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Supporting Information

# Streamlined Synthesis and Evaluation of Teichoic Acid Fragments

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# Supporting information

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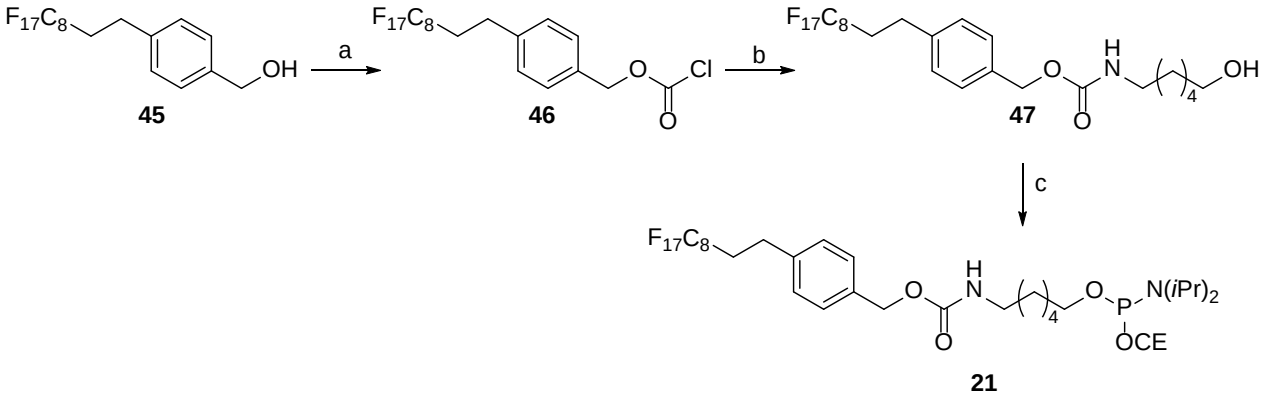
## Experimental

### General

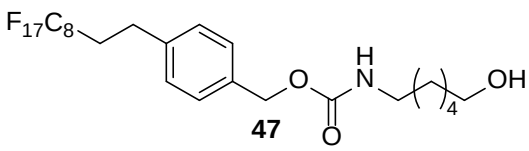
All chemicals (Acros, Fluka, Merck, Sigma-Aldrich, etc.) were used as received and reactions were carried out dry, under an argon atmosphere, at ambient temperature, unless stated otherwise. Column chromatography was performed on Screening Devices silica gel 60 (0.040-0.063 mm). TLC analysis was conducted on HPTLC aluminium sheets (Merck, silica gel 60, F245). Compounds were visualized by UV absorption (245 nm), by spraying with 20% $H_2SO_4$ in ethanol or with a solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ 25 g/l and $(NH_4)_4Ce(SO_4)_4\cdot 2H_2O$ 10 g/l, in 10% aqueous $H_2SO_4$ followed by charring at +/- 140 $^oC$. Some unsaturated compounds were visualized by spraying with a solution of $KMnO_4$ (2%) and $K_2CO_3$ (1%) in water. $^1H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded with a Bruker AV 400 (400, 101 and 162 MHz respectively) in MeOD, $CD_3CN$ or $D_2O$, with chemical shift (δ) relative to the residual solvent signal, TMS (external standard for $^{13}C$) and $H_3PO_4$. (external standard for $^{31}P$). High resolution mass spectra were recorded by direct injection (2 µl of a 2 µM solution in water/acetonitrile; 50/50; v/v and 0.1 % formic acid) on a mass spectrometer (Thermo Finnigan LTQ Orbitrap) equipped with an electrospray ion source in positive mode (source voltage 3.5 kV, sheath gas flow 10, capillary temperature 250 °C) with resolution R = 60000 at *m/z* 400 (mass range *m/z* = 150-2000) and dioctylphthalate (*m/z* = 391.28428) as a lock mass. The high resolution mass spectrometer was calibrated prior to measurements with a calibration mixture (Thermo Finnigan).

### Synthesis of fluorous benzyl spacer




**Scheme S1:** Synthesis of FCbz protected spacer phosphoramidite
*Reagents and conditions:* a) phosgene, THF, 0°C; b) $NaHCO_3$, 6-amino-1-hexanol, THF, $H_2O$, >98% over 2 steps; c) 2-cyanoethyl-*N,N*-diisopropylchlorophosphoramidite, DIPEA, DCM, 65%.

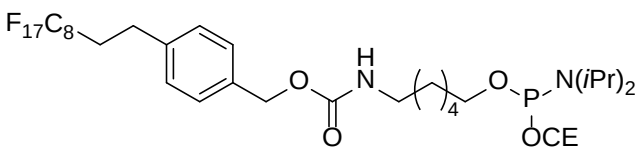
#### 4-(1H, 1H, 2H, 2H, perfluorodecyl)benzyl (6-hydroxyhexyl)carbamate (47)




4-(1H, 1H, 2H, 2H, perfluorodecyl)benzyl alcohol **45** (3.4 g, 6.2 mmol) was dissolved in THF (60 ml) and cooled to 0°C. Phosgene (20% in toluene, 9 ml, 17 mmol) was added and the mixture was stirred for 1.5 hours. The mixture was concentrated *in vacuo* yielding crude 4-(1H, 1H, 2H, 2H, perfluorodecyl)benzyl chloroformate **46** which was dissolved in a mixture of water and acetone (105 ml, 1/2, v/v). 6-aminohexan-1-ol (0.78 g, 6.7 mmol) and sodium bicarbonate (0.47 g, 5.6 mmol) were added and the mixture was stirred for 19 hours. The acetone was evaporated *in vacuo*, the solids were collected and washed with water. The residue was dried *in vacuo* giving 4-(1H, 1H, 2H, 2H, perfluorodecyl)benzyl (6-hydroxyhexyl)carbamate **47** (4,3 g, 6.2 mmol) in >98% yield. $^1H$ NMR (400 MHz, MeOD) δ 7.36 – 7.23 (m, 4H), 5.04 (s, 2H), 3.54 (t, *J* = 6.4 Hz, 2H), 3.10 (t, *J* = 6.9 Hz, 2H), 2.97 – 2.87 (m, 2H), 2.46 (tt, *J* = 17.6, 8.1 Hz, 2H), 1.59 – 1.44 (m, 4H), 1.44 –

1.23 (m, 4H); $^{13}$C NMR (101 MHz, MeOD) δ 129.5, 129.3, 67.0, 62.9, 49.6, 49.4, 49.2, 49.0, 48.8, 48.6, 48.4, 41.7, 33.6, 30.9, 27.6, 27.1, 26.6.

**4-(1H, 1H, 2H, 2H, perfluorodecyl)benzyl (6-*O*-([*N, N'*-di-isopropylamino]-2-cyanoethyl-phosphite)hexyl) carbamate (21)**



**21**

4-(1H, 1H, 2H, 2H, perfluorodecyl)benzyl (6-hydroxyhexyl)carbamate **47** (2.8 g, 4.0 mmol) was coevaporated with toluene three times and was dissolved in DCM (40 ml). DIPEA (1.0 ml, 6.0 mmol) and 3Å molsieves were added and the resulting suspension was stirred for 30 minutes. 2-Cyanoethyl N,N-diisopropylchlorophosphoramidite (1.0 ml, 4.8 mmol) was added and the reaction mixture was stirred for 3.5 hours. Water was added, the organic phase was washed with brine, dried over $Na_2SO_4$ and concentrated *in vacuo*. Flash column chromatography yielded phosphoramidite **21** (2.3 g, 2.6 mmol) in 65% yield. $^1$H NMR (400 MHz, $CD_3CN$) δ 7.39 – 7.13 (m, 4H), 5.66 (s, 1H), 5.00 (s, 2H), 3.85 – 3.68 (m, 2H), 3.69 – 3.49 (m, 4H), 3.08 (q, *J* = 6.4 Hz, 2H), 2.96 – 2.80 (m, 2H), 2.62 (t, *J* = 5.8 Hz, 2H), 2.55 – 2.33 (m, 2H), 1.68 – 1.51 (m, 2H), 1.52 – 1.41 (m, 2H), 1.41 – 1.22 (m, 5H), 1.17 (dd, *J* = 6.5, 2.8 Hz, 12H); $^{13}$C NMR (101 MHz, Acetone-$d_6$) δ 206.3, 157.2, 139.7, 136.9, 129.2, 129.1, 119.4, 119.0, 66.1, 64.2, 64.0, 59.4, 59.2, 43.7, 43.6, 41.5, 33.3, 33.1, 32.9, 31.9, 31.9, 30.7, 30.4, 30.2, 30.0, 29.8, 29.6, 29.5, 27.1, 26.6, 26.4, 24.9, 24.8, 20.8, 20.7, 1.2; $^{31}$P NMR (162 MHz, Acetone-$d_6$) δ 147.0.

## General procedure for automated solid phase synthesis

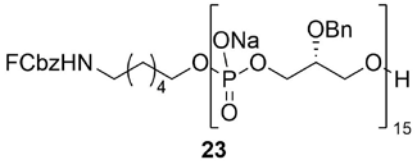
A small column containing highly cross-linked polystyrene based universal support resin (USP III PS, Glen research) was loaded in an automated synthesizer (Äkta oligopilot plus, GE healthcare). The resin was flushed with a solution of 3% dichloroacetic acid in toluene (15 ml, 3 min) followed by MeCN (5 ml, 1 min). A solution of phosphoramidite (0.1M in MeCN, 0.5 ml, 50 µmol) and a solution of 5-(Benzylthio)-1*H*-tetrazole (0.3M in MeCN, 0.75ml, 0.2 mmol) were added to the column and the mixture was recycled over the resin for 5 minutes. The resin was flushed with MeCN (5 ml, 1 min) and a solution of $I_2$ (0.05M in a mixture of pyridine and $H_2O$ (9/1 v/v), 2 ml, 1 min) subsequently. The resin was flushed with MeCN (5 ml, 1 min) and a capping mixture (1/1 mixture of cap A (0.5M $Ac_2O$ in MeCN) and cap B (*N*-methylimidazole, 2,6-lutidine, MeCN 1/1/9 v/v/v), 1 ml, 0.2 min) subsequently. The system was flushed with MeCN (5 ml, 1 min) and the cycle was repeated until the desired oligomer length was obtained. A solution of spacer-phosphoramidite (0.1 M in MeCN, 0.5 ml, 50 µmol) and a solution of 5-(Benzylthio)-1*H*-tetrazole (0.3M in MeCN, 0.75ml, 0.2 mmol) were added to the column and the mixture was recycled over the resin for 5 minutes. The resin was flushed with MeCN (5 ml, 1 min), a solution of $I_2$ (0.05M in a mixture of pyridine and $H_2O$ (9/1 v/v), 2 ml, 1 min) and MeCN (5 ml, 1 min) subsequently. The column was removed from the system and the resin was treated with $NH_3$ (2M in methanol, 10 ml) for 1 hour. Ammonia (25% in $H_2O$, 10 ml) was added and the mixture was rested for 1 hour. The mixture was passed over a filter and the resin was flushed with methanol (10 ml), $H_2O$ (10 ml), a mixture of (*t*-BuOH, MeCN and $H_2O$, 1/1/1 v/v/v, 10 ml) and acetonitrile (10 ml). The combined eluate was concentrated *in vacuo* and the residue was purified using reversed phase HPLC (C18, $NH_4OAc$). After repeated lyophilization, the product was eluted through a small column containing Dowex $Na^+$ cation-exchange resin (type: 50WX4-200, stored on 0.5 M NaOH in $H_2O$, flushed with $H_2O$ and MeOH before use).

## General procedure for global deprotection

The oligomer was dissolved in a mixture of water and dioxane (2 mM, 2/1 v/v). ~0.1ml AcOH was added and the mixture was purged of oxygen. Pd-black (~20 mg) was added and subsequently, the reaction mixture was treated with Hydrogen gas for 3 days. Celite was added to the mixture and after short sonication (20-30 sec) the mixture was filtered over celite and Chelex 100 resin and concentrated *in vacuo* The residue was purified by size-exclusion chromatography (HW40, dimensions: 16/60 mm, eluent: 0.15 M $NH_4OAc$). After repeated lyophilization, the product was eluted through a small column containing Dowex $Na^+$ cation-exchange resin (type: 50WX4-200, stored on 0.5 M NaOH in $H_2O$, flushed with $H_2O$ and MeOH before use).

## Analytical data for semi-protected pentadecamers 23-38

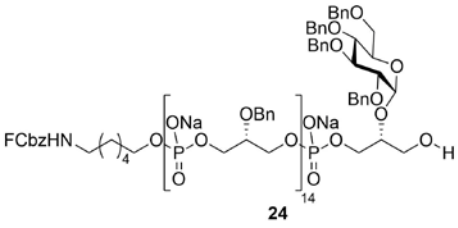
### Semi-Protected pentadecamer 23



**23**

Using the general procedure for automated solid phase synthesis, semi-protected pentadecamer **23** (8.0 mg, 1.7 µmol) was obtained in 17 % yield. $^1$H NMR (400MHz, $D_2O$): ð = 6.89-7.16 (m, 69H), 4.92 (s, 2H), 4.35-4.46 (m, 30H), 3.89-3.92 (m, 30H), 3.79-3.84 (m, 30H), 3.67-3.68 (m, 15H) 3.49-3.54 (m, 2H), 2.24 (s, 2H), 0.95-1.37 (m, 8H); $^{31}$P NMR (162MHz, $D_2O$): ð = 1.2, 1.1, 1.0; LCMS: $[C_{174}H_{219}F_{17}NO_{78}P_{15} + 2H]^{2+}$ requires 2181.5, found 2181.2.

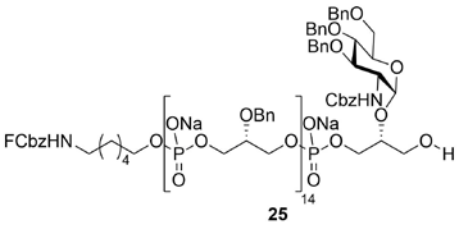
### Semi-protected pentadecamer 24



**24**

Using the general procedure for automated solid phase synthesis, semi-protected pentadecamer **24** (9.6 mg, 1.9 µmol) was obtained in 19 % yield. $^1$H NMR (400MHz, $D_2O$): ð = 6.78-7.33 (m, 94H), 4.71 (s, 1H), 3.96-4.19 (m, 38H), 3.14-3.73 (m, 81H) 2.72-2.94 (m, 4H), 2.24 (s, 2H), 0.92-1.21 (m, 8H); $^{31}$P NMR (162MHz, $D_2O$): ð = 1.1; LCMS: $[C_{201}H_{247}F_{17}NO_{83}P_{15} + 2H]^{2+}$ requires 2398.1, found 2398.2.

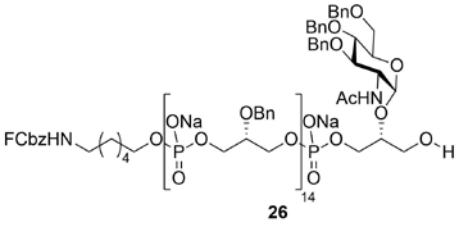
### Semi-protected pentadecamer 25



**25**

Using the general procedure for automated solid phase synthesis, semi-protected pentadecamer **25** (7.1 mg, 1.4 µmol) was obtained in 14 % yield. $^1$H NMR (400MHz, $D_2O$): ð = 6.72-7.13 (m, 94H), 4.95 (s, 1H), 4.20-4.35 (m, 38H), 3.76-3.82 (m, 60H), 3.42-3.62 (m, 21H), 2.60-2.87 (m, 4H), 2.20 (s, 2H), 1.62 (s, 2H), 0.70-1.35 (m, 8H); $^{31}$P NMR (162MHz, $D_2O$): ð = 1.0; LCMS: $[C_{202}H_{248}F_{17}N_2O_{84}P_{15} + 2H]^{2+}$ requires 2419.6, found 2419.9.

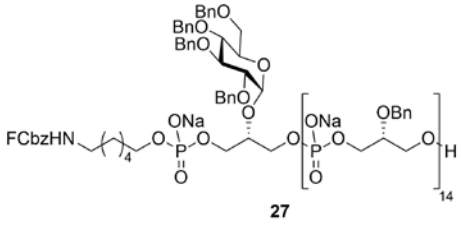
### Semi-protected pentadecamer 26



**26**

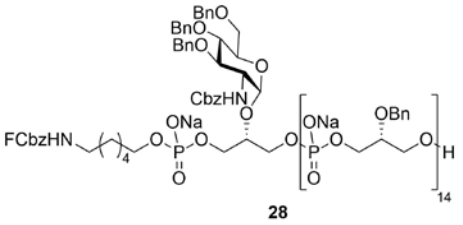
Using the general procedure for automated solid phase synthesis, semi-protected pentadecamer **26** (3.5 mg, 0.7 µmol) was obtained in 7 % yield. $^1$H NMR (400MHz, $D_2O$): ð = 6.82-7.17 (m, 94H), 4.96 (s, 1H), 4.32-4.36 (m, 38H), 3.75-4.05 (m, 60H), 3.35-3.70 (m, 21H), 2.75-3.00 (m, 4H), 2.32 (s, 2H), 1.97 (s, 3H), 1.80 (s, 2H), 0.80-1.34 (m, 8H); $^{31}$P NMR (162MHz, $D_2O$): ð = 1.0; LCMS: $[C_{196}H_{244}F_{17}N_2O_{83}P_{15} + 2H]^{2+}$ requires 2373.1, found 2373.3.

**Semi-protected pentadecamer 27**



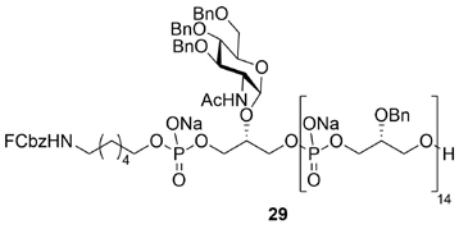
Using the general procedure for automated solid phase synthesis, semi-protected pentadecamer **27** (5.3 mg, 1.0 µmol) was obtained in 10 % yield. $^{1}$H NMR (400MHz, $D_2O$): ð = 6.37-7.12 (m, 94H), 4.70 (s, 1H), 4.16-4.29 (m, 38H), 3.66-3.83 (m, 60H), 3.22-3.60 (m, 21H), 2.83-2.92 (m, 4H), 2.11 (s, 2H), 1.63 (s, 2H), 0.92-1.21 (m, 8H); $^{31}$P NMR (162MHz, $D_2O$): ð = 1.0; LCMS: $[C_{201}H_{247}F_{17}NO_{83}P_{15} + 2H]^{2+}$ requires 2398.1, found 2397.7.

**Semi-protected pentadecamer 28**



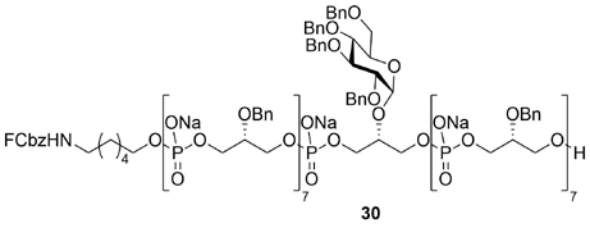
Using the general procedure for automated solid phase synthesis, semi-protected pentadecamer **28** (7.5 mg, 1.5 µmol) was obtained in 15 % yield. $^{1}$H NMR (400MHz, $D_2O$): ð = 6.81-7.13 (m, 94H), 4.98 (s, 1H), 4.26-4.28 (m, 38H), 3.76-3.98 (m, 60H), 3.31-3.59 (m, 21H), 2.70-2.95 (m, 4H), 2.11 (s, 2H), 1.48 (s, 2H), 1.00-1.24 (m, 8H); $^{31}$P NMR (162MHz, $D_2O$): ð = 1.0; LCMS: $[C_{202}H_{248}F_{17}N_2O_{84}P_{15} + 2H]^{2+}$ requires 2419.6, found 2419.1.

**Semi-protected pentadecamer 29**



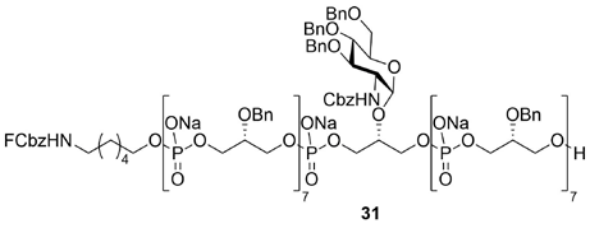
Using the general procedure for automated solid phase synthesis, semi-protected pentadecamer **29** (3.9 mg, 0.8 µmol) was obtained in 8% yield. $^{1}$H NMR (400MHz, $D_2O$): ð = 6.89-7.09 (m, 94H), 5.00 (s, 1H), 4.25-4.46 (m, 38H), 3.72-4.00 (m, 60H), 3.44-3.67 (m, 21H), 2.73-3.10 (m, 4H), 2.22 (s, 2H), 2.00 (s, 3H), 1.70 (m, 2H), 0.80-1.54 (m, 8H); $^{31}$P NMR (162MHz, $D_2O$): ð = 1.0; LCMS: $[C_{196}H_{244}F_{17}N_2O_{83}P_{15} + NH_4 + 2H]^{2+}$ requires 2381.1, found 2381.4.

**Semi-protected pentadecamer 30**



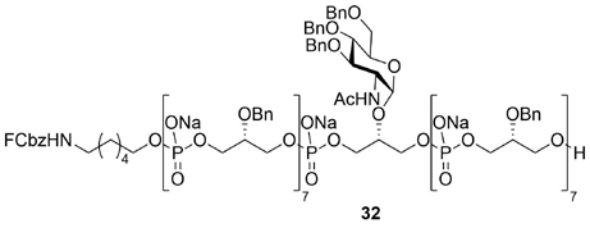
Using the general procedure for automated solid phase synthesis, semi-protected pentadecamer **30** (8.1 mg, 1.6 µmol) was obtained in 16 % yield. $^{1}$H NMR (400MHz, $D_2O$): ð = 6.49-6.97 (m, 94H), 4.18 (s, 38H), 3.71-3.77 (m, 60H), 3.30-3.60 (m, 21H), 2.89-2.78 (m, 2H), 2.16 (s, 2H), 1.60 (s, 2H), 0.83-1.25 (m, 8H); $^{31}$P NMR (162MHz, $D_2O$): ð = 1.1; LCMS: $[C_{201}H_{247}F_{17}NO_{83}P_{15} + 2H]^{2+}$ requires 2398.1, found 2397.7.

**Semi-protected pentadecamer 31**



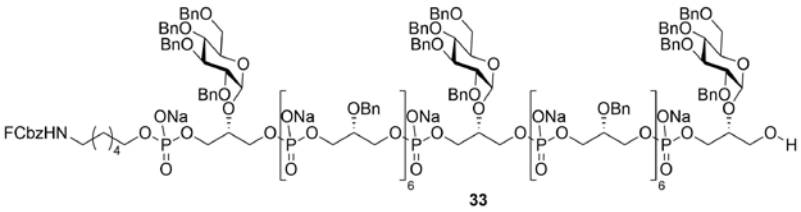
Using the general procedure for automated solid phase synthesis, semi-protected pentadecamer **31** (8.1 mg, 1.6 µmol) was obtained in 16 % yield. $^{1}$H NMR (400MHz, $D_2O$): ð = 6.69-6.96 (m, 94H), 4.90 (s, 1H), 4.17-4.26 (m, 38H), 3.60-3.98 (m, 60H), 3.42-3.48 (m, 21H), 2.60-2.85 (m, 4H), 2.11 (s, 2H), 1.62 (b, 2H), 0.80-1.30 (m, 8H); $^{31}$P NMR (162MHz, $D_2O$): ð = 1.0; LCMS: $[C_{202}H_{248}F_{17}N_2O_{84}P_{15} + 2H]^{2+}$ requires 2419.6, found 2419.9.

**Semi-protected pentadecamer 32**



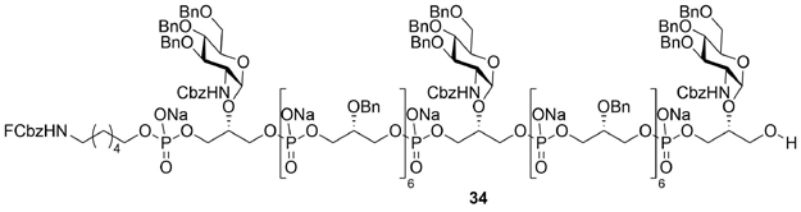
Using the general procedure for automated solid phase synthesis, semi-protected pentadecamer **32** (3.6 mg, 0.7 µmol) was obtained in 7 % yield. $^{1}$H NMR (400MHz, $D_2O$): ð = 6.81-7.16 (m, 94H), 5.03 (s, 1H), 4.25-4.50 (m, 38H), 3.75-4.19 (m, 60H), 3.32-3.76 (m, 21H), 2.71-3.00 (m, 4H), 2.31 (s, 2H), 1.99 (s, 3H), 1.50 (m, 2H), 0.86-1.37 (m, 8H); $^{31}$P NMR (162MHz, $D_2O$): ð = 1.0; LCMS: $[C_{196}H_{244}F_{17}N_2O_{83}P_{15} + 2H]^{2+}$ requires 2373.1, found 2373.3.

**Semi-protected pentadecamer 33**



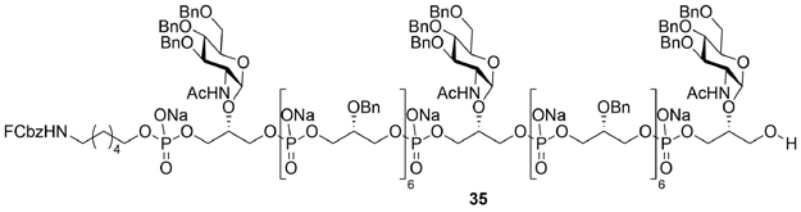
Using the general procedure for automated solid phase synthesis, semi-protected pentadecamer **33** (3.2 mg, 0.5 µmol) was obtained in 5 % yield. $^{31}$P NMR (162 MHz, $D_2O$) δ 0.8, 0.7, 0.6, 0.5; $^{1}$H NMR (400 MHz, $D_2O$) δ 7.14 – 6.59 (m, 234H), 6.41 – 6.20 (m, 3H), 5.06 (s, 1H), 5.01 – 4.88 (m, 2H), 4.57 – 4.06 (m, 50H), 4.05 – 3.59 (m, 111H), 3.59 – 3.25 (m, 35H), 3.23 – 3.05 (m, 5H), 2.86 – 2.57 (m, 3H), 2.29 – 2.02 (m, 3H), 1.75 – 1.43 (m, 4H), 1.43 – 1.18 (m, 7H), 1.18 – 0.71 (m, 18H); LCMS: $[C_{255}H_{303}F_{17}NO_{93}P_{15} + 2H]^{2+}$ requires 2829.7, found 2830.2.

**Semi-protected pentadecamer 34**



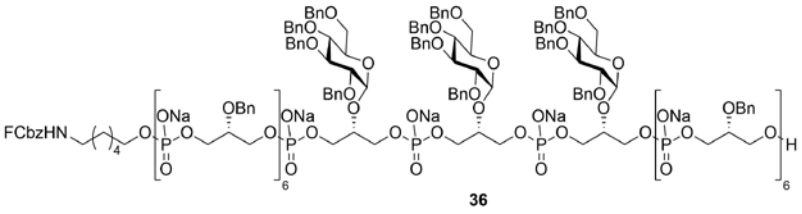
Using the general procedure for automated solid phase synthesis, semi-protected pentadecamer **34** (3.5 mg, 0.6 µmol) was obtained in 6 % yield. $^{1}$H NMR (400 MHz, $D_2O$) δ 7.29 – 6.61 (m, 227H), 6.48 – 6.22 (m, 3H), 5.19 – 5.00 (m, 3H), 4.58 – 4.12 (m, 43H), 4.12 – 3.69 (m, 106H), 3.69 – 3.21 (m, 41H), 3.05 – 2.82 (m, 3H), 2.72 (s, 2H), 2.36 – 2.08 (m, 4H), 1.83 – 1.55 (m, 4H), 1.55 – 1.37 (m, 4H), 1.37 – 0.76 (m, 18H); $^{31}$P NMR (162 MHz, $D_2O$) δ 1.3, 1.0; LCMS: $[C_{258}H_{306}F_{17}N_4O_{96}P_{15} + 3H]^{3+}$ requires 1929.8, found 1930.9.

**Semi-protected pentadecamer 35**



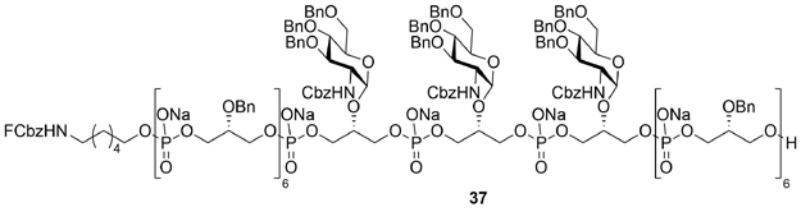
Using the general procedure for automated solid phase synthesis, semi-protected pentadecamer **35** (3.1 mg, 0.5 µmol) was obtained in 5 % yield. $^{1}$H NMR (400 MHz, $D_2O$) δ 7.26 – 6.61 (m, 116H), 6.58 – 6.32 (m, 3H), 5.07 – 4.90 (m, 3H), 4.56 – 4.19 (m, 37H), 4.19 – 3.73 (m, 79H), 3.73 – 3.22 (m, 33H), 2.94 (s, 2H), 2.72 (s, 1H), 2.44 – 2.11 (m, 4H), 2.09 – 1.85 (m, 16H), 1.85 – 0.59 (m, 35H); $^{31}$P NMR (162 MHz, MeOH) δ 0.9; LCMS: $[C_{240}H_{294}F_{17}N_4O_{93}P_{15} + 2H]^{2+}$ requires 2756.2, found 2756.3.

**Semi-protected pentadecamer 36**



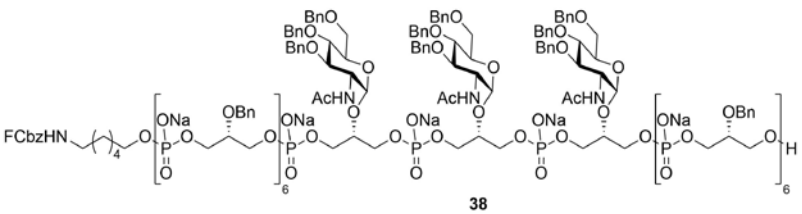
Using the general procedure for automated solid phase synthesis, semi-protected pentadecamer **36** (3.3 mg, 0.5 µmol) was obtained in 5 % yield. $^{1}$H NMR (400 MHz, $D_2O$) δ 7.34 – 6.42 (m, 205H), 6.39 – 6.16 (m, 3H), 5.33 – 4.85 (m, 3H), 4.59 – 4.01 (m, 47H), 4.01 – 3.60 (m, 91H), 3.60 – 3.21 (m, 34H), 2.88 – 2.69 (m, 3H), 2.69 – 2.38 (m, 8H), 2.18 – 2.00 (m, 3H), 1.65 – 0.56 (m, 23H); $^{31}$P NMR (162 MHz, $D_2O$) δ 1.3, 1.0, 0.1; LCMS: $[C_{255}H_{303}F_{17}NO_{93}P_{15} + 2H]^{2+}$ requires 2829.7, found 2830.3.

**Semi-protected pentadecamer 37**



Using the general procedure for automated solid phase synthesis, semi-protected pentadecamer **37** (4.7 mg, 0.8 µmol) was obtained in 8 % yield. $^{1}$H NMR (400 MHz, $D_2O$) δ 7.34 – 6.56 (m, 241H), 6.56 – 6.31 (m, 4H), 5.22 (s, 3H), 4.61 – 4.17 (m, 40H), 4.17 – 3.71 (m, 101H), 3.71 – 3.19 (m, 44H), 2.88 (s, 2H), 2.72 (s, 1H), 2.22 (s, 3H), 1.84 – 1.59 (m, 4H), 1.44 – 1.22 (m, 6H), 1.22 – 0.80 (m, 15H); $^{31}$P NMR (162 MHz, $D_2O$) δ 1.2, 1.0; LCMS: $[C_{258}H_{306}F_{17}N_4O_{96}P_{15} + 3H]^{3+}$ requires 1929.8, found 1930.9.

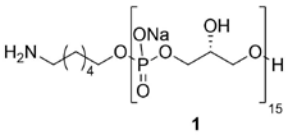
**Semi-protected pentadecamer 38**



Using the general procedure for automated solid phase synthesis, semi-protected pentadecamer **38** (4.1 mg, 0.7 µmol) was obtained in 7 % yield. $^{1}$H NMR (400 MHz, $D_2O$) δ 7.44 – 6.56 (m, 235H), 6.56 – 6.25 (m, 4H), 5.10 – 4.88 (m, 3H), 4.61 – 4.15 (m, 46H), 4.15 – 3.44 (m, 161H), 3.44 – 3.11 (m, 18H), 2.83 (s, 3H), 2.74 – 2.60 (m, 2H), 2.43 – 2.04 (m, 5H), 2.04 – 1.76 (m, 26H), 1.79 – 1.46 (m, 5H), 1.45 – 0.59 (m, 22H); $^{31}$P NMR (162 MHz, $D_2O$) δ 0.6, 0.5, 0.3; LCMS: $[C_{240}H_{294}F_{17}N_4O_{93}P_{15} + 2H]^{2+}$ requires 2756.2, found 2756.3.

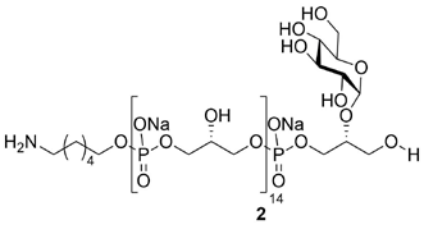
## Analytical data for deprotected pentadecamers 1-16

**Deprotected pentadecamer 1**



Using the general procedure for global deprotection on semi-protected pentadecamer **23** (8.0 mg, 1.7 µmol), deprotected pentadecamer **1** (3.1 mg, 1.7 µmol) was obtained in 66% yield. $^{1}$H NMR (400MHz, $D_2O$): ð =3.98-4.01 (m, 15H), 3.90-3.96 (m, 30H), 3.71-3.88 (m, 30H), 3.54-3.67 (m, 2H), 2.97 (t, *J* = 7.6 Hz, 2H), 1.61-1.67 (m, 4H), 1.39-1.40 (m, 4H); $^{31}$P NMR (162MHz, $D_2O$): ð = 1.3, 1.3, 1.2, 1.2; HRMS: $[C_{51}H_{120}NO_{76}P_{15} +H +NH_4]^{2+}$ requires 1223.10156, found 1223.10423.

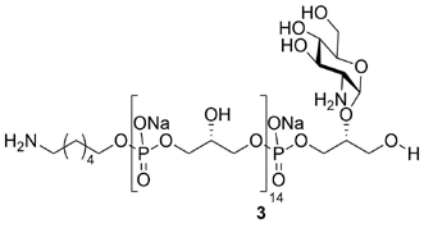
**Deprotected pentadecamer 2**



Using the general procedure for global deprotection on semi-protected pentadecamer **24** (8.9 mg, 1.7 µmol), deprotected pentadecamer **2** (3.0 mg, 1.0 µmol) was obtained in 60% yield. $^{1}$H NMR (400MHz, $D_2O$): ð = 5.13 (d, *J* = 4 Hz, 1H), 3.96-4.07

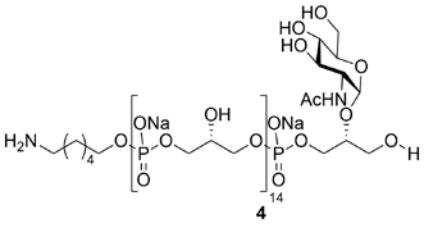
(m, 15H), 3.88-3.95 (m, 30H), 3.79-3.86 (m, 30H), 3.48-3.78 (m, 7H), 3.37 (t, *J* = 9.6 Hz, 1H), 2.96 (t, *J* = 7.6 Hz, 2H), 1.59-1.67 (m, 4H), 1.39-1.40 (m, 4H); $^{31}$P NMR (162MHz, $D_2O$): ð = 1.3, 1.3, 1.2; HRMS: $[C_{57}H_{133}N_2O_{81}P_{15} +2H]^{2+}$ requires 1304.12797, found 1304.13104.

**Deprotected pentadecamer 3**



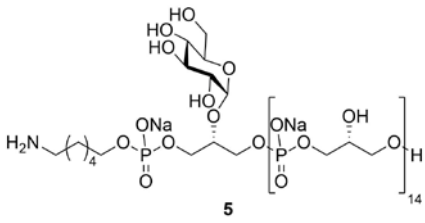
Using the general procedure for global deprotection on semi-protected pentadecamer **25** (4.2 mg, 0.8 µmol), deprotected pentadecamer **3** (2.0 mg, 0.7 µmol) was obtained in 86% yield. $^1$H NMR (400 MHz, $D_2O$) δ 5.04 (s, 1H), 4.16 – 4.05 (m, 2H), 4.01 – 3.91 (m, 26H), 3.91 – 3.84 (m, 48H), 3.84 – 3.71 (m, 64H), 3.71 – 3.62 (m, 11H), 3.58 (dd, *J* = 11.7, 4.2 Hz, 4H), 3.50 (dd, *J* = 11.8, 6.0 Hz, 3H), 3.36 – 3.24 (m, 2H), 2.97 – 2.81 (m, 2H), 1.68 – 1.46 (m, 4H), 1.46 – 1.28 (m, 4H); $^{31}$P NMR (162 MHz, $D_2O$) δ 0.7; HRMS: $[C_{57}H_{131}N_2O_{80}P_{15} +2H]^{2+}$ requires 1295.12269, found 1295.12402.

**Deprotected pentadecamer 4**



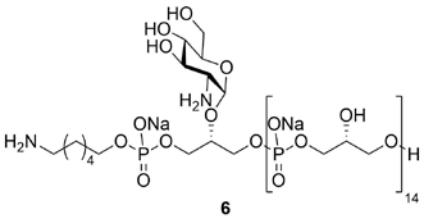
Using the general procedure for global deprotection on semi-protected pentadecamer **26** (2.5 mg, 0.5 µmol), deprotected pentadecamer **4** (0.6 mg, 0.2 µmol) was obtained in 41% yield. $^1$H NMR (400 MHz, $D_2O$) δ 4.95 (d, *J* = 2.9 Hz, 1H), 4.01 – 3.88 (m, 18H), 3.88 – 3.71 (m, 73H), 3.71 – 3.61 (m, 8H), 3.61 – 3.43 (m, 5H), 3.37 (m, 2H), 2.94 – 2.82 (m, 2H), 1.95 (s, 3H), 1.66 – 1.48 (m, 5H), 1.38 – 1.25 (m, 8H); $^{31}$P NMR (162 MHz, $D_2O$) δ 0.8, 0.7; HRMS: $[C_{59}H_{136}N_3O_{81}P_{15} +2H]^{2+}$ requires 1324.64124, found 1324.64430.

**Deprotected pentadecamer 5**



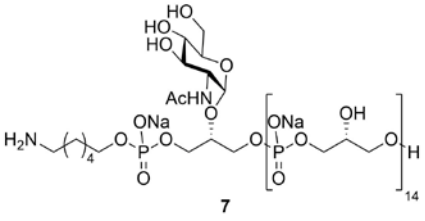
Using the general procedure for global deprotection on semi-protected pentadecamer **27** (5.3 mg, 1.0 µmol), deprotected pentadecamer **5** (2.5 mg, 0.9 µmol) was obtained in 83% yield. $^1$H NMR (400MHz, $D_2O$): ð = 5.12 (d, *J* = 3.6 Hz, 1H), 3.95-4.08 (m, 15H), 3.90-3.94 (m, 30H), 3.80-3.92 (m, 30H), 3.47-3.76 (m, 7H), 3.35 (t, *J* = 9.6 Hz, 1H), 2.96 (t, *J* = 7.4 Hz, 2H), 1.60-1.66 (m, 4H), 1.38-1.40 (m, 4H); $^{31}$P NMR (162MHz, $D_2O$): ð = 1.4, 1.3, 1.3, 1.3, 1.2; HRMS: $[C_{57}H_{133}N_2O_{81}P_{15} +2H]^{2+}$ requires 1304.12797, found 1304.13090.

**Deprotected pentadecamer 6**



Using the general procedure for global deprotection on semi-protected pentadecamer **28** (2.8 mg, 0.5 µmol), deprotected pentadecamer **6** (1.4 mg, 0.5 µmol) was obtained in 88% yield. $^1$H NMR (400 MHz, $D_2O$) δ 5.15 (s, 1H), 4.11 – 4.01 (m, 8H), 4.01 – 3.91 (m, 15H), 3.91 – 3.52 (m, 23H), 3.48 – 3.32 (m, 3H), 3.06 – 2.94 (m, 2H), 1.66 (s, 4H), 1.42 (s, 4H); $^{31}$P NMR (162 MHz, MeOH) δ 1.2; HRMS: $[C_{57}H_{131}N_2O_{80}P_{15} +H +NH_4]^{2+}$ requires 1303.63596, found 1303.63865.

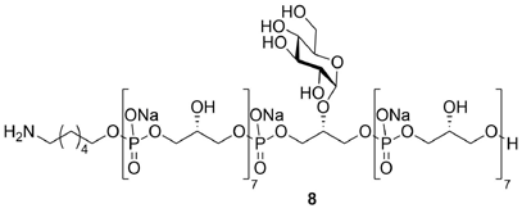
**Deprotected pentadecamer 7**



Using the general procedure for global deprotection on semi-protected pentadecamer **29** (2.3 mg, 0.5 µmol), deprotected pentadecamer **7** (0.5 mg, 0.2 µmol) was obtained in 36% yield. $^1$H NMR (400 MHz, $D_2O$) δ 4.95 (d, *J* = 3.2 Hz, 1H), 3.98 – 3.89

(m, 17H), 3.89 – 3.79 (m, 37H), 3.79 – 3.71 (m, 36H), 3.71 – 3.59 (m, 8H), 3.59 – 3.43 (m, 6H), 3.34 (t, *J* = 9.6 Hz, 2H), 2.93 – 2.83 (m, 2H), 1.95 (s, 3H), 1.63 – 1.45 (m, 4H), 1.35 – 1.24 (m, 4H); $^{31}$P NMR (162 MHz, $D_2O$) δ 0.7; HRMS: $[C_{59}H_{136}N_3O_{81}P_{15}$ +2H$]^{2+}$ requires 1324.64124, found 1324.64426.

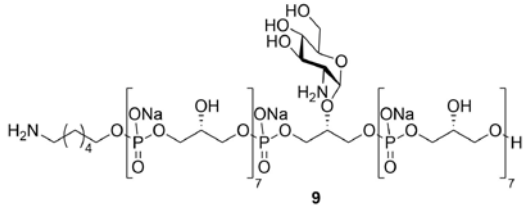
**Deprotected pentadecamer 8**



8

Using the general procedure for global deprotection on semi-protected pentadecamer **30** (8.1 mg, 1.6 µmol), deprotected pentadecamer **8** (2.3 mg, 0.8 µmol) was obtained in 51% yield. $^1$H NMR (400MHz, $D_2O$): δ = 5.14 (d, *J* = 3.6 Hz, 1H), 3.95-4.05 (m, 15H), 3.90-3.94 (m, 30H), 3.80-3.92 (m, 30H), 3.47-3.76 (m, 7H), 3.36 (t, *J* = 9.8 Hz, 1H), 2.96 (t, *J* = 7.4 Hz, 2H), 1.60-1.66 (m, 4H), 1.38-1.40 (m, 4H); $^{31}$P NMR (162MHz, $D_2O$): δ = 1.3, 1.3, 1.3, 1.3, 1.2, 1.2; HRMS: $[C_{57}H_{133}N_2O_{81}P_{15}$ +2H$]^{2+}$ requires 1304.12797, found 1304.13070.

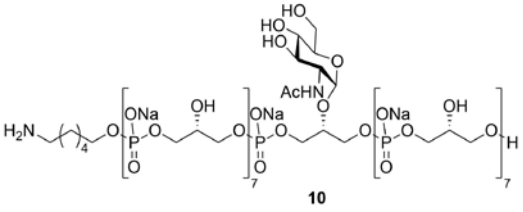
**Deprotected pentadecamer 9**



9

Using the general procedure for global deprotection on semi-protected pentadecamer **31** (8.1 mg, 1.6 µmol), deprotected pentadecamer **9** (3.6 mg, 1.2 µmol) was obtained in 79% yield. $^1$H NMR (400 MHz, $D_2O$) δ 5.24 (s, 1H), 4.09 – 3.87 (m, 16H), 3.87 – 3.80 (m, 21H), 3.80 – 3.60 (m, 30H), 3.60 – 3.53 (m, 1H), 3.53 – 3.42 (m, 2H), 3.34 (t, *J* = 9.6 Hz, 2H), 3.10 (s, 1H), 2.87 (t, *J* = 7.5 Hz, 2H), 1.67 – 1.46 (m, 4H), 1.36 – 1.25 (m, 4H); $^{31}$P NMR (162 MHz, $D_2O$) δ 0.8, 0.7; HRMS: $[C_{57}H_{134}N_3O_{80}P_{15}$ +2H$]^{2+}$ requires 1303.63596, found 1303.63917.

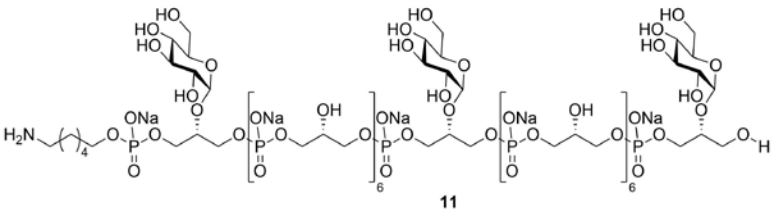
**Deprotected pentadecamer 10**



10

Using the general procedure for global deprotection on semi-protected pentadecamer **32** (3.9 mg, 0.8 µmol), deprotected pentadecamer **10** (0.9 mg, 0.3 µmol) was obtained in 39% yield. $^1$H NMR (400 MHz, $D_2O$) δ 4.97 (s, 1H), 3.99 – 3.88 (m, 19H), 3.88 – 3.80 (m, 30H), 3.80 – 3.59 (m, 49H), 3.56 (dd, *J* = 12.2, 3.9 Hz, 3H), 3.47 (dd, *J* = 11.8, 5.8 Hz, 3H), 3.35 (t, *J* = 9.8 Hz, 2H), 2.87 (t, *J* = 7.5 Hz, 2H), 1.96 (s, 3H), 1.67 – 1.44 (m, 4H), 1.37 – 1.24 (m, 4H); $^{31}$P NMR (162 MHz, $D_2O$) δ 0.8, 0.7; HRMS: $[C_{59}H_{136}N_3O_{81}P_{15}$ +2H$]^{2+}$ requires 1324.64124, found 1324.64473.

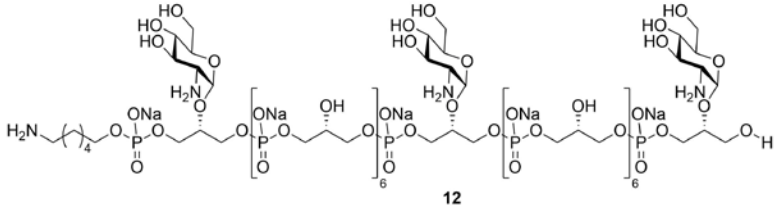
**Deprotected pentadecamer 11**



11

Using the general procedure for global deprotection on semi-protected pentadecamer **33** (2.5 mg, 0.4 µmol), deprotected pentadecamer **11** (1.1 mg, 0.3 µmol) was obtained in 79% yield. $^1$H NMR (400 MHz, $D_2O$) δ 5.20 – 5.09 (m, 3H), 4.13 – 3.98 (m, 27H), 3.98 – 3.92 (m, 31H), 3.92 – 3.79 (m, 42H), 3.79 – 3.64 (m, 15H), 3.59 – 3.45 (m, 7H), 3.45 – 3.30 (m, 8H), 2.99 (t, *J* = 7.3 Hz, 2H), 1.59 (d, *J* = 49.7 Hz, 8H); $^{31}$P NMR (162 MHz, $D_2O$) δ 1.3; HRMS: $[C_{69}H_{150}NO_{91}P_{15}$ +2H$]^{2+}$ requires 1457.66752, found 1457.67297.

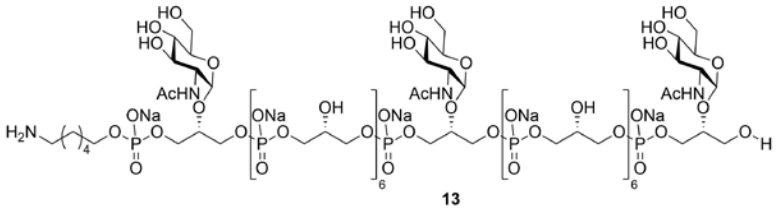
**Deprotected pentadecamer 12**



12

Using the general procedure for global deprotection on semi-protected pentadecamer **34** (2.1 mg, 0.4 μmol), deprotected pentadecamer **12** (0.9 mg, 0.3 μmol) was obtained in 81% yield. $^{1}$H NMR (400 MHz, $D_2O$) δ 5.15 – 4.96 (m, 3H), 4.11 – 3.90 (m, 22H), 3.89 – 3.82 (m, 28H), 3.82 – 3.71 (m, 29H), 3.71 – 3.46 (m, 18H), 3.38 – 3.22 (m, 4H), 2.96 – 2.85 (m, 2H), 1.57 (s, 4H), 1.34 (s, 4H); $^{31}$P NMR (162 MHz, $D_2O$) δ 1.4, 1.3, 1.0, 0.9; HRMS: $[C_{69}H_{153}N_4O_{88}P_{15}$ +2H$]^{2+}$ requires 1456.19149, found 1456.19606.

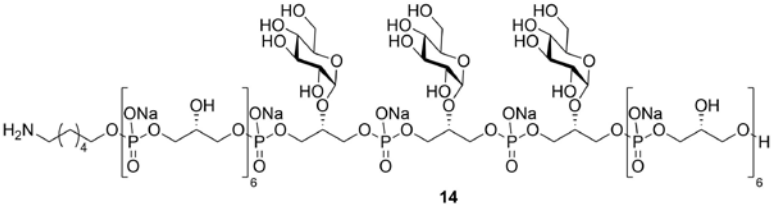
**Deprotected pentadecamer 13**



13

Using the general procedure for global deprotection on semi-protected pentadecamer **35** (1.7 mg, 0.3 μmol), deprotected pentadecamer **13** (0.8 mg, 0.2 μmol) was obtained in 84% yield. $^{1}$H NMR (400 MHz, $D_2O$) δ 4.98 (s, 3H), 4.12 (s, 3H), 4.00 – 3.82 (m, 47H), 3.82 – 3.62 (m, 42H), 3.62 – 3.45 (m, 8H), 3.45 – 3.31 (m, 5H), 2.89 (t, *J* = 6.7 Hz, 2H), 2.02 – 1.95 (m, 9H), 1.55 (s, 4H), 1.33 (s, 4H); $^{31}$P NMR (162 MHz, $D_2O$) δ 0.7, 0.6; HRMS: $[C_{75}H_{162}N_5O_{91}P_{15}$ +2H$]^{2+}$ requires 1527.72061, found 1527.72229.

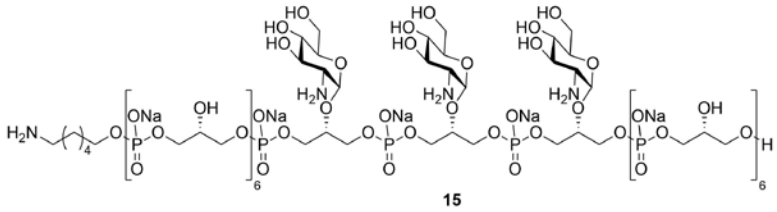
**Deprotected pentadecamer 14**



14

Using the general procedure for global deprotection on semi-protected pentadecamer **36** (3.3 mg, 0.5 μmol), deprotected pentadecamer **14** (1.1 mg, 0.3 μmol) was obtained in 63% yield. $^{1}$H NMR (400 MHz, $D_2O$) δ 5.08 (d, *J* = 3.6 Hz, 3H), 4.11 – 3.99 (m, 11H), 3.99 – 3.90 (m, 37H), 3.90 – 3.83 (m, 53H), 3.83 – 3.71 (m, 60H), 3.71 – 3.60 (m, 27H), 3.60 – 3.47 (m, 10H), 3.42 (dd, *J* = 9.7, 3.7 Hz, 9H), 3.29 (t, *J* = 9.6 Hz, 9H), 2.90 (t, *J* = 7.5 Hz, 2H), 1.60 (d, *J* = 29.3 Hz, 4H), 1.33 (s, 4H); $^{31}$P NMR (162 MHz, $D_2O$) δ 0.8, 0.7, 0.5, 0.4; HRMS: $[C_{69}H_{153}N_2O_{91}P_{15}$ +2H$]^{2+}$ requires 1466.18079, found 1466.18677.

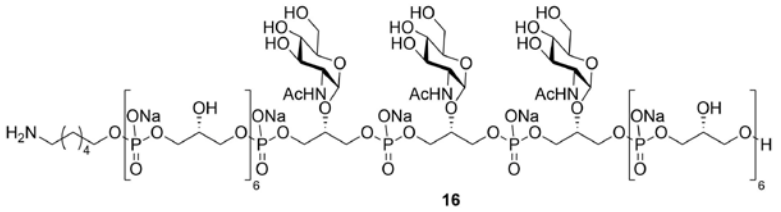
**Deprotected pentadecamer 15**



15

Using the general procedure for global deprotection on semi-protected pentadecamer **37** (4.7 mg, 0.8 μmol), deprotected pentadecamer **15** (1.6 mg, 0.5 μmol) was obtained in 64% yield. $^{1}$H NMR (400 MHz, $D_2O$) δ 5.21 – 5.02 (m, 3H), 4.13 – 3.93 (m, 28H), 3.93 – 3.85 (m, 38H), 3.85 – 3.73 (m, 44H), 3.73 – 3.47 (m, 20H), 3.42 – 3.26 (m, 6H), 2.99 – 2.73 (m, 7H), 1.66 – 1.48 (m, 4H), 1.41 – 1.26 (m, 4H); $^{31}$P NMR (162 MHz, $D_2O$) δ 0.8, 0.7, 0.5; HRMS: $[C_{69}H_{153}N_4O_{88}P_{15}$ +2H$]^{2+}$ requires 1456.19149, found 1456.19848.

**Deprotected pentadecamer 16**



16

Using the general procedure for global deprotection on semi-protected pentadecamer **37** (3.5 mg, 0.6 µmol), deprotected pentadecamer **1** (1.7 mg, 0.5 µmol) was obtained in 84% yield. $^{1}$H NMR (400 MHz, $D_2O$) δ 5.15 – 5.03 (m, 3H), 4.14 – 3.99 (m, 19H), 3.99 – 3.90 (m, 42H), 3.90 – 3.71 (m, 35H), 3.71 – 3.53 (m, 3H), 3.46 (t, *J* = 9.2 Hz, 3H), 2.99 (t, *J* = 7.5 Hz, 2H), 2.08 (s, 9H), 1.65 (s, 4H), 1.41 (s, 4H); $^{31}$P NMR (162 MHz, MeOH) δ 1.2, 0.7; HRMS $[C_{75}H_{159}N_4O_{91}P_{15} +2H]^{2+}$ requires 1519.20734, found 1519.20211.

## Generation and Serum analysis of microarrays

The amino-spacer equipped GTA-fragments were dissolved in spotting buffer (Nexterion Spot, Schott Nexterion) with 10% DMSO in 384-wells V-bottom plates (Genetix, New Milton, UK). The GTA-fragments were printed in three final concentrations (30µM, 10µM and 3µM) in triplicate on epoxysilane-coated glass slides (Slide E, Schott, Nexterion) by contact printing using the Omnigrid 100 microarrayer (Genomic Solutions, Ann Arbor, MI) equipped with SMP3 pins with uptake channels that deposit 0.7 nl at each contact. The slides were rested in a high humidity chamber for 18 hours and were stored in the dark until used. The slides were washed with PBS (3x) and subsequently all unreacted sites on the arrays were blocked by shaking the slides for 1 hour with ethanolamine (0.25 ml, 0.05M in PBS containing 20 mg/ml of BSA). The slides were flushed with PBS containing 5% of Tween® 20 and PBS containing 1% of Tween® 20 subsequently. After removal of the PBS containing 1% of Tween® 20, the arrays were shaken with the primary antibody dilutions (0.25 ml, diluted with PBS containing 1% of Tween® 20 and 10 mg/ml of BSA) for 60 minutes. The commercially available (IBT Bioservices) mouse anti-*S. epidermidis* monoclonal antibody was diluted 1:6000, normal rabbit serum (used as negative control), serum obtained from rabbits immunized with LTA isolated from *E. faecalis* strain 12030 and rabbit serum raised against the previously reported BSA-WH7 were used at a 1:500 dilution. The slides were flushed with PBS containing 5% of Tween® 20 and PBS containing 1% of Tween® 20 subsequently. After removal of the PBS containing 1% of Tween® 20, the arrays that were incubated with the monoclonal antibodies were shaken with goat anti-mouse IgM heavy chain secondary antibody, Alexa Fluor® 488 conjugate (Invitrogen, A21426) and goat anti-mouse IgG (H+L) secondary antibody, Alexa Fluor® 555 conjugate (Invitrogen, A21422), (0.25 ml, 0.5 µg/ml final dilution in PBS containing 1% of Tween® 20 and 10 mg/ml of BSA) all other slides were shaken with anti-rabbit IgM- and IgG secondary antibodies, labeled with DyLight 650 and DyLight 550 reporter groups, respectively (0.25 ml, 0.5 µg/ml final dilution in PBS containing 1% of Tween® 20 and 10 mg/ml of BSA) for 30 minutes in the dark. The slides were flushed with PBS containing 5% of Tween® 20, PBS and MilliQ subsequently. The slides were dried by centrifugation and were analyzed on fluorescence on 532 nm and 635 nm using a G2565BA scanner. Data and image analyses were performed with GenePix Pro 7.0 software (Molecular Devices, Sunnyvale, CA, USA) as described previously (J. Proteome Res., 8 (2009), pp. 4301–4310). Fluorescence intensities were quantified and corrected for background/non-specific antibody adhesion by subtracting the fluorescence at blank spots, where only spotting buffer was printed without GTA fragment. The average of the triplicate spots was normalized to the highest intensity on the array and visualized in bar graphs using Microsoft Excel.

## Additional array results

Using the aforementioned protocol, various sera were interrogated at various concentrations. A selection of the obtained data is shown below.

## Background and non-specific binding

To optimally correct for non-specific binding, two protocols were assessed. Anticipating on relatively weak antibody-antigen binding (as common for carbohydrate epitopes), the standard protocol, which replaces part of the Tween® 20 in the antibody-incubation buffer for BSA was evaluated and compared to a non-BSA protocol with increased Tween® 20 composition instead (6% of Tween® 20 in PBS).As can be seen from figure S1, both protocols give relatively low background labeling, but as anticipated, the BSA protocol outperforms the non-BSA protocol in absolute signal and allows for the detection of the presumably slightly weaker antibody interactions (like the binding of GTA fragments **2** and **8**). Most notably, no TA-IgM interactions could be visualized using the protocol without BSA. As a control for TA-recognition by pre-existing antibodies, serum obtained from non-immunized rabbits was used as negative control in both assessed protocols (with and without BSA in the antibody-incubation buffer). As can be seen in figures S1-C and S1-D, which show the measured fluorescence intensities normalized to the maximum measurable intensity, a similar trend is observed and the (already relatively weak) TA-binding is disturbed most when using an increased Tween® 20 concentration. Therefore, for further experimentation, the BSA protocol was adhered.

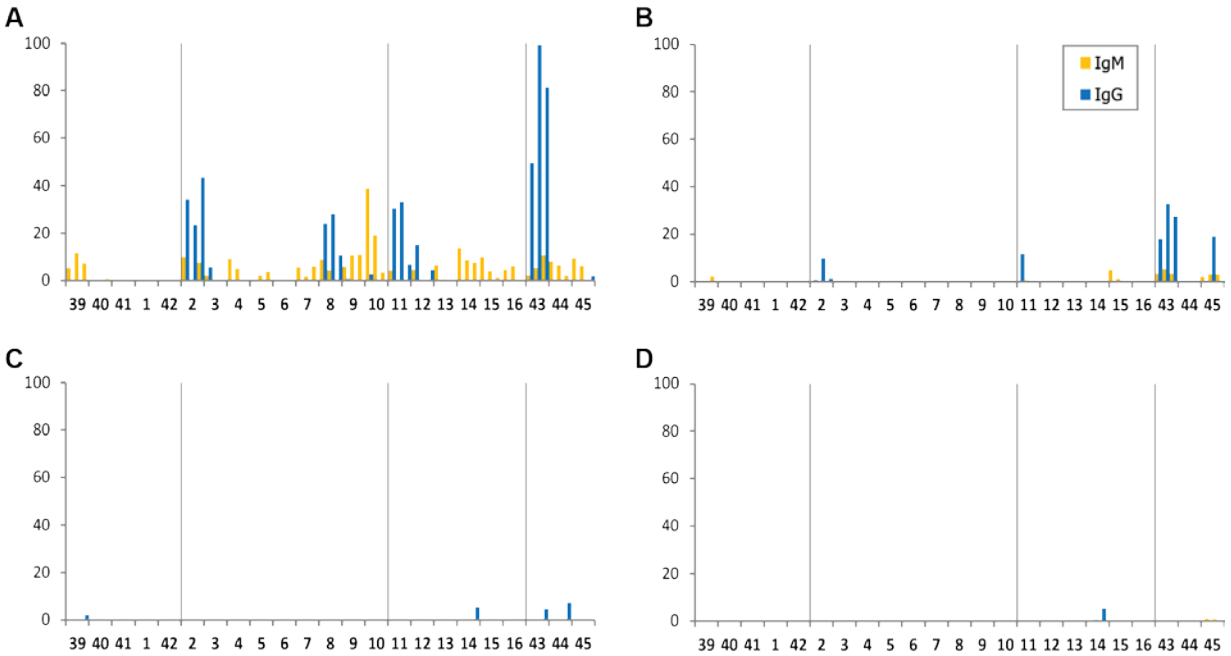



**Figure S1:** Interaction of the immobilized TA fragments by antibodies raised against our BSA-**43** conjugate in a 1:1000 dilution with (A) and without (B) BSA in the buffer and antibodies obtained from the blood of non-immunized rabbits in a 1:500 dilution with (C) and without (D) BSA in the buffer. Data are represented at three concentrations (30µM, 10µM and 3µM respectively, each spotted in triplicate) and are normalized to the highest intensity measured in the series with BSA in the buffer in the case of A and B or the highest measurable intensity in the case of C and D.

## Concentration screen

Antibody content in the used sera and the resulting signal when used on the arrays was assessed by executing a concentration screen on the used sera and monoclonal antibody. As anticipated, the monoclonal antibody required a much higher dilution factor than the rabbit sera. As can be seen in figure S2-A, a dilution of 1:6000 showed oversaturation of the fluorescence scanner with resulting lack of differentiation between the various TA fragments. Diluting up to 1:10000 (Figure S2-B) seemed to increase the “resolution” of the arrays and 1:20000 (Figure S2-C) further improved the differentiation. Diluting the sera further (up to 1:25000, Figure S2-D) did not seem to change the resolution significantly. A similar effect could be obtained by lowering the intensity of the excitation laser to 10%. With this method, at a 1:6000 dilution, the graph in figure 1C could be obtained.

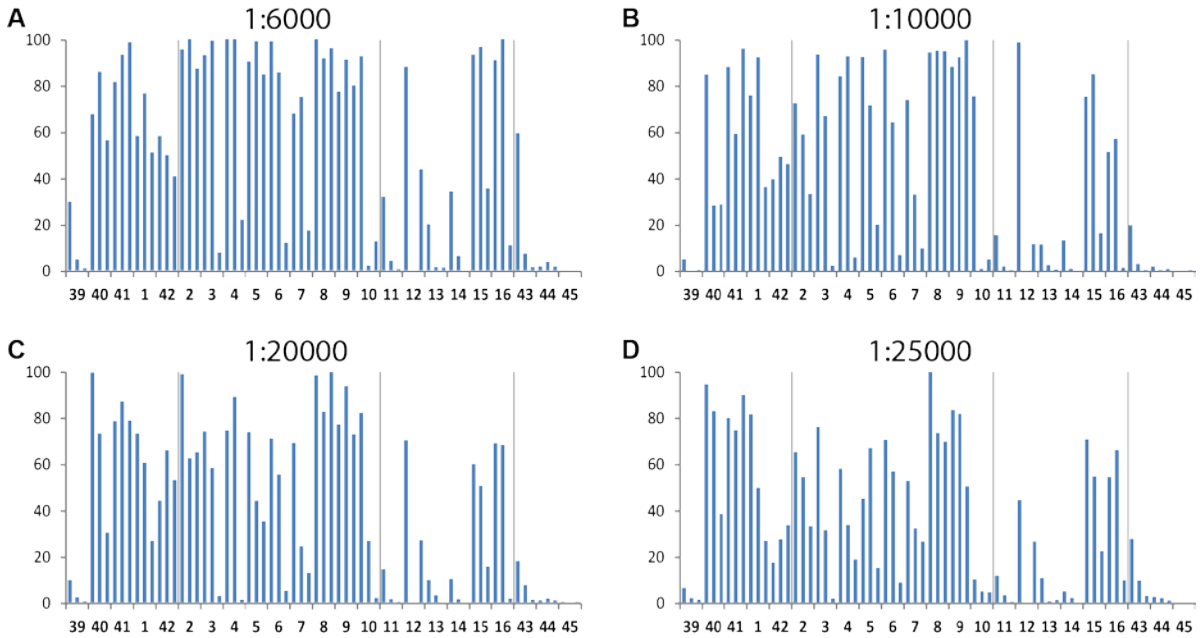
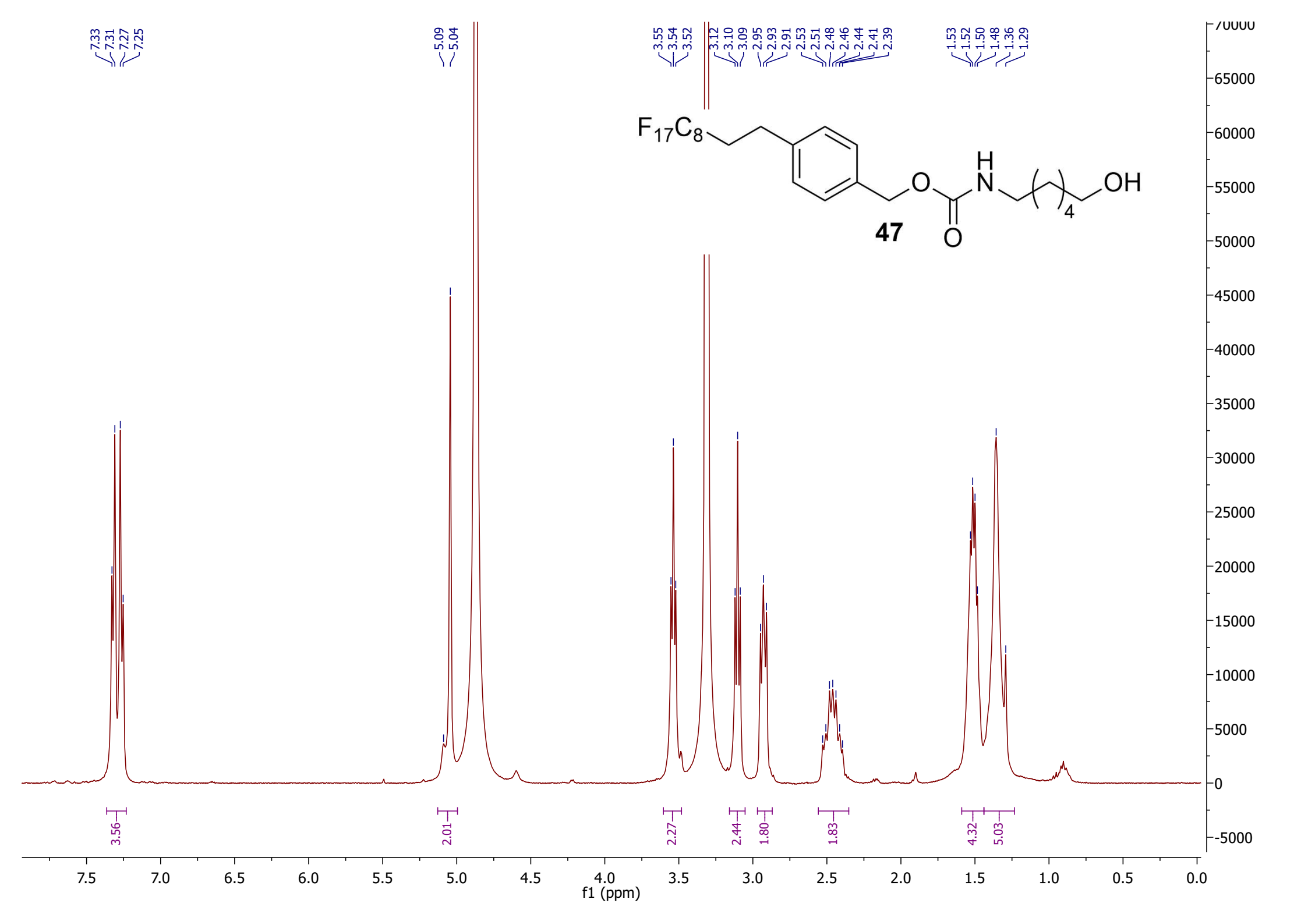



**Figure S2:** Interaction of the immobilized TA fragments with monoclonal antibodies against *S. epidermidis* LTA at varying dilutions (dilution shown above the representative graph). Data are represented at three concentrations (30µM, 10µM and 3µM respectively, each spotted in triplicate) and are normalized to the highest intensity.

## $^{1}$H and $^{31}$P NMR spectra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7.25
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3.55
3.54
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2.93
2.91
2.53
2.51
2.48
2.46
2.44
2.41
2.39
1.53
1.52
1.50
1.48
1.36
1.29
F17C8
O
H
N
OH
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O
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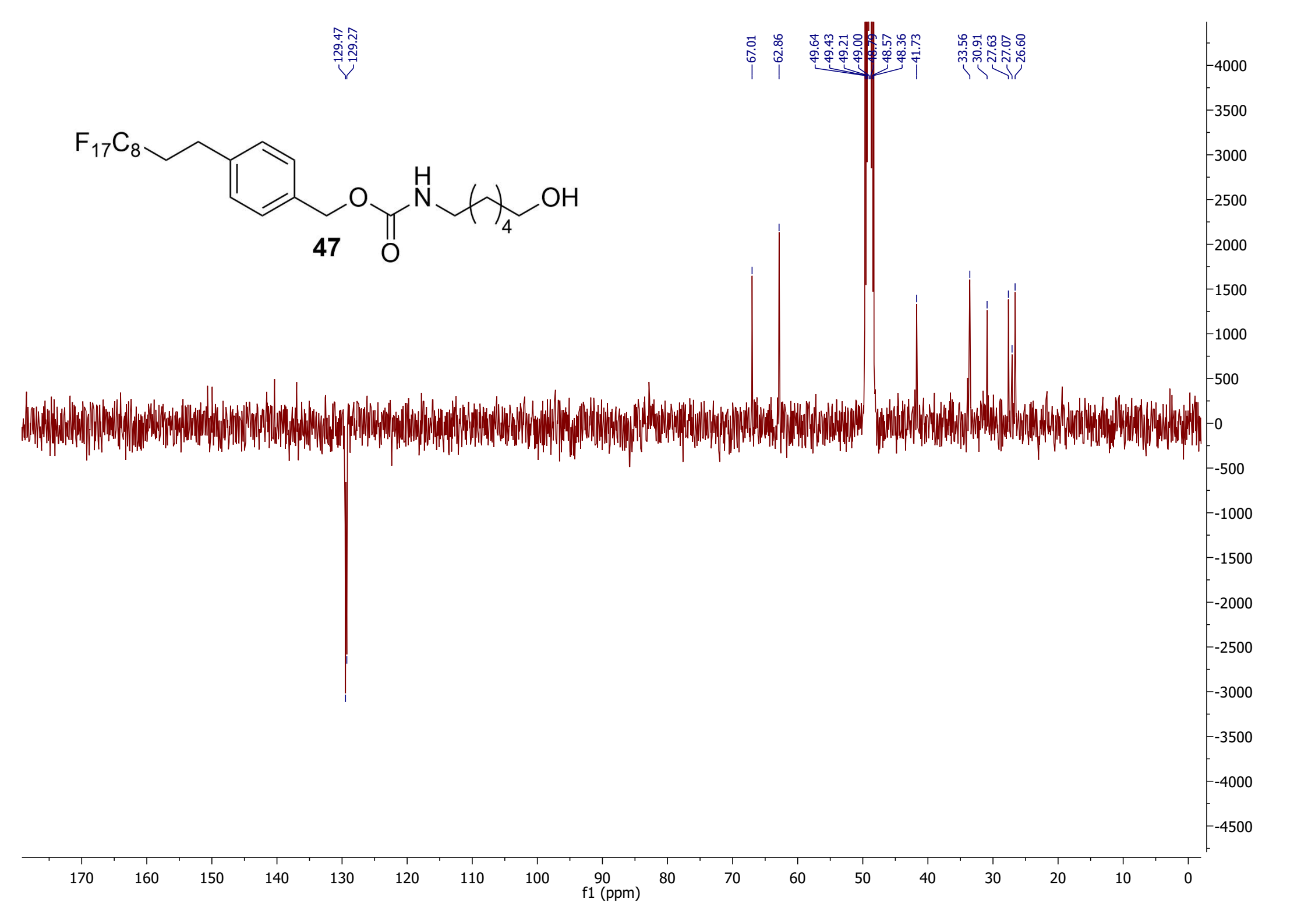
2.01
2.27
2.44
1.80
1.83
4.32
5.03
f1 (ppm)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33.56
30.91
27.63
27.07
26.60
F17C8
O
H
N
OH
4
O
47
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
-3000
-3500
-4000
-4500
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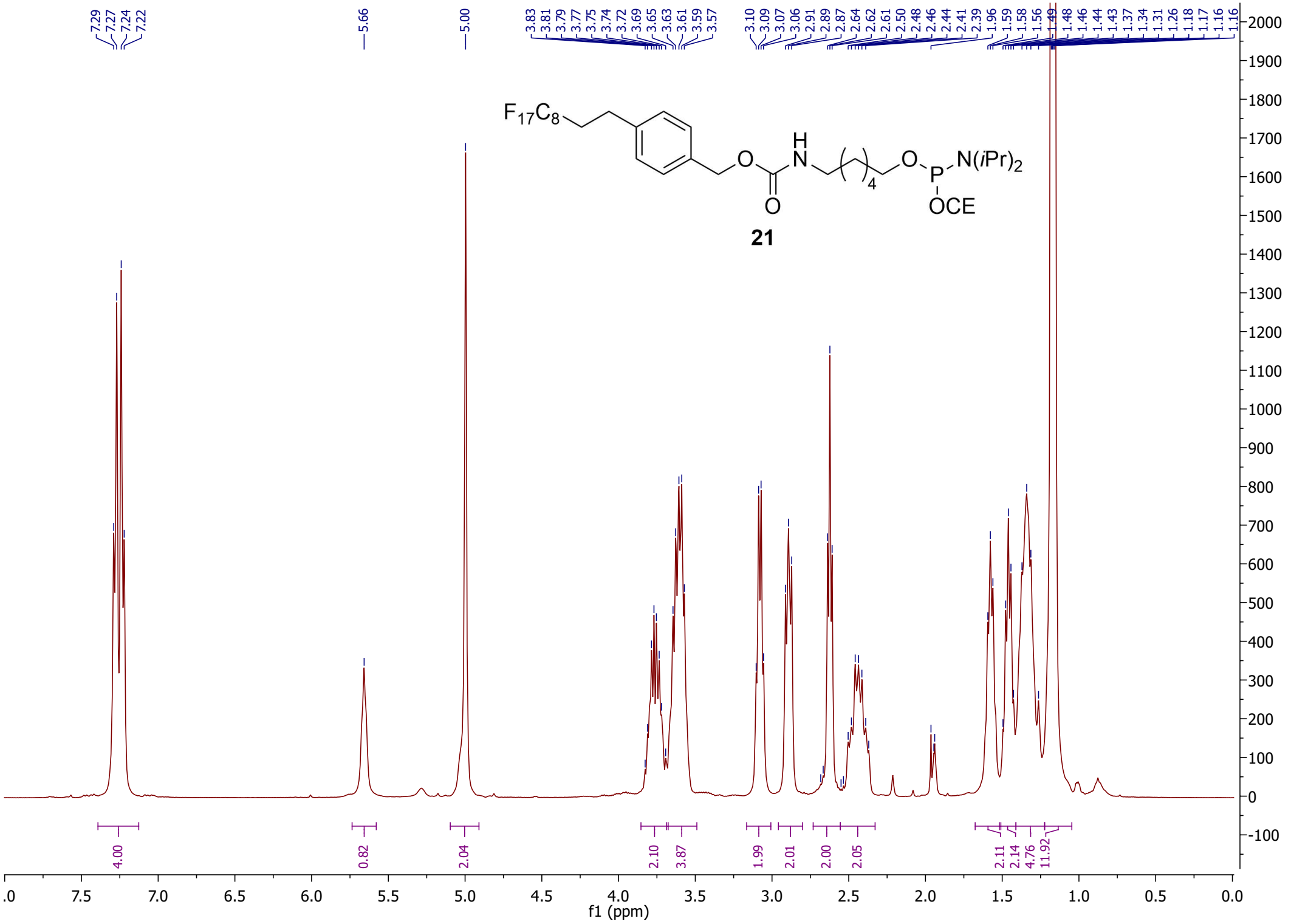
10
0
f1 (ppm)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3.63
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3.59
3.57
3.10
3.09
3.07
3.06
2.91
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2.87
2.64
2.62
2.61
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2.44
2.41
2.39
1.96
1.59
1.58
1.56
1.49
1.48
1.46
1.44
1.43
1.37
1.34
1.31
1.26
1.18
1.17
1.16
1.16
F17C8
O
H
N
O
4
O
P
N(iPr)2
OCE
O
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4.00
0.82
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2.10
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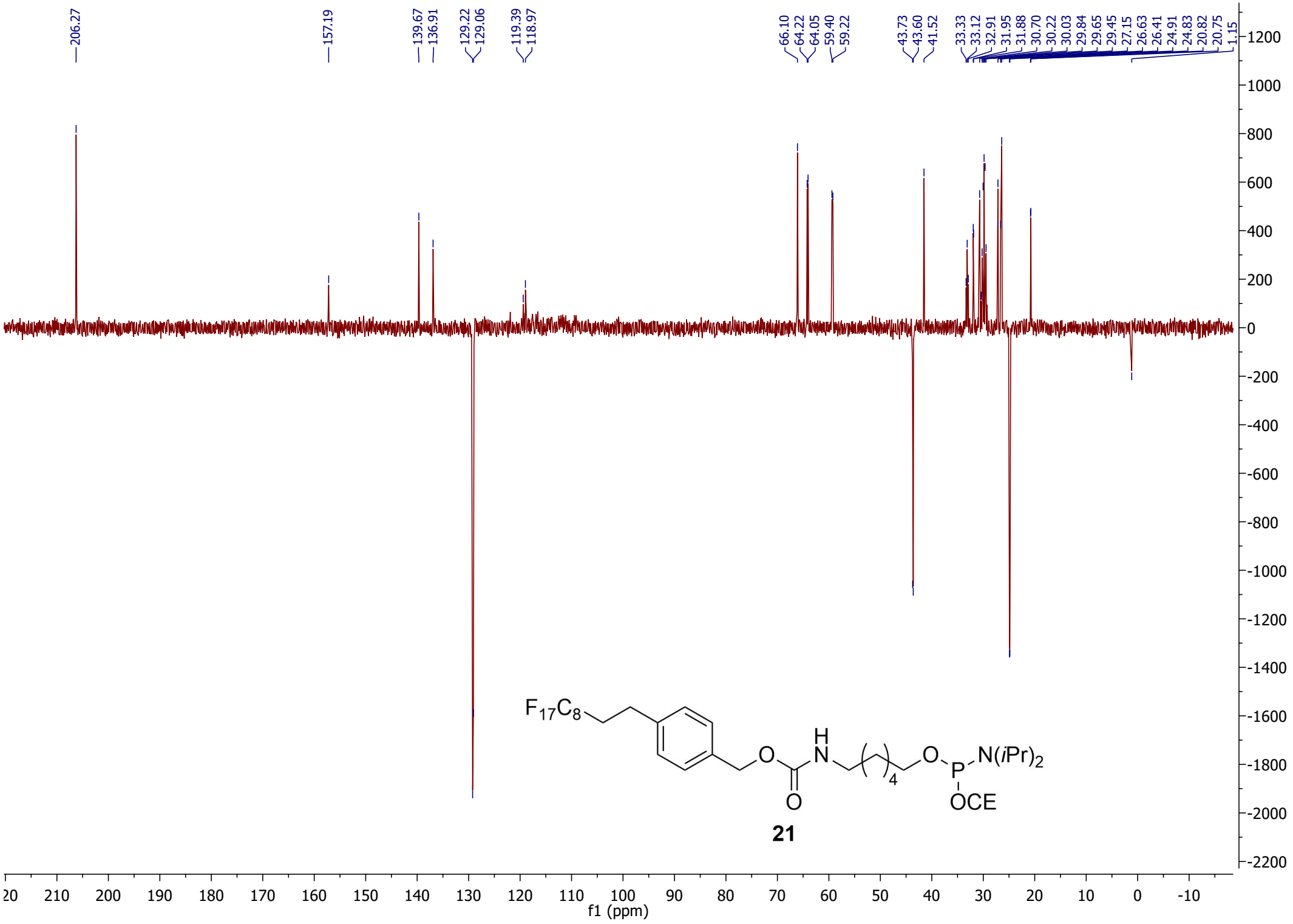
1.99
2.01
2.00
2.05
2.11
2.14
4.76
11.92
f1 (ppm)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129.06
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64.05
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43.73
43.60
41.52
33.33
33.12
32.91
31.95
31.88
30.70
30.22
30.03
29.84
29.65
29.45
27.15
26.63
26.41
24.91
24.83
20.82
20.75
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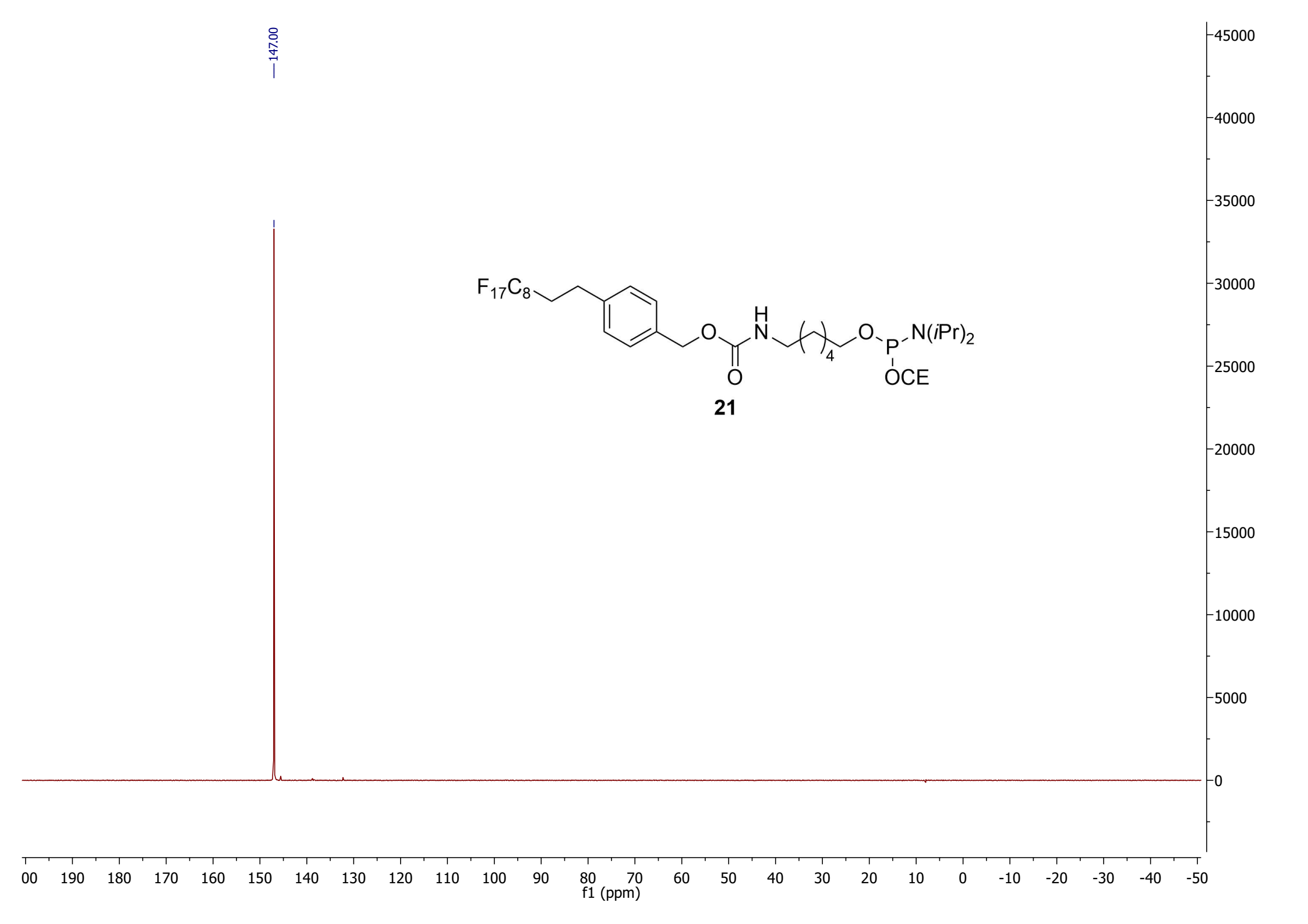
H
N
O
4
O
P
N(iPr)2
OCE
O

**21**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4
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OCE
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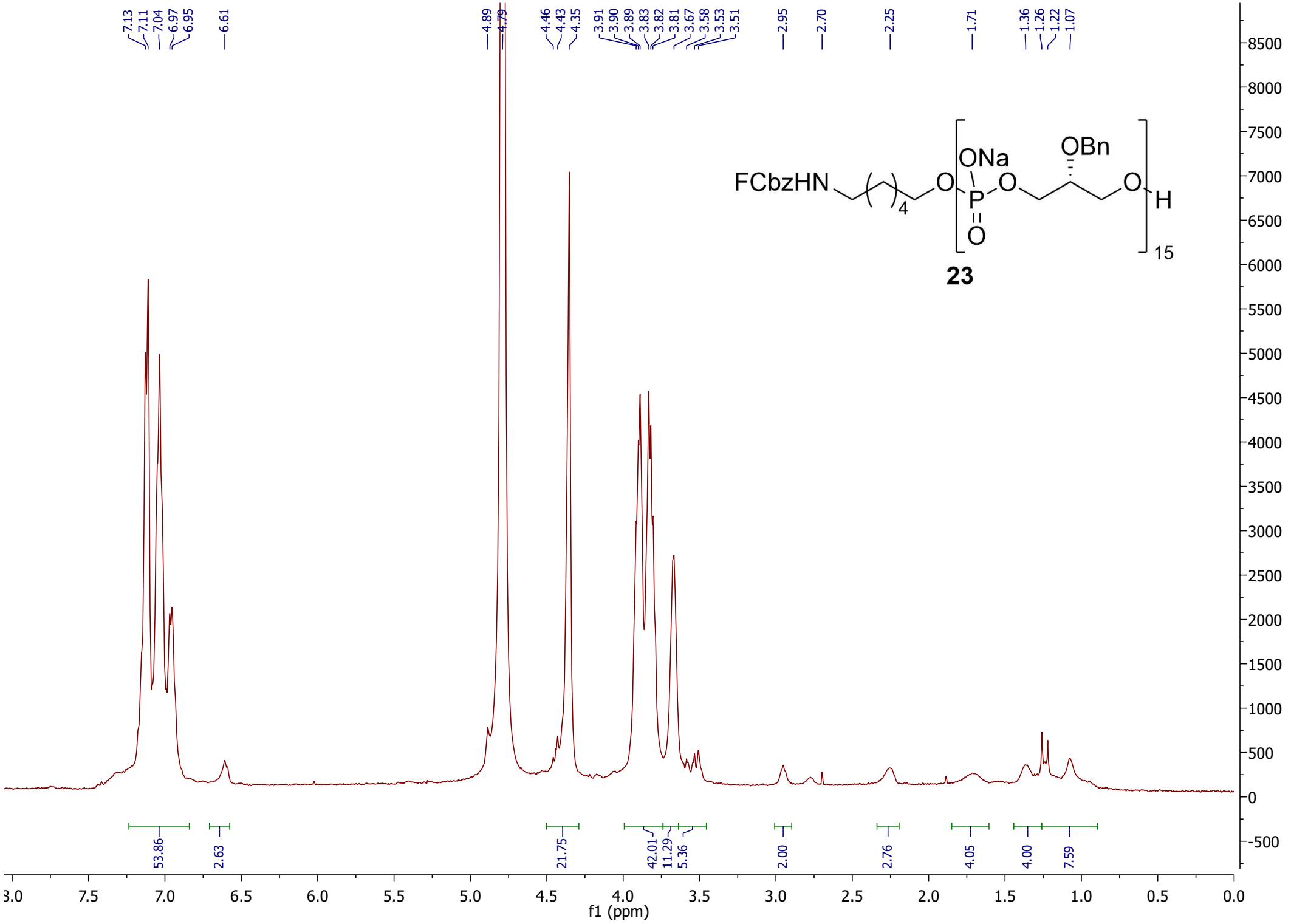
f1 (ppm)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3.89
3.83
3.82
3.81
3.67
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3.53
3.51
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2.70
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1.71
1.36
1.26
1.22
1.07
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ONa
OBn
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P
H
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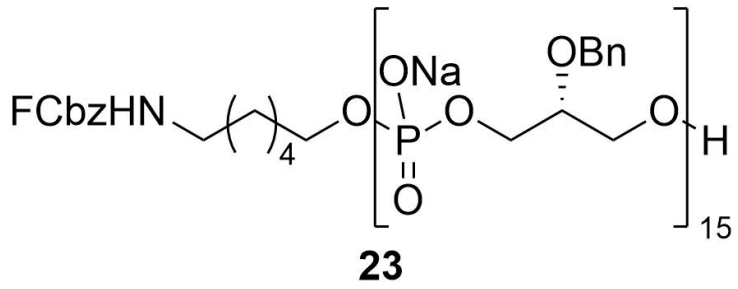
f1 (ppm)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ONa
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OBn
O
H
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**23**


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1000
500
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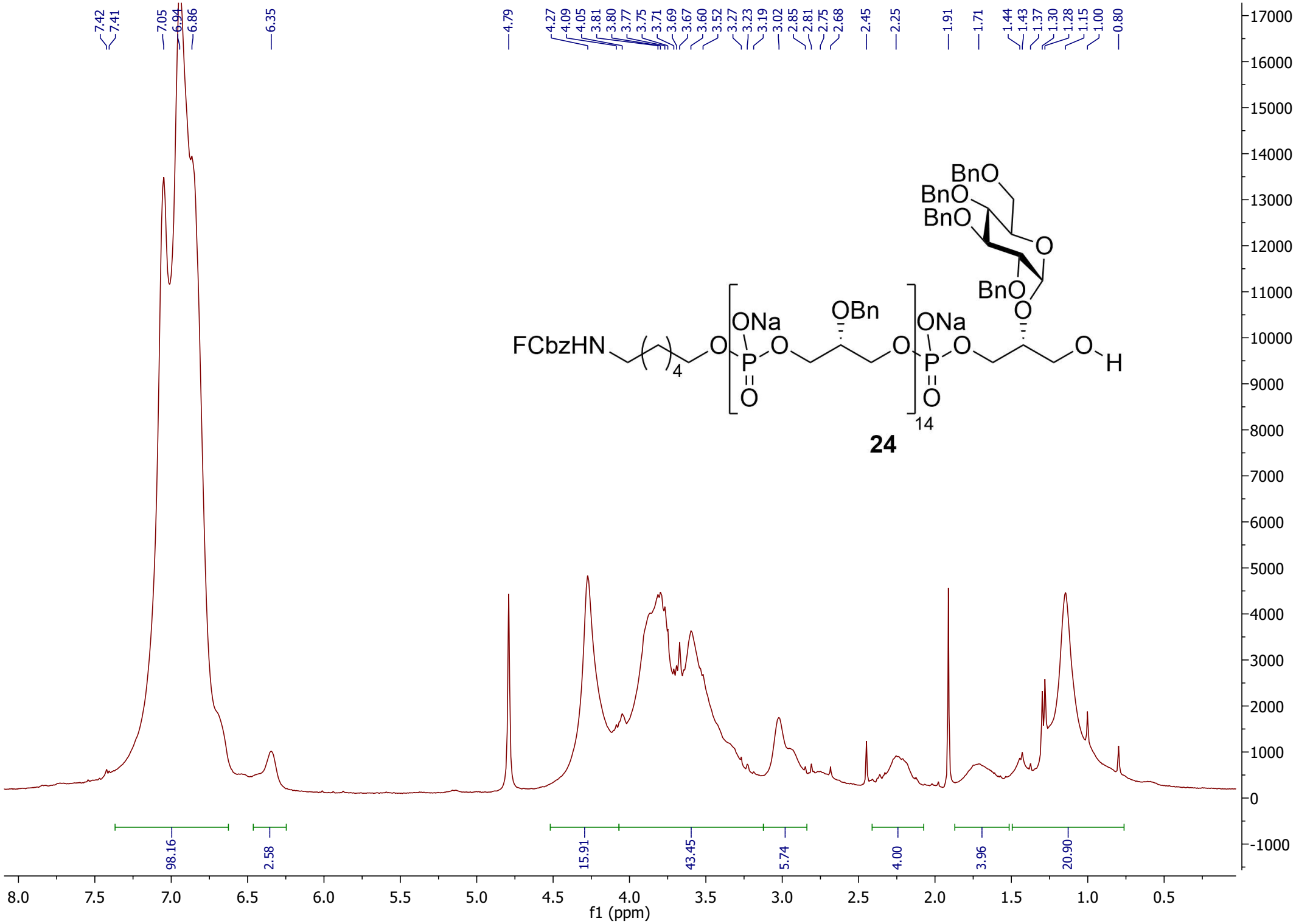
f1 (ppm)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3.71
3.69
3.67
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3.27
3.23
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BnO
BnO
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FCbzHN
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OBn
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ONa
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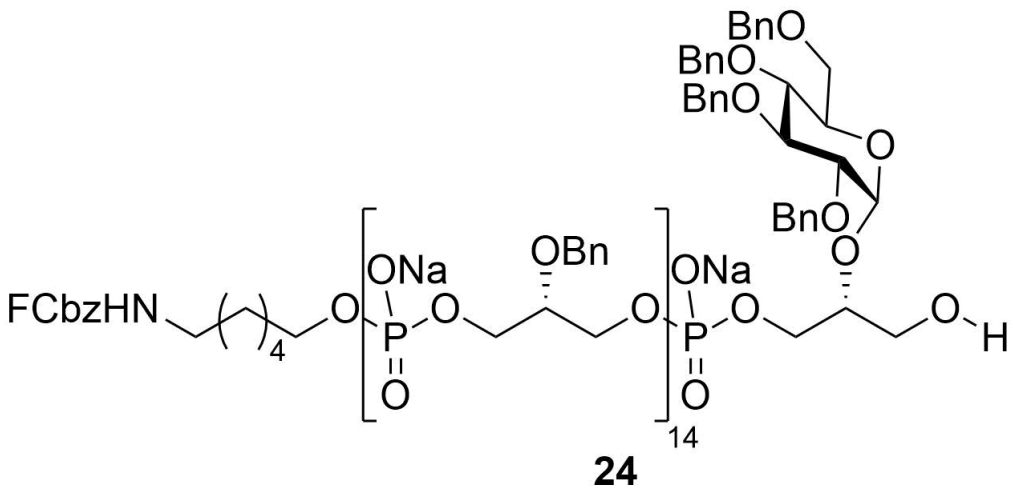
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P
O
14
O
O
H

**24**

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150
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130
120
110
100
90
80
70
60
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0
-10
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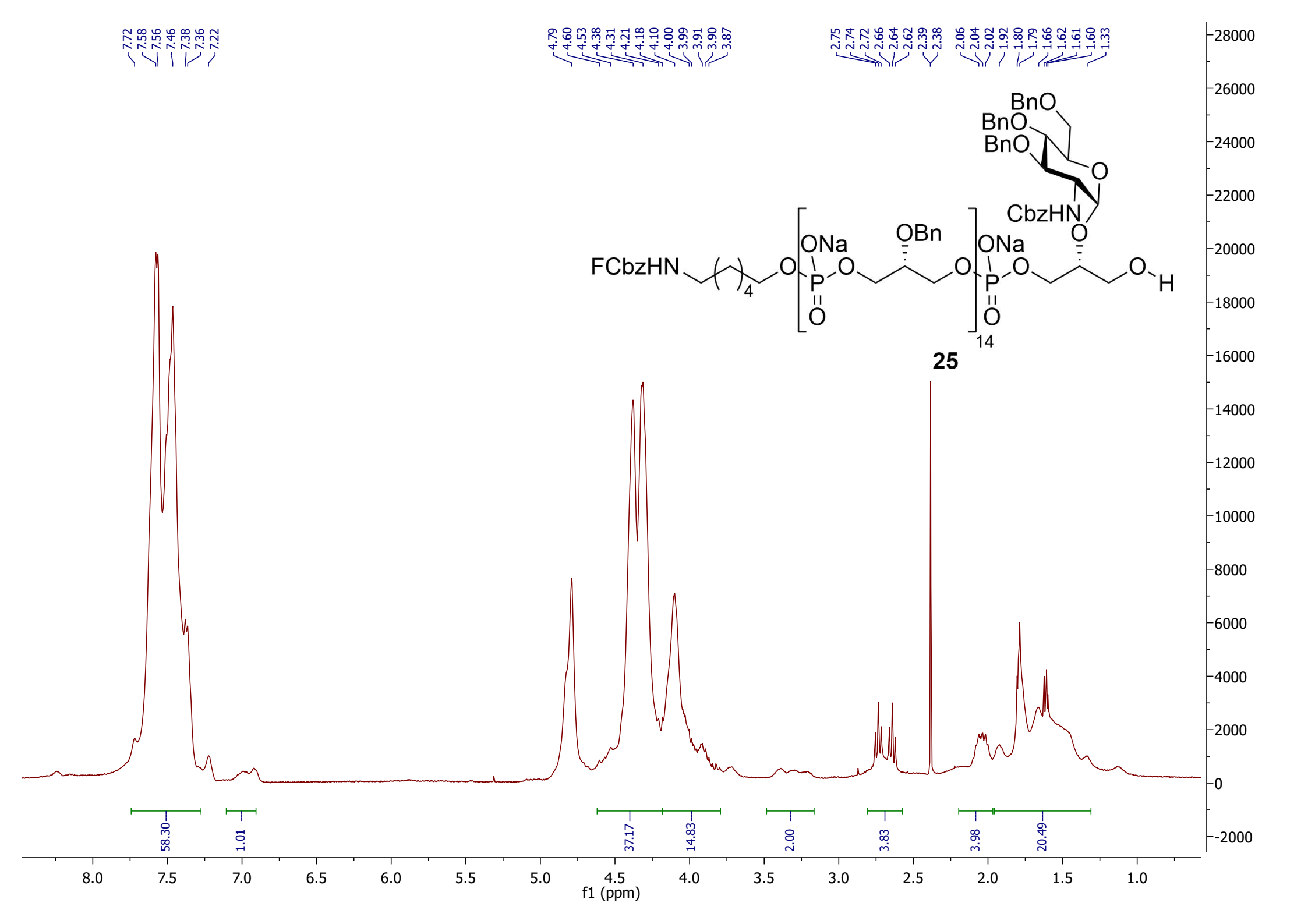
f1 (ppm)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2.02
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1.79
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1.62
1.61
1.60
1.33
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BnO
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FCbzHN
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P
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OBn
O
ONa
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P
O
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O
O
H
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14.83
2.00
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20.49
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7.5
7.0
6.5
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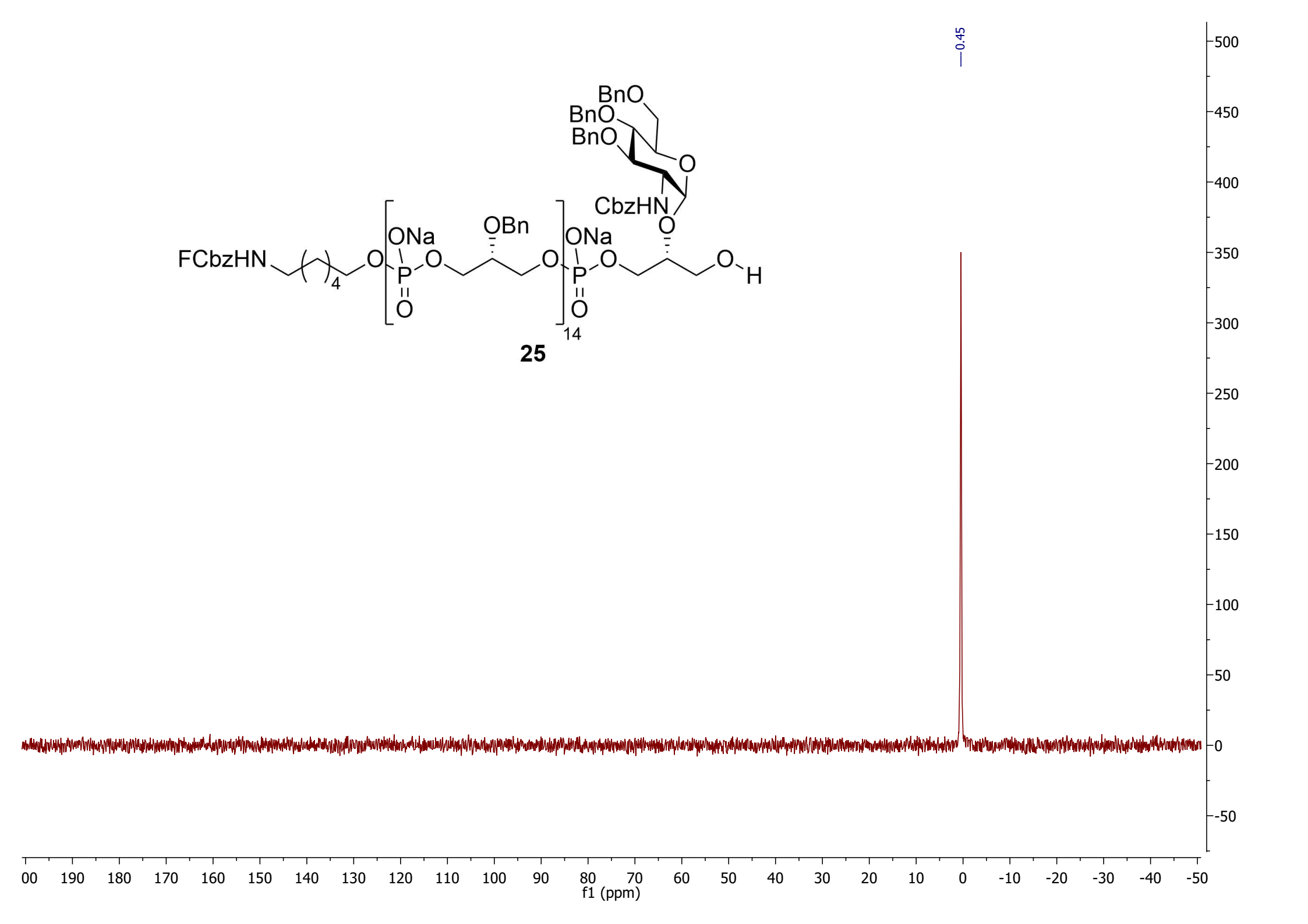
-2000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P
O
O
O
H
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500
450
400
350
300
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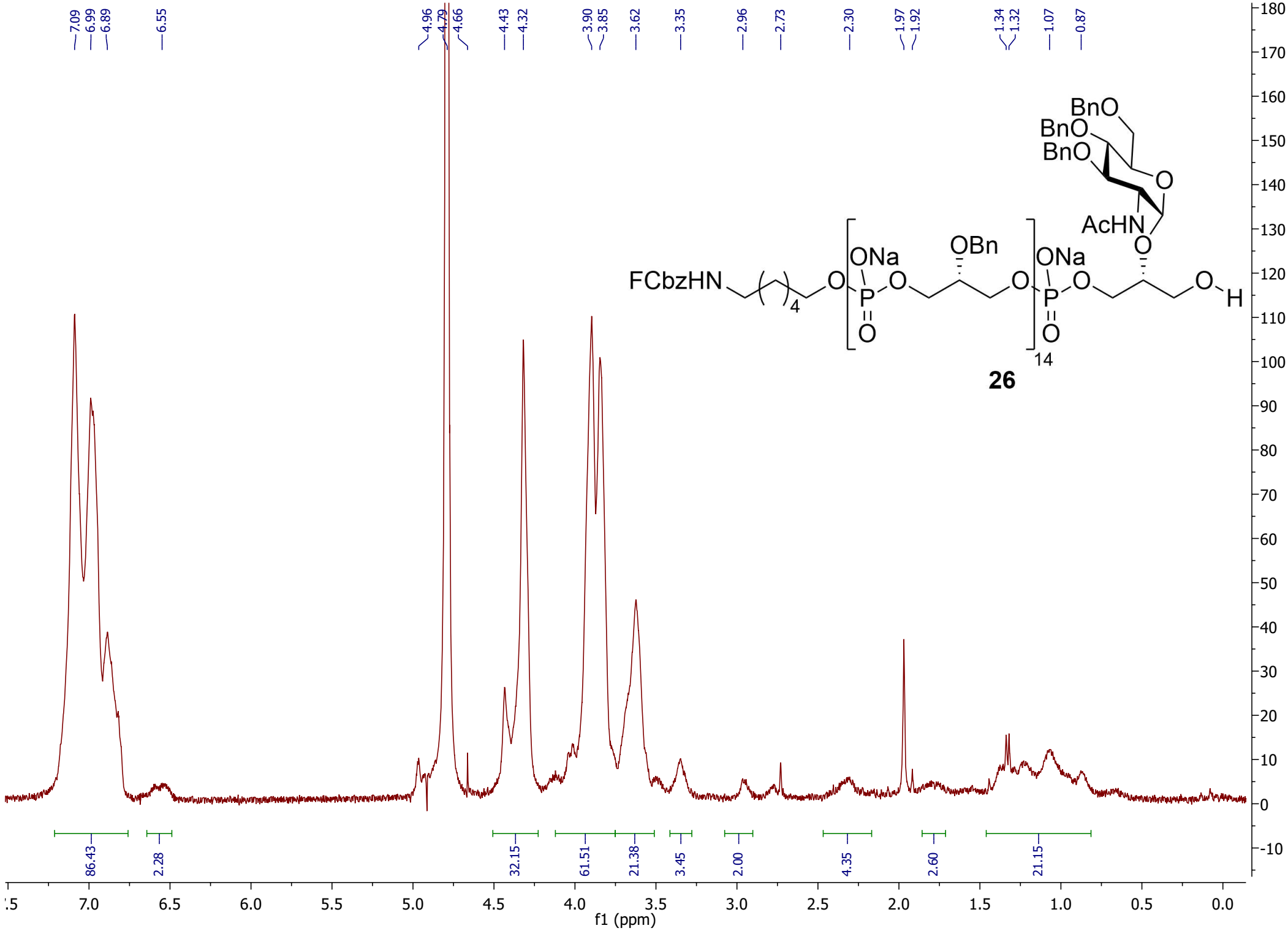
f1 (ppm)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2.96
2.73
2.30
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1.92
1.34
1.32
1.07
0.87
BnO
BnO
BnO
O
AcHN
O
FCbzHN
4
O
ONa
P
O
O
OBn
O
ONa
P
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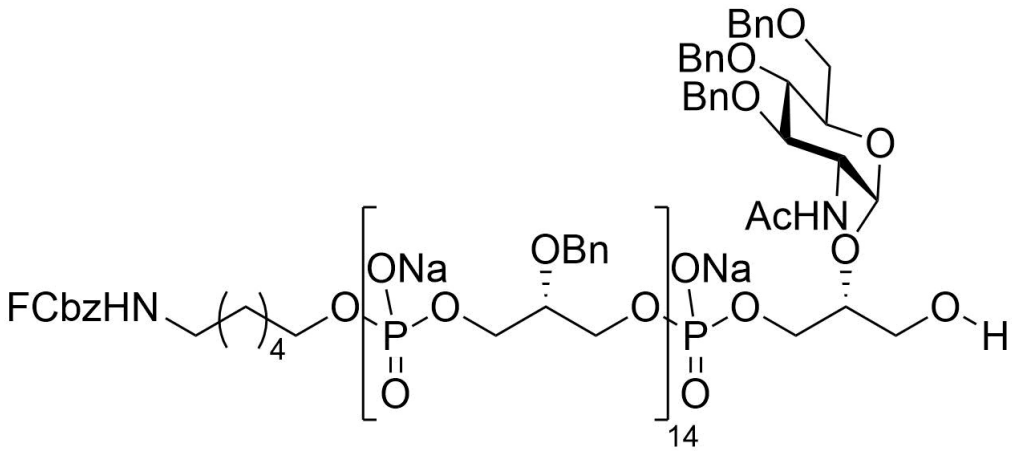
f1 (ppm)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BnO
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AcHN
O
OBn
ONa
ONa
FCbzHN
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O
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O
O
H
P
P
O
O
14

**26**

0.88
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
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400
200
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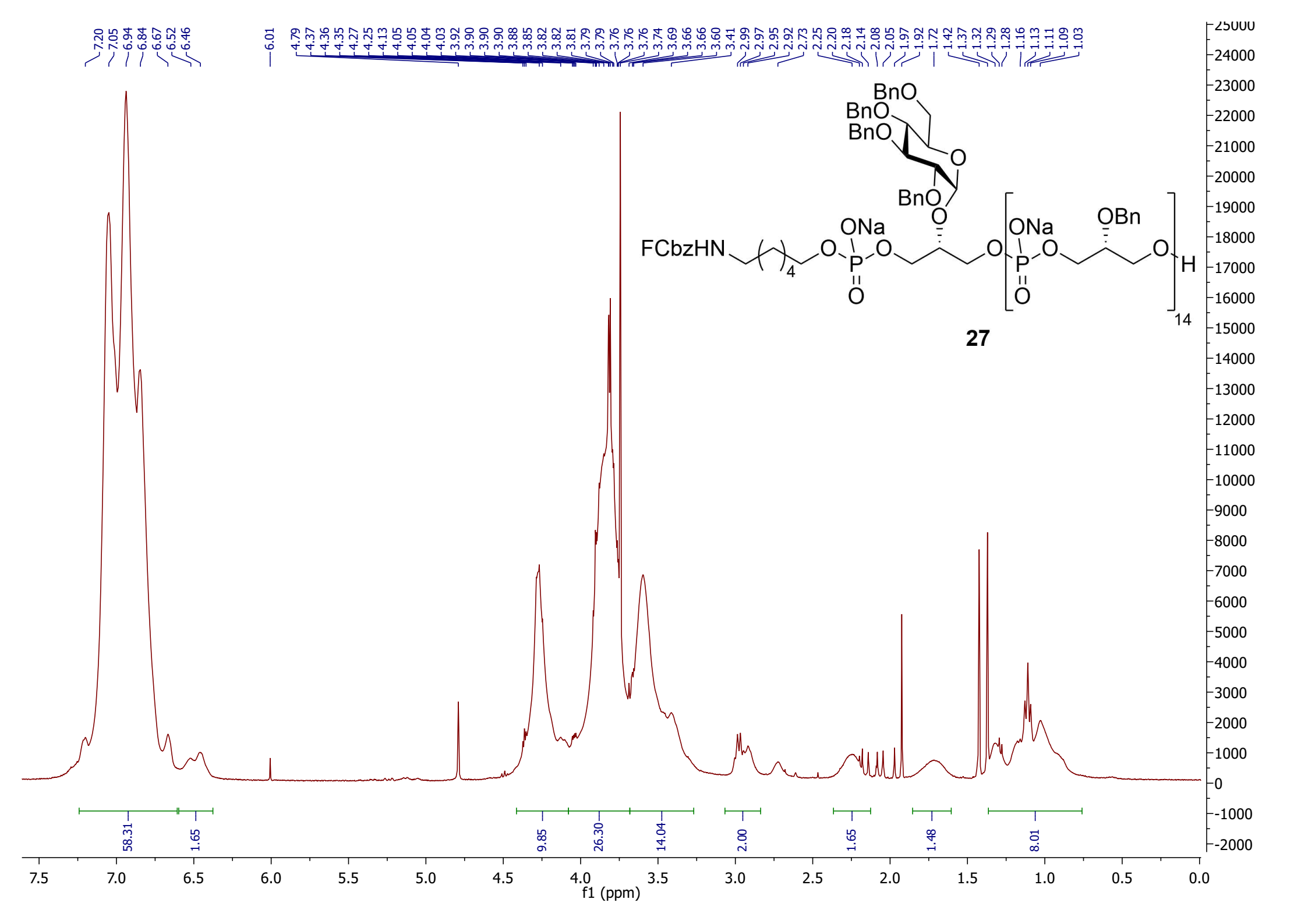
f1 (ppm)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4.27
4.25
4.13
4.05
4.04
4.03
3.92
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3.85
3.82
3.81
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1.37
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1.29
1.28
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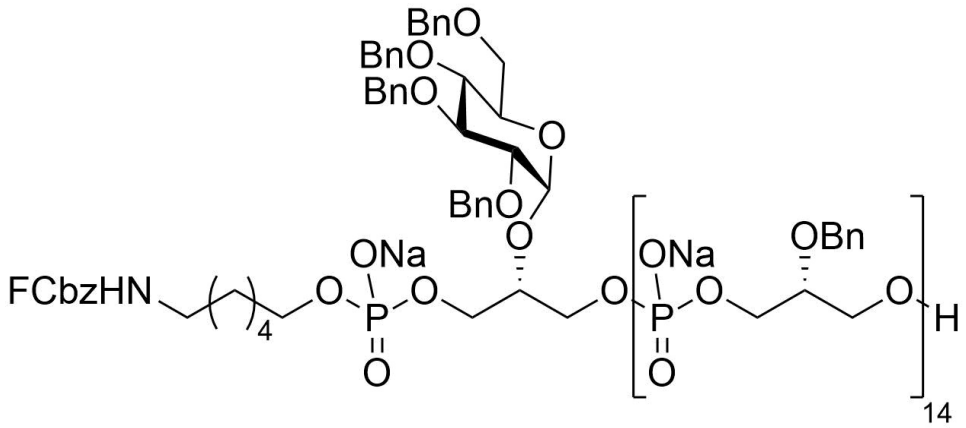
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BnO
BnO
BnO
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ONa
FCbzHN
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O
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O
ONa
O
P
O
O
OBn
O
H
14

**27**

0.51
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200
180
160
140
120
100
80
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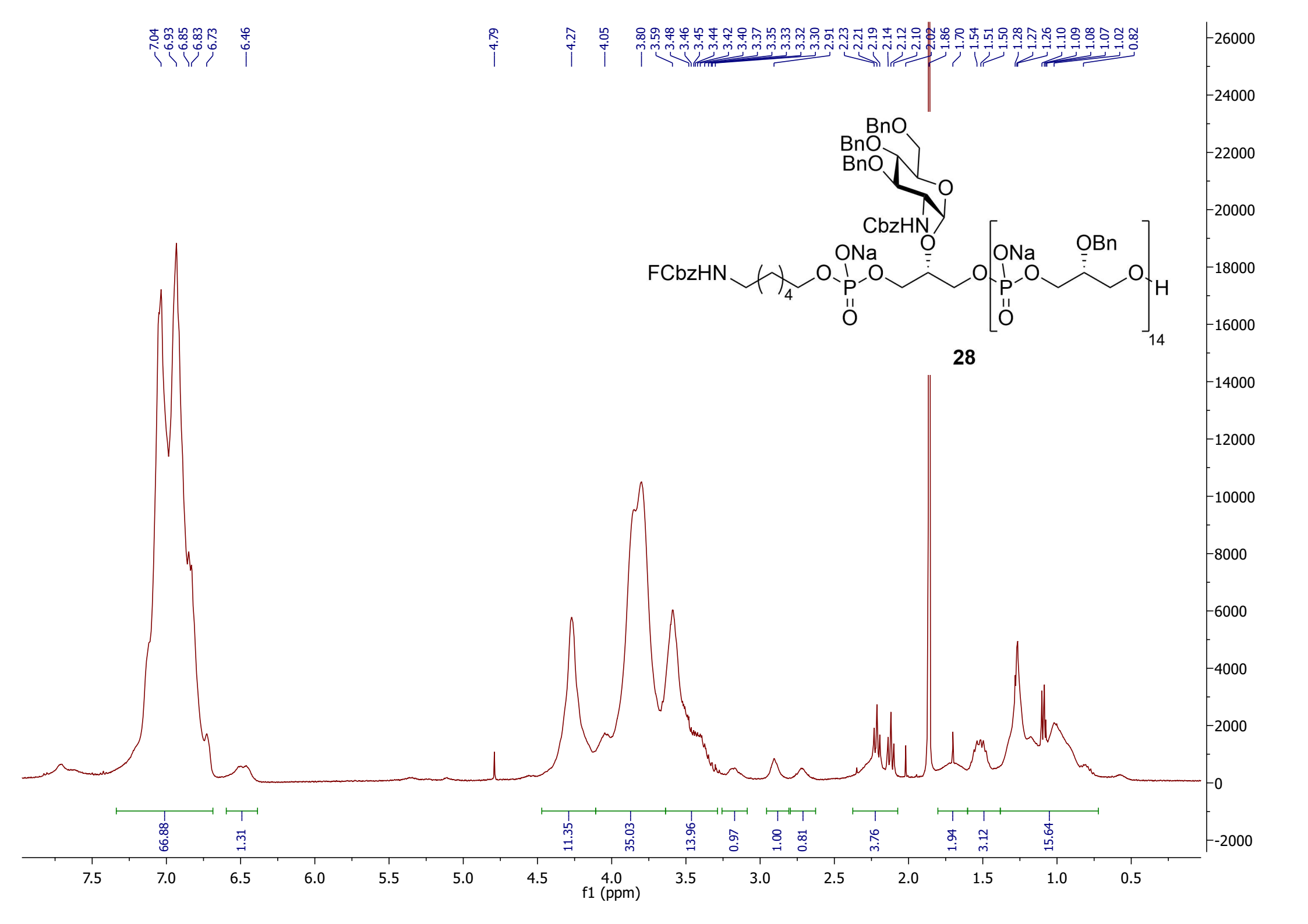
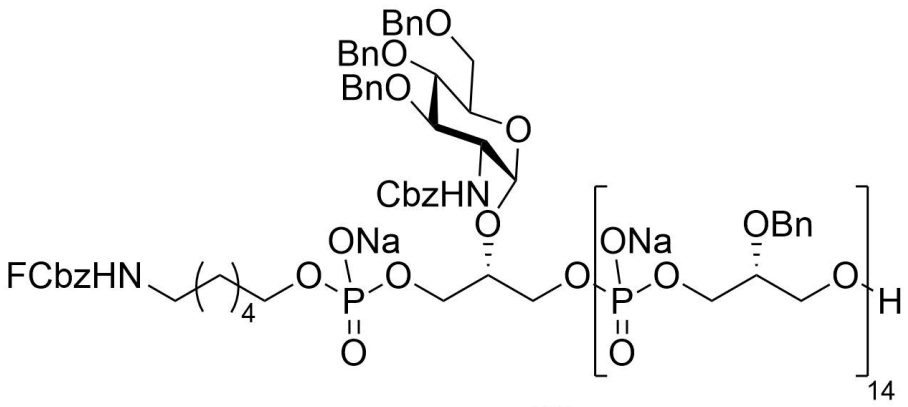
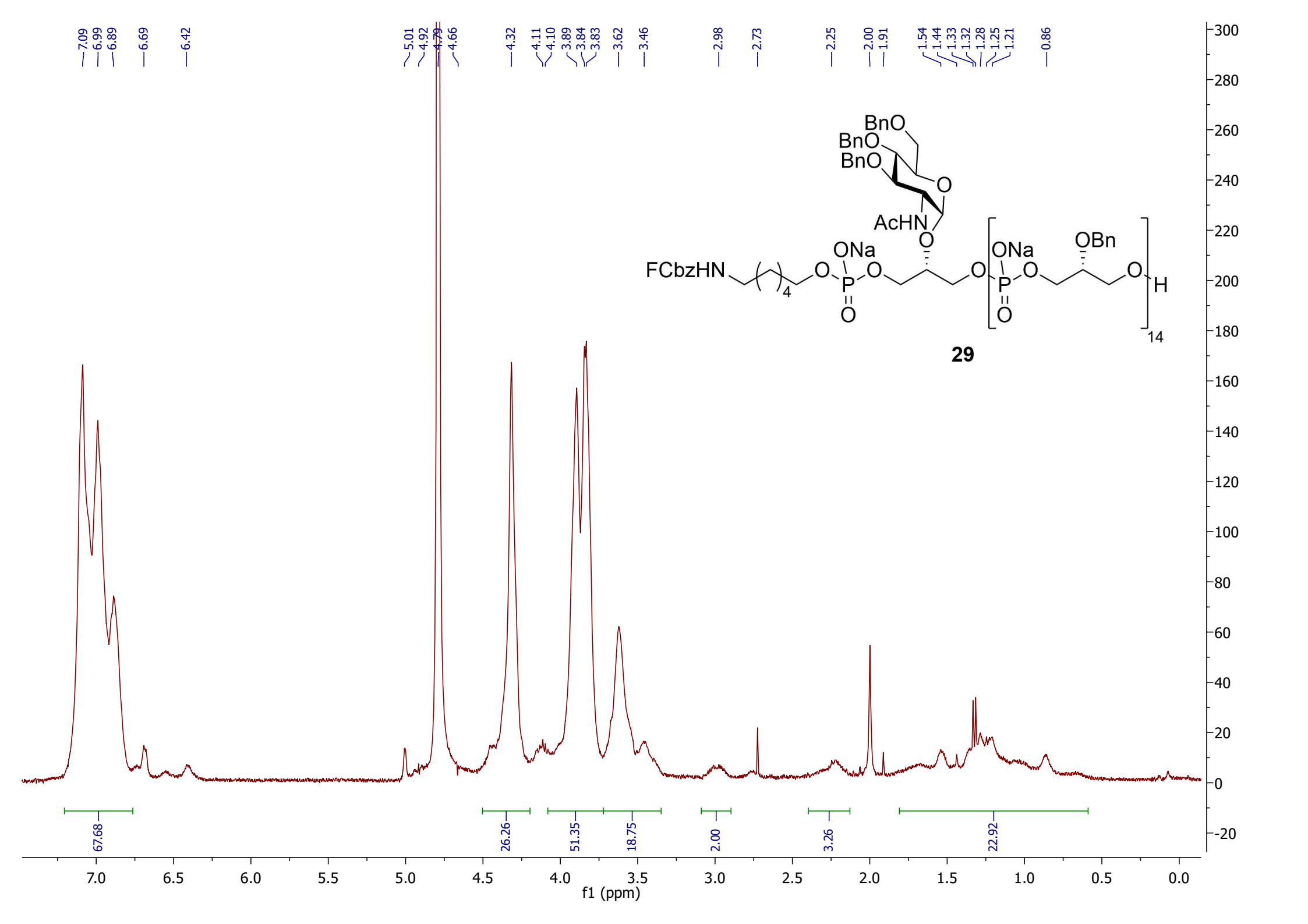
0
-20
-40
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

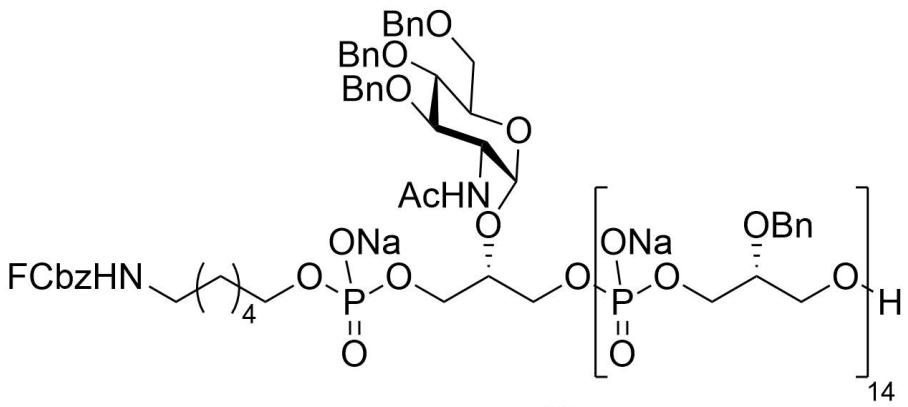

7.04
6.93
6.85
6.83
6.73
6.46
4.79
4.27
4.05
3.80
3.59
3.48
3.46
3.45
3.44
3.42
3.40
3.37
3.35
3.33
3.32
3.30
2.91
2.23
2.21
2.19
2.14
2.12
2.10
2.02
1.86
1.70
1.54
1.51
1.50
1.28
1.27
1.26
1.10
1.09
1.08
1.07
1.02
0.82
BnO
BnO
BnO
O
CbzHN
O
ONa
FCbzHN
4
O
P
O
O
O
ONa
P
O
O
OBn
O
H
14
28
66.88
1.31
11.35
35.03
13.96
0.97
1.00
0.81
3.76
1.94
3.12
15.64
f1 (ppm)


BnO
BnO
BnO
O
CbzHN
O
ONa
ONa
OBn
FCbzHN
4
O
P
O
O
O
P
O
O
O
H
14

**28**

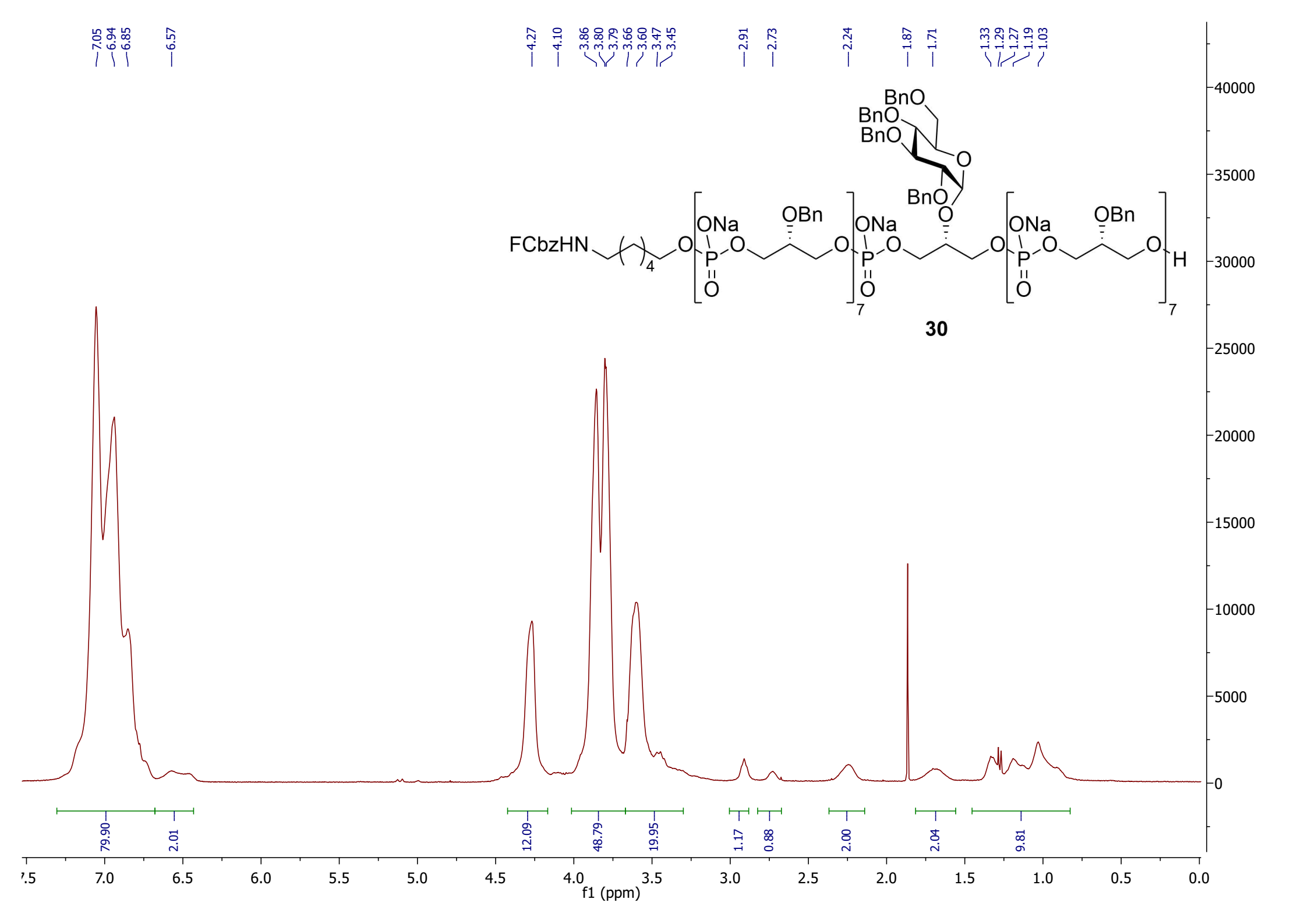
0.48
250
200
150
100
50
0
-50
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

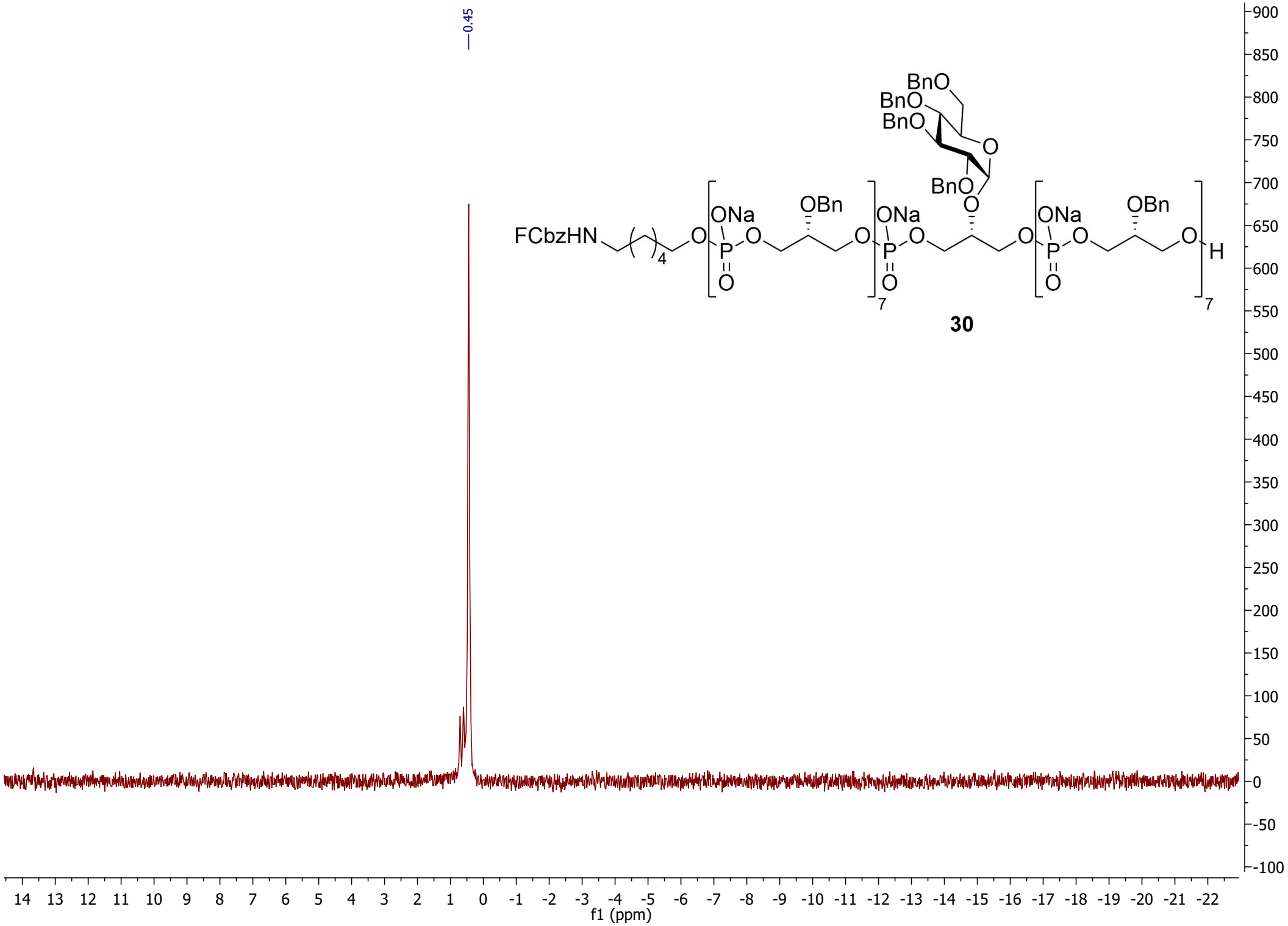

7.09
6.99
6.89
6.69
6.42
5.01
4.92
4.79
4.66
4.32
4.11
4.10
3.89
3.84
3.83
3.62
3.46
2.98
2.73
2.25
2.00
1.91
1.54
1.44
1.33
1.32
1.28
1.25
1.21
0.86
BnO
BnO
BnO
O
AcHN
O
ONa
ONa
OBn
FCbzHN
O
O
O
O
O
O
O
H
4
P
P
O
O
14
29
67.68
26.26
51.35
18.75
2.00
3.26
22.92
f1 (ppm)

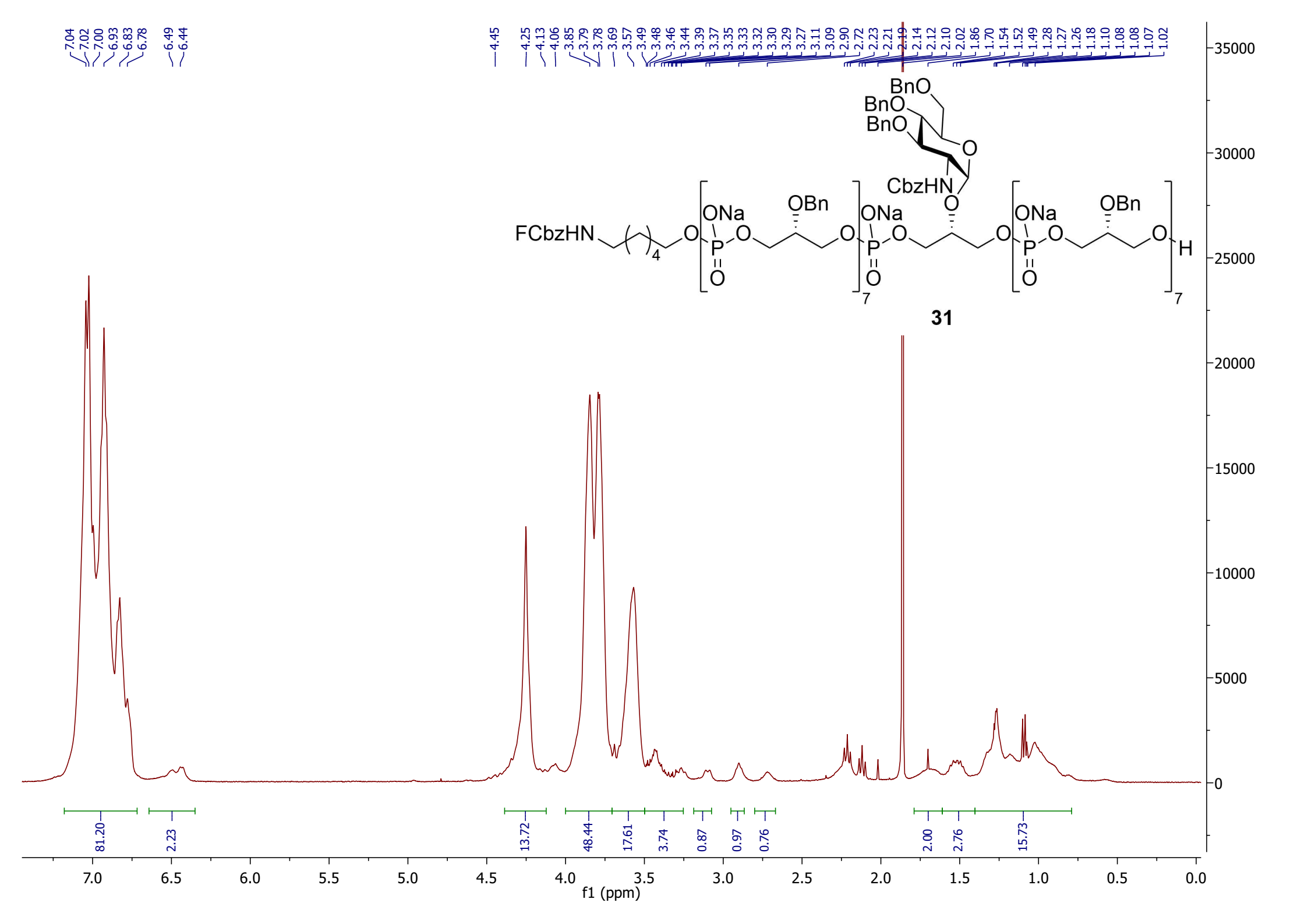

BnO
BnO
BnO
O
AcHN
O
ONa
ONa
OBn
FCbzHN
4
O
P
O
O
O
P
O
O
O
H
O
14

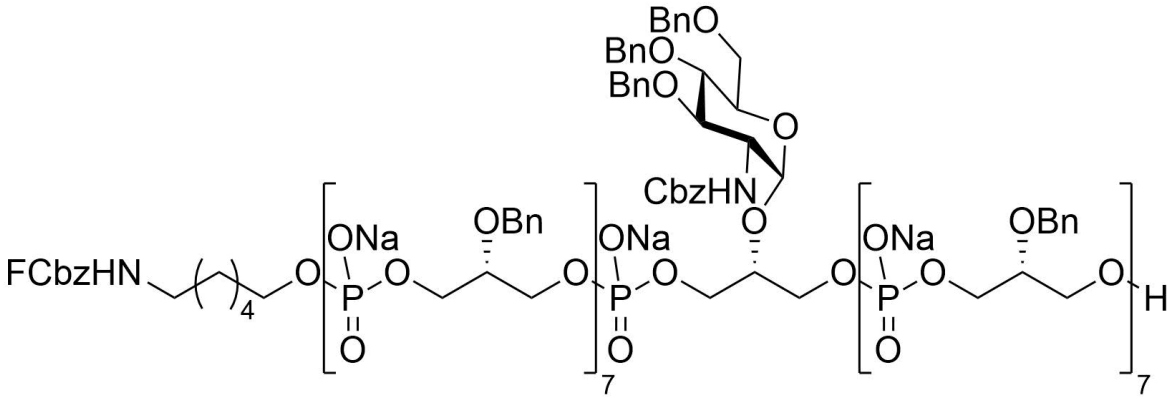
**29**


0.88
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)


7.05
6.94
6.85
6.57
4.27
4.10
3.86
3.80
3.79
3.66
3.60
3.47
3.45
2.91
2.73
2.24
1.87
1.71
1.33
1.29
1.27
1.19
1.03
BnO
BnO
BnO
BnO
O
FCbzHN
ONa
OBn
H
7
30
79.90
2.01
12.09
48.79
19.95
1.17
0.88
2.00
2.04
9.81
40000
35000
30000
25000
20000
15000
10000
5000
0
f1 (ppm)

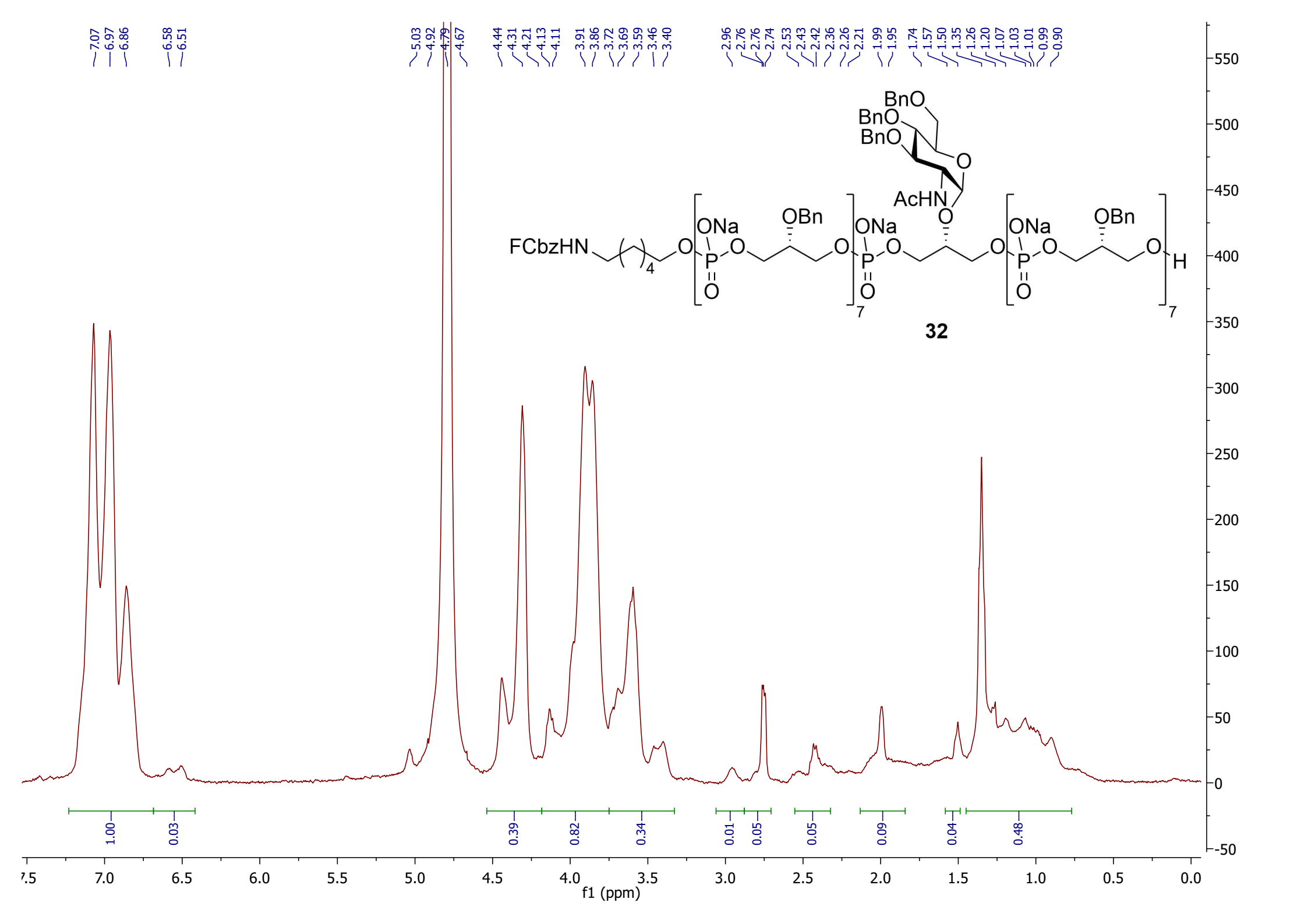

0.45
BnO
BnO
BnO
BnO
O
FCbzHN
4
O
ONa
OBn
P
O
7
H
30
f1 (ppm)

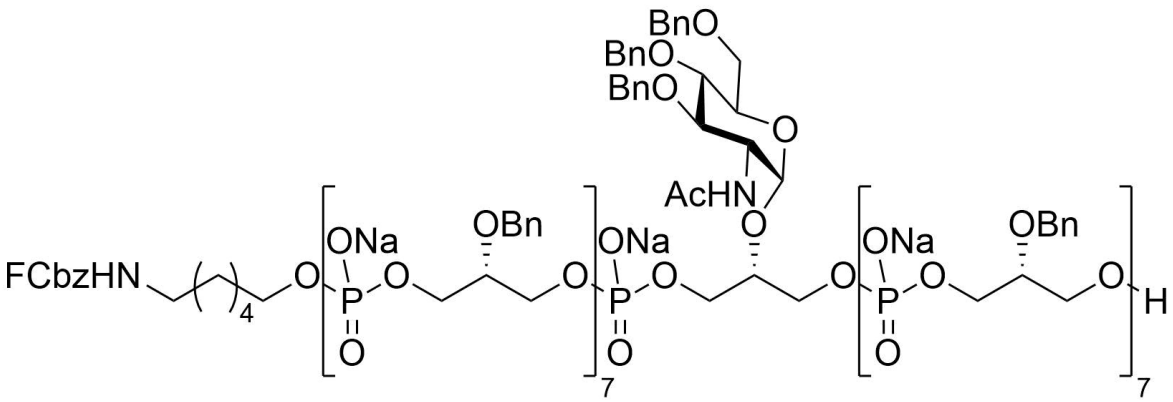

7.04
7.02
7.00
6.93
6.83
6.78
6.49
6.44
4.45
4.25
4.13
4.06
3.85
3.79
3.78
3.69
3.57
3.49
3.48
3.46
3.44
3.39
3.37
3.35
3.33
3.32
3.30
3.29
3.27
3.11
3.09
2.90
2.72
2.23
2.21
2.19
2.14
2.12
2.10
2.02
1.86
1.70
1.54
1.52
1.49
1.28
1.27
1.26
1.18
1.10
1.08
1.08
1.07
1.02
BnO
BnO
BnO
O
CbzHN
O
FCbzHN
4
O
ONa
O
P
O
O
OBn
O
7
H
31
81.20
2.23
13.72
48.44
17.61
3.74
0.87
0.97
0.76
2.00
2.76
15.73
f1 (ppm)


BnO
BnO
BnO
O
CbzHN
O
FCbzHN
4
O
ONa
P
O
O
OBn
O
7
ONa
P
O
O
O
ONa
P
O
O
OBn
O
7
H

**31**

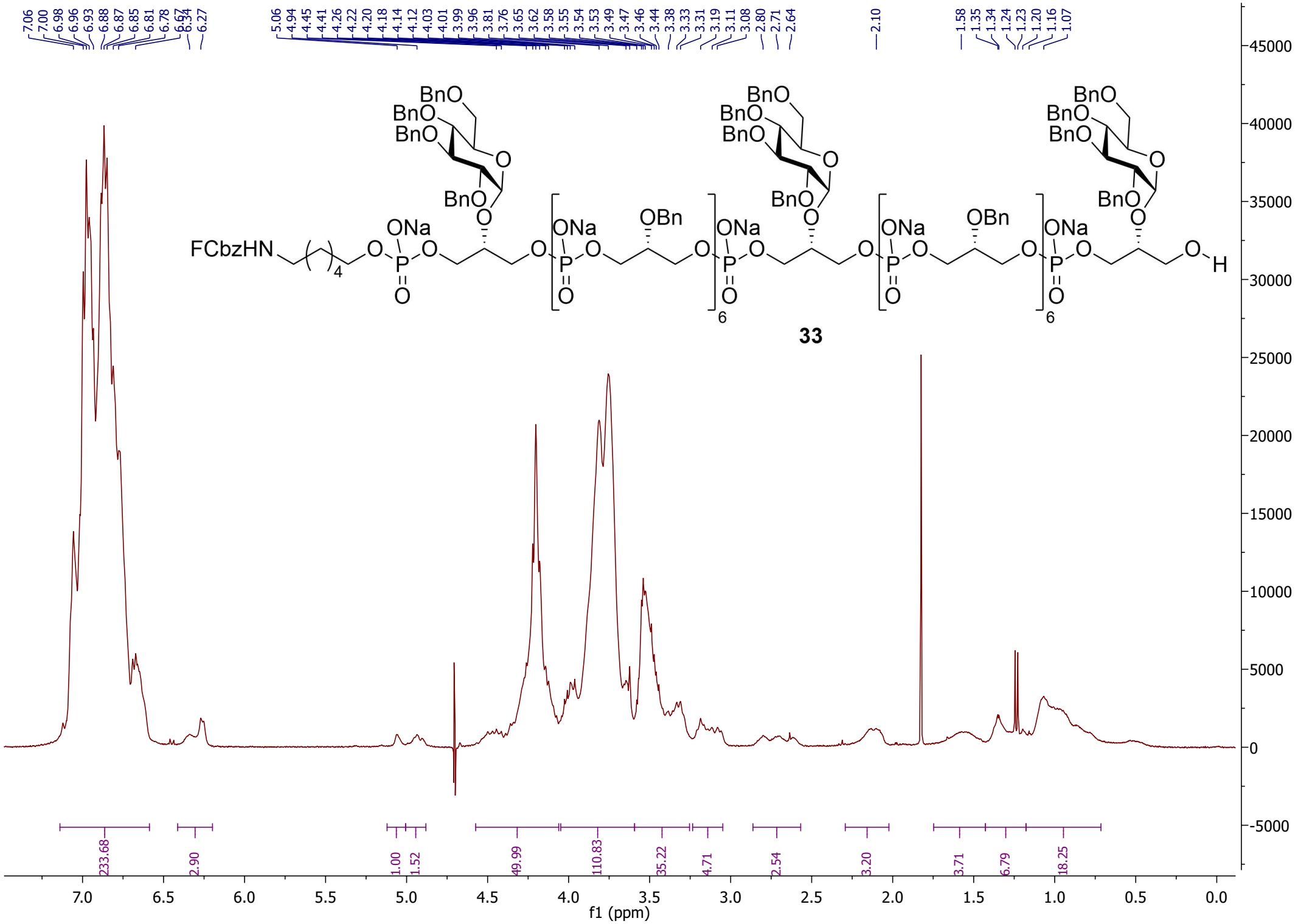

0.44
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
f1 (ppm)

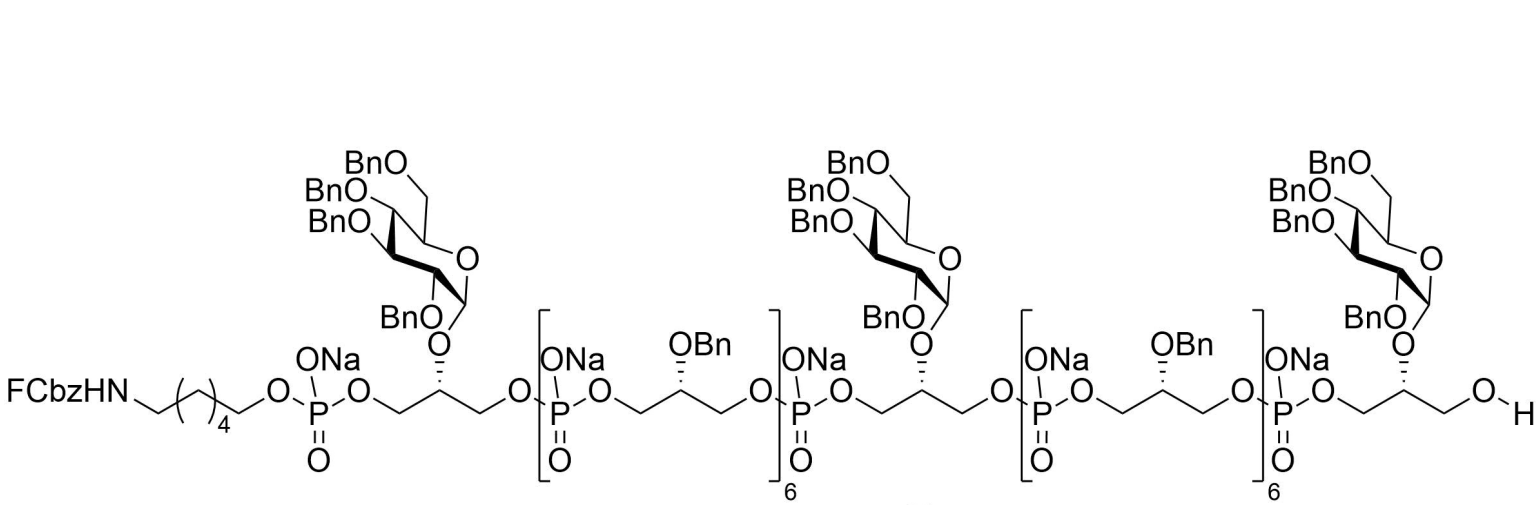

7.07
6.97
6.86
6.58
6.51
5.03
4.92
4.79
4.67
4.44
4.31
4.21
4.13
4.11
3.91
3.86
3.72
3.69
3.59
3.46
3.40
2.96
2.76
2.76
2.74
2.53
2.43
2.42
2.36
2.26
2.21
1.99
1.95
1.74
1.57
1.50
1.35
1.26
1.20
1.07
1.03
1.01
0.99
0.90
BnO
BnO
BnO
O
AcHN
O
FCbzHN
4
O
ONa
O
P
O
O
OBn
O
ONa
O
P
O
O
7
O
ONa
O
P
O
O
OBn
O
H
7
32
1.00
0.03
0.39
0.82
0.34
0.01
0.05
0.05
0.09
0.04
0.48
550
500
450
400
350
300
250
200
150
100
50
0
-50
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


BnO
BnO
BnO
O
AcHN
O
FCbzHN
4
O
ONa
P
O
O
OBn
O
7
ONa
P
O
O
O
O
ONa
P
O
O
OBn
O
7
H

**32**

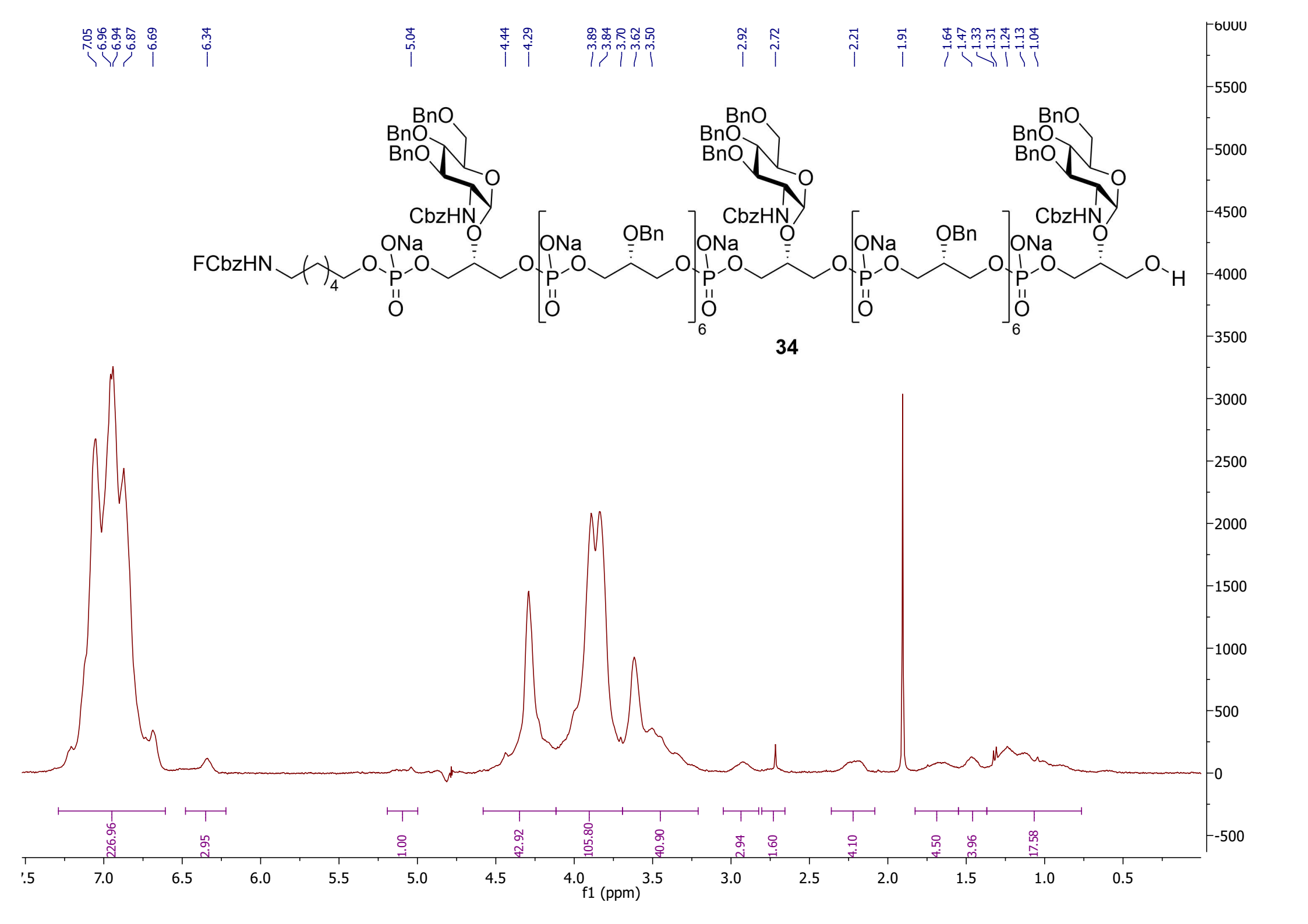

0.91
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

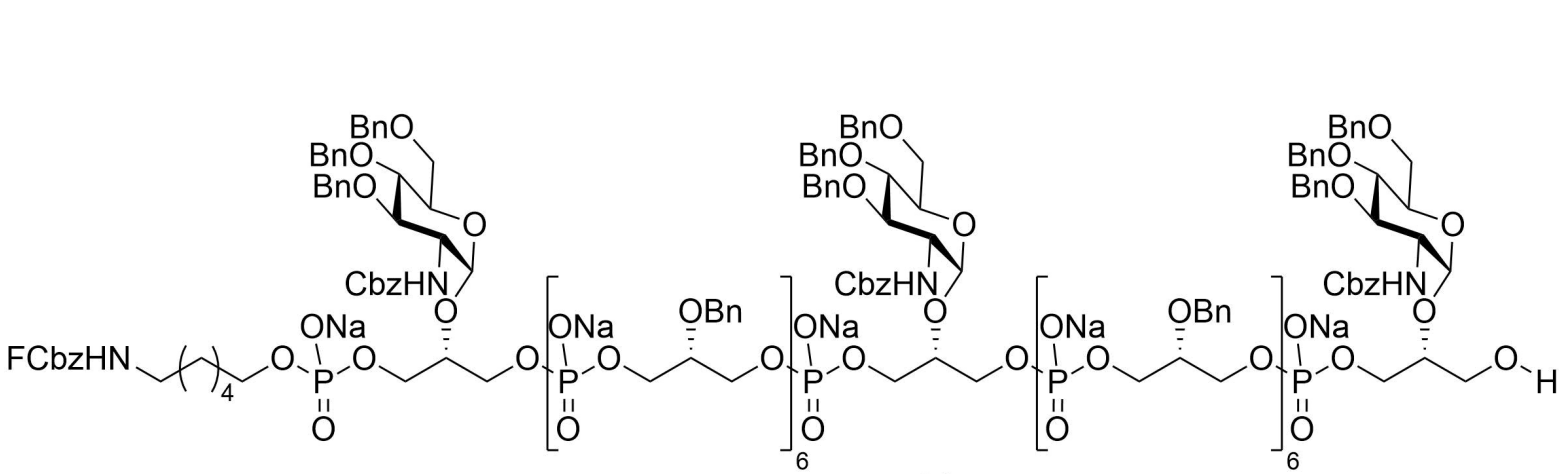

7.06 7.00 6.98 6.96 6.93 6.88 6.87 6.85 6.81 6.78 6.34 6.27
5.06 4.94 4.45 4.41 4.26 4.22 4.20 4.18 4.14 4.12 4.03 4.01 3.99 3.96 3.81 3.76 3.65 3.62 3.58 3.55 3.54 3.53 3.49 3.47 3.46 3.44 3.38 3.33 3.31 3.19 3.11 3.08 2.80 2.71 2.64
2.10
1.58 1.35 1.34 1.24 1.23 1.20 1.16 1.07
FCbzHN
BnO
ONa
OBn
O
P
H
4
6
33
233.68
2.90
1.00
1.52
49.99
110.83
35.22
4.71
2.54
3.20
3.71
6.79
18.25
f1 (ppm)


FCbzHN
BnO
ONa
OBn
O
P
H

**33**

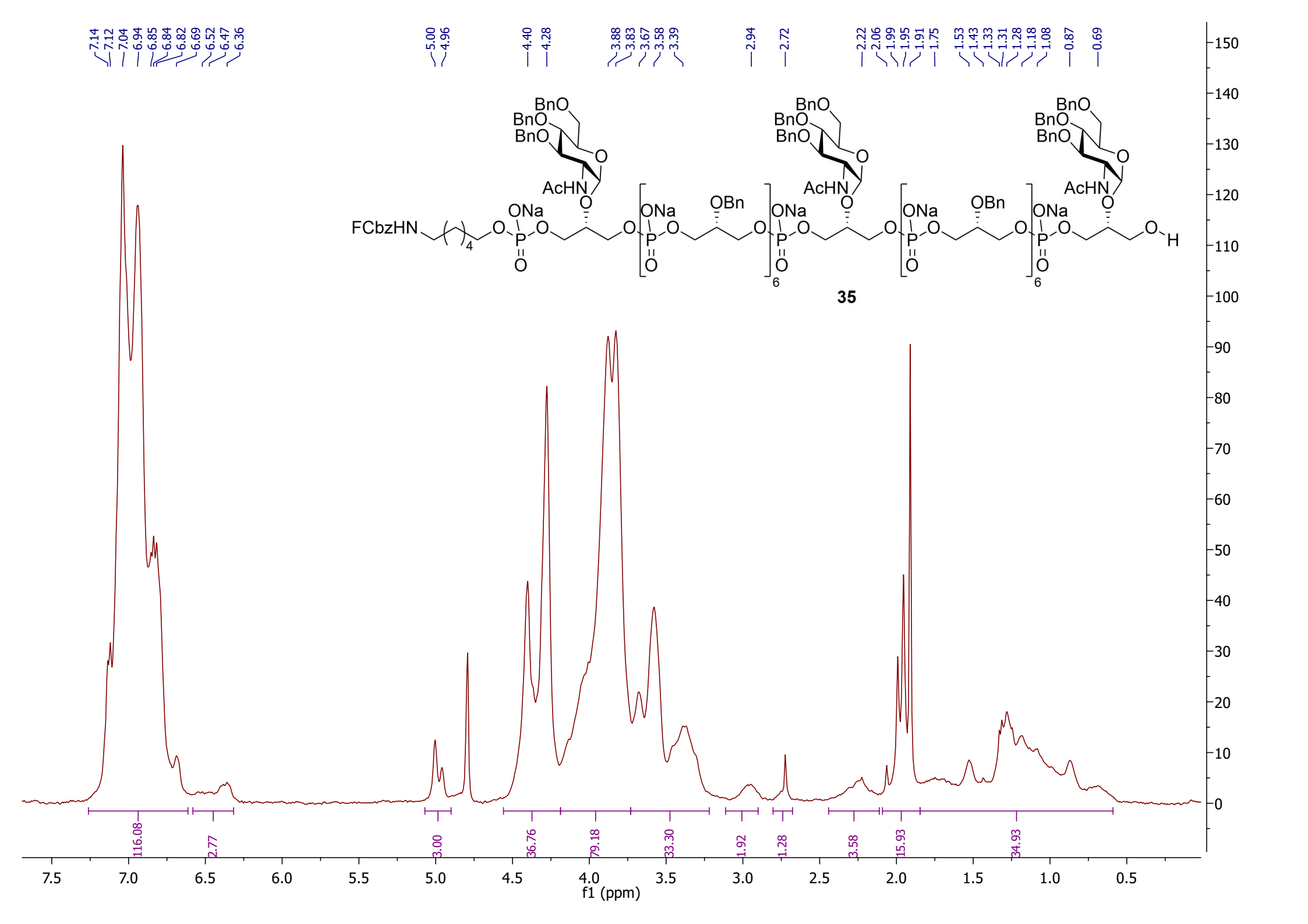

0.81
0.72
0.56
0.49
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
f1 (ppm)

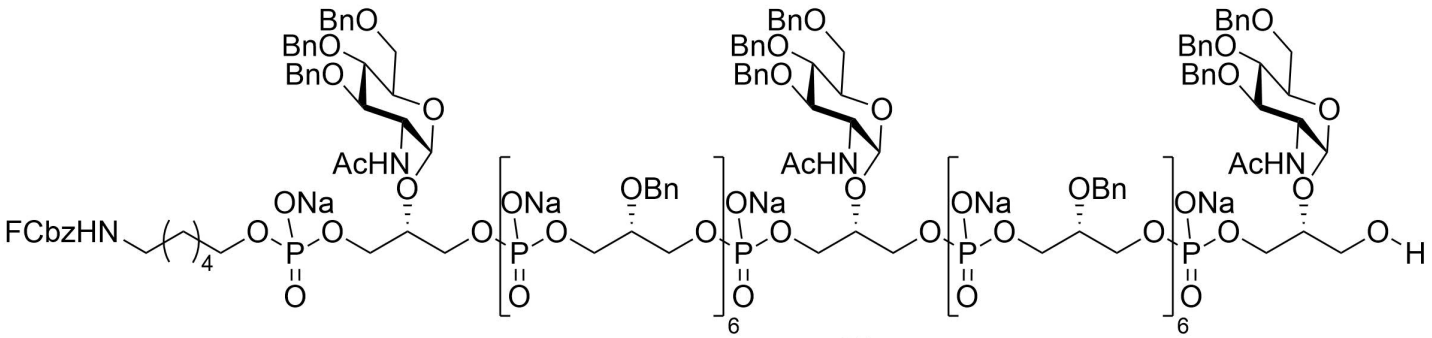

7.05
6.96
6.94
6.87
6.69
6.34
5.04
4.44
4.29
3.89
3.84
3.70
3.62
3.50
2.92
2.72
2.21
1.91
1.64
1.47
1.33
1.31
1.24
1.13
1.04
BnO
BnO
BnO
O
CbzHN
O
FCbzHN
4
ONa
O
P
O
OBn
6
H
34
226.96
2.95
1.00
42.92
105.80
40.90
2.94
1.60
4.10
4.50
3.96
17.58
f1 (ppm)


BnO
BnO
BnO
O
CbzHN
O
ONa
O
P
O
O
FCbzHN
4
OBn
6
H

**34**

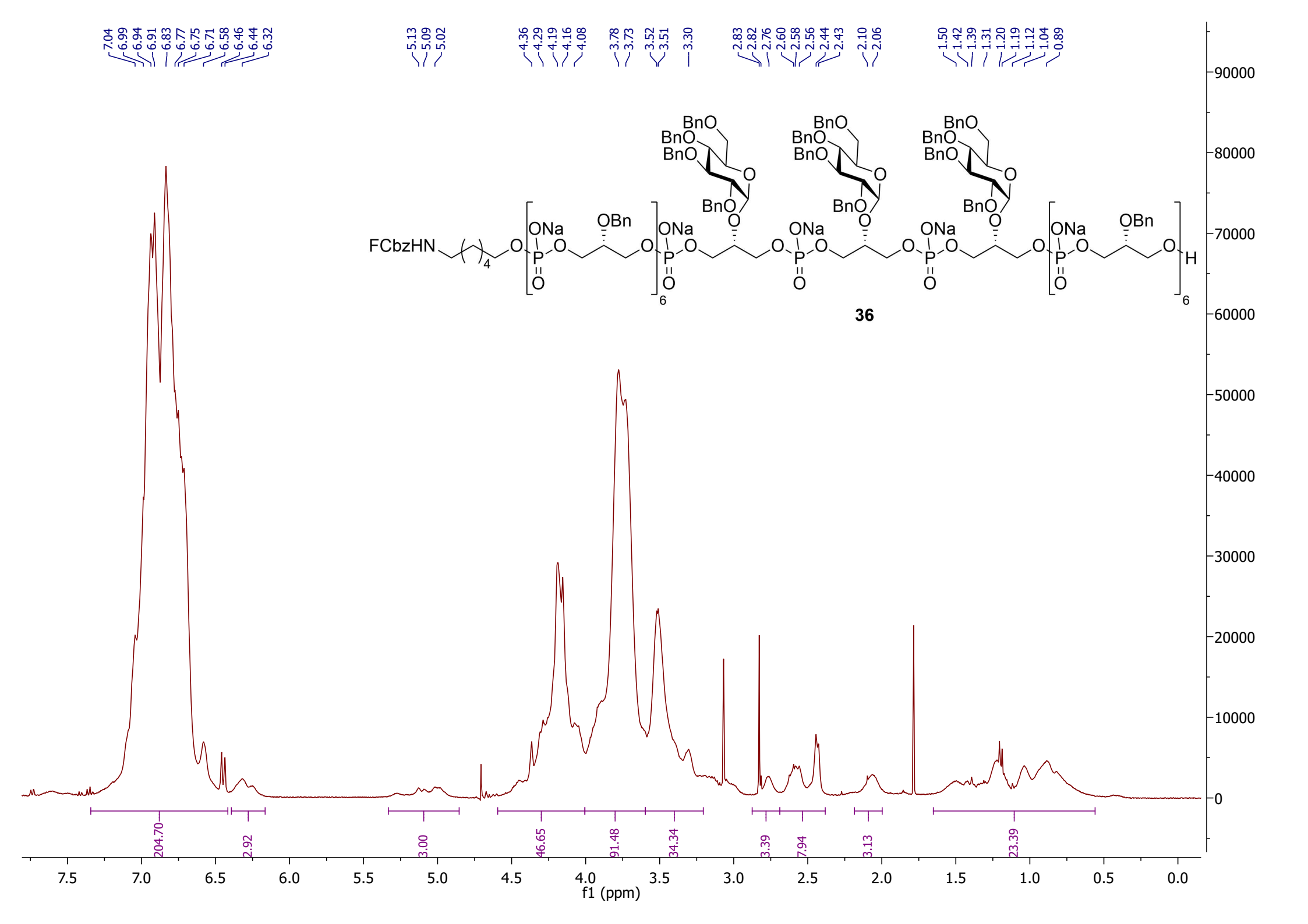

1.29
1.03
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
f1 (ppm)

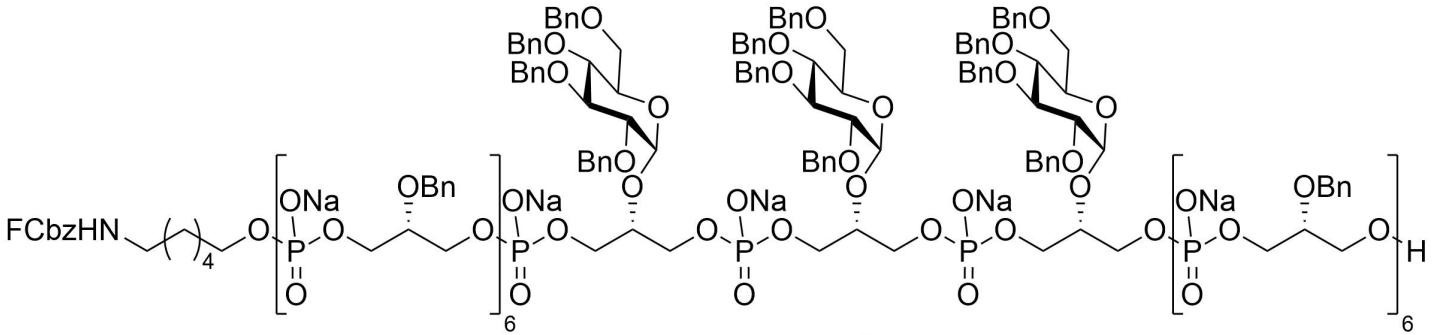

7.14
7.12
7.04
6.94
6.85
6.84
6.82
6.69
6.52
6.47
6.36
5.00
4.96
4.40
4.28
3.88
3.83
3.67
3.58
3.39
2.94
2.72
2.22
2.06
1.99
1.95
1.91
1.75
1.53
1.43
1.33
1.31
1.28
1.18
1.08
0.87
0.69
BnO
AcHN
ONa
OBn
FCbzHN
H
6
4
35
116.08
2.77
3.00
36.76
79.18
33.30
1.92
1.28
3.58
15.93
34.93
f1 (ppm)


BnO
BnO
BnO
O
AcHN
O
ONa
O
P
O
O
OBn
FCbzHN
4
6
H

**35**

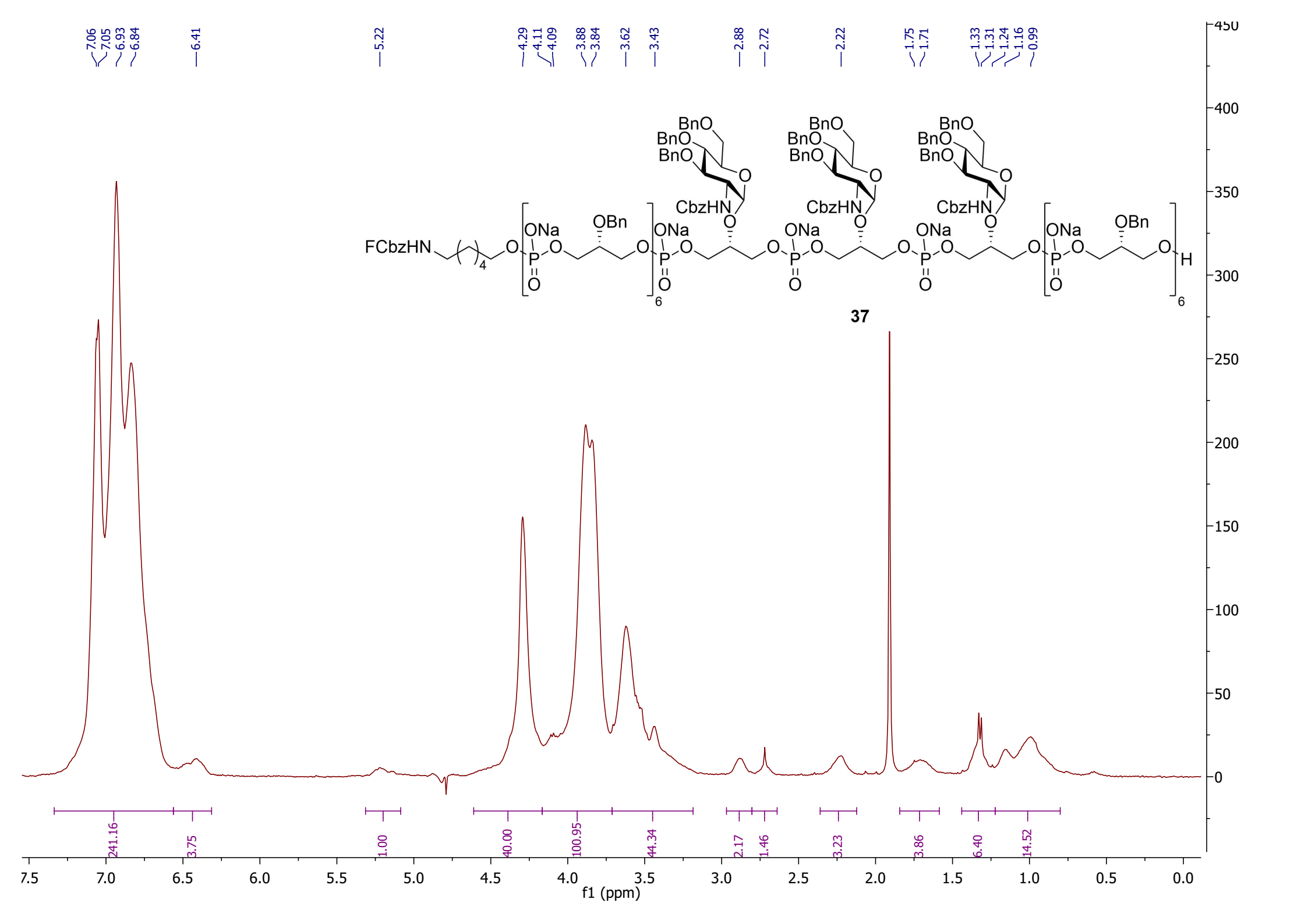

0.87
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

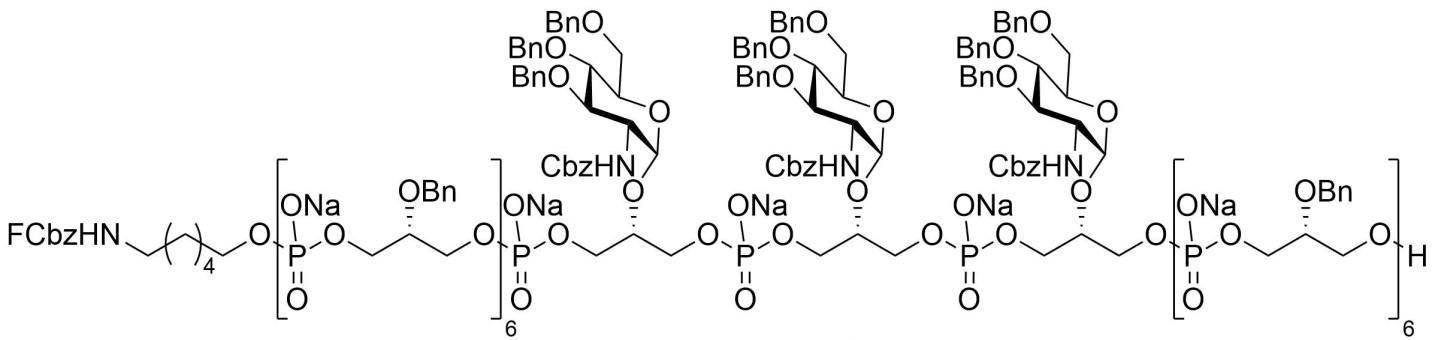

7.04
6.99
6.94
6.91
6.83
6.77
6.75
6.71
6.58
6.46
6.44
6.32
5.13
5.09
5.02
4.36
4.29
4.19
4.16
4.08
3.78
3.73
3.52
3.51
3.30
2.83
2.82
2.76
2.60
2.58
2.56
2.44
2.43
2.10
2.06
1.50
1.42
1.39
1.31
1.20
1.19
1.12
1.04
0.89
FCbzHN
ONa
OBn
BnO
H
6
4
36
204.70
2.92
3.00
46.65
91.48
34.34
3.39
7.94
3.13
23.39
f1 (ppm)


FCbzHN
ONa
OBn
BnO
O
P
O
H
6
4

**36**

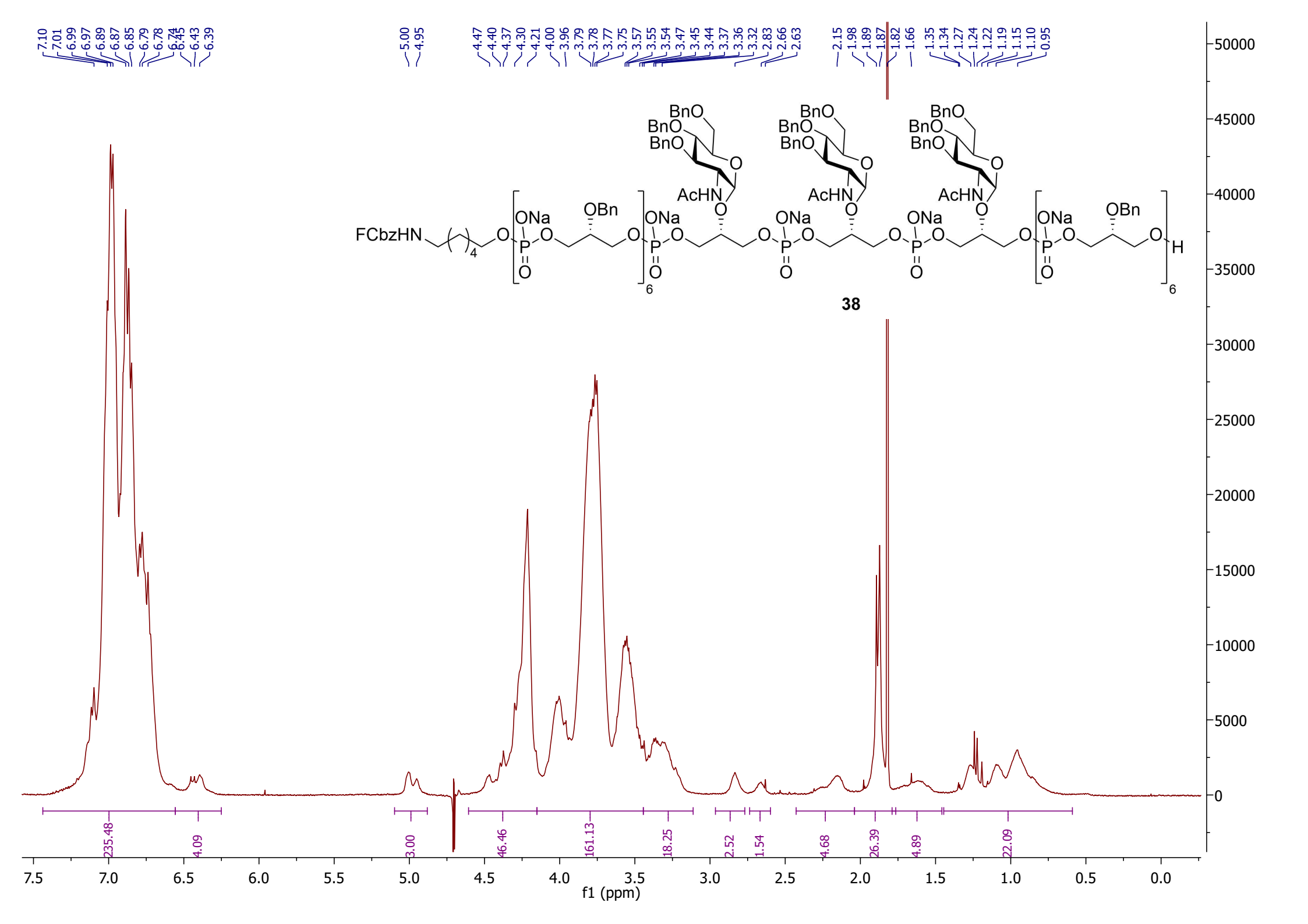

1.35
1.01
0.13
1000
900
800
700
600
500
400
300
200
100
0
-100
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
f1 (ppm)

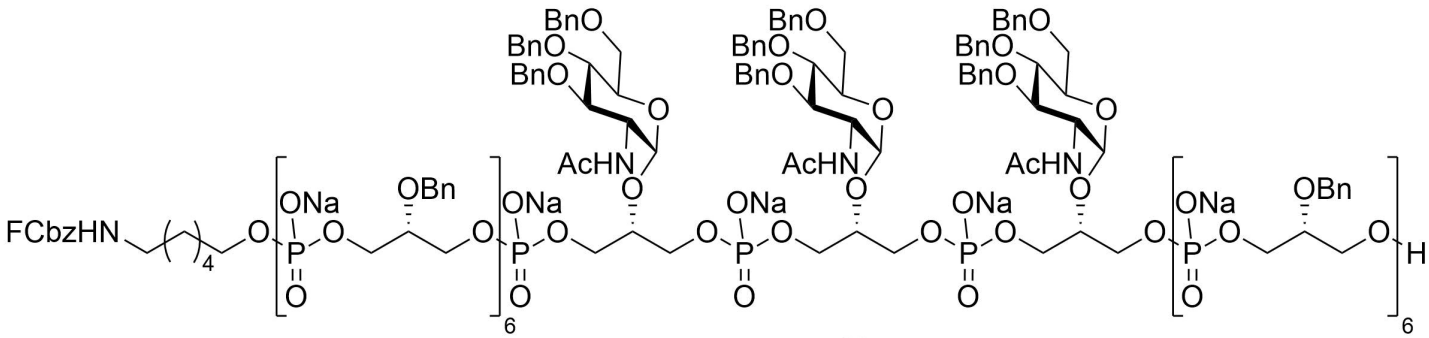

7.06
7.05
6.93
6.84
6.41
5.22
4.29
4.11
4.09
3.88
3.84
3.62
3.43
2.88
2.72
2.22
1.75
1.71
1.33
1.31
1.24
1.16
0.99
BnO
CbzHN
ONa
OBn
FCbzHN
H
37
241.16
3.75
1.00
40.00
100.95
44.34
2.17
1.46
3.23
3.86
6.40
14.52
f1 (ppm)


BnO
BnO
BnO
O
CbzHN
O
ONa
OBn
FCbzHN
4
P
O
6
H

**37**

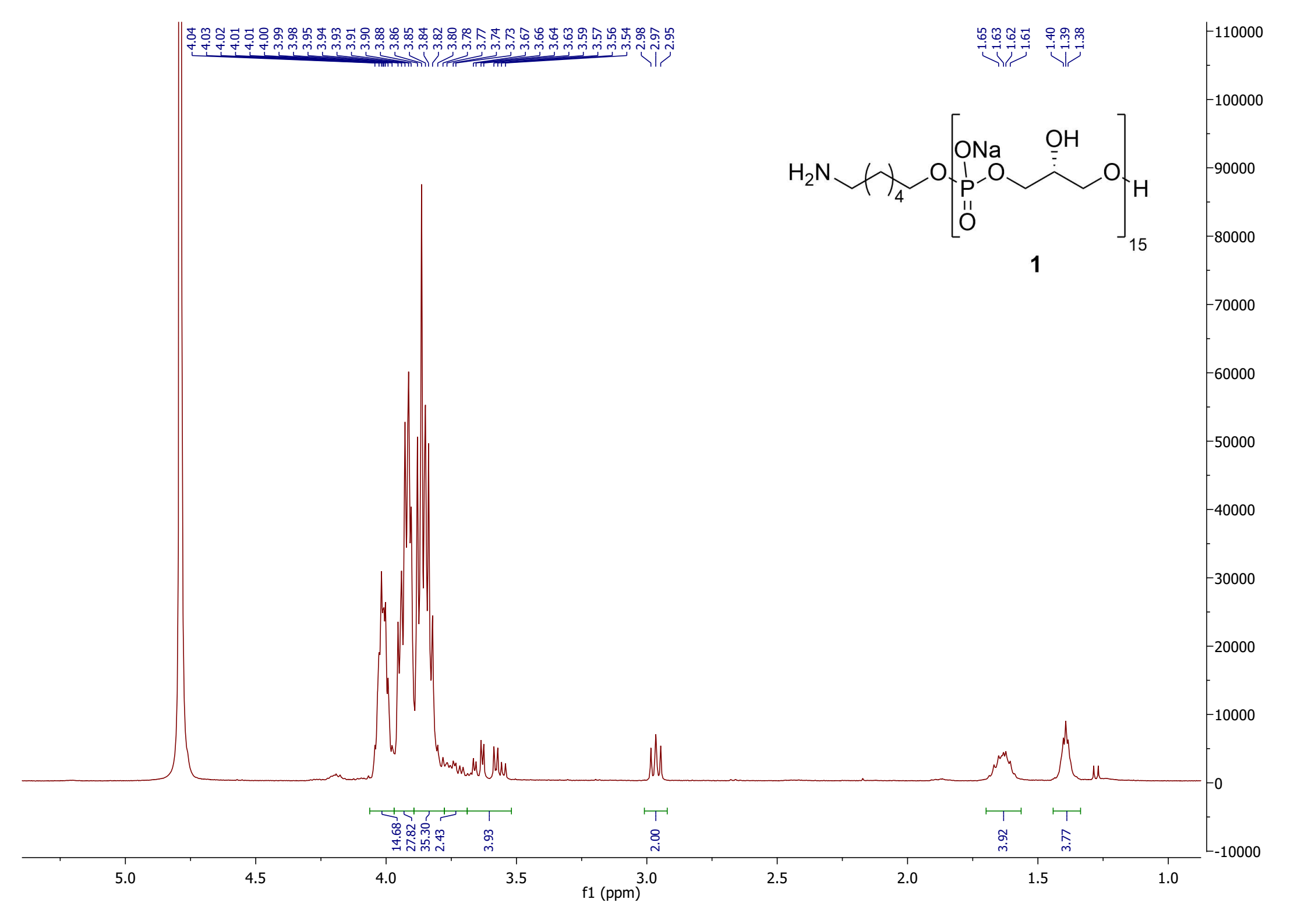

1.16
1.03
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
f1 (ppm)

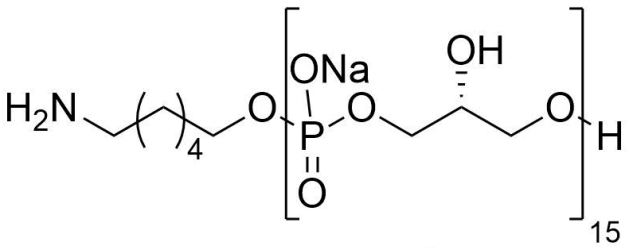

7.10
7.01
6.99
6.97
6.89
6.87
6.85
6.79
6.78
6.74
6.45
6.43
6.39
5.00
4.95
4.47
4.40
4.37
4.30
4.21
4.00
3.96
3.79
3.78
3.77
3.75
3.57
3.55
3.54
3.47
3.45
3.44
3.37
3.36
3.32
2.83
2.66
2.63
2.15
1.98
1.89
1.87
1.82
1.66
1.35
1.34
1.27
1.24
1.22
1.19
1.15
1.10
0.95
BnO
AcHN
FCbzHN
ONa
OBn
H
38
235.48
4.09
3.00
46.46
161.13
18.25
2.52
1.54
4.68
26.39
4.89
22.09
f1 (ppm)


FCbzHN
4
O
ONa
P
O
OBn
6
BnO
AcHN
H

**38**

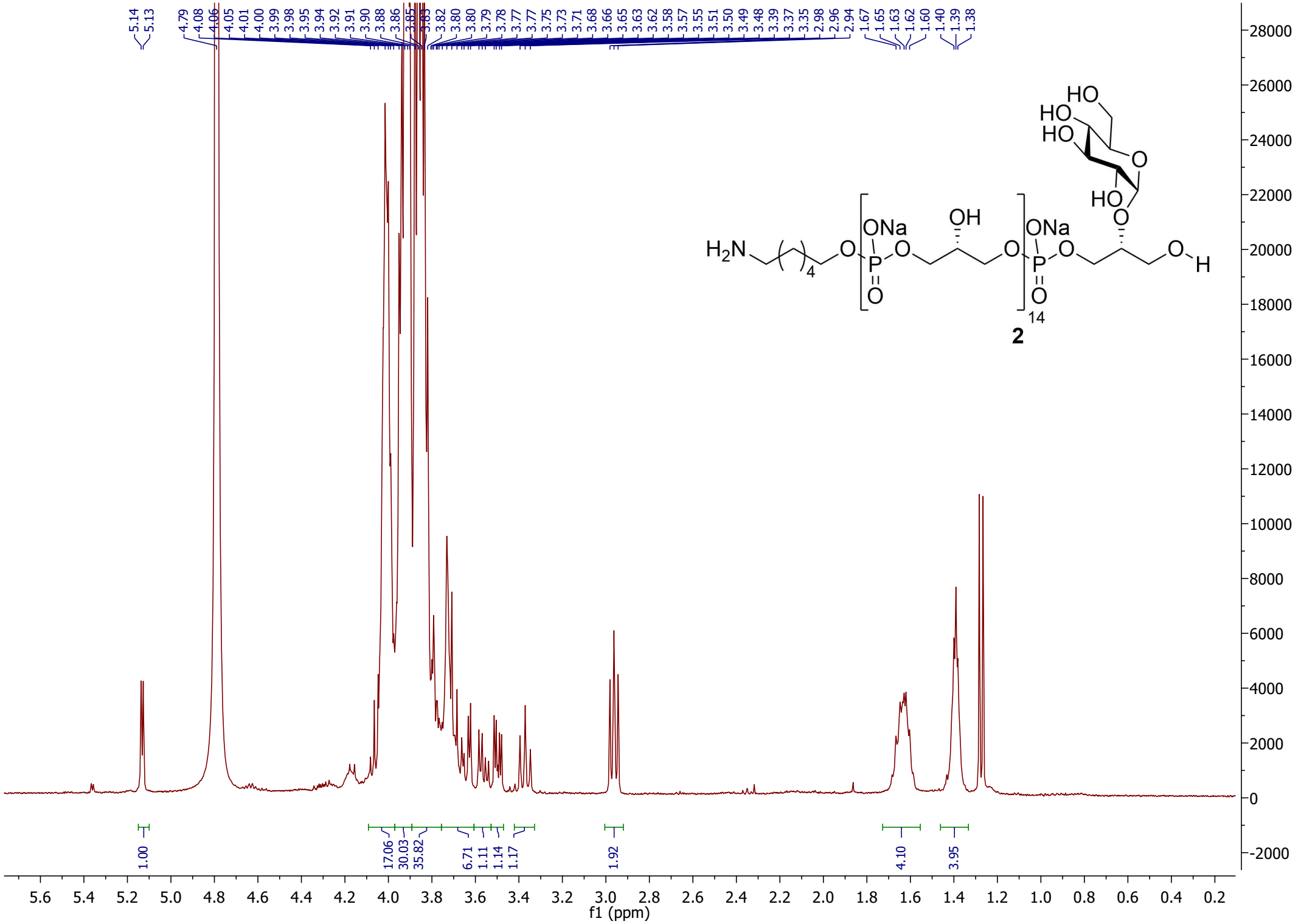

0.62
0.48
0.32
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
f1 (ppm)

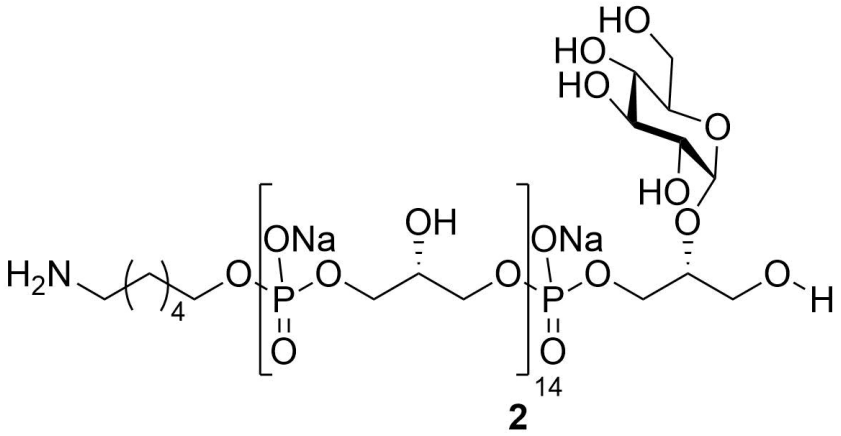

4.04 4.03 4.02 4.01 4.01 4.00 3.99 3.98 3.95 3.94 3.93 3.91 3.90 3.88 3.86 3.85 3.84 3.82 3.80 3.78 3.77 3.74 3.73 3.67 3.66 3.64 3.63 3.59 3.57 3.56 3.54 2.98 2.97 2.95
1.65 1.63 1.62 1.61 1.40 1.39 1.38
H2N
ONa
OH
O
P
O
H
4
15
1
14.68 27.82 35.30 2.43 3.93 2.00 3.92 3.77
f1 (ppm)


H2N
4
O
ONa
P
O
O
OH
O
H
15

**1**

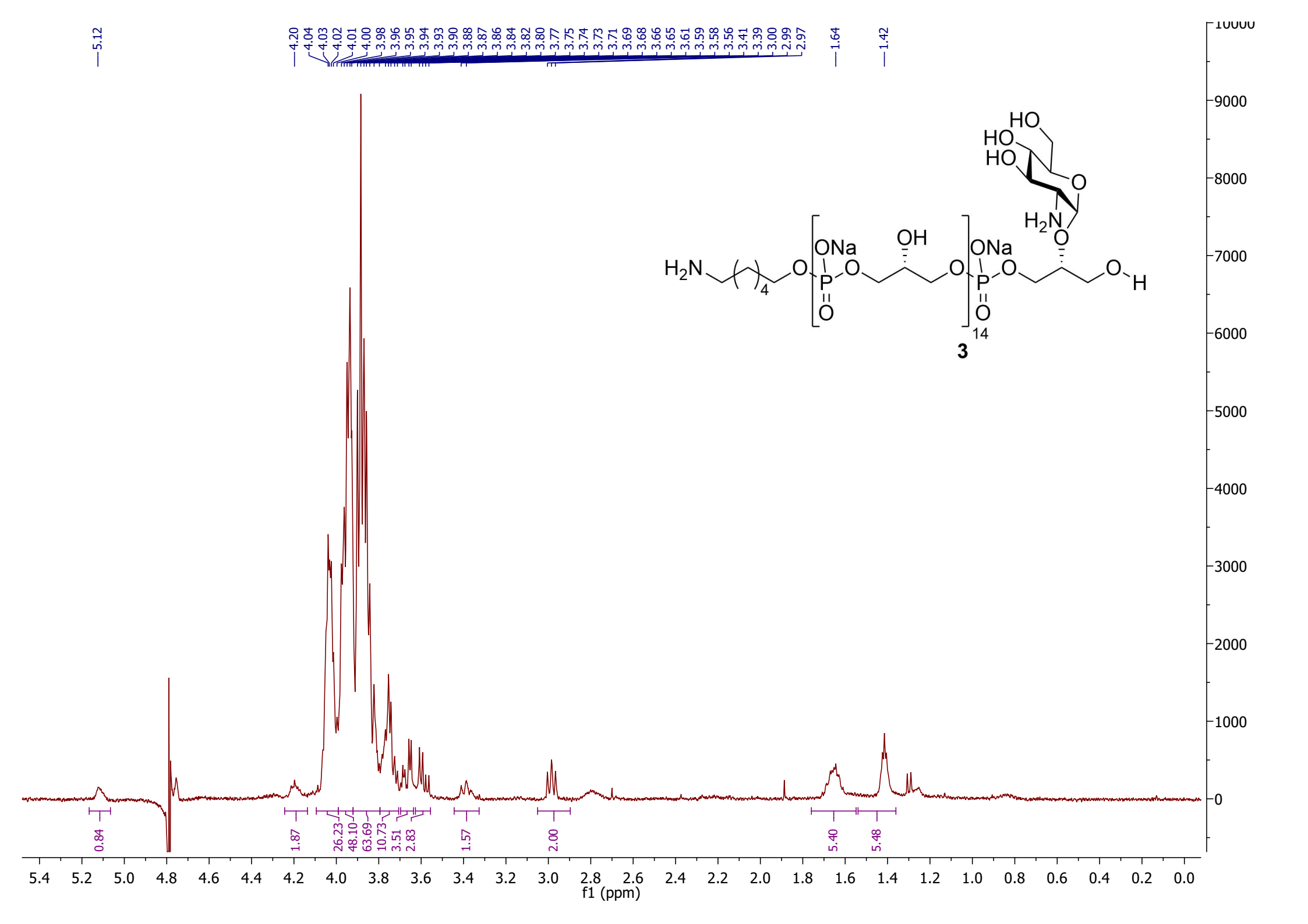

0.73
35000
30000
25000
20000
15000
10000
5000
0
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

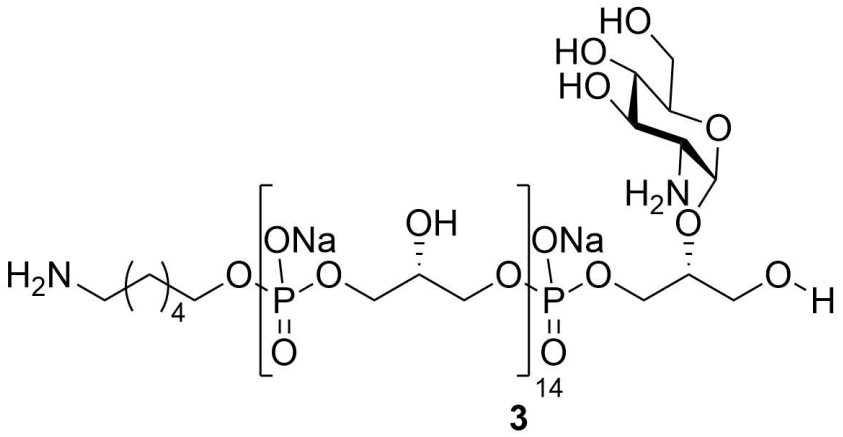

5.14
5.13
4.79
4.08
4.06
4.05
4.01
4.00
3.99
3.98
3.95
3.94
3.92
3.91
3.90
3.88
3.86
3.85
3.83
3.82
3.80
3.80
3.79
3.78
3.77
3.77
3.75
3.73
3.71
3.68
3.66
3.65
3.63
3.62
3.58
3.57
3.55
3.51
3.50
3.49
3.48
3.39
3.37
3.35
2.98
2.96
2.94
1.67
1.65
1.63
1.62
1.60
1.40
1.39
1.38
HO
HO
HO
O
HO
O
H2N
4
O
ONa
O
P
O
OH
O
ONa
O
P
O
O
14
O
O
H
2
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
1.00
17.06
30.03
35.82
6.71
1.11
1.14
1.17
1.92
4.10
3.95
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
f1 (ppm)


HO
HO
HO
O
HO
O
H2N
4
O
ONa
P
O
O
OH
O
ONa
P
O
O
O
O
H
14

**2**

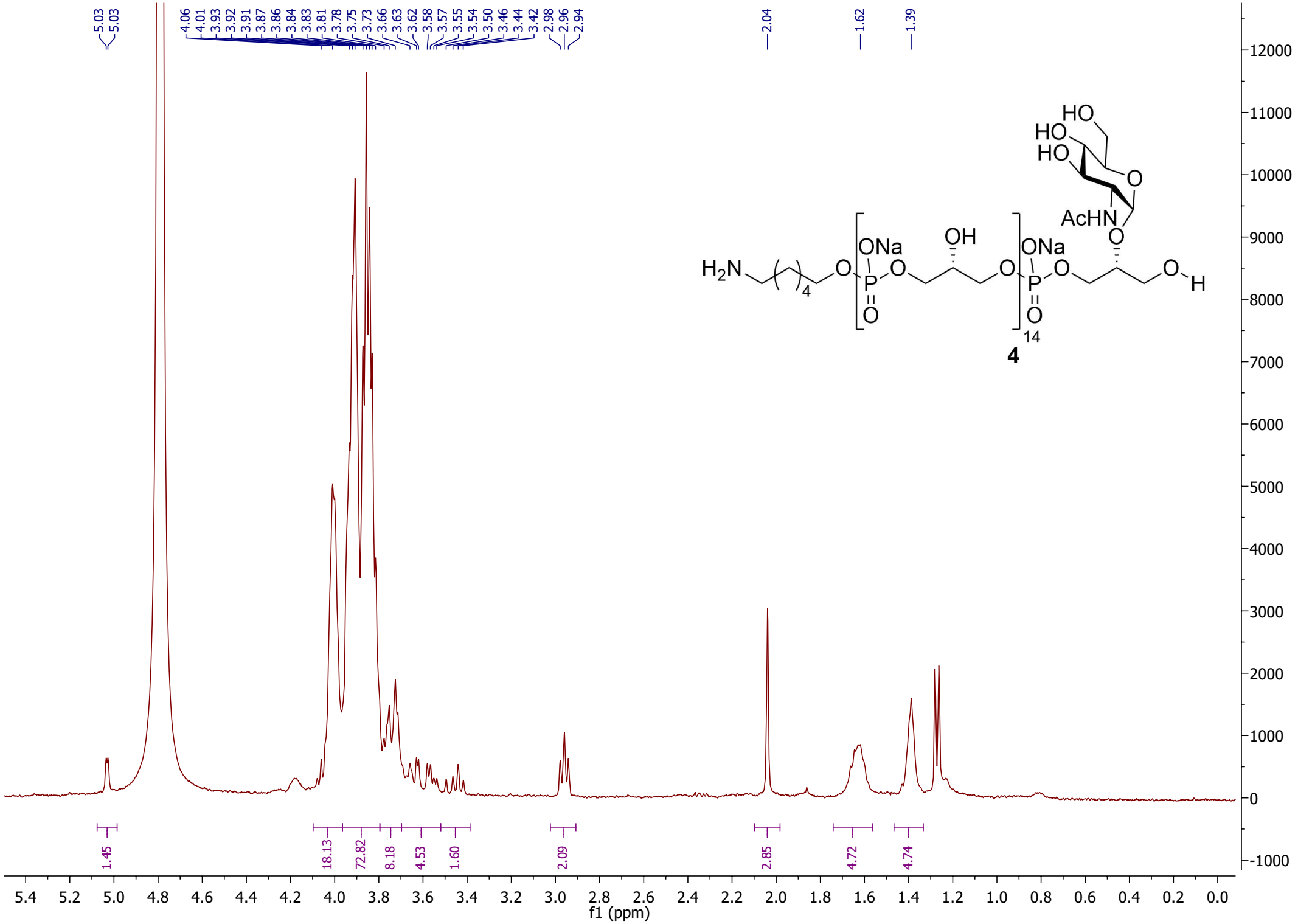

0.71
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

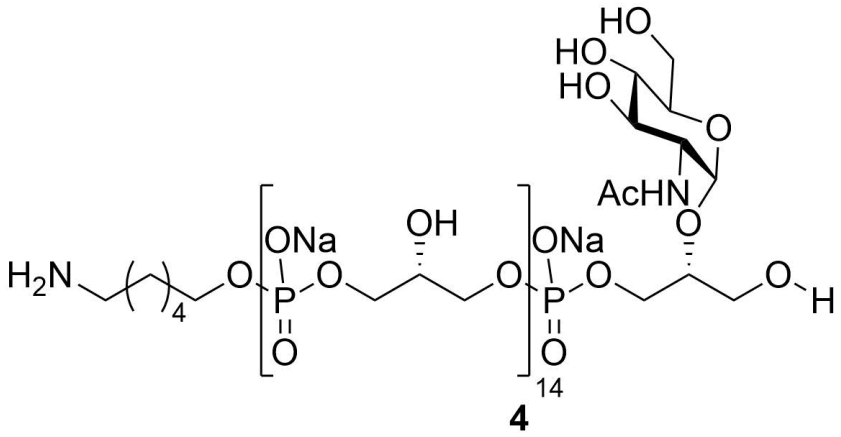

5.12
4.20
4.04
4.03
4.02
4.01
4.00
3.98
3.96
3.95
3.94
3.93
3.90
3.88
3.87
3.86
3.84
3.82
3.80
3.77
3.75
3.74
3.73
3.71
3.69
3.68
3.66
3.65
3.61
3.59
3.58
3.56
3.41
3.39
3.00
2.99
2.97
1.64
1.42
HO
HO
HO
O
H2N
O
H2N
4
O
ONa
O
P
O
OH
O
ONa
O
P
O
14
O
O
H
3
0.84
1.87
26.23
48.10
63.69
10.73
3.51
2.83
1.57
2.00
5.40
5.48
f1 (ppm)


HO
HO
HO
O
H2N
O
OH
ONa
ONa
H2N
4
O
P
O
O
O
O
P
O
O
O
H
14

**3**

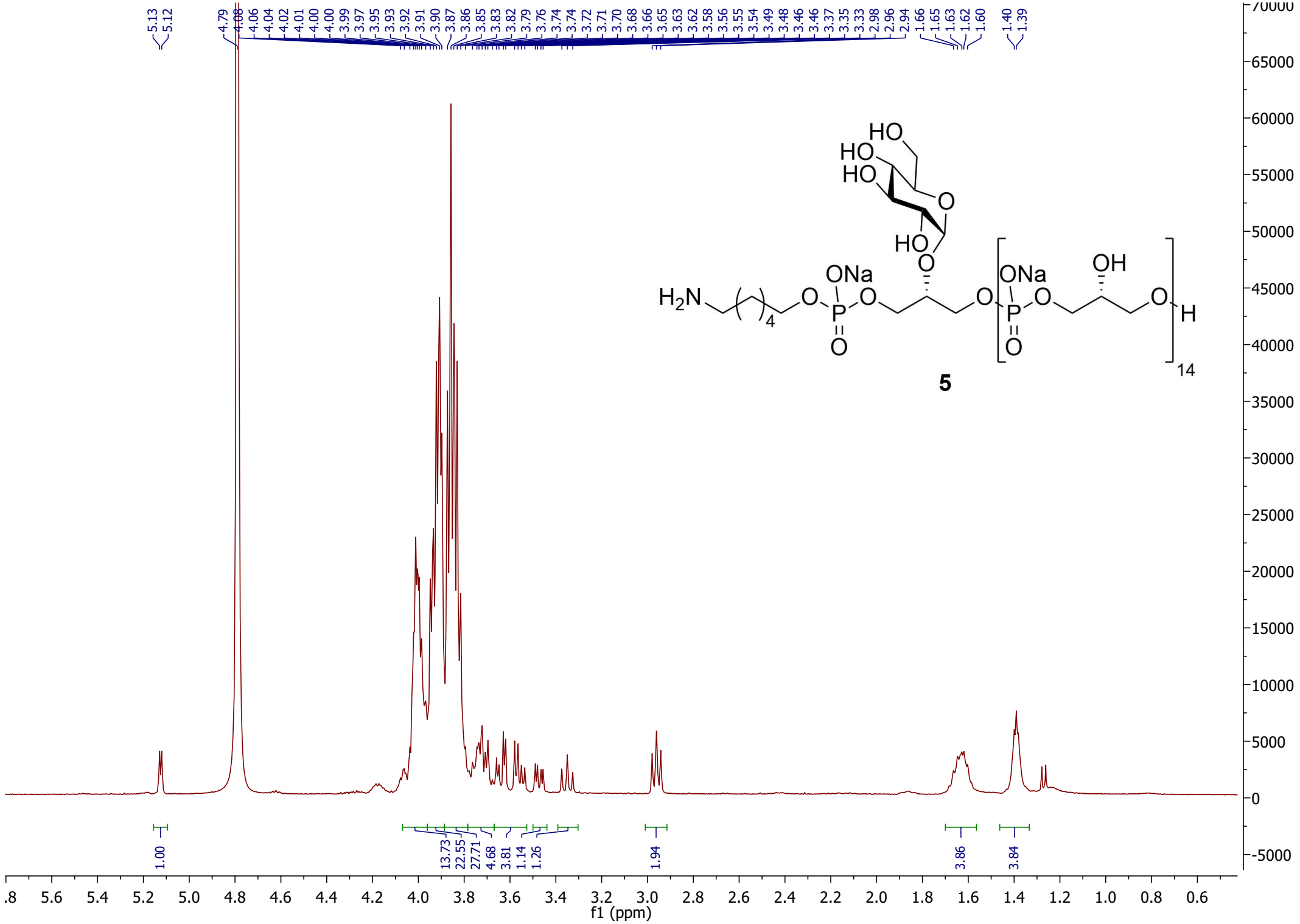
0.73
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
25
20
15
10
5
0
-5
-10
-15
-20
f1 (ppm)

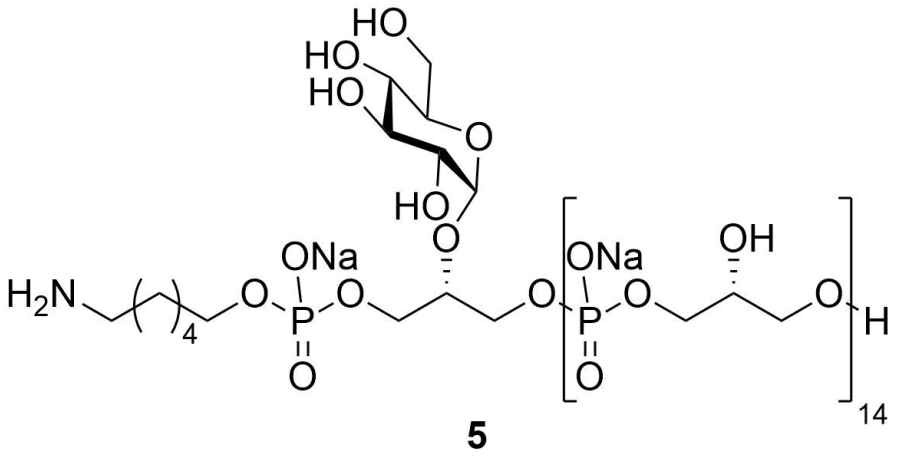

5.03
5.03
4.06
4.01
3.93
3.92
3.91
3.87
3.86
3.84
3.83
3.81
3.78
3.75
3.73
3.66
3.63
3.62
3.58
3.57
3.55
3.54
3.50
3.46
3.44
3.42
2.98
2.96
2.94
2.04
1.62
1.39
HO
HO
HO
O
AcHN
O
ONa
OH
ONa
H2N
4
O
P
O
O
O
P
O
O
O
H
14
4
1.45
18.13
72.82
8.18
4.53
1.60
2.09
2.85
4.72
4.74
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
f1 (ppm)


HO
HO
HO
O
AcHN
O
OH
ONa
ONa
$H_2N$
4
O
P
O
O
O
O
P
O
O
O
O
H
14

**4**

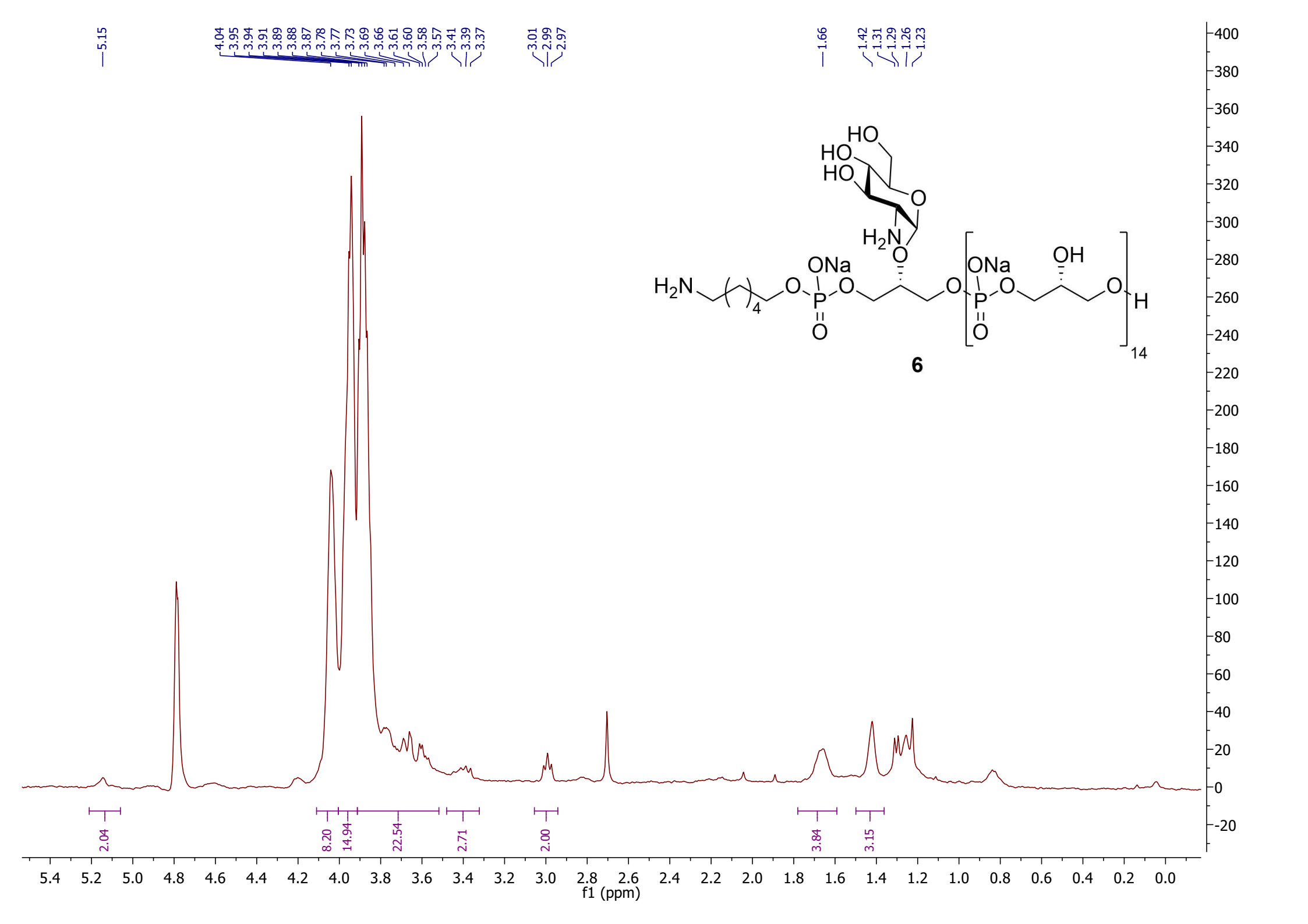

0.77
0.69
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

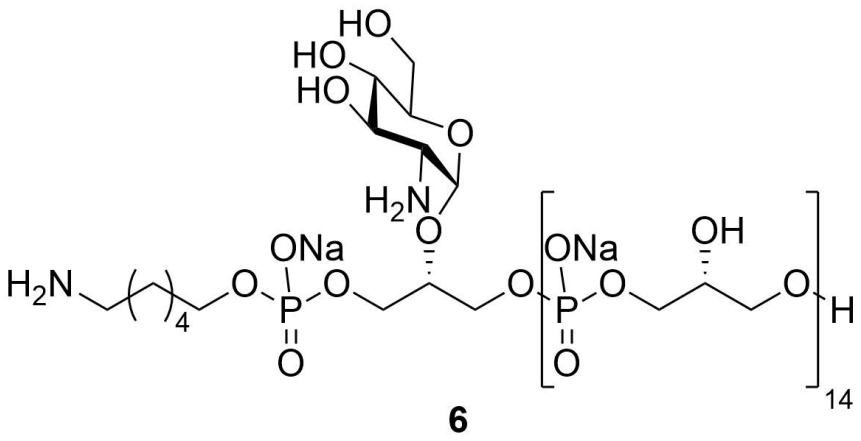

5.13
5.12
4.79
4.08
4.06
4.04
4.02
4.01
4.00
4.00
3.99
3.97
3.95
3.93
3.92
3.91
3.90
3.87
3.86
3.85
3.83
3.82
3.79
3.76
3.74
3.74
3.72
3.71
3.70
3.68
3.66
3.65
3.63
3.62
3.58
3.56
3.55
3.54
3.49
3.48
3.46
3.46
3.37
3.35
3.33
2.98
2.96
2.94
1.66
1.65
1.63
1.62
1.60
1.40
1.39
HO
HO
HO
O
HO
O
ONa
ONa
OH
H2N
4
O
P
O
O
O
O
O
O
O
P
O
O
O
H
14
5
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
1.00
13.73
22.55
27.71
4.68
3.81
1.14
1.26
1.94
3.86
3.84
.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
f1 (ppm)


HO
HO
HO
HO
O
O
ONa
ONa
OH
$H_2N$
4
O
P
O
O
O
O
O
O
O
H
14

**5**

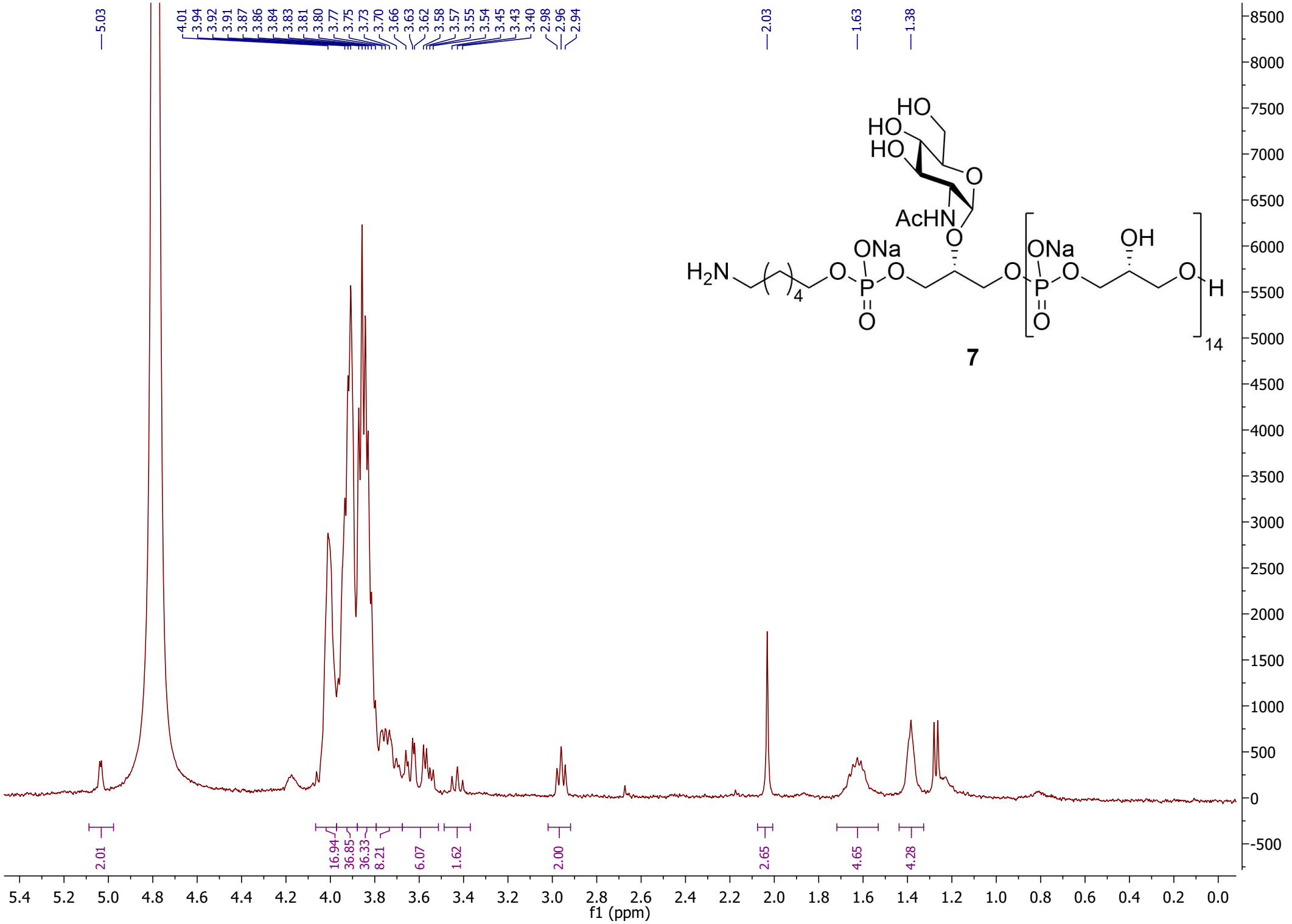

38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

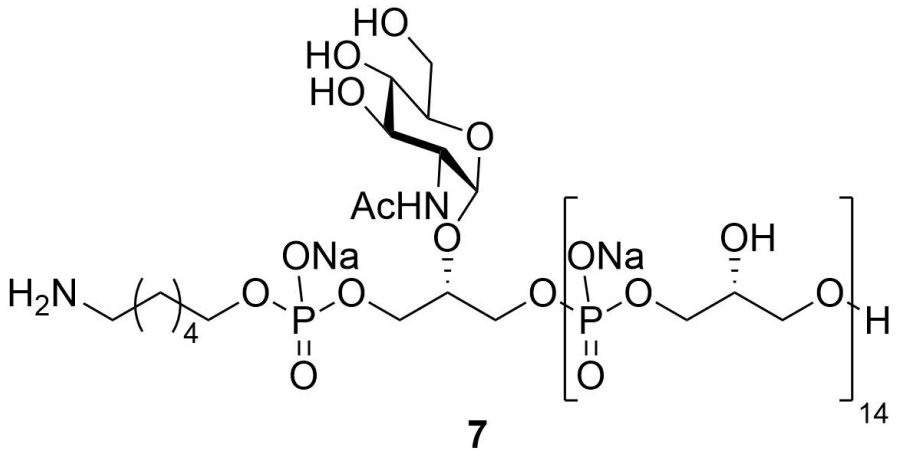

5.15
4.04
3.95
3.94
3.91
3.89
3.88
3.87
3.78
3.77
3.73
3.69
3.66
3.61
3.60
3.58
3.57
3.41
3.39
3.37
3.01
2.99
2.97
1.66
1.42
1.31
1.29
1.26
1.23
HO
HO
HO
O
H2N
O
ONa
ONa
OH
H2N
4
O
P
O
O
O
P
O
O
O
H
14
6
2.04
8.20
14.94
22.54
2.71
2.00
3.84
3.15
f1 (ppm)


HO
HO
HO
O
H2N
O
ONa
O
P
O
O
ONa
O
P
O
OH
O
H
14
H2N
4

**6**

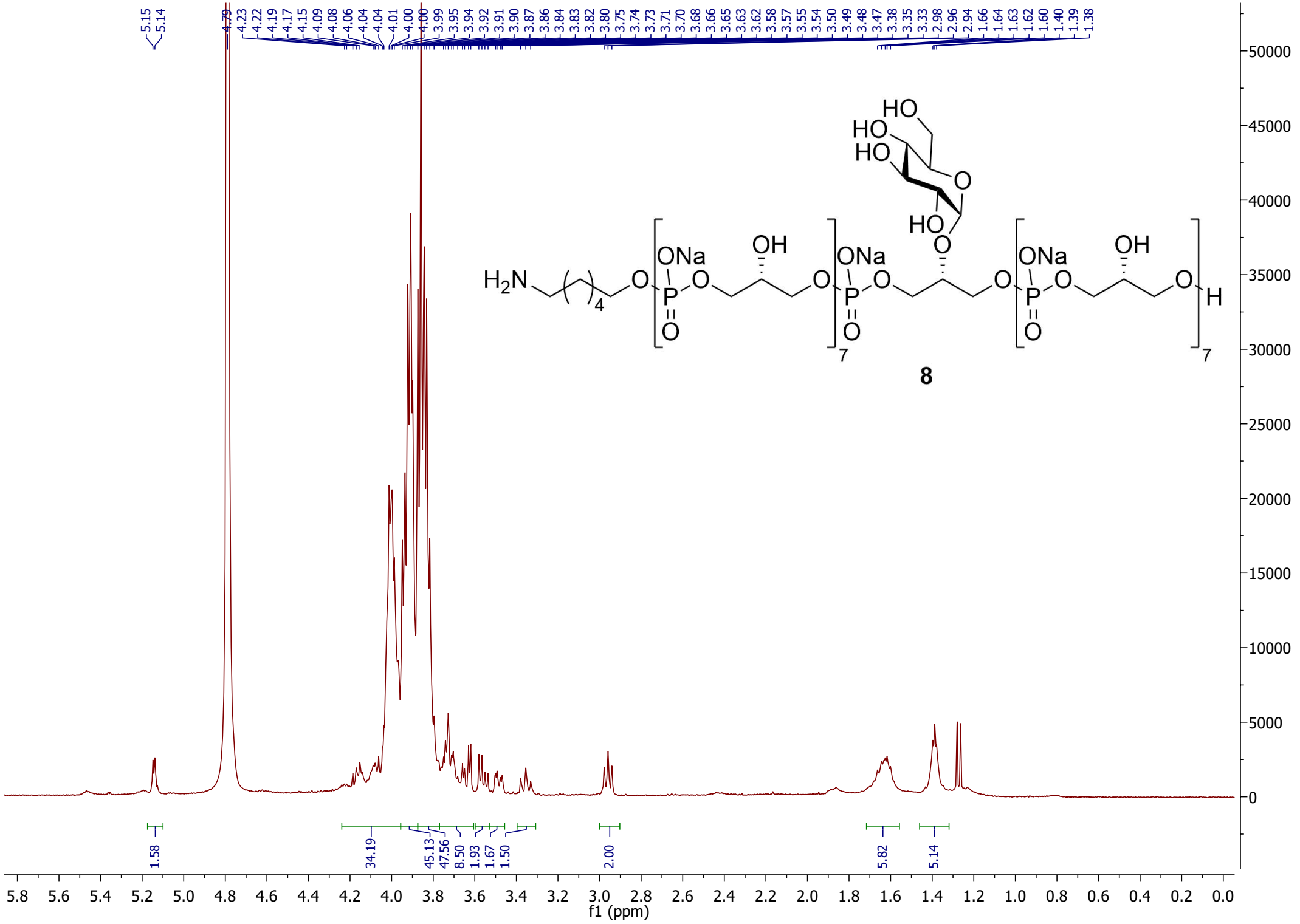

1.16
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

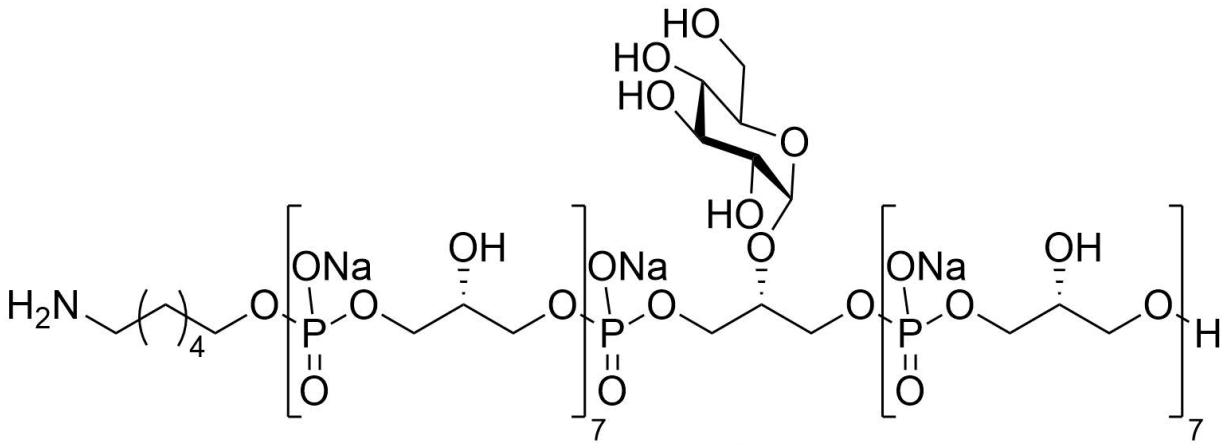

5.03
4.01
3.94
3.92
3.91
3.87
3.86
3.84
3.83
3.81
3.80
3.77
3.75
3.73
3.70
3.66
3.63
3.62
3.58
3.57
3.55
3.54
3.45
3.43
3.40
2.98
2.96
2.94
2.03
1.63
1.38
HO
HO
HO
O
AcHN
O
ONa
ONa
OH
H2N
4
O
P
O
O
O
O
O
P
O
O
O
H
14
7
2.01
16.94
36.85
36.33
8.21
6.07
1.62
2.00
2.65
4.65
4.28
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
f1 (ppm)


HO
HO
HO
O
AcHN
O
ONa
O
P
O
O
O
ONa
O
P
O
O
OH
O
H
$H_2N$
4
14

**7**

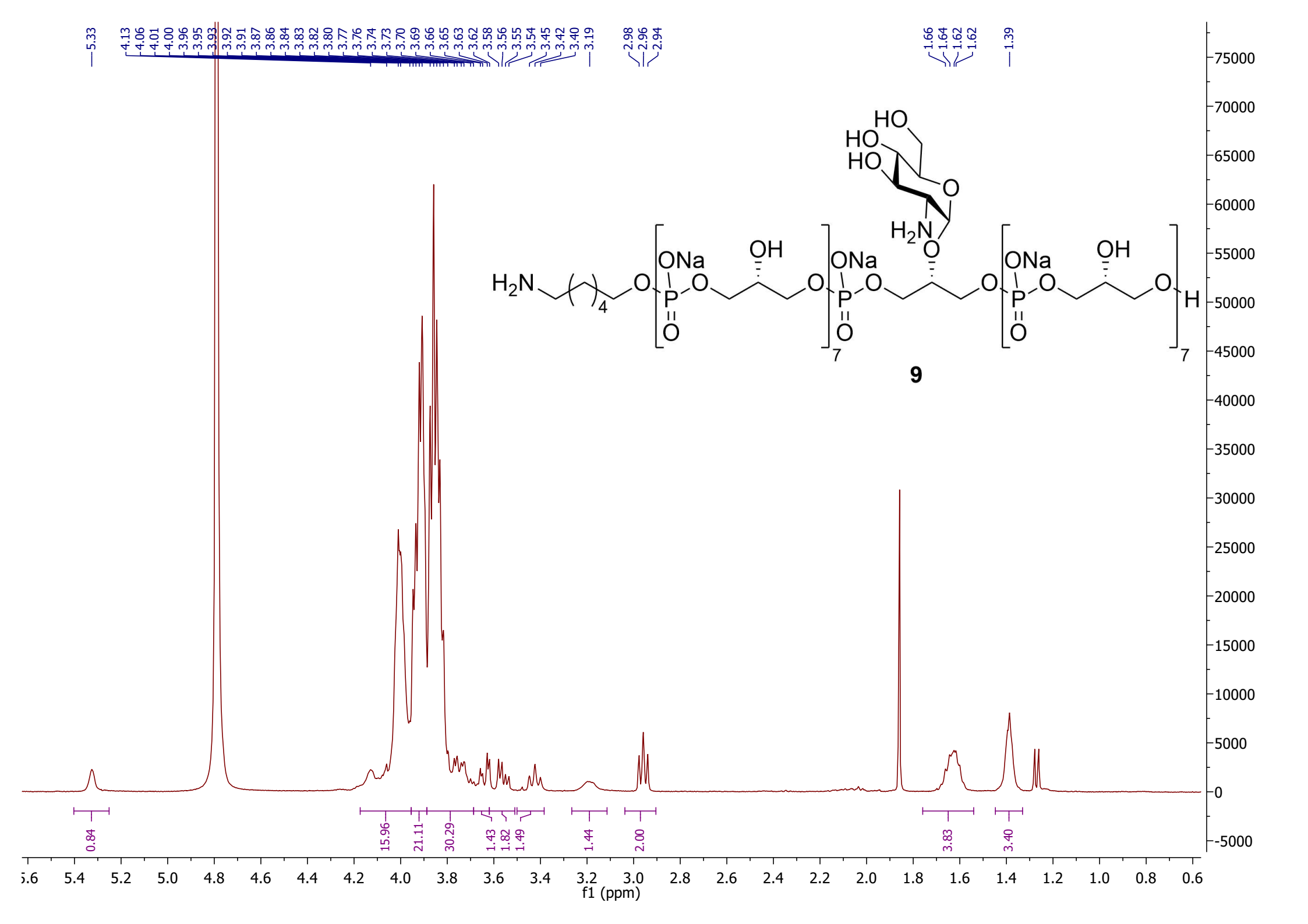

0.68
4000
3500
3000
2500
2000
1500
1000
500
0
-500
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

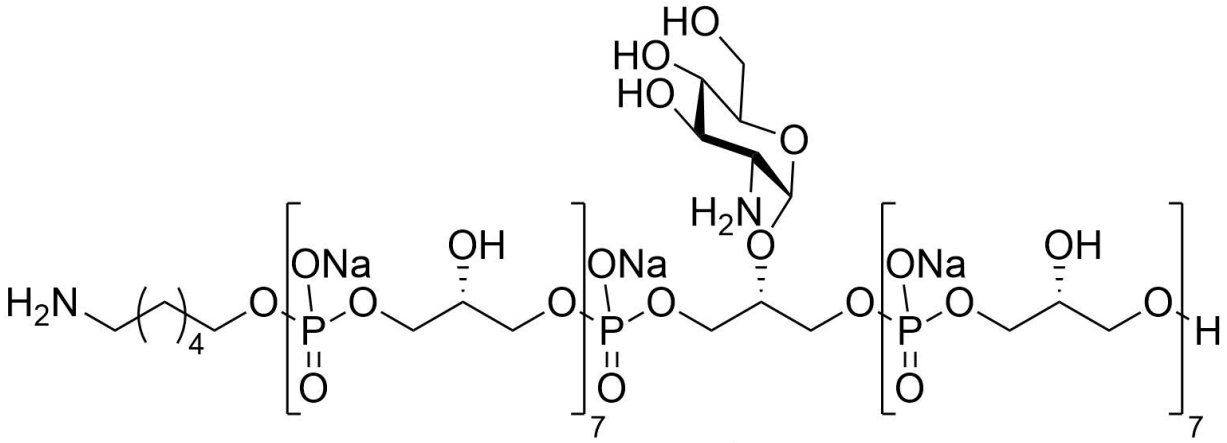

5.15
5.14
4.79
4.23
4.22
4.19
4.17
4.15
4.09
4.08
4.06
4.04
4.04
4.01
4.00
4.00
3.99
3.95
3.94
3.92
3.91
3.90
3.87
3.86
3.84
3.83
3.82
3.80
3.75
3.74
3.73
3.71
3.70
3.68
3.66
3.65
3.63
3.62
3.58
3.57
3.55
3.54
3.50
3.49
3.48
3.47
3.38
3.35
3.33
2.98
2.96
2.94
1.66
1.64
1.63
1.62
1.60
1.40
1.39
1.38
HO
HO
HO
O
HO
O
H2N
4
O
ONa
P
O
O
OH
7
H
8
1.58
34.19
45.13
47.56
8.50
1.93
1.67
1.50
2.00
5.82
5.14
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
f1 (ppm)


HO
HO
HO
O
HO
O
H2N
4
O
ONa
P
O
O
OH
O
7
ONa
P
O
O
O
ONa
P
O
O
OH
O
H
7

**8**

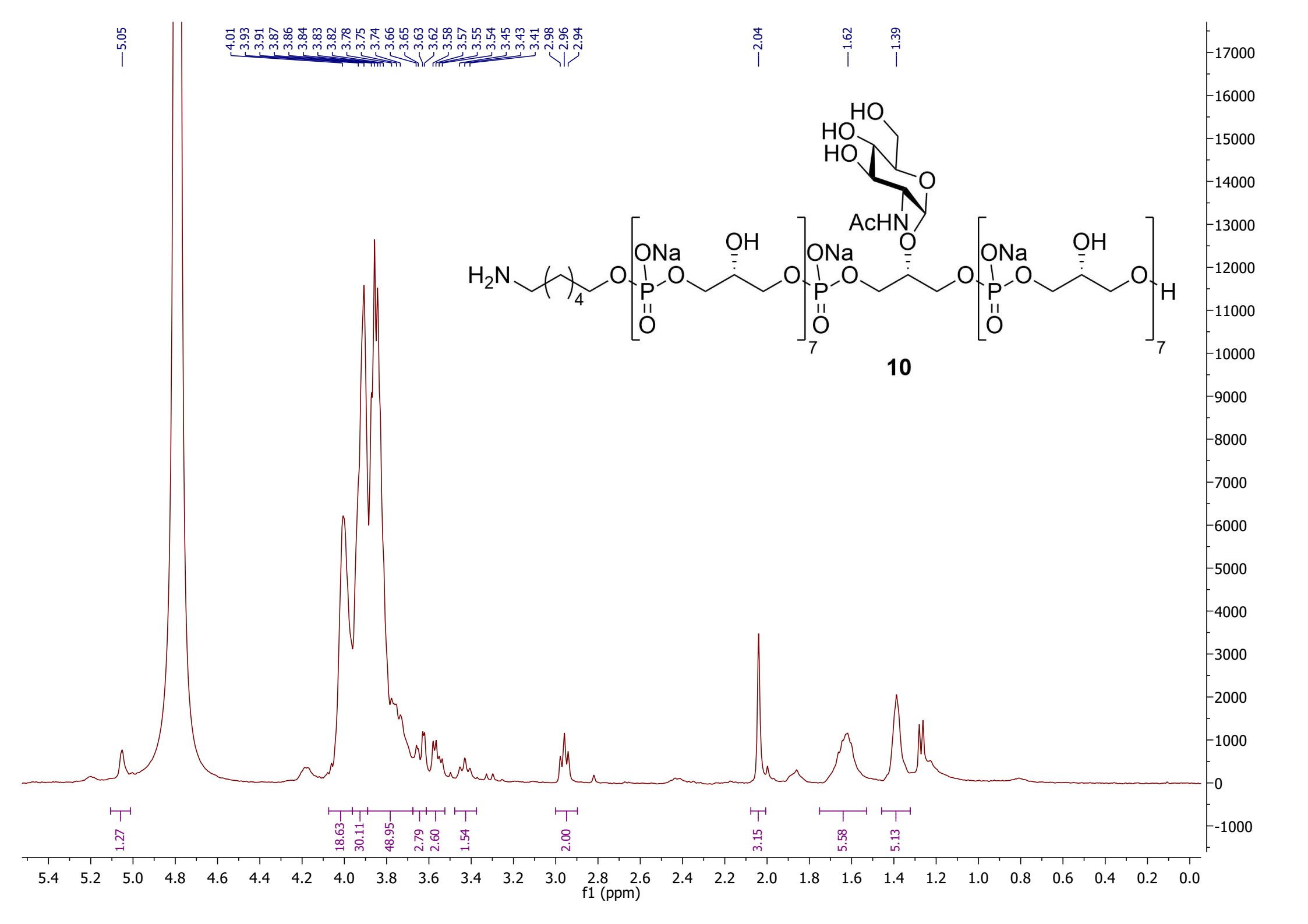

21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

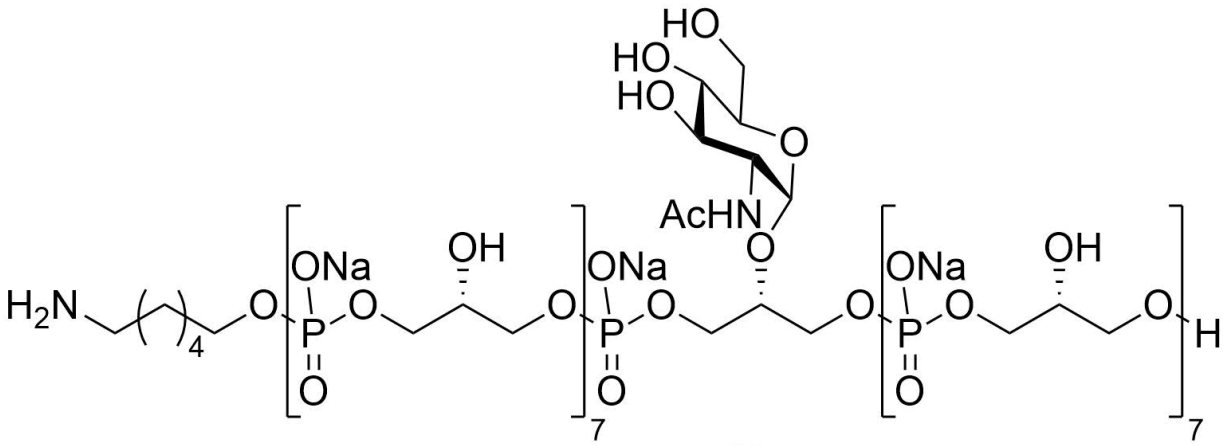

5.33
4.13
4.06
4.01
4.00
3.96
3.95
3.93
3.92
3.91
3.87
3.86
3.84
3.83
3.82
3.80
3.77
3.76
3.74
3.73
3.70
3.69
3.66
3.65
3.63
3.62
3.58
3.56
3.55
3.54
3.45
3.42
3.40
3.19
2.98
2.96
2.94
1.66
1.64
1.62
1.62
1.39
HO
HO
HO
O
H2N
O
ONa
OH
P
O
7
H
9
0.84
15.96
21.11
30.29
1.43
1.82
1.49
1.44
2.00
3.83
3.40
f1 (ppm)


HO
HO
HO
O
$H_2N$
O
$H_2N$
4
O
ONa
P
O
O
OH
O
ONa
P
O
O
O
ONa
P
O
O
OH
O
H
7
7

**9**

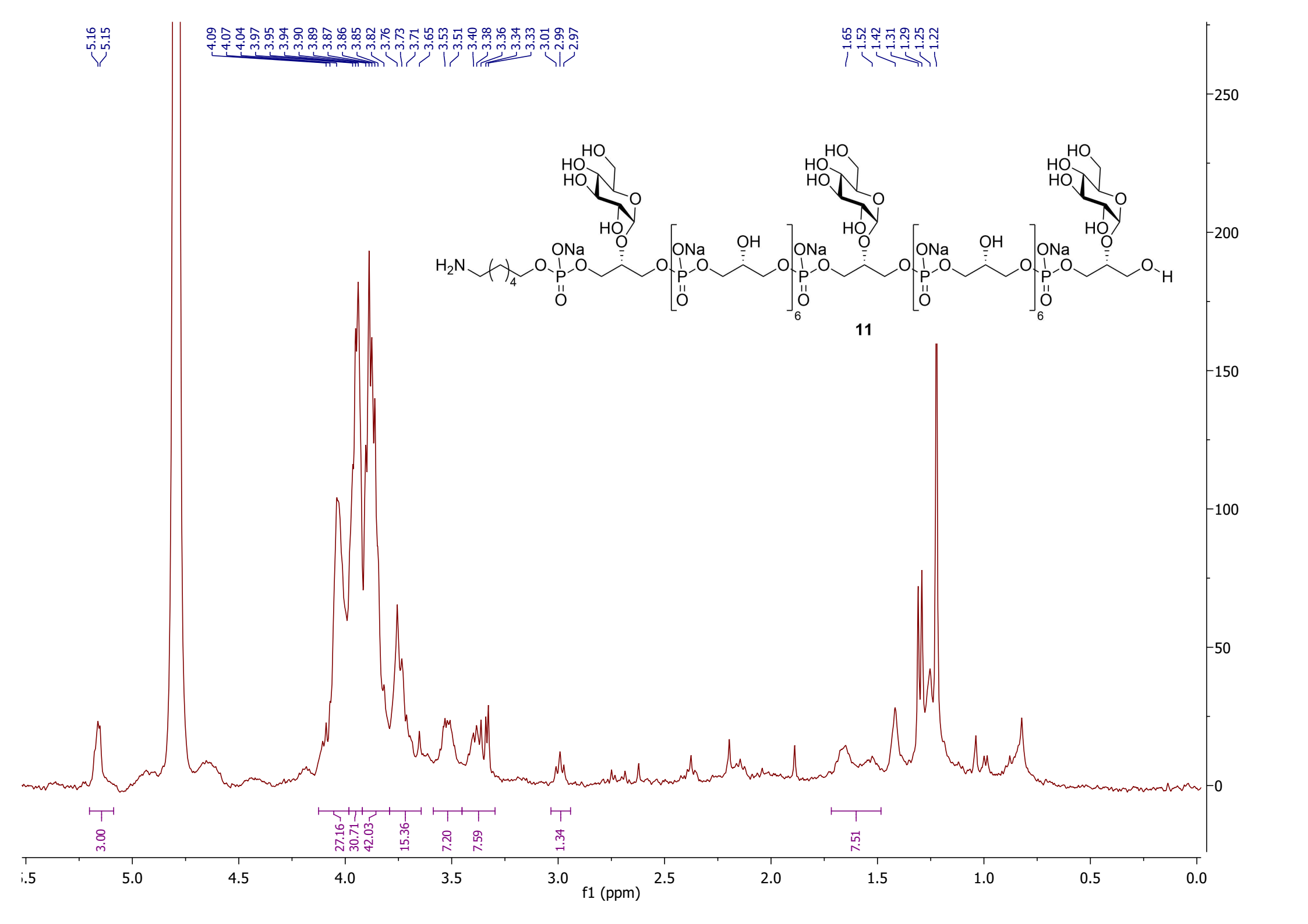

0.78
0.70
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

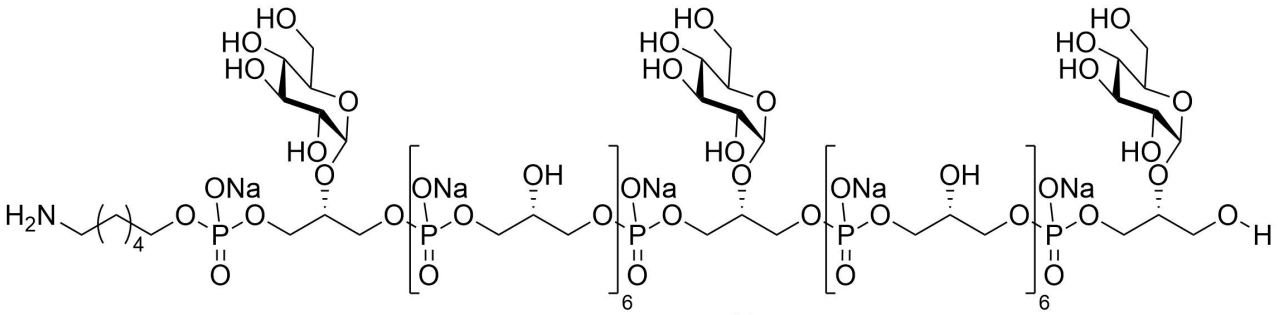

5.05
4.01
3.93
3.91
3.87
3.86
3.84
3.83
3.82
3.78
3.75
3.74
3.66
3.65
3.63
3.62
3.58
3.57
3.55
3.54
3.45
3.43
3.41
2.98
2.96
2.94
2.04
1.62
1.39
HO
HO
HO
O
AcHN
O
H2N
4
O
ONa
P
O
O
OH
7
H
10
1.27
18.63
30.11
48.95
2.79
2.60
1.54
2.00
3.15
5.58
5.13
f1 (ppm)


HO
HO
HO
O
AcHN
O
ONa
OH
ONa
ONa
OH
$H_2N$
4
O
P
O
7
H

**10**

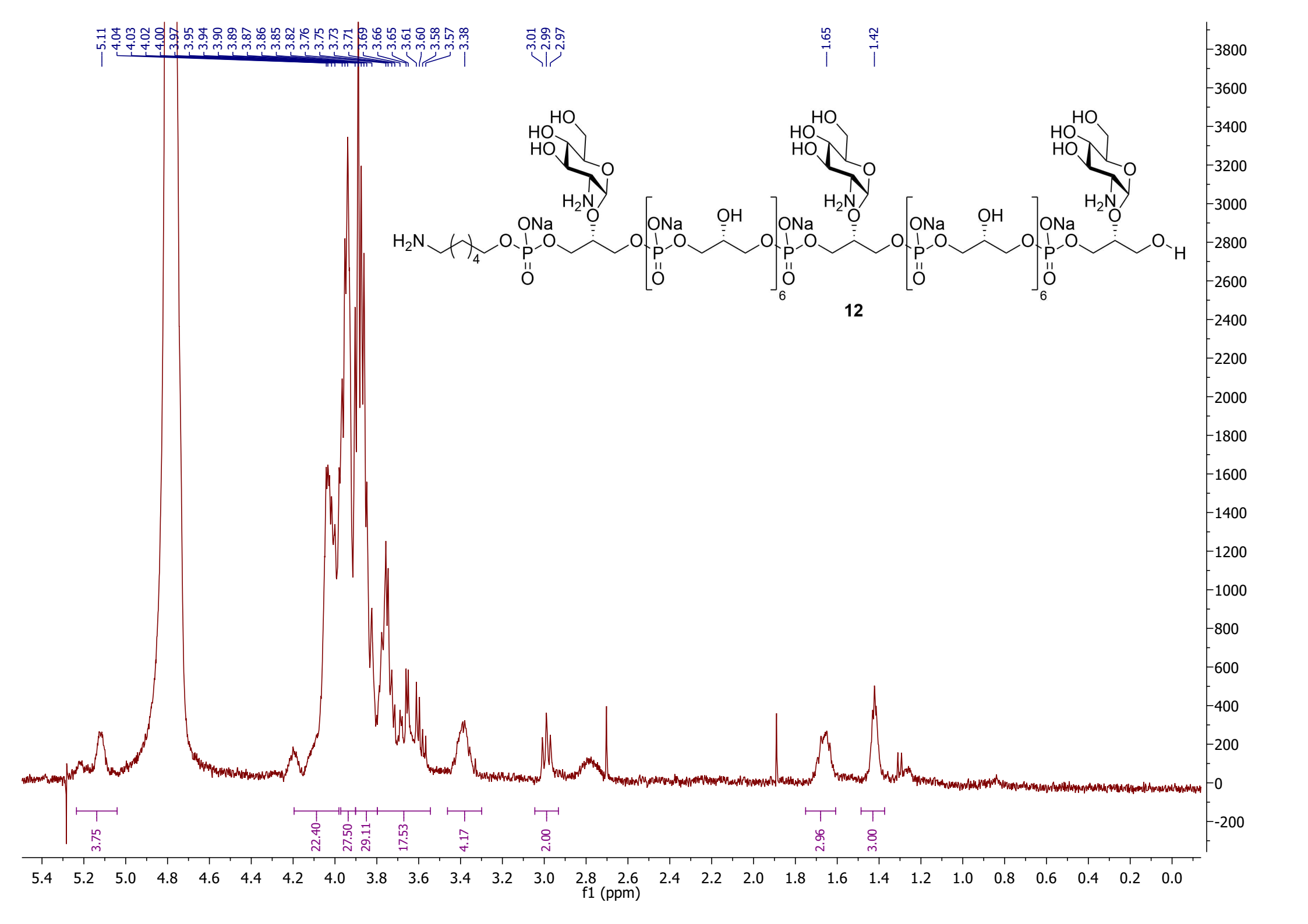

0.77
0.68
3500
3000
2500
2000
1500
1000
500
0
-500
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

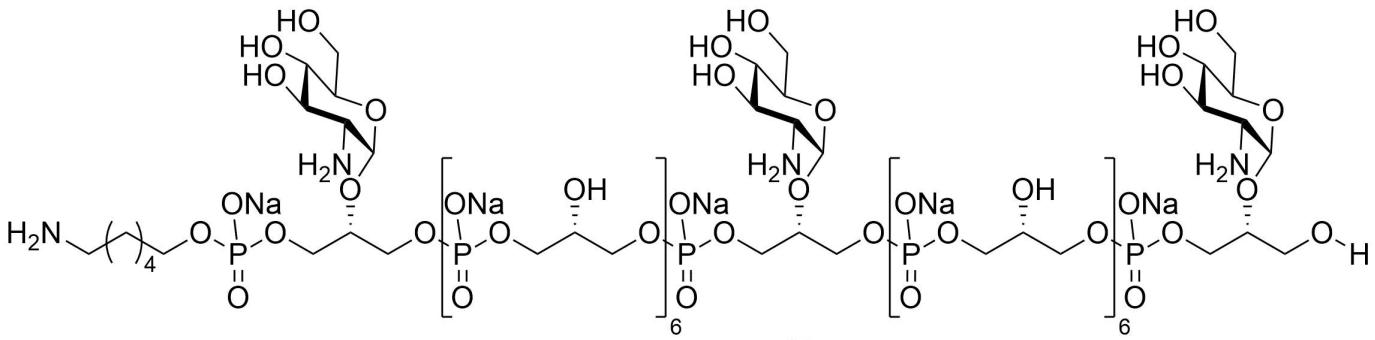

5.16
5.15
4.09
4.07
4.04
3.97
3.95
3.94
3.90
3.89
3.87
3.86
3.85
3.82
3.76
3.73
3.71
3.65
3.53
3.51
3.40
3.38
3.36
3.34
3.33
3.01
2.99
2.97
1.65
1.52
1.42
1.31
1.29
1.25
1.22
11
3.00
27.16
30.71
42.03
15.36
7.20
7.59
1.34
7.51
f1 (ppm)


HO
HO
HO
O
HO
O
ONa
OH
$H_2N$
4
P
O
6
H

**11**

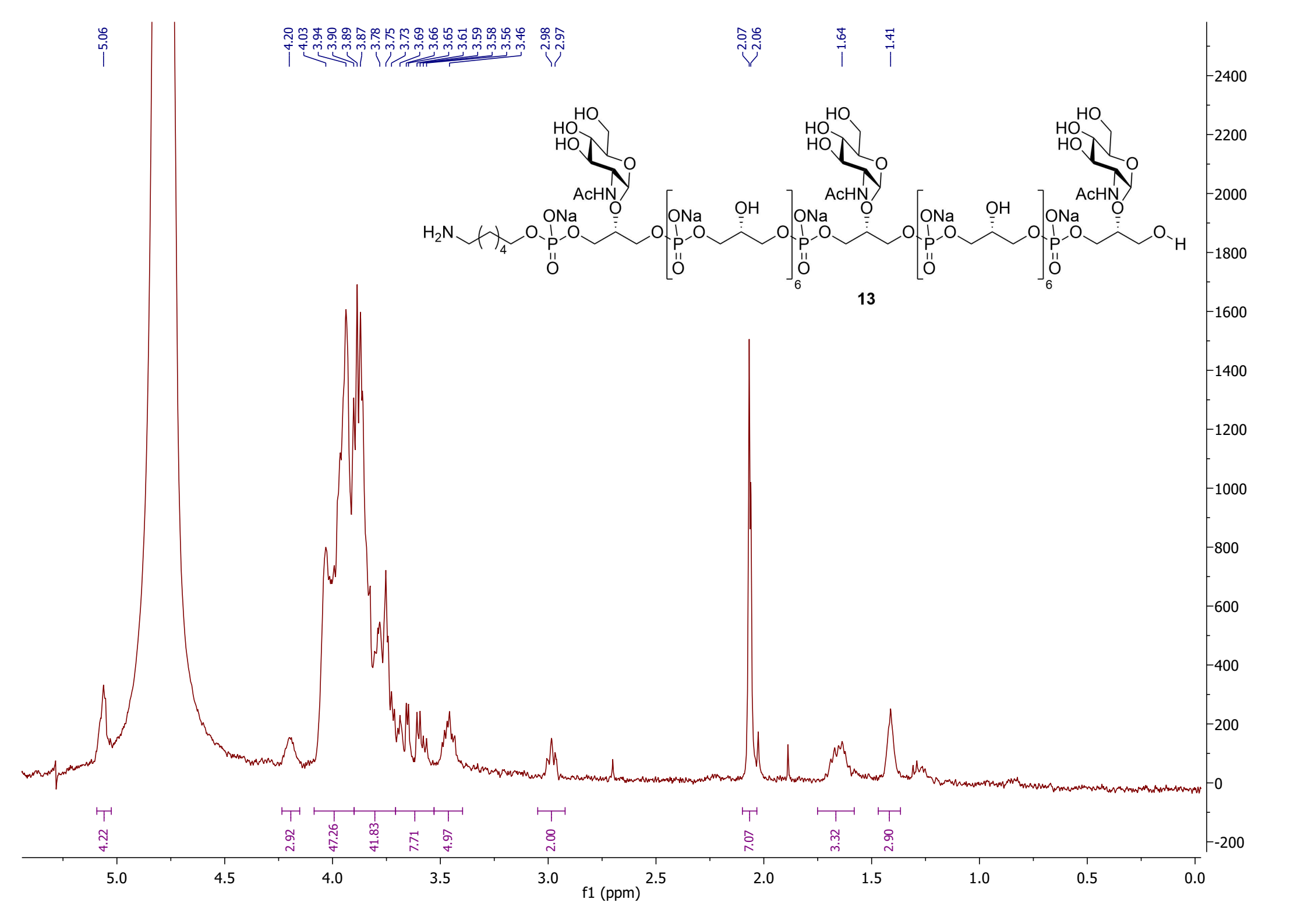

1.28
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

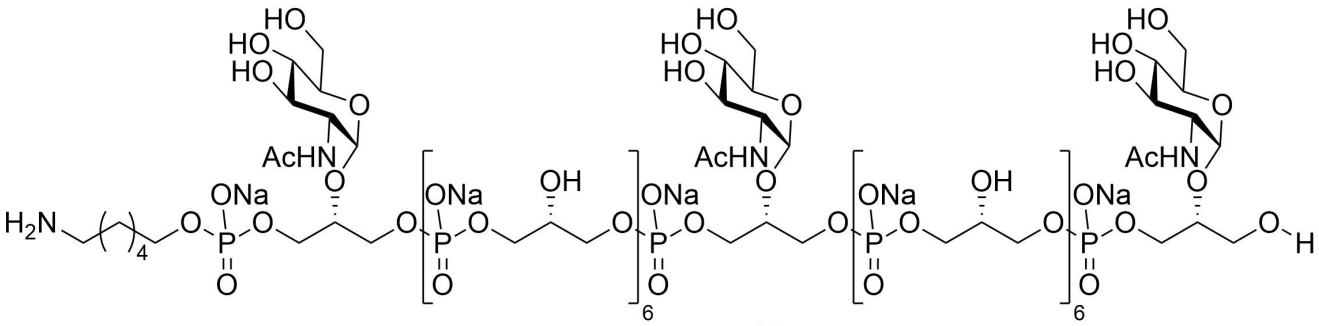

5.11
4.04
4.03
4.02
4.00
3.97
3.95
3.94
3.90
3.89
3.87
3.86
3.85
3.82
3.76
3.75
3.73
3.71
3.69
3.66
3.65
3.61
3.60
3.58
3.57
3.38
3.01
2.99
2.97
1.65
1.42
12
3.75
22.40
27.50
29.11
17.53
4.17
2.00
2.96
3.00
f1 (ppm)



**12**

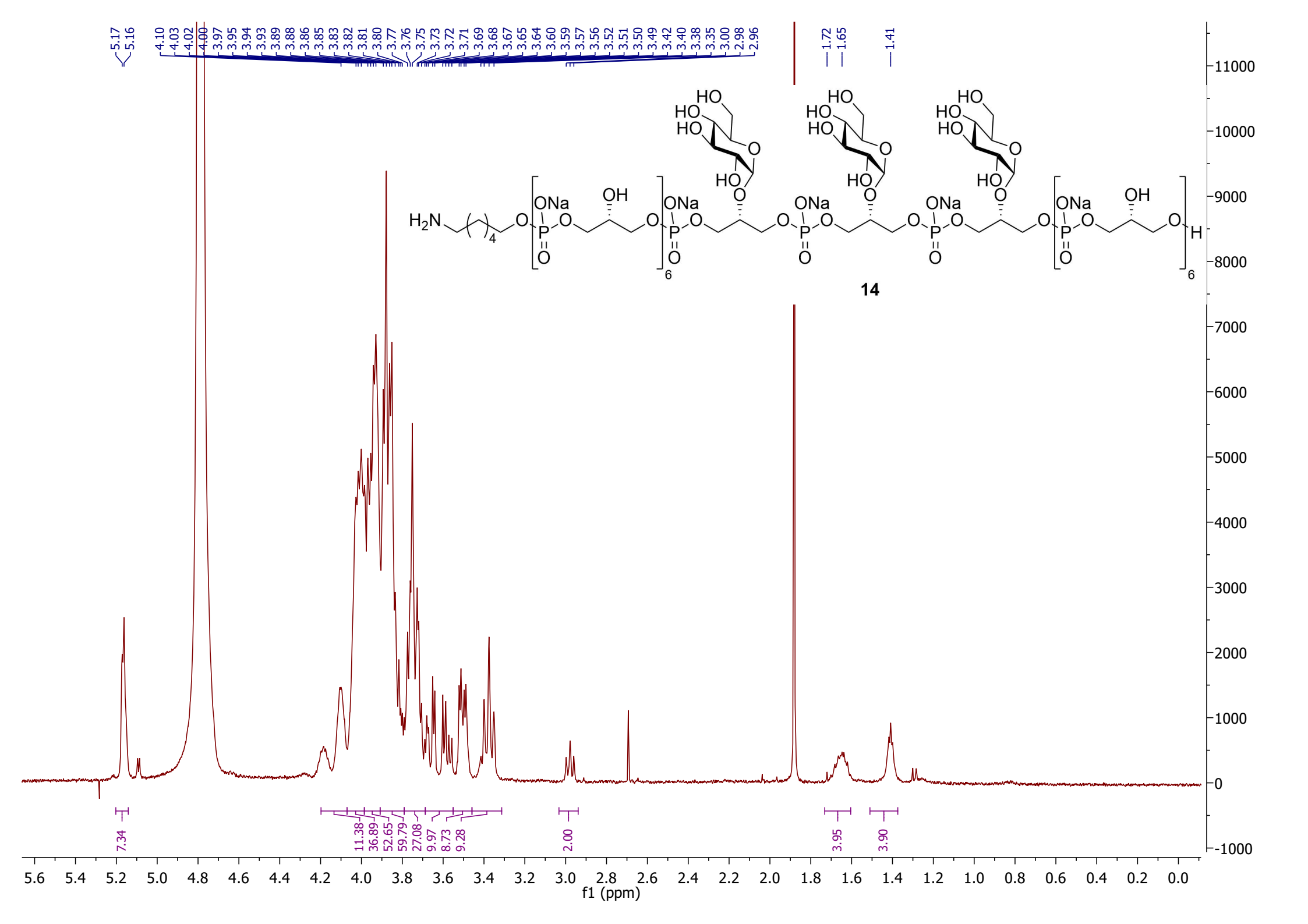

1.40
1.29
1.02
0.94
300000
250000
200000
150000
100000
50000
0
-50000
38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22
f1 (ppm)

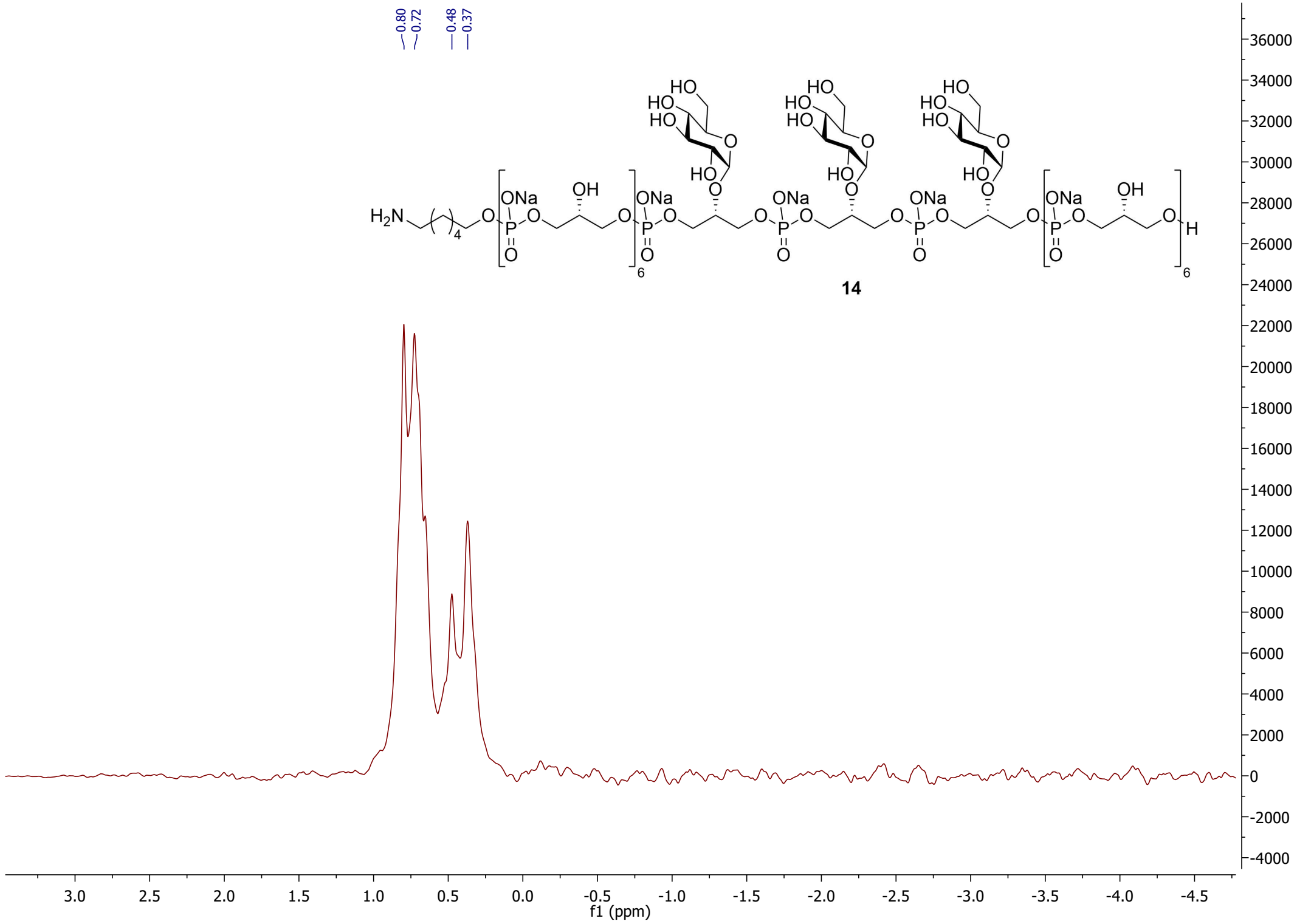

5.06
4.20
4.03
3.94
3.90
3.89
3.87
3.78
3.75
3.73
3.69
3.66
3.65
3.61
3.59
3.58
3.56
3.46
2.98
2.97
2.07
2.06
1.64
1.41
HO
HO
HO
O
AcHN
O
ONa
P
O
OH
$H_2N$
4
6
H
13
4.22
2.92
47.26
41.83
7.71
4.97
2.00
7.07
3.32
2.90
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

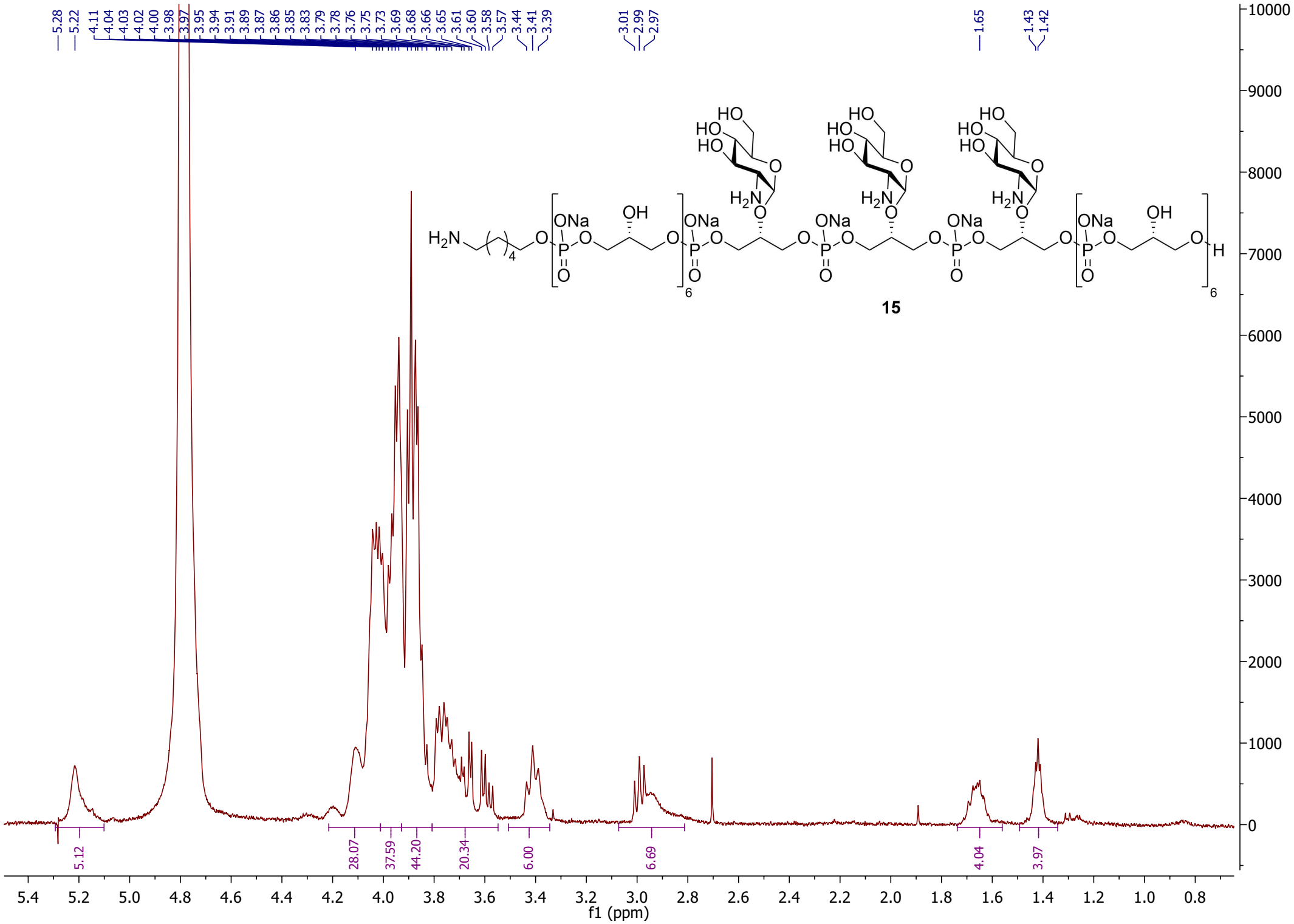


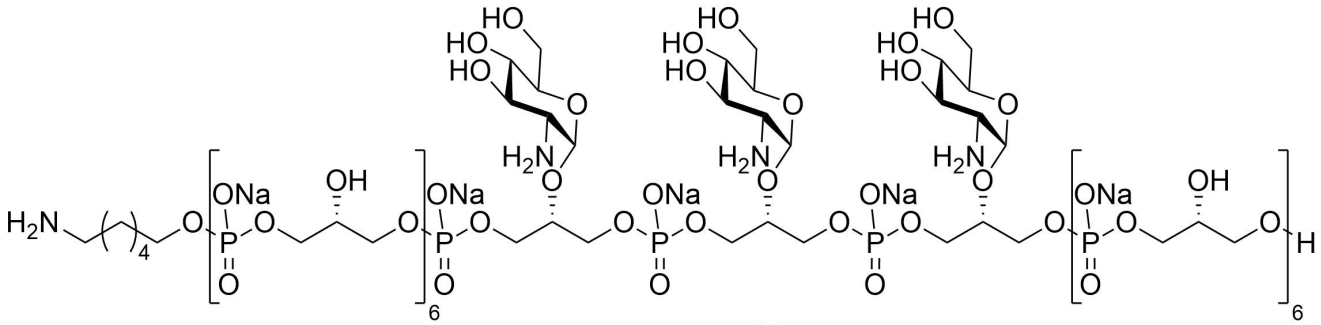
**13**


0.71
0.58
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)


5.17
5.16
4.10
4.03
4.02
4.00
3.97
3.95
3.94
3.93
3.89
3.88
3.86
3.85
3.83
3.82
3.81
3.80
3.77
3.76
3.75
3.73
3.72
3.71
3.69
3.68
3.67
3.65
3.64
3.60
3.59
3.57
3.56
3.52
3.51
3.50
3.49
3.42
3.40
3.38
3.35
3.00
2.98
2.96
1.72
1.65
1.41
HO
O
ONa
OH
P
H2N
H
6
4
14
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
7.34
11.38
36.89
52.65
59.79
27.08
9.97
8.73
9.28
2.00
3.95
3.90
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
f1 (ppm)

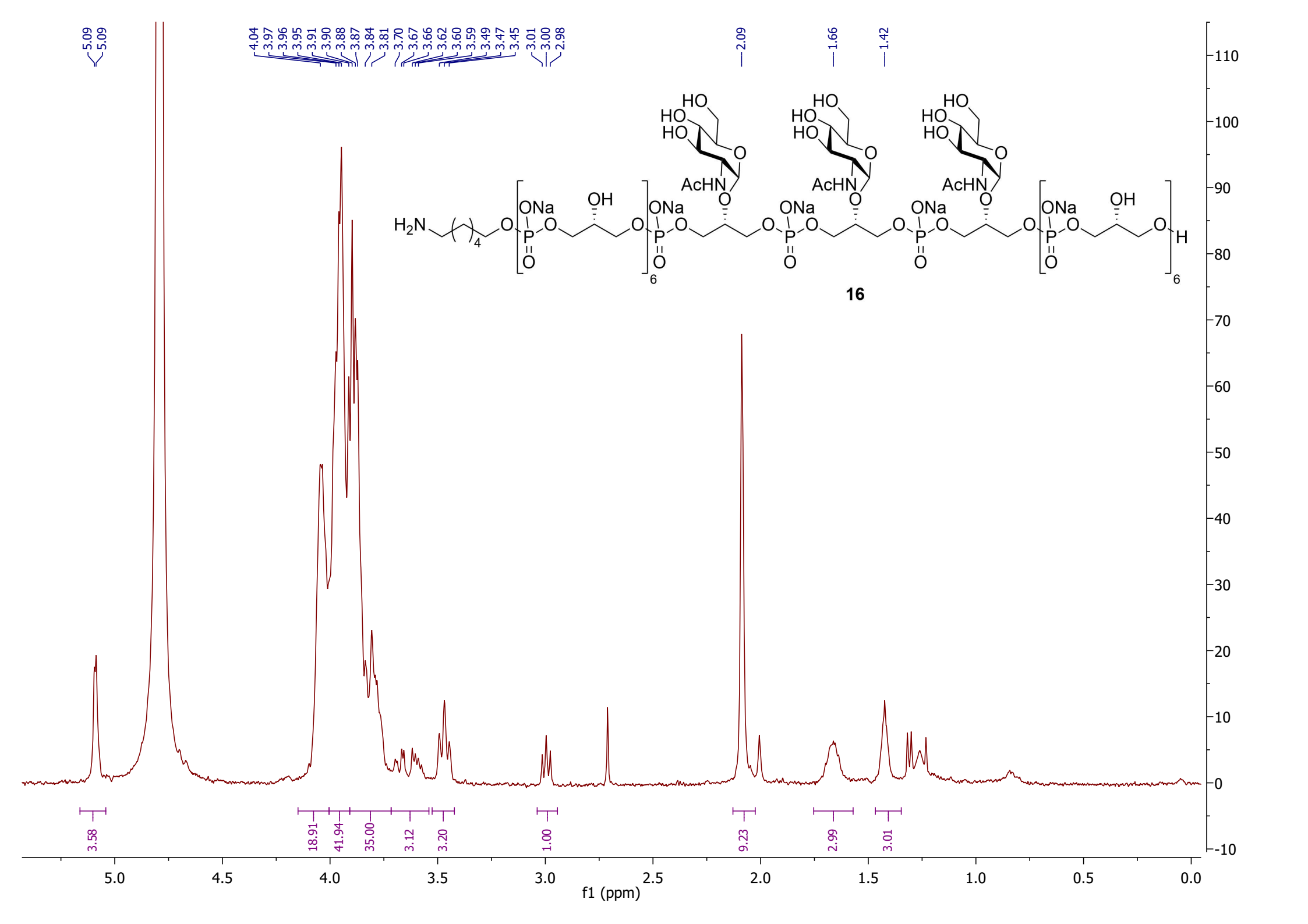

0.80
0.72
0.48
0.37
14
f1 (ppm)

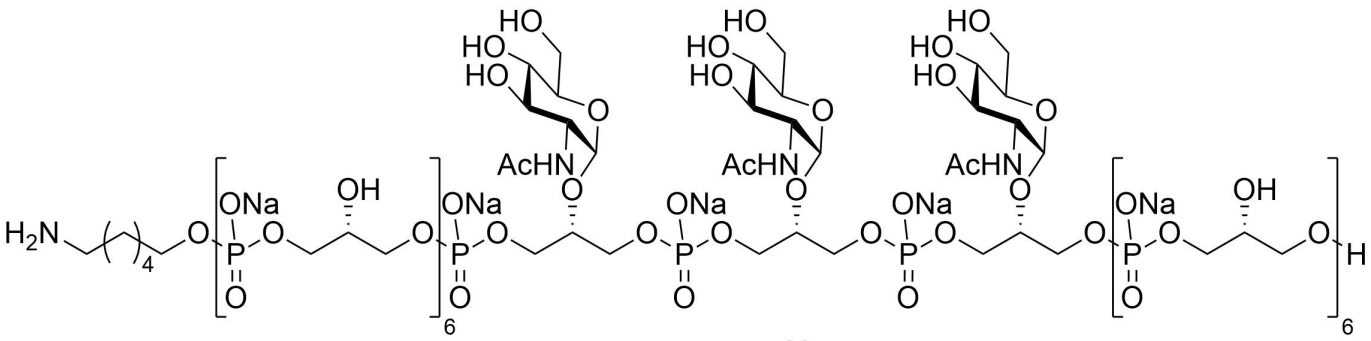

5.28
5.22
4.11
4.04
4.03
4.02
4.00
3.98
3.97
3.95
3.94
3.91
3.89
3.87
3.86
3.85
3.83
3.79
3.78
3.76
3.75
3.73
3.69
3.68
3.66
3.65
3.61
3.60
3.58
3.57
3.44
3.41
3.39
3.01
2.99
2.97
1.65
1.43
1.42
15
5.12
28.07
37.59
44.20
20.34
6.00
6.69
4.04
3.97
f1 (ppm)



**15**


0.80
0.71
0.53
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)


5.09
5.09
4.04
3.97
3.96
3.95
3.91
3.90
3.88
3.87
3.84
3.81
3.70
3.67
3.66
3.62
3.60
3.59
3.49
3.47
3.45
3.01
3.00
2.98
2.09
1.66
1.42
HO
HO
HO
O
AcHN
O
ONa
OH
O
P
O
H2N
4
6
H
16
3.58
18.91
41.94
35.00
3.12
3.20
1.00
9.23
2.99
3.01
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
110
100
90
80
70
60
50
40
30
20
10
0
-10


HO
HO
HO
AcHN
O
ONa
OH
P
O
$H_2N$
4
6
H

**16**

1.15
0.67
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)