SUPPORTING INFORMATION

Lipophilic sugar nucleotide synthesis by structure-based design of nucleotidylyltransferase substrates

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General Methods

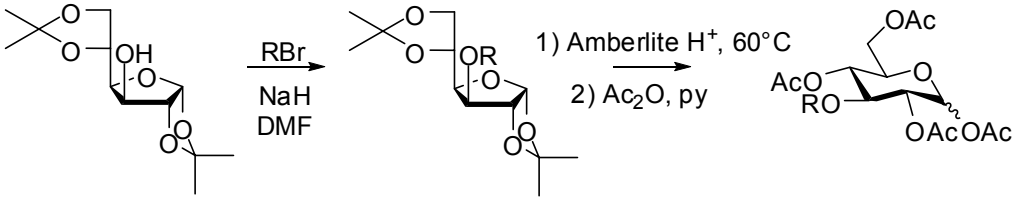
Dichloromethane and THF were dried over alumina (Innovative Technology) and stored over 3 Å molecular sieves. All other reagents and solvents were purchased and used without further purification. All reactions were monitored by thin layer chromatography (TLC) using Silicycle precoated silica gel plates (250 μm thickness). The TLC plates were visualized with a potassium permanganate solution (3 g potassium permanganate, 20 g potassium carbonate, 5 mL 5% aqueous sodium hydroxide, 300 mL distilled water), a phenol solution (10 g phenol, 5 mL H_2SO_4, 95 mL ethanol), or ultraviolet light (λ = 254 nm). Unless otherwise specified, flash chromatographic purification was performed on a Biotage SP1 HPFC. ^{1}H, ^{13}C and ^{31}P NMR spectra were obtained on a Bruker AVANCE-500 NMR Spectrometer operating at frequencies of 500.13 MHz, 125.76 MHz, and 202.45 MHz, respectively. Assignments are based on COSY and HSQC 2D NMR experiments. For chloroform-*d*, ^{1}H NMR chemical shifts are reported as δ in units of parts per million (ppm) downfield from tetramethylsilane (δ 0.0) and ^{13}C NMR chemical shifts are reported as δ in units of parts per million (ppm) relative to the residual solvent signal of chloroform-*d* (δ 77.16). For methanol-d_4, ^{1}H and ^{13}C NMR chemical shifts are reported as δ in units of parts per million (ppm) relative to the residual solvent signal of methanol-d_4 (δ 3.31 and δ 49.00, respectively). ^{31}P NMR chemical shifts are reported as δ in units of parts per million (ppm) relative to 85% H_3PO_4. Enzymatic reactions were monitored by HPLC performed on a

Hewlett Packard Series 1050 instrument with an Agilent Zorbax 5μm Rx-C18 column (150 cm x 4.6 cm). Compounds with a nucleotide base chromophore were monitored using a UV detector (λ = 254 nm). The linear gradient used was 90/10 A/B to 40/60 A/B over 8.0 min, followed by a plateau at 40/60 A/B from 8.0 to 10.0 min at 1.0 mL/min where A is an aqueous buffer containing 12 mM NBu_4Br, 10 mM KH_2PO_4, and 5% HPLC grade CH_3CN (pH 4.9) and B is HPLC CH_3CN except for assays containing compound **8f**, whereby the gradient was run to 80% CH_3CN instead of 60%. High resolution mass spectra were recorded on a micrOTOF instrument (Bruker Dalton) running in negative ion mode (ESI). Low resolution mass spectra were recorded on an LCQDuo ion trap instrument (Thermo Finnigan) running in positive mode (ESI).

An Agilent 1100 LC system was coupled to an Applied Biosystems-MDS SCIEX hybrid triple quadrupole linear ion trap (QTRAP 4000) mass spectrometer equipped with a Turbo V source for electrospray ionization for the ESI-MS/MS experiments. The sample was analyzed by flow-injection analysis in 75:25 (v/v) acetonitrile:de-ionized water using a flow-rate of 200 μL/min. Precursor ion scanning of m/z 323 ([UMP – H]-) and m/z 383 ([TDP – H]-) were used initially to selectively detect for uridine- and thymidine-linked sugar nucleotides, respectively, in the sample. ESI-MS/MS analysis in the enhanced product ion (EPI) mode was then performed to confirm the presence of the expected synthetic sugar nucleotide. The mass spectrometer settings for precursor ion scanning were: ionspray voltage 4.5 kV; mass range Q1 m/z 300 – 800; scan time 5 sec, Q1 and Q3 set to unit resolution. For the ESI-MS/MS experiments: ionspray voltage 4.5 kV; Q3 m/z 100–800; scan speed 1000 amu/sec; trap fill time was set to dynamic; Q1 and Q3 set to unit resolution. All acquisitions were made in the negative mode.

pKa values were measured in the following way: Using an IQ Scientific Instruments IQ150 fitted with an ISFET probe, a 0.01 M solution of the diammonium salt was adjusted to pH 10 with 0.2 M NaOH. Titration was done with 5 uL aliquots of 0.2 M HCl until pH 2, and the pKa values were determined by plotting in GraFit 5.0.4 (Erithacus Software Limited).

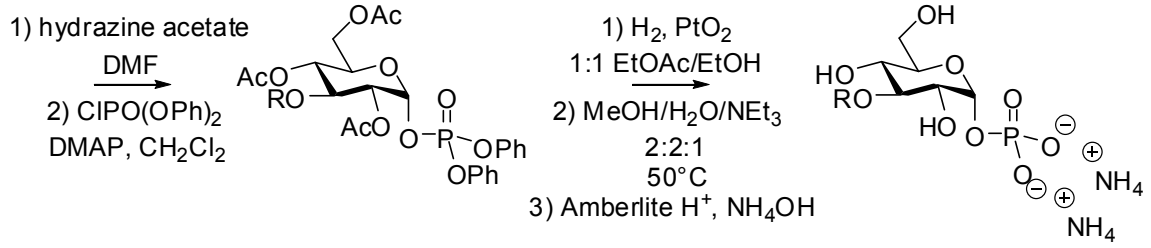
Chemical Synthesis



1

2b R = $(CH_2)_3CH_3$ (62%)
2c R = $(CH_2)_5CH_3$ (68%)
2d R = $(CH_2)_7CH_3$ (76%)
2e R = $(CH_2)_{11}CH_3$ (71%)
2f R = $(CH_2)_{15}CH_3$ (70%)
2g R = $CH_2CH(CH_3)_2$ (37%)
2h R = $CH_2CH(CH_2CH_3)_2$ (17%)

4a R = CH_3 (100%)
4b R = $(CH_2)_3CH_3$ (89%)
4c R = $(CH_2)_5CH_3$ (86%)
4d R = $(CH_2)_7CH_3$ (61%)
4e R = $(CH_2)_{11}CH_3$ (32%)
4f R = $(CH_2)_{15}CH_3$ (53%)
4g R = $CH_2CH(CH_3)_2$ (65%)
4h R = $CH_2CH(CH_2CH_3)_2$ (98%)

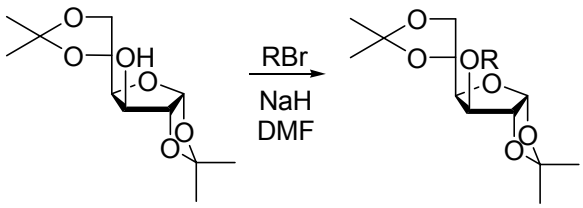


6a R = CH_3 (48%)
6b R = $(CH_2)_3CH_3$ (54%)
6c R = $(CH_2)_5CH_3$ (61%)
6d R = $(CH_2)_7CH_3$ (27%)
6e R = $(CH_2)_{11}CH_3$ (34%)
6f R = $(CH_2)_{15}CH_3$ (23%)
6g R = $CH_2CH(CH_3)_2$ (26%)
6h R = $CH_2CH(CH_2CH_3)_2$ (51%)

8a R = CH_3 (42%)
8b R = $(CH_2)_3CH_3$ (47%)
8c R = $(CH_2)_5CH_3$ (76%)
8d R = $(CH_2)_7CH_3$ (100%)
8e R = $(CH_2)_{11}CH_3$ (58%)
8f R = $(CH_2)_{15}CH_3$ (90%)
8g R = $CH_2CH(CH_3)_2$ (51%)
8h R = $CH_2CH(CH_2CH_3)_2$ (76%)

Overall yields: **8a** (20%), **8b** (14%), **8c** (21%), **8d** (21%), **8e** (3%), **8f** (4%), **8g** (3%), **8h** (6%).

General Procedure for Alkylation (2b-h)



1

2b R = $(CH_2)_3CH_3$ (62%)
2c R = $(CH_2)_5CH_3$ (68%)
2d R = $(CH_2)_7CH_3$ (76%)
2e R = $(CH_2)_{11}CH_3$ (71%)
2f R = $(CH_2)_{15}CH_3$ (70%)
2g R = $CH_2CH(CH_3)_2$ (37%)
2h R = $CH_2CH(CH_2CH_3)_2$ (17%)

To a stirring solution of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1**) (1.5 g, 5.76 mmol) in anhydrous DMF (15 mL) was added sodium hydride (0.42 g, 17 mmol) at 0ºC. After stirring at 0ºC for 10 min, the alkyl bromide (8.64 mmol) was added under a nitrogen atmosphere, and the mixture was stirred for another 30 min at 0ºC followed by 30 min at rt. The mixture was diluted with H_2O (50 mL) and extracted with dichloromethane (2 x 25 mL). The combined organic extracts were washed with brine (10 mL) and dried (Na_2SO_4), filtered and concentrated. Elution through a silica plug afforded the title compounds (**2b-h**).

3-*O*-Butyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (2b)[1]

Reaction with 1-bromobutane (0.93 mL, 8.64 mmol) followed by chromatographic purification (hexanes/EtOAc, 95:5) furnished compound **2b** as a colorless liquid (1.12 g, 62 %); R_F = 0.48 (hexanes/EtOAc, 85:15); ^{1}H NMR ($CDCl_3$) δ 5.87 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 4.52 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-2), 4.31 (dd, 1H, $J_{5,6}$ = 13.5 Hz, $J_{4,5}$ = 6.2 Hz, H-5), 4.13 (dd, 1H, $J_{4,5}$ = 7.4 Hz, $J_{3,4}$ = 3.0 Hz, H-4), 4.08 (ddd, 1H, $J_{5,6a}$ = 8.5 Hz, $^2J_{6a,6b}$ = 6.2 Hz, $^4J_{4,6a}$ = 0.7 Hz, H-6a), 3.98 (ddd, 1H, $J_{5,6b}$ = 8.5 Hz, $^2J_{6a,6b}$ = 6.0 Hz, $^4J_{4,6b}$ = 0.6 Hz, H-6b), 3.85 (d, 1H, $J_{3,4}$ = 3.0 Hz, H-3), 3.56 (m, 2H, OCH_2), 1.54 (m, 2H, OCH_2CH_2), 1.50, 1.42, 1.35, 1.32 (s, 12H, CH_3 x 4), 1.38 (m, 2H, $OCH_2CH_2CH_2$), 0.91 (t, 3H, J = 7.5 Hz, $(CH_2)_3CH_3$); ^{13}C NMR ($CDCl_3$) δ 111.8, 109.0 ($C(CH_3)_2$ x 2) 105.4 (C-1), 82.7 (C-2), 82.3 (C-3), 81.4 (C-4), 72.7 (C-5), 70.5 (OCH_2), 67.4 (C-6), 31.9 (OCH_2CH_2), 27.0, 26.9, 26.4, 25.5 ($C(CH_3)_2$ x 2), 19.4 ($OCH_2CH_2CH_2$), 14.0 ($(CH_2)_3CH_3$); LRMS *m/z* calcd for $C_{16}H_{28}O_6$ $[M+Na]^+$: 339.2. Found 339.2.

3-*O*-Hexyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (2c)[1]

Reaction with 1-bromohexane (1.21 mL, 8.64 mmol) followed by chromatographic purification (hexanes/EtOAc, 91:9) furnished compound **2c** as a colorless liquid (1.35 g, 68 %); R_F = 0.22 (hexanes/EtOAc, 95:5); ^{1}H NMR ($CDCl_3$) δ 5.87 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 4.52 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-2), 4.31 (dd, 1H, $J_{5,6}$ = 13.5 Hz, $J_{4,5}$ = 6.1 Hz, H-5), 4.13 (dd, 1H, $J_{4,5}$ = 7.4 Hz, $J_{3,4}$ = 3.1 Hz, H-4), 4.08 (ddd, 1H, $J_{5,6a}$ = 8.4 Hz, $^2J_{6a,6b}$

[1] Ikekawa, T.; Irinoda, K.; Saze, K.; Katori, T.; Matsuda, H.; Ohkawa, M.; Kosik, M. *Chem. Pharm. Bull.* **1987**, *35*, 2894-2899.

= 6.2 Hz, $^{4}J_{4,6a}$ = 0.7 Hz, H-6a), 3.98 (dd, 1H, $J_{5,6b}$ = 8.7 Hz, $^{2}J_{6a,6b}$ = 6.0 Hz, H-6b), 3.85 (d, 1H, $J_{3,4}$ = 3.1 Hz, H-3), 3.55 (m, 2H, OC*H*$_2$), 1.55 (m, 2H, OCH$_2$C*H*$_2$), 1.50, 1.42, 1.35, 1.32 (s, 12H, CH$_3$ x 4), 1.38-1.24 (m, 6H, OCH$_2$CH$_2$(C*H*$_2$)$_3$CH$_3$), 0.89 (t, 3H, *J* = 6.7 Hz, (CH$_2$)$_5$C*H*$_3$); ^{13}C NMR (CDCl$_3$) δ 111.8, 109.0 (*C*(CH$_3$)$_2$ x 2) 105.4 (C-1), 82.7 (C-2), 82.3 (C-3), 81.4 (C-4), 72.7 (C-5), 70.9 (O*C*H$_2$), 67.4 (C-6), 31.7 (OCH$_2$*C*H$_2$), 29.8 (OCH$_2$CH$_2$*C*H$_2$), 27.0, 26.9, 26.4, 25.5 (C(*C*H$_3$)$_2$ x 2), 25.9 (O(CH$_2$)$_3$*C*H$_2$CH$_2$CH$_3$), 22.7 (O(CH$_2$)$_4$*C*H$_2$CH$_3$), 14.2 ((CH$_2$)$_5$*C*H$_3$); LRMS *m/z* calcd for $C_{18}H_{32}O_6$ [M+Na]$^+$: 367.2. Found 367.2.

3-*O*-Octyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (2d)[1]

Reaction with 1-bromooctane (1.49 mL, 8.64 mmol) followed by chromatographic purification (hexanes/EtOAc, 93:7) furnished compound **2d** as a colorless liquid (1.64 g, 76 %); R_F = 0.38 (hexanes/EtOAc, 90:10); ^{1}H NMR (CDCl$_3$) δ 5.87 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.52 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-2), 4.31 (dd, 1H, $J_{5,6}$ = 13.5 Hz, $J_{4,5}$ = 6.1 Hz, H-5), 4.13 (dd, 1H, $J_{4,5}$ = 7.5 Hz, $J_{3,4}$ = 3.1 Hz, H-4), 4.08 (dd, 1H, $J_{5,6a}$ = 8.5 Hz, $^{2}J_{6a,6b}$ = 6.3 Hz, H-6a), 3.98 (dd, 1H, $J_{5,6b}$ = 8.5 Hz, $^{2}J_{6a,6b}$ = 6.0 Hz, H-6b), 3.85 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-3), 3.55 (m, 2H, OC*H*$_2$), 1.55 (m, 2H, OCH$_2$C*H*$_2$), 1.49, 1.42, 1.35, 1.32 (s, 12H, CH$_3$ x 4), 1.38-1.21 (m, 10H, OCH$_2$CH$_2$(C*H*$_2$)$_5$CH$_3$), 0.88 (t, 3H, *J* = 7.1 Hz, (CH$_2$)$_7$C*H*$_3$); ^{13}C NMR (CDCl$_3$) δ 111.8, 109.0 (*C*(CH$_3$)$_2$ x 2) 105.4 (C-1), 82.7 (C-2), 82.3 (C-3), 81.4 (C-4), 72.7 (C-5), 70.9 (O*C*H$_2$), 67.4 (C-6), 32.0, 29.5, 29.4, 26.2, 22.8 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 29.9 (OCH$_2$*C*H$_2$(*C*H$_2$)$_5$CH$_3$), 27.0, 26.9, 26.4, 25.5 (C(*C*H$_3$)$_2$ x 2), 14.2 ((CH$_2$)$_7$*C*H$_3$); LRMS *m/z* calcd for $C_{20}H_{36}O_6$ [M+Na]$^+$: 395.2. Found 395.3.

3-*O*-Dodecyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (2e)[1]

Reaction with 1-bromododecane (2.07 mL, 8.64 mmol) followed by chromatographic purification (hexanes/EtOAc, 93:7) furnished compound **2e** as a colorless liquid (1.75 g, 71 %); R_F = 0.19 (hexanes/EtOAc, 95:5); ^{1}H NMR (CDCl$_3$) δ 5.87 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.52 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-2), 4.30 (dd, 1H, $J_{5,6}$ = 13.6 Hz, $J_{4,5}$ = 6.2 Hz, H-5), 4.12 (dd, 1H, $J_{4,5}$ = 7.5 Hz, $J_{3,4}$ = 3.1 Hz, H-4), 4.08 (dd, 1H, $J_{5,6a}$ = 8.5 Hz, $^{2}J_{6a,6b}$ = 6.3 Hz, H-6a), 3.98 (dd, 1H, $J_{5,6b}$ = 8.5 Hz, $^{2}J_{6a,6b}$ = 6.0 Hz, H-6b), 3.85 (d, 1H, $J_{3,4}$ = 3.1 Hz, H-3), 3.55 (m, 2H,

OC*H*$_2$), 1.55 (m, 2H, OCH$_2$C*H*$_2$), 1.49, 1.42, 1.35, 1.31 (s, 12H, CH$_3$ x 4), 1.37-1.21 (m, 18H, OCH$_2$CH$_2$(C*H*$_2$)$_9$CH$_3$), 0.88 (t, 3H, J = 6.6 Hz, (CH$_2$)$_{11}$C*H*$_3$); ^{13}C NMR (CDCl$_3$) δ 111.8, 109.0 (*C*(CH$_3$)$_2$ x 2) 105.4 (C-1), 82.7 (C-2), 82.3 (C-3), 81.4 (C-4), 72.7 (C-5), 70.9 (O*C*H$_2$), 67.4 (C-6), 32.0, 29.9, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 26.4, 22.8 (OCH$_2$(*C*H$_2$)$_{10}$CH$_3$), 27.0, 26.9, 26.2, 25.5 (C(*C*H$_3$)$_2$ x 2), 14.2 ((CH$_2$)$_{11}$*C*H$_3$); LRMS *m/z* calcd for C$_{24}$H$_{44}$O$_6$ [M+Na]$^+$: 451.3. Found 451.3.

3-*O*-Hexadecyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (2f)[1]

Reaction with 1-bromohexadecane (3.52 mL, 11.5 mmol) followed by chromatographic purification (hexanes/EtOAc, 90:10) furnished compound **2f** as a colorless liquid (1.95 g, 70 %); R$_F$ = 0.40 (hexanes/EtOAc, 90:10); ^{1}H NMR (CDCl$_3$) δ 5.87 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.52 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-2), 4.30 (ddd, 1H, $J_{4,5}$ = 7.3 Hz, $J_{5,6a}$ = 6.2 Hz, $J_{5,6b}$ = 6.2 Hz, H-5), 4.13 (dd, 1H, $J_{4,5}$ = 7.4 Hz, $J_{3,4}$ = 3.1 Hz, H-4), 4.08 (dd, 1H, $J_{5,6a}$ = 8.5 Hz, $^2J_{6a,6b}$ = 6.2 Hz, H-6a), 3.97 (dd, 1H, $J_{5,6b}$ = 8.5 Hz, $^2J_{6a,6b}$ = 6.0 Hz, H-6b), 3.85 (d, 1H, $J_{3,4}$ = 3.1 Hz, H-3), 3.55 (m, 2H, OC*H*$_2$), 1.55 (m, 2H, OCH$_2$C*H*$_2$), 1.49, 1.42, 1.35, 1.31 (s, 12H, CH$_3$ x 4), 1.37-1.21 (m, 26H, OCH$_2$CH$_2$(C*H*$_2$)$_{13}$CH$_3$), 0.88 (t, 3H, J = 7.0 Hz, (CH$_2$)$_{15}$C*H*$_3$); ^{13}C NMR (CDCl$_3$) δ 111.8, 109.0 (*C*(CH$_3$)$_2$ x 2) 105.4 (C-1), 82.7 (C-2), 82.3 (C-3), 81.4 (C-4), 72.7 (C-5), 70.9 (O*C*H$_2$), 67.4 (C-6), 32.1, 29.9, 29.9, 29.9, 29.8, 29.8, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 26.2, 22.8 (OCH$_2$(*C*H$_2$)$_{14}$CH$_3$), 27.0, 26.9, 26.4, 25.5 (C(*C*H$_3$)$_2$ x 2), 14.2 ((CH$_2$)$_{15}$*C*H$_3$); LRMS *m/z* calcd for C$_{28}$H$_{52}$O$_6$ [M+Na]$^+$: 507.4. Found 507.4.

1,2:5,6-Di-*O*-Isopropylidene-3-*O*-(2-methylpropyl)-α-D-glucofuranose (2g)

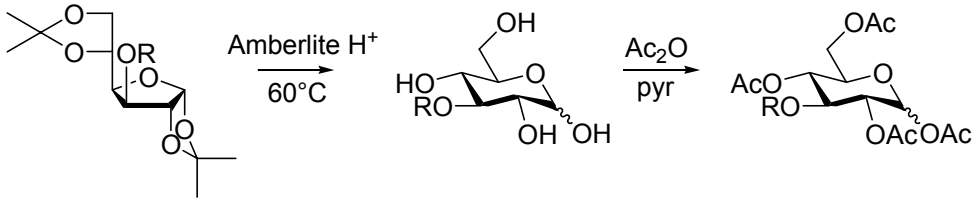
Reaction with 1-bromo-2-methylpropane (2.51 mL, 23.0 mmol) followed by chromatographic purification (hexanes/EtOAc, 90:10) furnished compound **2g** as a colorless liquid (0.67 g, 37 %); R$_F$ = 0.86 (hexanes/EtOAc, 66:33); ^{1}H NMR (CDCl$_3$) δ 5.87 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.52 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-2), 4.33 (dd, 1H, $J_{5,6}$ = 13.5 Hz, $J_{4,5}$ = 6.2 Hz, H-5), 4.14 (dd, 1H, $J_{4,5}$ = 7.4 Hz, $J_{3,4}$ = 3.1 Hz, H-4), 4.08 (dd, 1H, $J_{5,6a}$ = 8.5 Hz, $^2J_{6a,6b}$ = 6.2 Hz, H-6a), 3.97 (dd, 1H, $J_{5,6b}$ = 8.5 Hz, $^2J_{6a,6b}$ = 6.2 Hz, H-6b), 3.84 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-3), 3.37 (dd, 1H, J = 6.5 Hz, ^2J = 9.0 Hz, OC*H*$_{2a}$), 3.28 (dd, 1H, J = 6.5 Hz, ^2J = 9.0 Hz, OC*H*$_{2b}$), 1.84

(nonet, 1H, J = 6.7 Hz, $OCH_2CH(CH_3)_2$), 1.50, 1.42, 1.35, 1.32 (s, 12H, CH_3 x 4), 0.91 (d, 3H, J = 3.8 Hz, CH_{3a}), 0.90 (d, 3H, J = 3.8 Hz, CH_{3b}); ^{13}C NMR ($CDCl_3$) δ 111.7, 108.9 ($C(CH_3)_2$ x 2) 105.3 (C-1), 82.4 (C-2), 82.3 (C-3), 81.3 (C-4), 77.3 (OCH_2), 72.6 (C-5), 67.3 (C-6), 28.6 (OCH_2CH), 26.9, 26.8, 26.3, 25.4 ($C(CH_3)_2$ x 2), 19.3, 19.2 ($OCH_2CH(CH_3)_2$); LRMS *m/z* calcd for $C_{16}H_{28}O_6$ $[M+Na]^+$: 339.2. Found 339.1.

1,2:5,6-Di-*O*-Isopropylidene-3-*O*-(2-ethylbutyl)-α-D-glucofuranose (2h)

Reaction with 1-bromo-2-ethylbutane (1.61 mL, 11.5 mmol) followed by chromatographic purification (hexanes/EtOAc, 91:9) furnished compound **2h** as a colorless liquid (0.34 g, 17 %); R_F = 0.67 (hexanes/EtOAc, 80:20); ^{1}H NMR ($CDCl_3$) δ 5.86 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.51 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-2), 4.30 (dd, 1H, $J_{5,6}$ = 13.6 Hz, $J_{4,5}$ = 6.2 Hz, H-5), 4.13 (dd, 1H, $J_{4,5}$ = 7.4 Hz, $J_{3,4}$ = 3.1 Hz, H-4), 4.08 (dd, 1H, $J_{5,6a}$ = 8.5 Hz, $^2J_{6a,6b}$ = 6.3 Hz, H-6a), 3.96 (dd, 1H, $J_{5,6b}$ = 8.4 Hz, $^2J_{6a,6b}$ = 6.2 Hz, H-6b), 3.83 (d, 1H, $J_{3,4}$ = 3.1 Hz, H-3), 3.50 (dd, 1H, J = 5.3 Hz, ^2J = 9.0 Hz, OCH_{2a}), 3.40 (dd, 1H, J = 5.4 Hz, ^2J = 9.0 Hz, OCH_{2b}), 1.50, 1.42, 1.34, 1.32 (s, 12H, CH_3 x 4), 1.45-1.28 (m, 5H, $OCH_2CH(CH_2CH_3)_2$), 0.88 (t, 3H, J = 7.4 Hz, CH_{3a}), 0.90 (t, 3H, J = 7.4 Hz, CH_{3b}); ^{13}C NMR ($CDCl_3$) δ 111.9, 109.0 ($C(CH_3)_2$ x 2) 105.5 (C-1), 82.5 (C-2), 82.5 (C-3), 81.6 (C-4), 72.8 (OCH_2), 72.7 (C-5), 67.5 (C-6), 41.5 (OCH_2CH), 27.0, 26.9, 26.4, 25.5 ($C(CH_3)_2$ x 2), 23.5, 23.5 ($OCH_2CH(CH_2CH_3)_2$), 11.3, 11.2 ($OCH_2CH(CH_2CH_3)_2$); LRMS *m/z* calcd for $C_{18}H_{32}O_6$ $[M+Na]^+$: 367.2. Found 367.2.

General Procedure for Hydrolysis and Acetylation (3a-h and 4a-h, respectively)



2b R = $(CH_2)_3CH_3$
2c R = $(CH_2)_5CH_3$
2d R = $(CH_2)_7CH_3$
2e R = $(CH_2)_{11}CH_3$
2f R = $(CH_2)_{15}CH_3$
2g R = $CH_2CH(CH_3)_2$
2h R = $CH_2CH(CH_2CH_3)_2$

3a R = CH_3
3b R = $(CH_2)_3CH_3$
3c R = $(CH_2)_5CH_3$
3d R = $(CH_2)_7CH_3$
3e R = $(CH_2)_{11}CH_3$
3f R = $(CH_2)_{15}CH_3$
3g R = $CH_2CH(CH_3)_2$
3h R = $CH_2CH(CH_2CH_3)_2$

4a R = CH_3 (100%)
4b R = $(CH_2)_3CH_3$ (89%)
4c R = $(CH_2)_5CH_3$ (86%)
4d R = $(CH_2)_7CH_3$ (61%)
4e R = $(CH_2)_{11}CH_3$ (32%)
4f R = $(CH_2)_{15}CH_3$ (53%)
4g R = $CH_2CH(CH_3)_2$ (65%)
4h R = $CH_2CH(CH_2CH_3)_2$ (98%)

To a solution of 3-*O*-alkyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**2b-h**) (1.5 g) in 5:1 MeOH/H_2O (30 mL) was added Amberlite IR-120 PLUS(H) ion exchange resin (45 g) and the reaction was stirred overnight at 60ºC. The reaction mixture was then filtered and concentrated to dryness. The hydrolyzed intermediate (**3b-h**) was immediately reacted without further purification. Under a nitrogen atmosphere, a solution of the 3-*O*-alkyl-D-glucopyranose (**3a-h**) in anhydrous pyridine (20 mL) was charged with acetic anhydride (3.0 mL) and stirred overnight at rt. This mixture was then diluted with H_2O (50 mL) and extracted with dichloromethane (2 x 25 mL). The combined organic extracts were washed with brine (10 mL) and dried (Na_2SO_4), filtered and concentrated to afford the acetylated product (**4a-h**).

1,2,4,6-Tetra-*O*-acetyl-3-*O*-methyl-α-D-glucopyranose (4a)

Compound **4a** was obtained as a colorless liquid (2.80 g, 100 %); R_F = 0.46 (hexanes/EtOAc, 67:33); ^{1}H NMR ($CDCl_3$) δ 6.29 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.08 (dd, 1H, $J_{4,5}$ = 10.2 Hz, $J_{3,4}$ = 9.6 Hz, H-4), 5.00 (dd, 1H, $J_{2,3}$ = 9.9 Hz, $J_{1,2}$ = 3.6 Hz, H-2), 4.20 (dd, 1H, $^2J_{6a,6b}$ = 12.5 Hz, $J_{5,6a}$ = 4.5 Hz, H-6a), 4.07 (dd, 1H, $^2J_{6a,6b}$ = 12.3 Hz, $J_{5,6b}$ = 2.3 Hz, H-6b), 4.01 (ddd, 1H, $J_{4,5}$ = 10.2 Hz, $J_{5,6a}$ = 4.2 Hz, $J_{5,6b}$ = 2.2 Hz, H-5), 3.72 (dd, 1H, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 9.8 Hz, H-3), 3.47 (s, 3H, C*H*$_3$), 2.17, 2.11, 2.09, 2.07 (s, 12H, C(O)C*H*$_3$ x 4); ^{13}C NMR ($CDCl_3$) δ 170.8, 169.7, 169.4, 168.9 (*C*(O)CH_3 x 4), 89.6 (C-1), 78.3 (C-3), 71.2 (C-2), 70.4 (C-5), 69.1 (C-4), 61.9 (C-6),

60.2 (*C*H_3), 21.0, 20.9, 20.8, 20.8 (C(O)*C*H_3 x 4); LRMS *m/z* calcd for $C_{15}H_{22}O_{10}$ $[M+Na]^+$: 385.1. Found 385.1.

1,2,4,6-Tetra-*O*-acetyl-3-*O*-butyl-β-D-glucopyranose (4b)

Compound **4b** was obtained as a colorless liquid (1.74 g, 89 %); R_F = 0.46 (hexanes/EtOAc, 67:33); ^{1}H NMR ($CDCl_3$) δ 5.64 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1), 5.09 (dd, 1H, $J_{2,3}$ = 9.4 Hz, $J_{1,2}$ = 8.3 Hz, H-2), 5.09 (dd, 1H, $J_{4,5}$ = 9.5 Hz, $J_{3,4}$ = 9.4 Hz, H-4), 4.23 (dd, 1H, $^2J_{6a,6b}$ = 12.5 Hz, $J_{5,6a}$ = 4.9 Hz, H-6a), 4.09 (dd, 1H, $^2J_{6a,6b}$ = 12.5 Hz, $J_{5,6b}$ = 2.3 Hz, H-6b), 3.72 (ddd, 1H, $J_{4,5}$ = 9.8 Hz, $J_{5,6a}$ = 4.7 Hz, $J_{5,6b}$ = 2.2 Hz, H-5), 3.56 (dd, 1H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 3.54 (m, 2H, OC*H*$_2$), 2.11, 2.09, 2.08, 2.08 (s, 12H, C(O)C*H*$_3$ x 4), 1.46 (m, 2H, OCH_2CH_2), 1.30 (m, 2H, $OCH_2CH_2CH_2$), 0.88 (t, 3H, *J* = 7.3 Hz, $(CH_2)_3CH_3$); ^{13}C NMR ($CDCl_3$) δ 170.9, 169.4, 169.4, 169.2 (*C*(O)CH_3 x 4), 92.2 (C-1), 80.4 (C-3), 73.2 (C-5), 72.4 (OCH_2), 71.7 (C-2), 69.2 (C-4), 62.0 (C-6), 32.3 (OCH_2CH_2), 21.0, 20.9, 20.9, 20.9 (C(O)*C*H_3 x 4), 19.1 ($OCH_2CH_2CH_2$), 14.0 ($O(CH_2)_3CH_3$); LRMS *m/z* calcd for $C_{18}H_{28}O_{10}$ $[M+Na]^+$: 427.2. Found 427.2.

1,2,4,6-Tetra-*O*-acetyl-3-*O*-hexyl-β-D-glucopyranose (4c)

Compound **4c** was obtained as a white solid (1.62 g, 86 %); R_F = 0.26 (hexanes/EtOAc, 80:20); ^{1}H NMR ($CDCl_3$) δ 5.64 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1), 5.10 (dd, 1H, $J_{2,3}$ = 9.4 Hz, $J_{1,2}$ = 8.3 Hz, H-2), 5.08 (dd, 1H, $J_{4,5}$ = 9.5 Hz, $J_{3,4}$ = 9.6 Hz, H-4), 4.23 (dd, 1H, $^2J_{6a,6b}$ = 12.5 Hz, $J_{5,6a}$ = 4.9 Hz, H-6a), 4.09 (dd, 1H, $^2J_{6a,6b}$ = 12.5 Hz, $J_{5,6b}$ = 2.3 Hz, H-6b), 3.72 (ddd, 1H, $J_{4,5}$ = 9.9 Hz, $J_{5,6a}$ = 4.9 Hz, $J_{5,6b}$ = 2.4 Hz, H-5), 3.57 (dd, 1H, $J_{2,3}$ = 9.4 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 3.53 (m, 2H, OC*H*$_2$), 2.11, 2.09, 2.08, 2.08 (s, 12H, C(O)C*H*$_3$ x 4), 1.46 (p, 2H, *J* = 7.5 Hz, OCH_2CH_2), 1.26 (m, 6H, $OCH_2CH_2(CH_2)_3CH_3$), 0.88 (t, 3H, *J* = 6.9 Hz, $O(CH_2)_5CH_3$); ^{13}C NMR ($CDCl_3$) δ 170.9, 169.4, 169.3, 169.2 (*C*(O)CH_3 x 4), 92.2 (C-1), 80.4 (C-3), 73.2 (C-5), 72.8 (OCH_2), 71.6 (C-2), 69.1 (C-4), 61.9 (C-6), 31.7, 25.7, 22.7 ($OCH_2CH_2(CH_2)_3CH_3$), 30.3 ($OCH_2CH_2(CH_2)_3CH_3$), 21.0, 20.9, 20.9, 20.9 (C(O)*C*H_3 x 4), 14.1 ($O(CH_2)_5CH_3$); LRMS *m/z* calcd for $C_{20}H_{32}O_{10}$ $[M+Na]^+$: 455.2. Found 455.1.

1,2,4,6-Tetra-*O*-acetyl-3-*O*-octyl-β-D-glucopyranose (4d)[2]

Diethyl ether was used instead of dichloromethane as an extraction solvent *en route* to compound **4d**, a white solid (1.21 g, 61 %); R_F = 0.32 (hexanes/EtOAc, 75:25); ^{1}H NMR ($CDCl_3$) δ 5.64 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1), 5.08 (dd, 1H, $J_{2,3}$ = 9.3 Hz, $J_{1,2}$ = 8.2 Hz, H-2), 5.08 (dd, 1H, $J_{4,5}$ = 9.6 Hz, $J_{3,4}$ = 9.6 Hz, H-4), 4.22 (dd, 1H, $^2J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 4.9 Hz, H-6a), 4.09 (dd, 1H, $^2J_{6a,6b}$ = 12.2 Hz, $J_{5,6b}$ = 2.2 Hz, H-6b), 3.72 (ddd, 1H, $J_{4,5}$ = 9.9 Hz, $J_{5,6a}$ = 4.9 Hz, $J_{5,6b}$ = 2.2 Hz, H-5), 3.57 (dd, 1H, $J_{2,3}$ = 9.3 Hz, $J_{3,4}$ = 9.3 Hz, H-3), 3.53 (m, 2H, OCH_2), 2.10, 2.08, 2.08, 2.07 (s, 12H, C(O)CH_3 x 4), 1.46 (m, 2H, OCH_2CH_2), 1.33-1.20 (m, 10H, $OCH_2CH_2(CH_2)_5CH_3$), 0.88 (t, 3H, J = 7.1 Hz, $(CH_2)_7CH_3$); ^{13}C NMR ($CDCl_3$) δ 170.8, 169.4, 169.3, 169.1 (C(O)CH_3 x 4), 92.2 (C-1), 80.4 (C-3), 73.2 (C-5), 72.7 (OCH_2), 71.7 (C-2), 69.2 (C-4), 62.0 (C-6), 31.9, 29.5, 29.3, 26.1, 22.7 ($OCH_2CH_2(CH_2)_5CH_3$), 30.3 ($OCH_2CH_2(CH_2)_5CH_3$), 21.0, 20.9, 20.9, 20.9 (C(O)CH_3 x 4), 14.2 ($O(CH_2)_7CH_3$); LRMS *m/z* calcd for $C_{22}H_{36}O_{10}$ $[M+Na]^+$: 483.2. Found 483.2.

1,2,4,6-Tetra-*O*-acetyl-3-*O*-dodecyl-β-D-glucopyranose (4e)[2]

Diethyl ether was used instead of dichloromethane as an extraction solvent and the reaction mixture was purified by column chromatography (hexanes/EtOAc, 75:25). Compound **4e** was obtained as a white solid (0.58 g, 32 %); R_F = 0.21 (hexanes/EtOAc, 80:20); ^{1}H NMR ($CDCl_3$) δ 5.64 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1), 5.09 (dd, 1H, $J_{2,3}$ = 9.3 Hz, $J_{1,2}$ = 9.4 Hz, H-2), 5.07 (dd, 1H, $J_{4,5}$ = 9.5 Hz, $J_{3,4}$ = 9.5 Hz, H-4), 4.22 (dd, 1H, $^2J_{6a,6b}$ = 12.5 Hz, $J_{5,6a}$ = 5.1 Hz, H-6a), 4.10 (dd, 1H, $^2J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 2.1 Hz, H-6b), 3.72 (ddd, 1H, $J_{4,5}$ = 9.9 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 2.3 Hz, H-5), 3.56 (dd, 1H, $J_{2,3}$ = 9.4 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 3.53 (m, 2H, OCH_2), 2.10, 2.08, 2.08, 2.07 (s, 12H, C(O)CH_3 x 4), 1.46 (m, 2H, OCH_2CH_2), 1.33-1.19 (m, 18H, $OCH_2CH_2(CH_2)_9CH_3$), 0.88 (t, 3H, J = 7.0 Hz, $(CH_2)_{11}CH_3$); ^{13}C NMR ($CDCl_3$) δ 170.9, 169.4, 169.3, 169.1 (C(O)CH_3 x 4), 92.2 (C-1), 80.4 (C-3), 73.2 (C-5), 72.8 (OCH_2), 71.7 (C-2), 69.2 (C-4), 62.0 (C-6), 32.1, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 26.1, 22.8 ($OCH_2CH_2(CH_2)_9CH_3$), 30.3 ($OCH_2CH_2(CH_2)_9CH_3$), 21.0, 20.9, 20.9, 20.9 (C(O)CH_3 x 4), 14.2 ($O(CH_2)_{11}CH_3$); LRMS *m/z* calcd for $C_{26}H_{44}O_{10}$ $[M+Na]^+$: 539.3. Found 539.2.

[2] Miethchen, R.; Gabriel, T.; Peters, D.; Holz, J.; Michalik, M. *Carbohydr. Res.* **1991**, *214*, 331-6.

1,2,4,6-Tetra-*O*-acetyl-3-*O*-hexadecyl-β-D-glucopyranose (4f)[2]

Hydrolysis of the isopropylidene functionality was performed at 85ºC and chloroform was used instead of dichloromethane as an extraction solvent for the acetylation. Compound **4f** was obtained as a white solid (0.80 g, 53 %); R_F = 0.62 (hexanes/EtOAc, 67:33); ^{1}H NMR ($CDCl_3$) δ 5.64 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1), 5.08 (dd, 1H, $J_{2,3}$ = 9.3 Hz, $J_{1,2}$ = 9.4 Hz, H-2), 5.07 (dd, 1H, $J_{4,5}$ = 9.5 Hz, $J_{3,4}$ = 9.5 Hz, H-4), 4.22 (dd, 1H, $^2J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 4.9 Hz, H-6a), 4.10 (dd, 1H, $^2J_{6a,6b}$ = 12.5 Hz, $J_{5,6b}$ = 2.3 Hz, H-6b), 3.72 (ddd, 1H, $J_{4,5}$ = 9.9 Hz, $J_{5,6a}$ = 4.9 Hz, $J_{5,6b}$ = 2.3 Hz, H-5), 3.56 (dd, 1H, $J_{2,3}$ = 9.3 Hz, $J_{3,4}$ = 9.3 Hz, H-3), 3.52 (m, 2H, OC*H*$_2$), 2.10, 2.08, 2.08, 2.07 (s, 12H, C(O)C*H*$_3$ x 4), 1.46 (m, 2H, OCH_2CH_2), 1.33-1.19 (m, 26H, $OCH_2CH_2(CH_2)_{13}CH_3$), 0.88 (t, 3H, J = 7.0 Hz, $(CH_2)_{15}CH_3$); ^{13}C NMR ($CDCl_3$) δ 170.9, 169.4, 169.3, 169.1 (*C*(O)CH_3 x 4), 92.2 (C-1), 80.5 (C-3), 73.2 (C-5), 72.8 (O*C*H_2), 71.7 (C-2), 69.2 (C-4), 62.0 (C-6), 32.1, 29.8, 29.8, 29.8, 29.8, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 26.1, 22.8 ($OCH_2CH_2(CH_2)_{13}CH_3$), 30.3 ($OCH_2CH_2(CH_2)_9CH_3$), 21.0, 20.9, 20.9, 20.9 (C(O)*C*H_3 x 4), 14.2 ($O(CH_2)_{15}CH_3$); LRMS *m/z* calcd for $C_{30}H_{52}O_{10}$ $[M+Na]^+$: 595.3. Found 595.3.

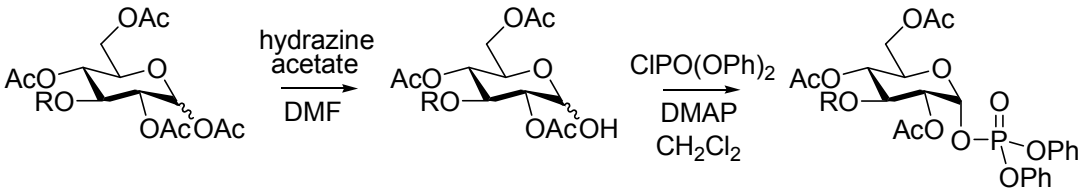
1,2,4,6-Tetra-*O*-acetyl-3-*O*-(2-methylpropyl)-β-D-glucopyranose (4g)

Compound **4g** was obtained as a colorless liquid (1.25 g, 65 %); R_F = 0.44 (hexanes/EtOAc, 67:33); ^{1}H NMR ($CDCl_3$) δ 5.64 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1), 5.11 (m, 1H, H-2), 5.09 (m, 1H, H-4), 4.22 (dd, 1H, $^2J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 4.9 Hz, H-6a), 4.09 (dd, 1H, $^2J_{6a,6b}$ = 12.5 Hz, $J_{5,6b}$ = 2.3 Hz, H-6b), 3.72 (ddd, 1H, $J_{4,5}$ = 9.9 Hz, $J_{5,6a}$ = 4.5 Hz, $J_{5,6b}$ = 2.4 Hz, H-5), 3.56 (dd, 1H, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 9.2 Hz, H-3), 3.30 (dd, 2H, J = 6.3 Hz, ^2J = 2.2 Hz, OC*H*$_2$), 2.10, 2.08, 2.08, 2.07 (s, 12H, C(O)C*H*$_3$ x 4), 1.74 (nonet, 1H, J = 6.6 Hz, OCH_2CH), 0.84 (d, 6H, J = 6.7 Hz, $OCH_2CH(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 170.7, 169.3, 169.2, 169.0 (*C*(O)CH_3 x 4), 92.0 (C-1), 80.4 (C-3), 79.4 (O*C*H_2), 73.0 (C-5), 71.5 (C-2), 69.1 (C-4), 61.8 (C-6), 28.9 (OCH_2CH), 20.9, 20.8, 20.8, 20.8 (C(O)*C*H_3 x 4), 19.1, 19.0 ($OCH_2CH(CH_3)_2$); LRMS *m/z* calcd for $C_{18}H_{28}O_{10}$ $[M+Na]^+$: 427.2. Found 427.2.

1,2,4,6-Tetra-*O*-acetyl-3-*O*-(2-ethylbutyl)-β-D-glucopyranose (4h)

Compound **4h** was obtained as a white solid (0.98 g, 98 %); R_F = 0.47 (hexanes/EtOAc, 67:33); ^{1}H NMR ($CDCl_3$) δ 5.64 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1), 5.10 (dd, 1H, $J_{2,3}$ = 9.4 Hz, $J_{1,2}$ = 8.3 Hz, H-2), 5.09 (dd, 1H, $J_{4,5}$ = 9.6 Hz, $J_{3,4}$ = 9.6 Hz, H-4), 4.22 (dd, 1H, $^2J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 5.0 Hz, H-6a), 4.09 (dd, 1H, $^2J_{6a,6b}$ = 12.5 Hz, $J_{5,6b}$ = 2.3 Hz, H-6b), 3.72 (ddd, 1H, $J_{4,5}$ = 9.9 Hz, $J_{5,6a}$ = 4.9 Hz, $J_{5,6b}$ = 2.3 Hz, H-5), 3.56 (dd, 1H, $J_{2,3}$ = 9.3 Hz, $J_{3,4}$ = 9.3 Hz, H-3), 3.46 (dd, 2H, J = 4.4 Hz, ^2J = 2.6 Hz, OCH_2), 2.10, 2.08, 2.08, 2.07 (s, 12H, C(O)CH_3 x 4), 1.27 (m, 5H, $OCH_2CH(CH_2CH_3)_2$), 0.83 (t, 6H, J = 7.3 Hz, $OCH_2CH(CH_2CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 170.9, 169.4, 169.3, 169.1 (*C*(O)CH_3 x 4), 92.2 (C-1), 80.4 (C-3), 74.9 (O*C*H_2), 73.2 (C-5), 71.8 (C-2), 69.4 (C-4), 61.9 (C-6), 42.0 (OCH_2CH), 23.1, 23.1 ($OCH_2CH(CH_2CH_3)_2$), 21.0, 20.9, 20.9, 20.8 (C(O)CH_3 x 4), 11.2, 11.2 ($OCH_2CH(CH_2CH_3)_2$); LRMS *m/z* calcd for $C_{20}H_{32}O_{10}$ $[M+Na]^+$: 455.2. Found 455.2.

General Procedure for Selective Deacetylation and Phosphorylation (5a-h and 6a-h, respectively)



4a R = CH_3	**5a** R = CH_3 (72%)	**6a** R = CH_3 (67%)
4b R = $(CH_2)_3CH_3$	**5b** R = $(CH_2)_3CH_3$ (79%)	**6b** R = $(CH_2)_3CH_3$ (68%)
4c R = $(CH_2)_5CH_3$	**5c** R = $(CH_2)_5CH_3$ (82%)	**6c** R = $(CH_2)_5CH_3$ (74%)
4d R = $(CH_2)_7CH_3$	**5d** R = $(CH_2)_7CH_3$ (62%)	**6d** R = $(CH_2)_7CH_3$ (44%)
4e R = $(CH_2)_{11}CH_3$	**5e** R = $(CH_2)_{11}CH_3$ (59%)	**6e** R = $(CH_2)_{11}CH_3$ (58%)
4f R = $(CH_2)_{15}CH_3$	**5f** R = $(CH_2)_{15}CH_3$ (41%)	**6f** R = $(CH_2)_{15}CH_3$ (55%)
4g R = $CH_2CH(CH_3)_2$	**5g** R = $CH_2CH(CH_3)_2$ (39%)	**6g** R = $CH_2CH(CH_3)_2$ (66%)
4h R = $CH_2CH(CH_2CH_3)_2$	**5h** R = $CH_2CH(CH_2CH_3)_2$ (65%)	**6h** R = $CH_2CH(CH_2CH_3)_2$ (78%)

To a stirring solution of the acetylated glucopyranose (**4a-h**) (2.41 mmol) in anhydrous DMF (10 mL) was added hydrazine acetate (0.33 g, 3.62 mmol) and the solution subsequently heated to 60ºC for 15 min. The mixture was then stirred for 1 hr at rt before being diluted with H_2O (20 mL) and extracted with dichloromethane (2 x 20 mL). The combined organic layers were washed with brine (10 mL) and dried (Na_2SO_4), filtered and concentrated. The major product was purified by flash chromatography to give the selectively deacetylated pyranose (**5a-h**). Under a nitrogen atmosphere, a solution of the selectively

deacetylated product (**5a-h**) (1.49 mmol) and 4-dimethylaminopyridine (438 mg, 3.58 mmol) in anhydrous dichloromethane (8 mL) was stirred for 15 min at rt. The flask was cooled to -10ºC and charged with diphenyl chlorophosphate (464 μL, 2.24 mmol). After 1.5 hr, the mixture was diluted with H_2O (20 mL) and extracted with dichloromethane (2 x 15 mL). The combined organic extracts were washed with brine (10 mL) and dried (Na_2SO_4), filtered and concentrated. Purification by flash chromatography afforded the title compounds (**6a-g**).

Diphenyl 2,4,6-tri-*O*-acetyl-3-*O*-methyl-α-D-glucopyranosyl-1-phosphate (6a)

Compound **5a**[3] (R_F = 0.28 (hexanes/EtOAc, 60:40)), a colorless liquid, was provided by silica gel chromatography (hexanes/EtOAc, 60:40) (556 mg, 72%) and immediately carried onto the subsequent phosphorylation. Chromatographic purification (hexanes/EtOAc, 72:28) furnished compound **6a** as a colorless liquid (552 mg, 67%); R_F = 0.36 (hexanes/EtOAc, 67:33); ^{1}H NMR ($CDCl_3$) δ 7.38-7.20 (m, 10H, Ph x 2), 6.06 (dd, 1H, $^1J_{C,H}$ = 180 Hz, $J_{1,P}$ = 6.5 Hz, $J_{1,2}$ = 3.3 Hz, H-1), 5.07 (dd, 1H, $J_{4,5}$ = 10.2 Hz, $J_{3,4}$ = 9.6 Hz, H-4), 4.90 (ddd, 1H, $J_{2,3}$ = 10.0 Hz, $J_{1,2}$ = 3.1 Hz, $^4J_{1,P}$ = 3.1 Hz, H-2), 4.14 (dd, 1H, $^2J_{6a,6b}$ = 12.5 Hz, $J_{5,6a}$ = 4.3 Hz, H-6a), 4.02 (ddd, 1H, $J_{4,5}$ = 10.4 Hz, $J_{5,6a}$ = 4.2 Hz, $J_{5,6b}$ = 2.1 Hz, H-5), 3.90 (dd, 1H, $J_{6a,6b}$ = 12.2 Hz, $J_{5,6b}$ = 2.2 Hz, H-6b), 3.73 (dd, 1H, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 9.7 Hz, H-3), 3.45 (s, 3H, CH_3), 2.10, 2.00, 1.94 (s, 9H, C(O)CH_3 x 3); ^{13}C NMR ($CDCl_3$) δ 170.8, 170.0, 169.4, (*C*(O)CH_3 x 3), 150.6-120.1 (12C, Ph x 2), 95.6 (d, $^2J_{1,P}$ = 6.3 Hz, C-1), 77.9 (C-3), 71.9 (d, $^3J_{1,P}$ = 7.1 Hz, C-2), 70.3 (C-5), 68.7 (C-4), 61.5 (C-6), 60.6 (CH_3), 20.9, 20.8, 20.7 (C(O)*C*H_3 x 3); ^{31}P NMR ($CDCl_3$) δ -13.98 (s, 1P, P-1); LRMS *m/z* calcd for $C_{25}H_{29}O_{12}P$ $[M+Na]^+$: 575.1. Found 575.0.

Diphenyl 2,4,6-tri-*O*-acetyl-3-*O*-butyl-α-D-glucopyranosyl-1-phosphate (6b)

Compound **5b** (R_F = 0.43 (hexanes/EtOAc, 67:33)), a colorless liquid, was provided by silica gel chromatography (hexanes/EtOAc, 72:28) (690 mg, 79%) and immediately carried onto the subsequent phosphorylation. Chromatographic purification (hexanes/EtOAc, 78:22) furnished compound **6b** as a colorless

[3] Han, X. B.; Jiang, H.; Schmidt, R. R. *Liebigs Ann. Chem.* **1993**, *8*, 853-8.

liquid (602 mg, 68%); R_F = 0.26 (hexanes/EtOAc, 75:25); ^{1}H NMR ($CDCl_3$) δ 7.38-7.20 (m, 10H, Ph x 2), 6.06 (dd, 1H, $^1J_{C,H}$ = 183 Hz, $J_{1,P}$ = 6.6 Hz, $J_{1,2}$ = 3.3 Hz, H-1), 5.08 (dd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{3,4}$ = 10.0 Hz, H-4), 4.90 (ddd, 1H, $J_{2,3}$ = 10.0 Hz, $J_{1,2}$ = 3.2 Hz, $^4J_{1,P}$ = 3.2 Hz, H-2), 4.14 (dd, 1H, $^2J_{6a,6b}$ = 12.5 Hz, $J_{5,6a}$ = 4.2 Hz, H-6a), 4.01 (ddd, 1H, $J_{4,5}$ = 10.3 Hz, $J_{5,6a}$ = 4.1 Hz, $J_{5,6b}$ = 2.1 Hz, H-5), 3.89 (dd, 1H, $J_{6a,6b}$ = 12.5 Hz, $J_{5,6b}$ = 2.2 Hz, H-6b), 3.79 (dd, 1H, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 9.8 Hz, H-3), 3.56 (m, 2H, OC*H*$_2$), 2.08, 2.00, 1.92 (s, 9H, C(O)C*H*$_3$ x 3), 1.46 (m, 2H, OCH_2CH_2), 1.30 (m, 2H, $OCH_2CH_2CH_2$), 0.89 (t, 3H, J = 7.5 Hz, $(CH_2)_3CH_3$); ^{13}C NMR ($CDCl_3$) δ 170.7, 169.9, 169.3, (*C*(O)CH_3 x 3), 150.5-120.1 (12C, Ph x 2), 95.7 (d, $^2J_{1,P}$ = 6.0 Hz, C-1), 76.5 (C-3), 73.0 (O*C*H_2), 72.1 (d, $^3J_{1,P}$ = 7.1 Hz, C-2), 70.3 (C-5), 68.9 (C-4), 61.5 (C-6), 32.3 (OCH_2CH_2), 20.8, 20.7, 20.6 (C(O)*C*H_3 x 3), 19.1 ($OCH_2CH_2CH_2$), 13.9 ($(CH_2)_3CH_3$); ^{31}P NMR ($CDCl_3$) δ -14.00 (s, 1P, P-1); LRMS *m/z* calcd for $C_{28}H_{35}O_{12}P$ $[M+Na]^+$: 617.2. Found 617.2.

Diphenyl 2,4,6-tri-*O*-acetyl-3-*O*-hexyl-α-D-glucopyranosyl-1-phosphate (6c)

Diethyl ether was used instead of dichloromethane as an extraction solvent *en route* to compound **5c** (R_F = 0.30 (hexanes/EtOAc, 70:30)), a colorless liquid, which was provided by silica gel chromatography (hexanes/EtOAc, 63:37) (772 mg, 82%) and immediately carried onto the subsequent phosphorylation. Diethyl ether was again used instead of dichloromethane as an extraction solvent for compound **6c**, a colorless liquid, which was isolated by chromatographic purification (hexanes/EtOAc, 75:25) (538 mg, 58%); R_F = 0.29 (hexanes/EtOAc, 75:25); ^{1}H NMR ($CDCl_3$) δ 7.38-7.20 (m, 10H, Ph x 2), 6.06 (dd, 1H, $^1J_{C,H}$ = 180 Hz, $J_{1,P}$ = 6.5 Hz, $J_{1,2}$ = 3.4 Hz, H-1), 5.08 (dd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{3,4}$ = 10.0 Hz, H-4), 4.90 (ddd, 1H, $J_{2,3}$ = 9.9 Hz, $J_{1,2}$ = 3.0 Hz, $^4J_{1,P}$ = 3.0 Hz, H-2), 4.14 (dd, 1H, $^2J_{6a,6b}$ = 12.5 Hz, $J_{5,6a}$ = 4.2 Hz, H-6a), 4.01 (ddd, 1H, $J_{4,5}$ = 10.4 Hz, $J_{5,6a}$ = 4.1 Hz, $J_{5,6b}$ = 2.0 Hz, H-5), 3.89 (dd, 1H, $J_{6a,6b}$ = 12.6 Hz, $J_{5,6b}$ = 2.1 Hz, H-6b), 3.79 (dd, 1H, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 9.7 Hz, H-3), 3.55 (m, 2H, OC*H*$_2$), 2.08, 2.00, 1.92 (s, 9H, C(O)C*H*$_3$ x 3), 1.47 (m, 2H, OCH_2CH_2), 1.28 (m, 6H, $OCH_2CH_2(CH_2)_3CH_3$), 0.88 (t, 3H, J = 6.8 Hz, $O(CH_2)_5CH_3$); ^{13}C NMR ($CDCl_3$) δ 170.8, 169.9, 169.3, (*C*(O)CH_3 x 3), 150.5-120.1 (12C, Ph x 2), 95.7 (d, $^2J_{1,P}$ = 6.0 Hz, C-1), 76.5 (C-3), 73.4 (O*C*H_2), 72.1 (d, $^3J_{1,P}$ = 7.3 Hz, C-2), 70.4 (C-5), 68.9 (C-4), 61.5 (C-6), 31.7, 25.8, 22.7 ($OCH_2CH_2(CH_2)_3CH_3$), 30.3 (OCH_2CH_2),

20.9, 20.8, 20.6 (C(O)*C*H$_3$ x 3), 14.2 (O(CH$_2$)$_5$*C*H$_3$); ^{31}P NMR (CDCl$_3$) δ -14.00 (s, 1P, P-1); LRMS *m/z* calcd for $C_{30}H_{39}O_{12}P$ $[M+Na]^+$: 645.2. Found 645.1.

Diphenyl 2,4,6-tri-*O*-acetyl-3-*O*-octyl-α-D-glucopyranosyl-1-phosphate (6d)

Diethyl ether was used instead of dichloromethane as an extraction solvent *en route* to compound **5d** (R_F = 0.27 (hexanes/EtOAc, 67:33)), a colorless liquid which was provided by silica gel chromatography (hexanes/EtOAc, 63:37) (625 mg, 62%) and immediately carried onto the subsequent phosphorylation. Chromatographic purification (hexanes/EtOAc, 81:19) furnished compound **6d** as a colorless liquid (717 mg, 74%); R_F = 0.45 (hexanes/EtOAc, 67:33); ^{1}H NMR (CDCl$_3$) δ 7.38-7.20 (m, 10H, Ph x 2), 6.06 (dd, 1H, $^1J_{C,H}$ = 181 Hz, $J_{1,P}$ = 6.6 Hz, $J_{1,2}$ = 3.4 Hz, H-1), 5.08 (dd, 1H, $J_{4,5}$ = 10.2 Hz, $J_{3,4}$ = 10.2 Hz, H-4), 4.90 (ddd, 1H, $J_{2,3}$ = 10.1 Hz, $J_{1,2}$ = 3.2 Hz, $^4J_{1,P}$ = 3.2 Hz, H-2), 4.14 (dd, 1H, $^2J_{6a,6b}$ = 12.5 Hz, $J_{5,6a}$ = 4.2 Hz, H-6a), 4.01 (ddd, 1H, $J_{4,5}$ = 10.2 Hz, $J_{5,6a}$ = 3.9 Hz, $J_{5,6b}$ = 2.0 Hz, H-5), 3.89 (dd, 1H, $J_{6a,6b}$ = 12.6 Hz, $J_{5,6b}$ = 2.1 Hz, H-6b), 3.78 (dd, 1H, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 9.8 Hz, H-3), 3.55 (m, 2H, OC*H*$_2$), 2.08, 2.00, 1.92 (s, 9H, C(O)C*H*$_3$ x 3), 1.47 (m, 2H, OCH$_2$C*H*$_2$), 1.34-1.19 (m, 10H, OCH$_2$CH$_2$(C*H*$_2$)$_5$CH$_3$), 0.88 (t, 3H, *J* = 7.1 Hz, (CH$_2$)$_7$C*H*$_3$); ^{13}C NMR (CDCl$_3$) δ 170.8, 169.9, 169.3, (*C*(O)CH$_3$ x 3), 150.6-120.1 (12C, Ph x 2), 95.7 (d, $^2J_{1,P}$ = 6.1 Hz, C-1), 76.5 (C-3), 73.5 (O*C*H$_2$), 72.1 (d, $^3J_{1,P}$ = 7.2 Hz, C-2), 70.4 (C-5), 68.9 (C-4), 61.5 (C-6), 32.0, 29.5, 29.4, 26.1, 22.8 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 30.3 (OCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$), 20.9, 20.8, 20.6 (C(O)*C*H$_3$ x 3), 14.2 ((CH$_2$)$_7$*C*H$_3$); ^{31}P NMR (CDCl$_3$) δ -14.00 (s, 1P, P-1); LRMS *m/z* calcd for $C_{32}H_{43}O_{12}P$ $[M+Na]^+$: 673.2. Found 673.3.

Diphenyl 2,4,6-tri-*O*-acetyl-3-*O*-dodecyl-α-D-glucopyranosyl-1-phosphate (6e)

Diethyl ether was used instead of dichloromethane as an extraction solvent *en route* to compound **5e**[4] (R_F = 0.29 (hexanes/EtOAc, 67:33)), a colorless liquid, which was not purified by silica gel chromatography (675 mg, 59%). For the phosphorylation, diethyl ether was again used instead of dichloromethane as an extraction solvent, which was isolated by chromatographic purification (hexanes/EtOAc, 80:20) to furnish compound **6e**

[4] Miethchen, R.; Holz, J.; Prade, H.; Peters, D. *Ger. (East)* **1991**, 3 pp.

as a colorless liquid (463 mg, 44%); R_F = 0.38 (hexanes/EtOAc, 75:25); ^{1}H NMR ($CDCl_3$) δ 7.38-7.20 (m, 10H, Ph x 2), 6.05 (dd, 1H, $^1J_{C,H}$ = 180 Hz, $J_{1,P}$ = 6.6 Hz, $J_{1,2}$ = 3.4 Hz, H-1), 5.08 (dd, 1H, $J_{4,5}$ = 10.3 Hz, $J_{3,4}$ = 9.7 Hz, H-4), 4.90 (ddd, 1H, $J_{2,3}$ = 10.0 Hz, $J_{1,2}$ = 3.1 Hz, $^4J_{1,P}$ = 3.1 Hz, H-2), 4.14 (dd, 1H, $^2J_{6a,6b}$ = 12.5 Hz, $J_{5,6a}$ = 4.2 Hz, H-6a), 4.01 (ddd, 1H, $J_{4,5}$ = 10.4 Hz, $J_{5,6a}$ = 4.1 Hz, $J_{5,6b}$ = 2.1 Hz, H-5), 3.89 (dd, 1H, $J_{6a,6b}$ = 12.5 Hz, $J_{5,6b}$ = 2.1 Hz, H-6b), 3.79 (dd, 1H, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 9.8 Hz, H-3), 3.55 (m, 2H, OC*H*$_2$), 2.08, 2.00, 1.92 (s, 9H, C(O)C*H*$_3$ x 3), 1.47 (m, 2H, OCH_2CH_2), 1.33-1.19 (m, 18H, $OCH_2CH_2(CH_2)_9CH_3$), 0.88 (t, 3H, *J* = 6.7 Hz, $O(CH_2)_{11}CH_3$); ^{13}C NMR ($CDCl_3$) δ 170.8, 169.9, 169.3, (*C*(O)CH_3 x 3), 150.6-120.1 (12C, Ph x 2), 95.7 (d, $^2J_{1,P}$ = 6.1 Hz, C-1), 76.6 (C-3), 73.5 (O*C*H_2), 72.1 (d, $^3J_{1,P}$ = 7.3 Hz, C-2), 70.4 (C-5), 68.9 (C-4), 61.5 (C-6), 32.1, 29.8, 29.8, 29.8, 29.8, 29.6, 29.5, 26.1, 22.8 ($OCH_2CH_2(CH_2)_9CH_3$), 30.4 ($OCH_2CH_2(CH_2)_9CH_3$), 20.9, 20.8, 20.7 (C(O)*C*H_3 x 3), 14.2 ($O(CH_2)_{11}CH_3$); ^{31}P NMR ($CDCl_3$) δ -14.00 (s, 1P, P-1); LRMS *m/z* calcd for $C_{36}H_{51}O_{12}P$ $[M+Na]^+$: 729.3. Found 729.1.

Diphenyl 2,4,6-tri-*O*-acetyl-3-*O*-hexadecyl-α-D-glucopyranosyl-1-phosphate (6f)

Chloroform was used instead of dichloromethane as an extraction solvent *en route* to compound **5f**[4] (R_F = 0.21 (hexanes/EtOAc, 67:33)), a white solid, which was provided by silica gel chromatography (hexanes/EtOAc, 67:33) (524 mg, 41%) and immediately carried onto the subsequent phosphorylation. Chromatographic purification (hexanes/EtOAc, 80:20) furnished compound **6f** as a colorless liquid (625 mg, 55%); R_F = 0.25 (hexanes/EtOAc, 80:20); ^{1}H NMR ($CDCl_3$) δ 7.39-7.18 (m, 10H, Ph x 2), 6.06 (dd, 1H, $^1J_{C,H}$ = 180 Hz, $J_{1,P}$ = 6.6 Hz, $J_{1,2}$ = 3.3 Hz, H-1), 5.08 (dd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{3,4}$ = 10.0 Hz, H-4), 4.90 (ddd, 1H, $J_{2,3}$ = 10.0 Hz, $J_{1,2}$ = 3.0 Hz, $^4J_{1,P}$ = 3.0 Hz, H-2), 4.14 (dd, 1H, $^2J_{6a,6b}$ = 12.6 Hz, $J_{5,6a}$ = 4.3 Hz, H-6a), 4.01 (ddd, 1H, $J_{4,5}$ = 10.3 Hz, $J_{5,6a}$ = 3.9 Hz, $J_{5,6b}$ = 2.1 Hz, H-5), 3.89 (dd, 1H, $J_{6a,6b}$ = 12.5 Hz, $J_{5,6b}$ = 2.2 Hz, H-6b), 3.79 (dd, 1H, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 9.8 Hz, H-3), 3.54 (m, 2H, OC*H*$_2$), 2.08, 2.00, 1.92 (s, 9H, C(O)C*H*$_3$ x 3), 1.47 (m, 2H, OCH_2CH_2), 1.33-1.19 (m, 26H, $OCH_2CH_2(CH_2)_{13}CH_3$), 0.88 (t, 3H, *J* = 7.1 Hz, $O(CH_2)_{15}CH_3$); ^{13}C NMR ($CDCl_3$) δ 170.8, 169.9, 169.3, (*C*(O)CH_3 x 3), 150.6-120.1 (12C, Ph x 2), 95.7 (d, $^2J_{1,P}$ = 6.2 Hz, C-1), 76.5 (C-3), 73.4 (O*C*H_2), 72.1 (d, $^3J_{1,P}$ = 7.2 Hz, C-2), 70.4 (C-5), 68.9 (C-4), 61.5 (C-6), 32.0, 29.8, 29.8, 29.8, 29.8,

29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 26.1, 22.8 ($OCH_2CH_2(\mathit{C}H_2)_{13}CH_3$), 30.3 ($OCH_2\mathit{C}H_2(CH_2)_{13}CH_3$), 20.9, 20.7, 20.6 ($C(O)\mathit{C}H_3$ x 3), 14.2 ($O(CH_2)_{15}\mathit{C}H_3$); ^{31}P NMR ($CDCl_3$) δ -14.00 (s, 1P, P-1); LRMS *m/z* calcd for $C_{40}H_{59}O_{12}P$ $[M+Na]^+$: 785.4. Found 785.4.

Diphenyl 2,4,6-tri-*O*-acetyl-3-*O*-(2-methylpropyl)-α-D-glucopyranosyl-1-phosphate (6g)

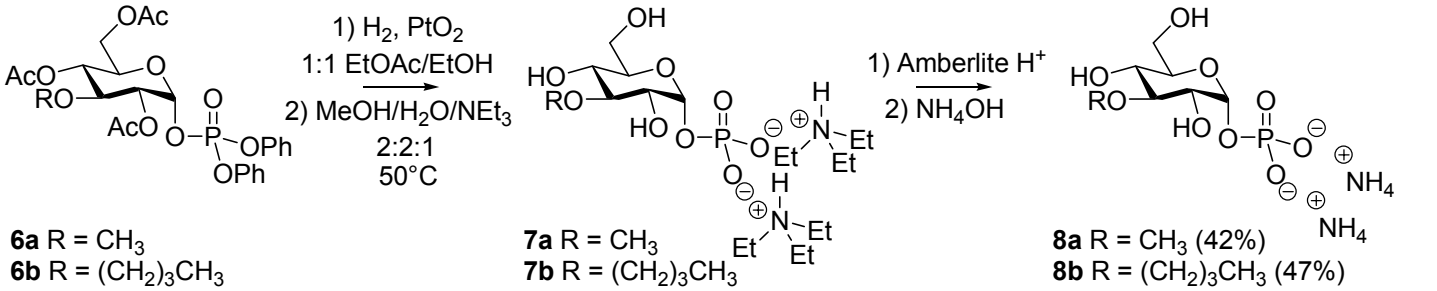
Compound **5g** (R_F = 0.23 (hexanes/EtOAc, 67:33)), a colorless liquid, was provided by silica gel chromatography (hexanes/EtOAc, 60:40) (341 mg, 39%) and immediately carried onto the subsequent phosphorylation. Chromatographic purification (hexanes/EtOAc, 71:29) furnished compound **6g** as a colorless liquid (585 mg, 66%); R_F = 0.36 (hexanes/EtOAc, 66:33); ^{1}H NMR ($CDCl_3$) δ 7.39-7.18 (m, 10H, Ph x 2), 6.05 (dd, 1H, $^1J_{C,H}$ = 180 Hz, $J_{1,P}$ = 6.5 Hz, $J_{1,2}$ = 3.2 Hz, H-1), 5.10 (dd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{3,4}$ = 10.0 Hz, H-4), 4.92 (ddd, 1H, $J_{2,3}$ = 9.9 Hz, $J_{1,2}$ = 3.0 Hz, $^4J_{1,P}$ = 3.0 Hz, H-2), 4.14 (dd, 1H, $^2J_{6a,6b}$ = 12.6 Hz, $J_{5,6a}$ = 4.2 Hz, H-6a), 4.01 (ddd, 1H, $J_{4,5}$ = 10.4 Hz, $J_{5,6a}$ = 4.2 Hz, $J_{5,6b}$ = 2.3 Hz, H-5), 3.90 (dd, 1H, $J_{6a,6b}$ = 12.5 Hz, $J_{5,6b}$ = 2.2 Hz, H-6b), 3.78 (dd, 1H, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 9.8 Hz, H-3), 3.37 (dd, 1H, J = 6.2 Hz, ^2J = 8.4 Hz, $OC\mathit{H}_{2a}$), 3.28 (dd, 1H, J = 6.4 Hz, ^2J = 8.8 Hz, $OC\mathit{H}_{2b}$), 2.08, 2.00, 1.92 (s, 9H, $C(O)C\mathit{H}_3$ x 3), 1.75 (nonet, 1H, J = 6.6 Hz, $OCH_2C\mathit{H}$), 0.84 (d, 6H, J = 6.6 Hz, $OCH_2CH(C\mathit{H}_3)_2$); ^{13}C NMR ($CDCl_3$) δ 170.8, 170.0, 169.3, ($\mathit{C}(O)CH_3$ x 3), 150.6-120.2 (12C, Ph x 2), 95.8 (d, $^2J_{1,P}$ = 6.1 Hz, C-1), 80.3 ($O\mathit{C}H_2$), 76.7 (C-3), 72.1 (d, $^3J_{1,P}$ = 7.2 Hz, C-2), 70.4 (C-5), 68.9 (C-4), 61.5 (C-6), 29.0 ($OCH_2\mathit{C}H$), 20.9, 20.8, 20.6 ($C(O)\mathit{C}H_3$ x 3), 19.2, 19.2 ($OCH_2CH(\mathit{C}H_3)_2$); ^{31}P NMR ($CDCl_3$) δ -14.00 (s, 1P, P-1); LRMS *m/z* calcd for $C_{28}H_{35}O_{12}P$ $[M+Na]^+$: 617.2. Found 617.2.

Diphenyl 2,4,6-tri-*O*-acetyl-3-*O*-(2-ethylbutyl)-α-D-glucopyranosyl-1-phosphate (6h)

Compound **5h** (R_F = 0.23 (hexanes/EtOAc, 67:33)), a white solid, was provided by silica gel chromatography (hexanes/EtOAc, 61:39) (612 mg, 65%) and immediately carried onto the subsequent phosphorylation. Chromatographic purification (hexanes/EtOAc, 78:22) furnished compound **6h** as a colorless liquid (724 mg, 78%); R_F = 0.24 (hexanes/EtOAc, 78:22); ^{1}H NMR ($CDCl_3$) δ 7.39-7.17 (m, 10H, Ph x 2), 6.05 (dd, 1H, $^1J_{C,H}$ =

180 Hz, $J_{1,P}$ = 6.6 Hz, $J_{1,2}$ = 3.4 Hz, H-1), 5.09 (dd, 1H, $J_{4,5}$ = 10.2 Hz, $J_{3,4}$ = 9.5 Hz, H-4), 4.91 (ddd, 1H, $J_{2,3}$ = 10.0 Hz, $J_{1,2}$ = 3.2 Hz, $^{4}J_{1,P}$ = 3.2 Hz, H-2), 4.13 (dd, 1H, $^{2}J_{6a,6b}$ = 12.6 Hz, $J_{5,6a}$ = 4.4 Hz, H-6a), 4.01 (ddd, 1H, $J_{4,5}$ = 10.4 Hz, $J_{5,6a}$ = 4.2 Hz, $J_{5,6b}$ = 2.1 Hz, H-5), 3.89 (dd, 1H, $J_{6a,6b}$ = 12.5 Hz, $J_{5,6b}$ = 2.2 Hz, H-6b), 3.78 (dd, 1H, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 9.7 Hz, H-3), 3.52 (dd, 1H, J = 4.6 Hz, ^{2}J = 9.0 Hz, OCH_{2a}), 3.42 (dd, 1H, J = 4.4 Hz, ^{2}J = 8.8 Hz, OCH_{2b}), 2.08, 2.00, 1.92 (s, 9H, C(O)CH_3 x 3), 1.28 (m, 5H, $OCH_2CH(CH_2CH_3)_2$), 0.83 (t, 6H, J = 7.0 Hz, $OCH_2CH(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 170.8, 170.0, 169.3, (C(O)CH_3 x 3), 150.5-120.2 (12C, Ph x 2), 95.7 (d, $^{2}J_{1,P}$ = 6.1 Hz, C-1), 76.6 (C-3), 75.4 (OCH_2), 72.3 (d, $^{3}J_{1,P}$ = 7.3 Hz, C-2), 70.4 (C-5), 69.0 (C-4), 61.5 (C-6), 42.0 (OCH_2CH), 23.2, 23.2 ($OCH_2CH(CH_2CH_3)_2$), 20.9, 20.8, 20.6 (C(O)CH_3 x 3), 11.3, 11.3 ($OCH_2CH(CH_2CH_3)_2$); ^{31}P NMR ($CDCl_3$) δ -13.99 (s, 1P, P-1); LRMS *m/z* calcd for $C_{30}H_{39}O_{12}P$ $[M+Na]^+$: 645.2. Found 645.2.

General Procedure for Deprotection and Ion Exchange (7a-h and 8a-h, respectively)



6a R = CH_3
6b R = $(CH_2)_3CH_3$
6c R = $(CH_2)_5CH_3$
6d R = $(CH_2)_7CH_3$
6e R = $(CH_2)_{11}CH_3$
6f R = $(CH_2)_{15}CH_3$
6g R = $CH_2CH(CH_3)_2$
6h R = $CH_2CH(CH_2CH_3)_2$

7a R = CH_3
7b R = $(CH_2)_3CH_3$
7c R = $(CH_2)_5CH_3$
7d R = $(CH_2)_7CH_3$
7e R = $(CH_2)_{11}CH_3$
7f R = $(CH_2)_{15}CH_3$
7g R = $CH_2CH(CH_3)_2$
7h R = $CH_2CH(CH_2CH_3)_2$

8a R = CH_3 (42%)
8b R = $(CH_2)_3CH_3$ (47%)
8c R = $(CH_2)_5CH_3$ (76%)
8d R = $(CH_2)_7CH_3$ (100%)
8e R = $(CH_2)_{11}CH_3$ (58%)
8f R = $(CH_2)_{15}CH_3$ (90%)
8g R = $CH_2CH(CH_3)_2$ (51%)
8h R = $CH_2CH(CH_2CH_3)_2$ (76%)

A solution of phosphorylated pyranoside (0.384 mmol) and platinium (IV) oxide (0.242 mmol) in 1:1 EtOH/EtOAc (4 mL) was shaken under H_2 in a Parr apparatus at 54 PSI for 2 h. The reaction mixture was filtered through Celite and concentrated. The residue was taken up in 2:2:1 MeOH/H_2O/NEt_3 (10 mL) and stirred at 50ºC for 36 h. Again, the mixture was concentrated and the residue was partitioned between H_2O (10 mL) and EtOAc (10 mL). The aqueous layer containing the triethyl ammonium salt (**7a-h**) was passed through Amberlite IR-120 PLUS(H) ion exchange resin. The resulting acidic aqueous fraction was immediately

adjusted to pH 8 with NH_4OH 0.1 M, concentrated to 5 mL, and lyophilized. Titration with NH_4OH 0.1 M and lyophilization was repeated twice more to remove NH_4OAc and isolate the ammonium salt (**8a-h**).

3-*O*-Methyl-α-D-glucopyranosyl phosphate diammonium salt (8a)[5]

Deacetylation was performed at rt and compound **8a** was isolated as a colorless foam (50 mg, 42%); ^{1}H NMR (D_2O) δ 5.35 (dd, 1H, $^1J_{C,H}$ = 176 Hz, $J_{1,P}$ = 7.2 Hz, $J_{1,2}$ = 3.0 Hz, H-1), 3.80 (ddd, 1H, $J_{4,5}$ = 9.6 Hz, $J_{5,6b}$ = 4.7 Hz, $J_{5,6a}$ = 2.0 Hz, H-5), 3.75 (dd, 1H, $^2J_{6a,6b}$ = 12.2 Hz, $J_{5,6a}$ = 2.0 Hz, H-6a), 3.65 (dd, 1H, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 4.9 Hz, H-6b), 3.52 (s, 3H, C*H*$_3$), 3.47 (m, 1H, H-2), 3.44 (m, 1H, H-3), 3.39 (m, 1H, H-4); ^{13}C NMR (D_2O) δ 94.2 (d, $^2J_{1,P}$ = 5.7 Hz, C-1), 82.8 (C-3), 72.3 (C-5), 71.4 (d, $^3J_{1,P}$ = 7.5 Hz, C-2), 69.0 (C-4), 60.5 (C-6), 60.0 (*C*H$_3$); ^{31}P NMR (D_2O) δ 0.77 (s, 1P, P-1); HRMS *m/z* calcd for $C_7H_{13}O_9P^{2-}$ $[M+H]^-$: 273.0386. Found 273.0390.

3-*O*-Butyl-α-D-glucopyranosyl phosphate diammonium salt (8b)

Compound **8b** was obtained as a colorless foam (63 mg, 47%); ^{1}H NMR (D_2O) δ 5.33 (dd, 1H, $^1J_{C,H}$ = 172 Hz, $J_{1,P}$ = 7.4 Hz, $J_{1,2}$ = 3.4 Hz, H-1), 3.79 (ddd, 1H, $J_{4,5}$ = 10.1 Hz, $J_{5,6b}$ = 5.0 Hz, $J_{5,6a}$ = 2.2 Hz, H-5), 3.75 (dd, 1H, $^2J_{6a,6b}$ = 12.5 Hz, $J_{5,6a}$ = 2.2 Hz, H-6a), 3.72 (t, 2H, J = 6.7 Hz, OC*H*$_2$), 3.63 (dd, 1H, $J_{6a,6b}$ = 12.5 Hz, $J_{5,6b}$ = 5.2 Hz, H-6b), 3.50 (dd, 1H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.2 Hz, H-3), 3.42 (ddd, 1H, $J_{2,3}$ = 9.6 Hz, $J_{1,2}$ = 3.3 Hz, $^4J_{2,P}$ = 2.0 Hz, H-2), 3.33 (dd, 1H, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.6 Hz, H-4), 1.49 (p, 2H, J = 7.0 Hz, OCH_2CH_2), 1.26 (sextet, 2H, J = 7.5 Hz, $O(CH_2)_2CH_2CH_3$), 0.79 (t, 3H, J = 7.8 Hz, $O(CH_2)_3CH_3$); ^{13}C NMR (D_2O) δ 94.1 (d, $^2J_{1,P}$ = 5.5 Hz, C-1), 81.5 (C-3), 73.1 (OCH_2), 72.3 (C-5), 71.8 (d, $^3J_{1,P}$ = 7.4 Hz, C-2), 69.3 (C-4), 60.7 (C-6), 31.5 (OCH_2CH_2), 18.5 ($OCH_2CH_2CH_2$), 13.1 ($O(CH_2)_3CH_3$); ^{31}P NMR (D_2O) δ 1.32 (s, 1P, P-1); HRMS *m/z* calcd for $C_{10}H_{19}O_9P^{2-}$ $[M+H]^-$: 315.0856. Found 315.0856.

3-*O*-Hexyl-α-D-glucopyranosyl phosphate diammonium salt (8c)

[5] Jiang, J.; Albermann, C.; Thorson, J. *ChemBioChem.* **2003**, *4*, 443-446.

Compound **8c** was obtained as a colorless foam (110 mg, 76%); ^{1}H NMR (D_2O) δ 5.34 (dd, 1H, $^{1}J_{C,H}$ = 173 Hz, $J_{1,P}$ = 6.9 Hz, $J_{1,2}$ = 3.0 Hz, H-1), 3.78 (m, 1H, H-5), 3.74 (m, 1H, H-6a), 3.70 (t, 2H, J = 6.6 Hz, OCH_2), 3.64 (dd, 1H, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6b}$ = 4.5 Hz, H-6b), 3.49 (dd, 1H, $J_{2,3}$ = 9.3 Hz, $J_{3,4}$ = 9.3 Hz, H-3), 3.44 (ddd, 1H, $J_{2,3}$ = 9.7 Hz, H-2), 3.35 (dd, 1H, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 1.50 (p, 2H, J = 7.0 Hz, OCH_2CH_2), 1.22 (m, 6H, $OCH_2CH_2(CH_2)_3CH_3$), 0.76 (m, 3H, $O(CH_2)_5CH_3$); ^{13}C NMR (D_2O) δ 94.4 (d, $^{2}J_{1,P}$ = 5.7 Hz, C-1), 81.4 (C-3), 73.4 (OCH_2), 72.4 (C-5), 71.6 (d, $^{3}J_{1,P}$ = 7.7 Hz, C-2), 69.1 (C-4), 60.6 (C-6), 30.9, 24.8, 22.0 ($OCH_2CH_2(CH_2)_3CH_3$), 29.2 (OCH_2CH_2), 13.4 ($O(CH_2)_5CH_3$); ^{31}P NMR (D_2O) δ 0.41 (s, 1P, P-1); HRMS *m/z* calcd for $C_{12}H_{23}O_9P^{2-}$ $[M+H]^-$: 343.1169. Found 343.1176.

3-*O*-Octyl-α-D-glucopyranosyl phosphate diammonium salt (8d)

Diethyl ether was used instead of ethyl acetate as an extraction solvent *en route* to compound **8d**, a colorless foam (66 mg, 42%); ^{1}H NMR (D_2O) δ 5.36 (dd, 1H, $^{1}J_{C,H}$ = 173 Hz, $J_{1,P}$ = 7.2 Hz, $J_{1,2}$ = 3.2 Hz, H-1), 3.78 (ddd, 1H, $J_{4,5}$ = 9.8 Hz, $J_{5,6b}$ = 5.0 Hz, $J_{5,6a}$ = 2.1 Hz, H-5), 3.75 (m, 1H, H-6a), 3.72 (t, 2H, J = 7.0 Hz, OCH_2), 3.66 (dd, 1H, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6b}$ = 4.9 Hz, H-6b), 3.50 (m, 1H, H-3), 3.45 (m, 1H, H-2), 3.37 (dd, 1H, $J_{3,4}$ = 9.4 Hz, $J_{4,5}$ = 9.4 Hz, H-4), 1.50 (p, 2H, J = 7.2 Hz, OCH_2CH_2), 1.30-1.12 (m, 10H, $OCH_2CH_2(CH_2)_5CH_3$), 0.77 (t, 3H, J = 7.0 Hz, $(CH_2)_7CH_3$); ^{13}C NMR (D_2O) δ 94.6 (d, $^{2}J_{1,P}$ = 5.9 Hz, C-1), 81.4 (C-3), 73.5 (OCH_2), 72.5 (C-5), 71.5 (d, $^{3}J_{1,P}$ = 7.7 Hz, C-2), 69.1 (C-4), 60.5 (C-6), 31.1, 28.5, 28.4, 25.1, 22.0 ($OCH_2CH_2(CH_2)_5CH_3$), 29.3 (OCH_2CH_2), 13.4 ($O(CH_2)_7CH_3$); ^{31}P NMR (D_2O) δ 0.12 (s, 1P, P-1); HRMS *m/z* calcd for $C_{14}H_{28}O_9P^{2-}$ $[M+H]^-$: 371.1482. Found 371.1490.

3-*O*-Dodecyl-α-D-glucopyranosyl phosphate diammonium salt (8e)

Deacetylation was performed at 70ºC instead of 50ºC and diethyl ether was used instead of ethyl acetate as an extraction solvent. Triethylamine (1 mL) was added before rotary evaporation to suppress the surfactant-like behavior of the salt. After the third NH_4OAc sublimation, the residue was dissolved in water and filtered through a short pad of Bio-Rad Chelex 100. The solution was then passed through Amberlite IR-120 PLUS(H) ion exchange resin, titrated with NH_4OH 0.1 M, and lyophilized to forge compound **8e** as a colorless foam (103

mg, 58%); ^{1}H NMR (MeOD) δ 5.48 (dd, 1H, $^{1}J_{C,H}$ = 173 Hz, $J_{1,P}$ = 6.9 Hz, $J_{1,2}$ = 3.3 Hz, H-1), 3.85 (ddd, 1H, $J_{4,5}$ = 9.8 Hz, $J_{5,6b}$ = 5.7 Hz, $J_{5,6a}$ = 2.1 Hz, H-5), 3.81 (m, 2H, OCH_2), 3.80 (m, 1H, H-6a), 3.63 (dd, 1H, $J_{6a,6b}$ = 11.6 Hz, $J_{5,6b}$ = 5.5 Hz, H-6b), 3.47 (dd, 1H, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 9.0 Hz, H-3), 3.42 (ddd, 1H, $J_{2,3}$ = 9.6 Hz, $J_{1,2}$ = 3.0 Hz, $^{4}J_{1,P}$ = 3.0 Hz, H-2), 3.32 (m, 1H, H-4), 1.62 (p, 2H, J = 7.3 Hz, OCH_2CH_2), 1.41-1.23 (m, 18H, $OCH_2CH_2(CH_2)_9CH_3$), 0.90 (t, 3H, J = 7.0 Hz, $(CH_2)_{11}CH_3$); ^{13}C NMR (MeOD) δ 96.6 (d, $^{2}J_{1,P}$ = 6.2 Hz, C-1), 83.6 (C-3), 74.6 (OCH_2), 74.5 (C-5), 74.0 (d, $^{3}J_{1,P}$ = 7.5 Hz, C-2), 71.4 (C-4), 62.8 (C-6), 33.1, 30.8, 30.8, 30.8, 30.8, 30.7, 30.5, 27.1, 23.7 ($OCH_2CH_2(CH_2)_9CH_3$), 31.4 (OCH_2CH_2), 14.4 ($O(CH_2)_{11}CH_3$); ^{31}P NMR (MeOD) δ -1.86 (s, 1P, P-1); HRMS *m/z* calcd for $C_{18}H_{35}O_9P^{2-}$ $[M+H]^-$: 427.2108. Found 427.2115.

3-*O*-Hexadecyl-α-D-glucopyranosyl phosphate diammonium salt (8f)

Deacetylation was performed at 70ºC instead of 50ºC and diethyl ether was used instead of ethyl acetate as an extraction solvent. Triethylamine (1 mL) was added before rotary evaporation to suppress the surfactant-like behavior of the salt. After the third NH_4OAc sublimation, the residue was dissolved in water and filtered through a short pad of Bio-Rad Chelex 100. The solution was then passed through Amberlite IR-120 PLUS(H) ion exchange resin, titrated with NH_4OH 0.1 M, and lyophilized to forge compound **8f** as a colorless foam (179 mg, 90%). Coupling constants are omitted from the ^{1}H NMR spectrum because of the compound's inherent insolubility in a variety of NMR solvents led to significant line-broadening; ^{1}H NMR (D_2O) δ 5.44 (d, 1H, $^{1}J_{C,H}$ = 174 Hz, H-1), 3.86 (m, 1H, H-5), 3.86 (m, 1H, H-6a), 3.74 (m, 2H, OCH_2), 3.69 (m, 1H, H-6b), 3.56 (m, 1H, H-2), 3.52 (m, 1H, H-3), 3.39 (m, 1H, H-4), 1.58 (m, 2H, OCH_2CH_2), 1.42-1.15 (m, 26H, $OCH_2CH_2(CH_2)_{13}CH_3$), 0.84 (m, 3H, $(CH_2)_{15}CH_3$); ^{13}C NMR (D_2O) δ 94.9 (d, $^{2}J_{1,P}$ = 5.1 Hz, C-1), 81.0 (C-3), 72.7 (C-5), 72.2 (OCH_2), 71.1 (d, $^{3}J_{1,P}$ = 7.3 Hz, C-2), 69.4 (C-4), 61.0 (C-6), 32.1, 30.3, 30.3, 30.3, 30.3, 30.3, 30.3, 30.3, 30.1, 30.1, 30.0, 29.7, 26.2, 22.7 ($OCH_2(CH_2)_{14}CH_3$), 13.8 ($O(CH_2)_{15}CH_3$); ^{31}P NMR (D_2O) δ -0.57 (s, 1P, P-1); HRMS *m/z* calcd for $C_{22}H_{43}O_9P^{2-}$ $[M+H]^-$: 483.2734. Found 483.2708.

3-*O*-(2-Methylpropyl)-α-D-glucopyranosyl phosphate diammonium salt (8g)

Compound **8g** was obtained as a colorless foam (69 mg, 51%); ^{1}H NMR (D_2O) δ 5.29 (dd, 1H, $^{1}J_{C,H}$ = 171 Hz, $J_{1,P}$ = 7.3 Hz, $J_{1,2}$ = 3.3 Hz, H-1), 3.76 (ddd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6b}$ = 4.8 Hz, $J_{5,6a}$ = 1.8 Hz, H-5), 3.72 (dd, 1H, $^{2}J_{6a,6b}$ = 12.3 Hz, $J_{5,6a}$ = 1.9 Hz, H-6a), 3.60 (dd, 1H, $J_{6a,6b}$ = 12.1 Hz, $J_{5,6b}$ = 5.2 Hz, H-6b), 3.47 (dd, 1H, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 3.46 (d, 2H, J = 6.1 Hz, OC*H*$_2$), 3.41 (m, 1H, H-2), 3.31 (dd, 1H, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 1.74 (nonet, 1H, J = 6.5 Hz, OCH_2CH), 0.81, 0.81 (d, 3H, J = 6.7 Hz, $OCH_2CH(CH_3)_2$); ^{13}C NMR (D_2O) δ 94.0 (d, $^{2}J_{1,P}$ = 5.6 Hz, C-1), 81.7 (C-3), 80.1 (OCH_2), 72.2 (C-5), 71.8 (d, $^{3}J_{1,P}$ = 7.2 Hz, C-2), 69.3 (C-4), 60.7 (C-6), 28.2 (OCH_2CH), 18.6, 18.6 ($OCH_2CH(CH_3)_2$); ^{31}P NMR (D_2O) δ 1.76 (s, 1P, P-1); HRMS *m/z* calcd for $C_{10}H_{19}O_9P^{2-}$ $[M+H]^-$: 315.0856. Found 315.0869.

3-*O*-(2-Ethylbutyl)-α-D-glucopyranosyl phosphate diammonium salt (8h)

Compound **8h** was obtained as a colorless foam (145 mg, 76%); ^{1}H NMR (D_2O) δ 5.32 (dd, 1H, $^{1}J_{C,H}$ = 172 Hz, $J_{1,P}$ = 4.6 Hz, $J_{1,2}$ = 3.0 Hz, H-1), 3.79 (m, 1H, H-5), 3.75 (d, 1H, $^{2}J_{6a,6b}$ = 12.6 Hz, H-6a), 3.63 (m, 1H, H-6b), 3.61 (m, 2H, OC*H*$_2$), 3.49 (dd, 1H, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 9.2 Hz, H-3), 3.42 (d, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 3.33 (dd, 1H, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 9.2 Hz, H-4), 1.39 (m, 1H, $OCH_2CH(CH_2CH_3)_2$), 1.25 (m, 4H, $OCH_2CH(CH_2CH_3)_2$), 0.76 (t, 6H, J = 6.7 Hz, $OCH_2CH(CH_2CH_3)_2$); ^{13}C NMR (D_2O) δ 94.1 (d, $^{2}J_{1,P}$ = 5.6 Hz, C-1), 81.7 (C-3), 75.7 (OCH_2), 72.3 (C-5), 71.8 (d, $^{3}J_{1,P}$ = 7.3 Hz, C-2), 69.3 (C-4), 60.7 (C-6), 41.0 (OCH_2CH), 22.5, 22.4 ($OCH_2CH(CH_2CH_3)_2$), 10.2, 10.2 ($OCH_2CH(CH_2CH_3)_2$); ^{31}P NMR (D_2O) δ 1.62 (s, 1P, P-1); HRMS *m/z* calcd for $C_{12}H_{23}O_9P^{2-}$ $[M+H]^-$: 343.1169. Found 343.1159.

^{1}H, ^{13}C and ^{31}P NMR Spectra of compounds 6a-h and 8a-h

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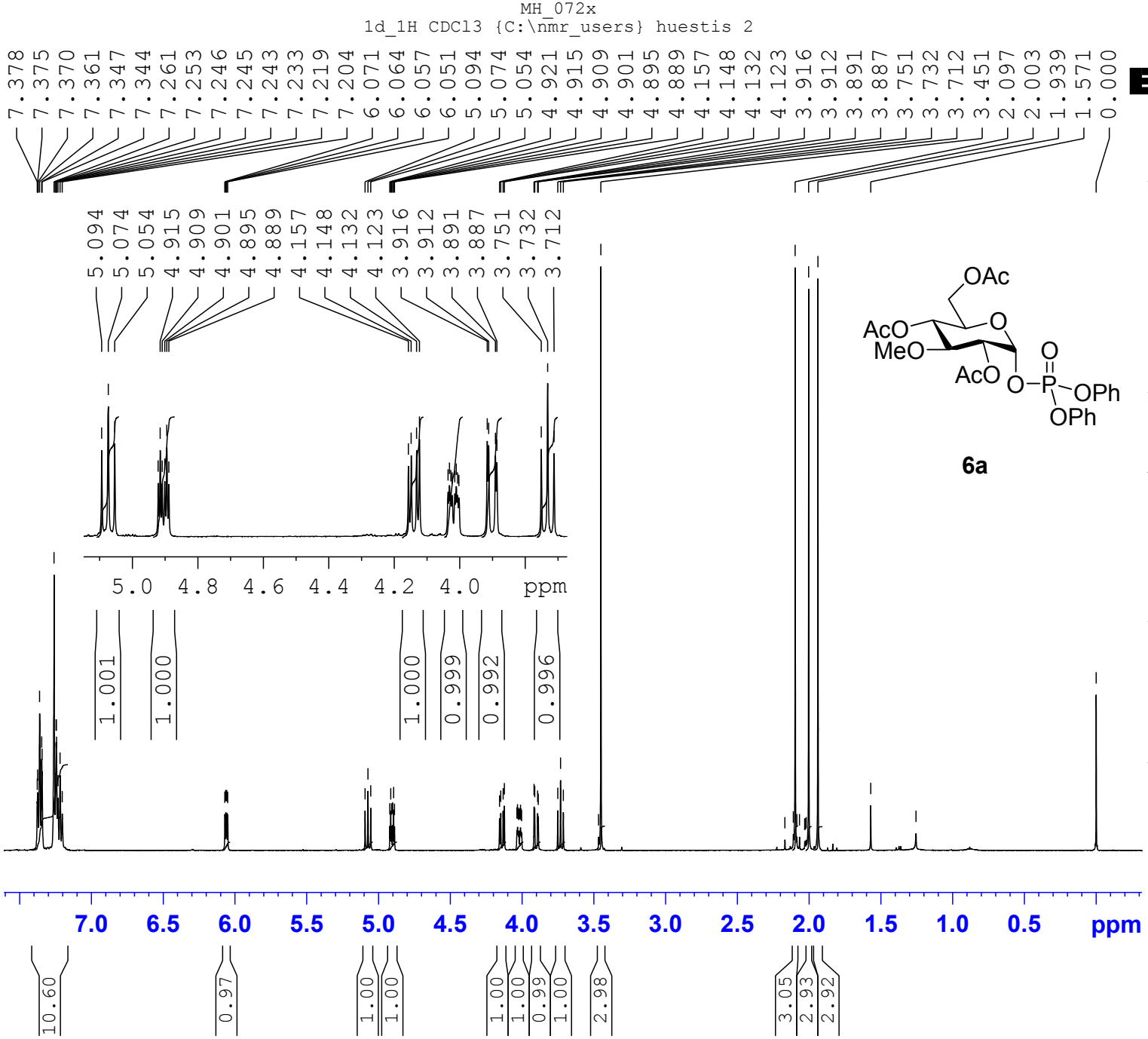

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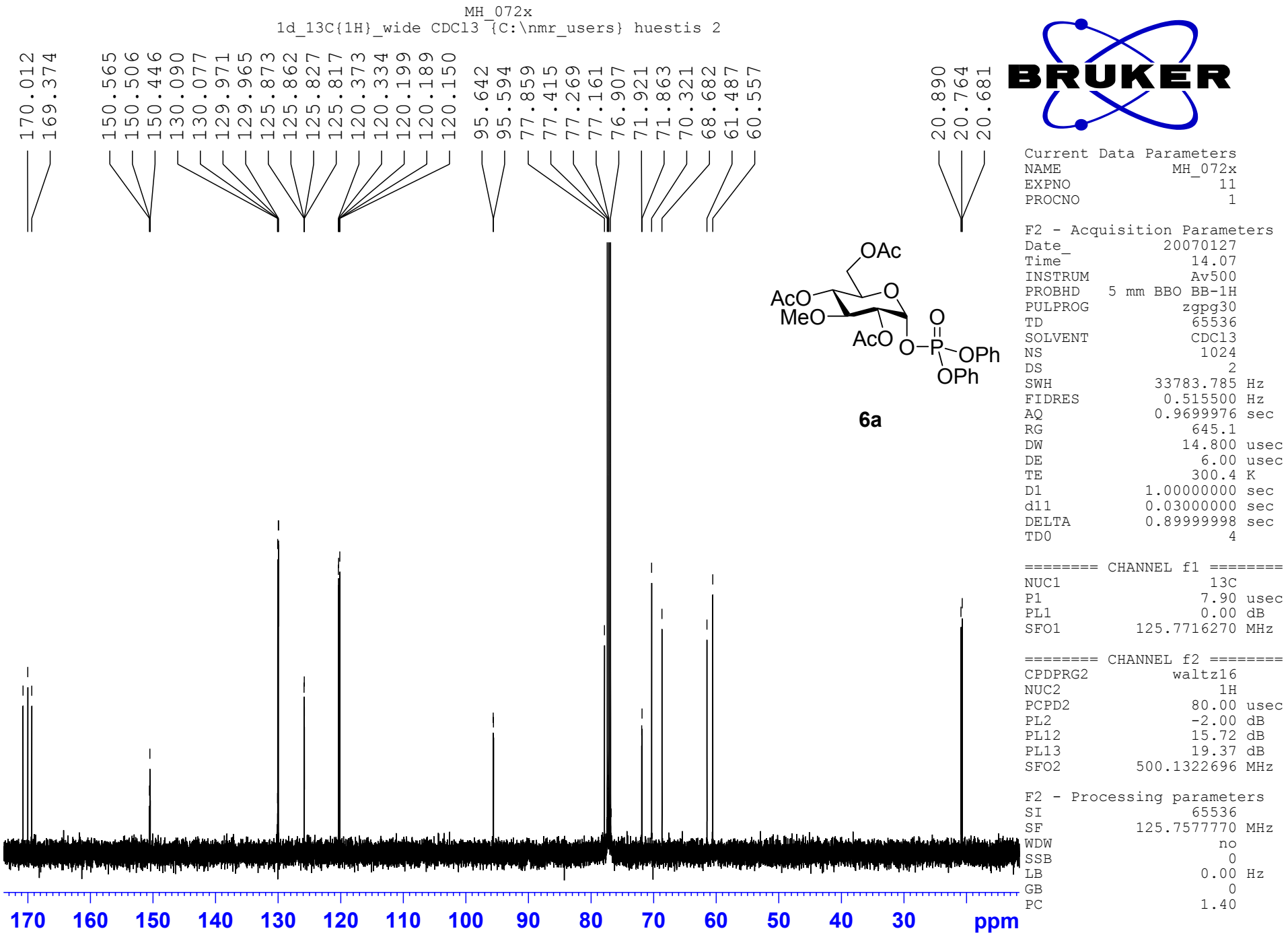


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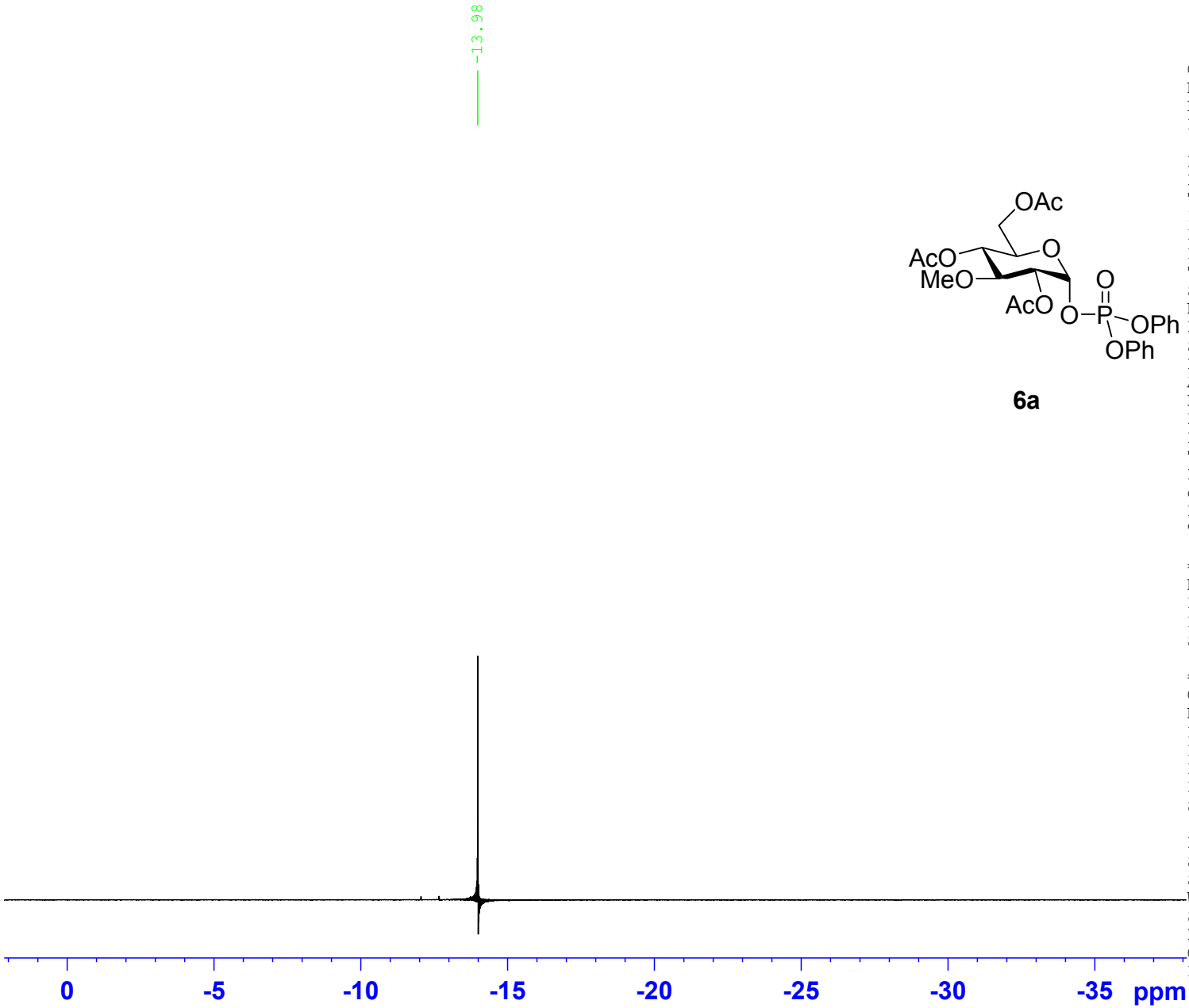

6a

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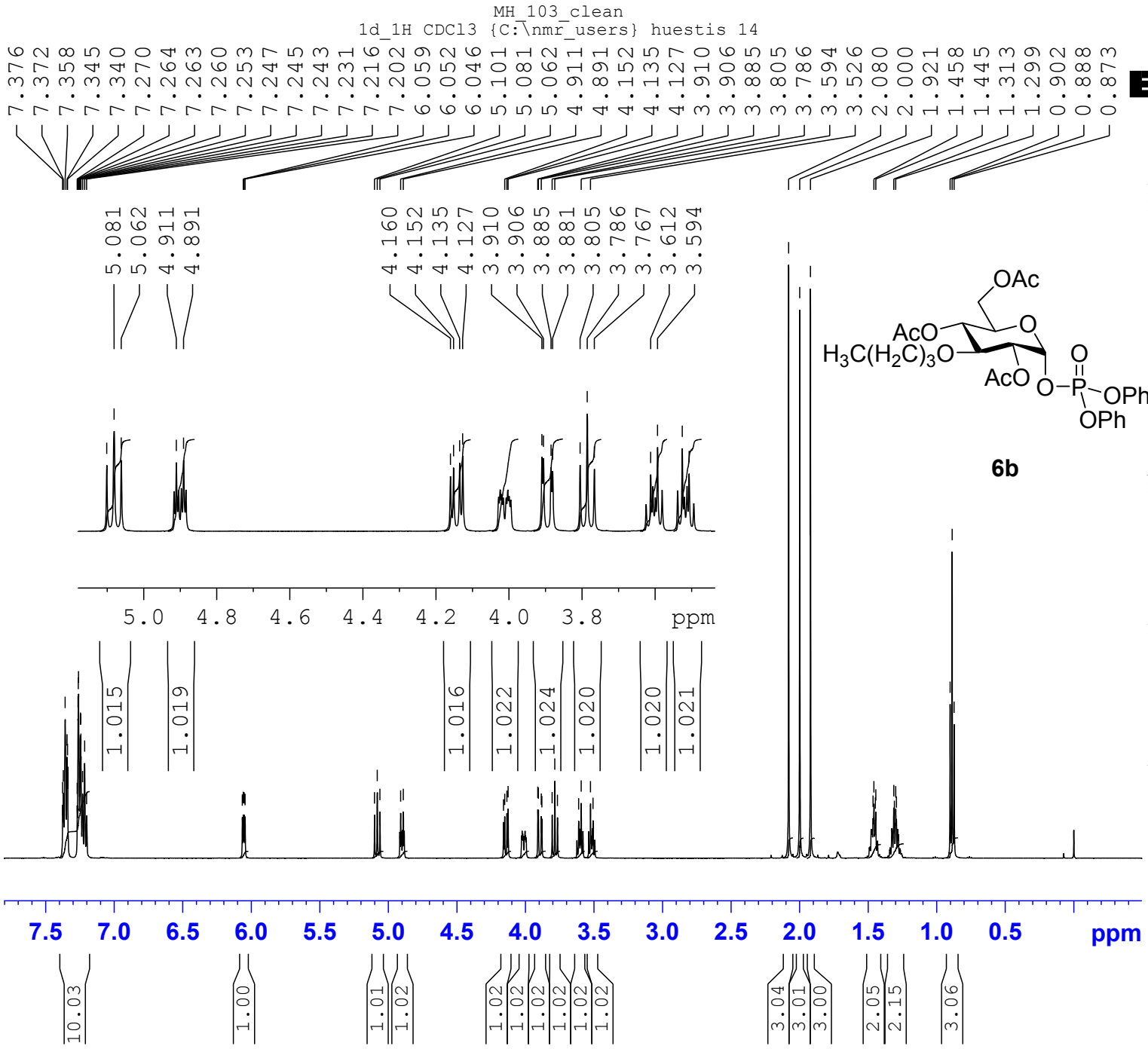

6b

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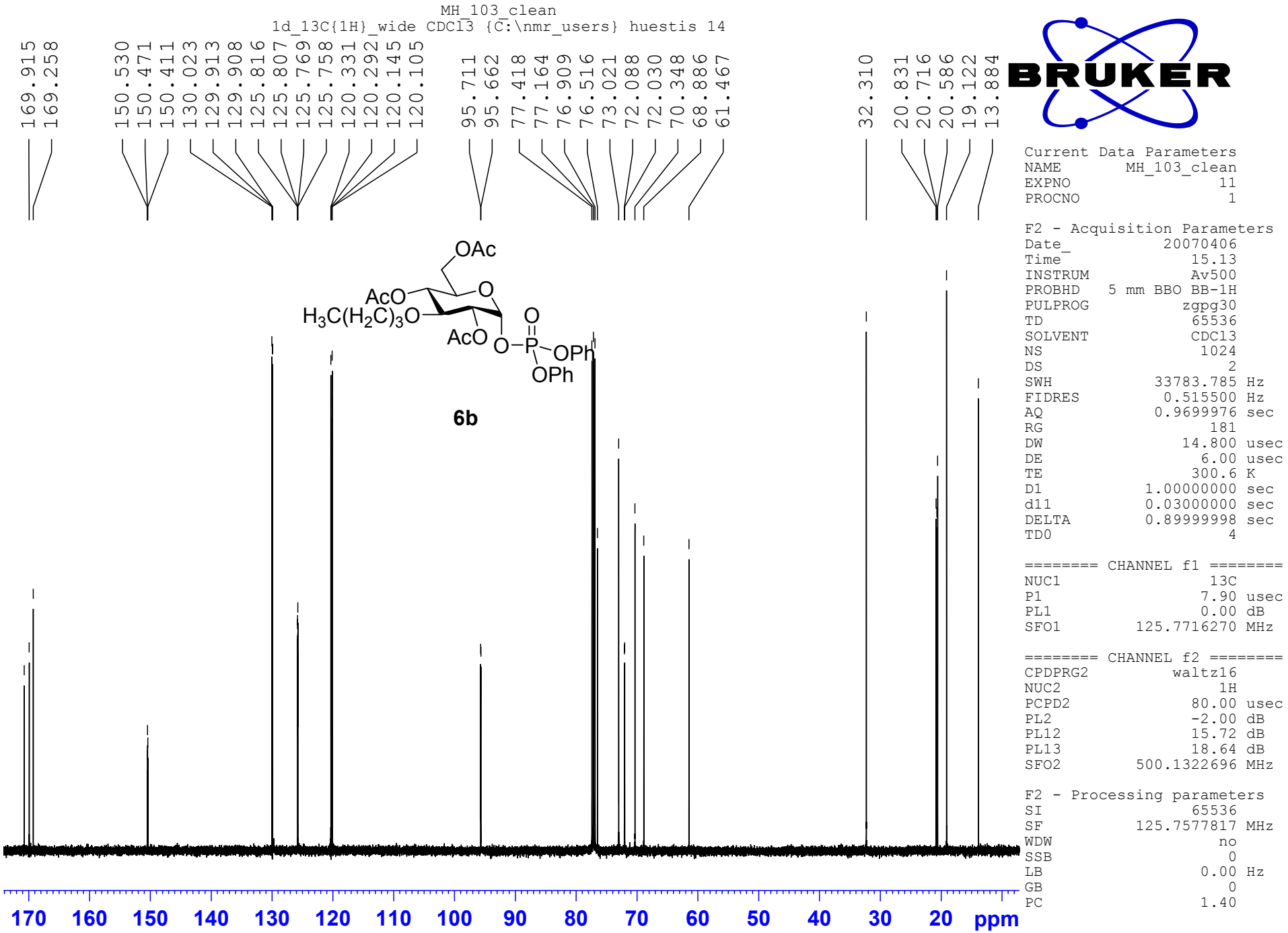

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TE 300.6 K
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d11 0.03000000 sec
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PL12 15.72 dB
PL13 18.64 dB
SFO2 500.1322696 MHz

F2 - Processing parameters
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SSB 0
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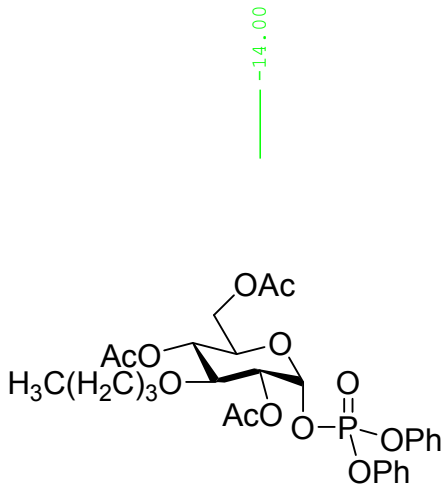
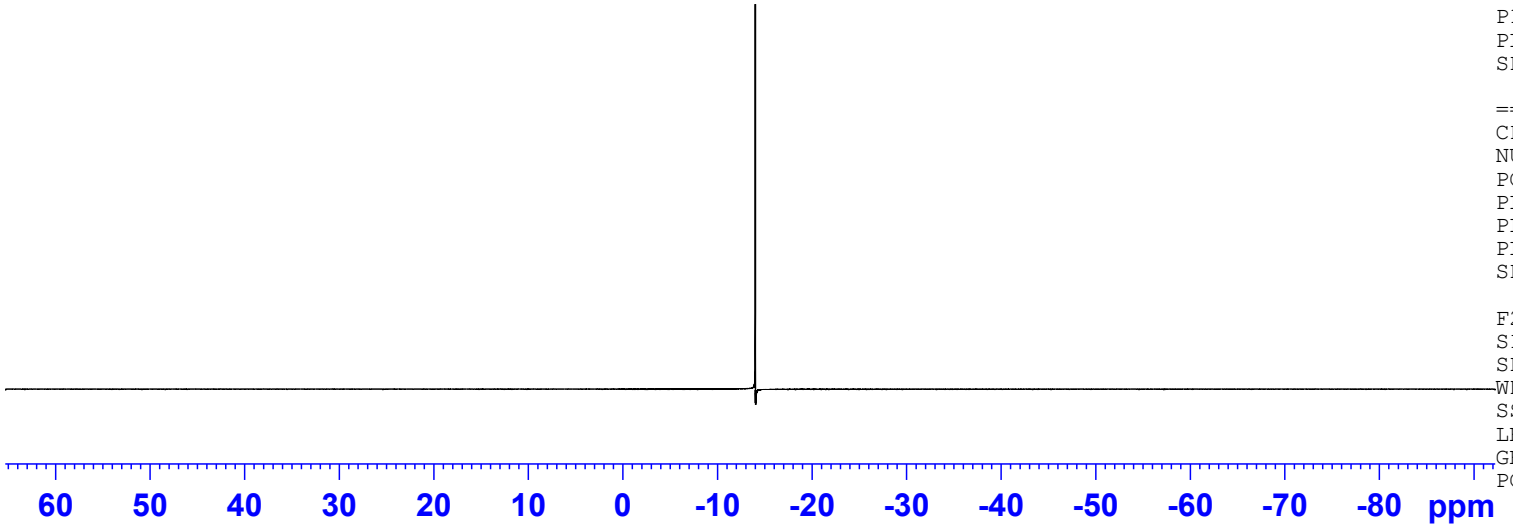
GB 0
PC 1.40

MH_103_clean
1d_31P{1H} CDCl3 {C:\nmr_users} huestis 14



6b



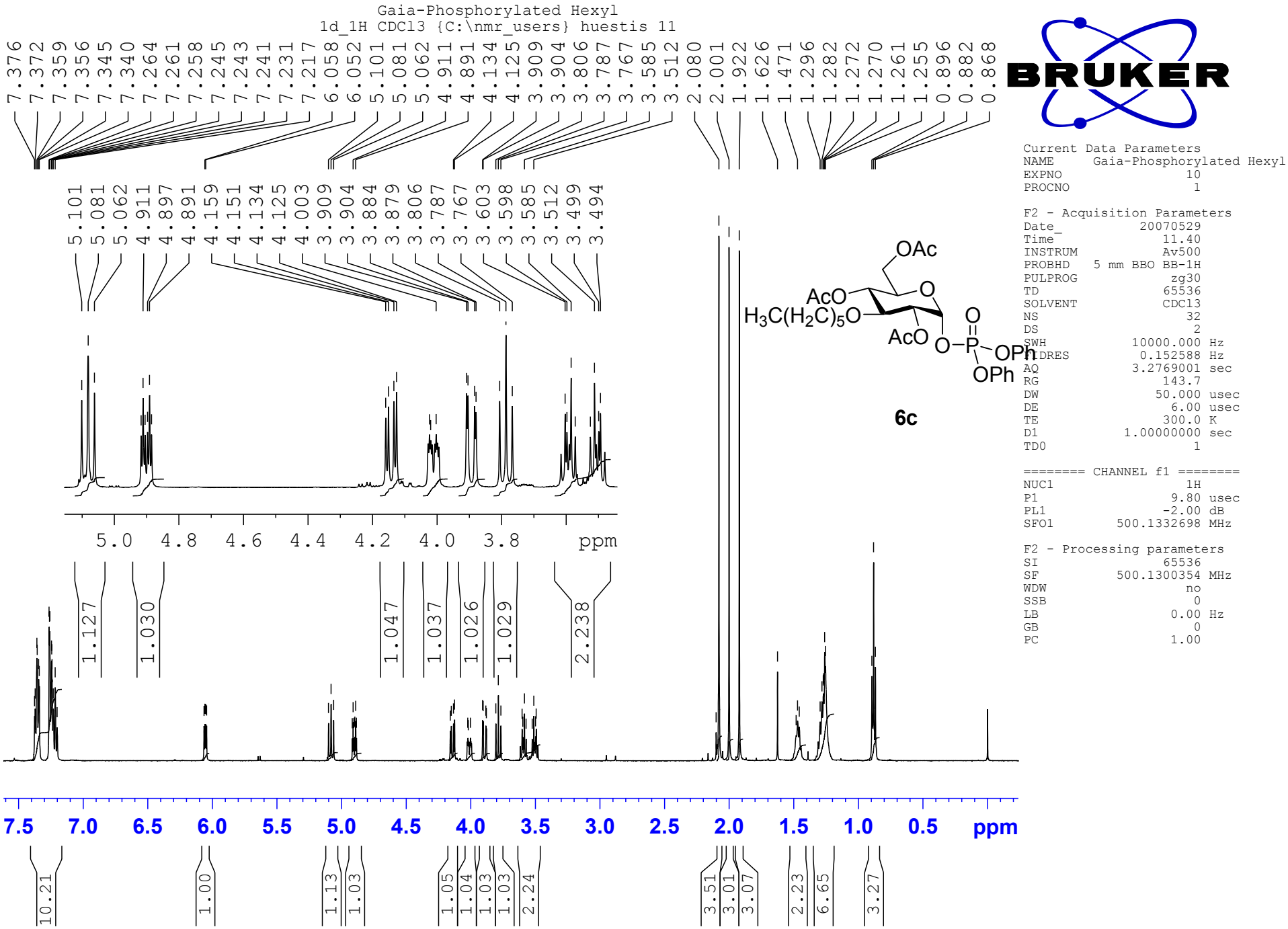
Current Data Parameters
NAME MH_103_clean
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070406
Time 15.48
INSTRUM Av500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 0
SWH 98039.219 Hz
FIDRES 1.495960 Hz
AQ 0.3342887 sec
RG 8192
DW 5.100 usec
DE 6.00 usec
TE 300.4 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 2

======== CHANNEL f1 ========
NUC1 31P
P1 8.41 usec
PL1 0.50 dB
SFO1 202.4664658 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 15.72 dB
PL13 18.64 dB
SFO2 500.1322696 MHz

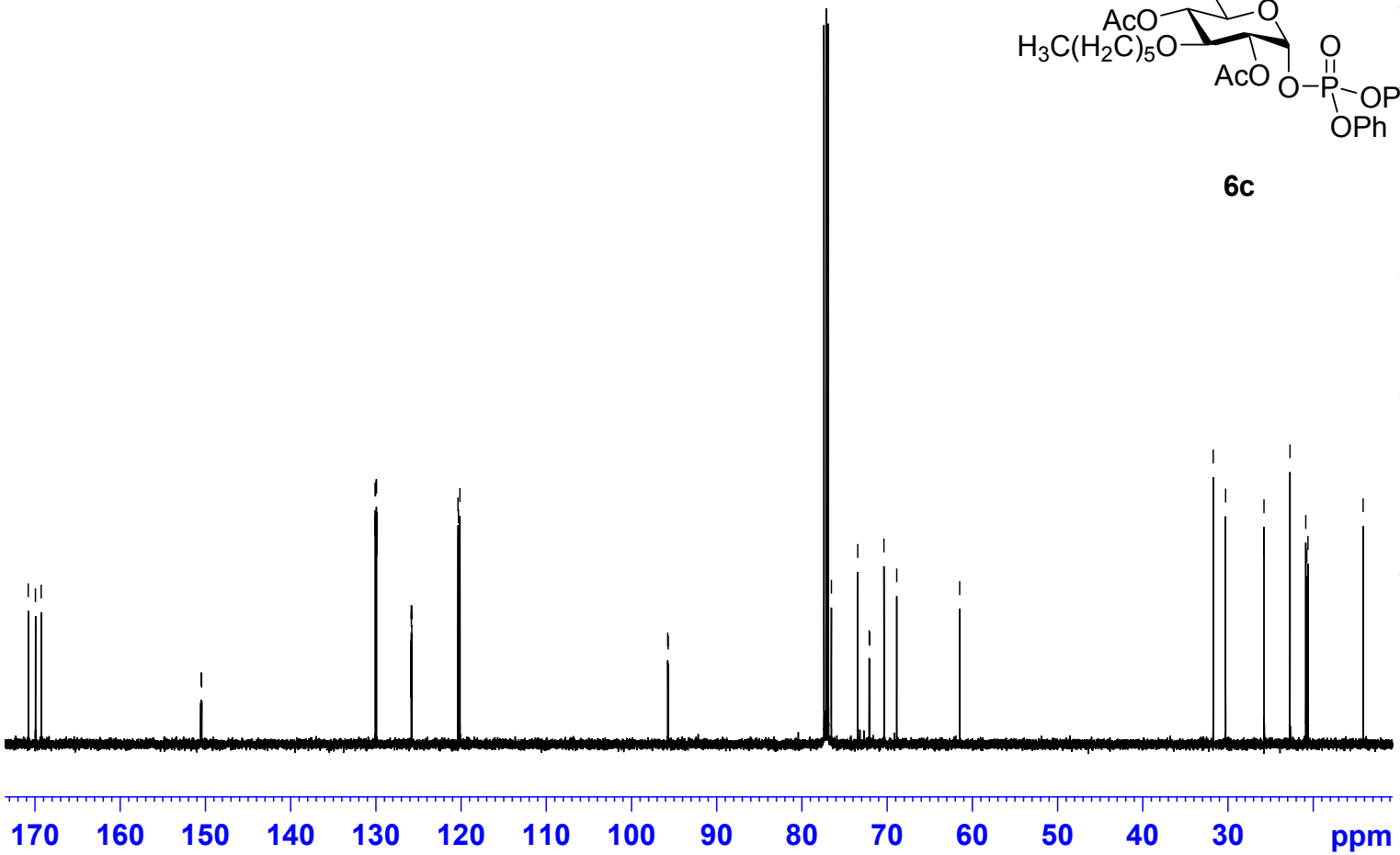
F2 - Processing parameters
SI 65536
SF 202.4563430 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00




```
Current Data Parameters
NAME      Gaia-Phosphorylated Hexyl
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070529
Time                11.40
INSTRUM           Av500
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            10000.000 Hz
FIDRES             0.152588 Hz
AQ             3.2769001 sec
RG                 143.7
DW                50.000 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.80 usec
PL1               -2.00 dB
SFO1        500.1332698 MHz

F2 - Processing parameters
SI                 65536
SF          500.1300354 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                 1.00
```

Gaia-Phosphorylated Hexyl
1d_13C{1H}_wide CDCl3 {C:\nmr_users} huestis 11

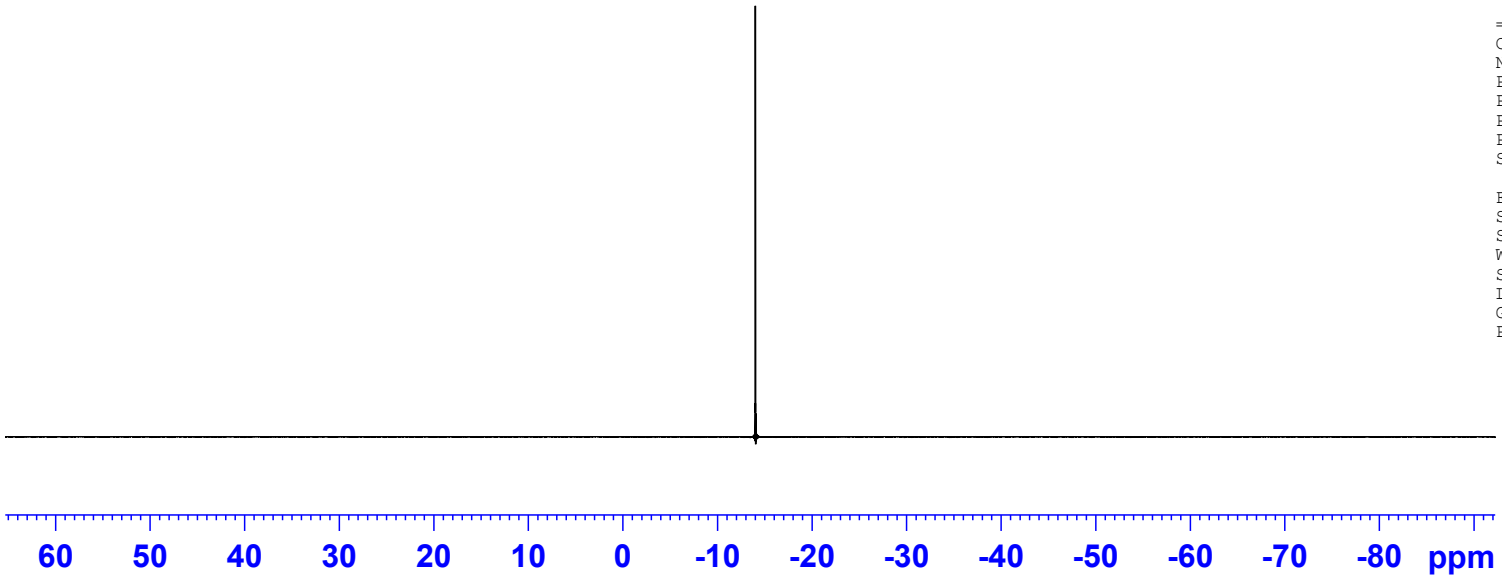
169.945
169.269
150.492
150.434
130.055
130.050
129.941
129.935
125.843
125.834
125.791
125.781
120.358
120.320
120.172
120.132
95.742
95.693
76.545
73.445
72.107
72.049
70.372
68.879
61.487
31.743
30.280
25.776
22.729
20.879
20.751

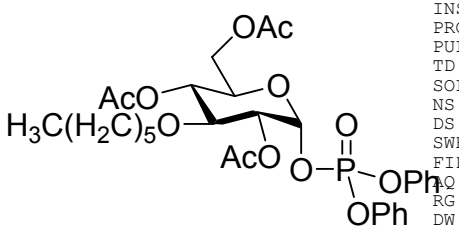


6c

```
Current Data Parameters
NAME      Gaia-Phosphorylated Hexyl
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070529
Time                11.50
INSTRUM             Av500
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     2
SWH            33783.785 Hz
FIDRES             0.515500 Hz
AQ                 0.9699976 sec
RG                   574.7
DW                  14.800 usec
DE                   6.00 usec
TE                   300.4 K
D1              1.00000000 sec
d11             0.03000000 sec
DELTA           0.89999998 sec
TD0                    4

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.90 usec
PL1                  0.00 dB
SFO1          125.7716270 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2               80.00 usec
PL2                 -2.00 dB
PL12                15.72 dB
PL13                18.64 dB
SFO2          500.1322696 MHz

F2 - Processing parameters
SI                 65536
SF            125.7577788 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.40
```

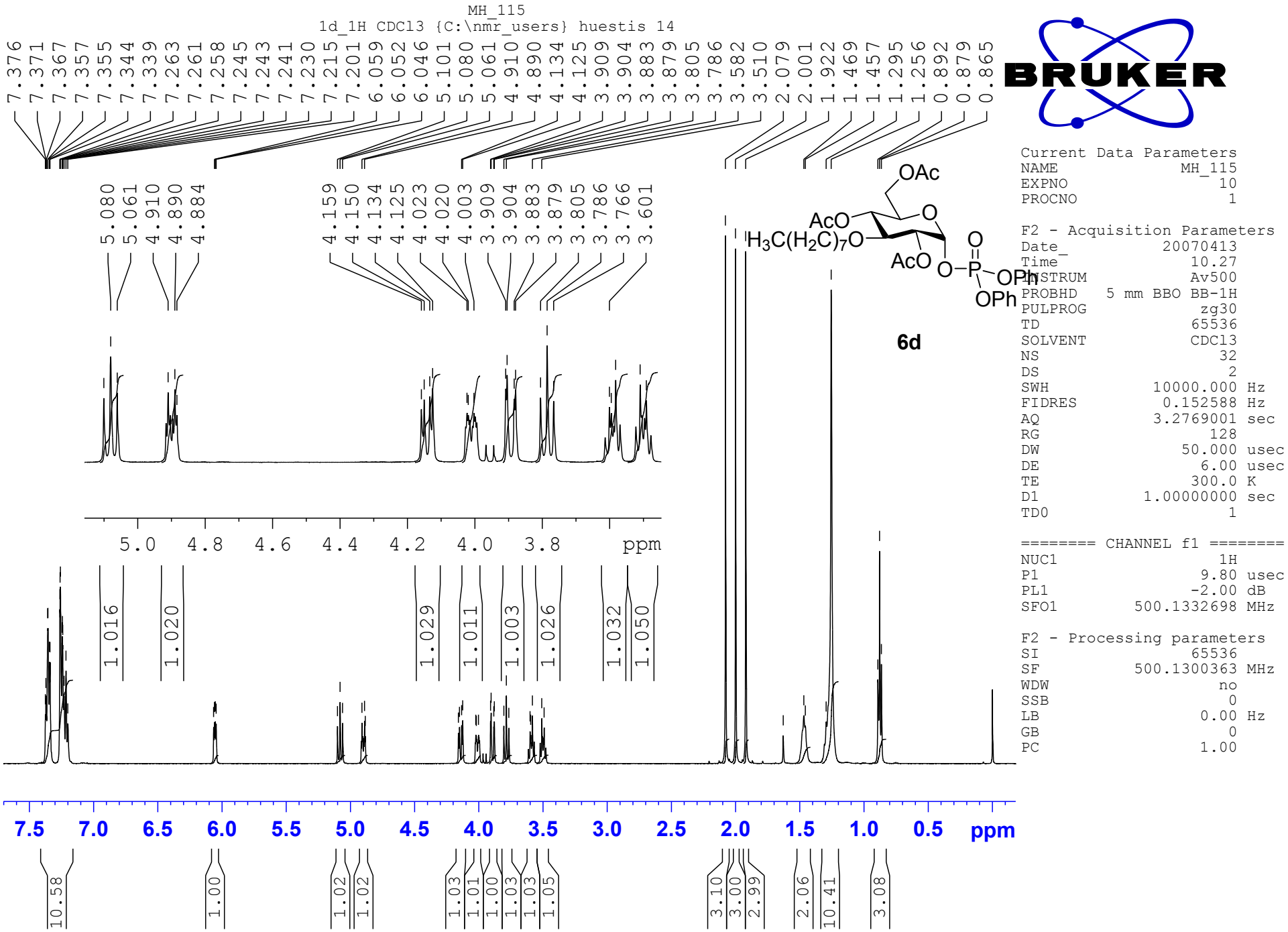
Gaia-Phosphorylated Hexyl
1d_31P{1H} CDCl3 {C:\nmr_users} huestis 11



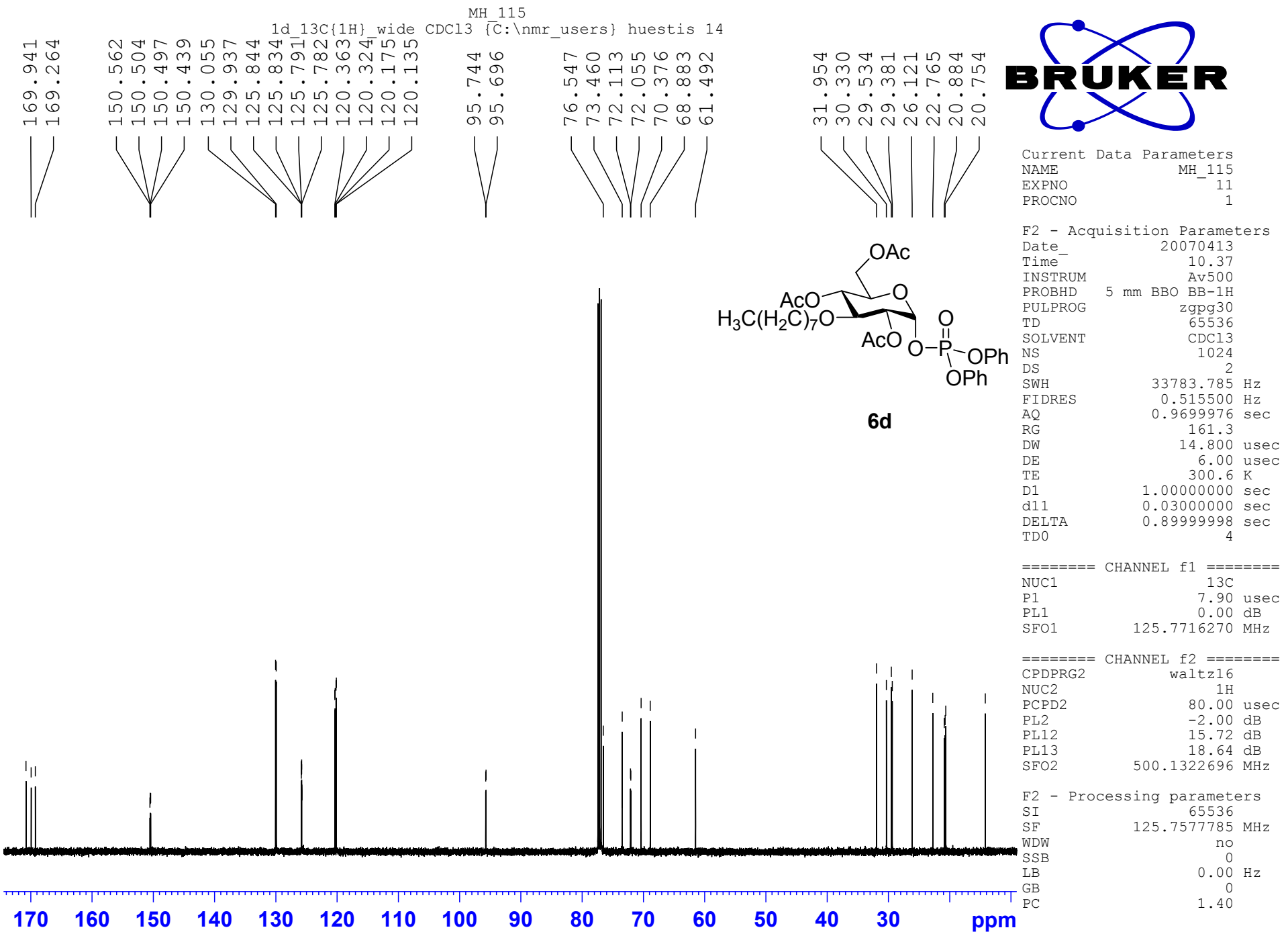


6c

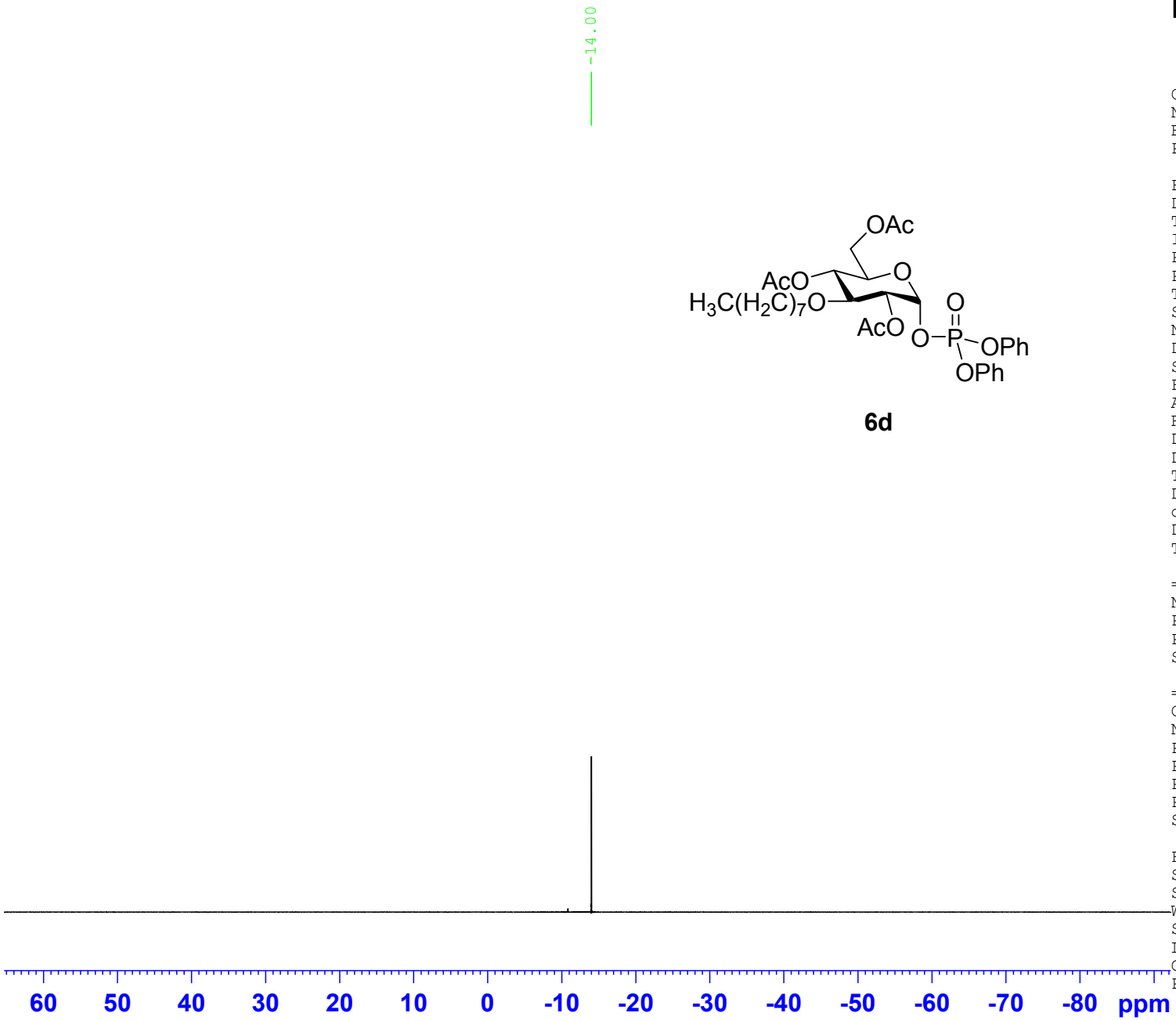
```
Current Data Parameters
NAME      Gaia-Phosphorylated Hexyl
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_           20070529
Time               12.24
INSTRUM            Av500
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     0
SWH            98039.219 Hz
FIDRES          1.495960 Hz
AQ             0.3342887 sec
RG                9195.2
DW                 5.100 usec
DE                 6.00 usec
TE                300.4 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
TD0                    2

======== CHANNEL f1 ========
NUC1                 31P
P1                  8.41 usec
PL1                 0.50 dB
SFO1         202.4664658 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               15.72 dB
PL13               18.64 dB
SFO2         500.1322696 MHz

F2 - Processing parameters
SI                 65536
SF           202.4563430 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```




```
Current Data Parameters
NAME                  MH_115
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_               20070413
Time                   10.27
INSTRUM                Av500
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH              10000.000 Hz
FIDRES               0.152588 Hz
AQ                3.2769001 sec
RG                      128
DW                   50.000 usec
DE                    6.00 usec
TE                   300.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.80 usec
PL1                   -2.00 dB
SFO1           500.1332698 MHz

F2 - Processing parameters
SI                    65536
SF             500.1300363 MHz
WDW                      no
SSB                       0
LB                    0.00 Hz
GB                        0
PC                    1.00
```

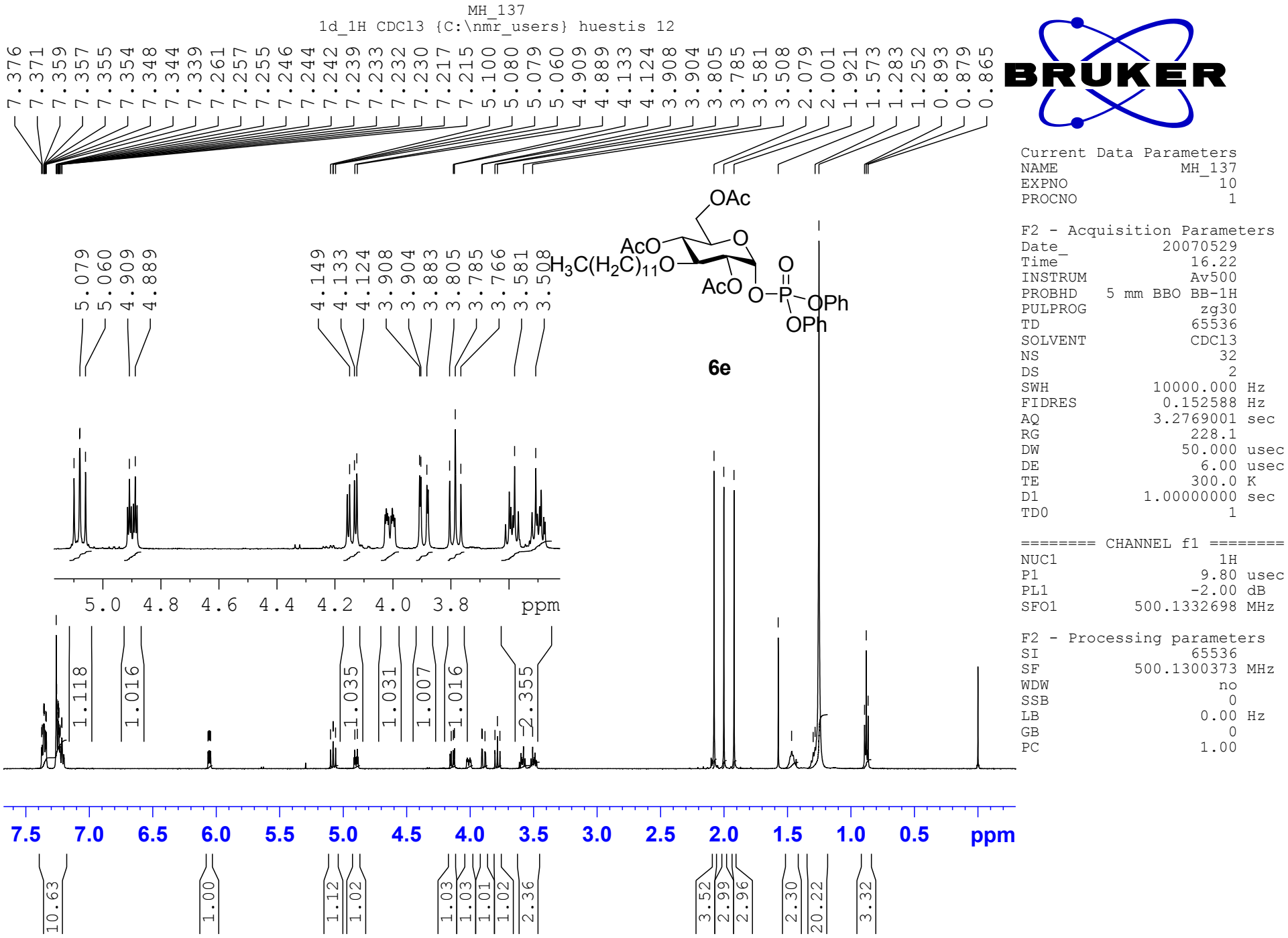

MH_115
1d_13C{1H}_wide CDCl3 {C:\nmr_users} huestis 14
169.941
169.264
150.562
150.504
150.497
150.439
130.055
129.937
125.844
125.834
125.791
125.782
120.363
120.324
120.175
120.135
95.744
95.696
76.547
73.460
72.113
72.055
70.376
68.883
61.492
31.954
30.330
29.534
29.381
26.121
22.765
20.884
20.754
OAc
AcO
O
H3C(H2C)7O
AcO
O
O
P
OPh
OPh
6d
Current Data Parameters
NAME MH_115
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070413
Time 10.37
INSTRUM Av500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 2
SWH 33783.785 Hz
FIDRES 0.515500 Hz
AQ 0.9699976 sec
RG 161.3
DW 14.800 usec
DE 6.00 usec
TE 300.6 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 4
======== CHANNEL f1 ========
NUC1 13C
P1 7.90 usec
PL1 0.00 dB
SFO1 125.7716270 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 15.72 dB
PL13 18.64 dB
SFO2 500.1322696 MHz
F2 - Processing parameters
SI 65536
SF 125.7577785 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

MH_115
1d_31P{1H} CDCl3 {C:\nmr_users} huestis 14

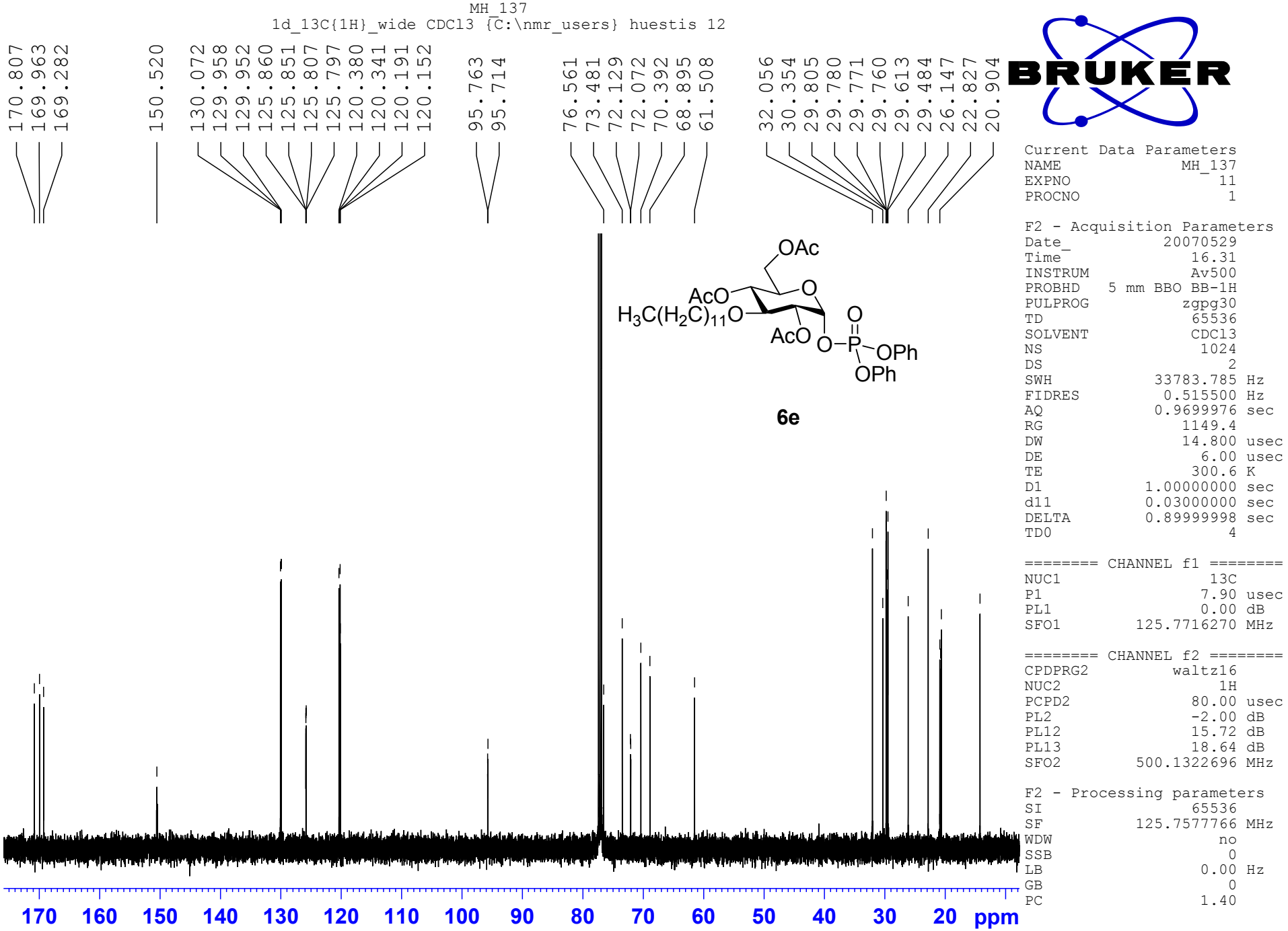


6d

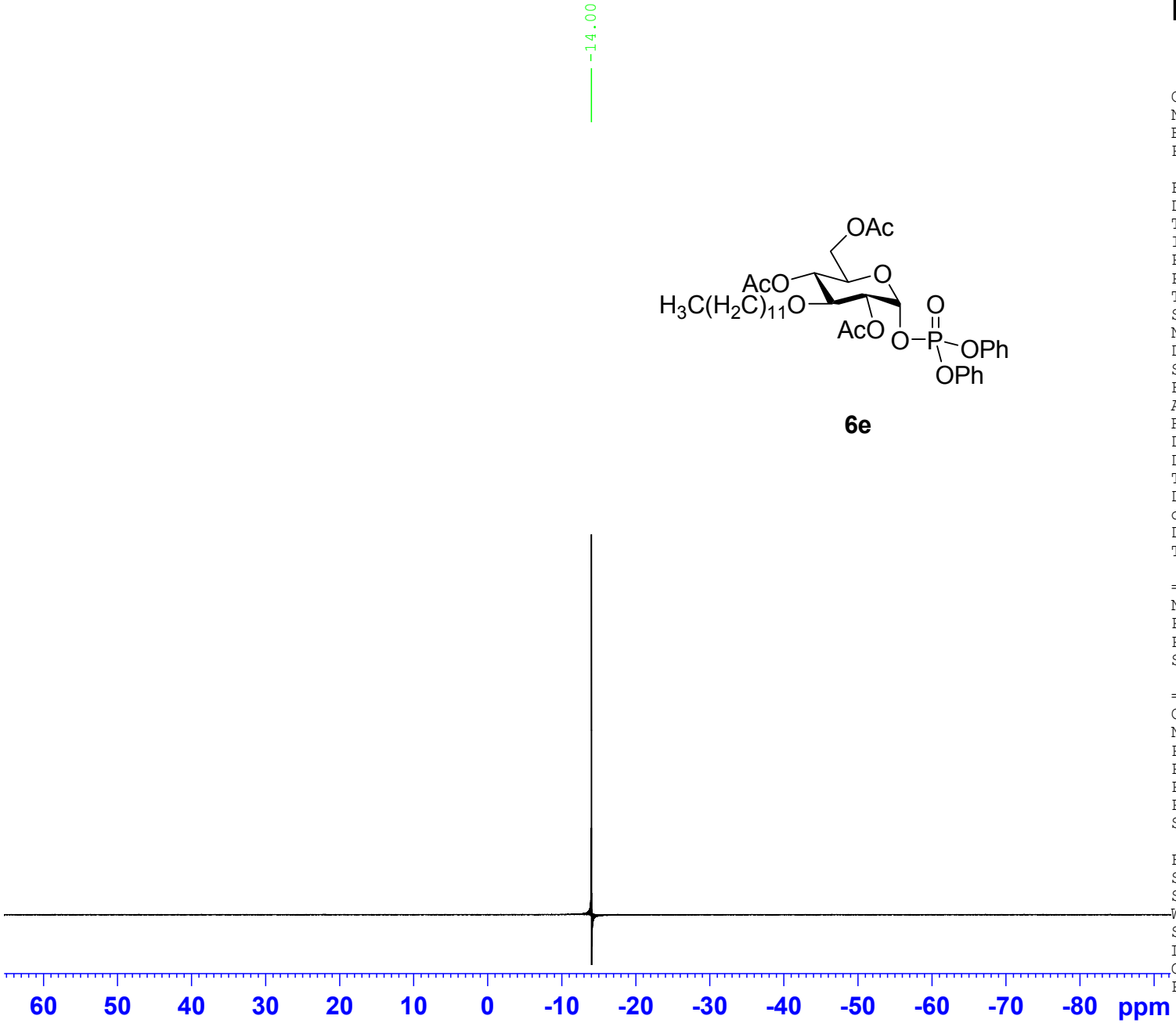
```
Current Data Parameters
NAME                 MH_115
EXPNO                    12
PROCNO                    1

F2 - Acquisition Parameters
Date_              20070413
Time                 11.11
INSTRUM              Av500
PROBHD   5 mm BBO BB-1H
PULPROG              zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     512
DS                       0
SWH              98039.219 Hz
FIDRES            1.495960 Hz
AQ                0.3342887 sec
RG                  10321.3
DW                    5.100 usec
DE                    6.00 usec
TE                   300.4 K
D1             1.00000000 sec
d11            0.03000000 sec
DELTA          0.89999998 sec
TD0                      2

======== CHANNEL f1 ========
NUC1                   31P
P1                    8.41 usec
PL1                   0.50 dB
SFO1          202.4664658 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2                80.00 usec
PL2                  -2.00 dB
PL12                 15.72 dB
PL13                 18.64 dB
SFO2          500.1322696 MHz

F2 - Processing parameters
SI                    65536
SF            202.4563430 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00
```




```
Current Data Parameters
NAME                  MH_137
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20070529
Time                  16.22
INSTRUM               Av500
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH              10000.000 Hz
FIDRES               0.152588 Hz
AQ                3.2769001 sec
RG                    228.1
DW                   50.000 usec
DE                    6.00 usec
TE                   300.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    9.80 usec
PL1                  -2.00 dB
SFO1           500.1332698 MHz

F2 - Processing parameters
SI                    65536
SF             500.1300373 MHz
WDW                      no
SSB                       0
LB                    0.00 Hz
GB                        0
PC                    1.00
```


MH_137
1d_13C{1H}_wide CDCl3 {C:\nmr_users} huestis 12
170.807
169.963
169.282
150.520
130.072
129.958
129.952
125.860
125.851
125.807
125.797
120.380
120.341
120.191
120.152
95.763
95.714
76.561
73.481
72.129
72.072
70.392
68.895
61.508
32.056
30.354
29.805
29.780
29.771
29.760
29.613
29.484
26.147
22.827
20.904
OAc
AcO
O
H3C(H2C)11O
AcO
O
P
O
OPh
OPh
6e
Current Data Parameters
NAME MH_137
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070529
Time 16.31
INSTRUM Av500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 2
SWH 33783.785 Hz
FIDRES 0.515500 Hz
AQ 0.9699976 sec
RG 1149.4
DW 14.800 usec
DE 6.00 usec
TE 300.6 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 4
======== CHANNEL f1 ========
NUC1 13C
P1 7.90 usec
PL1 0.00 dB
SFO1 125.7716270 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 15.72 dB
PL13 18.64 dB
SFO2 500.1322696 MHz
F2 - Processing parameters
SI 65536
SF 125.7577766 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

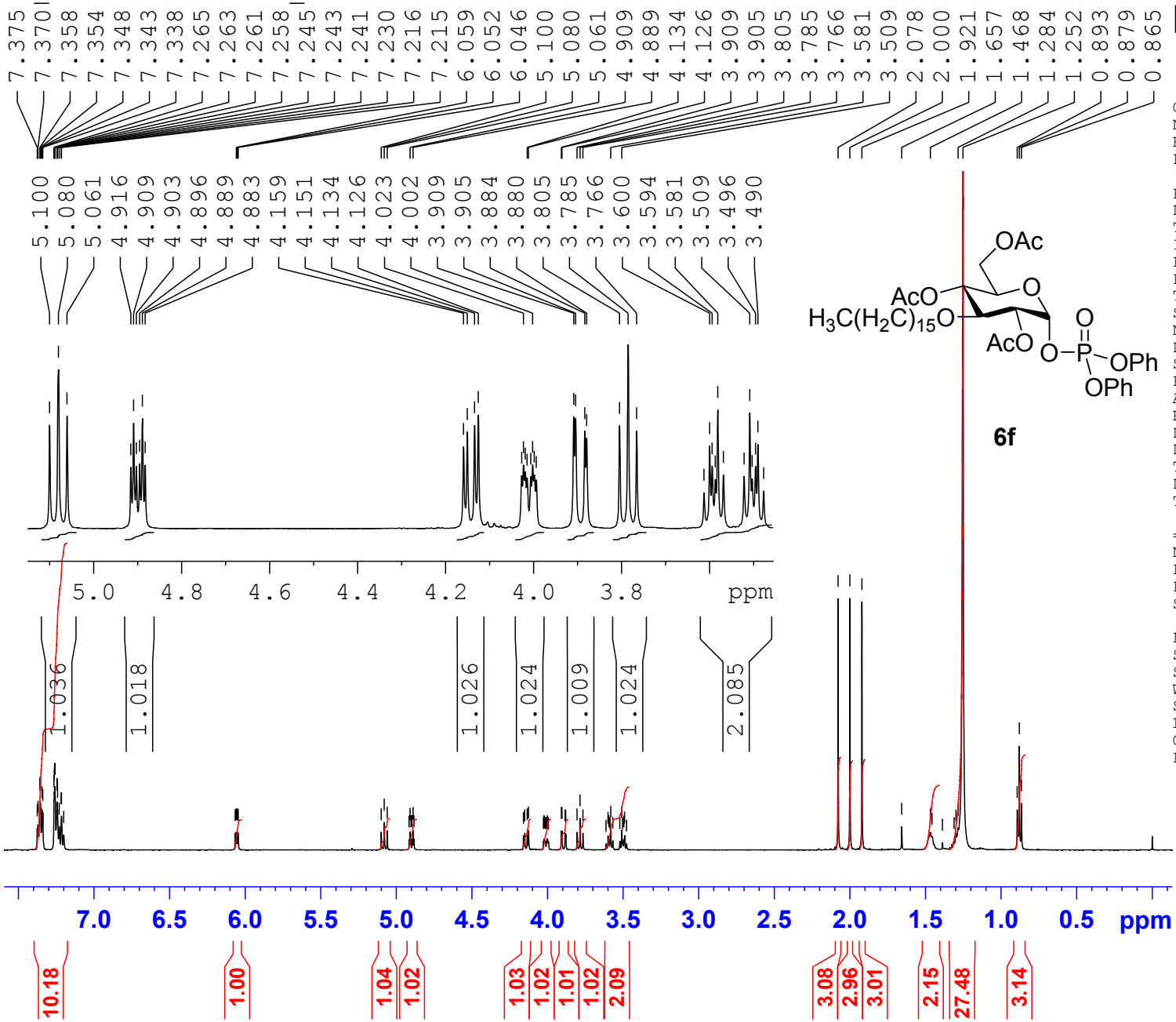
MH_137
1d_31P{1H} CDCl3 {C:\nmr_users} huestis 12



6e

```
Current Data Parameters
NAME                  MH_137
EXPNO                     12
PROCNO                     1

F2 - Acquisition Parameters
Date_               20070529
Time                   17.05
INSTRUM                Av500
PROBHD   5 mm BBO BB-1H
PULPROG                zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       512
DS                         0
SWH                98039.219 Hz
FIDRES              1.495960 Hz
AQ                  0.3342887 sec
RG                     7298.2
DW                     5.100 usec
DE                     6.00 usec
TE                     300.4 K
D1                 1.00000000 sec
d11                0.03000000 sec
DELTA              0.89999998 sec
TD0                        2

======== CHANNEL f1 ========
NUC1                     31P
P1                     8.41 usec
PL1                    0.50 dB
SFO1            202.4664658 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                80.00 usec
PL2                  -2.00 dB
PL12                 15.72 dB
PL13                 18.64 dB
SFO2            500.1322696 MHz

F2 - Processing parameters
SI                     65536
SF              202.4563430 MHz
WDW                       no
SSB                        0
LB                    0.00 Hz
GB                         0
PC                     1.00
```

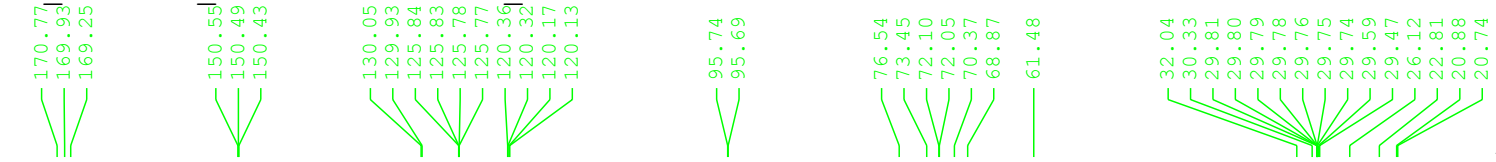
Gaia-hexadecyl phos_2
1d_1H CDCl3 {C:\nmr_users} huestis 27

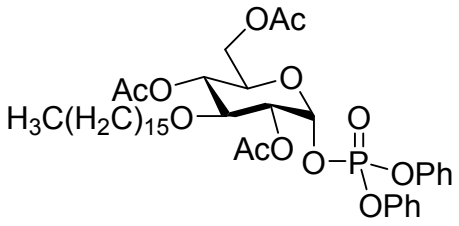


6f

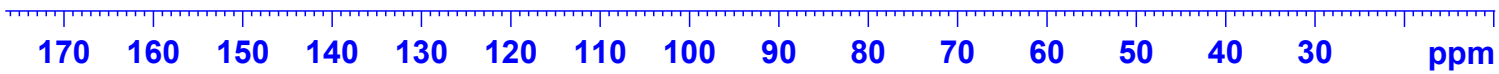
```
Current Data Parameters
NAME      Gaia-hexadecyl phos_2
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_           20070704
Time                10.19
INSTRUM           Av500
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2769001 sec
RG                  80.6
DW                 50.000 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.80 usec
PL1                -2.00 dB
SFO1        500.1332698 MHz

F2 - Processing parameters
SI                 65536
SF          500.1300353 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  0.75
```

Gaia-hexadecyl phos_2
1d_13C{1H}_d CDCl3 {C:\nmr_users} huestis 27



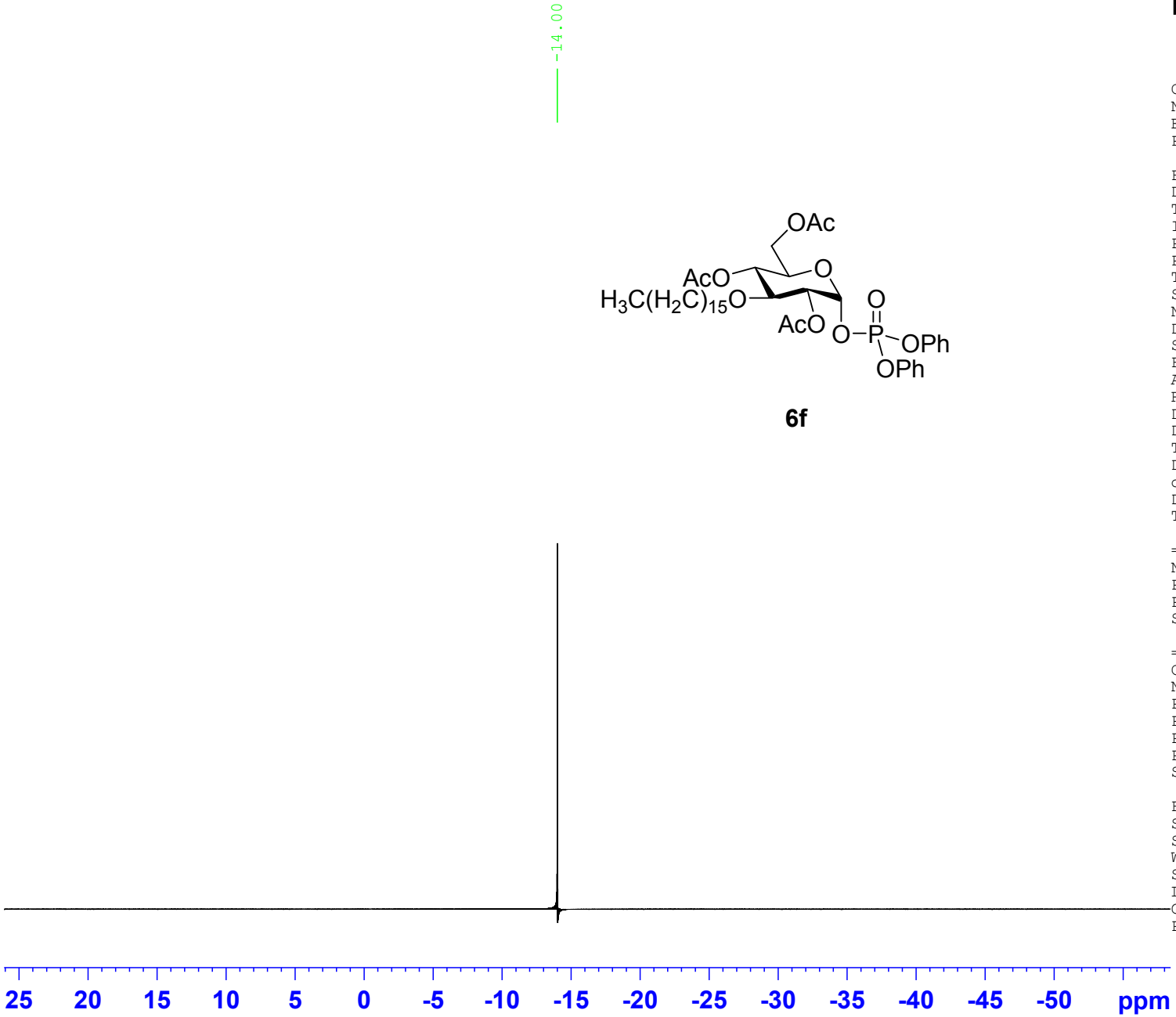


6f



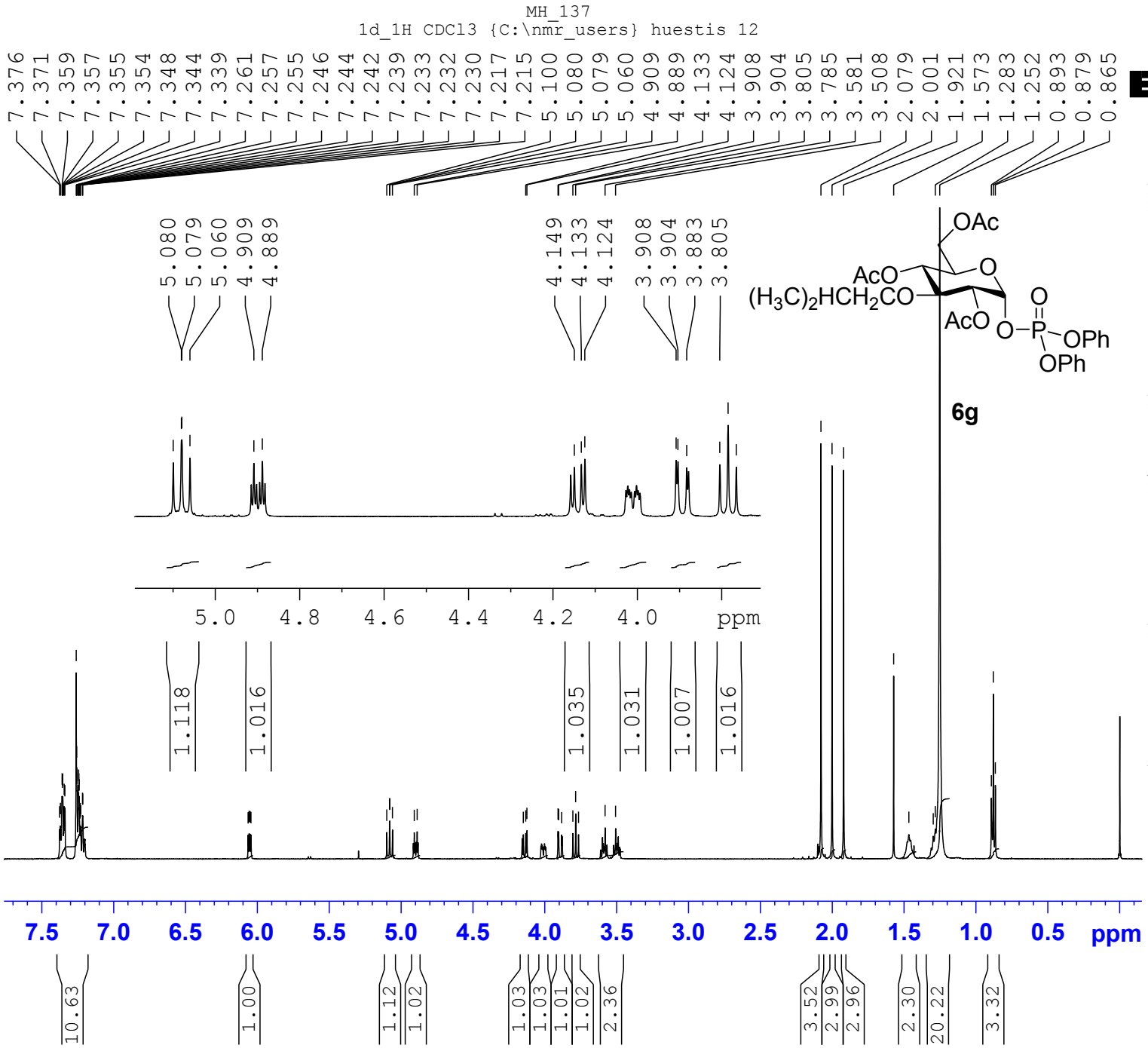

```
Current Data Parameters
NAME      Gaia-hexadecyl phos_2
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameters
Date_             20070704
Time                10.27
INSTRUM             Av500
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 54048
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH            33783.785 Hz
FIDRES          0.625070 Hz
AQ              0.7999752 sec
RG                10321.3
DW                 14.800 usec
DE                 21.14 usec
TE                 300.4 K
D1             1.00000000 sec
d11            0.03000000 sec
DELTA          0.89999998 sec
TD0                     4

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.90 usec
PL1                  0.00 dB
SFO1         125.7716273 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               15.72 dB
PL13               18.64 dB
SFO2         500.1322696 MHz

F2 - Processing parameters
SI                  65536
SF           125.7577794 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   0.75
```

Gaia-hexadecyl phos_2
1d_31P{1H}_d CDCl3 {C:\nmr_users} huestis 27

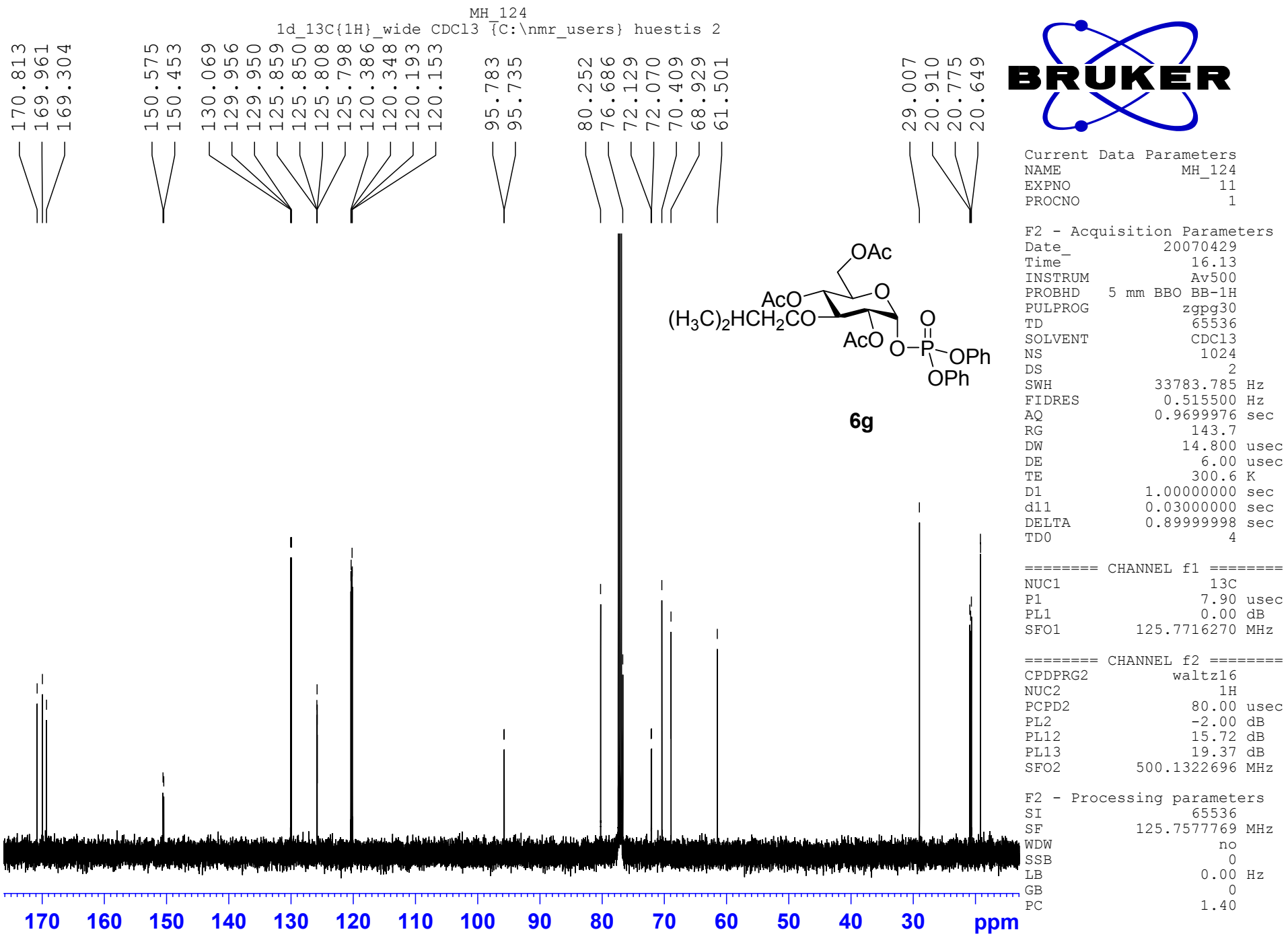


6f

```
Current Data Parameters
NAME      Gaia-hexadecyl phos_2
EXPNO                   14
PROCNO                   1

F2 - Acquisition Parameters
Date_             20070705
Time                 7.54
INSTRUM             Av500
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            98039.219 Hz
FIDRES          1.495960 Hz
AQ             0.3342887 sec
RG                9195.2
DW                 5.100 usec
DE                 7.29 usec
TE                 300.6 K
D1            1.00000000 sec
d11           0.03000000 sec
DELTA         0.89999998 sec
TD0                    2

======== CHANNEL f1 ========
NUC1                  31P
P1                   8.41 usec
PL1                  0.50 dB
SFO1         202.4664658 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               15.72 dB
PL13               18.64 dB
SFO2         500.1322696 MHz

F2 - Processing parameters
SI                 65536
SF           202.4563430 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  0.75
```




```
Current Data Parameters
NAME                  MH_133
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_               20070529
Time                   16.22
INSTRUM                Av500
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH             10000.000 Hz
FIDRES              0.152588 Hz
AQ                3.2769001 sec
RG                    228.1
DW                 50.000 usec
DE                  6.00 usec
TE                  300.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                   9.80 usec
PL1                 -2.00 dB
SFO1          500.1332698 MHz

F2 - Processing parameters
SI                    65536
SF              500.1300373 MHz
WDW                      no
SSB                       0
LB                   0.00 Hz
GB                        0
PC                     1.00
```



Current Data Parameters

NAME	MH_124
EXPNO	11
PROCNO	1

F2 - Acquisition Parameters

Date_	20070429
Time	16.13
INSTRUM	Av500
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	2
SWH	33783.785 Hz
FIDRES	0.515500 Hz
AQ	0.9699976 sec
RG	143.7
DW	14.800 usec
DE	6.00 usec
TE	300.6 K
D1	1.00000000 sec
d11	0.03000000 sec
DELTA	0.89999998 sec
TD0	4

======== CHANNEL f1 ========

NUC1	13C
P1	7.90 usec
PL1	0.00 dB
SFO1	125.7716270 MHz

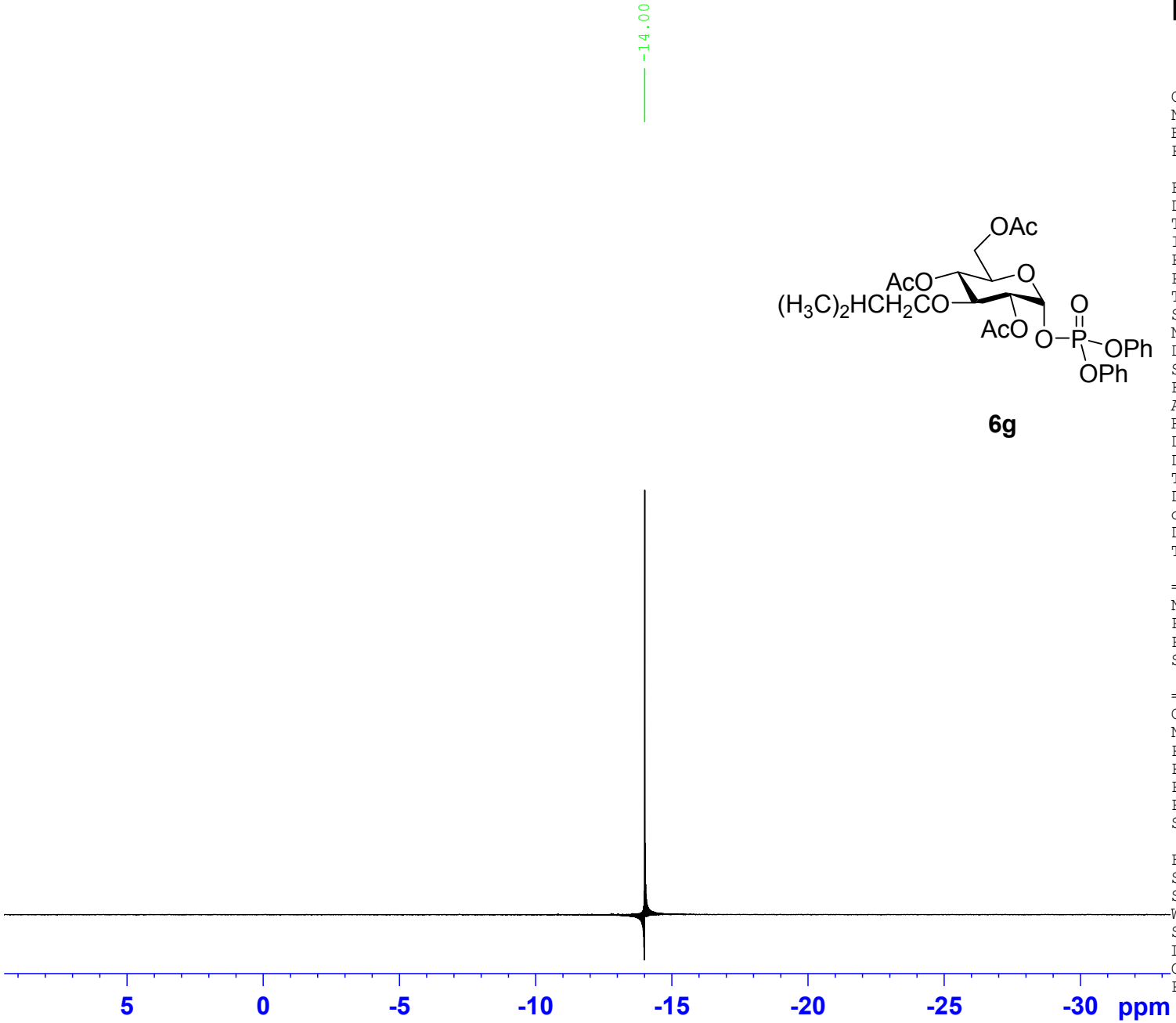
======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.00 dB
PL12	15.72 dB
PL13	19.37 dB
SFO2	500.1322696 MHz

F2 - Processing parameters

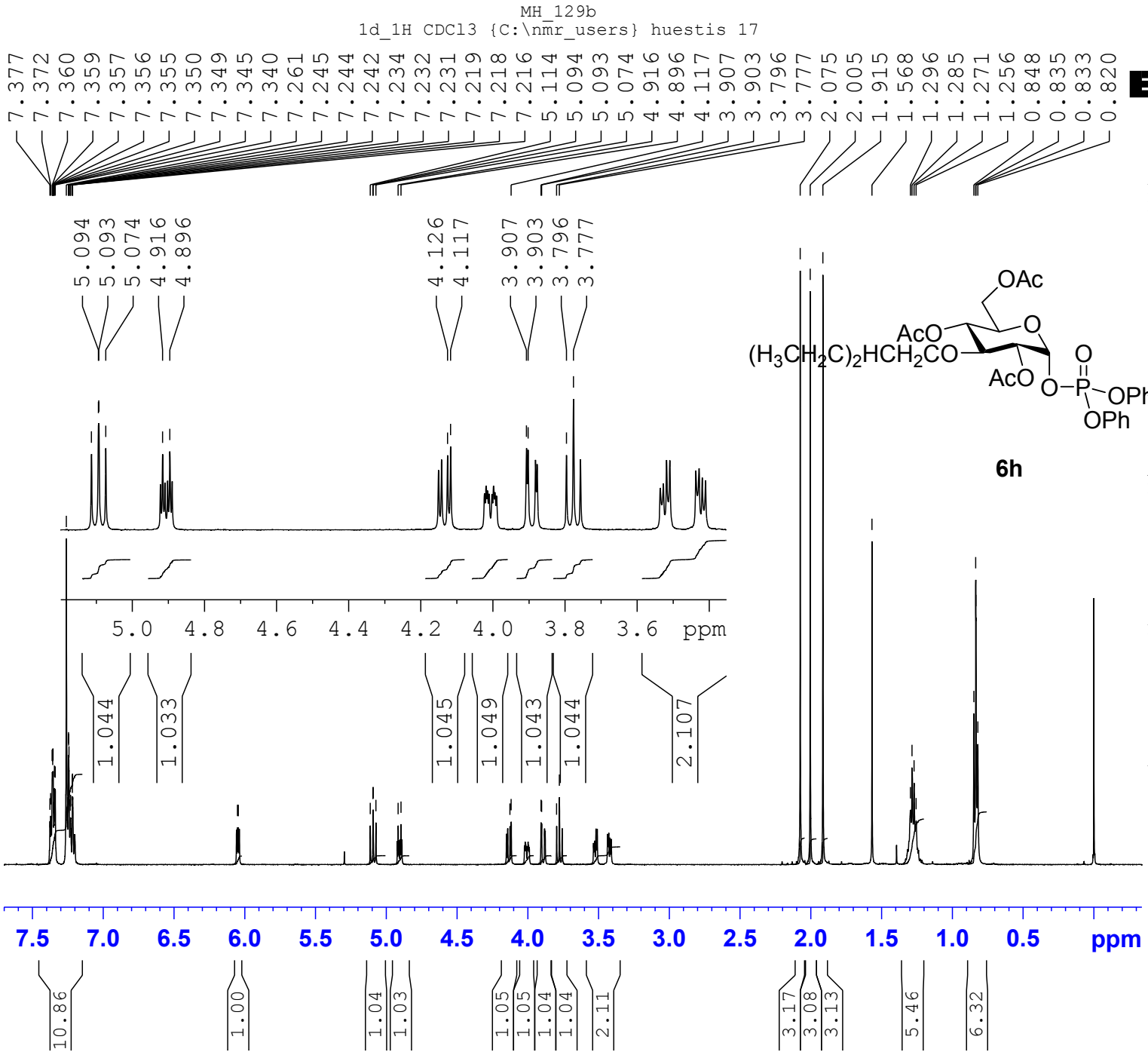
SI	65536
SF	125.7577769 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40

MH_124
1d_31P{1H} CDCl3 {C:\nmr_users} huestis 2



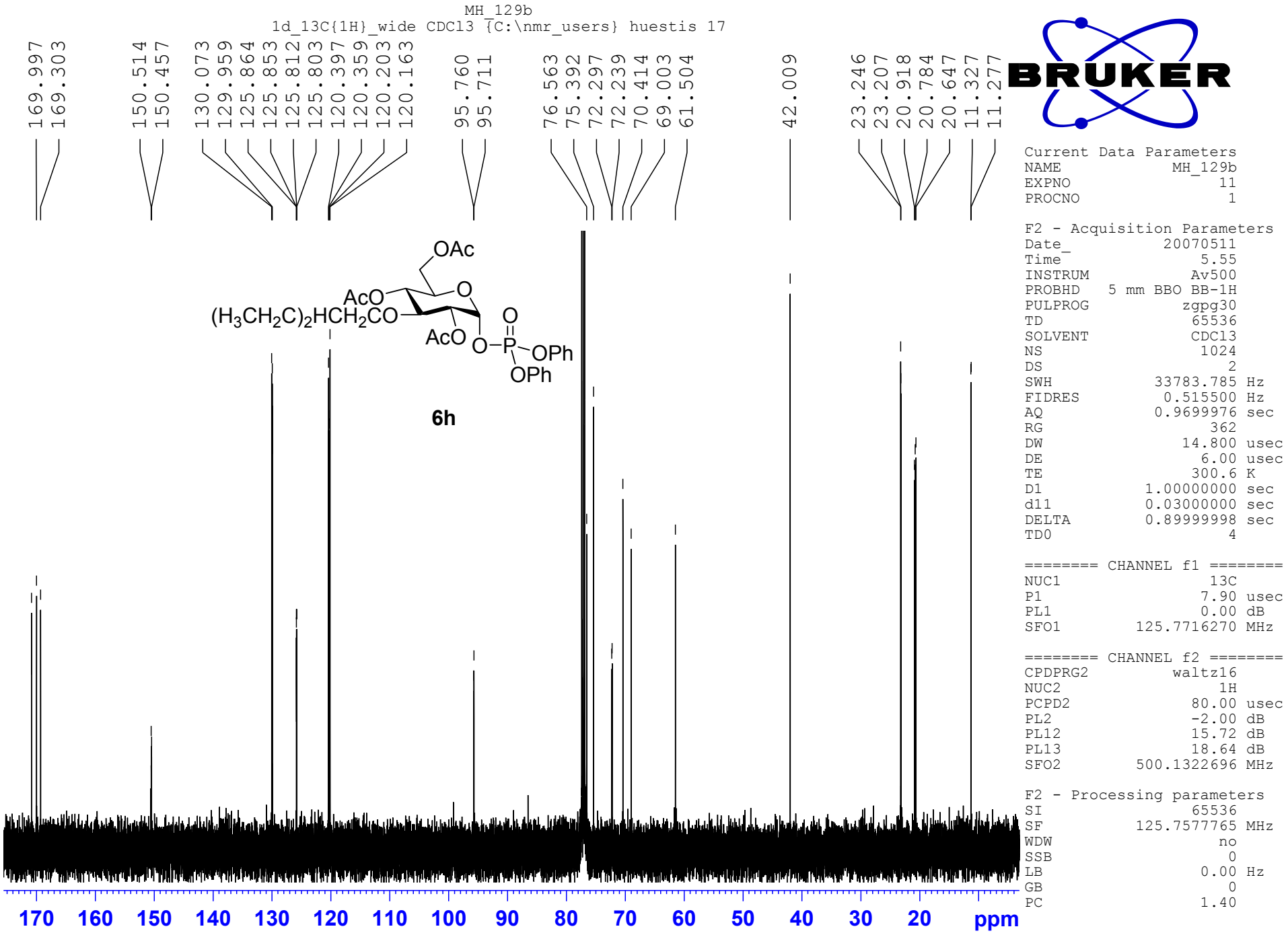
6g

```
Current Data Parameters
NAME                 MH_124
EXPNO                    12
PROCNO                    1

F2 - Acquisition Parameters
Date_              20070429
Time                  16.47
INSTRUM               Av500
PROBHD   5 mm BBO BB-1H
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      512
DS                        0
SWH              98039.219 Hz
FIDRES            1.495960 Hz
AQ                0.3342887 sec
RG                   7298.2
DW                    5.100 usec
DE                    6.00 usec
TE                   300.4 K
D1             1.00000000 sec
d11            0.03000000 sec
DELTA          0.89999998 sec
TD0                       2

======== CHANNEL f1 ========
NUC1                    31P
P1                    8.41 usec
PL1                   0.50 dB
SFO1          202.4664658 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -2.00 dB
PL12                 15.72 dB
PL13                 19.37 dB
SFO2          500.1322696 MHz

F2 - Processing parameters
SI                    65536
SF            202.4563430 MHz
WDW                      no
SSB                       0
LB                    0.00 Hz
GB                        0
PC                    1.00
```



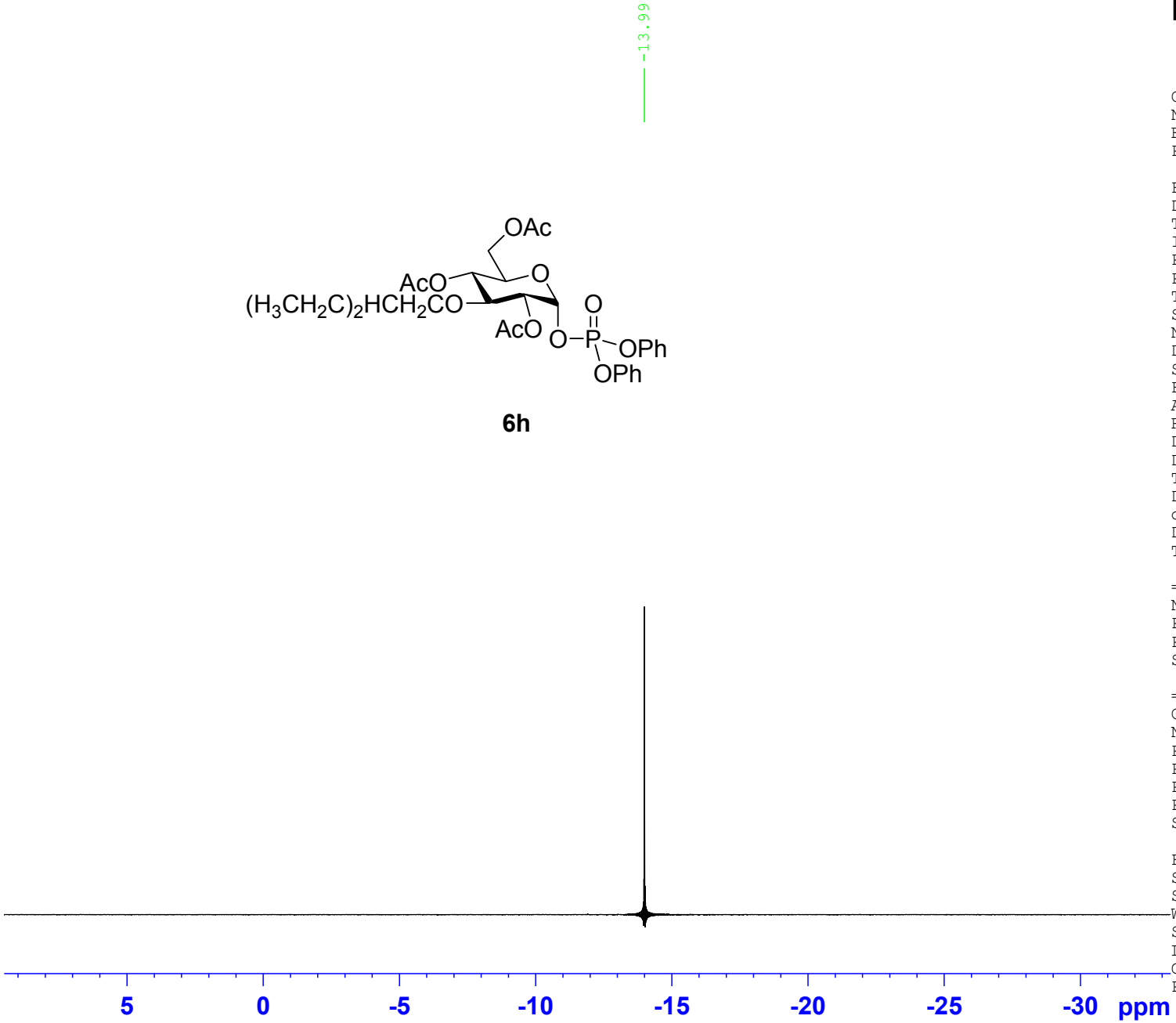
6h

```
Current Data Parameters
NAME                  MH_129b
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_               20070511
Time                    5.44
INSTRUM                Av500
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH              10000.000 Hz
FIDRES               0.152588 Hz
AQ                3.2769001 sec
RG                      362
DW                   50.000 usec
DE                    6.00 usec
TE                   300.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    9.80 usec
PL1                  -2.00 dB
SFO1           500.1332698 MHz

F2 - Processing parameters
SI                    65536
SF             500.1300376 MHz
WDW                      no
SSB                       0
LB                    0.00 Hz
GB                        0
PC                     1.00
```




```
Current Data Parameters
NAME                  MH_129b
EXPNO                      11
PROCNO                      1

F2 - Acquisition Parameters
Date_               20070511
Time                    5.55
INSTRUM                Av500
PROBHD    5 mm BBO BB-1H
PULPROG               zgpg30
TD                     65536
SOLVENT                CDCl3
NS                      1024
DS                         2
SWH               33783.785 Hz
FIDRES             0.515500 Hz
AQ                 0.9699976 sec
RG                       362
DW                    14.800 usec
DE                     6.00 usec
TE                     300.6 K
D1                1.00000000 sec
d11               0.03000000 sec
DELTA             0.89999998 sec
TD0                        4

======== CHANNEL f1 ========
NUC1                     13C
P1                    7.90 usec
PL1                   0.00 dB
SFO1           125.7716270 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                80.00 usec
PL2                  -2.00 dB
PL12                 15.72 dB
PL13                 18.64 dB
SFO2           500.1322696 MHz

F2 - Processing parameters
SI                     65536
SF             125.7577765 MHz
WDW                       no
SSB                        0
LB                    0.00 Hz
GB                         0
PC                      1.40
```

MH_129b
1d_31P{1H} CDCl3 {C:\nmr_users} huestis 17



6h

Current Data Parameters
NAME MH_129b
EXPNO 12
PROCNO 1

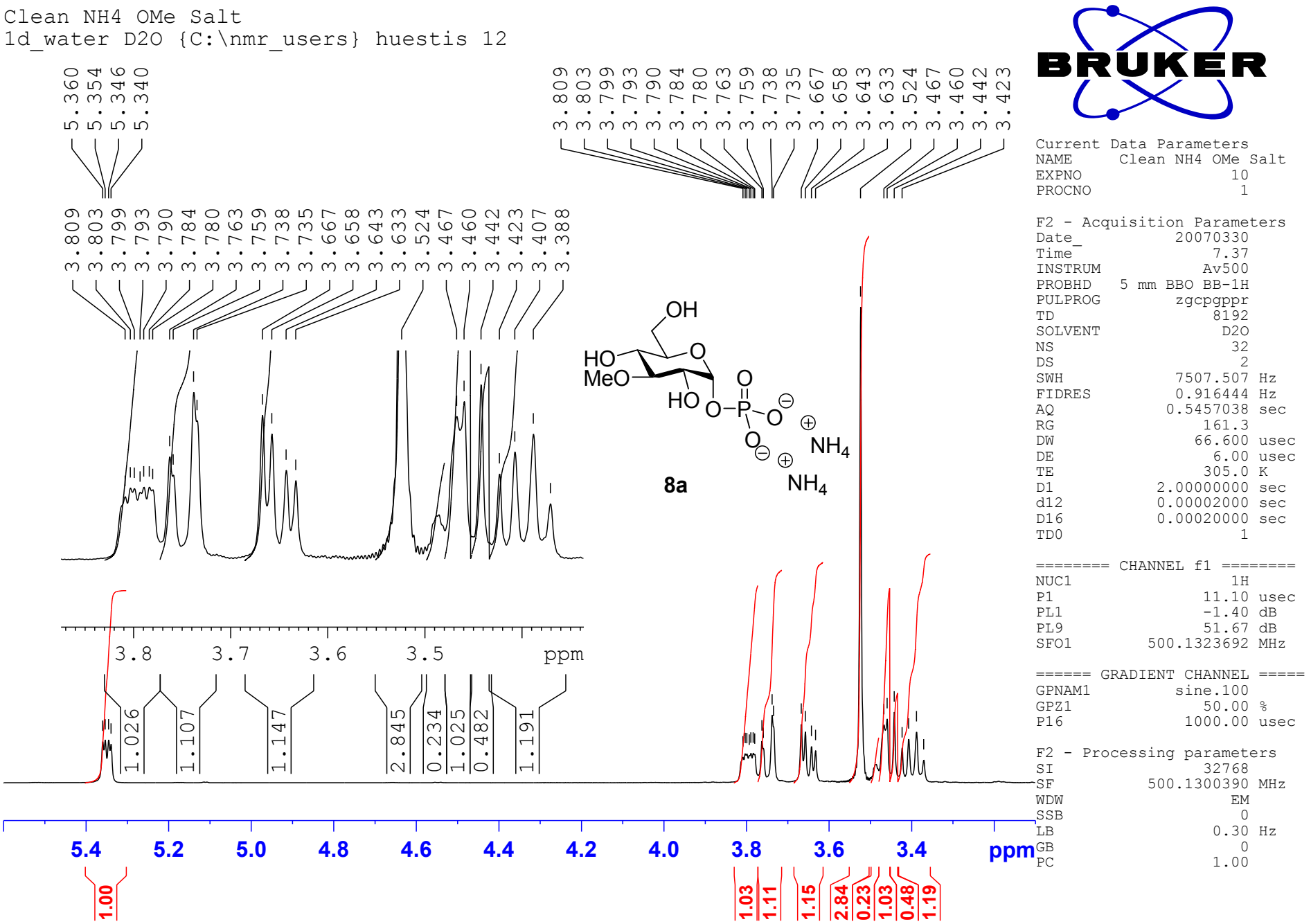
F2 - Acquisition Parameters
Date_ 20070511
Time 6.28
INSTRUM Av500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 0
SWH 98039.219 Hz
FIDRES 1.495960 Hz
AQ 0.3342887 sec
RG 6502
DW 5.100 usec
DE 6.00 usec
TE 300.6 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 2

======== CHANNEL f1 ========
NUC1 31P
P1 8.41 usec
PL1 0.50 dB
SFO1 202.4664658 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 15.72 dB
PL13 18.64 dB
SFO2 500.1322696 MHz

F2 - Processing parameters
SI 65536
SF 202.4563430 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

Clean NH4 OMe Salt
1d_water D2O {C:\nmr_users} huestis 12



Current Data Parameters

NAME	Clean NH4 OMe Salt
EXPNO	10
PROCNO	1

F2 - Acquisition Parameters

Date_	20070330
Time	7.37
INSTRUM	Av500
PROBHD	5 mm BBO BB-1H
PULPROG	zgcpgppr
TD	8192
SOLVENT	D2O
NS	32
DS	2
SWH	7507.507 Hz
FIDRES	0.916444 Hz
AQ	0.5457038 sec
RG	161.3
DW	66.600 usec
DE	6.00 usec
TE	305.0 K
D1	2.00000000 sec
d12	0.00002000 sec
D16	0.00020000 sec
TD0	1

======== CHANNEL f1 ========

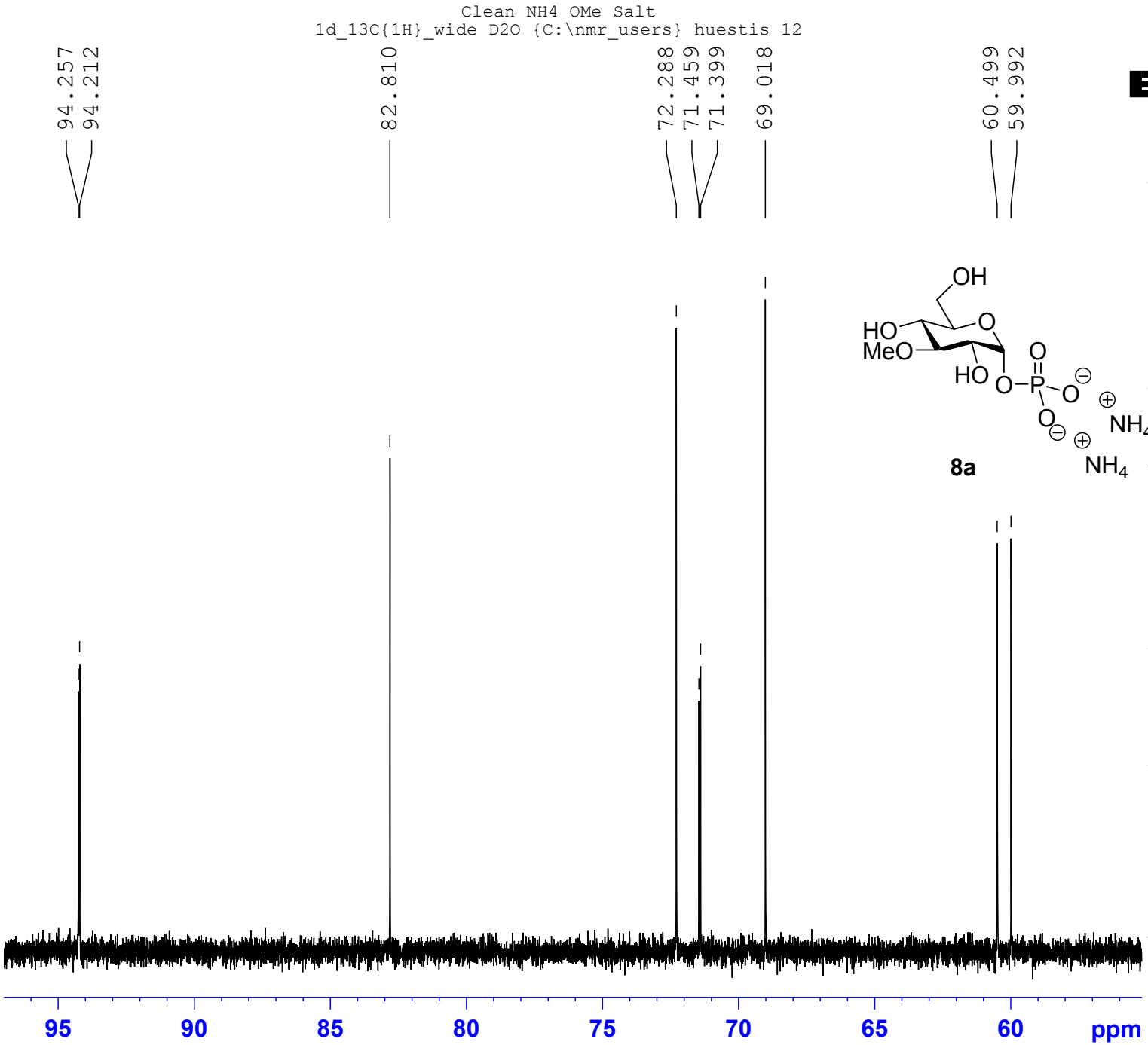
NUC1	1H
P1	11.10 usec
PL1	-1.40 dB
PL9	51.67 dB
SFO1	500.1323692 MHz

====== GRADIENT CHANNEL =====

GPNAM1	sine.100
GPZ1	50.00 %
P16	1000.00 usec

F2 - Processing parameters

SI	32768
SF	500.1300390 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



BRUKER

Current Data Parameters
NAME Clean NH4 OMe Salt
EXPNO 11
PROCNO 1

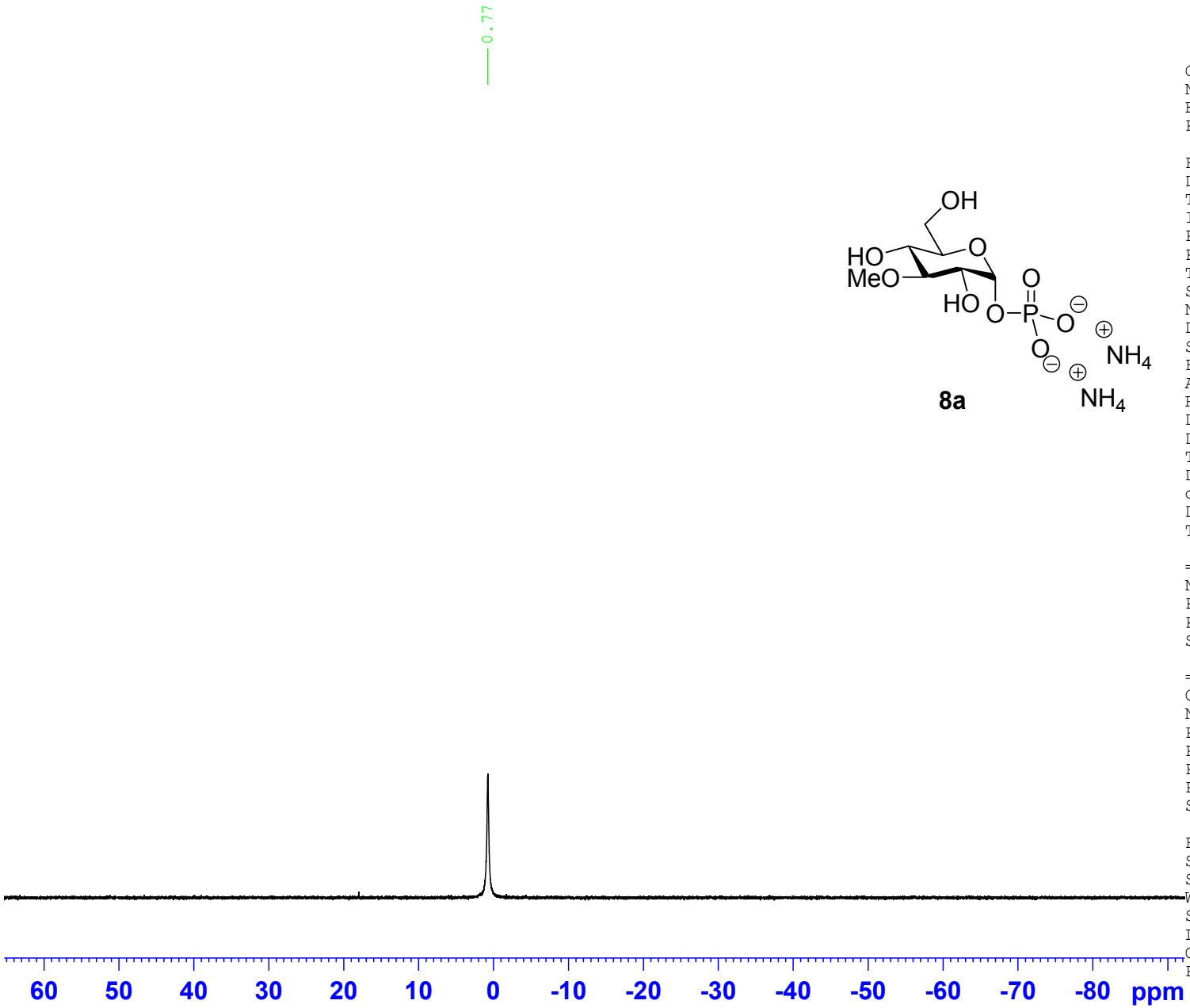
F2 - Acquisition Parameters
Date_ 20070330
Time 7.47
INSTRUM Av500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT D2O
NS 1024
DS 2
SWH 33783.785 Hz
FIDRES 0.515500 Hz
AQ 0.9699976 sec
RG 912.3
DW 14.800 usec
DE 6.00 usec
TE 300.6 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P1 7.90 usec
PL1 0.00 dB
SFO1 125.7716270 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.40 dB
PL12 15.83 dB
PL13 19.37 dB
SFO2 500.1322696 MHz

F2 - Processing parameters
SI 65536
SF 125.7577930 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

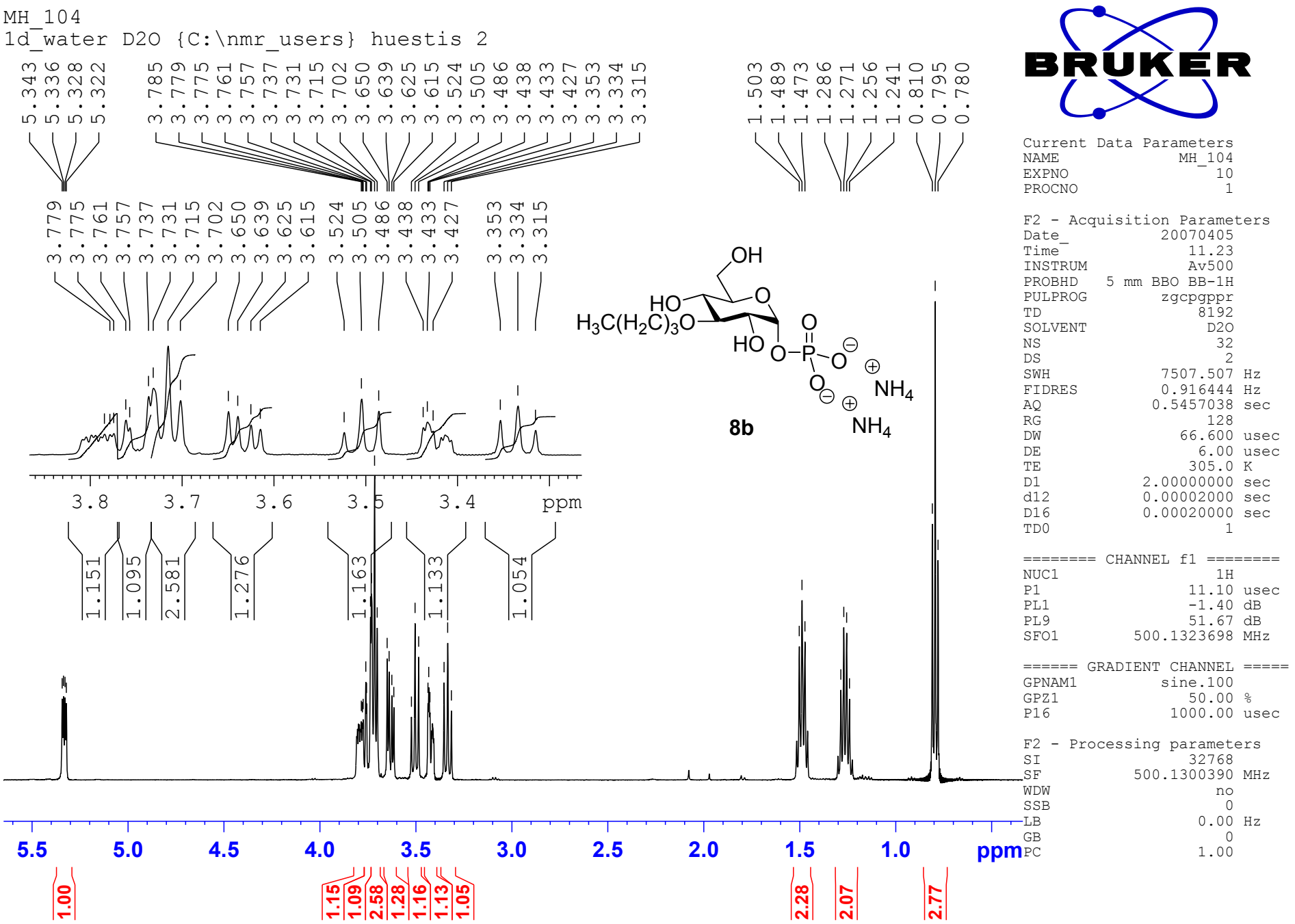
Clean NH4 OMe Salt
1d_31P{1H} D2O {C:\nmr_users} huestis 12



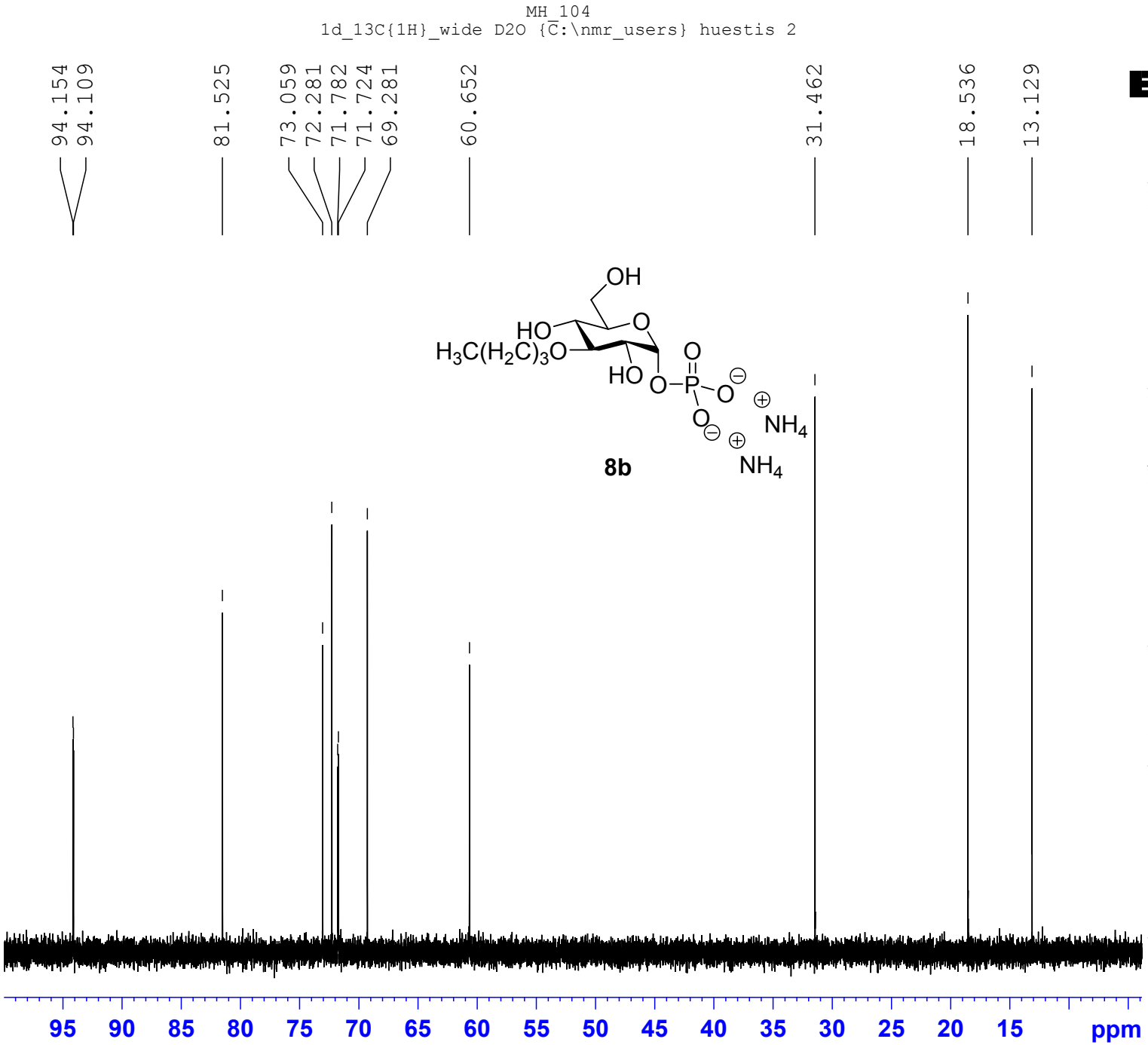
8a

```
Current Data Parameters
NAME      Clean NH4 OMe Salt
EXPNO                   13
PROCNO                   1

F2 - Acquisition Parameters
Date_           20070330
Time                8.23
INSTRUM            Av500
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT              D2O
NS                   512
DS                     0
SWH           98039.219 Hz
FIDRES         1.495960 Hz
AQ            0.3342887 sec
RG               7298.2
DW                5.100 usec
DE                6.00 usec
TE               300.4 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
TD0                    2

======== CHANNEL f1 ========
NUC1                 31P
P1                  8.41 usec
PL1                 0.50 dB
SFO1        202.4664658 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -1.40 dB
PL12               15.83 dB
PL13               19.37 dB
SFO2        500.1322696 MHz

F2 - Processing parameters
SI                 65536
SF          202.4563430 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

MH_104
1d_water D2O {C:\nmr_users} huestis 2




```
Current Data Parameters
NAME                  MH_104
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20070405
Time                  11.23
INSTRUM               Av500
PROBHD    5 mm BBO BB-1H
PULPROG           zgcpgppr
TD                    8192
SOLVENT               D2O
NS                      32
DS                       2
SWH               7507.507 Hz
FIDRES            0.916444 Hz
AQ                0.5457038 sec
RG                      128
DW                  66.600 usec
DE                   6.00 usec
TE                  305.0 K
D1              2.00000000 sec
d12             0.00002000 sec
D16             0.00020000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  11.10 usec
PL1                 -1.40 dB
PL9                 51.67 dB
SFO1          500.1323698 MHz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPZ1                50.00 %
P16               1000.00 usec

F2 - Processing parameters
SI                    32768
SF            500.1300390 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```



Current Data Parameters
NAME MH_104
EXPNO 11
PROCNO 1

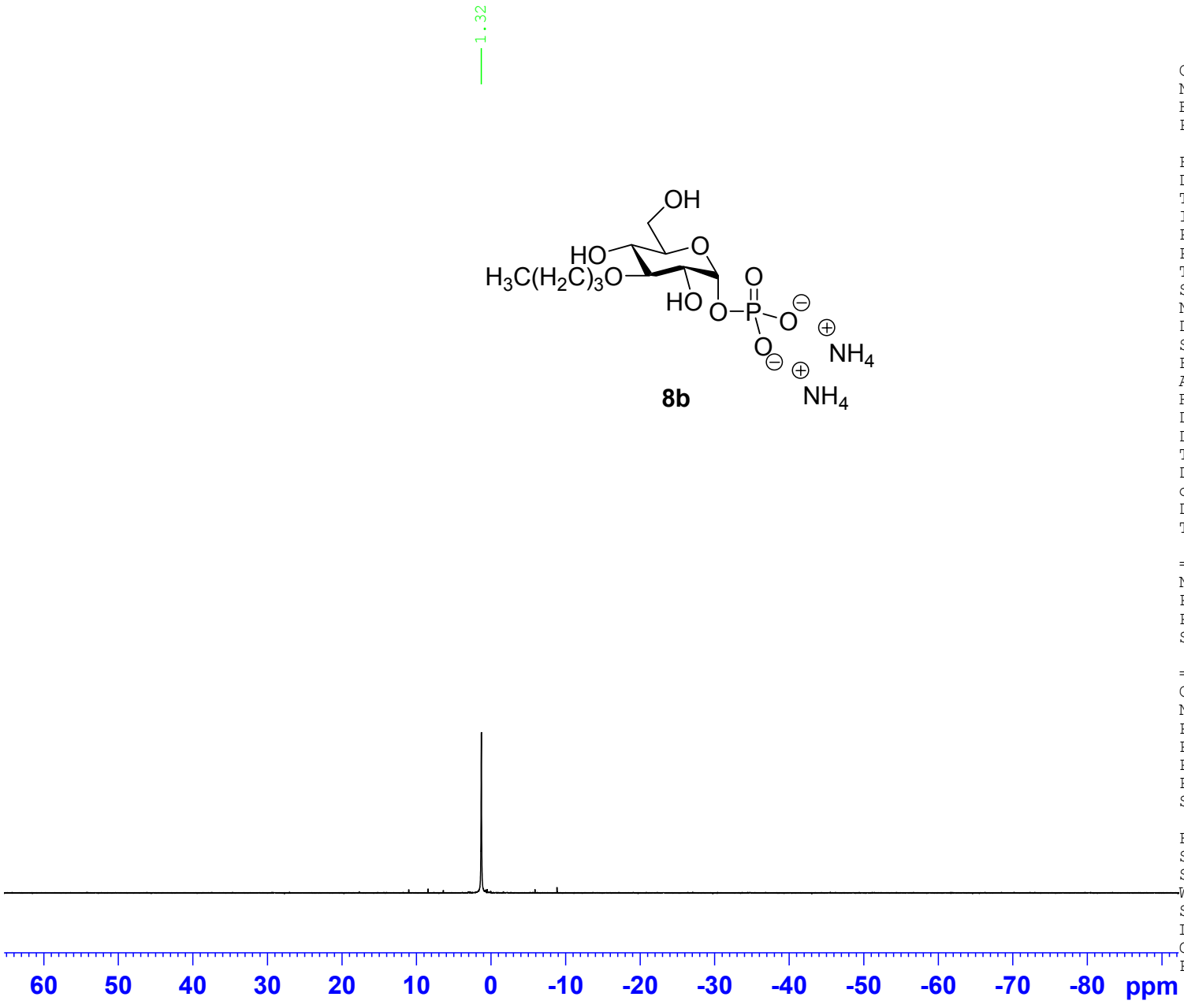
F2 - Acquisition Parameters
Date_ 20070405
Time 11.32
INSTRUM Av500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT D2O
NS 1024
DS 2
SWH 33783.785 Hz
FIDRES 0.515500 Hz
AQ 0.9699976 sec
RG 1024
DW 14.800 usec
DE 6.00 usec
TE 300.6 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P1 7.90 usec
PL1 0.00 dB
SFO1 125.7716270 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.40 dB
PL12 15.83 dB
PL13 19.37 dB
SFO2 500.1322696 MHz

F2 - Processing parameters
SI 65536
SF 125.7577930 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

MH_104
1d_31P{1H} D2O {C:\nmr_users} huestis 2



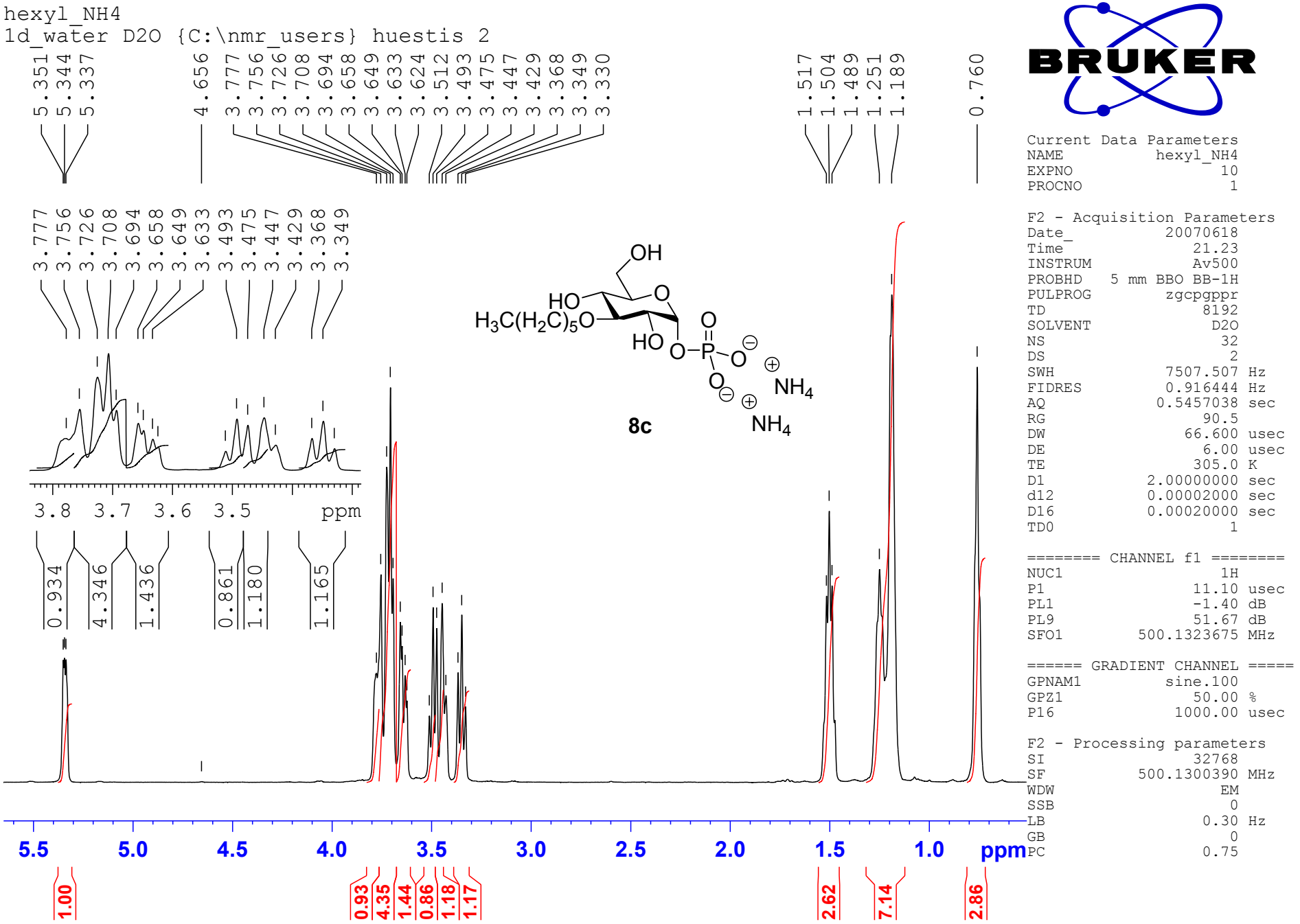
Current Data Parameters
NAME MH_104
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070405
Time 12.06
INSTRUM Av500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT D2O
NS 512
DS 0
SWH 98039.219 Hz
FIDRES 1.495960 Hz
AQ 0.3342887 sec
RG 10321.3
DW 5.100 usec
DE 6.00 usec
TE 300.6 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 2

======== CHANNEL f1 ========
NUC1 31P
P1 8.41 usec
PL1 0.50 dB
SFO1 202.4664658 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.40 dB
PL12 15.83 dB
PL13 19.37 dB
SFO2 500.1322696 MHz

F2 - Processing parameters
SI 65536
SF 202.4563430 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00



Current Data Parameters
NAME hexyl_NH4
EXPNO 10
PROCNO 1

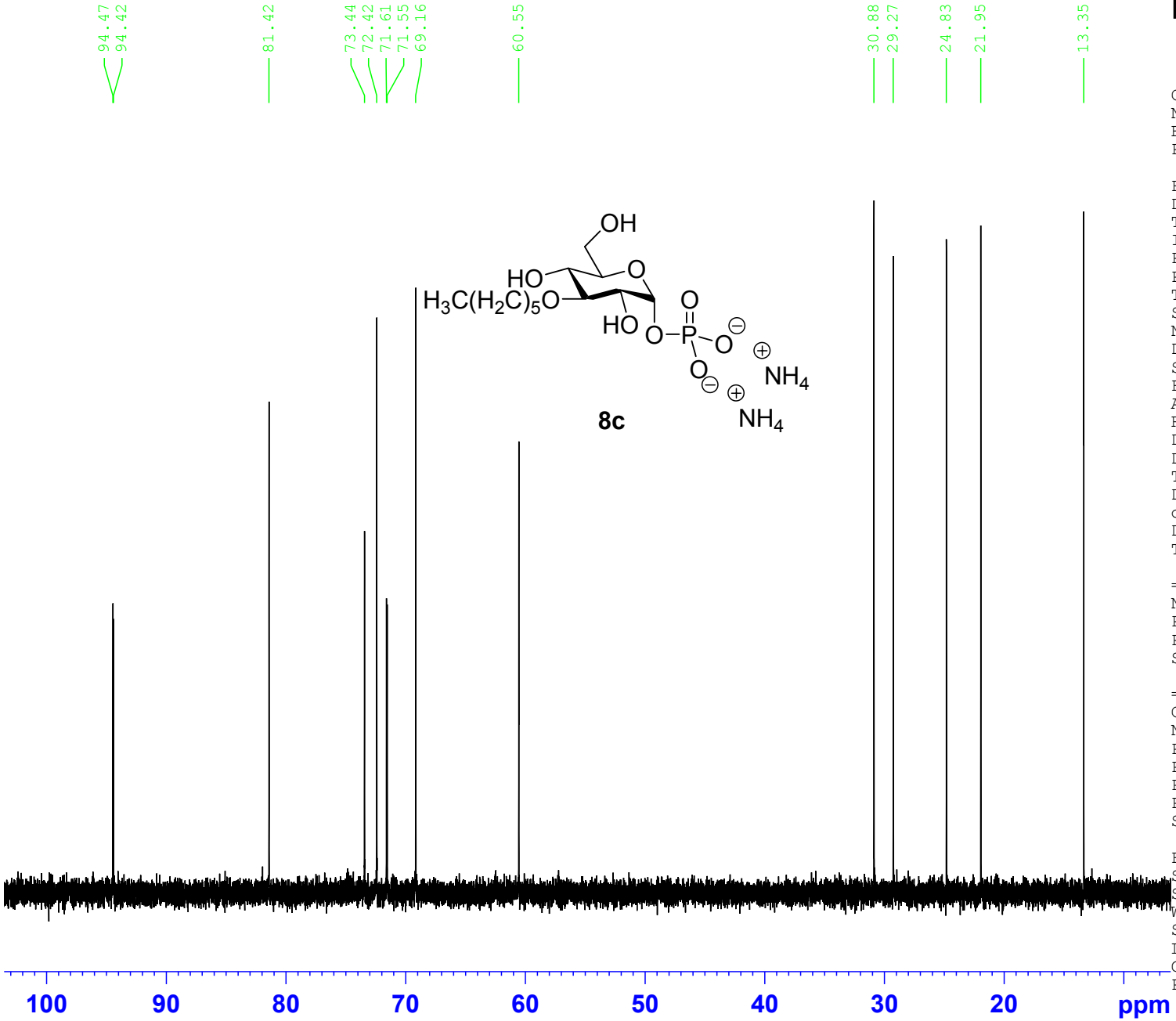
F2 - Acquisition Parameters
Date_ 20070618
Time 21.23
INSTRUM Av500
PROBHD 5 mm BBO BB-1H
PULPROG zgcpgppr
TD 8192
SOLVENT D2O
NS 32
DS 2
SWH 7507.507 Hz
FIDRES 0.916444 Hz
AQ 0.5457038 sec
RG 90.5
DW 66.600 usec
DE 6.00 usec
TE 305.0 K
D1 2.00000000 sec
d12 0.00002000 sec
D16 0.00020000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 11.10 usec
PL1 -1.40 dB
PL9 51.67 dB
SFO1 500.1323675 MHz

====== GRADIENT CHANNEL =====
GPNAM1 sine.100
GPZ1 50.00 %
P16 1000.00 usec

F2 - Processing parameters
SI 32768
SF 500.1300390 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.75

hexyl_NH4
1d_13C{1H}_n D2O {C:\nmr_users} huestis 2



Current Data Parameters
NAME hexyl_NH4
EXPNO 12
PROCNO 1

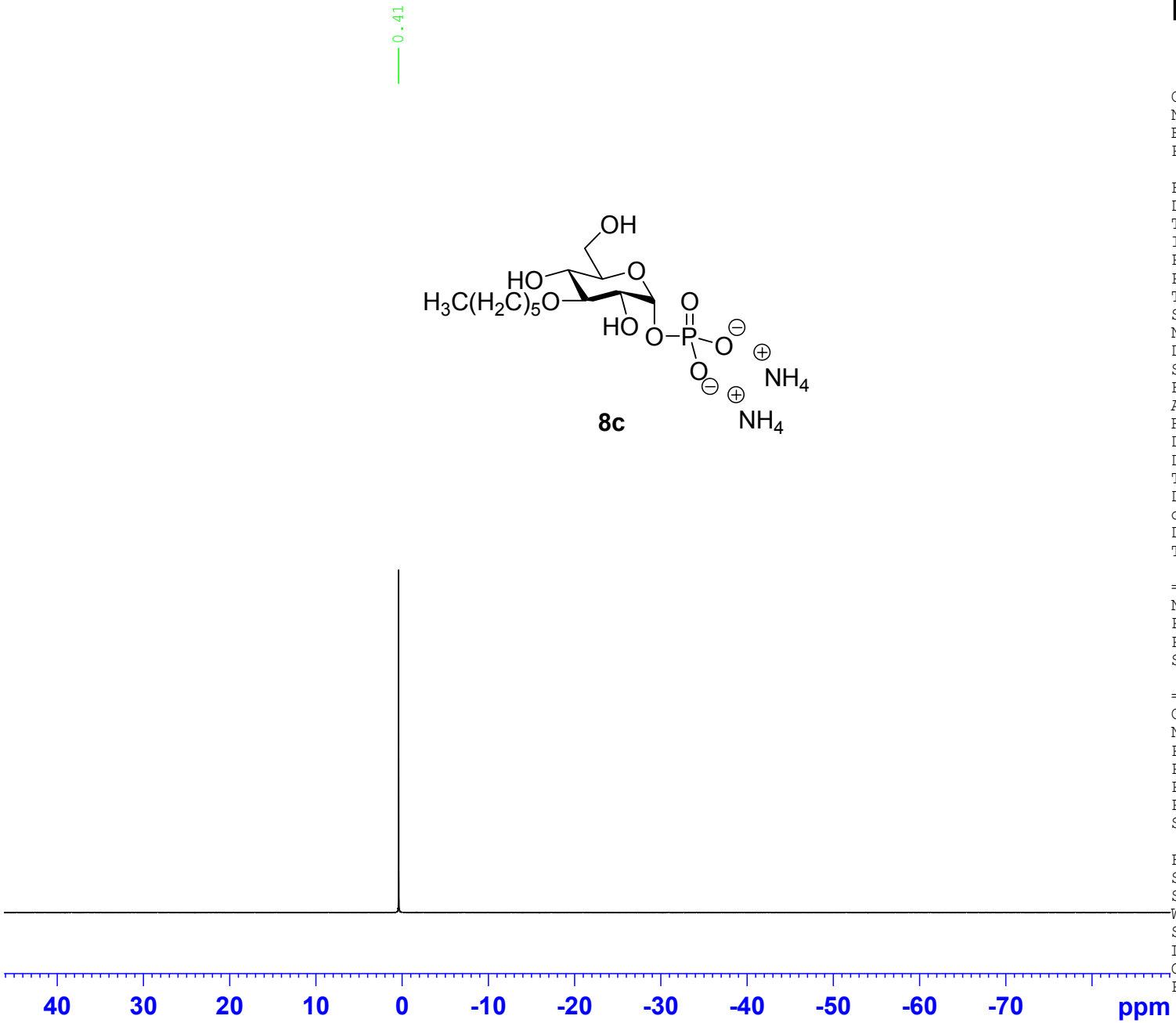
F2 - Acquisition Parameters
Date_ 20070618
Time 21.37
INSTRUM Av500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 54048
SOLVENT D2O
NS 1024
DS 4
SWH 33783.785 Hz
FIDRES 0.625070 Hz
AQ 0.7999752 sec
RG 9195.2
DW 14.800 usec
DE 21.14 usec
TE 300.4 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P1 7.90 usec
PL1 0.00 dB
SFO1 125.7716273 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.40 dB
PL12 15.83 dB
PL13 19.37 dB
SFO2 500.1322696 MHz

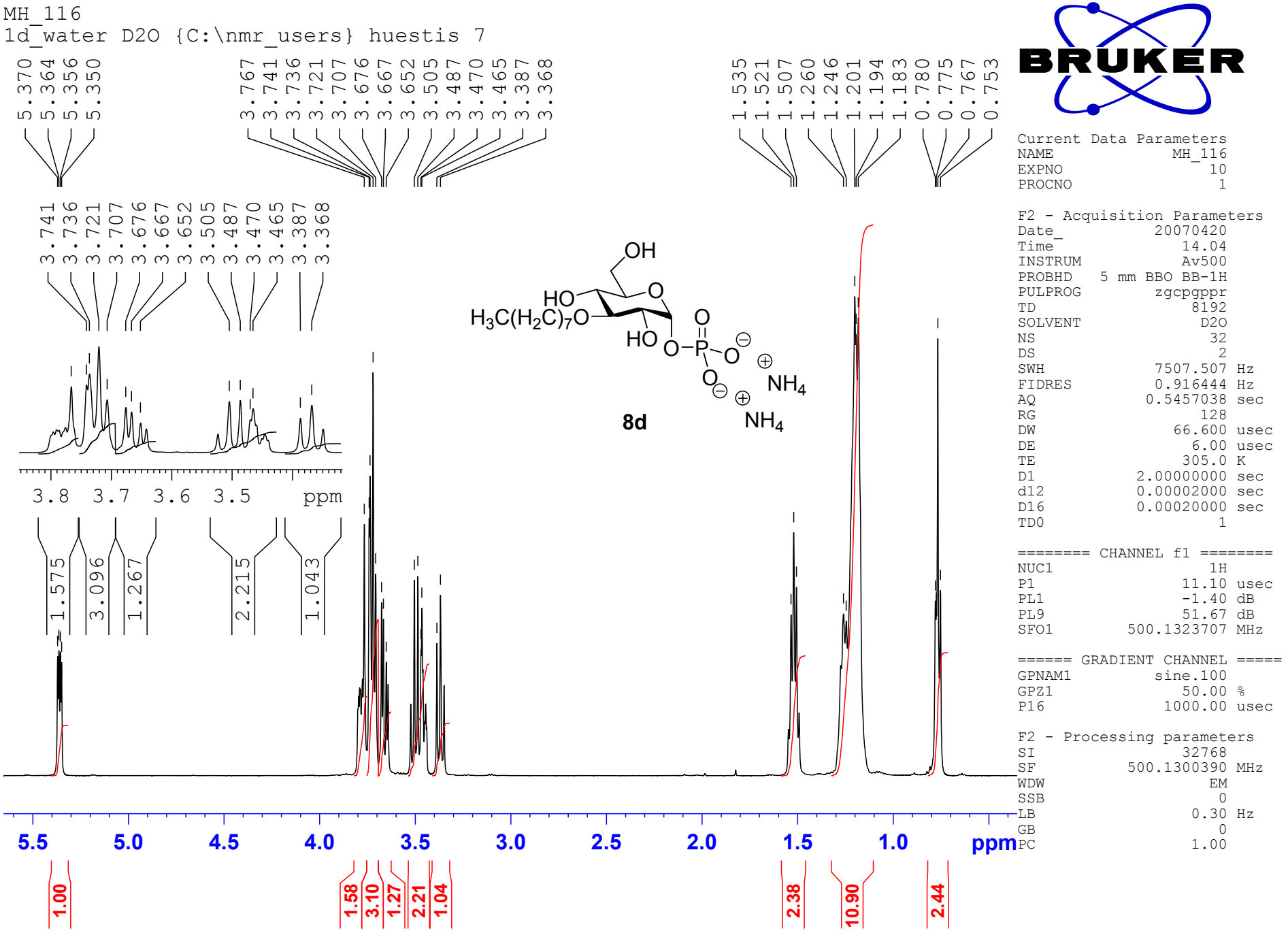
F2 - Processing parameters
SI 65536
SF 125.7577930 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.75

hexyl_NH4
1d_31P{1H}_d D2O {C:\nmr_users} huestis 2



8c

```
Current Data Parameters
NAME          hexyl_NH4
EXPNO                13
PROCNO                1

F2 - Acquisition Parameters
Date_          20070618
Time              22.09
INSTRUM           Av500
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT             D2O
NS                  512
DS                    4
SWH           98039.219 Hz
FIDRES         1.495960 Hz
AQ            0.3342887 sec
RG               9195.2
DW                5.100 usec
DE                7.29 usec
TE               300.4 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
TD0                   2

======== CHANNEL f1 ========
NUC1                 31P
P1                8.41 usec
PL1               0.50 dB
SFO1        202.4664658 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            80.00 usec
PL2              -1.40 dB
PL12             15.83 dB
PL13             19.37 dB
SFO2        500.1322696 MHz

F2 - Processing parameters
SI                65536
SF          202.4563430 MHz
WDW                  no
SSB                   0
LB                0.00 Hz
GB                    0
PC                0.75
```



Current Data Parameters

NAME	MH_116
EXPNO	10
PROCNO	1

F2 - Acquisition Parameters

Date_	20070420
Time	14.04
INSTRUM	Av500
PROBHD	5 mm BBO BB-1H
PULPROG	zgcpgppr
TD	8192
SOLVENT	D2O
NS	32
DS	2
SWH	7507.507 Hz
FIDRES	0.916444 Hz
AQ	0.5457038 sec
RG	128
DW	66.600 usec
DE	6.00 usec
TE	305.0 K
D1	2.00000000 sec
d12	0.00002000 sec
D16	0.00020000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	1H
P1	11.10 usec
PL1	-1.40 dB
PL9	51.67 dB
SFO1	500.1323707 MHz

====== GRADIENT CHANNEL =====

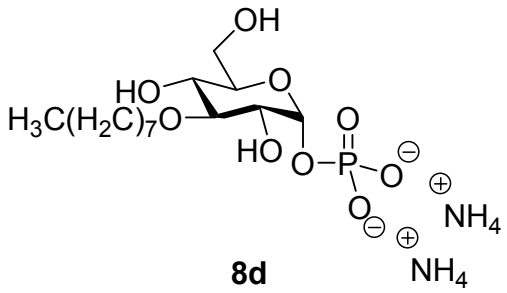
GPNAM1	sine.100
GPZ1	50.00 %
P16	1000.00 usec

F2 - Processing parameters

SI	32768
SF	500.1300390 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

MH_116
1d_13C{1H}_wide D2O {C:\nmr_users} huestis 7

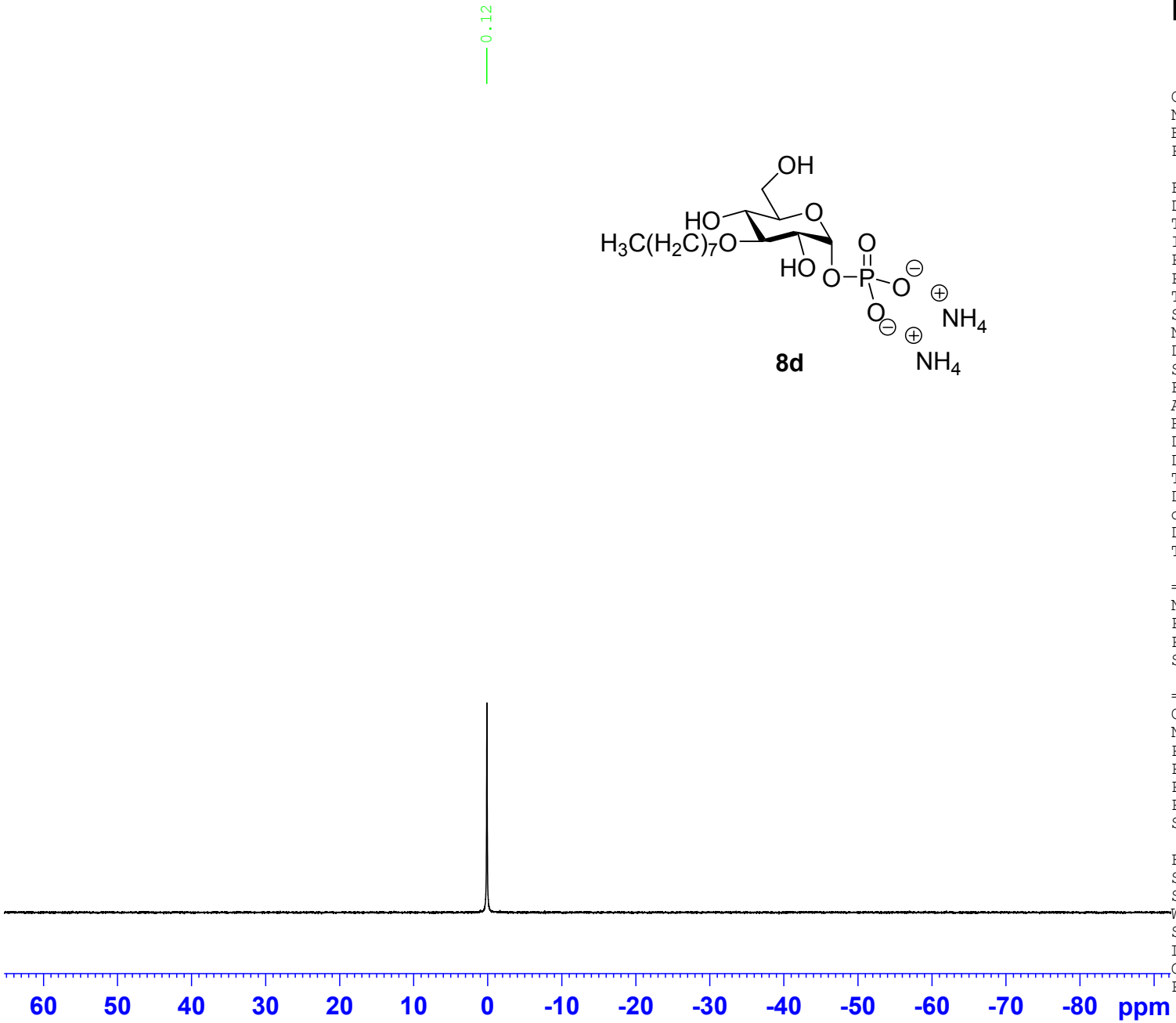
94.578
94.530
81.400
73.486
72.467
71.580
71.518
69.136
60.519
31.134
29.303
28.527
28.427
25.155
22.033
13.427



8d

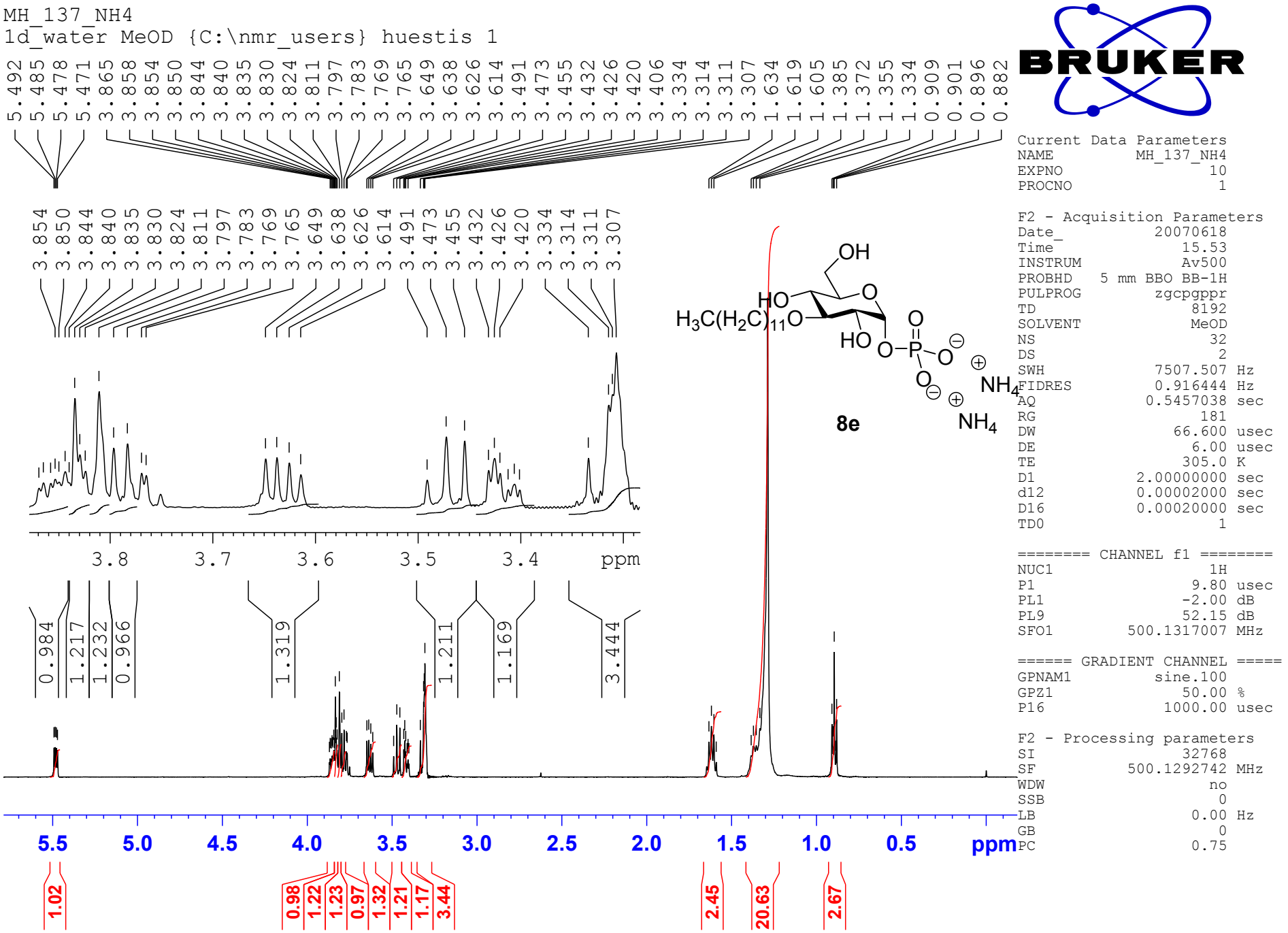

```
Current Data Parameters
NAME                  MH_116
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20070420
Time                  14.14
INSTRUM               Av500
PROBHD    5 mm BBO BB-1H
PULPROG              zgpg30
TD                    65536
SOLVENT                D2O
NS                     1024
DS                        2
SWH              33783.785 Hz
FIDRES            0.515500 Hz
AQ                0.9699976 sec
RG                     1024
DW                  14.800 usec
DE                   6.00 usec
TE                   300.4 K
D1              1.00000000 sec
d11             0.03000000 sec
DELTA           0.89999998 sec
TD0                       4

======== CHANNEL f1 ========
NUC1                    13C
P1                   7.90 usec
PL1                  0.00 dB
SFO1          125.7716270 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               80.00 usec
PL2                 -1.40 dB
PL12                15.83 dB
PL13                19.37 dB
SFO2          500.1322696 MHz

F2 - Processing parameters
SI                    65536
SF            125.7577930 MHz
WDW                      no
SSB                       0
LB                   0.00 Hz
GB                        0
PC                    1.40
```

MH_116
1d_31P{1H} D2O {C:\nmr_users} huestis 7



8d

```
Current Data Parameters
NAME                  MH_116
EXPNO                     12
PROCNO                     1

F2 - Acquisition Parameters
Date_               20070420
Time                   14.48
INSTRUM                Av500
PROBHD   5 mm BBO BB-1H
PULPROG                zgpg30
TD                     65536
SOLVENT                  D2O
NS                         512
DS                           0
SWH                98039.219 Hz
FIDRES              1.495960 Hz
AQ                  0.3342887 sec
RG                    10321.3
DW                      5.100 usec
DE                      6.00 usec
TE                     300.6 K
D1                 1.00000000 sec
d11                0.03000000 sec
DELTA              0.89999998 sec
TD0                          2

======== CHANNEL f1 ========
NUC1                      31P
P1                      8.41 usec
PL1                     0.50 dB
SFO1             202.4664658 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2                    -1.40 dB
PL12                   15.83 dB
PL13                   19.37 dB
SFO2             500.1322696 MHz

F2 - Processing parameters
SI                         65536
SF               202.4563430 MHz
WDW                           no
SSB                            0
LB                          0.00 Hz
GB                             0
PC                          1.00
```



Current Data Parameters
NAME MH_137_NH4
EXPNO 10
PROCNO 1

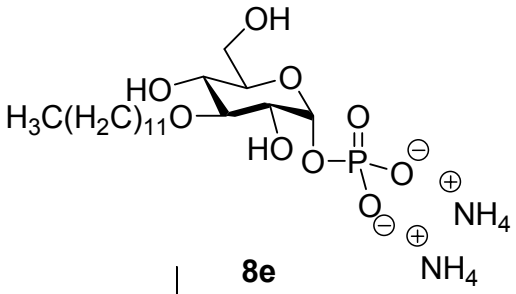
F2 - Acquisition Parameters
Date_ 20070618
Time 15.53
INSTRUM Av500
PROBHD 5 mm BBO BB-1H
PULPROG zgcpgppr
TD 8192
SOLVENT MeOD
NS 32
DS 2
SWH 7507.507 Hz
FIDRES 0.916444 Hz
AQ 0.5457038 sec
RG 181
DW 66.600 usec
DE 6.00 usec
TE 305.0 K
D1 2.00000000 sec
d12 0.00002000 sec
D16 0.00020000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 9.80 usec
PL1 -2.00 dB
PL9 52.15 dB
SFO1 500.1317007 MHz

====== GRADIENT CHANNEL =====
GPNAM1 sine.100
GPZ1 50.00 %
P16 1000.00 usec

F2 - Processing parameters
SI 32768
SF 500.1292742 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.75

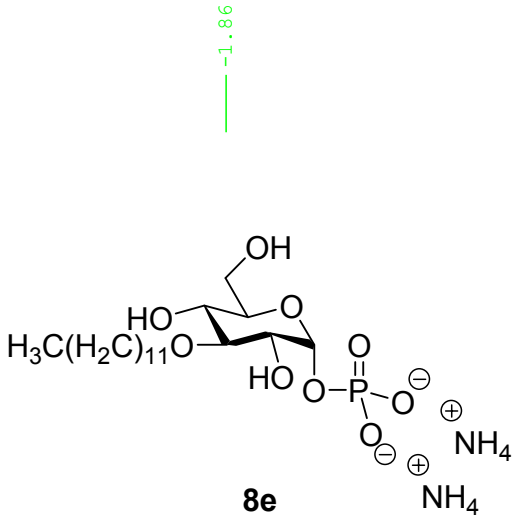
MH_137_NH4
1d_13C{1H}_n_MeOD_{C:\nmr_users}_huestis_1



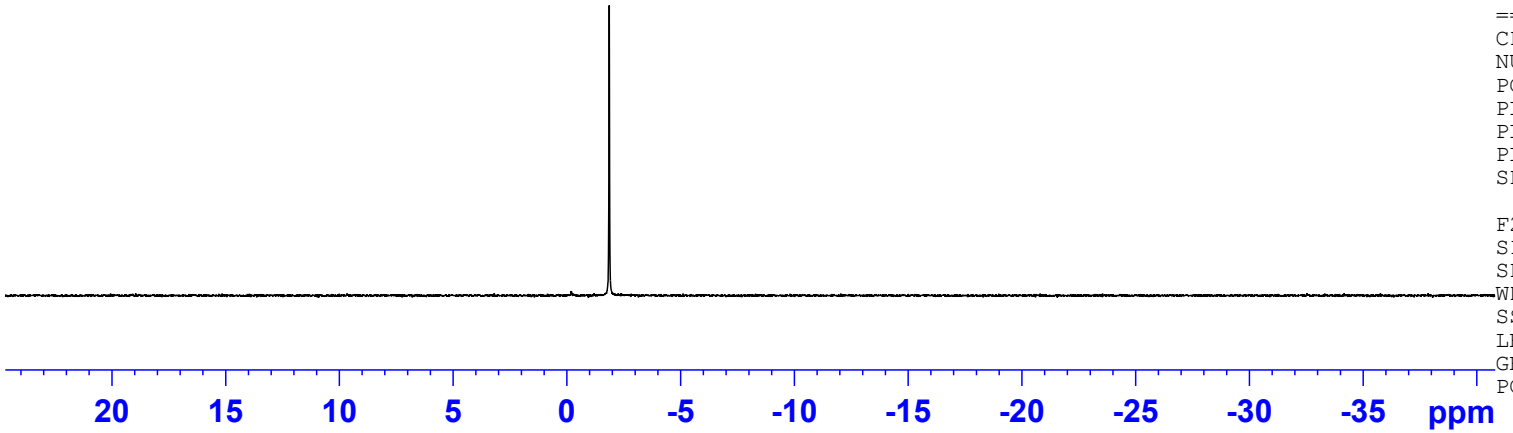
8e

```
Current Data Parameters
NAME          MH_137_NH4
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070618
Time              17.50
INSTRUM           Av500
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                54048
SOLVENT             MeOD
NS                 1024
DS                    4
SWH           33783.785 Hz
FIDRES         0.625070 Hz
AQ             0.7999752 sec
RG                9195.2
DW                14.800 usec
DE                21.14 usec
TE                300.4 K
D1             1.00000000 sec
d11            0.03000000 sec
DELTA          0.89999998 sec
TD0                   4

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.90 usec
PL1                 0.00 dB
SFO1         125.7716273 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               15.72 dB
PL13               19.37 dB
SFO2         500.1322696 MHz

F2 - Processing parameters
SI                 65536
SF           125.7576190 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  0.75
```

MH_137_NH4
1d_31P{1H}_d MeOD {C:\nmr_users} huestis 1

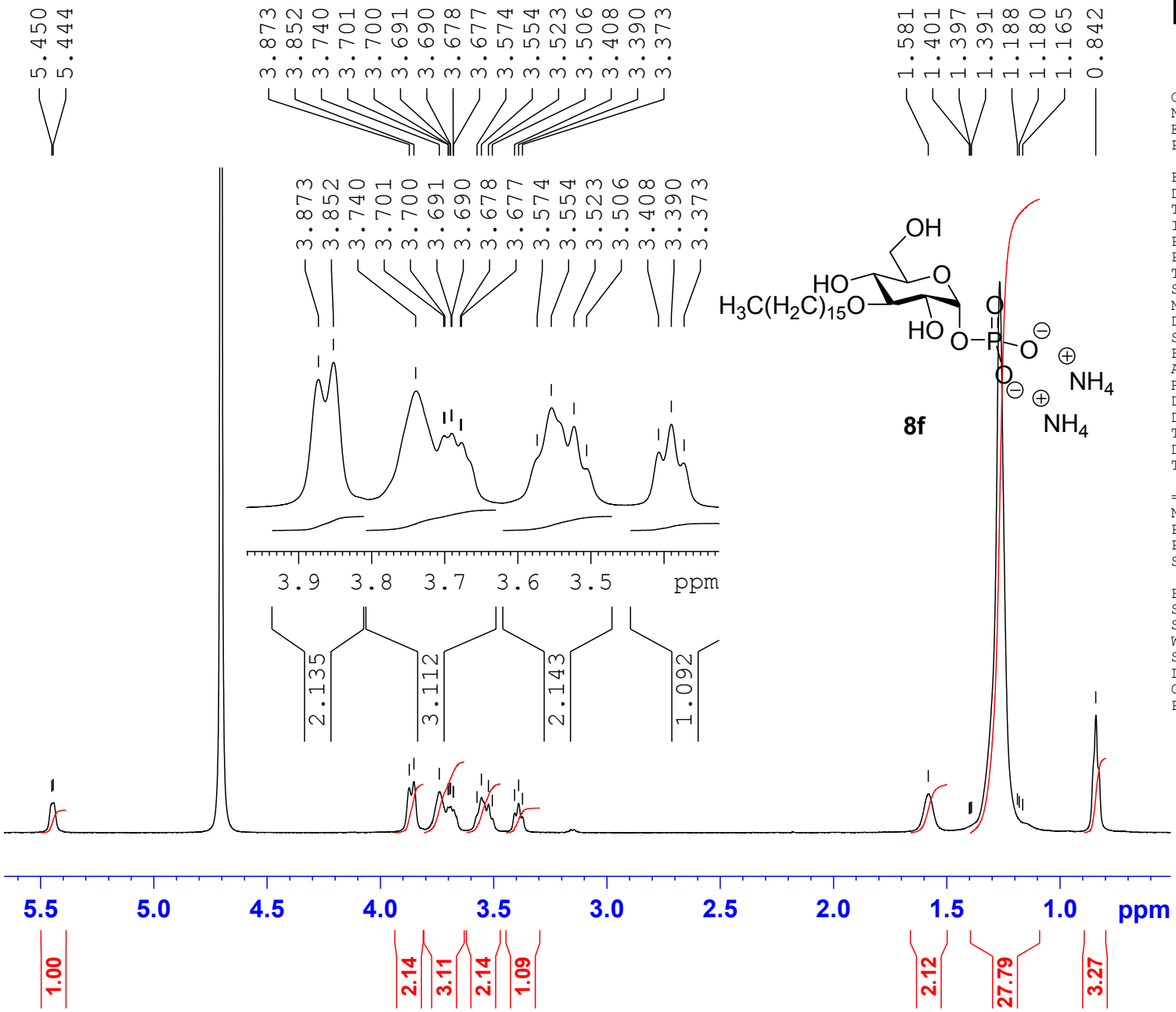


8e




```
Current Data Parameters
NAME          MH_137_NH4
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070618
Time              16.01
INSTRUM           Av500
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT             MeOD
NS                  512
DS                    4
SWH           98039.219 Hz
FIDRES         1.495960 Hz
AQ            0.3342887 sec
RG               9195.2
DW                5.100 usec
DE                7.29 usec
TE                300.4 K
D1            1.00000000 sec
d11           0.03000000 sec
DELTA         0.89999998 sec
TD0                   2

======== CHANNEL f1 ========
NUC1                 31P
P1                8.41 usec
PL1               0.50 dB
SFO1        202.4664658 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            80.00 usec
PL2              -2.00 dB
PL12             15.72 dB
PL13             19.37 dB
SFO2        500.1322696 MHz

F2 - Processing parameters
SI                65536
SF          202.4563430 MHz
WDW                  no
SSB                   0
LB                0.00 Hz
GB                    0
PC                0.75
```

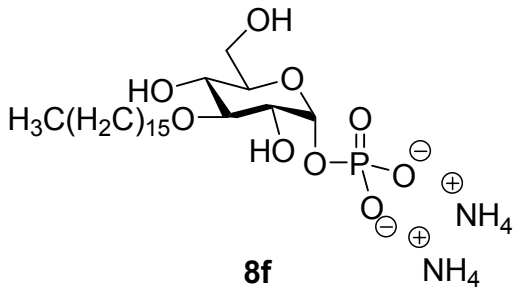
Gaia-4,6-benzylidene
1d_1H D2O {C:\nmr_users} huestis 4




```
Current Data Parameters
NAME      Hexadecyl deprotected 3
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070719
Time                2.00
INSTRUM            Av500
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT              D2O
NS                   128
DS                     2
SWH           10000.000 Hz
FIDRES            0.152588 Hz
AQ             3.2769001 sec
RG                 228.1
DW                50.000 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.80 usec
PL1                -2.00 dB
SFO1         500.1332698 MHz

F2 - Processing parameters
SI                 65536
SF           500.1300190 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  0.75
```

hexadecyl deprotected carbon
1d_13C{1H}_n D2O {C:\nmr_users} huestis 3

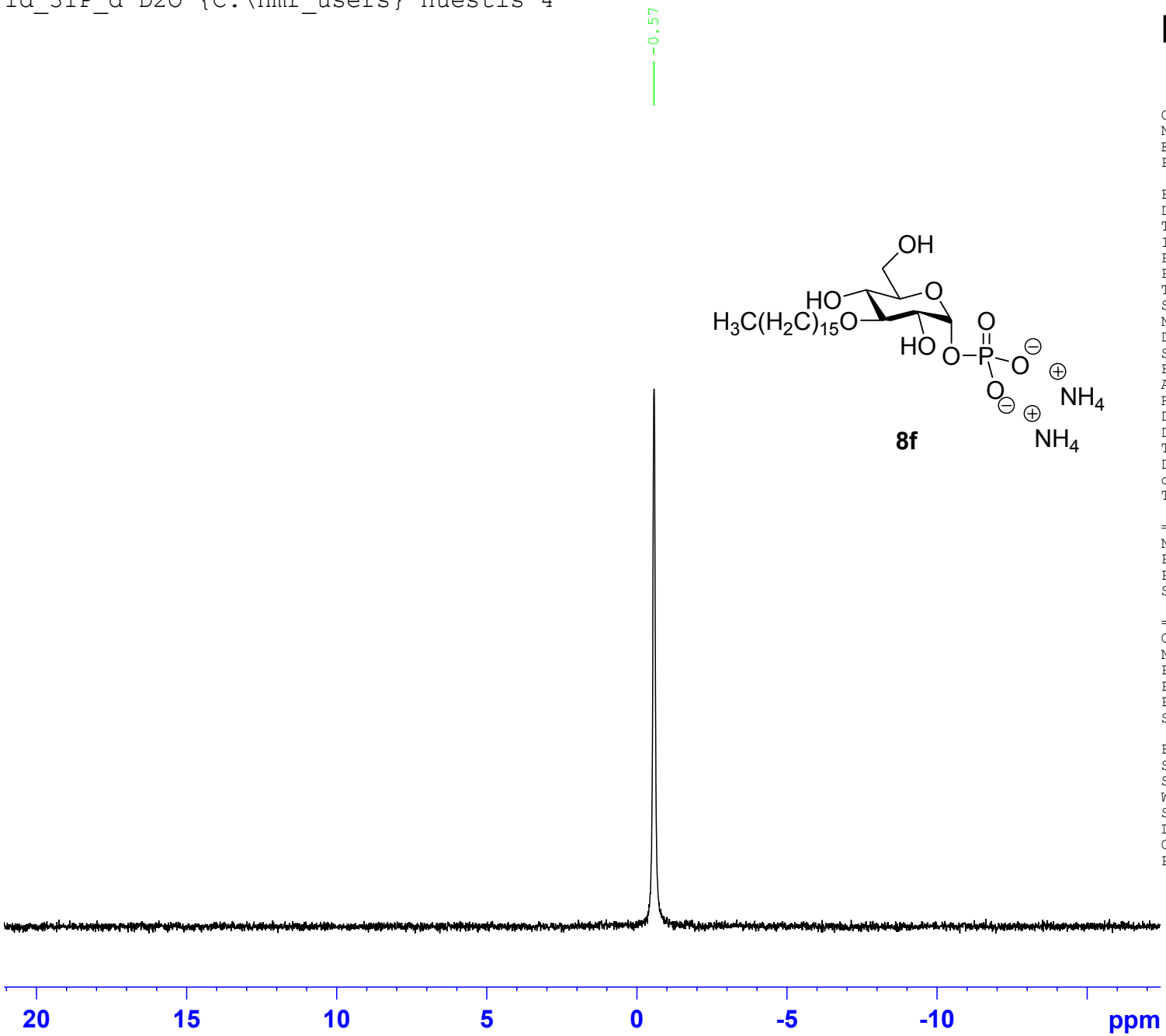
94.89 94.84 81.03 72.72 72.27 71.12 71.11 69.37 61.09 61.07 32.12 30.27 30.09 29.99 29.96 29.77 29.71 26.15 22.73 13.87 13.83



8f


```
Current Data Parameters
NAME      hexadecyl deprotected carbon
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070724
Time              18.18
INSTRUM           Av500
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                54048
SOLVENT             D2O
NS                 8192
DS                    4
SWH           33783.785 Hz
FIDRES         0.625070 Hz
AQ             0.7999752 sec
RG               10321.3
DW                14.800 usec
DE                21.14 usec
TE                296.6 K
D1            1.00000000 sec
d11           0.03000000 sec
DELTA         0.89999998 sec
TD0                   32

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.90 usec
PL1                 0.00 dB
SFO1         125.7716273 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               15.72 dB
PL13               18.64 dB
SFO2         500.1322696 MHz

F2 - Processing parameters
SI                65536
SF           125.7577930 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 0.75
```

Gaia-4,6-benzylidene
1d_31P_d D2O {C:\nmr_users} huestis 4



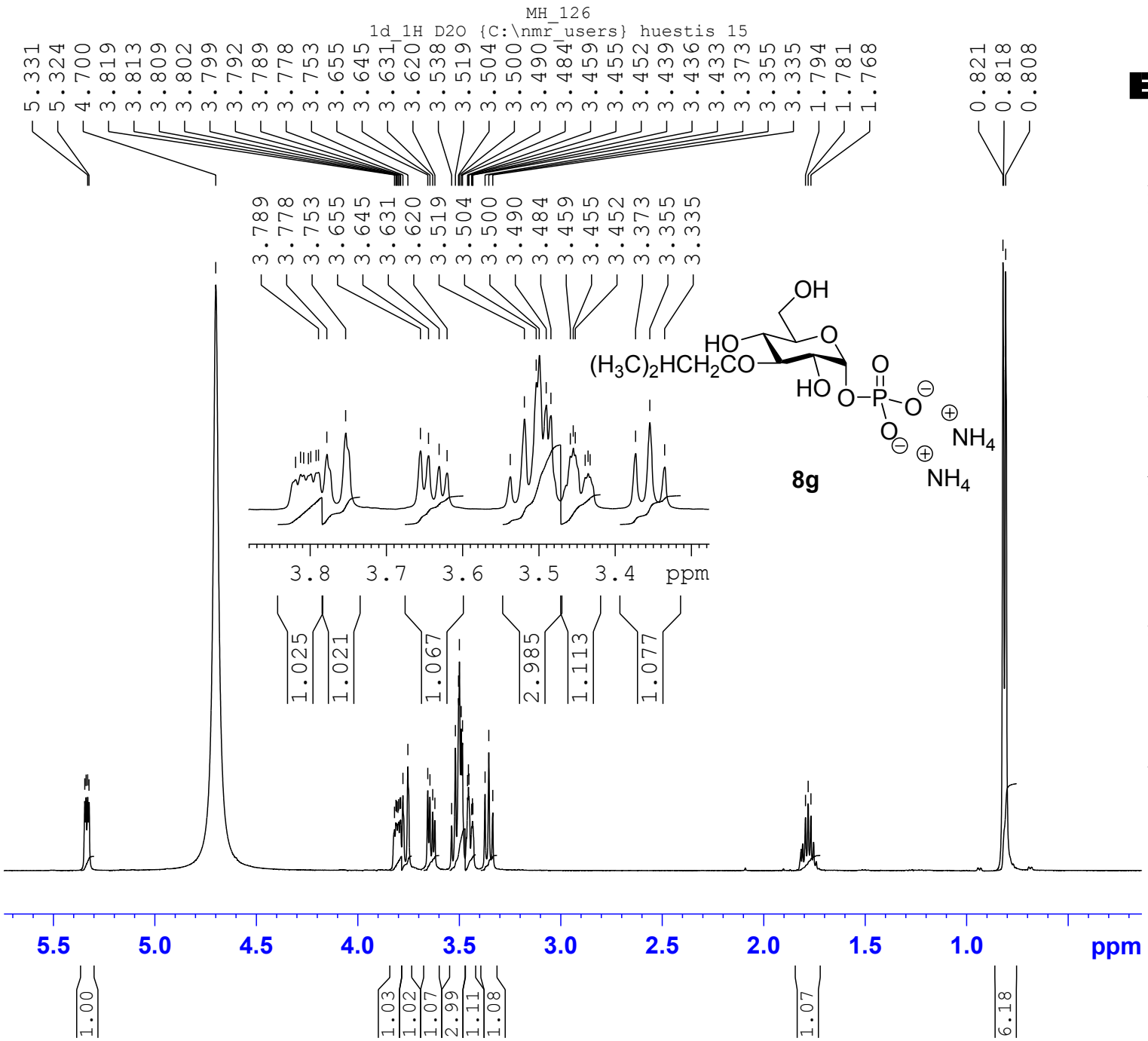
Current Data Parameters
NAME Hexadecyl deprotected 3
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070719
Time 1.33
INSTRUM Av500
PROBHD 5 mm BBO BB-1H
PULPROG zggd30
TD 65536
SOLVENT D2O
NS 1024
DS 2
SWH 98039.219 Hz
FIDRES 1.495960 Hz
AQ 0.3342887 sec
RG 7298.2
DW 5.100 usec
DE 7.29 usec
TE 300.6 K
D1 1.00000000 sec
d11 0.03000000 sec
TD0 4

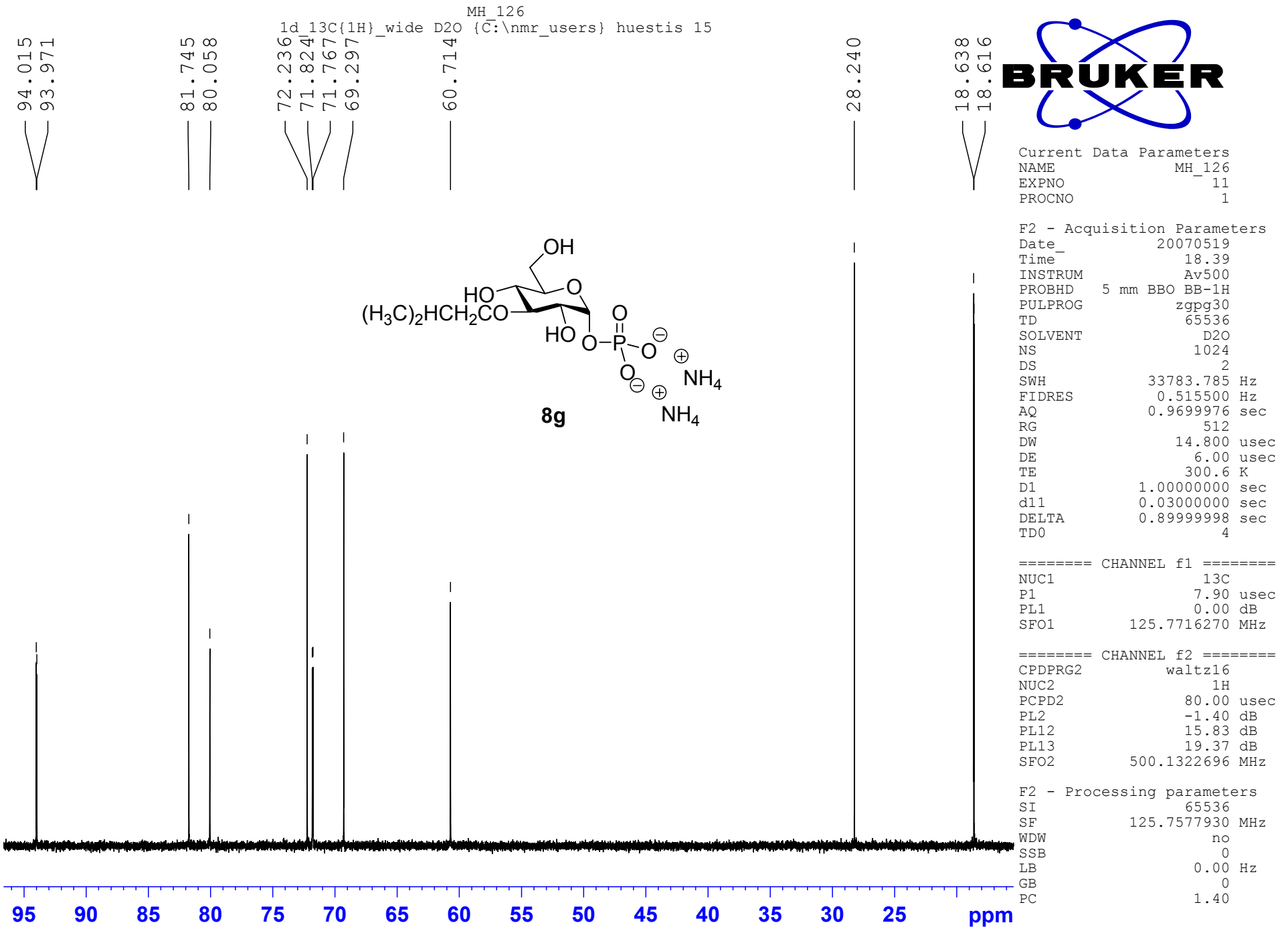
======== CHANNEL f1 ========
NUC1 31P
P1 8.41 usec
PL1 0.50 dB
SFO1 202.4664652 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 15.72 dB
SFO2 500.1322696 MHz

F2 - Processing parameters
SI 65536
SF 202.4563430 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.75




```
Current Data Parameters
NAME                  MH_126
EXPNO                     15
PROCNO                     1

F2 - Acquisition Parameters
Date_              20070519
Time                  22.08
INSTRUM               Av500
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT                D2O
NS                        64
DS                         2
SWH              10000.000 Hz
FIDRES               0.152588 Hz
AQ                3.2769001 sec
RG                     71.8
DW                   50.000 usec
DE                    6.00 usec
TE                   300.0 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                    11.10 usec
PL1                   -1.40 dB
SFO1          500.1332698 MHz

F2 - Processing parameters
SI                        65536
SF            500.1300190 MHz
WDW                         no
SSB                          0
LB                    0.00 Hz
GB                           0
PC                    1.00
```



Current Data Parameters
NAME MH_126
EXPNO 11
PROCNO 1

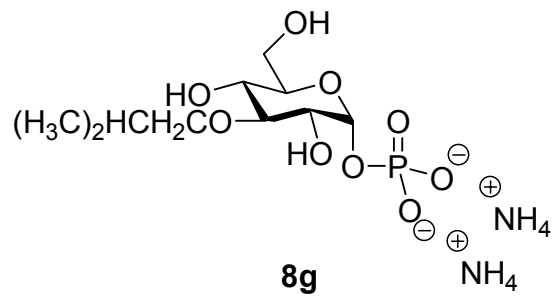
F2 - Acquisition Parameters
Date_ 20070519
Time 18.39
INSTRUM Av500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT D2O
NS 1024
DS 2
SWH 33783.785 Hz
FIDRES 0.515500 Hz
AQ 0.9699976 sec
RG 512
DW 14.800 usec
DE 6.00 usec
TE 300.6 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P1 7.90 usec
PL1 0.00 dB
SFO1 125.7716270 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.40 dB
PL12 15.83 dB
PL13 19.37 dB
SFO2 500.1322696 MHz

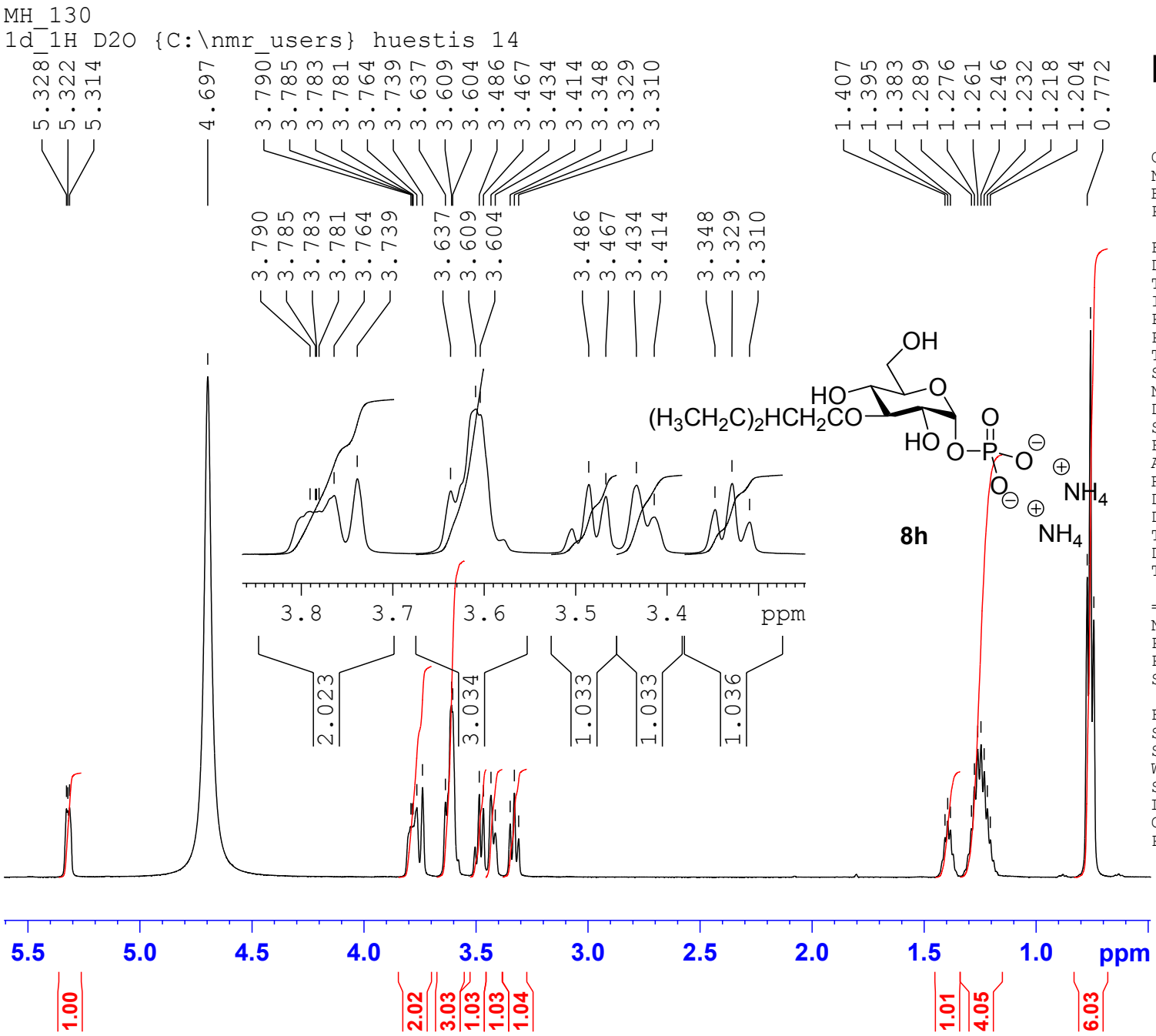
F2 - Processing parameters
SI 65536
SF 125.7577930 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

MH_126
1d_31P{1H} D2O {C:\nmr_users} huestis 15



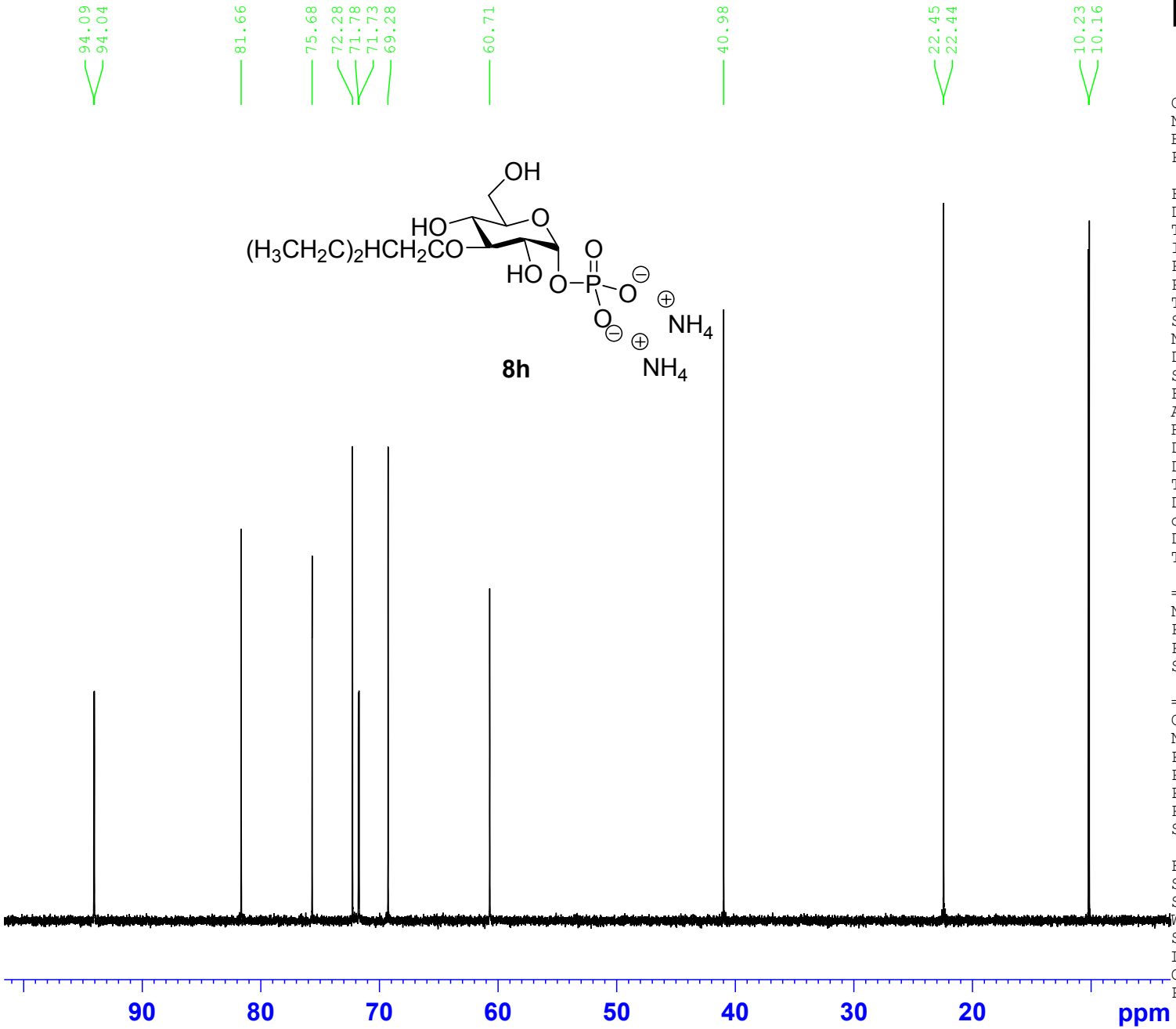
8g


```
Current Data Parameters
NAME                 MH_126
EXPNO                    12
PROCNO                    1

F2 - Acquisition Parameters
Date_             20070519
Time                 19.13
INSTRUM              Av500
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT                D2O
NS                       512
DS                         0
SWH              98039.219 Hz
FIDRES            1.495960 Hz
AQ                0.3342887 sec
RG                    6502
DW                   5.100 usec
DE                   6.00 usec
TE                  300.6 K
D1              1.00000000 sec
d11             0.03000000 sec
DELTA           0.89999998 sec
TD0                        2

======== CHANNEL f1 ========
NUC1                    31P
P1                     8.41 usec
PL1                    0.50 dB
SFO1          202.4664658 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -1.40 dB
PL12                 15.83 dB
PL13                 19.37 dB
SFO2          500.1322696 MHz

F2 - Processing parameters
SI                     65536
SF            202.4563430 MHz
WDW                       no
SSB                        0
LB                    0.00 Hz
GB                         0
PC                     1.00
```




```
Current Data Parameters
NAME                  MH_130
EXPNO                     13
PROCNO                     1

F2 - Acquisition Parameters
Date_              20070607
Time                   2.42
INSTRUM               Av500
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT                 D2O
NS                       32
DS                        2
SWH             10000.000 Hz
FIDRES              0.152588 Hz
AQ                3.2769001 sec
RG                       57
DW                  50.000 usec
DE                   6.00 usec
TE                   300.0 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    9.80 usec
PL1                  -2.00 dB
SFO1           500.1332698 MHz

F2 - Processing parameters
SI                    65536
SF             500.1300190 MHz
WDW                      no
SSB                       0
LB                    0.00 Hz
GB                        0
PC                     0.75
```

MH_130
1d_13C{1H}_n D2O {C:\nmr_users} huestis 14



Current Data Parameters
NAME MH_130
EXPNO 11
PROCNO 1

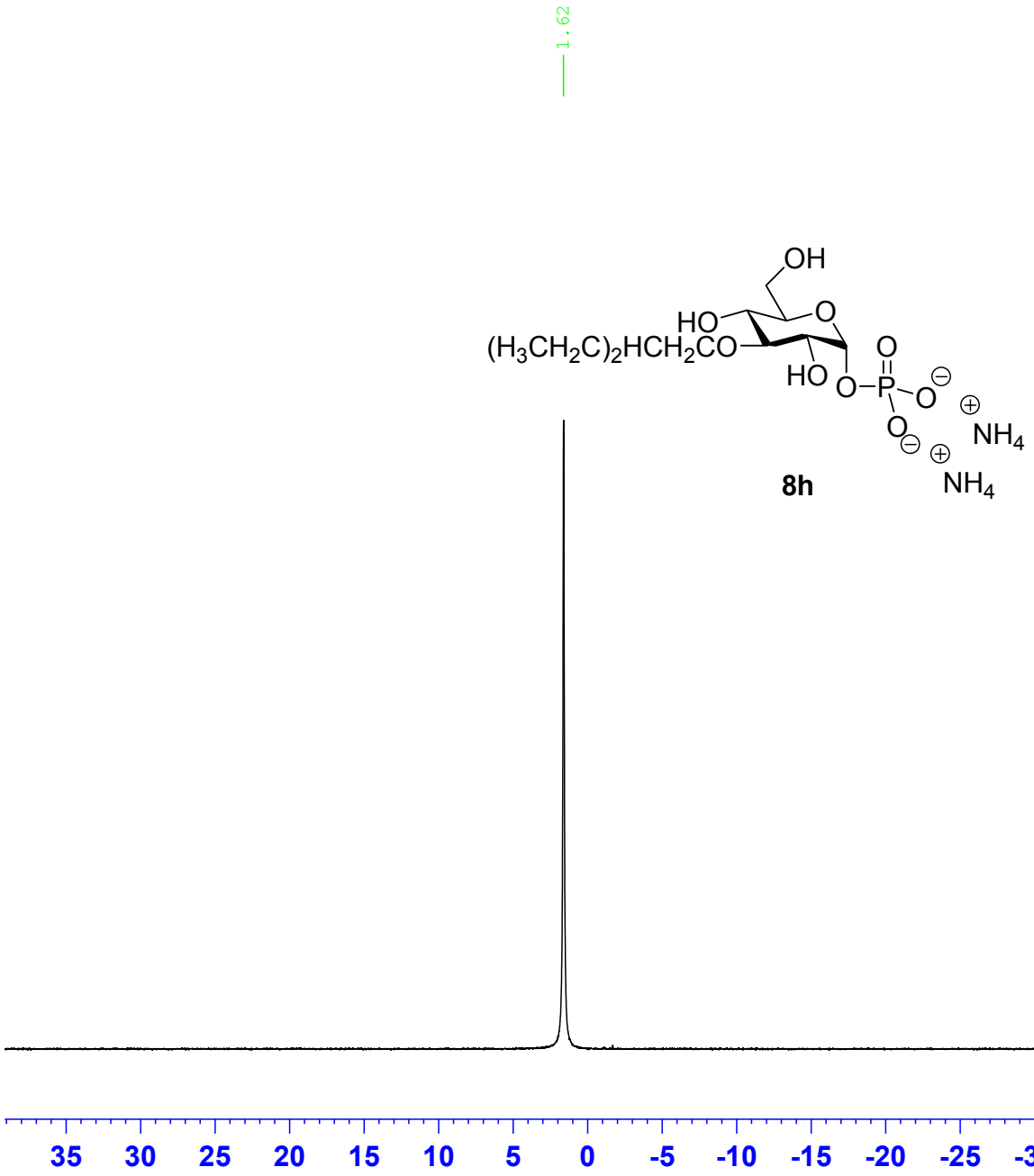
F2 - Acquisition Parameters
Date_ 20070607
Time 2.01
INSTRUM Av500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 54048
SOLVENT D2O
NS 1024
DS 4
SWH 33783.785 Hz
FIDRES 0.625070 Hz
AQ 0.7999752 sec
RG 9195.2
DW 14.800 usec
DE 21.14 usec
TE 300.4 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 4

======== CHANNEL f1 ========
NUC1 13C
P1 7.90 usec
PL1 0.00 dB
SFO1 125.7716273 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 15.72 dB
PL13 18.64 dB
SFO2 500.1322696 MHz

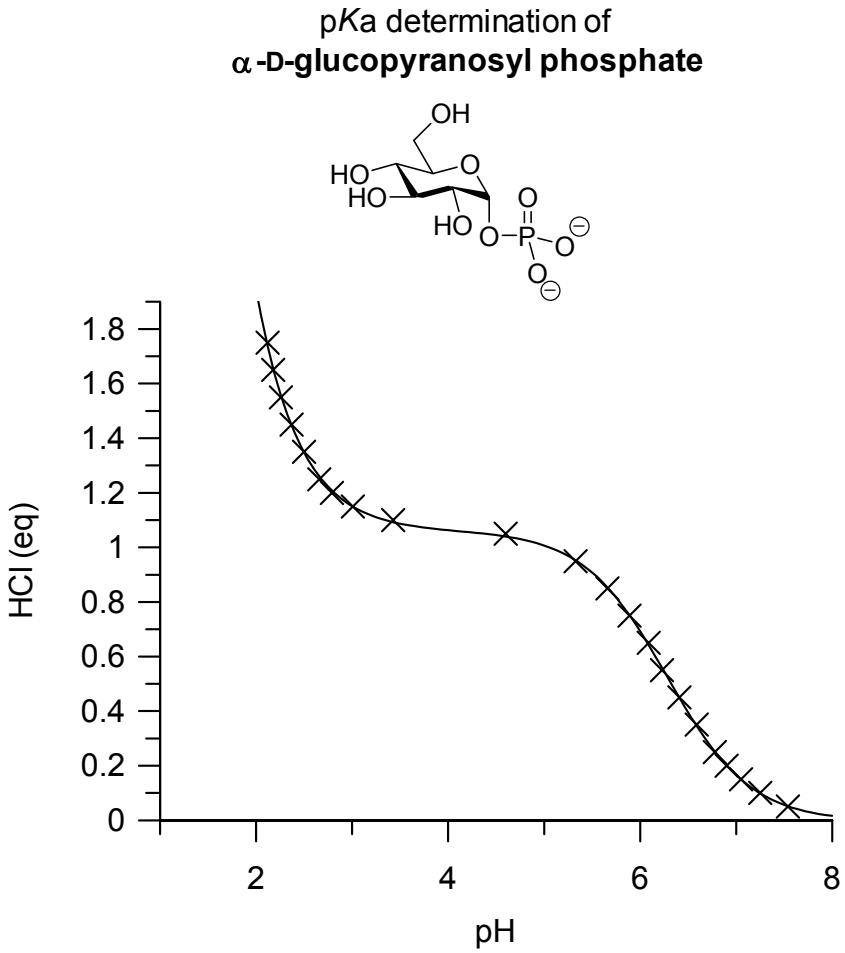
F2 - Processing parameters
SI 65536
SF 125.7577930 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.75

MH_130
1d_31P{1H} D2O {C:\nmr_users} huestis 14




```
Current Data Parameters
NAME                 MH_130
EXPNO                    12
PROCNO                    1

F2 - Acquisition Parameters
Date_              20070607
Time                   2.33
INSTRUM               Av500
PROBHD   5 mm BBO BB-1H
PULPROG              zgpg30
TD                    65536
SOLVENT                D2O
NS                       512
DS                         4
SWH              98039.219 Hz
FIDRES            1.495960 Hz
AQ                0.3342887 sec
RG                      8192
DW                   5.100 usec
DE                   7.29 usec
TE                   300.4 K
D1              1.00000000 sec
d11             0.03000000 sec
DELTA           0.89999998 sec
TD0                        2

======== CHANNEL f1 ========
NUC1                    31P
P1                   8.41 usec
PL1                  0.50 dB
SFO1          202.4664658 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               80.00 usec
PL2                 -2.00 dB
PL12                15.72 dB
PL13                18.64 dB
SFO2          500.1322696 MHz

F2 - Processing parameters
SI                     65536
SF            202.4563430 MHz
WDW                       no
SSB                        0
LB                   0.00 Hz
GB                         0
PC                    0.75
```

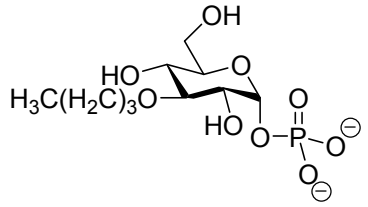
Determination of p*K*a2 for α-D-glucopyranosyl phosphate and compounds 8b, 8d, 8e and 8g



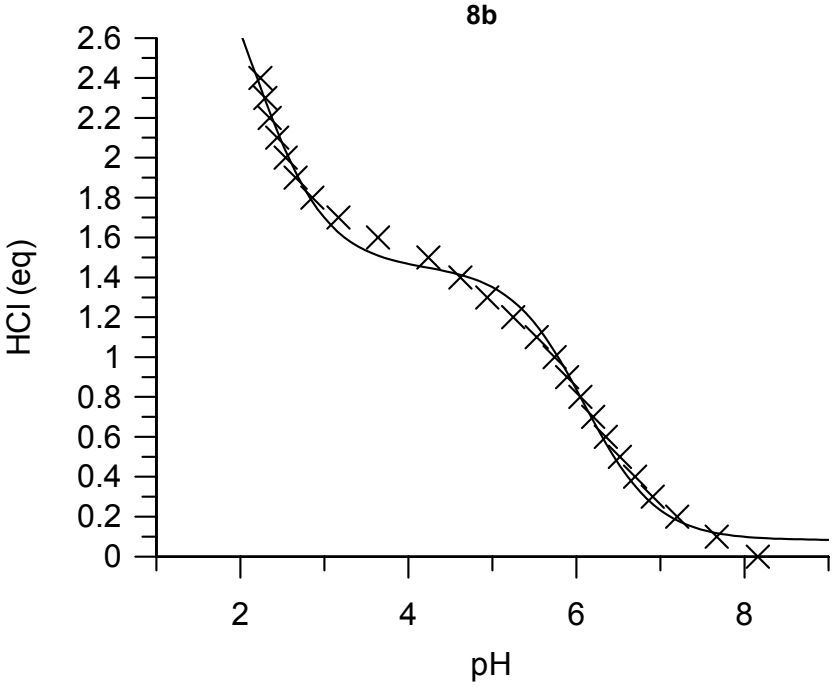
Parameter	Value	Std. Error
pKa 1	0.6783	0.0547
Lower Limit	20.5268	2.2855
Middle Limit	1.0593	0.0031
Upper Limit	-0.0042	0.0048
pKa 2	6.2798	0.0081

p*K*a determination of

3-*O*-Butyl-α-D-glucopyranosyl phosphate



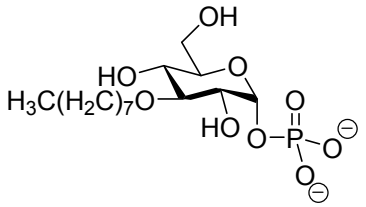
8b



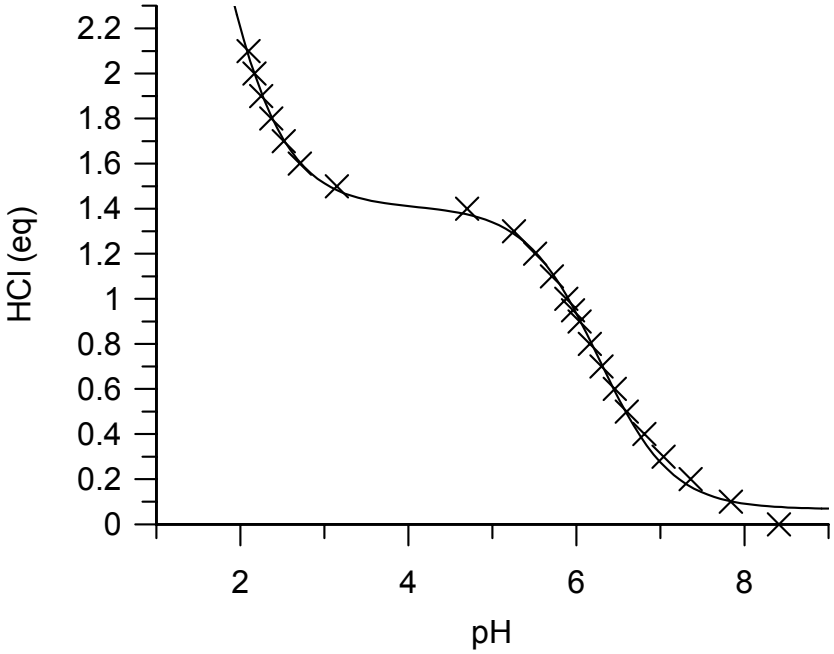
Parameter	Value	Std. Error
pKa 1	2.1514	0.1808
Lower Limit	3.4621	0.4900
Middle Limit	1.4506	0.0281
Upper Limit	0.0822	0.0304
pKa 2	6.0911	0.0461

p*K*a determination of

3-*O*-Octyl-α-D-glucopyranosyl phosphate



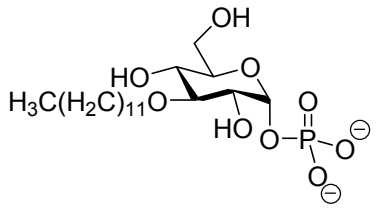
8d



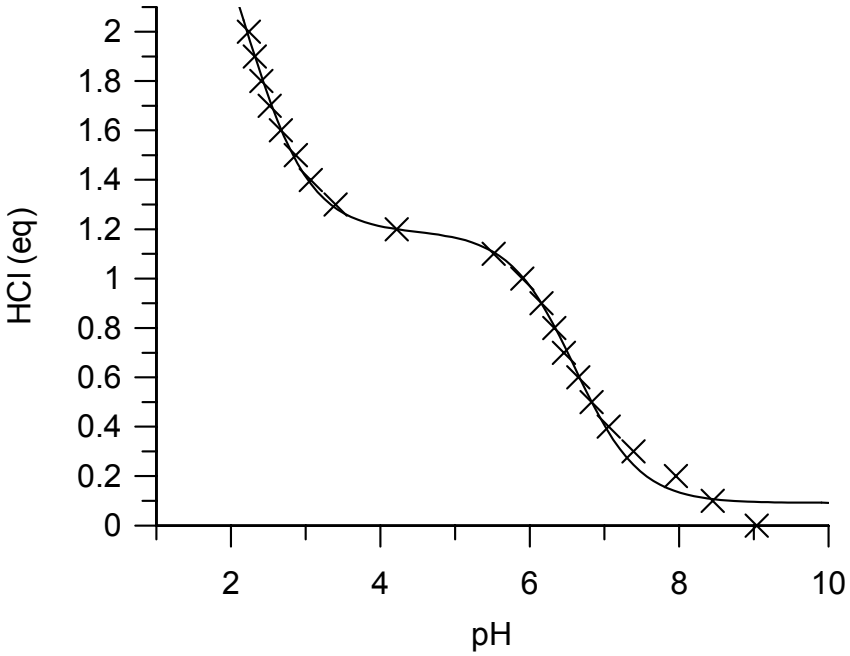
Parameter	Value	Std. Error
pKa 1	1.5658	0.0856
Lower Limit	4.3730	0.4395
Middle Limit	1.4079	0.0152
Upper Limit	0.0668	0.0156
pKa 2	6.2651	0.0232

p*K*a determination of

3-*O*-Dodecyl-α-D-glucopyranosyl phosphate



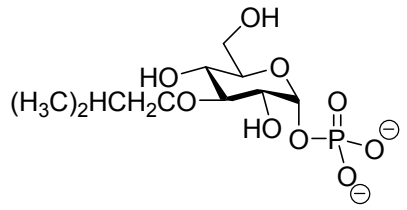
8e



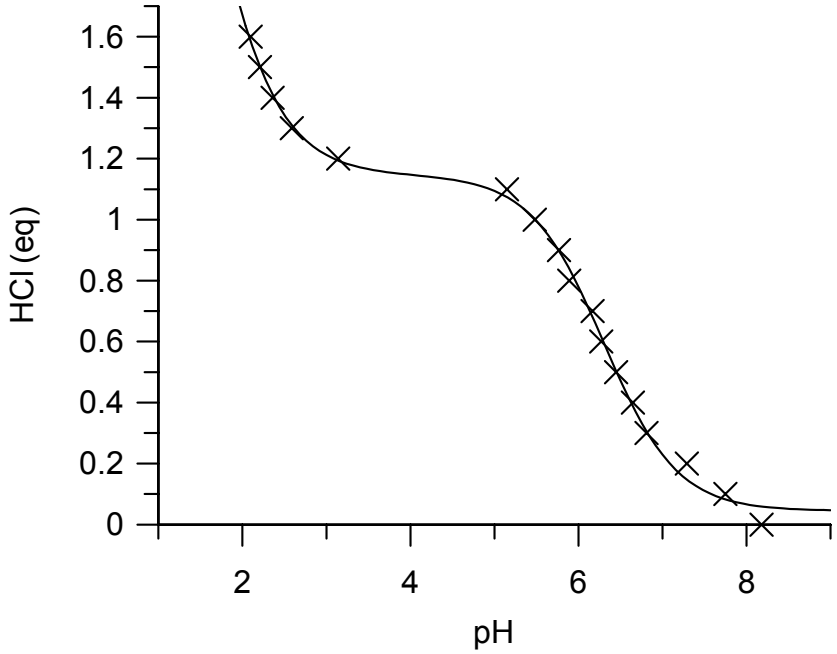
Parameter	Value	Std. Error
pKa 1	2.1883	0.1443
Lower Limit	2.8675	0.3209
Middle Limit	1.1894	0.0234
Upper Limit	0.0913	0.0202
pKa 2	6.6034	0.0411

p*K*a determination of

3-*O*-(2-methylpropyl)-α-D-glucopyranosyl phosphate



8g

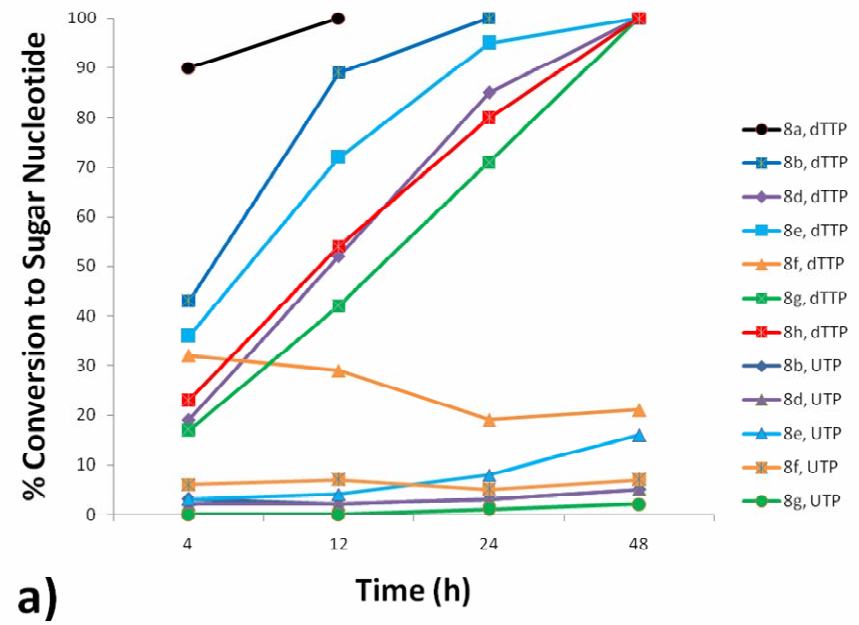


Parameter	Value	Std. Error
pKa 1	1.4930	0.1630
Lower Limit	3.3633	0.6249
Middle Limit	1.1457	0.0193
Upper Limit	0.0446	0.0186
pKa 2	6.3039	0.0349

Enzymatic Synthesis

General Procedure for nucleotidylyltransferase-catalyzed synthesis of sugar nucleotides (9a-h, 10a-h)

Enzymatic reactions were performed by the method of Timmons ($MgCl_2$, 1.0 mM NTP, 2.0 mM S1P, 0.5EU inorganic pyrophosphatase, 2EU nucleotidylyltransferase in Tris-HCl buffer – total 50 µL)[6] except that $MgCl_2$ was used at a final concentration of 5.5 mM and incubations were performed at 41ºC.



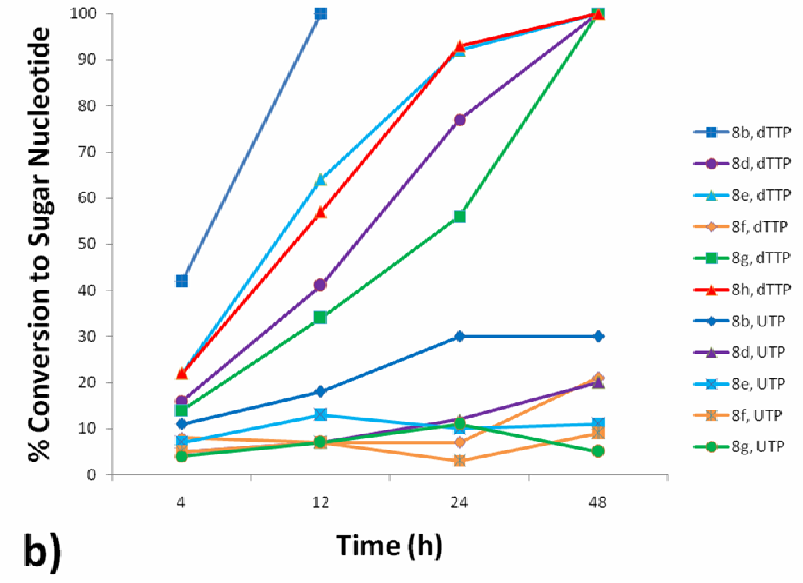


Figure S1. a) Selected data for nucleotidylyltransferase-catalyzed conversion of sugar-1-phosphates (8a-h) to sugar nucleotides (9a-h, 10a-h) using a) Cps2L b) RmlA3.

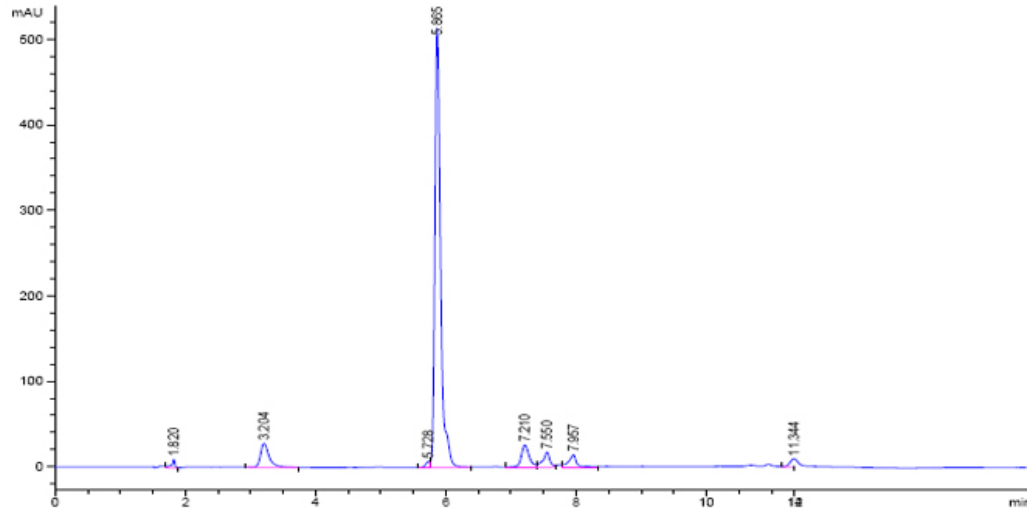
[6] Timmons, S. C.; Mosher, R. H.; Knowles, S. A.; Jakeman, D. L. *Org. Lett.* **2007**, *9*, 857-860.

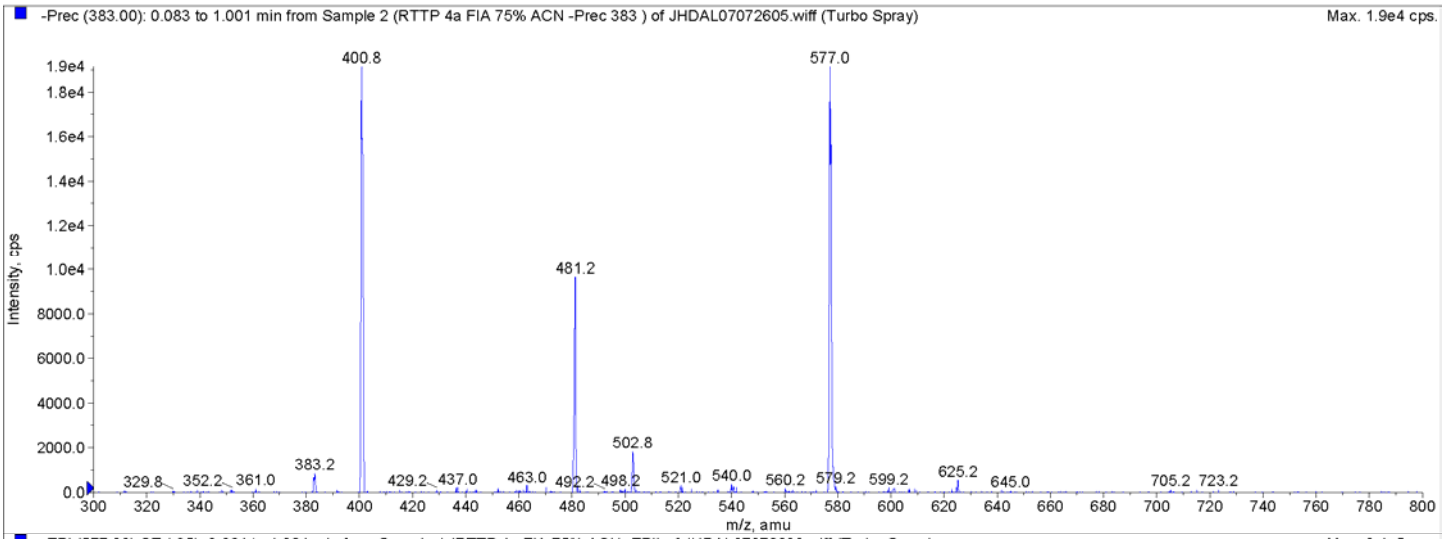
Enzyme	Sugar-1-Phosphate	NTP	% Conv. (4 hr)	% Conv. (12 hr)	% Conv. (24 hr)	% Conv (48 hr)	Sugar Nucleotide retention time (min)
Cps2L	**8a**	dTTP	90	100			5.82
Cps2L	**8b**	dTTP	43	89	100		6.73
Cps2L	**8c**	dTTP	[c]	[c]	[c]	[c]	7.50
Cps2L	**8d**	dTTP	19	52	85	100	8.28
Cps2L	**8e**	dTTP	36	72	95	100	9.77
Cps2L	**8f**	dTTP	32	29	19	21	9.25[a]
Cps2L	**8g**	dTTP	17	42	71	100	6.75
Cps2L	**8h**	dTTP	23	54	80	100	7.35
Cps2L	**8a**	UTP	[b]	[b]	[b]	[b]	5.75
Cps2L	**8b**	UTP	3	2	3	5	6.69
Cps2L	**8c**	UTP	[c]	[c]	6	10	7.48
Cps2L	**8d**	UTP	2	2	3	5	8.26
Cps2L	**8e**	UTP	3	4	8	16	9.77
Cps2L	**8f**	UTP	6	7	5	7	9.27[a]
Cps2L	**8g**	UTP	0	0	1	2	6.66
Cps2L	**8h**	UTP	1	[c]	[c]	[c]	7.32
RmlA3	**8a**	dTTP	28	[b]	[b]	[b]	5.82
RmlA3	**8b**	dTTP	42	100			6.73
RmlA3	**8c**	dTTP	[c]	[c]	[c]	[c]	7.50
RmlA3	**8d**	dTTP	16	41	77	100	8.28
RmlA3	**8e**	dTTP	22	64	92	100	9.77
RmlA3	**8f**	dTTP	8	7	7	21	9.25[a]
RmlA3	**8g**	dTTP	14	34	56	100	6.75
RmlA3	**8h**	dTTP	22	57	93	100	7.35
RmlA3	**8a**	UTP	[b]	[b]	7	[b]	5.75
RmlA3	**8b**	UTP	11	18	30	breakdown	6.69
RmlA3	**8c**	UTP	[c]	9	13	14	7.48
RmlA3	**8d**	UTP	5	7	12	20	8.26
RmlA3	**8e**	UTP	7	13	10	11	9.77
RmlA3	**8f**	UTP	5	7	3	9	9.27[a]
RmlA3	**8g**	UTP	4	7	11	5	6.66
RmlA3	**8h**	UTP	5	[c]	[c]	[c]	7.32

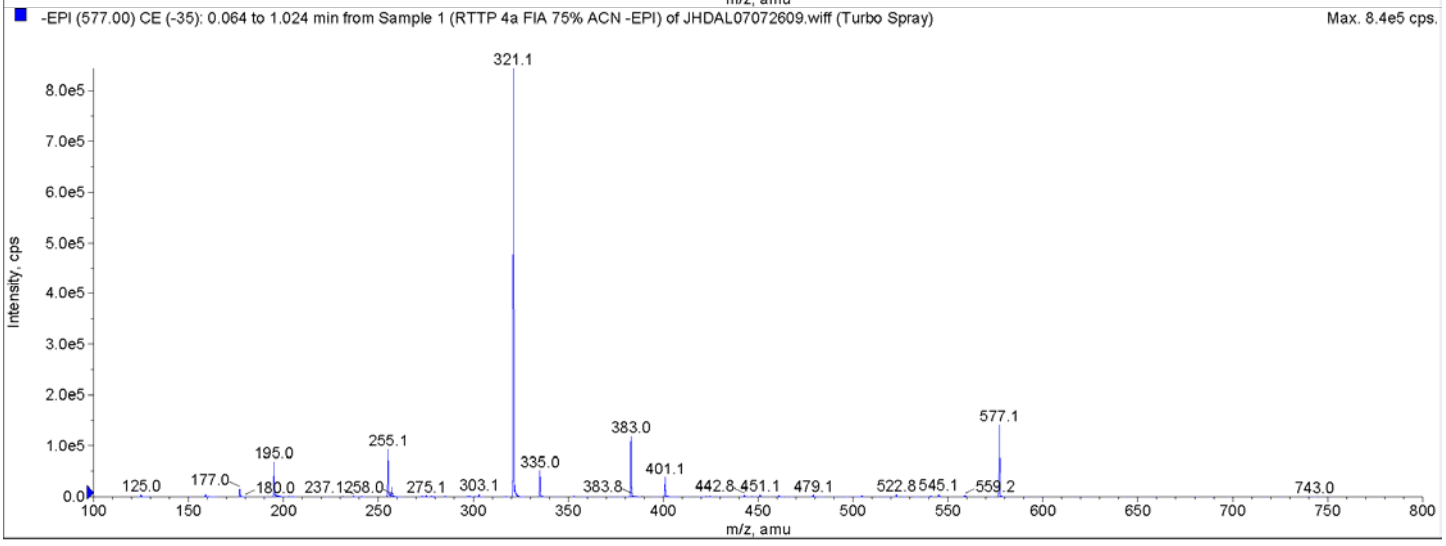
Table S1. Nucleotidylyltransferase-catalyzed conversion of sugar-1-phosphates (8a-h) to sugar nucleotides (9a-h, 10a-h). [a]alternate buffer gradient used (see General Methods). [b]inaccurate integration due to co-elution with NDP. [c]inaccurate integration due to co-elution with NTP.

3-*O*-Methyl-dTDP-α-D-glucose (9a)

LRMS *m/z* calcd for $C_{17}H_{26}N_2O_{16}P_2^{2-}$ $[M+H]^-$: 577.1. Found 577.0. EPI fragments: 321.1.

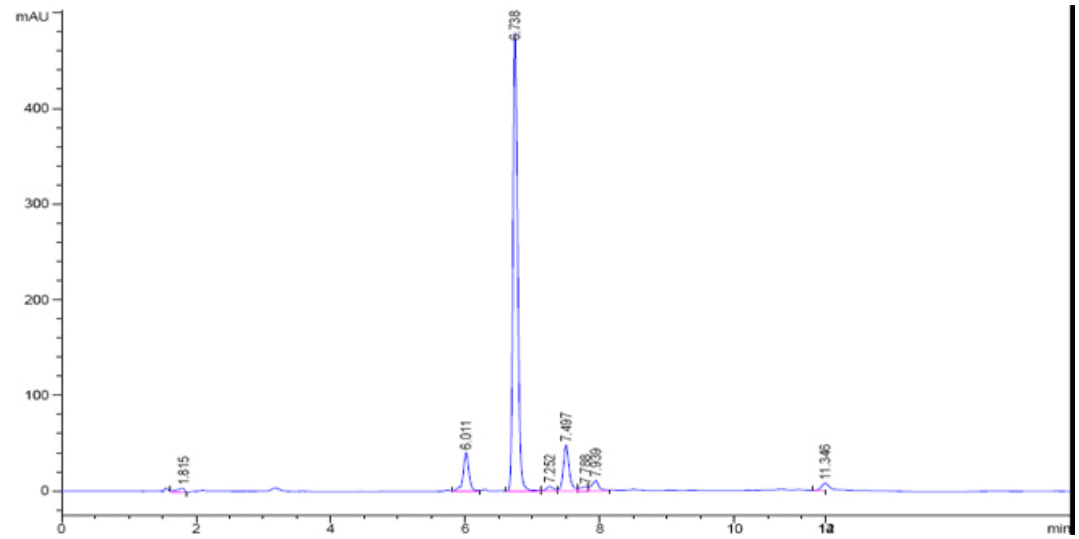


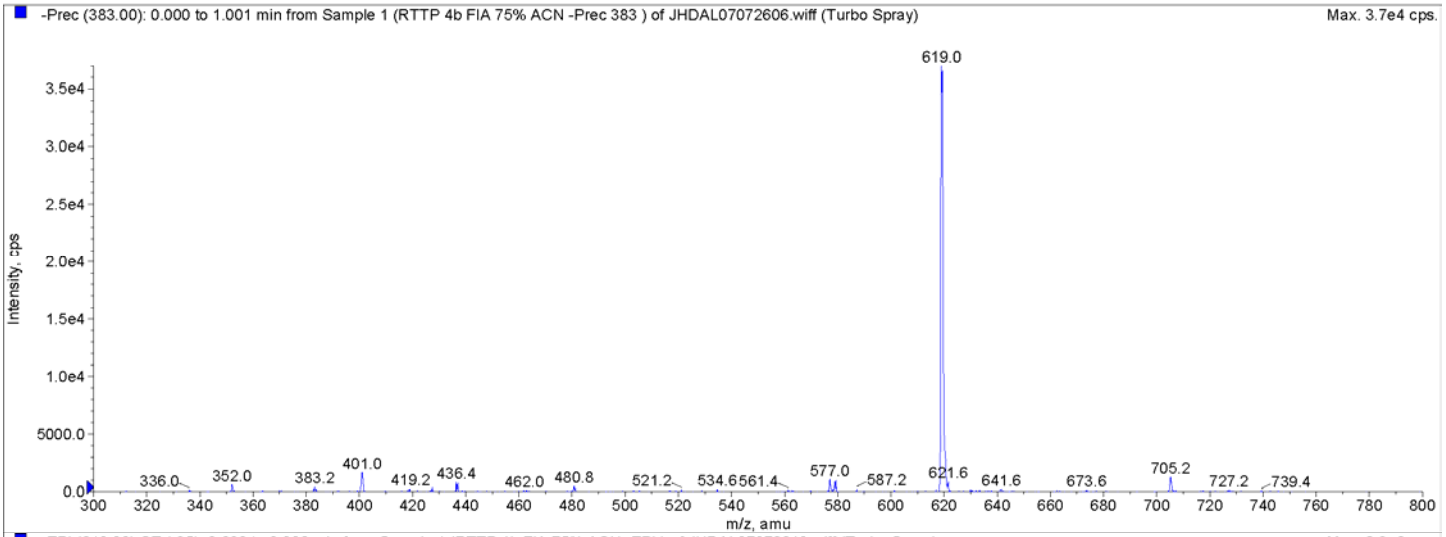


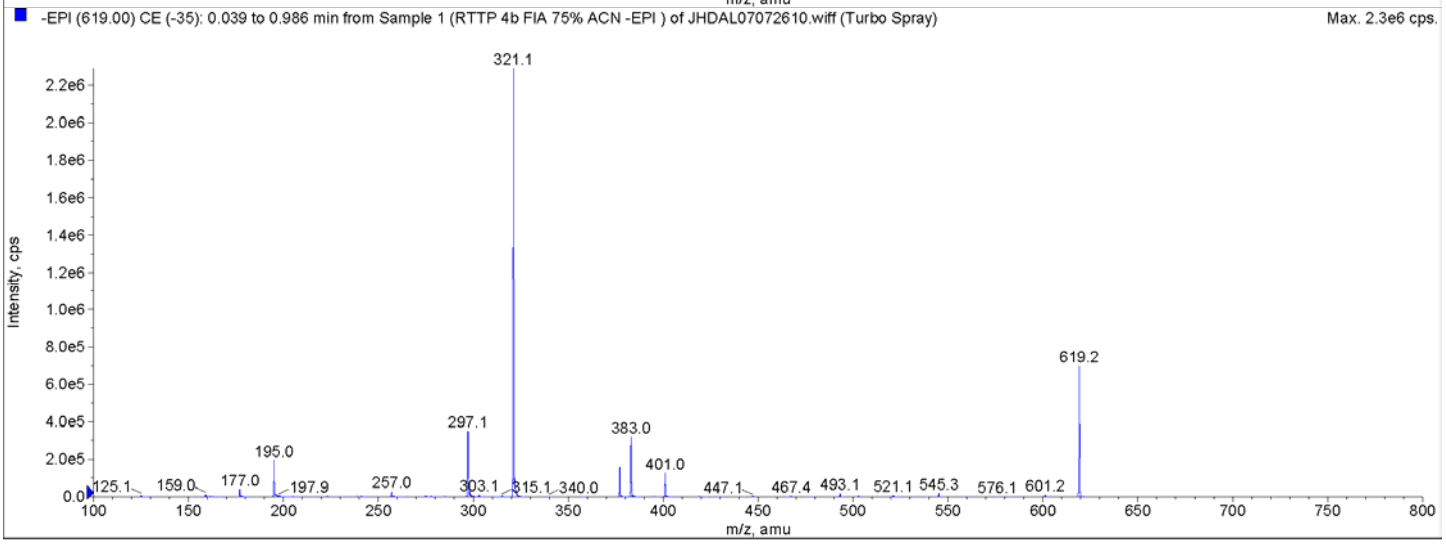


3-*O*-Butyl-dTDP-α-D-glucose (9b)

LRMS *m/z* calcd for $C_{20}H_{32}N_2O_{16}P_2^{2-}$ $[M+H]^-$: 619.1. Found 619.0. EPI fragments: 321.1.

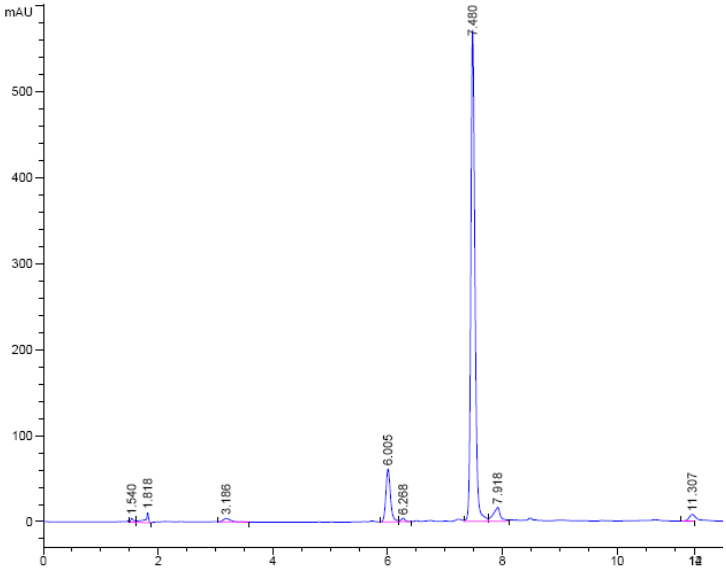


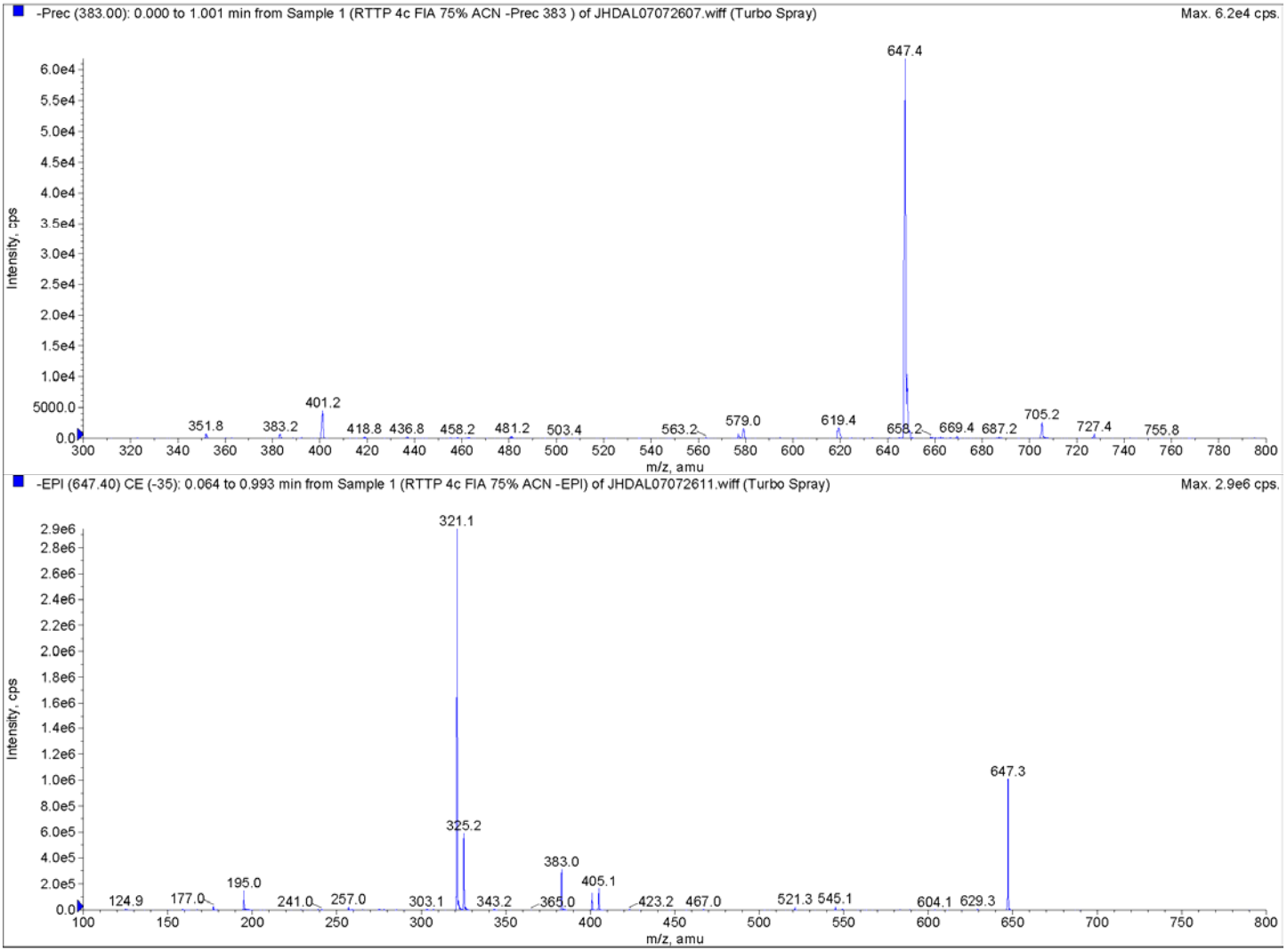




3-*O*-Hexyl-dTDP-α-D-glucose (9c)

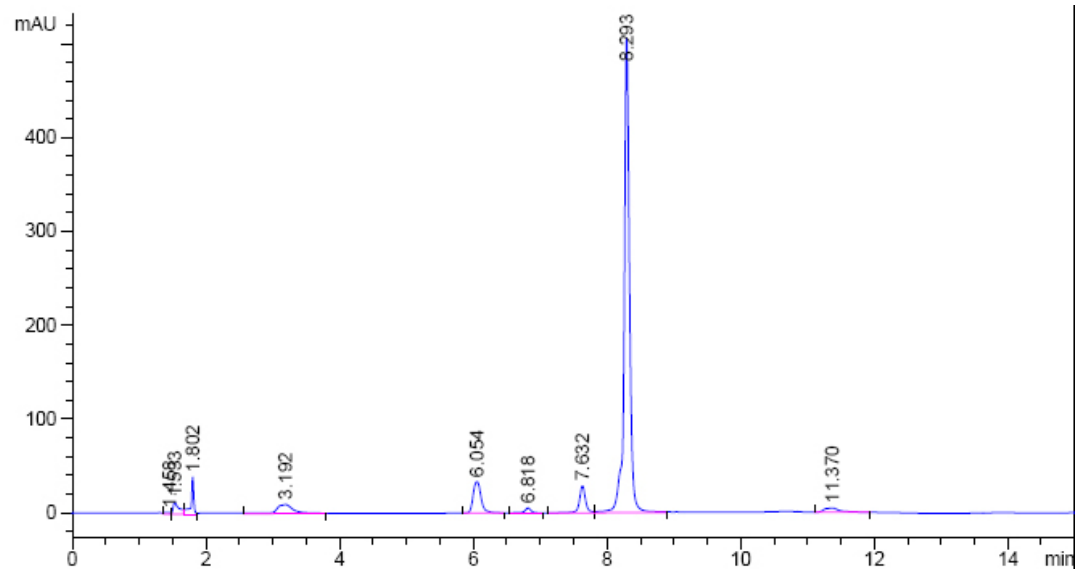
LRMS *m/z* calcd for $C_{22}H_{36}N_2O_{16}P_2^{2-}$ $[M+H]^-$: 647.2. Found 647.4. EPI fragments: 321.1.

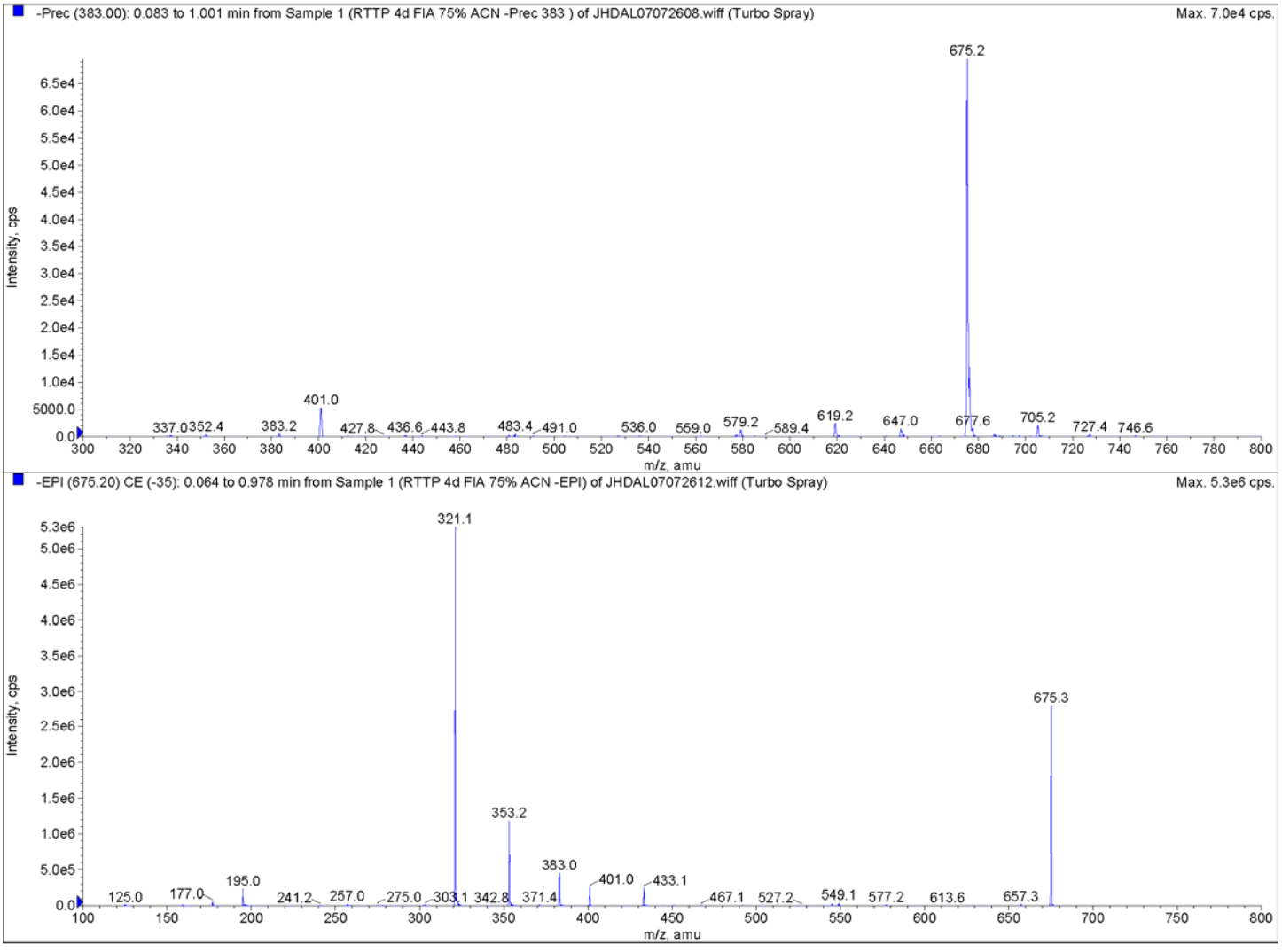




3-*O*-Octyl-dTDP-α-D-glucose (9d)

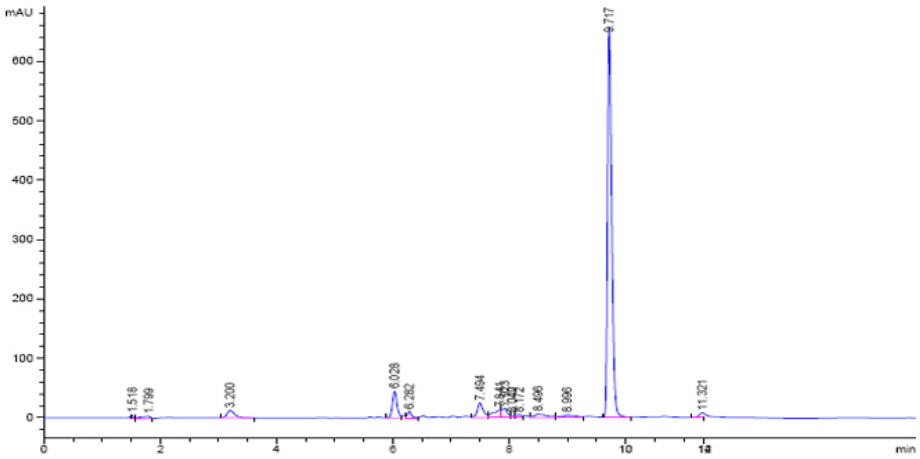
LRMS *m/z* calcd for $C_{24}H_{40}N_2O_{16}P_2^{2-}$ $[M+H]^-$: 675.2. Found 675.2. EPI fragments: 321.1.

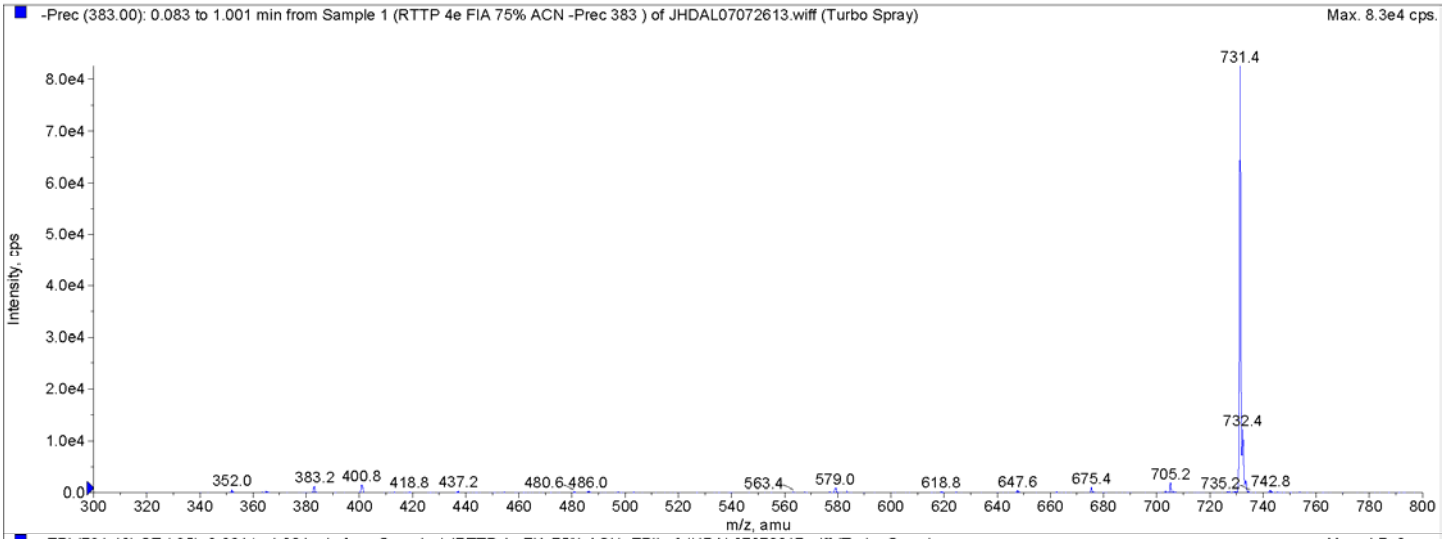


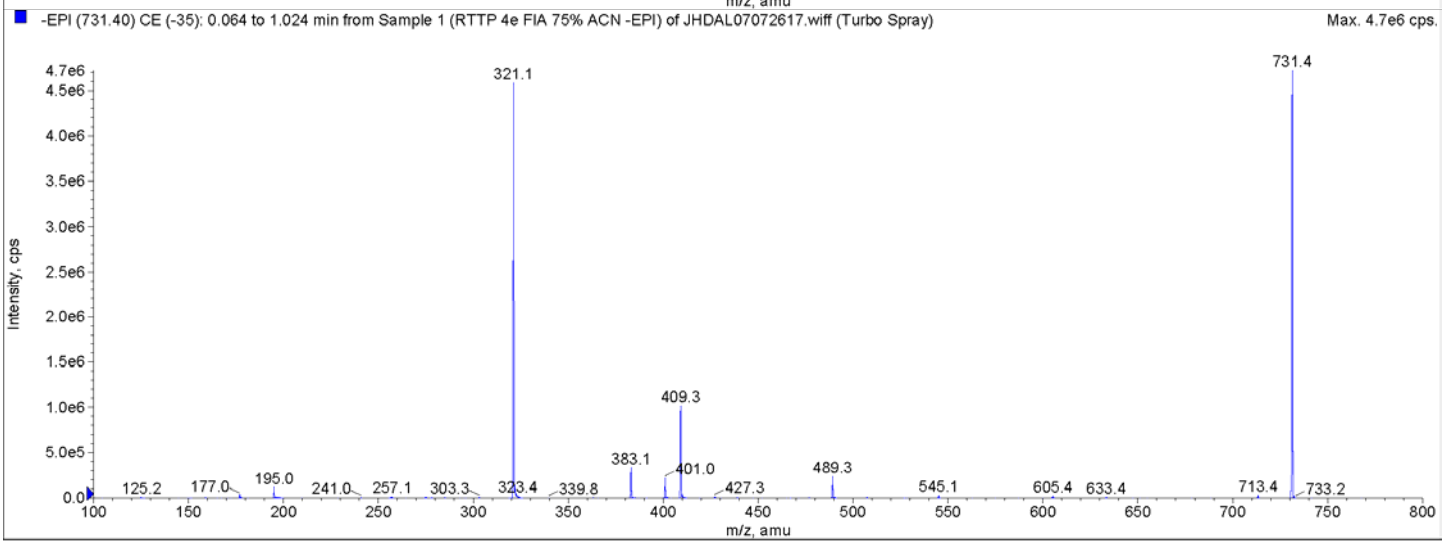


3-*O*-Dodecyl-dTDP-α-D-glucose (9e)

LRMS *m/z* calcd for $C_{28}H_{48}N_2O_{16}P_2^{2-}$ $[M+H]^-$: 731.3. Found 731.4. EPI fragments: 321.1.

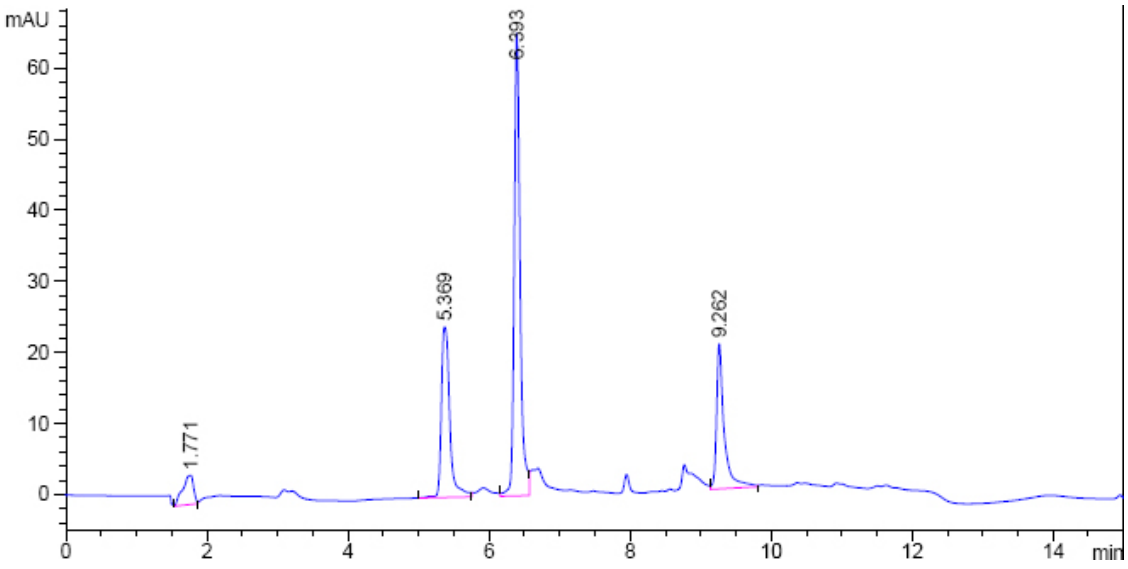


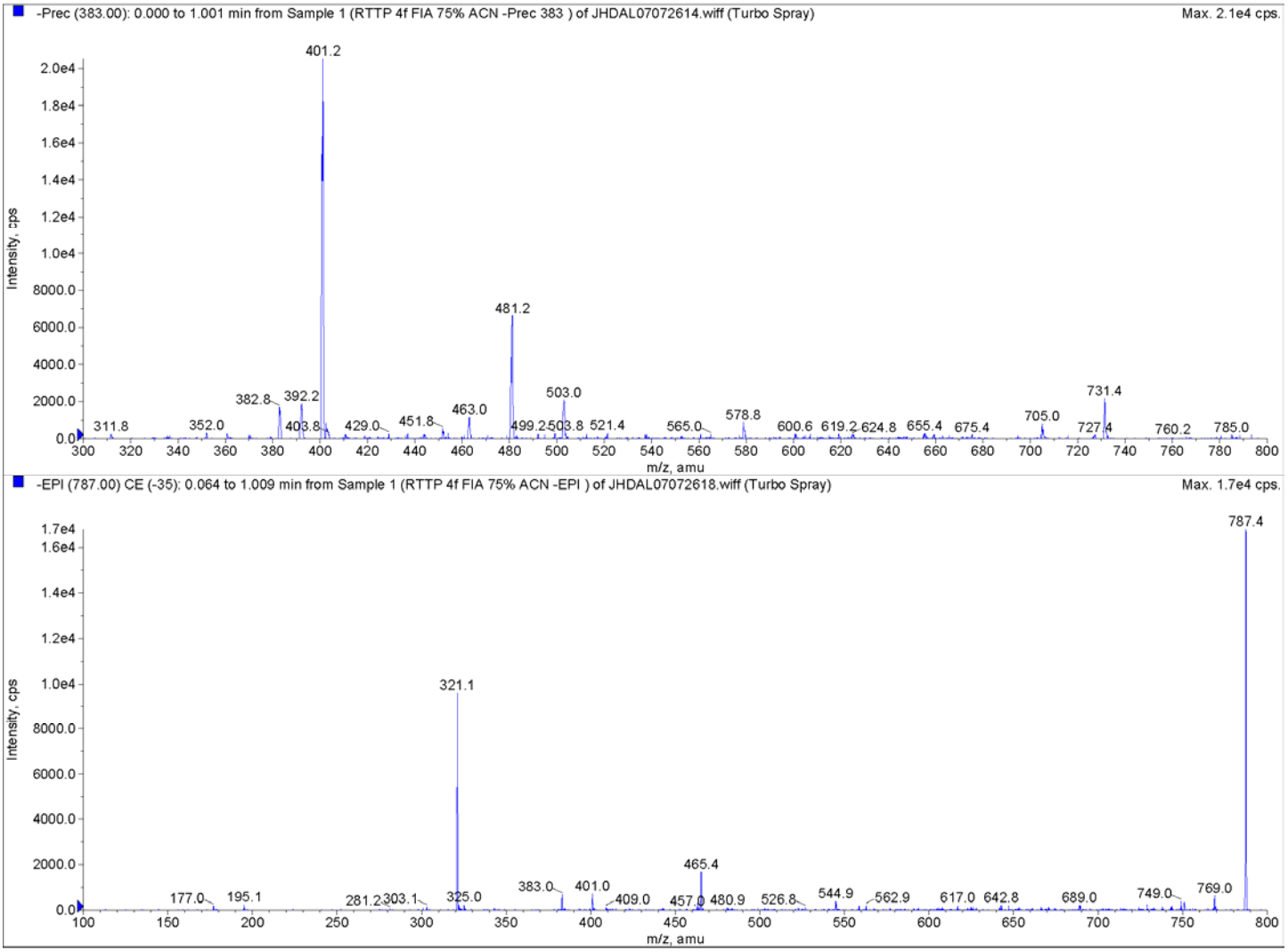




3-*O*-Hexadecyl-dTDP-α-D-glucose (9f)

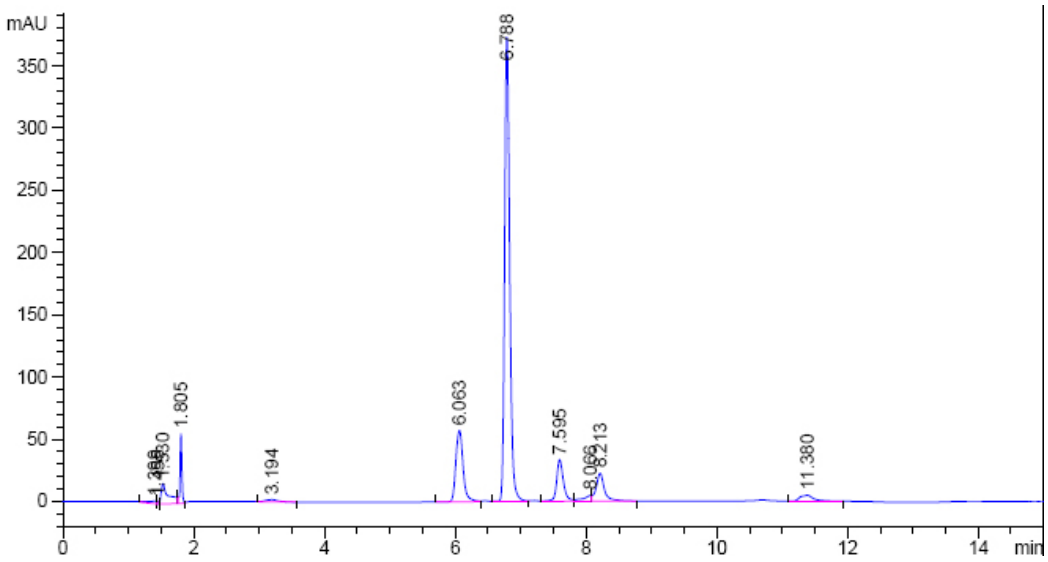
LRMS *m/z* calcd for $C_{32}H_{56}N_2O_{16}P_2^{2-}$ $[M+H]^-$: 787.3. Found 787.4. EPI fragments: 321.1.

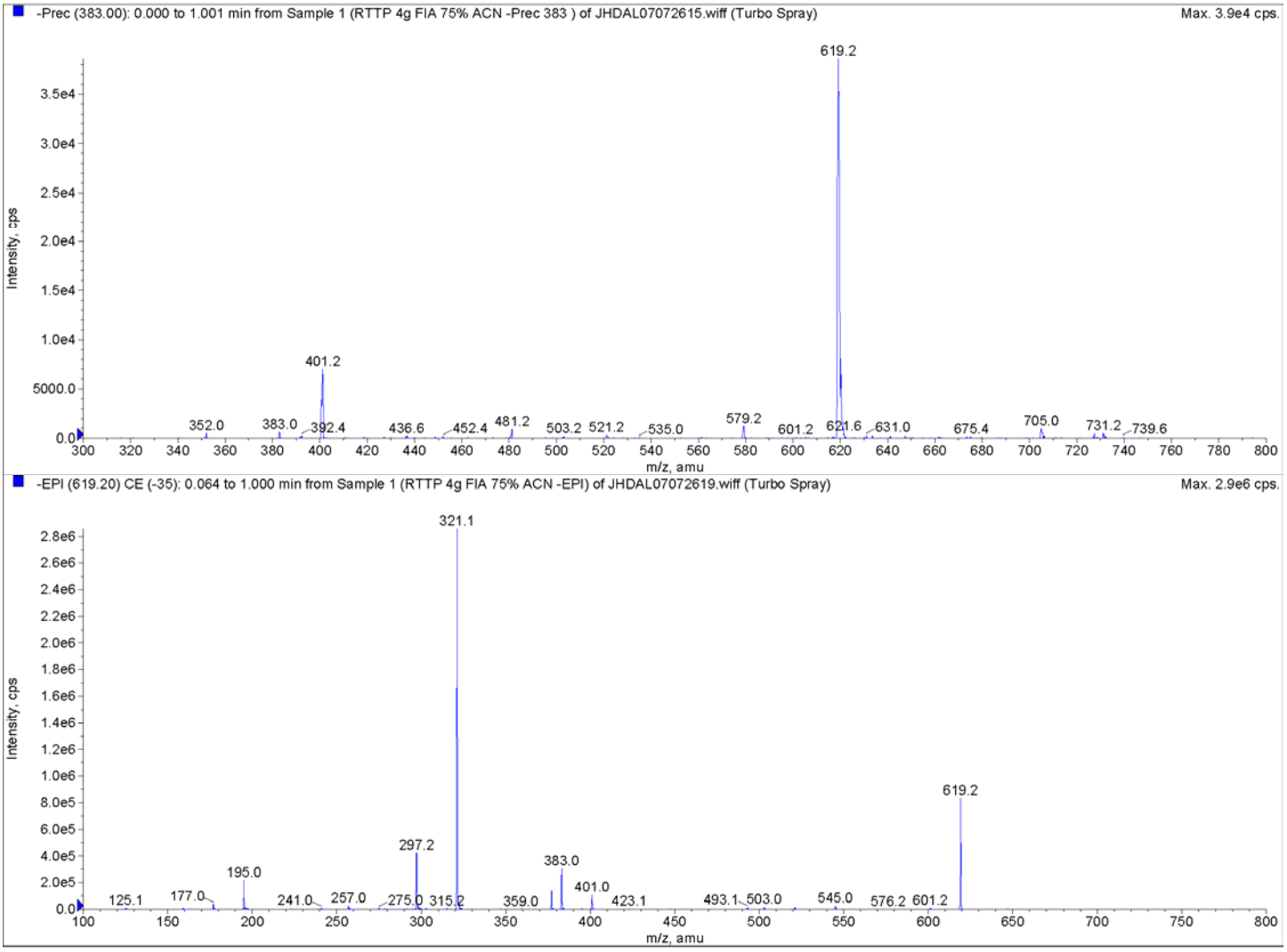




3-*O*-(2-Methylpropyl)-dTDP-α-D-glucose (9g)

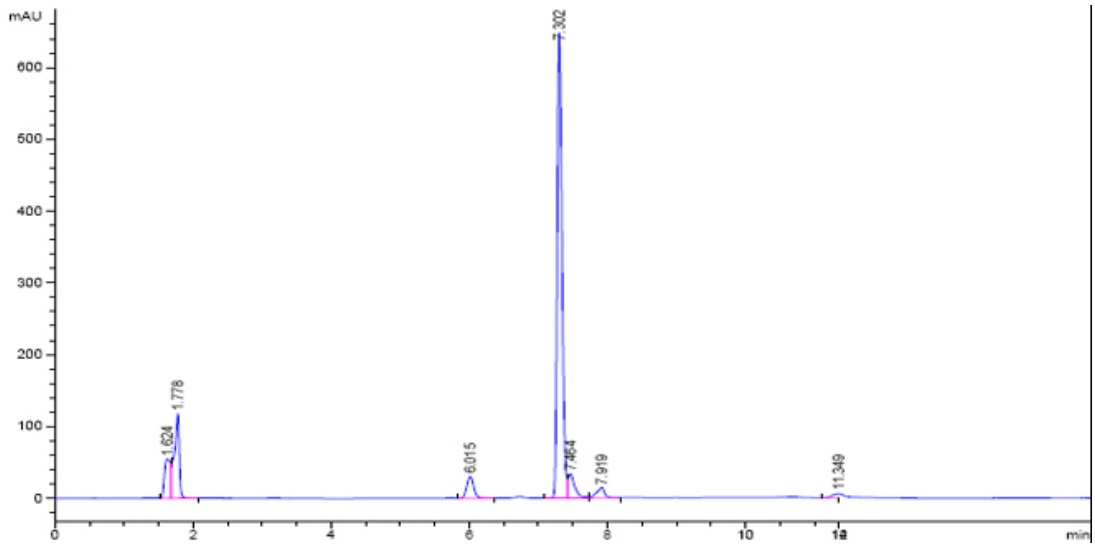
LRMS *m/z* calcd for $C_{20}H_{32}N_2O_{16}P_2^{2-}$ $[M+H]^-$: 619.1. Found 619.2. EPI fragments: 321.1.

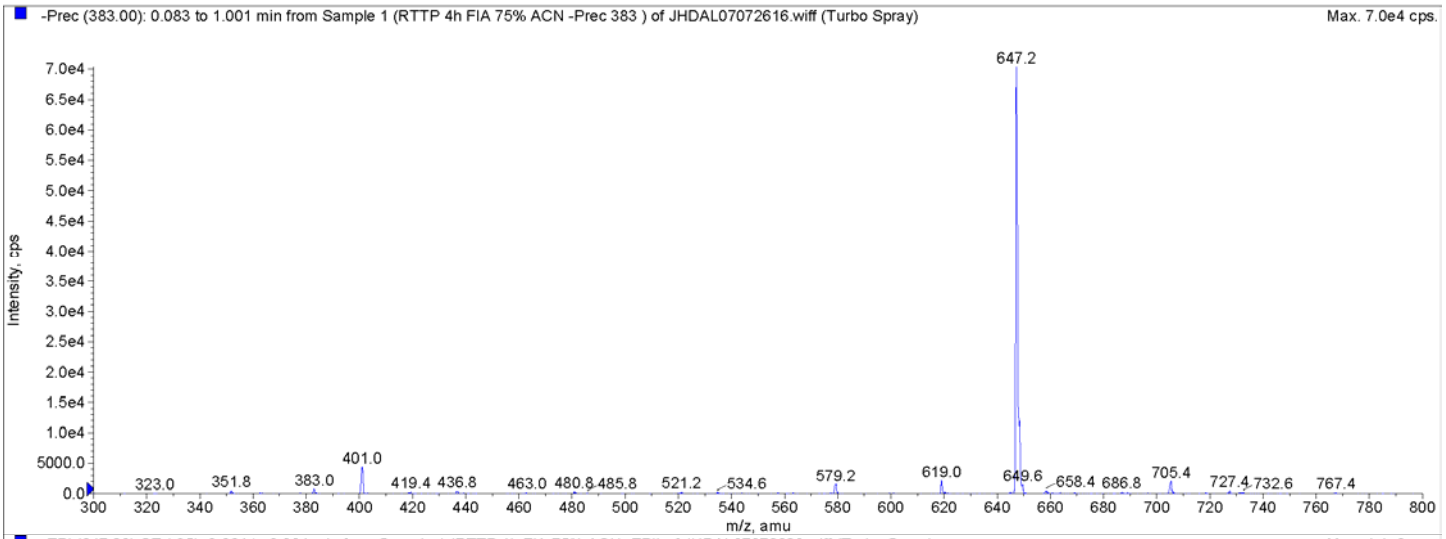




3-*O*-(2-Ethylbutyl)-dTDP-α-D-glucose (9h)

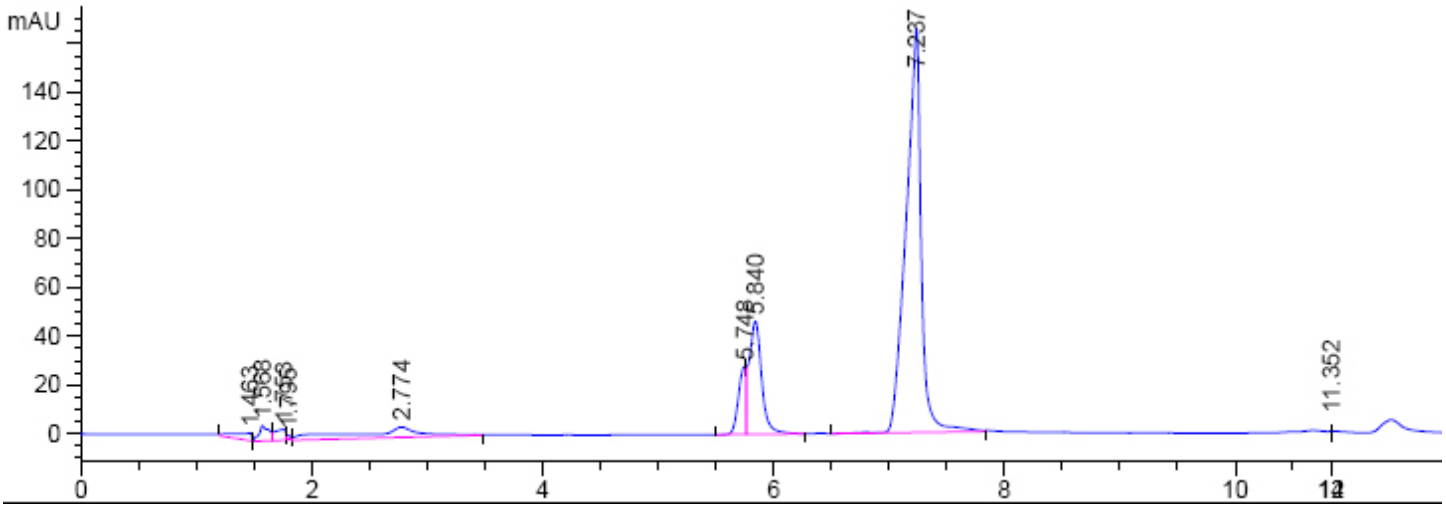
LRMS *m/z* calcd for $C_{22}H_{36}N_2O_{16}P_2^{2-}$ $[M+H]^-$: 647.2. Found 647.2. EPI fragments: 321.1.

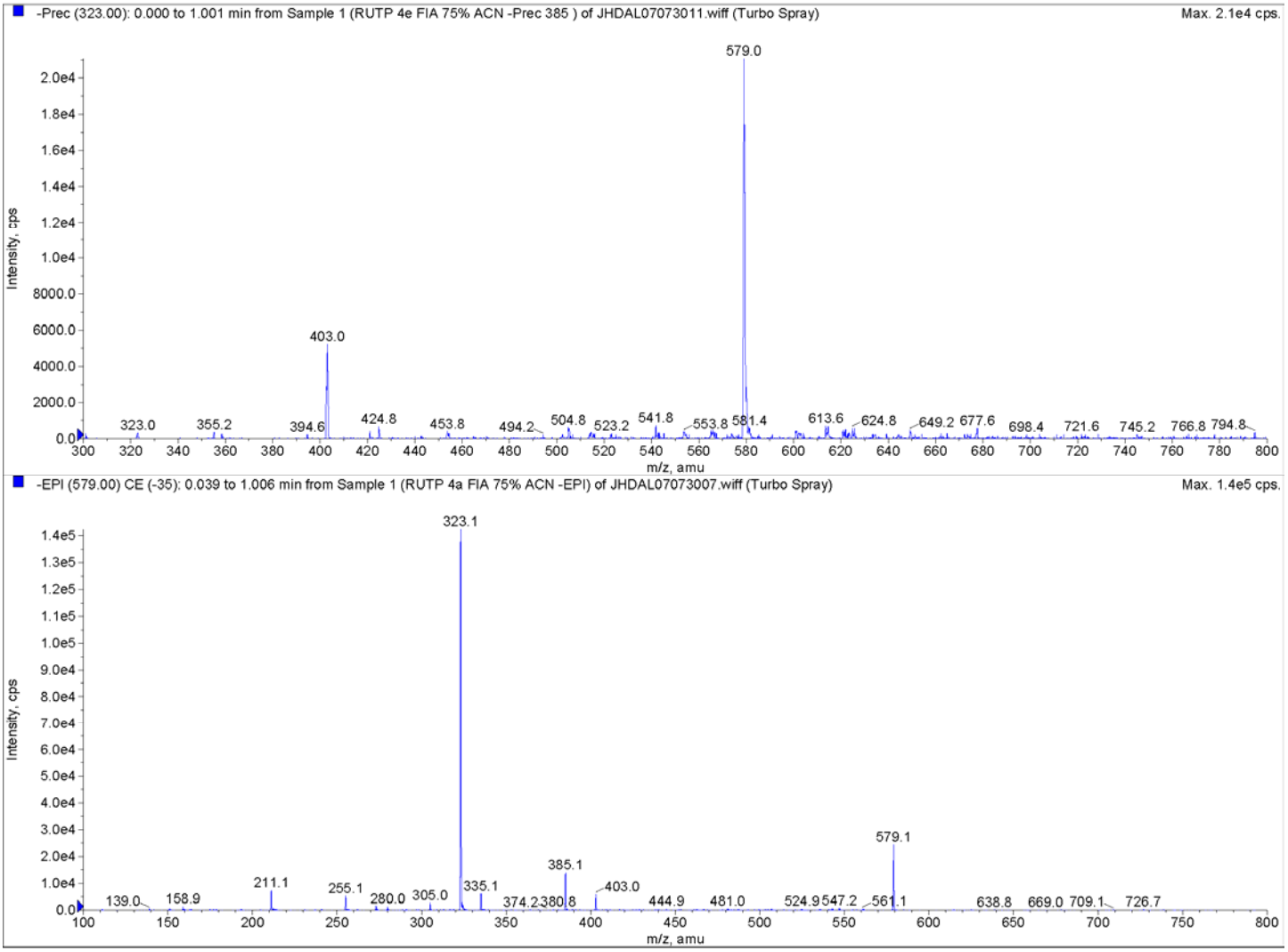




3-*O*-Methyl-UDP-α-D-glucose (10a)

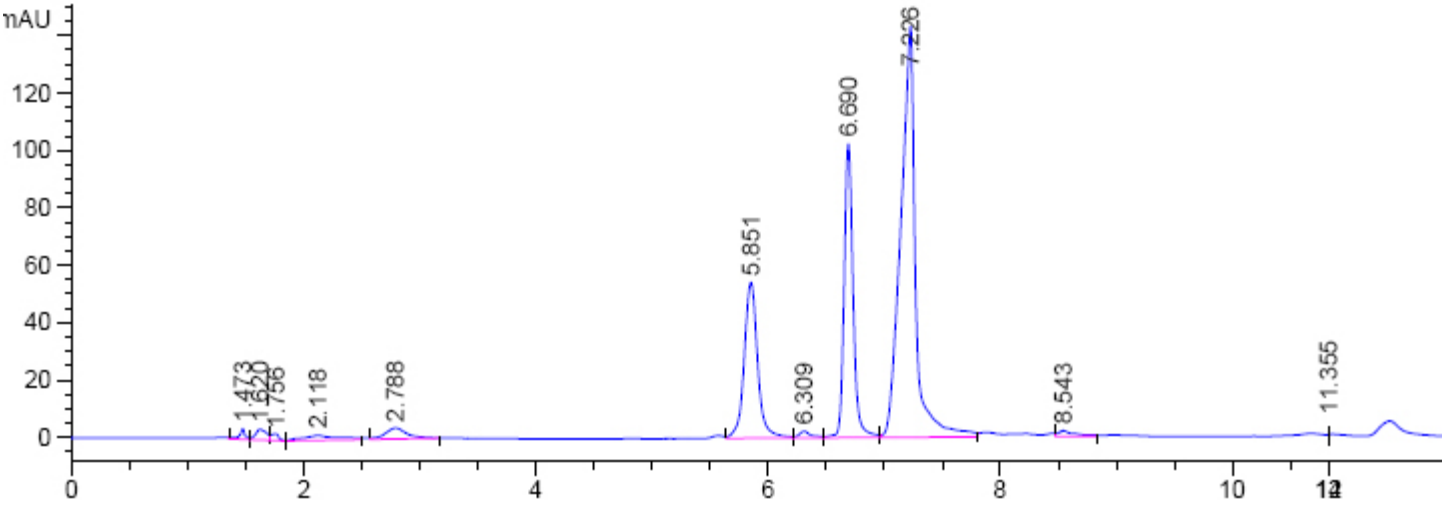
LRMS *m/z* calcd for $C_{16}H_{24}N_2O_{17}P_2^{2-}$ $[M+H]^-$: 579.1. Found 579.1. EPI fragments: 323.1.

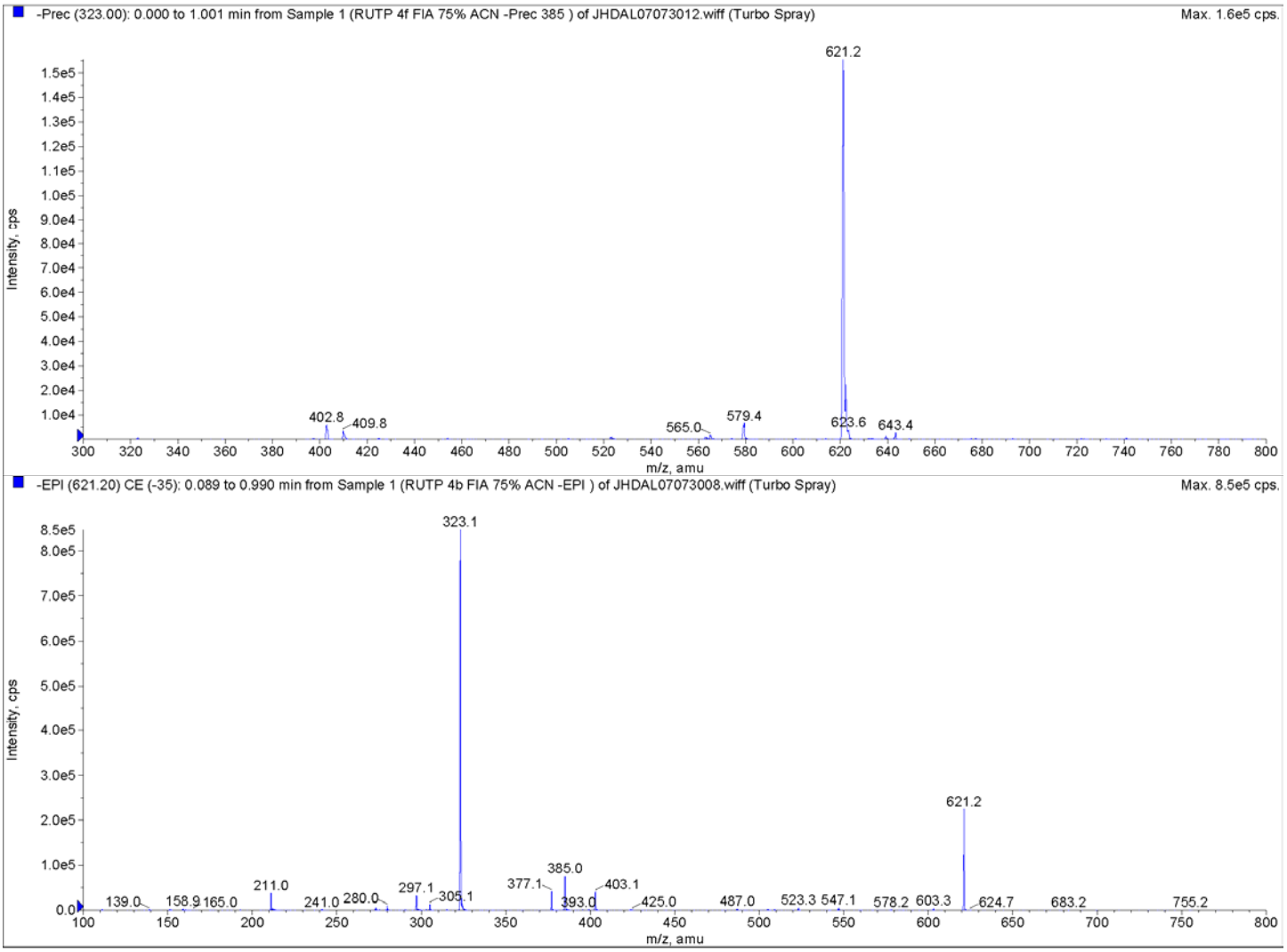




3-*O*-Butyl-UDP-α-D-glucose (10b)

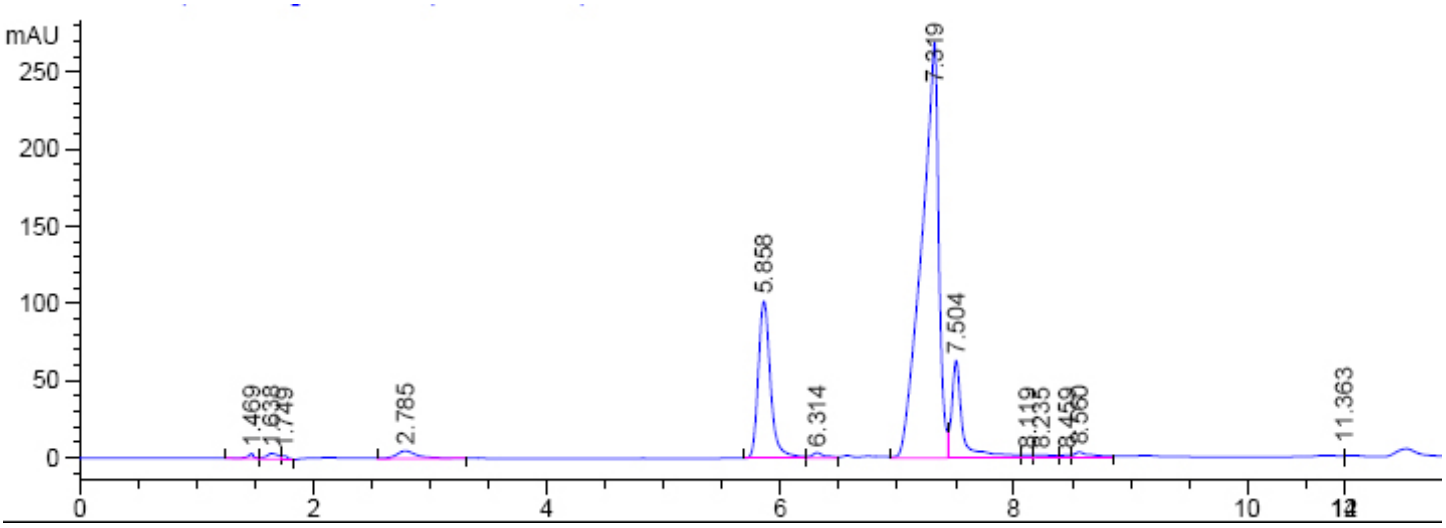
LRMS *m/z* calcd for $C_{19}H_{30}N_2O_{17}P_2^{2-}$ $[M+H]^-$: 621.1. Found 621.2. EPI fragments: 323.1.

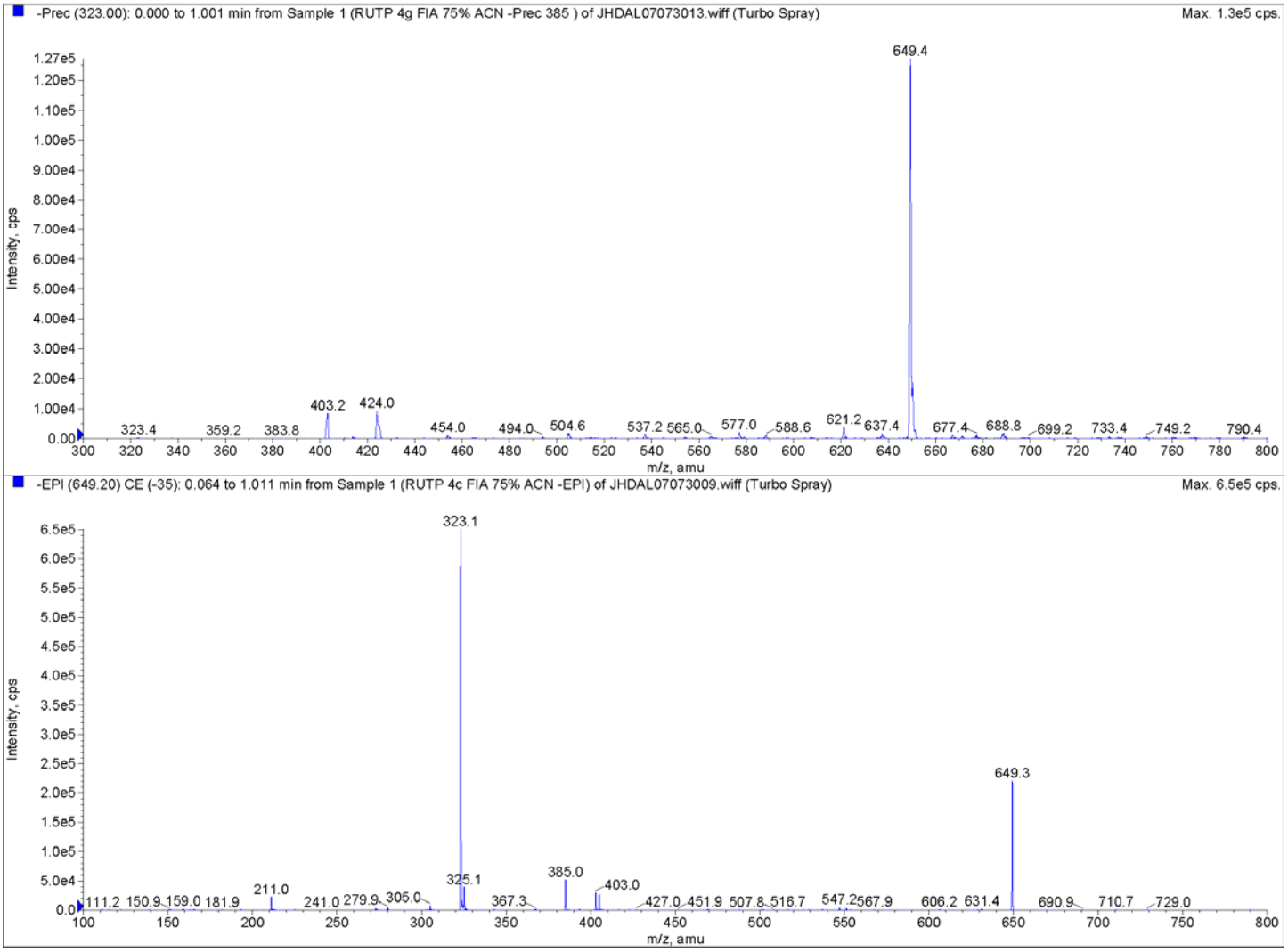




3-*O*-Hexyl-UDP-α-D-glucose (10c)

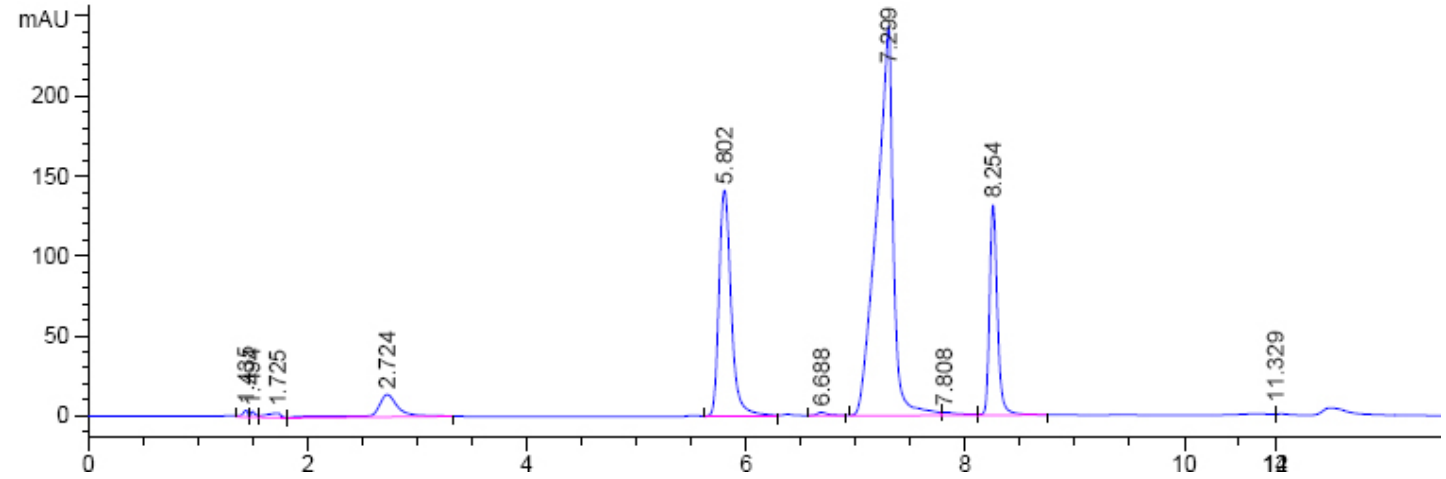
LRMS *m/z* calcd for $C_{21}H_{34}N_2O_{17}P_2^{2-}$ $[M+H]^-$: 649.1. Found 649.3. EPI fragments: 323.1.

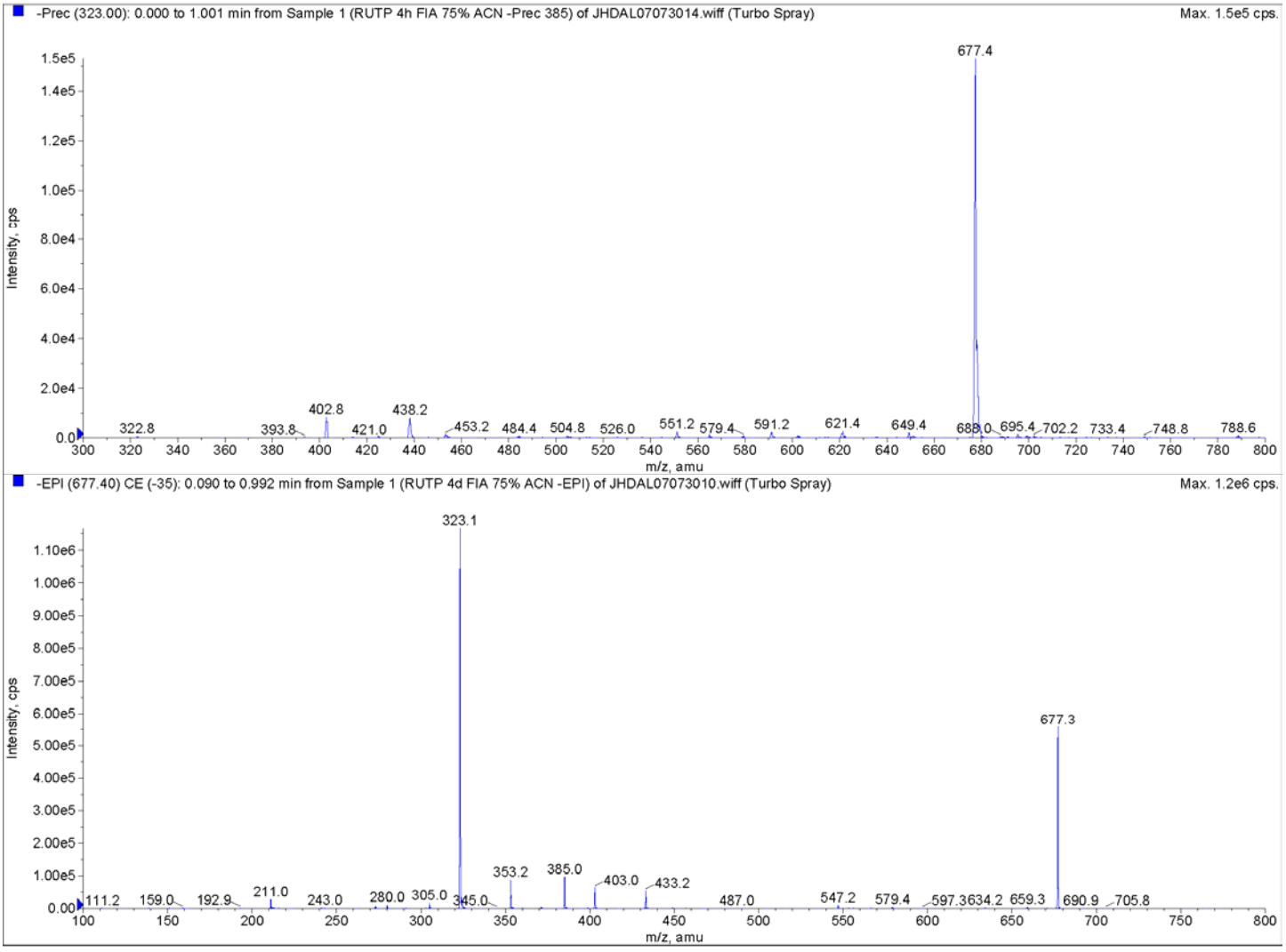




3-*O*-Octyl-UDP-α-D-glucose (10d)

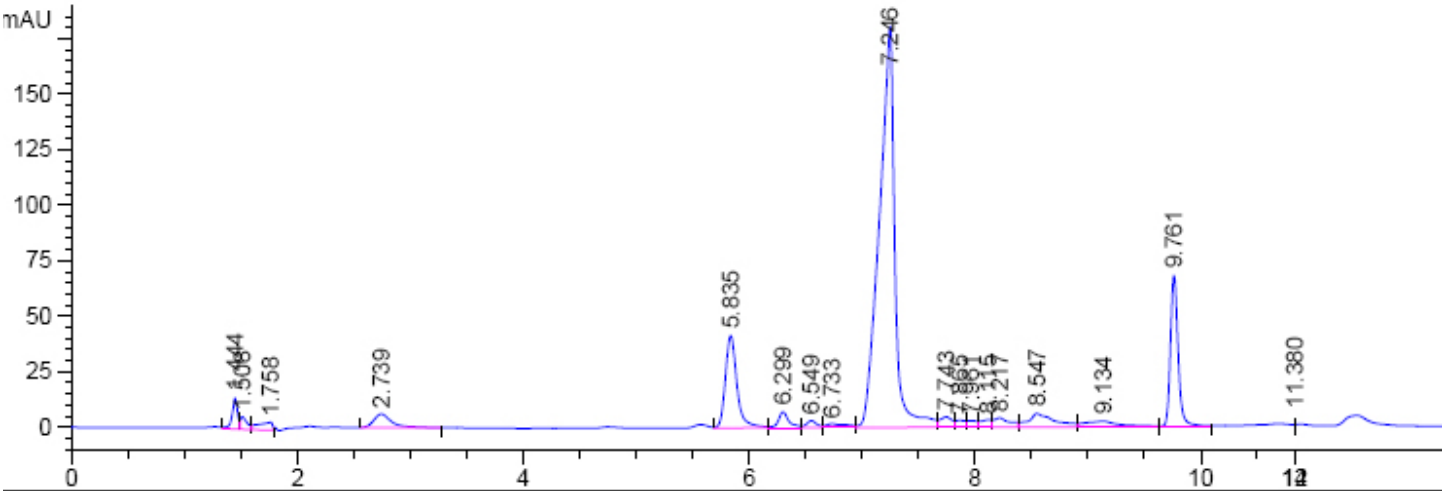
LRMS *m/z* calcd for $C_{23}H_{38}N_2O_{17}P_2^{2-}$ $[M+H]^-$: 677.2. Found 677.3. EPI fragments: 323.1.

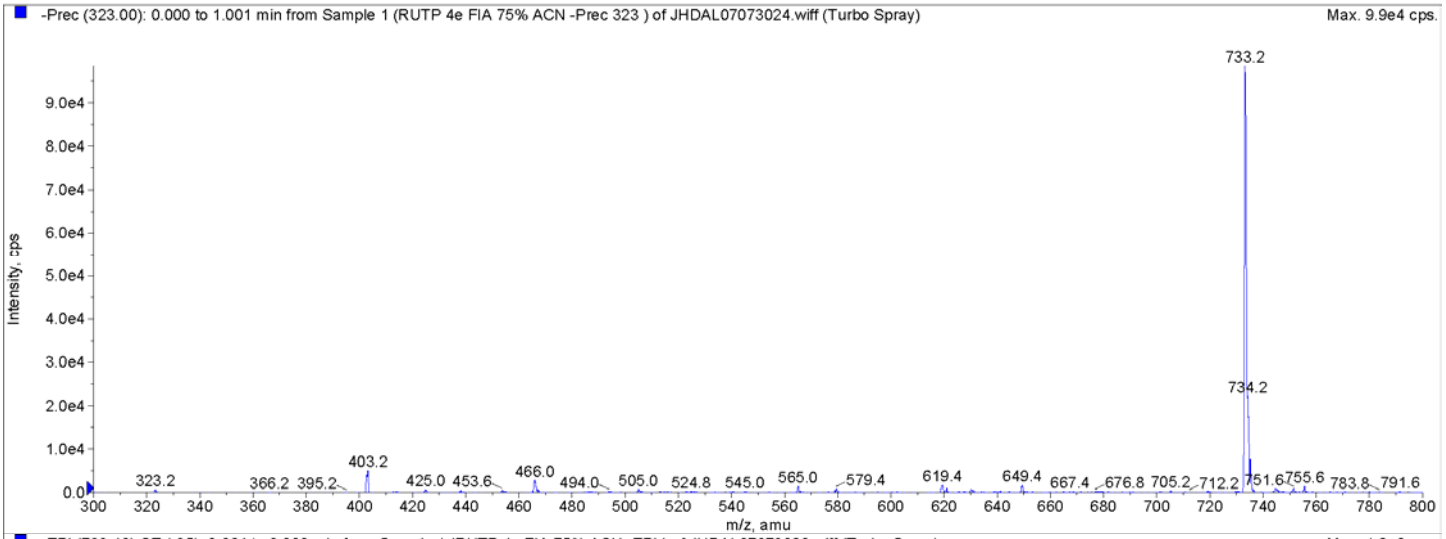


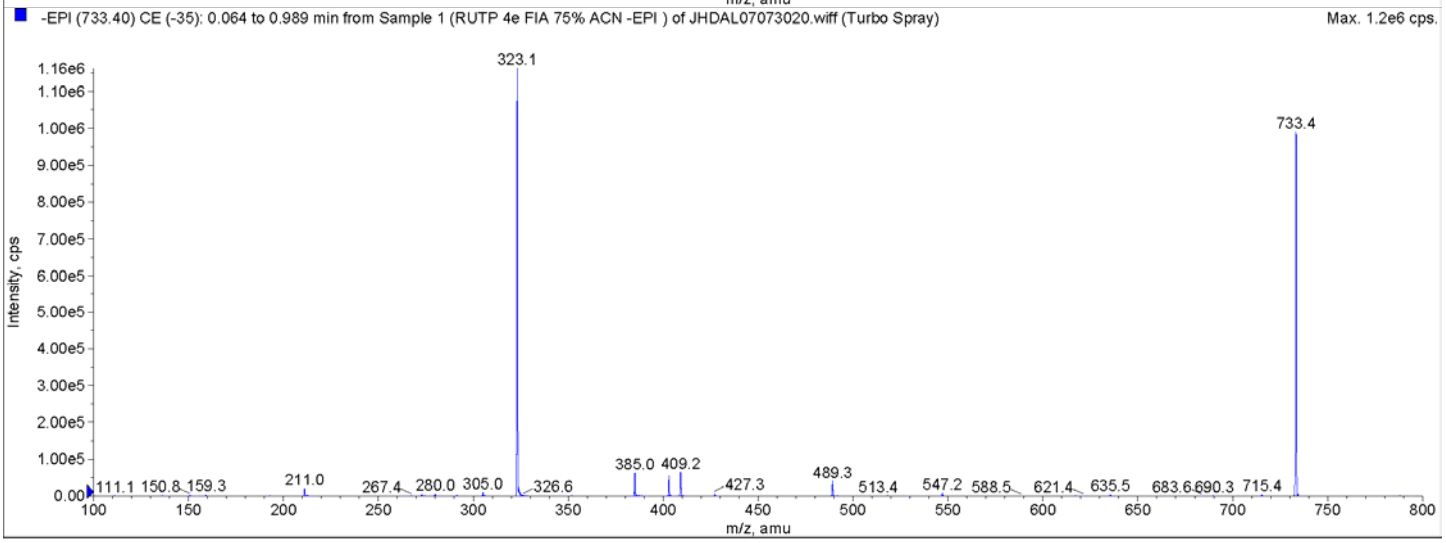


3-*O*-Dodecyl-UDP-α-D-glucose (10e)

LRMS *m/z* calcd for $C_{27}H_{46}N_2O_{17}P_2^{2-}$ $[M+H]^-$: 733.2. Found 733.2. EPI fragments: 323.1.

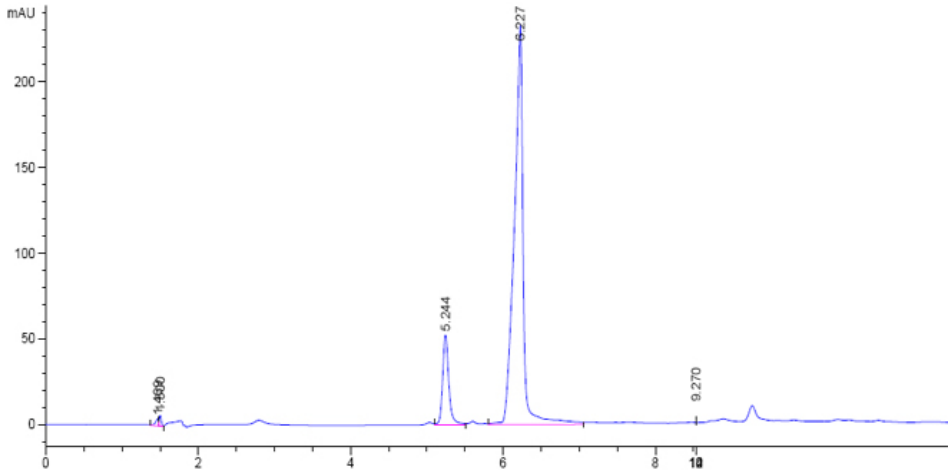


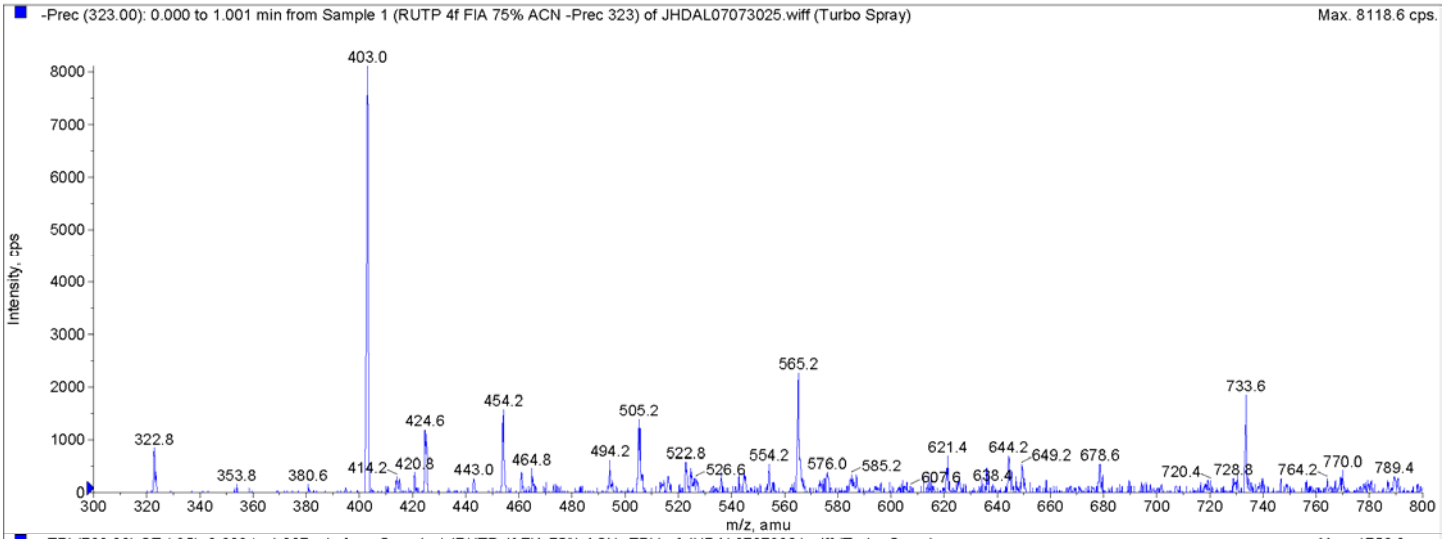




3-*O*-Hexadecyl-UDP-*α*-D-glucose (10f)

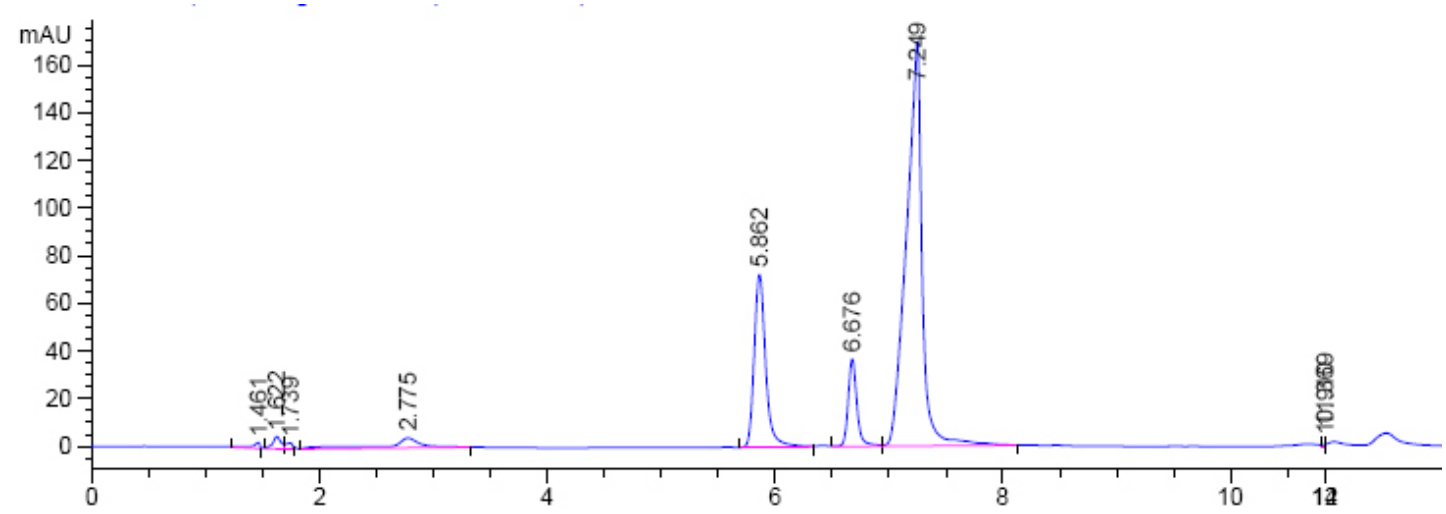
LRMS *m/z* calcd for $C_{31}H_{54}N_2O_{17}P_2^{2-}$ $[M+H]^-$: 789.3. Found 789.4. EPI fragments: 323.1.

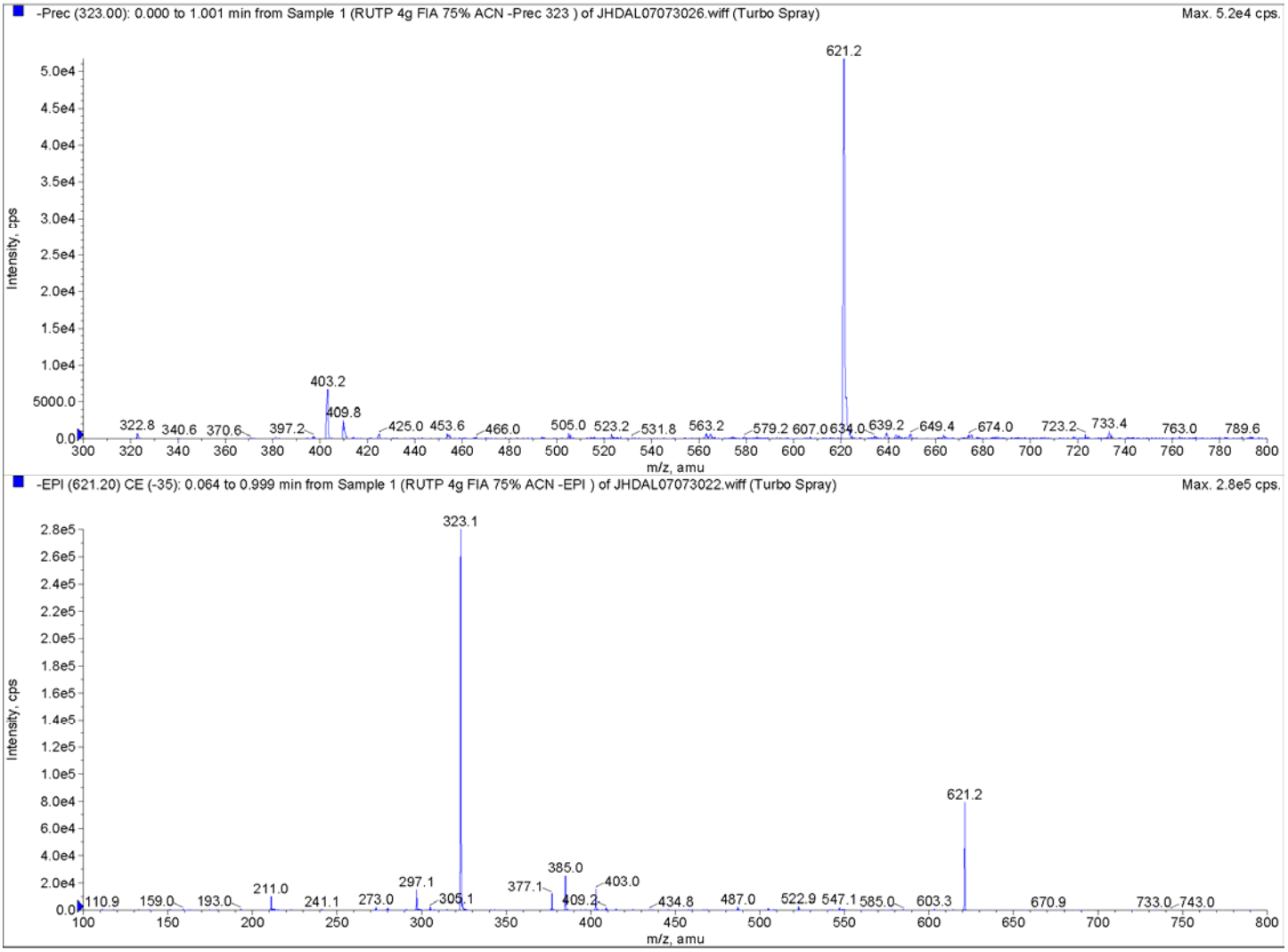




3-*O*-(2-Methylpropyl)-UDP-α-D-glucose (10g)

LRMS *m/z* calcd for $C_{19}H_{30}N_2O_{17}P_2^{2-}$ $[M+H]^-$: 621.1. Found 621.2. EPI fragments: 323.1.





3-*O*-(2-Ethylbutyl)-UDP-α-D-glucose (10h)

LRMS *m/z* calcd for $C_{21}H_{34}N_2O_{17}P_2^{2-}$ $[M+H]^-$: 649.1. Found 649.3. EPI fragments: 323.1.