Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Protecting group free glycosylation of phosphatidic acid in aqueous media

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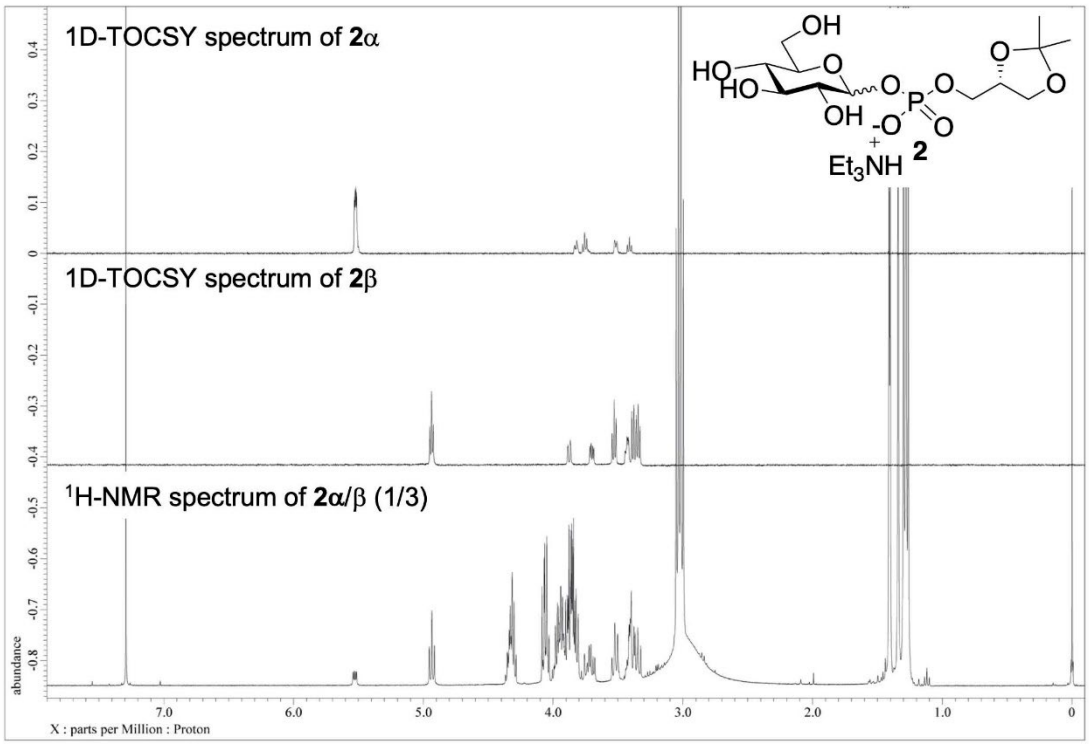
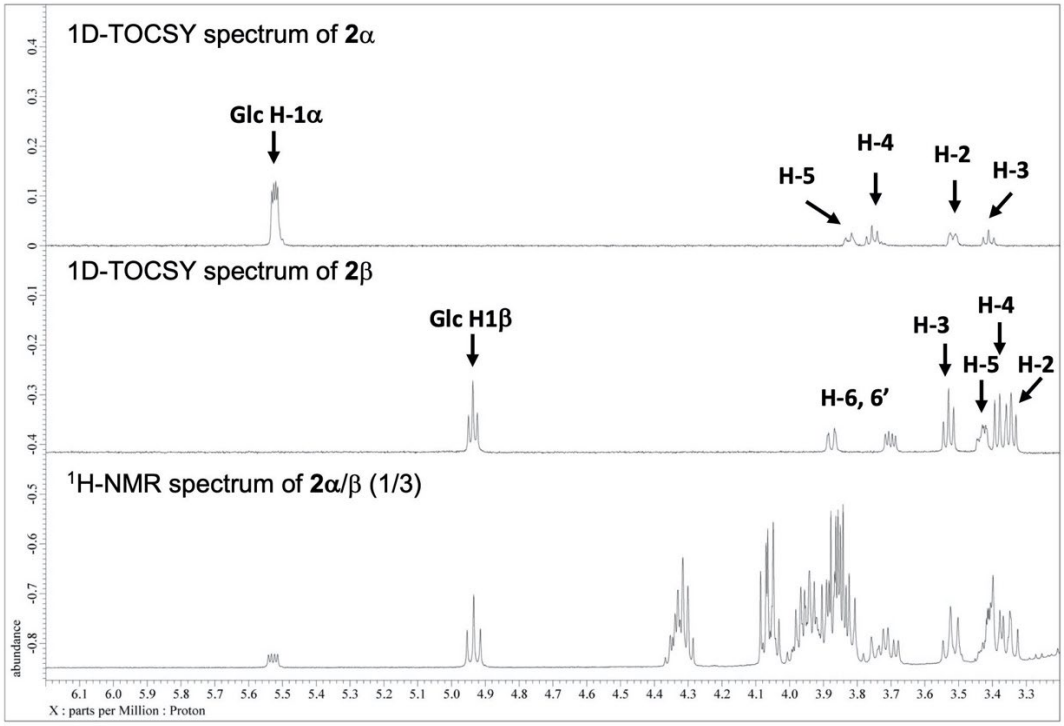
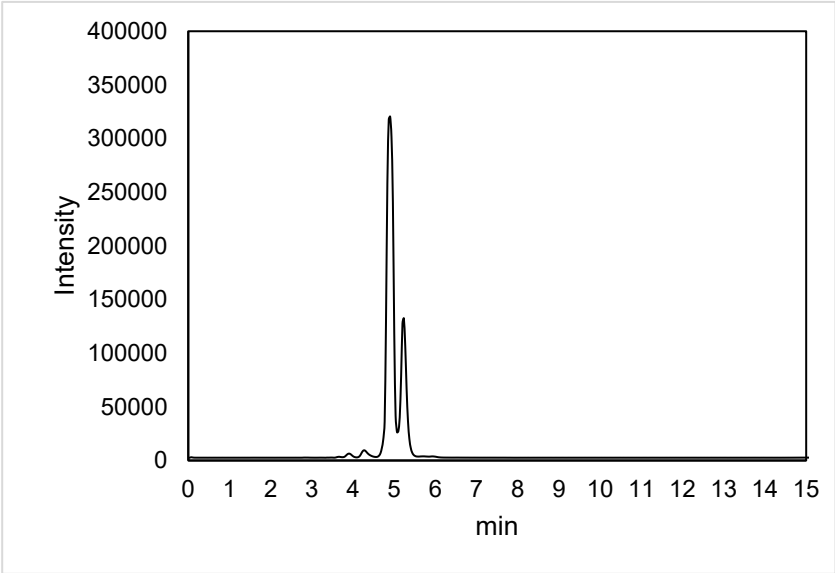


1-2. ^{1}H-NMR and 1D-TOCSY spectra of reaction mixture 2 (expansion of pyranose ring region)



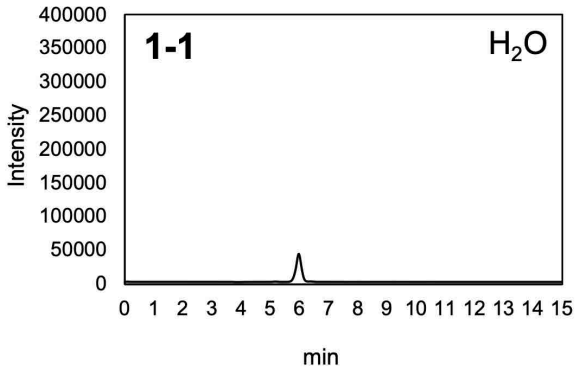
1-3. LC-MS analysis of reaction mixture 2

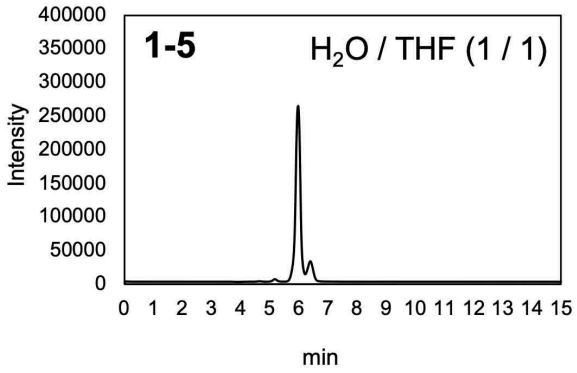


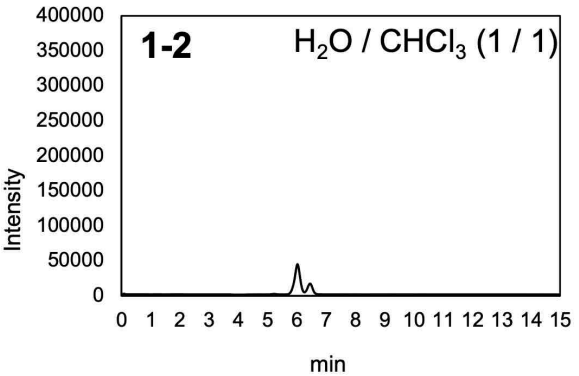
Analytical conditions: solvent system A: 5 mM ammonium formate in water pH4, solvent system B: 5 mM ammonium formate in water/acetonitrile = 5/95 v/v pH4, solvent B = 80% isocratic, column: TOSOH Amide 80, 2.0 mmI.D. x 15 cm 3 μm, flow rate: 200 uL/min, Oven temperature: 40 ^{o}C, Ionization mode: ESI negative, The MS detector was run in SIM mode, m/z = 373.10, 358.10 and 387.10, sample: The reaction mixture was diluted with 2,500 times by mixed solvent (solvent A/B=30/70) and injected 3 μL.

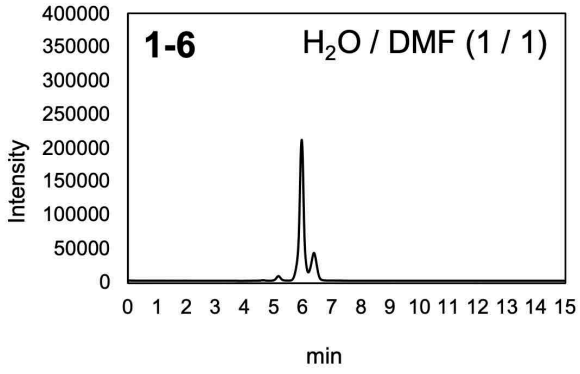
2. LCMS analysis of DMC mediated coupling reaction

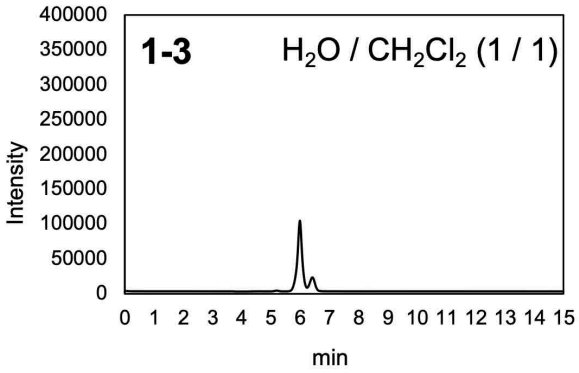
2-1. Solvent effect on coupling reaction (for Table 1 entry1-15)

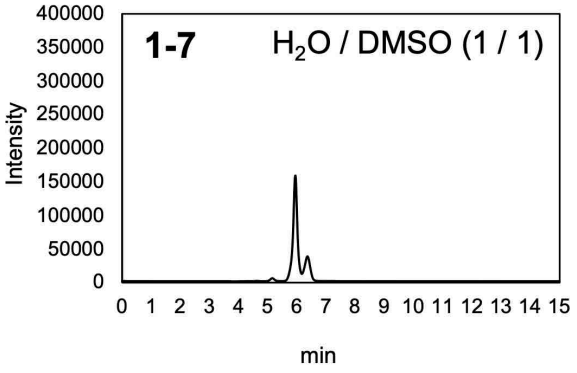


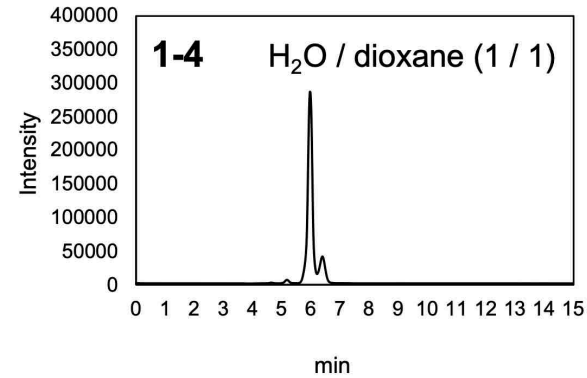


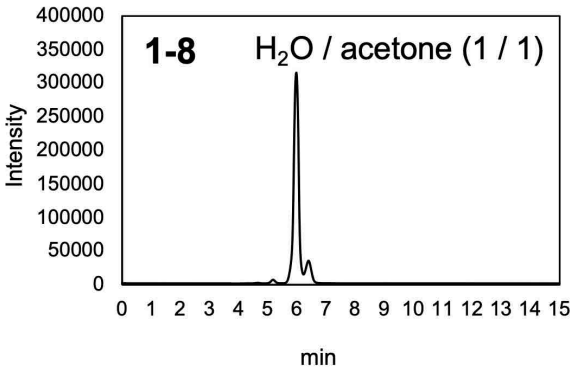


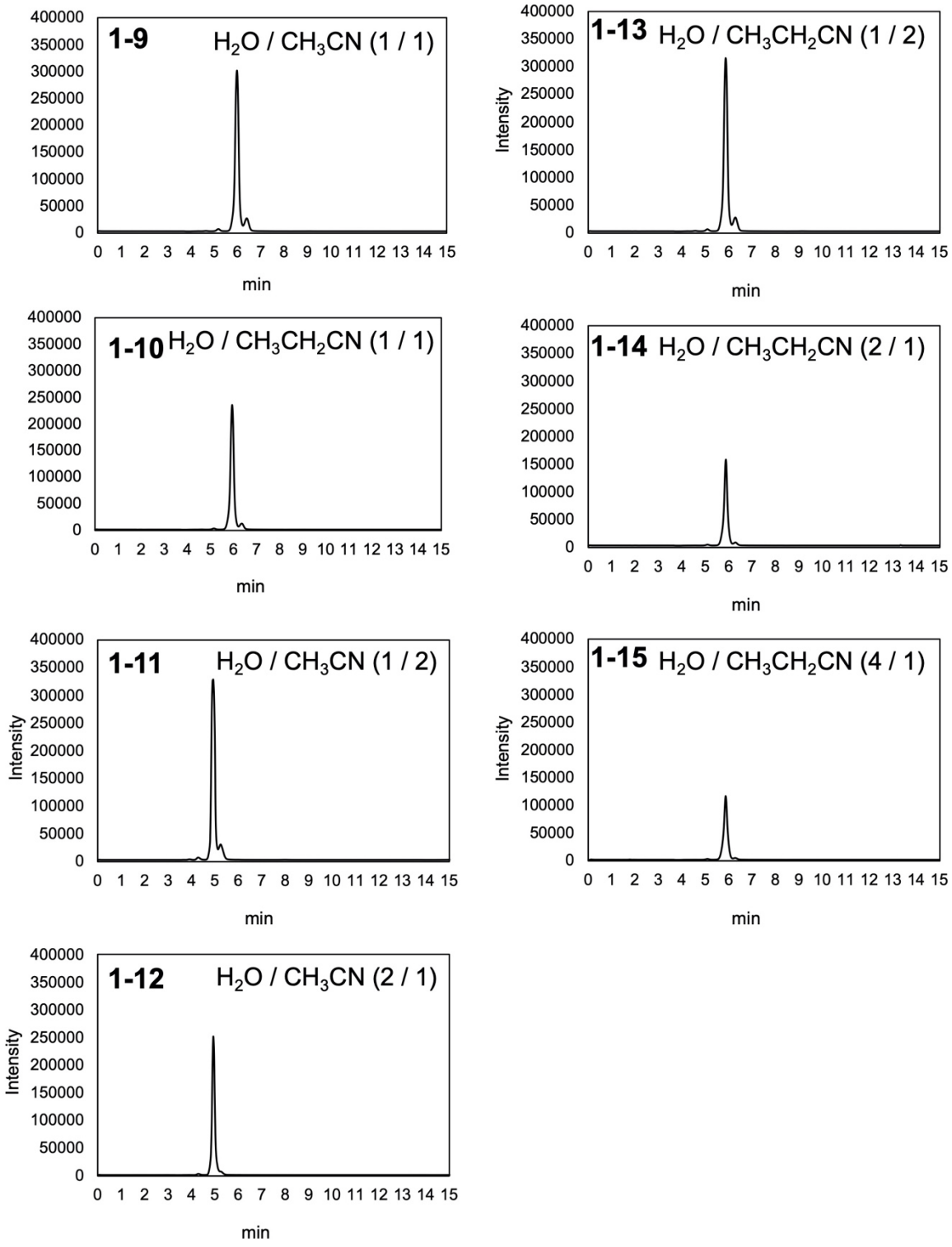








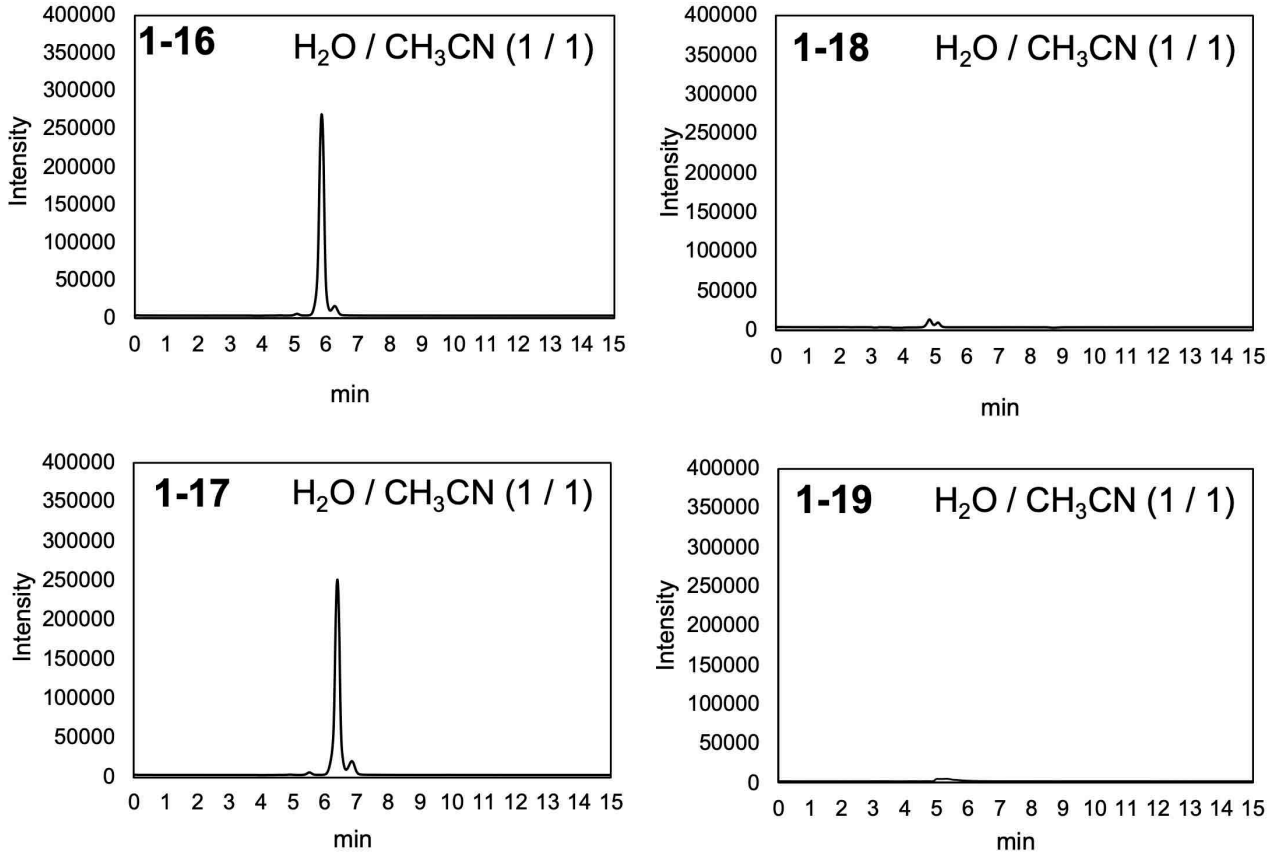




Analytical conditions: solvent system A: 5 mM ammonium formate in water pH 4, solvent system B: 5 mM ammonium formate in water/acetonitrile = 5/95 v/v, pH 4, solvent B = 80% isocratic, column: TOSOH Amide 80 3 μm, 2.0 mmI.D. x 15 cm, flow rate: 200 μL/min, column oven temperature: 40 °C, Ionization mode: ESI negative, The MS detector was run in SIM mode, m/z = 373.10, sample: The reaction mixture was diluted with 500 times by mixed solvent (solvent A/B=30/70) and injected 3 μL.

Figure S1

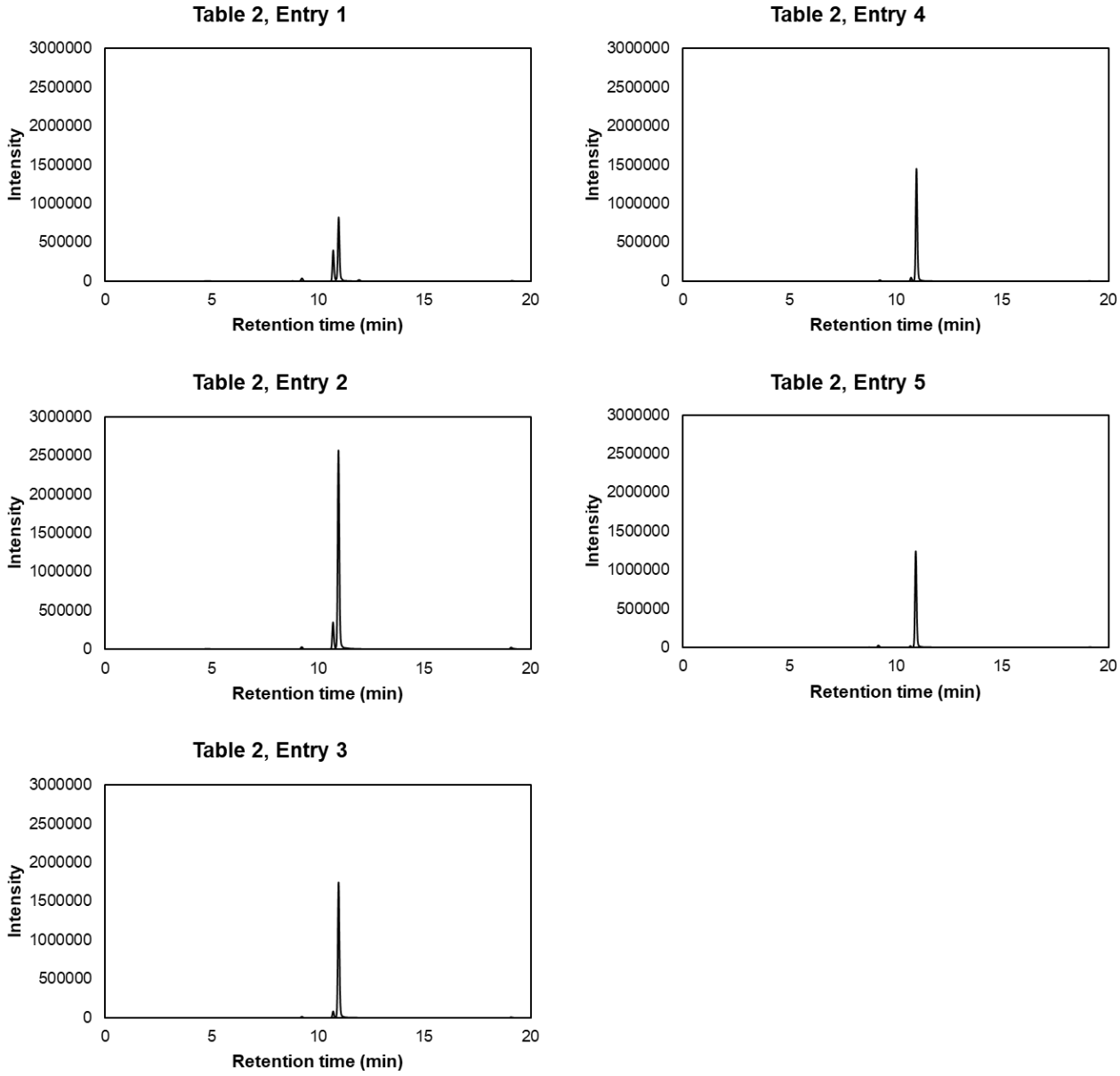
2-1-2. Solvent effect on coupling reaction (for Table 1 entry16-19)



Analytical conditions: solvent system A: 5 mM ammonium formate in water pH 4, solvent system B: 5 mM ammonium formate in water/acetonitrile = 5/95 v/v, pH 4, solvent B = 80% isocratic, column: TOSOH Amide 80 3 μm, 2.0 mmI.D. x 15 cm, flow rate: 200 μL/min, column oven temperature: 40 °C, Ionization mode: ESI negative, The MS detector was run in SIM mode, m/z = 373.10 for entry 16,17, m/z = 357.10 for entry 18, and m/z = 387.10 for entry 19, sample: The reaction mixture was diluted with 500 times by mixed solvent (solvent A/B=30/70) and injected 3 μL.

Figure S2

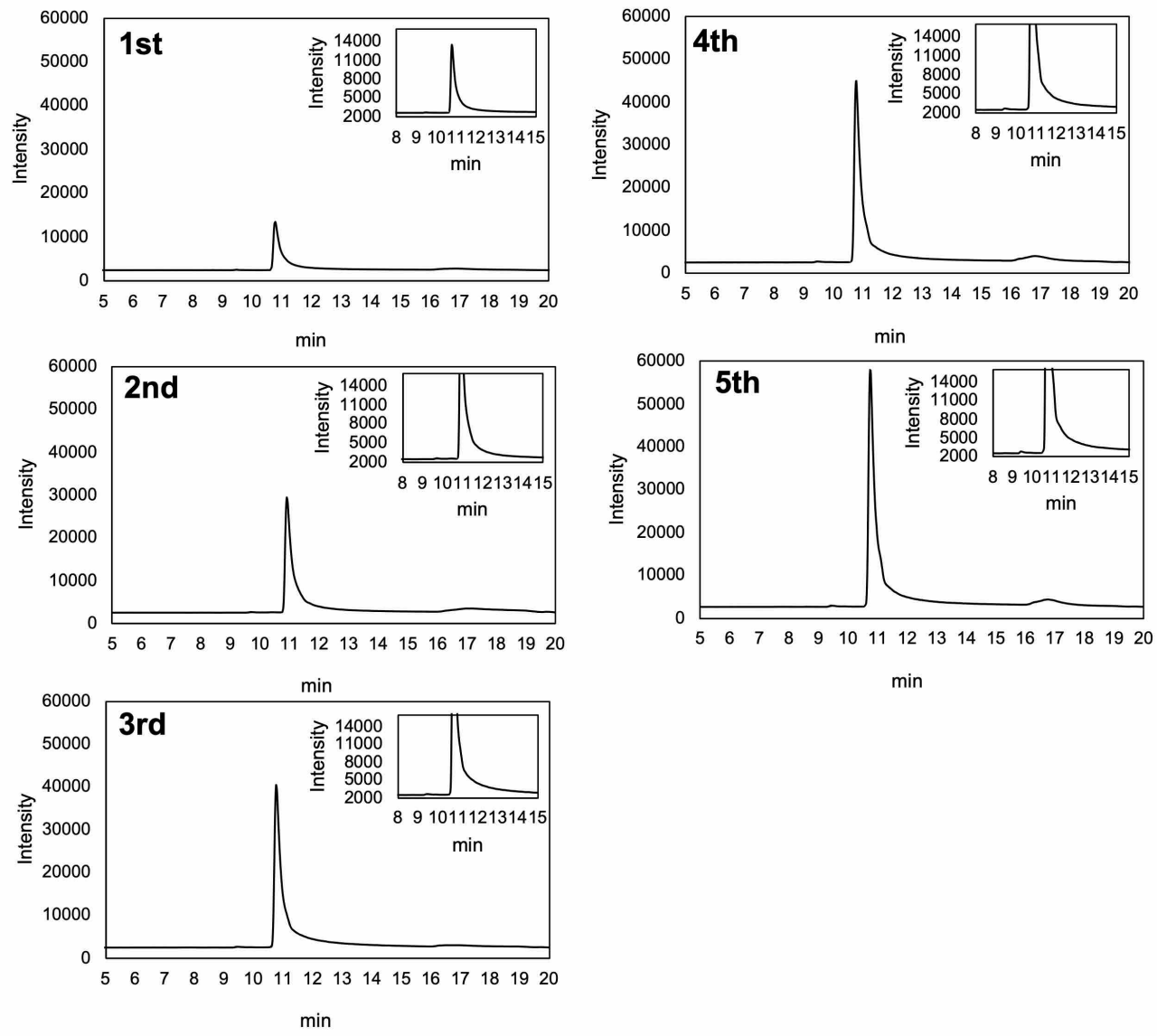
2-2. Solvent effect on coupling reaction for the synthesis of PtdGlc (**4**) analyzed by supercritical fluid chromatography triple quadrupole mass spectrometry (SFC/QqQMS).



Analytical conditions: Analytical conditions: mobile phase A: CO_2, mobile phase B: 0.1% w/v ammonium acetate in MeOH/H_2O = 95/5 v/v, mobile phase B = 1% (0-1 min), 1-65% (1-12 min), 65% (12-18 min), 65-1% (18-18.1min), 1% (18.1-20min), column: Waters Torus DEA, 1.7 µm, 3.0 mm I.D. x 10 cm, flow rate: 1 mL/min, Oven temperature: 50 °C, back pressure: 10 MPa, ionization mode: ESI negative, The MS/MS detector was run in MRM mode, m/z = 893.5 > 283.2, sample: The reaction mixture was diluted with 50,000 times by MeOH and injected 1 µL.

Figure S3

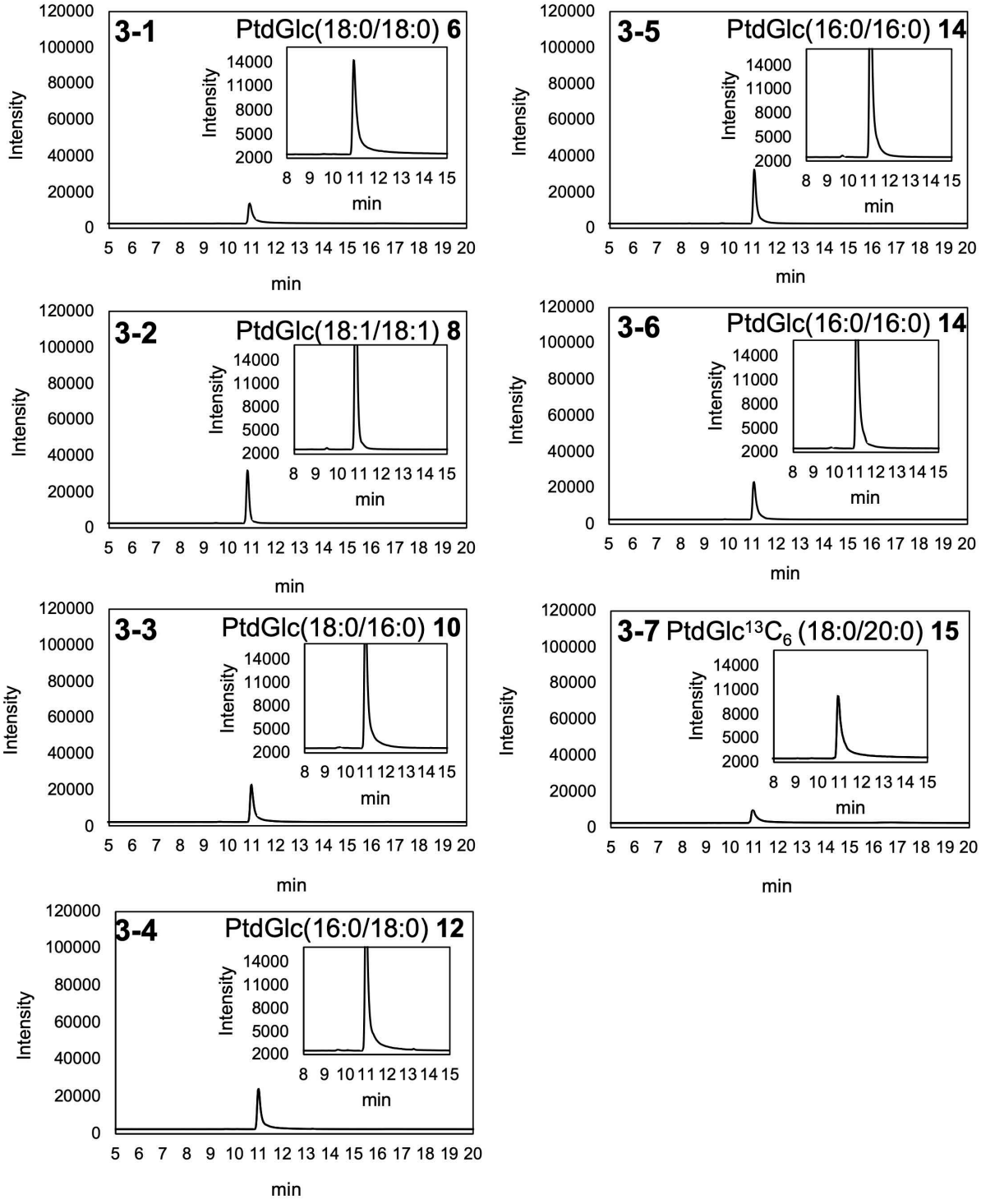
2-3. Stepwise addition of DMC and glucose (for Figure 1).



Analytical conditions: solvent system A: 5 mM ammonium formate in water/methanol/acetonitrile = 1/3/96 v/v pH 7, solvent system B: 20 mM ammonium formate in water/methanol = 10/90 v/v pH 7, solvent B = 0-20% gradient, 15min, column: Waters BEH Amide 2.1 mm I.D. x 15 cm, 1.7 µm, flow rate: 600 µL/min, Oven temperature: 40 °C, Ionization mode: ESI negative, The MS detector was run in SIM mode, m/z = 893.61, sample: The reaction mixture was diluted with 500 times by mixed solvent (solvent A/B=30/70) and injected 3 µL.

Figure S4

2-4. Synthesis of PtdGlc derivatives (for Table 3).



Analytical conditions: solvent system A: 5 mM ammonium formate in water/methanol/acetonitrile = 1/3/96 v/v, pH 7, solvent system B: 20 mM ammonium formate in water/methanol = 10/90 v/v, pH 7, solvent B = 0-20% gradient, 15min, column: Waters BEH Amide 2.1 mm I.D. x 15 cm, 1.7 µm, flow rate: 600 µL/min, Oven temperature: 40 °C, Ionization mode: ESI negative, The MS detector was run in SIM mode, m/z = 865.58 for entry 1, 861.54 for entry 2, 850.55 for entry 3 and 4, 809.52 for entry 5-7, and 837.55 for entry 8, sample: The reaction mixture was diluted with 50,000 times by MeOH and injected 1 µL.

Figure S5

3. Experimental Procedure

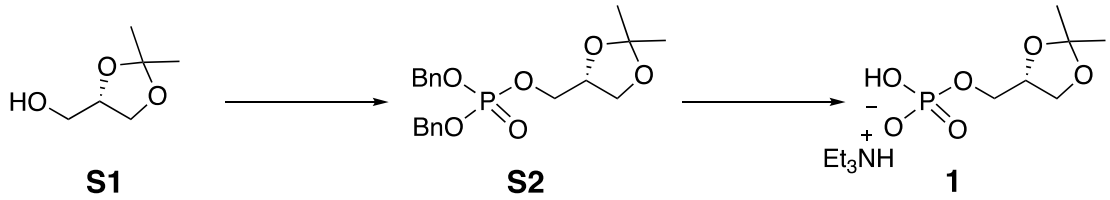
3-1. General information

All reactions sensitive to moisture were carried out under anhydrous conditions using argon atmosphere and anhydrous solvents, unless stated otherwise. Solvents and other reagents were purchased from Kanto Chemical Co., Inc (Tokyo, Japan), Tokyo Chemical Industry (Tokyo, Japan) and Wako Pure Chemical Industries Ltd. (Tokyo, Japan) and used without further purification. 1,2-di-*O*-palmityl-*sn*-glycerol-3-phosphate sodium salt was purchased from Sigma-Aldrich-Merck (Darmstadt, Germany). Analytical thin layer chromatography was developed on TLC Silica gel 60 F_{254} plate (Merck, Darmstadt, Germany). Silica gel column chromatography was performed on Silica gel 60 N (40–100 mesh or 100–210 mesh, Kanto Chemical Co., Inc, Tokyo, Japan), Hi-Flash column (YAMAZEN, Osaka, Japan), or Iatrobeads 6RS-8060 Mitsubishi Chemical Medience Co., Tokyo, Japan). High-performance liquid chromatograph (HPLC) was performed on a Shimadzu Prominence HPLC system equipped with a UV detector SPD-20A (Shimadzu Co., Ltd., Kyoto, Japan). ESI-MS were recorded in negative ion mode on an LCMS-2020 equipped with a Nexera X2 HPLC system (Shimadzu Co., Ltd., Kyoto, Japan). MALDI-TOF MS were recorded in high-resolution mode with positive or negative ion mode, as indicated, on an AXIMA-Performance (Shimadzu Co., Ltd., Kyoto, Japan). High-resolution mass spectrometry was performed on a Waters Synapt G2-S HDMS spectrometer. NMR spectra were recorded with a JEOL ECA-600 spectrometer (JEOL, Tokyo, Japan; ^{1}H: 600 MHz, ^{13}C: 150 MHz, ^{31}P: 243 MHz). ^{1}H NMR spectra were referenced to TMS (0.00 ppm), ^{13}C NMR spectra were referenced to the central peak of $CDCl_3$ (77.16 ppm) and ^{31}P NMR spectra were referenced to 85% H_3PO_4 (0.00 ppm). The relative alpha anomer content was determined as the respective integral ratio (R) of the anomeric signals in the 1H NMR spectrum. The signal to noise ratio (SNR) of each signal was calculated with Delta software (JEOL). The relative uncertainty of the ratio R ($\Delta R/R$) was estimated according to

$$\frac{\Delta R}{R} = \sqrt{\left(\frac{1}{SNR_A}\right)^2 + \left(\frac{1}{SNR_B}\right)^2}$$

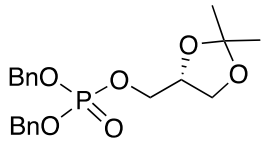
where SNR_A and SNR_B are the signal to noise ratio of the alpha and beta anomeric signals respectively. The lower limit of detection was defined as SNR>3. ^{1}H NMR signals marked with a triangle are derived from LH20.

3-2. Synthesis of triethylammonium (*R*)-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl hydrogen phosphate: **1**



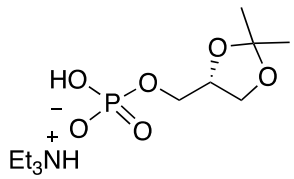
S1 **S2** **1**

3-2-1. dibenzyl [(*R*)-2,2-dimethyl-1,3-dioxolan-4-yl]methyl phosphate: **S2**



To a solution of (*S*)-(+)-(2,2-dimethyl-1,3-dioxolan-4-yl)methanol **S1** (250 mg, 1.89 mmol) in 19 mL of dry CH_2Cl_2 was added dibenzyl diisopropylphosphoramidite (1.89 mL, 1.96 g, 5.67 mmol) and 1*H*-tetrazole (469 mg, 6.69 mmol) at 0 °C and stirred at 25 °C for 30 min. The reaction mixture was cooled to 0°C and treated with 2 mL of 35% aq. H_2O_2 and subsequently warmed to 25 °C and stirred for 30 min. The resulting mixture was diluted with $CHCl_3$ and washed with saturated aq. $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was purified by flash silica gel column chromatography with hexane/EtOAc (100/0 to 1/100, *v/v*) to give **S2** (618 mg, 1.57 mmol, 83% in 2 steps); R_f = 0.20 (hexane/EtOAc = 2/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38-7.32 (m, 10H, Ar), 5.09-5.02 (m, 4H, -CH_2Ph), 4.23-4.19 (m, 1H, *sn*-2), 4.02-3.97 (m, 2H, *sn*-3$_a$, *sn*-1$_a$), 3.94-3.91 (m, 1H, *sn*-3$_b$), 3.74-3.72 (m, 1H, sn-1$_b$), 1.38 (s, 3H, -C(CH_3)$_2$), 1.33 (s, 3H, -C(CH_3)$_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.86, 135.81 (*ipso*), 128.74, 128.14 (Ar), 109.97 (-*C*(CH$_3$)$_2$), 74.05 (d, $^3J_{CP}$ = 8.7 Hz, *sn*-2), 69.57 (d, $^2J_{CP}$ = 5.7 Hz, -*C*H$_2$Ph), 67.58 (d, $^2J_{CP}$ = 5.7 Hz, *sn*-3), 66.25 (*sn*-1), 26.84 (-C(*C*H$_3$)$_2$), 25.38 (-C(*C*H$_3$)$_2$); ^{31}P NMR (243 MHz, $CDCl_3$) δ -0.43 ppm; MALDI-TOF MS calcd for $C_{20}H_{25}NaO_6P$ $[M+Na]^+$ *m/z* 415.13, $C_{20}H_{25}KO_6P$ $[M+K]^+$ *m/z* 431.10, found *m/z* 415.62, 431.63.

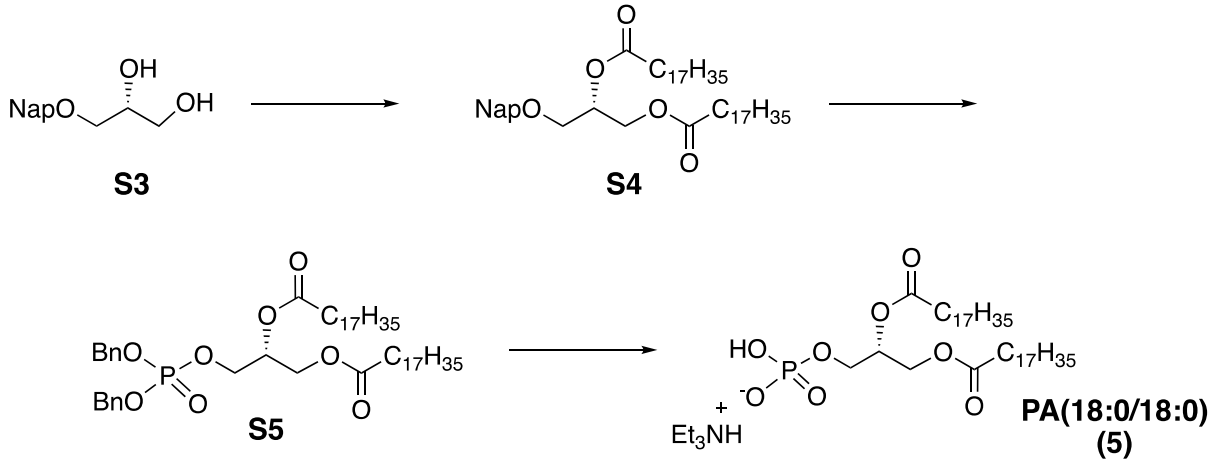
3-2-2. (*R*)-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl hydrogen phosphate triethylammonium salt: **1**



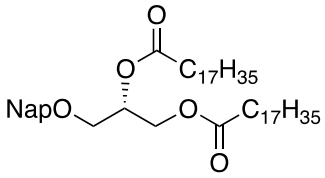
A suspension of 10% Pd/C catalyst (256 mg) in 30 mL of EtOH containing the compound **S2** (618 mg, 1.57 mmol) was stirred at 35 °C for 11 h under a hydrogen atmosphere. Subsequently, TEA (240 μL) was added at 0 °C and the resulting mixture was stirred for 1 h. The suspension was filtered over a bed of Celite, and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Iatrobeads 6RS-8060 No.1104) with $CHCl_3$/MeOH/H_2O/TEA (100/0/0/1, 89/11/0/0.2, 80/20/0/0.2, 67/33/5/0.2, *v/v*) to give **1** (460 mg, 1.47 mmol, 93%); R_f = 0.50 ($CHCl_3$/MeOH = 1/1, 1% TEA); ^{1}H NMR (600 MHz, $CDCl_3$, CD_3OD 3%) δ 4.34-4.30 (m, 1H, *sn*-2), 4.08-4.06 (m, 1H, *sn*-1$_a$), 3.99-3.95 (m, 1H, *sn*-3$_a$), 3.87-3.84 (m, 2H, *sn*-1$_b$, *sn*-3$_b$), 3.10-3.06 (m, 6H,

N-(C*H*$_2$-CH$_3$)$_3$), 1.40 (s, 3H, -C(C*H*$_3$)$_2$), 1.34 (s, 3H, -C(C*H*$_3$)$_2$), 1.31 (t, 9H, *J* = 7.2 Hz, *J* = 7.2 Hz, N-(CH$_2$-C*H*$_3$)$_3$); ^{13}C NMR (150 MHz, $CDCl_3$, CD_3OD 3%) δ 109.26 (-*C*(CH$_3$)$_2$), 74.87 (d, $^3J_{CP}$ = 8.6 Hz, *sn*-2), 67.20 (*sn*-1), 65.84 (d, $^2J_{CP}$ = 5.9 Hz, *sn*-3), 45.60 (N-(*C*H$_2$-CH$_3$)$_3$), 26.97 (-C(*C*H$_3$)$_2$), 25.54 (-C(*C*H$_3$)$_2$), 8.63 (N-(CH$_2$-*C*H$_3$)$_3$); ^{31}P NMR (243 MHz, $CDCl_3$, CD_3OD 3%) δ 2.00 ppm; ESI MS calcd for $C_6H_{12}O_6P$ [M-NHEt$_3$]$^-$ *m/z* 211.04, found *m/z* 211.08.; HRMS calcd for [$C_6H_{12}O_6P$]$^-$ requires *m/z* 211.0376; found 211.0369.

3-3. Synthesis of PA(18:0/18:0): **5**

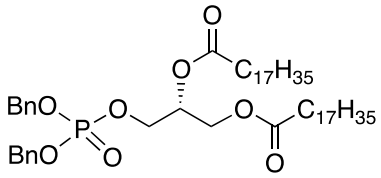


3-3-1. 1, 2-di-*O*-stearoyl-3-*O*-(2-naphtylmethyl)-*sn*-glycerol: **S4**



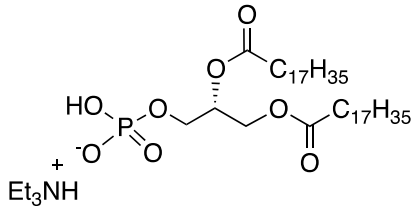
A mixture of 3-O-(2-Naphthylmethyl)-sn-glycerol [Ref S1] (**S3**) (104 mg, 448 μmol), stearic acid (277 mg, 974 μmol) and DMAP (36 mg, 295 μmol) in dry CH_2Cl_2 (13 mL) was treated with EDC (182 mg, 949 μmol) at 0 °C under argon. The mixture was warmed to 40 °C and stirred at 40 °C for 14 h. The reaction was quenched with CH_3OH at 0 °C. The mixture was diluted with CH_2Cl_2 and washed with 1 M HCl, brine, saturated aq. $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was purified by flash silica gel column chromatography with hexane/EtOAc (100/0 to 87/13, *v/v*) to give **S4** (261 mg, 341 μmol, 76%); R_f = 0.58 (hexane/EtOAc = 5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83-7.43 (m, 7H, Ar), 5.28-5.25 (m, 1H, *sn*-2), 4.73-4.67 (m, 2H, -C*H*$_2$Nap), 4.37-4.35 (m, 1H, *sn*-1$_a$), 4.22-4.19 (m, 1H, *sn*-1$_b$), 3.65-3.60 (m, 2H, *sn*-3), 2.32 (t, 2H, *J* = 7.8 Hz, *J* = 7.8 Hz, FA), 2.24 (t, 2H, *J* = 7.2 Hz, *J* = 7.8 Hz, FA), 1.63-1.54 (m, 4H, FA), 1.35-1.25 (m, 56H, FA), 0.88 (t, 6H, *J* = 6.6 Hz, *J* = 7.2 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.58, 173.29 (CO), 135.31, 133.35, 133.18, 128.41, 128.00, 127.85, 126.66, 126.32, 126.12, 125.73 (Ar), 73.56 (-*C*H$_2$Nap), 70.15 (*sn*-2), 68.37 (*sn*-3), 62.77 (*sn*-1), 34.50, 34.26, 32.08, 29.86, 29.82, 29.79, 29.65, 29.52, 29.45, 29.43, 29.27, 25.11, 25.02, 22.84, 14.27 (FA) ppm; MALDI-TOF MS calcd for $C_{50}H_{84}NaO_5$ [M+Na]$^+$ *m/z* 787.62, $C_{50}H_{84}KO_5$ [M+K]$^+$ *m/z* 803.60, found *m/z* 788.27, 804.24.

3-3-2. 1,2-di-*O*-stearyl-3-*O*-di-*O*-benzylphosphate-*sn*-glycerol: **S5**



To a solution of compound **S4** (131 mg, 171 μmol) in CH_2Cl_2/H_2O (9/1, 5 mL) was treated with DDQ (197 mg, 868 μmol) at 0 °C and stirred at 25 °C for 1 h. The reaction mixture was diluted with $CHCl_3$ and washed with water, saturated aq. $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was purified by flash silica gel column chromatography with hexane/EtOAc (100/0 to 83/17, *v/v*) to give a 1,2-di-*O*-stearoyl-*sn*-glycerol. The crude diacyl glycerol was dissolved with CH_2Cl_2 (1.4 mL) treate with dibenzyl diisopropylphosphoramidite (141 μL, 146 mg, 424 μmol) and 1*H*-tetrazole (36 mg, 514 μmol) at 0 °C and stirred at 25 °C for 30 min. The reaction mixture was cooled to 0°C and treated with H_2O_2 (35% aq., 250 μL) and subsequently warmed to 25 °C and stirred for 30 min. The mixture was diluted with CH_2Cl_2 and washed with saturated aq. $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was recrystallized from EtOH (16 mL) to give **S5** (134 mg, 152 μmol, 89% in 3 steps); R_f = 0.34 (hexane/EtOAc = 3/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.31 (m, 10H, Ar), 5.18-5.14 (m, 1H, *sn*-2), 5.07-5.00 (m, 4H, -C*H*$_2$Ph), 4.26-4.24 (m, 1H, *sn*-1$_a$), 4.14-4.06 (m, 3H, *sn*-3, *sn*-1$_b$), 2.28-2.25 (m, 4H, FA), 1.61-1.55 (m, 4H, FA), 1.35-1.25 (m, 56H, FA), 0.88 (t, 6H, *J* = 7.2 Hz, *J* = 7.2 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.36, 172.96 (CO), 135.78, 135.72 (*ipso*), 128.77, 128.12 (Ar), 69.64 (d, $^2J_{CP}$ = 5.7 Hz, -*C*H$_2$Ph), 69.44 (d, $^3J_{CP}$ = 7.2 Hz, *sn*-2), 65.52 (d, $^2J_{CP}$ = 4.2 Hz, *sn*-3), 61.74 (*sn*-1), 34.28, 34.15, 32.08, 29.86, 29.82, 29.79, 29.64, 29.52, 29.43, 29.28, 29.23, 24.98, 24.96, 22.84, 14.27 (FA); ^{31}P NMR (243 MHz, $CDCl_3$) δ -0.49 ppm; MALDI-TOF MS calcd for $C_{53}H_{89}NaO_8P$ $[M+Na]^+$ *m/z* 907.62, $C_{53}H_{89}KO_8P$ $[M+K]^+$ *m/z* 923.59, found *m/z* 908.83, 924.78.

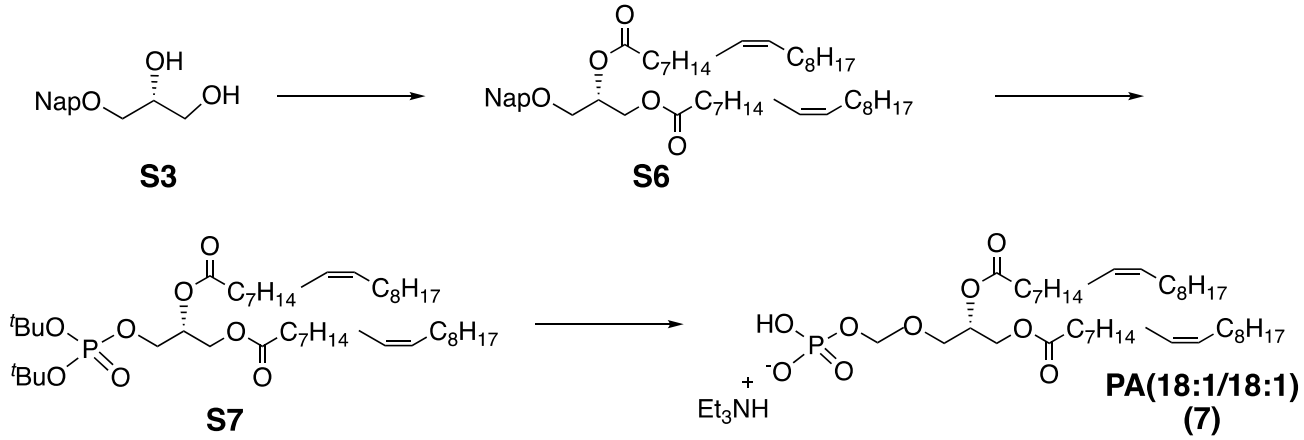
3-3-3. Synthesis of PA (18:0/18:0): 1, 2-di-*O*-stearyl-*sn*-glycerol-3-phosphate triethylammonium salt (**5**)



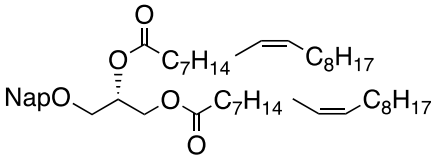
A suspension of 10% Pd/C catalyst (291 mg) in EtOAc/EtOH (5/1, 43.2 mL) containing compound **S5** (121 mg, 137 μmol) was stirred at 35 °C for 24 h under a hydrogen atmosphere. Subsequently, the suspension was treated with of TEA (21 μL) and stirred for 1 h. The resulting suspension was filtered over a bed of Celite, and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Iatrobeads 6RS-8060 No.1104) with $CHCl_3$/MeOH/H_2O/TEA (100/0/0/1 to 89/11/0/0.2, 80/20/0/0.2, 67/33/5/0.2 *v/v*) to give **6** (81.1 mg, 101 μmol, 74%); R_f = 0.31 ($CHCl_3$/MeOH = 5/1, 1% TEA); ^{1}H NMR (600 MHz, $CDCl_3$, CD_3OD 3%) δ 5.25-5.22 (m, 1H, *sn*-2), 4.39-4.37 (m, 1H, *sn*-1$_a$), 4.20-4.17 (m, 1H, *sn*-1$_b$), 4.02-4.01 (m, 2H, *sn*-3), 3.13-3.09 (m, 6H, N-(C*H*$_2$-CH$_3$)$_3$), 2.32-2.28 (m, 4H, FA), 1.62-1.65 (m, 4H, FA), 1.38 (t, 9H, *J* = 7.2 Hz, *J* = 7.2 Hz, N-(CH$_2$-C*H*$_3$)$_3$), 1.31-1.25 (m, 56H, FA), 0.88 (t, 6H, *J* = 7.2 Hz, *J* = 7.2 Hz, FA); ^{13}C NMR (150 MHz,

$CDCl_3$, CD_3OD 3%) δ 173.76, 173.38 (CO), 70.36 (d, $^3J_{CP}$ = 7.2 Hz, *sn*-2), 63.54 (d, $^2J_{CP}$ = 4.2 Hz, *sn*-3), 62.69 (*sn*-1), 45.91 (N-(*C*H_2-CH_3)$_3$), 34.32, 34.17, 32.00, 29.78, 29.74, 29.60, 29.44, 29.40, 29.23, 24.96, 24.93, 22.76, 14.17 (FA), 8.57 (N-(CH_2-*C*H_3)$_3$); ^{31}P NMR (243 MHz, $CDCl_3$, CD_3OD 3%) δ 0.30 ppm; MALDI-TOF MS calcd for $C_{39}H_{77}NaO_8P$ $[M+Na]^+$ *m/z* 727.53, $C_{39}H_{76}Na_2O_8P$ $[M-H+Na_2]^+$ *m/z* 749.51, $C_{39}H_{76}KNaO_8P$ $[M-H+KNa]^+$ *m/z* 765.48, found *m/z* 728.29, 750.29, 766.33. ; HRMS calcd for $[C_{39}H_{76}O_8P]^-$ requires *m/z* 703.5283; found 703.5265.

3-4. Synthesis of PA(18:1/18:1): **7**

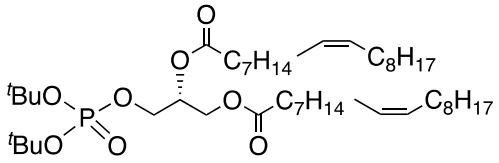


3-4-1. Synthesis of 1,2-di-*O*-oleyl-3-*O*-(2-naphtylmethyl)-*sn*-glycerol: **S6**



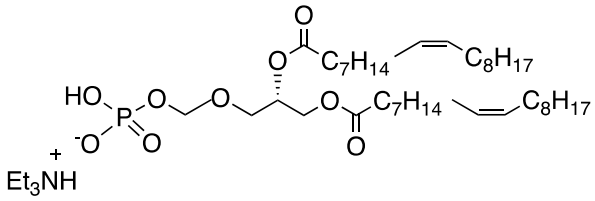
S3 (100 mg, 431 μmol), oleic acid (280 mg, 991 μmol) and DMAP (38 mg, 300 μmol) were dissolved in dry CH_2Cl_2 (13 mL) under argon and treated with EDC (220 mg, 1.15 mmol) at 0 °C. The reaction mixture was warmed to 40 °C and stirred at 40 °C for 14 h. Subsequently, the reaction was quenched with CH_3OH at 0 °CC. The mixture was diluted with CH_2Cl_2 and washed with 1 M HCl, brine, saturated aq. $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was purified by flash silica gel column chromatography with hexane/EtOAc (100/0 to 95/5, *v/v*) to give **S6** (307 mg, 403 μmol, 94%); R_f = 0.58 (hexane/EtOAc = 5/1); H NMR (600 MHz, $CDCl_3$) δ 7.83-7.43 (m, 7H, Ar), 5.37-5.31 (m, 4H, olefin), 5.28-5.25 (m, 1H, *sn*-2), 4.73-4.67 (m, 2H, -C*H*$_2$Nap), 4.37-4.34 (m, 1H, *sn*-1$_a$), 4.22-4.19 (m, 1H, *sn*-1$_b$), 3.65-3.60 (m, 2H, *sn*-3), 2.32 (t, 2H, *J* = 7.2 Hz, *J* = 8.4 Hz, FA), 2.24 (t, 2H, *J* = 7.2 Hz, *J* = 7.8 Hz, FA), 2.02-1.98 (m, 8H, FA), 1.64-1.54 (m, 4H, FA), 1.36-1.26 (m, 40H, FA), 0.88 (t, 6H, *J* = 6.6 Hz, *J* = 7.2 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.54, 173.25 (CO), 135.31, 133.35, 133.18 (Ar), 130.16, 129.87 (olefin), 128.41, 128.00, 127.85, 126.66, 126.33, 126.13, 125.74 (Ar), 73.56 (-*C*H_2Nap), 70.16 (*sn*-2), 68.35 (*sn*-3), 62.77 (*sn*-1), 34.47, 34.23, 32.05, 29.92, 29.86, 29.68, 29.48, 29.35, 29.32, 29.28, 29.23, 27.37, 27.32, 25.09, 24.99, 22.83, 14.27 (FA) ppm.

3-4-2. Synthesis of 1,2-di-*O*-oleyl-3-*O*-di-*O*-*t*-butylphosphate-*sn*-glycerol: **S7**



A solution of compound **S6** (100 mg, 131 μmol) in CH_2Cl_2/H_2O (9/1, 4 mL) was treated with DDQ (151 mg, 665 μmol) at 0 °C and stirred at 25 °C for 30min. The mixture was diluted with $CHCl_3$ and washed with water, saturated aq. $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was purified by flash silica gel column chromatography with hexane/EtOAc (100/0 to 83/17, *v/v*) to give 1,2-di-*O*-oleoyl-*sn*-glycerol intermediate. The crude diacyl glycerol intermediate was dissolved in CH_2Cl_2 (1.1 mL), treated with di-*t*-butyl diisopropylphosphoramidite (106 μL, 94 mg, 340 μmol) and 1*H*-tetrazole (32 mg, 460 μmol) at 0 °C and stirred at 25 °C for 25 min. Subsequently, the reaction mixture was cooled to 0 °C, treated with H_2O_2 (35% aq., 200 μL), warmed to 25 °C and stirred for 15 min. The mixture was diluted with $CHCl_3$ and washed with saturated aq. $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was purified by flash silica gel column chromatography with hexane/EtOAc (100/0 to 70/30, *v/v*) to give **S7** (75 mg, 92 μmol, 70% in 3 steps); R_f = 0.49 (hexane/EtOAc = 2/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.37-5.31 (m, 4H, olefin), 5.24-5.21 (m, 1H, *sn*-2), 4.37-4.34 (m, 1H, *sn*-1_a), 4.18-4.15 (m, 1H, *sn*-1_b), 4.10-4.04 (m, 2H, *sn*-3), 2.33-2.29 (m, 4H, FA), 2.02-1.99 (m, 8H, FA), 1.64-1.59 (m, 4H, FA), 1.49 (s, 9H, -C(C*H*$_3$)$_3$), 1.48 (s, 9H, -C(C*H*$_3$)$_3$), 1.35-1.24 (m, 40H, FA), 0.88 (t, 6H, *J* = 7.2 Hz, *J* = 6.6 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.42, 172.99 (CO), 130.16, 129.85 (olefin), 82.90 (d, $^2J_{CP}$ = 7.2 Hz, -*C*(CH$_3$)$_3$), 82.85 (d, $^2J_{CP}$ = 8.6 Hz, -*C*(CH$_3$)$_3$), 69.73 (d, $^3J_{CP}$ = 8.7 Hz, *sn*-2), 64.49 (d, ^2J = 5.9 Hz, *sn*-3), 62.15 (*sn*-1), 34.34, 34.19, 32.04 (FA), 29.98, 29.95 (-C(*C*H$_3$)$_3$), 29.91, 29.86, 29.67, 29.47, 29.34, 29.27, 29.25, 29.22 (FA); ^{31}P NMR (243 MHz, $CDCl_3$) δ -9.39 ppm; MALDI-TOF MS calcd for $C_{47}H_{89}NaO_8P$ $[M+Na]^+$ *m/z* 835.62, $C_{47}H_{89}KO_8P$ $[M+K]^+$ *m/z* 851.59, found *m/z* 836.85, 852.82.

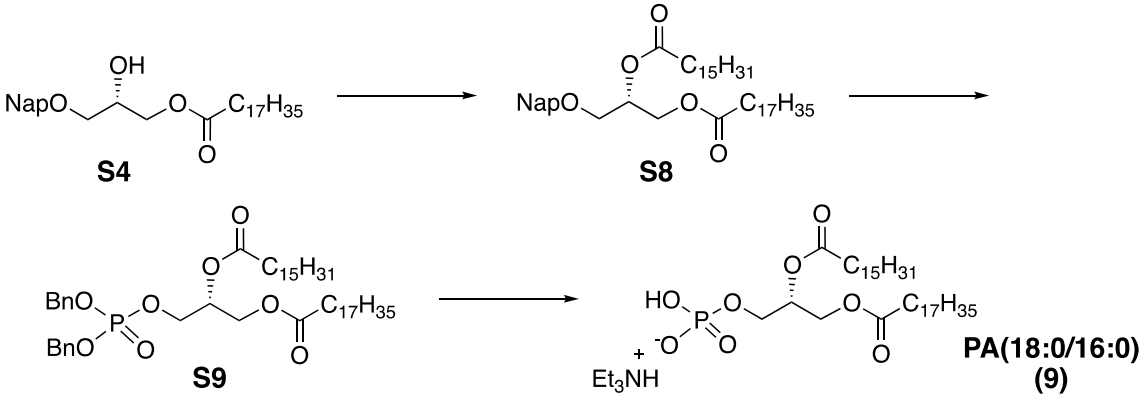
3-4-3. Synthesis of PA (18:1/18:1): 1, 2-di-*O*-oleoyl-*sn*-glycerol-3-phosphate triethylammonium salt (**7**)



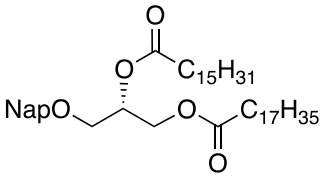
A solution of compound **S7** (33 mg, 40.0 μmol) in CH_2Cl_2 (330 μL) was treated with trifluoroacetic acid (TFA, 77 μL) at 0 °C and stirred at 25 °C for 10 min. The organic solvent was removed by nitrogen gas. The residue was dissolved CH_2Cl_2 (1 mL) and treated with methanolic ammonia (2 M, 1 mL). The organic solvent was removed by nitrogen gas and the residue was purified by silica gel column chromatography (Iatrobeads 6RS-8060 No.1104) with $CHCl_3$/MeOH/H_2O/TEA (100/0/0/1 to 89/11/0/0.2, 80/20/0/0.2, 67/33/5/0.2 *v/v*) to give **7** (30.2 mg, 37.6 μmol, 94%); R_f = 0.31 ($CHCl_3$/MeOH = 5/1, 1% TEA); ^{1}H NMR (600 MHz, $CDCl_3$, CD_3OD 3%) δ 5.37-5.31 (m, 4H, olefin), 5.25-5.22 (m, 1H, *sn*-2), 4.39-4.36 (m, 1H, *sn*-1_a), 4.20-4.17 (m, 1H, *sn*-1_b), 4.03-4.01 (m, 2H, *sn*-3), 3.09-3.05 (m,

6H, N-(CH_2-CH$_3$)$_3$), 2.33-2.28 (m, 4H, FA), 2.03-1.99 (m, 8H, FA), 1.62-1.57 (m, 4H, FA), 1.32 (t, 9H, J = 7.2 Hz, J = 7.2 Hz, N-(CH$_2$-CH_3)$_3$), 1.34-1.24 (m, 40H, FA), 0.88 (t, 6H, J = 6.6 Hz, J = 7.2 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$, CD_3OD 3%) δ 173.74, 173.37 (CO), 130.08, 129.79 (olefin), 70.26 (d, $^3J_{CP}$ = 8.6 Hz, *sn*-2), 63.72 (d, $^2J_{CP}$ = 3.0 Hz, *sn*-3), 62.61 (*sn*-1), 45.72 (N-(*C*H$_2$-CH$_3$)$_3$), 34.28, 34.13, 31.98, 29.84, 29.60, 29.39, 29.32, 29.31, 29.25, 29.20, 29.18, 27.30, 27.27, 24.93, 24.91, 22.76, 14.17 (FA), 8.45 (N-(CH$_2$-*C*H$_3$)$_3$); ^{31}P NMR (243 MHz, $CDCl_3$, CD_3OD 3%) δ 0.43 ppm; MALDI-TOF MS calcd for $C_{39}H_{73}NaO_8P$ $[M+Na]^+$ *m/z* 723.49, $C_{39}H_{72}Na_2O_8P$ $[M+Na_2]^+$ *m/z* 745.48, $C_{39}H_{72}KNaO_8P$ $[M+KNa]^+$ *m/z* 761.45, found *m/z* 724.25, 746.28, 762.29.; HRMS calcd for $[C_{39}H_{72}O_8P]^-$ requires *m/z* 699.4970; found 699.4966.

3-5. Synthesis of PA(18:0/16:0): **9**

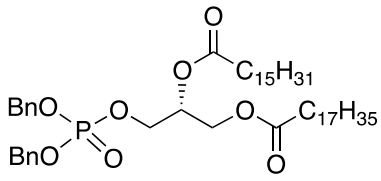


3-5-1. Synthesis of 1-*O*-stearyl-2-*O*-palmityl-3-*O*-(2-naphtylmethyl)-*sn*-glycerol: **S8**



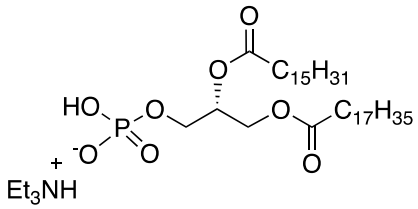
A solution of 1-O-stearyl-3-O-(2-naphtylmethyl)-sn-glycerol [Ref S1] (**S4**) (129 mg, 259 μmol) in CH_2Cl_2 (5 mL) was stirred at 0 °C, and then treated with palmitic acid (141 mg, 550 μmol), DMAP (14 mg, 110 μmol) and EDC (110 mg, 574 μmol). The resulting mixture was stirred at 25 °C for 2 h. The reaction was quenched with MeOH (250 μL), diluted with CH_2Cl_2 and washed with 1 N HCl, brine, aq. $NaHCO_3$ and brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/EtOAc, 100/0 to 88/12) to give **S8** (185 mg, 251 μmol, 97%): Rf 0.46 (toluene/EtOAc (5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84-7.43 (m, 7H, Ar), 5.28-5.25 (m, 1H, *sn*-2), 4.73-4.67 (m, 2H, -CH_2Nap), 4.37-4.35 (m, 1H, *sn*-1$_a$), 4.22-4.19 (m, 1H, *sn*-1$_b$), 3.65-3.60 (m, 2H, *sn*-3), 2.32 (t, 2H, J = 7.2 Hz, J = 8.4 Hz, FA), 2.24 (t, 2H, J = 7.2 Hz, J = 7.8 Hz, FA), 1.63-1.54 (m, 4H, FA), 1.35-1.24 (m, 52H, FA), 0.88 (t, 6H, J = 6.6 Hz, J = 7.2 Hz, FA) ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.58, 173.28 (CO), 135.30, 133.35, 133.17, 128.40, 128.00, 127.84, 126.65, 126.32, 126.12, 125.73 (Ar), 73.55 (-*C*H$_2$Nap), 70.14 (*sn*-2), 68.35 (*sn*-3), 62.76 (*sn*-1), 34.49, 34.25, 32.07, 29.85, 29.81, 29.78, 29.64, 29.52, 29.44, 29.42, 29.26, 25.10, 25.01, 22.84, 14.27 (FA) ppm ; MALDI-TOF MS calcd for $C_{48}H_{80}NaO_5$ $[M+Na]^+$ *m/z* 759.59, $C_{48}H_{80}KO_5$ $[M+K]^+$ *m/z* 775.56, found *m/z* 760.63, 776.63.

3-5-2. Synthesis of 1-*O*-stearoyl-2-*O*-palmitoyl-3-*O*-(di-*O*-benzylphosphate)-*sn*-glycerol **S9**



A solution of compound **S8** (100 mg, 131 μmol) in CH_2Cl_2/H_2O (9/1, 4 mL) was treated with DDQ (165 mg, 727 μmol) at 0 °C and stirred at 25 °C for 40 min. The resulting mixture was diluted with $CHCl_3$ and washed with water, saturated aq. $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was purified by flash silica gel column chromatography with hexane/EtOAc (100/0 to 83/17, *v/v*) to give 1-*O*-stearoyl-2-*O*-palmitoyl-*sn*-glycerol intermediate. The diacyl glycerol intermediate was dissolved in CH_2Cl_2 (1.4 mL), treated with dibenzyl diisopropylphosphoramidite (142 μL, 147 mg, 425 μmol) and 1*H*-tetrazole (39 mg, 560 μmol) at 0 °C and stirred at 25 °C for 25 min. The reaction mixture was cooled to 0 °C, treated with H_2O_2 (35% aq, 250 μL) and the resulting mixture was warmed to 25 °C and stirred for 15 min. Subsequently, the mixture was diluted with $CHCl_3$ and washed with saturated aq. $NaHCO_3$, and brine. The resulting residue was recrystallized from EtOH (7 mL) to give **S9** (95 mg, 110 μmol, 81% in 3 steps); Rf 0.51 (hexane/EtOAc (5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38-7.32 (m, 10H, Ar), 5.18-5.14 (m, 1H, *sn*-2), 5.07-5.00 (m, 4H, -C*H*$_2$Ph), 4.26-4.24 (m, 1H, *sn*-1$_a$), 4.13-4.06 (m, 3H, *sn*-3, *sn*-1$_b$), 2.28-2.24 (m, 4H, FA), 1.60-1.55 (m, 4H, FA), 1.35-1.25 (m, 52H, FA), 0.88 (t, 6H, *J* = 6.6 Hz, *J* = 7.2 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.35, 172.95 (CO), 135.75, 135.72 (*ipso*), 128.76, 128.12 (Ar), 69.63 (d, $^2J_{CP}$ = 5.7 Hz, -*C*H$_2$Ph), 69.43 (d, $^3J_{CP}$ = 7.2 Hz, *sn*-2), 65.52 (d, $^2J_{CP}$ = 5.7 Hz, *sn*-3), 61.73 (*sn*-1), 34.26, 34.14, 32.06, 29.84, 29.80, 29.78, 29.63, 29.51, 29.42, 29.26, 29.22, 24.97, 24.95, 22.83, 14.26 (FA); ^{31}P NMR (243 MHz, $CDCl_3$) δ -0.49 ppm; MALDI-TOF MS calcd for $C_{51}H_{85}NaO_8P$ $[M+Na]^+$ *m/z* 879.59, $C_{51}H_{85}KO_8P$ $[M+K]^+$ *m/z* 895.56, found *m/z* 880.92, 896.93.

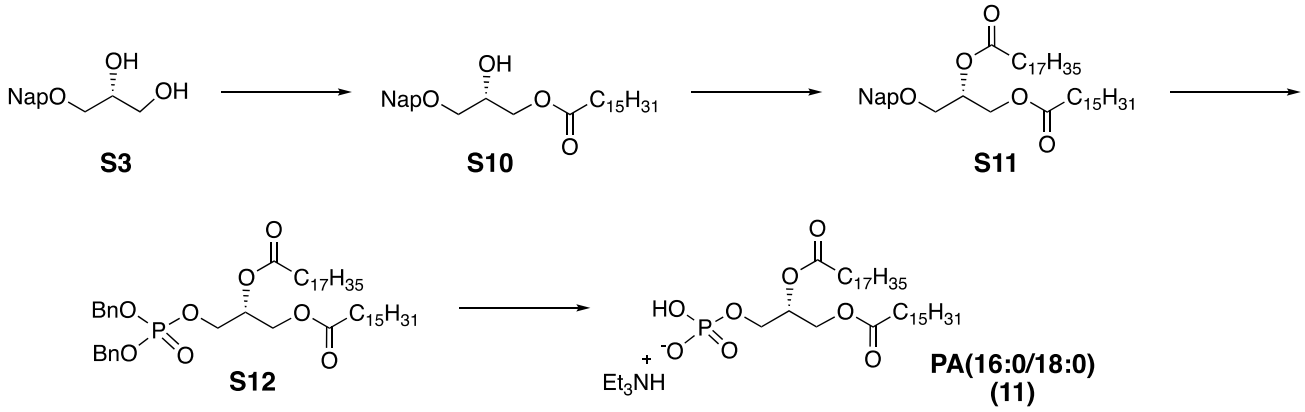
3-5-3. Synthesis of PA (18:0/16:0): 1-*O*-stearoyl-2-*O*-palmityol-*sn*-glycerol-3-phosphate triethylammonium salt (**9**)



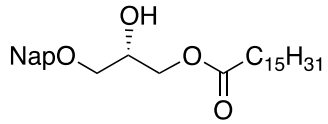
A suspension of 10% Pd/C catalyst (180 mg) in of EtOAc/EtOH (5/1, 28 mL) containing compound **S9** (74 mg, 86 μmol) was stirred at 35 °C for 23 h under a hydrogen atmosphere. Subsequently, the suspension was treated with TEA (13 μL) and stirred for 1 h. The resulting suspension was filtered over a bed of Celite, and the filtrate was concentrated *in vacuo.* The residue was purified by silica gel column chromatography (Iatrobeads 6RS-8060 No.1104) with $CHCl_3$/MeOH/H_2O/TEA (100/0/0/1 to 89/11/0/0.2, 80/20/0/0.2, 67/33/5/0.2 *v/v*) to give **9** (60 mg, 77 μmol, 90%); R_f = 0.23 ($CHCl_3$/MeOH = 5/1, 1% TEA); ^{1}H NMR (600 MHz, $CDCl_3$, CD_3OD 3%) δ 5.25-5.21 (m, 1H, *sn*-2), 4.39-4.36 (m, 1H, *sn*-1$_a$), 4.20-4.17 (m, 1H, *sn*-1$_b$), 4.03-4.01 (m, 2H, *sn*-3), 3.09-3.06 (m, 6H, N-(C*H*$_2$-CH$_3$)$_3$), 2.32-2.28 (m, 4H, FA), 1.61-1.56 (m, 4H, FA), 1.31 (t, 9H, *J* = 7.2 Hz, *J* = 7.2 Hz, N-(CH$_2$-

C*H*$_3$)$_3$), 1.35-1.25 (m, 52H, FA), 0.88 (t, 6H, *J* = 7.2 Hz, *J* = 7.2 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$, CD_3OD 3%) δ 173.79, 173.41 (CO), 70.30 (d, $^3J_{CP}$ = 8.7 Hz, *sn*-2), 63.63 (d, $^2J_{CP}$ = 4.2 Hz, *sn*-3), 62.65 (*sn*-1), 45.68 (N-(*C*H$_2$-CH$_3$)$_3$), 34.31, 34.17, 32.01, 29.79, 29.75, 29.61, 29.45, 29.42, 29.40, 29.24, 29.21, 24.96, 22.77, 14.18 (FA), 8.44 (N-(CH$_2$-*C*H$_3$)$_3$); ^{31}P NMR (243 MHz, $CDCl_3$, CD_3OD 3%) δ 0.33 ppm; MALDI-TOF MS calcd for $C_{37}H_{73}NaO_8P$ $[M+Na]^+$ *m/z* 699.49, $C_{37}H_{72}Na_2O_8P$ $[M+Na_2]^+$ *m/z* 721.48, $C_{37}H_{72}KNaO_8P$ $[M+KNa]^+$ *m/z* 737.45, found *m/z* 700.20, 722.19, 738.18. ; HRMS calcd for $[C_{37}H_{72}O_8P]^-$ requires *m/z* 675.4970; found 675.4972.

3-6. Synthesis of PA (16:0/18:0): **11**

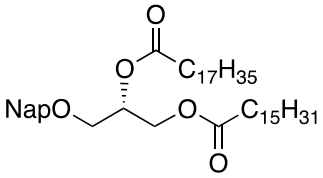


3-6-1. Synthesis of 1-*O*-palmitoyl-3-*O*-(2-naphtylmethyl)-*sn*-glycerol: **S10**



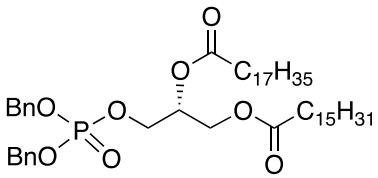
A solution of **S3** (101 mg, 435 μmol) in CH_2Cl_2 (13 mL) was stirred at 0 °C, and treated with palmitic acid (137 mg, 534 μmol), DMAP (19 mg, 160 μmol) and EDC (114 mg, 595 μmol) at 0 °C. The reaction mixture was stirred at 25 °C for 1.5 h and subsequently quenched with MeOH (500 μL). The resulting mixture was diluted with CH_2Cl_2 and washed with 1 M HCl, brine, aq. $NaHCO_3$ and brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (toluene/EtOAc, 100/0 to 90/10, *v/v*) to give **S10** (152 mg, 323 μmol, 74%); R_f =0.45 (toluene/EtOAc, 5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85-7.44 (m, 7H, Ar), 4.72 (s, 2H, -C*H*$_2$Nap), 4.21-4.19 (m, 1H, *sn*-1$_a$), 4.17-4.14 (m, 1H, *sn*-1$_b$), 4.08-4.04 (m, 1H, *sn*-2), 3.61-3.58 (m, 1H, *sn*-3$_a$), 3.55-3.52 (m, 1H, *sn*-3$_b$), 2.55 (d, 1H, *J* = 4.8 Hz, OH-*sn*-2), 2.29 (t, 2H, *J* = 7.8 Hz, *J* = 7.8 Hz, FA), 1.61-1.56 (m, 2H, FA), 1.35-1.25 (m, 24H, FA), 0.88 (t, 3H, *J* = 6.6 Hz, *J* = 7.2 Hz, FA) ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.12 (CO), 135.25, 133.35, 133.20, 128.49, 128.01, 127.86, 126.77, 126.37, 126.17, 125.79 (Ar), 73.77 (-*C*H$_2$Nap), 70.98 (*sn*-3), 69.12 (*sn*-2), 65.47 (*sn*-1), 34.28, 32.07, 29.84, 29.80, 29.75, 29.60, 29.51, 29.39, 29.26, 25.04, 22.84, 14.27 (FA) ppm; MALDI-TOF MS calcd for $C_{30}H_{46}NaO_4$ $[M+Na]^+$ *m/z* 493.33, $C_{30}H_{46}KO_4$ $[M+K]^+$ *m/z* 509.30, found *m/z* 493.93, 509.91.

3-6-2. Synthesis of 1-*O*-palmitoyl-2-*O*-stearoyl-3-*O*-(2-naphtylmethyl)-*sn*-glycerol**: S11**



A solution of **S10** (76 mg, 161 μmol) in CH_2Cl_2 (3 mL) was stirred at 0 °C, and treated with stearic acid (109 mg, 383 μmol), DMAP (7.5 mg, 61 μmol) and EDC (64 mg, 330 μmol). The reaction mixture was stirred at 25 °C for 2 h and subsequently quenched with MeOH (250 μL). The resulting mixture was diluted with CH_2Cl_2 and washed with 1 M HCl, brine, aq. $NaHCO_3$ and brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexane/EtOAc, 100/0 to 88/12) to give **S11** (109 mg, 148 μmol, 92%): R_f =0.38 (hexane/EtOAc (5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83-7.43 (m, 7H, Ar), 5.28-5.25 (m, 1H, *sn*-2), 4.73-4.67 (m, 2H, -C*H*$_2$Nap), 4.37-4.35 (m, 1H, *sn*-1$_a$), 4.22-4.19 (m, 1H, *sn*-1$_b$), 3.65-3.60 (m, 2H, *sn*-3), 2.32 (t, 2H, *J* = 7.8 Hz, *J* = 7.8 Hz, FA), 2.24 (t, 2H, *J* = 7.8 Hz, *J* = 7.8 Hz, FA), 1.63-1.54 (m, 4H, FA), 1.35-1.24 (m, 52H, FA), 0.88 (t, 6H, *J* = 6.6 Hz, *J* = 7.2 Hz, FA) ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.57, 173.28 (CO), 135.30, 133.35, 133.18, 128.40, 128.00, 127.84, 126.65, 126.32, 126.12, 125.73 (Ar), 73.55 (-*C*H$_2$Nap), 70.14 (*sn*-2), 68.35 (*sn*-3), 62.76 (*sn*-1), 34.49, 34.25, 32.07, 29.85, 29.81, 29.78, 29.64, 29.52, 29.45, 29.42, 29.26, 25.11, 25.01, 22.84, 14.27 (FA) ppm; MALDI-TOF MS calcd for $C_{48}H_{80}NaO_5$ $[M+Na]^+$ *m/z* 759.59, $C_{48}H_{80}KO_5$ $[M+K]^+$ *m/z* 775.56, found *m/z* 760.62, 776.62.

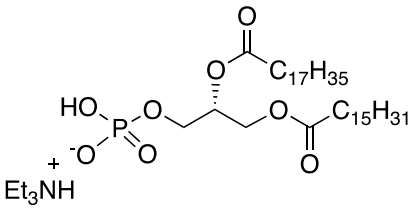
3-6-3. Synthesis of 1-*O*-palmitoyl-2-*O*-stearoyl-3-*O*-(di-*O*-benzylphosphate)-*sn*-glycerol: **S12**



A solution of compound **S11** (90 mg, 122 μmol) in CH_2Cl_2/H_2O (9/1, 3.4 mL) was treated with DDQ (167 mg, 736 μmol) at 0 °C and the reaction mixture was stirred at 25 °C for 40 min. Subsequently, the mixture was diluted with $CHCl_3$ and washed with water, saturated aq. $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was purified by flash silica gel column chromatography with hexane/EtOAc (100/0 to 83/17, *v/v*) to give the desired 1-*O*-palmitoyl-2-*O*-stearyl-*sn*-glycerol intermediate. The diacyl glycerol intermediate was dissolved with CH_2Cl_2 (1 mL), treated with dibenzyl diisopropylphosphoramidite (142 μL, 147 mg, 425 μmol) and 1*H*-tetrazole (28 mg, 402 μmol) at 0 °C and stirred at 25 °C for 20 min. Subsequently, the reaction mixture was cooled to 0 °C, treated with H_2O_2 (35% aq., 180 μL) and the resulting mixture was warmed to 25 °C and stirred for 15 min. The mixture was diluted with $CHCl_3$ and washed with saturated aq. $NaHCO_3$, and brine. The resulting residue was recrystallized from EtOH (5 mL) to give **S12** (79 mg, 92 μmol, 75% in 3 steps); R_f =0.54 (hexane/EtOAc (2/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38-7.32 (m, 10H, Ar), 5.18-5.14 (m, 1H, *sn*-2), 5.07-5.00 (m, 4H, -C*H*$_2$Ph), 4.26-4.24 (m, 1H, *sn*-1$_a$), 4.13-4.06 (m, 3H, *sn*-3, *sn*-1$_b$), 2.28-2.24 (m, 4H, FA), 1.59-1.55 (m, 4H, FA), 1.35-1.24 (m, 52H, FA), 0.88 (t, 6H, *J* = 6.6 Hz, *J* = 7.2 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.35, 172.96 (CO), 135.75, 135.72 (*ipso*), 128.76, 128.12 (Ar), 69.64 (d,

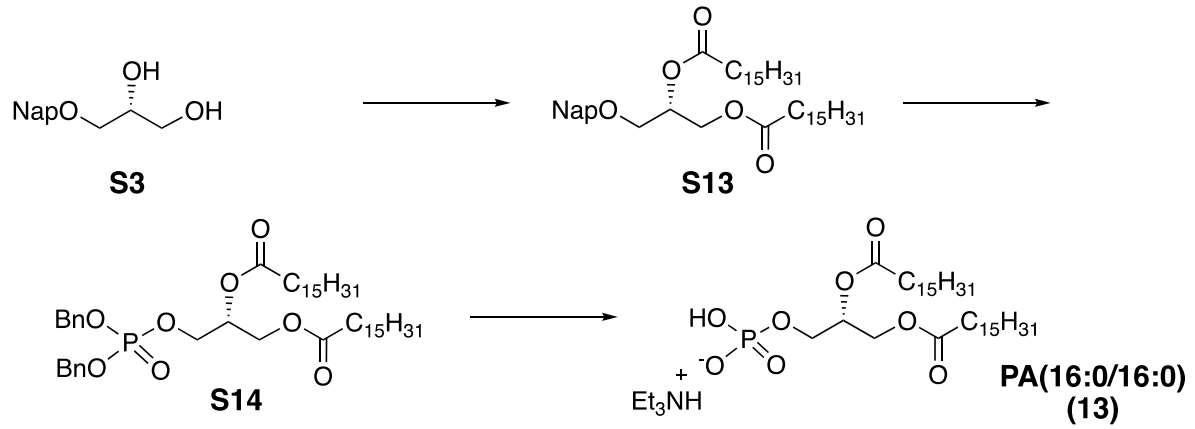
$^{2}J_{CP}$ = 5.7 Hz, -*C*H$_2$Ph), 69.43 (d, $^{3}J_{CP}$ = 7.2 Hz, *sn*-2), 65.52 (d, $^{2}J_{CP}$ = 5.7 Hz, *sn*-3), 61.73 (*sn*-1), 34.26, 34.14, 32.06, 29.84, 29.80, 29.63, 29.51, 29.42, 29.26, 29.22, 24.97, 24.95, 22.83, 14.26 (FA); ^{31}P NMR (243 MHz, $CDCl_3$) δ -0.51 ppm; MALDI-TOF MS calcd for $C_{51}H_{85}NaO_8P$ $[M+Na]^+$ *m/z* 879.59, $C_{51}H_{85}KO_8P$ $[M+K]^+$ *m/z* 895.56, found *m/z* 880.78, 896.81.

3-6-4. Synthesis of PA (16:0/18:0):1-*O*-palmitoyl-2-*O*-stearoyl-*sn*-glycerol-3-phosphate triethylammonium salt (**11**)

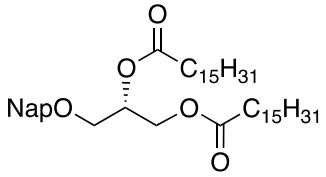


A suspension of 10% Pd/C catalyst (161 mg) in EtOAc/EtOH (5/1, 23 mL) containing compound **S12** (63 mg, 73.7 μmol) was stirred at 35 °C for 25 h under a hydrogen atmosphere. Subsequenlty the suspension was treated with TEA (13 μL) and stirred for 1 h. The resulting suspension was filtered over a bed of Celite, and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Iatrobeads 6RS-8060 No.1104) with $CHCl_3$/MeOH/H_2O/TEA (100/0/0/1 to 89/11/0/0.2, 80/20/0/0.2, 67/33/5/0.2 *v/v*) to give **11** (49 mg, 62.6 μmol, 85%); R_f = 0.30 ($CHCl_3$/MeOH = 5/1, 1% TEA); ^{1}H NMR (600 MHz, $CDCl_3$, CD_3OD 3%) δ 5.25-5.22 (m, 1H, *sn*-2), 4.40-4.37 (m, 1H, *sn*-1$_a$), 4.20-4.17 (m, 1H, *sn*-1$_b$), 4.03-3.97 (m, 2H, *sn*-3), 3.09-3.05 (m, 6H, N-(C*H*$_2$-CH$_3$)$_3$), 2.31-2.28 (m, 4H, FA), 1.62-1.56 (m, 4H, FA), 1.31 (t, 9H, *J* = 7.2 Hz, *J* = 7.2 Hz, N-(CH$_2$-C*H*$_3$)$_3$), 1.35-1.25 (m, 52H, FA), 0.88 (t, 6H, *J* = 7.2 Hz, *J* = 7.2 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$, CD_3OD 3%) δ 173.79, 173.40 (CO), 70.48 (d, $^{3}J_{CP}$ = 8.7 Hz, *sn*-2), 63.36 (d, $^{2}J_{CP}$ = 4.2 Hz, *sn*-3), 62.80 (*sn*-1), 45.60 (N-(*C*H$_2$-CH$_3$)$_3$), 34.34, 34.18, 32.00, 29.79, 29.75, 29.60, 29.45, 29.40, 29.24, 24.97, 24.94, 22.77, 14.18 (FA), 8.43 (N-(CH$_2$-*C*H$_3$)$_3$); ^{31}P NMR (243 MHz, $CDCl_3$, CD_3OD 3%) δ 0.38 ppm; MALDI-TOF MS calcd for $C_{37}H_{73}NaO_8P$ $[M+Na]^+$ *m/z* 699.49, $C_{37}H_{72}Na_2O_8P$ $[M+Na_2]^+$ *m/z* 721.48, $C_{37}H_{72}KNaO_8P$ $[M+KNa]^+$ *m/z* 737.45, found *m/z* 700.22, 722.25, 738.18. ; HRMS calcd for $[C_{37}H_{72}O_8P]^-$ requires *m/z* 675.4970; found 675.4985.

3-7. Synthesis of PA (16:0/16:0): **13**

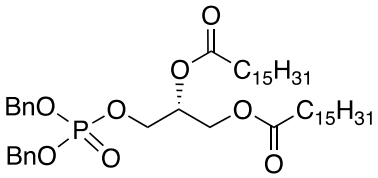


3-7-1. Synthesis of 1, 2-di-*O*-palmitoyl -3-*O*-(2-naphtylmethyl)-*sn*-glycerol: **S13**



S3 (104 mg, 448 μmol), palmitic acid (258 mg, 1.01 mmol) and DMAP (37 mg, 300 μmol) were dissolved in dry CH_2Cl_2 (13 mL) under argon and treated with EDC (202 mg, 1.05 mmol) at 0 °C. The reaction mixture was warmed to 40 °C and stirred at 40 °C for 15 h. The reaction was quenched with CH_3OH at 0 °C, diluted with CH_2Cl_2 and washed with 1 M HCl, brine, saturated aq. $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was purified by flash silica gel column chromatography with hexane/EtOAc (100/0 to 88/12, *v/v*) to give **S13** (221 mg, 312 μmol, 70%); R_f = 0.58 (hexane/EtOAc = 5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83-7.43 (m, 7H, Ar), 5.28-5.25 (m, 1H, *sn*-2), 4.73-4.67 (m, 2H, -CH_2Nap), 4.37-4.35 (m, 1H, *sn*-1$_a$), 4.22-4.19 (m, 1H, *sn*-1$_b$), 3.65-3.61 (m, 2H, *sn*-3), 2.32 (t, 2H, *J* = 7.2 Hz, *J* = 7.8 Hz, FA), 2.24 (t, 2H, *J* = 7.8 Hz, *J* = 7.8 Hz, FA), 1.63-1.54 (m, 4H, FA), 1.34-1.24 (m, 48H, FA), 0.88 (t, 6H, *J* = 6.6 Hz, *J* = 7.2 Hz, FA) ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.58, 173.29 (CO), 135.31, 133.35, 133.18, 128.41, 128.01, 127.85, 126.66, 126.33, 126.13, 125.74 (Ar), 73.56 (-*C*H_2Nap), 70.15 (*sn*-2), 68.36 (*sn*-3), 62.77 (*sn*-1), 34.50, 34.26, 32.08, 29.85, 29.82, 29.79, 29.64, 29.52, 29.45, 29.43, 29.27, 25.11, 25.02, 22.84, 14.27 (FA) ppm; MALDI-TOF MS calcd for $C_{46}H_{76}NaO_5$ $[M+Na]^+$ *m/z* 731.56, $C_{46}H_{76}KO_5$ $[M+K]^+$ *m/z* 747.53, found *m/z* 732.53, 748.53.

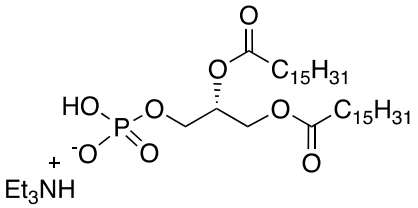
3-7-2. Synthesis of 1, 2-di-*O*-palmitoyl-3-*O*-(di-*O*-benzylphosphate)-*sn*-glycerol: **S14**



A solution of compound **S13** (111 mg, 157 μmol) in CH_2Cl_2/H_2O (9/1, 4 mL) was treated with DDQ (177 mg, 780 μmol) at 0 °C and the reaction mixture was stirred at 25 °C for 45 min. Subsequently, the mixture was diluted with $CHCl_3$ and washed with water, saturated aq. $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was purified by flash silica gel column chromatography with hexane/EtOAc (100/0 to 83/17, *v/v*) to give the desired 1,2-di-*O*-palmitoyl-*sn*-glycerol intermediate. The diacyl glycerol intermediate was dissolved in CH_2Cl_2 (1.5 mL), treated with dibenzyl diisopropylphosphoramidite (148 μL, 153 mg, 442 μmol) and 1*H*-tetrazole (36 mg, 514 μmol) at 0 °C and stirred at 25 °C for 30 min. The reaction mixture was cooled to 0°C, treated with H_2O_2 (35% aq., 260 μL) and the reaction mixture was warmed to 25 °C and stirred for 20 min. Subsequently, the mixture was diluted with $CHCl_3$ and washed with saturated aq. $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was recrystallized from EtOH (16 mL) to give **S14** (112 mg, 135 μmol, 86% in 3 steps); R_f = 0.48 (hexane/EtOAc = 2/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38-7.32 (m, 10H, Ar), 5.18-

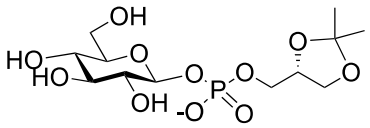
5.14 (m, 1H, *sn*-2), 5.07-5.00 (m, 4H, -CH_2Ph), 4.26-4.24 (m, 1H, *sn*-1$_a$), 4.13-4.06 (m, 3H, *sn*-3, *sn*-1$_b$), 2.28-2.24 (m, 4H, FA), 1.60-1.55 (m, 4H, FA), 1.35-1.24 (m, 48H, FA), 0.88 (t, 6H, J = 6.6 Hz, J = 7.2 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.35, 172.95 (CO), 135.77, 135.71 (*ipso*), 128.76, 128.11 (Ar), 69.63 (d, $^2J_{CP}$ = 5.7 Hz, -*C*H$_2$Ph), 69.43 (d, $^3J_{CP}$ = 7.2 Hz, *sn*-2), 65.51 (d, $^2J_{CP}$ = 4.4 Hz, *sn*-3), 61.73 (*sn*-1), 34.26, 34.14, 32.06, 29.84, 29.80, 29.78, 29.63, 29.51, 29.42, 29.26, 29.22, 24.97, 24.95, 22.83, 14.26 (FA); ^{31}P NMR (243 MHz, $CDCl_3$) δ -0.49 ppm; MALDI-TOF MS calcd for $C_{49}H_{81}NaO_8P$ $[M+Na]^+$ *m/z* 851.56, $C_{49}H_{81}KO_8P$ $[M+K]^+$ *m/z* 867.53, found *m/z* 852.69, 868.68.

3-7-3. Synthesis of PA (16:0/16:0):1, 2-di-*O*-palmitoyl-*sn*-glycerol-3-phosphate triethylammonium salt (**13**)



A suspension of 10% Pd/C catalyst (211 mg) in EtOAc/EtOH (5/1, 29 mL) containing compound **S14** (81 mg, 91.8 μmol) was stirred at 35 °C for 24 h under a hydrogen atmosphere. Subsequently, the suspension was treated with TEA (21 μL) and stirred for 1 h. The suspension was filtered over a bed of Celite, and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Iatrobeads 6RS-8060 No.1104) with $CHCl_3$/MeOH/H_2O/TEA (100/0/0/1 to 89/11/0/0.2, 80/20/0/0.2, 67/33/5/0.2 *v/v*) to give **13** (59 mg, 73.4 μmol, 80%); R_f = 0.23 ($CHCl_3$/MeOH = 5/1, 1% TEA); ^{1}H NMR (600 MHz, $CDCl_3$, CD_3OD 3%) δ 5.25-5.22 (m, 1H, *sn*-2), 4.39-4.36 (m, 1H, *sn*-1$_a$), 4.20-4.17 (m, 1H, *sn*-1$_b$), 4.02-4.00 (m, 2H, *sn*-3), 3.09-3.05 (m, 6H, N-(CH_2-CH$_3$)$_3$), 2.32-2.28 (m, 4H, FA), 1.62-1.56 (m, 4H, FA), 1.32 (t, 9H, J = 7.2 Hz, J = 7.2 Hz, N-(CH$_2$-CH_3)$_3$), 1.30-1.25 (m, 48H, FA), 0.88 (t, 6H, J = 7.2 Hz, J = 7.2 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$, CD_3OD 3%) δ 173.78, 173.39 (CO), 70.40 (d, $^3J_{CP}$ = 8.7 Hz, *sn*-2), 63.52 (d, $^2J_{CP}$ = 4.4 Hz, *sn*-3), 62.74 (*sn*-1), 45.66 (N-(*C*H$_2$-CH$_3$)$_3$), 34.34, 34.19, 32.02, 29.80, 29.76, 29.62, 29.46, 29.41, 29.25, 24.98, 24.95, 22.78, 14.19 (FA), 8.46 (N-(CH$_2$-*C*H$_3$)$_3$); ^{31}P NMR (243 MHz, $CDCl_3$, CD_3OD 3%) δ 0.43 ppm.; MALDI-TOF MS calcd for $C_{35}H_{69}NaO_8P$ $[M+Na]^+$ *m/z* 671.46, $C_{35}H_{68}Na_2O_8P$ $[M+Na_2]^+$ *m/z* 693.44, $C_{35}H_{69}KO_8P$ $[M+K]^+$ *m/z* 687.44, $C_{35}H_{68}KNaO_8P$ $[M+KNa]^+$ *m/z* 709.42, found *m/z* 672.42, 694.48, 688.46, 710.52.; HRMS calcd for $[C_{35}H_{68}O_8P]^-$ requires *m/z* 647.4657; found 647.4665.

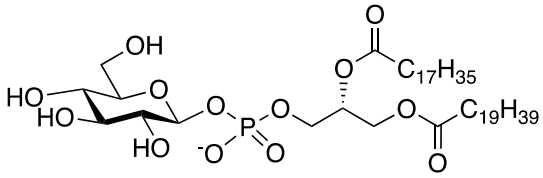
3-8. Synthesis of 2,2-dimethyl-1,3-dioxolan-4-ylmethyl phosphatidyl glucoside: **2**



2,2-Dimethyl-1,3-dioxolan-4-ylmethyl phosphatidic acid: **1** (15 mg, 48 μmol), D-glucose (26 mg, 144 μmol) and TEA (240 μL, 1.72 mmol) were dissolved in CH_3CN/H_2O (1/4, 796 μL) and treated with DMC (72.8 mg, 431 μmol) at 0 °C. The reaction mixture was stirred at 4 °C for 1 h. The mixture was passed over a solid phase extraction column

(Strata^{TM}-X 33 μm Polymeric Reversed Phase) with H_2O/MeOH (100/0 to 97/3). All fractions containing **2** were pooled and concentrated *in vacuo.* The residue was purified by silica gel column chromatography (Iatrobeads 6RS-8060 No.1104) with $CHCl_3$/MeOH/H_2O/TEA (100/0/0/1 to 89/11/0/0.2, 80/20/0/0.2, 67/33/5/0.2 *v/v*) to give **2** (10 mg, 44%); R_f = 0.55 ($CHCl_3$/MeOH = 1/1, 1% TEA); ^{1}H NMR (600 MHz, $CDCl_3$, CD_3OD 3%): δ 4.94 (t, 1H, H-1), 4.36-4.32 (m, 1H, *sn*-2), 4.06-4.04 (m, 1H, *sn*-1$_a$), 3.99-3.96 (m, 1H, *sn*-3$_a$), 3.93-3.87 (m, 3H, *sn*-3$_b$, *sn*-1$_b$, H-6), 3.71-3.68 (m, 1H, H-6'), 3.53 (t, 1H, H-3), 3.45-3.37 (m, 2H, H-5, H-4), 3.35 (t, 1H, H-2), 3.11-3.08 (m, 6H, N-(*C*H$_2$-CH$_3$)$_3$), 1.41 (s, 3H, -C*H*$_3$Isop), 1.34 (s, 3H, -C*H*$_3$Isop), 1.31 (t, 9H, N-(CH$_2$-C*H*$_3$)$_3$); ^{13}C NMR (150 MHz, $CDCl_3$, CD_3OD 3%): δ 109.58 (Isopropylidene), 98.41 (d, $^2J_{CP}$ = 5.8 Hz, C-1), 77.09 (C-5), 76.40 (C-3), 74.82 (d, $^3J_{CP}$ = 8.6 Hz, *sn*-2), 74.38 (d, $^3J_{CP}$ = 7.1 Hz, C-2), 70.30 (C-4), 66.50 (*sn*-1), 66.08 (d, $^2J_{CP}$ = 4.4 Hz, *sn*-3), 62.14 (C-6), 45.76 (N-(*C*H$_2$-CH$_3$)$_3$), 26.83 (-*C*H$_3$Isop), 25.35 (-*C*H$_3$Isop), 8.59 (N-(CH$_2$-*C*H$_3$)$_3$); ^{31}P NMR (243 MHz, $CDCl_3$, CD_3OD 3%) δ -2.08 ppm: ESI MS calcd for $[C_{12}H_{22}O_{11}P]^-$ requires *m/z* 373.09; found 373.13.; HRMS calcd for $[C_{12}H_{22}O_{11}P]^-$ requires *m/z* 373.0905; found 373.0898.

3-9. Synthesis of phosphatidyl glucoside (PtdGlc) (18:0/20:0): **4**

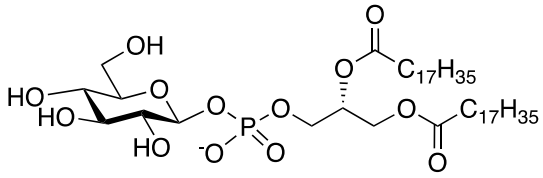


PA(18:0/20:0) (**3**) (Ref S1)(5.0 mg, 6 μmol), D-glucose (3.3 mg, 18 μmol) and TEA (30 μL, 215 mmol) were suspended in propionitrile/H_2O (1/5, 90 μL) and treated with DMC (9.1 mg, 55 μmol) at 0 °C. The reaction mixture was stirred at 4 °C for 1 h. Subsequently, the mixture was subjected to silica gel column chromatography (Iatrobeads 6RS-8060 No.1104) and eluted with $CHCl_3$/MeOH/TEA (100/0/1 to 89/11/0.2, 80/20/0.2, *v/v*). All fractions containing **4** were collected and concentrated *in vacuo.* The residue was purified by gel permeation column chromatography (Sephadex LH20) with $CHCl_3$/MeOH/TEA (50/50/1, *v/v*) to give **4** (2.1 mg, 35%);^{1}H NMR (600 MHz, $CDCl_3$/CD_3OD = 2/1) δ 5.28-5.25 (m, 1H, *sn*-2), 4.84 (t, 1H, *J* = 7.8 Hz, *J* = 7.8 Hz, H-1), 4.44-4.43 (m, 1H, *sn*-1$_a$), 4.20-4.17 (m, 1H, *sn*-1$_b$), 4.10-4.03 (m, 2H, *sn*-3), 3.90-3.88 (m, 1H, H-6), 3.67-3.64 (m, 1H, H-6'), 3.47-3.37 (m, 2H, H-3, H-5), 3.32-3.28 (m, 2H, H-4, H-2), 3.16-3.13 (m, 6H, N-(*C*H$_2$-CH$_3$)$_3$), 2.34-2.30 (m, 4H, FA), 1.64-1.58 (m, 4H, FA), 1.34 (t, 9H, *J* = 7.8 Hz, *J* = 7.2 Hz, N-(CH$_2$-C*H*$_3$)$_3$), 1.33-1.27 (m, 60H, FA), 0.89 (t, 6H, *J* = 6.6 Hz, *J* = 7.2 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$/CD_3OD = 2/1) δ 173.83, 173.43 (CO), 97.88 (d, $^2J_{CP}$ = 5.7 Hz, C-1), 76.84 (C-5), 75.98 (C-3), 73.95 (d, $^3J_{CP}$ = 7.2 Hz, C-2), 70.27 (d, $^3J_{CP}$ = 8.7 Hz, *sn*-2), 69.91 (C-4), 63.55 (d, $^2J_{CP}$ = 4.4 Hz, *sn*-3), 62.55 (*sn*-1), 61.60 (C-6), 46.00 (N-(*C*H$_2$-CH$_3$)$_3$), 33.99, 33.83, 31.65, 29.42, 29.38, 29.26, 29.09, 29.06, 28.88, 24.64, 24.60, 22.38, 13.63 (FA), 8.19 (N-(CH$_2$-*C*H$_3$)$_3$); ^{31}P NMR (243 MHz, $CDCl_3$/CD_3OD = 2/1) δ -2.73 ppm; ESI MS calcd for $[C_{47}H_{90}O_{13}P]^-$ requires *m/z* 893.61; found 893.59. HR-MS calcd for $[C_{47}H_{90}O_{13}P]^-$ requires *m/z* 893.6124; found 893.6143.; HRMS calcd for $[C_{47}H_{90}O_{13}P]^-$ requires *m/z* 893.6124; found 893.6139. These data are consistent with previously reported [Ref BMCL].

3-10. Synthesis of PtdGlc (**4**) by stepwise addition of DMC and D-glucose.

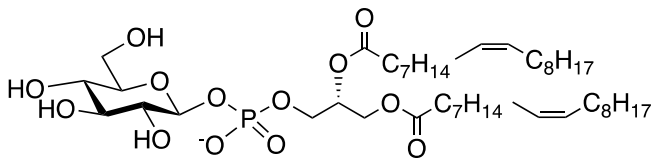
PA(18:0/20:0) (**3**) (5.0 mg, 6 μmol), D-glucose (3.3 mg, 18 μmol) and TEA (30 μL, 215 mmol) were suspended in propionitrile/H_2O (1/5, 90 μL) and treated with DMC (9.1 mg, 55 μmol) at 0 °C. The reaction mixture was stirred at 4 °C for 15 min. Subsequently, 4 times a solution of glucose (3.3 mg, 18 μmol), DMC (9.1 mg, 55 μmol), and TEA (15 μL, 108 mmol) in H_2O/CH_3CH_2CN (5:1, total volume 45 μL) was added to the reaction mixture in 15 min intervals. The final reaction mixture was applied to silica gel column chromatography (Iatrobeads 6RS-8060 No.1104) and eluted with $CHCl_3$/MeOH/TEA (100/0/1 to 89/11/0.2, 80/20/0.2, *v/v*). All fractions containing **4** were collected and concentrated *in vacuo*. The residue was purified by gel permeation column chromatography (Sephadex LH20) with $CHCl_3$/MeOH/TEA (50/50/1, *v/v*) to give **4** (4.8 mg, 81%).

3-11. Synthesis of PtdGlc (18:0/18:0): **6**



PA(18:0/18:0) **5** (1.0 mg, 1.2 μmol), D-glucose (0.65 mg, 3.6 μmol) and TEA (6 μL, 43 mmol) were suspended in propionitrile/H_2O (1/5, 18 μL), treated with DMC (1.8 mg, 11 μmol) at 0 °C and stirred at 4 °C for 1 h. The reaction mixture was applied to silica gel column chromatography (Iatrobeads 6RS-8060 No.1104) and eluted with $CHCl_3$/MeOH/TEA (100/0/1 to 89/11/0.2, 80/20/0.2, *v/v*). All fractions containing **6** were collected and concentrated *in vacuo*. The residue was purified by gel permeation column chromatography (Sephadex LH20) with $CHCl_3$/MeOH/TEA (50/50/1, *v/v*) to give **6** (0.38 mg, 32%);^{1}H NMR (600 MHz, $CDCl_3$ / CD_3OD = 2 / 1): δ 5.28-5.25 (m, 1H, *sn*-2), 4.85 (t, 1H, *J* = 7.8 Hz, *J* = 7.8 Hz, H-1), 4.45-4.44 (m, 1H, *sn*-1_a), 4.20-4.17 (m, 1H, *sn*-1_b), 4.10-4.03 (m, 2H, *sn*-3), 3.88-3.86 (m, 1H, H-6), 3.69-3.66 (m, 1H, H-6'), 3.46-3.42 (m, 1H, H-3), 3.38-3.37 (m, 1H, H-5), 3.33-3.28 (m, 2H, H-4, H-2), 3.16-3.12 (m, 6H, N-(C*H*$_2$-CH$_3$)$_3$), 2.34-2.30 (m, 4H, FA), 1.64-1.58 (m, 4H, FA), 1.33 (t, 9H, *J* = 7.2 Hz, *J* = 7.8 Hz, N-(CH$_2$-C*H*$_3$)$_3$), 1.31-1.27 (m, 56H, FA), 0.89 (t, 6H, *J* = 6.6 Hz, *J* = 6.6 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$ / CD_3OD = 2 / 1): δ 173.84, 173.43 (CO), 97.90 (d, $^2J_{CP}$ = 7.2 Hz, C-1), 76.85 (C-5), 76.01 (C-3), 73.97 (d, $^3J_{CP}$ = 8.6 Hz, C-2), 70.28 (d, $^3J_{CP}$ = 7.1 Hz, *sn*-2), 69.92 (C-4), 63.55 (d, $^2J_{CP}$ = 4.4 Hz, *sn*-3), 62.56 (*sn*-1), 61.62 (C-6), 46.06 (N-(*C*H$_2$-CH$_3$)$_3$), 34.00, 33.83, 31.66, 29.43, 29.39, 29.28, 29.09, 28.88, 24.64, 24.60, 22.39, 13.63 (FA), 8.20 (N-(CH$_2$-*C*H$_3$)$_3$); ^{31}P NMR (243 MHz, $CDCl_3$ / CD_3OD = 2 / 1) δ -2.76 ppm: ESI MS calcd for $[C_{45}H_{86}O_{13}P]^-$ requires *m/z* 865.58; found 865.65.; HRMS calcd for $[C_{45}H_{86}O_{13}P]^-$ requires *m/z* 865.5811; found 865.5809.

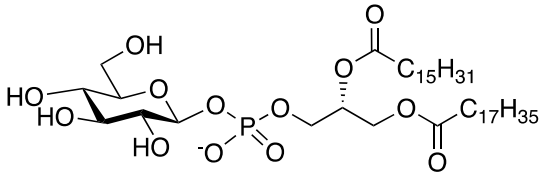
3-12. Synthesis of PtdGlc (18:1/18:1): **8**



PA(18:1/18:1) **7** (5.0 mg, 6 μmol), D-glucose (3.3 mg, 18 μmol) and TEA (30 μL, 215 mmol) were suspended in

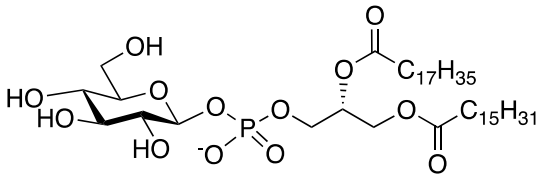
propionitrile/H_2O (1/5, 90 μL), treated with DMC (9.1 mg, 55 μmol) at 0 °C and stirred at 4 °C for 1 h. The mixture was applied to silica gel column chromatography (Iatrobeads 6RS-8060 No.1104) and eluted with $CHCl_3$/MeOH/TEA (100/0/1 to 89/11/0.2, 80/20/0.2, *v/v*). All fractions containing **8** were collected and concentrated *in vacuo*. The residue was purified by gel permeation column chromatography (Sephadex LH20) with $CHCl_3$/MeOH/TEA (50/50/1, *v/v*) to give **8** (1.8 mg, 29%); ^{1}H NMR (600 MHz, $CDCl_3$ / CD_3OD = 2 / 1): δ 5.38-5.32 (m, 4H, olefin), 5.28-5.25 (m, 1H, *sn*-2), 4.85 (t, 1H, *J* = 7.8 Hz, *J* = 7.8 Hz, H-1), 4.44-4.43 (m, 1H, *sn*-1_a), 4.20-4.17 (m, 1H, *sn*-1_b), 4.10-4.03 (m, 2H, *sn*-3), 3.89-3.87 (m, 1H, H-6), 3.69-3.66 (m, 1H, H-6'), 3.48-3.37 (m, 2H, H-3, H-5), 3.33-3.28 (m, 2H, H-4, H-2), 3.17-3.13 (m, 6H, N-(CH_2-CH_3)$_3$), 2.34-2.30 (m, 4H, FA), 2.04-2.00 (m, 8H, FA), 1.64-1.58 (m, 4H, FA), 1.35 (t, 9H, *J* = 7.8 Hz, *J* = 7.2 Hz, N-(CH_2-CH_3)$_3$), 1.34-1.28 (m, 44H, FA), 0.89 (t, 6H, *J* = 6.6 Hz, *J* = 7.2 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$ / CD_3OD = 2 / 1): δ 173.77, 173.37 (CO), 129.70, 129.42 (olefin), 97.96 (d, $^2J_{CP}$ = 5.7 Hz, C-1), 76.87 (C-5), 76.06 (C-3), 74.00 (d, $^3J_{CP}$ = 7.1 Hz, C-2), 70.29 (, $^3J_{CP}$ = 8.6 Hz, *sn*-2), 69.89 (C-4), 63.56 (d, $^2J_{CP}$ = 4.2 Hz, *sn*-3), 62.57 (*sn*-1), 61.63 (C-6), 46.03 (N-(CH_2-CH_3)$_3$), 33.96, 33.80, 31.62, 29.47, 29.23, 29.03, 28.98, 28.94, 28.88, 28.87, 28.84, 28.15, 26.90, 25.40, 24.61, 24.58, 22.37, 13.62 (FA), 8.18 (N-(CH_2-CH_3)$_3$); ^{31}P NMR (243 MHz, $CDCl_3$ / CD_3OD = 2 / 1) δ -2.92 ppm: ESI MS calcd for $[C_{45}H_{82}O_{13}P]^-$ requires *m/z* 861.55; found 861.52.; HRMS calcd for $[C_{45}H_{82}O_{13}P]^-$ requires *m/z* 861.5498; found 861.5509.

3-13. Synthesis of PtdGlc (18:0/16:0): **10**



PA(18:0/16:0) **9** (1.0 mg, 1.2 μmol), D-glucose (0.65 mg, 3.6 μmol) and TEA (6 μL, 43 mmol) were suspended in propionitrile/H_2O (1/5, 18 μL), treated with DMC (1.8 mg, 11 μmol) at 0 °C and stirred at 4 °C for 1 h. The mixture was applied to silica gel column chromatography (Iatrobeads 6RS-8060 No.1104) and eluted with $CHCl_3$/MeOH/TEA (100/0/1 to 89/11/0.2, 80/20/0.2, *v/v*). All fractions containing **10** were collected and concentrated *in vacuo*. The residue was purified by gel permeation column chromatography (Sephadex LH20) with $CHCl_3$/MeOH/TEA (50/50/1, *v/v*) to give **10** (0.34 mg, 28%);^{1}H NMR (600 MHz, $CDCl_3$ / CD_3OD = 2 / 1): δ 5.28-5.25 (m, 1H, *sn*-2), 4.84 (t, 1H, *J* = 7.2 Hz, *J* = 7.8 Hz, H-1), 4.46-4.43 (m, 1H, *sn*-1_a), 4.20-4.17 (m, 1H, *sn*-1_b), 4.10-4.03 (m, 2H, *sn*-3), 3.90-3.87 (m, 1H, H-6), 3.68-3.65 (m, 1H, H-6'), 3.47-3.41 (m, 1H, H-3), 3.39-3.37 (m, 1H, H-5), 3.32-3.28 (m, 2H, H-4, H-2), 3.16-3.13 (m, 6H, N-(CH_2-CH_3)$_3$), 2.34-2.30 (m, 4H, FA), 1.64-1.58 (m, 4H, FA), 1.34 (t, 9H, *J* = 7.2 Hz, *J* = 7.8 Hz, N-(CH_2-CH_3)$_3$), 1.32-1.27 (m, 52H, FA), 0.89 (m, 6H, *J* = 6.6 Hz, *J* = 7.2 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$ / CD_3OD = 2 / 1): δ 173.82, 173.42 (CO), 97.89 (d, $^2J_{CP}$ = 5.7 Hz, C-1), 76.85 (C-5), 76.00 (C-3), 73.97 (d, $^3J_{CP}$ = 7.2 Hz, C-2), 70.27 (d, $^3J_{CP}$ = 8.7 Hz, *sn*-2), 69.90 (C-4), 63.52 (d, $^2J_{CP}$ = 4.4 Hz, *sn*-3), 62.55 (*sn*-1), 61.60 (C-6), 45.99 (N-(CH_2-CH_3)$_3$), 33.97, 33.82, 31.64, 29.41, 29.25, 29.07, 28.87, 24.62, 24.60, 22.37, 13.61 (FA), 8.18 (N-(CH_2-CH_3)$_3$); ^{31}P NMR (243 MHz, $CDCl_3$ / CD_3OD = 2 / 1) δ -2.76 ppm: ESI MS calcd for $[C_{43}H_{82}O_{13}P]^-$ requires *m/z* 837.55; found 837.57.; HRMS calcd for $[C_{43}H_{82}O_{13}P]^-$ requires *m/z* 837.5498; found 837.5498.

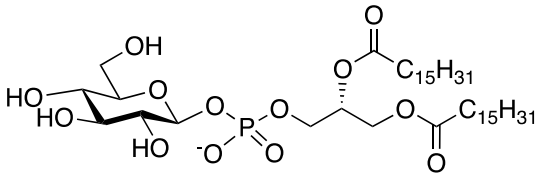
3-14. Synthesis of PtdGlc (16:0/18:0): **12**



PA(16:0/18:) **11** (5.0 mg, 6 μmol), D-glucose (3.3 mg, 18 μmol) and TEA (30 μL, 215 mmol) were suspended in propionitrile/H_2O (1/5, 90 μL), treated with DMC (9.1 mg, 55 μmol) at 0 °C and stirred at 4 °C for 1 h. The mixture was applied to silica gel column chromatography (Iatrobeads 6RS-8060 No.1104) and eluted with $CHCl_3$/MeOH/TEA (100/0/1 to 89/11/0.2, 80/20/0.2, *v/v*). All fractions containing **12** were collected and concentrated *in vacuo*. The residue was purified by gel permeation column chromatography (Sephadex LH20) with $CHCl_3$/MeOH/TEA (50/50/1, *v/v*) to give **12** (1.6 mg, 27%); ^{1}H NMR (600 MHz, $CDCl_3$ / CD_3OD = 2 / 1): δ 5.28-5.25 (m, 1H, *sn*-2), 4.84 (t, 1H, *J* = 7.8 Hz, *J* = 7.8 Hz, H-1), 4.45-4.43 (m, 1H, *sn*-1$_a$), 4.20-4.17 (m, 1H, *sn*-1$_b$), 4.10-4.03 (m, 2H, *sn*-3), 3.89-3.86 (m, 1H, H-6), 3.69-3.66 (m, 1H, H-6'), 3.48-3.41 (m, 1H, H-3), 3.39-3.37 (m, 1H, H-5), 3.33-3.28 (m, 2H, H-4, H-2), 3.18-3.15 (m, 6H, N-(C*H*$_2$-CH$_3$)$_3$), 2.34-2.30 (m, 4H, FA), 1.64-1.58 (m, 4H, FA), 1.36 (t, 9H, *J* = 7.2 Hz, *J* = 7.8 Hz, N-(CH$_2$-C*H*$_3$)$_3$), 1.33-1.27 (m, 52H, FA), 0.89 (t, *J* = 6.6 Hz, *J* = 7.2 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$ / CD_3OD = 2 / 1): δ 173.81, 173.41 (CO), 97.93 (d, $^2J_{CP}$ = 5.9 Hz, C-1), 76.86 (C-5), 76.04 (C-3), 73.99 (d, $^3J_{CP}$ = 8.6 Hz, C-2), 70.27 (d, $^3J_{CP}$ = 8.7 Hz, *sn*-2), 69.88 (C-4), 63.54 (d, $^2J_{CP}$ = 5.7 Hz, *sn*-3), 62.55 (*sn*-1), 61.62 (C-6), 46.12 (N-(*C*H$_2$-CH$_3$)$_3$), 33.98, 33.82, 31.64, 29.41, 29.36, 29.26, 29.24, 29.07, 29.04, 28.87, 28.85, 24.63, 24.59, 22.37, 13.61 (FA), 8.19 (N-(CH$_2$-*C*H$_3$)$_3$) ; ^{31}P NMR (243 MHz, $CDCl_3$ / CD_3OD = 2 / 1) δ -2.90 ppm: ESI MS calcd for $[C_{43}H_{82}O_{13}P]^-$ requires *m/z* 837.55; found 837.59.; HRMS calcd for $[C_{43}H_{82}O_{13}P]^-$ requires *m/z* 837.5498; found 837.5472.

3-15. Synthesis of PtdGlc (16:0/16:0): **14**

3-15-1. Using 1,2-di-*O*-palmitoyl-*sn*-glycerol-3-phosphate triethylammonium salt.



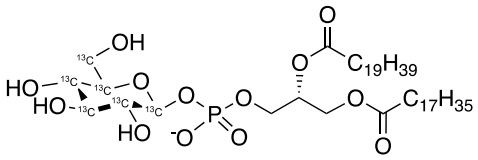
PA(16:0/16:0) **13** (10 mg, 12 μmol), D-glucose (6.5 mg, 36 μmol) and TEA (60 μL, 430 mmol) were suspended in propionitrile/H_2O (1/5, 180 μL), treated with DMC (1.8 mg, 11 μmol) at 0 °C and stirred at 4 °C for 1 h. The mixture was applied to silica gel column chromatography (Iatrobeads 6RS-8060 No.1104) and eluted with $CHCl_3$/MeOH/TEA (100/0/1 to 89/11/0.2, 80/20/0.2, *v/v*). All fractions containing **14** were collected and concentrated *in vacuo*. The residue was purified by gel permeation column chromatography (Sephadex LH20) with $CHCl_3$/MeOH/TEA (50/50/1, *v/v*) to give **14** (3.9 mg, 31%);^{1}H NMR (600 MHz, $CDCl_3$ / CD_3OD = 2 / 1): δ 5.28-5.25 (m, 1H, *sn*-2), 4.85 (t, 1H, *J* = 7.2 Hz, *J* = 7.8 Hz, H-1), 4.48-4.43 (m, 1H, *sn*-1$_a$), 4.20-4.17 (m, 1H, *sn*-1$_b$), 4.10-4.02 (m, 2H, *sn*-3), 3.89-3.86 (m, 1H, H-6), 3.69-3.66 (m, 1H, H-6'), 3.47-3.42 (m, 1H, H-3), 3.39-3.37 (m, 1H, H-5), 3.33-3.28 (m, 2H, H-4, H-2), 3.14-3.10 (m, 6H, N-(C*H*$_2$-CH$_3$)$_3$), 2.34-2.30 (m, 4H, FA), 1.64-1.58 (m, 4H, FA),

1.33 (t, 9H, *J* = Hz, *J* = Hz, N-(CH_2-CH_3)$_3$), 1.32-1.27 (m, 48H, FA), 0.89 (t, 6H, *J* = 7.2 Hz, *J* = 6.6 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$ / CD_3OD = 2 / 1): δ 173.82, 173.41 (CO), 97.94 (d, $^2J_{CP}$ = 5.7 Hz, C-1), 76.88 (C-5), 76.06 (C-3), 74.00 (d, $^3J_{CP}$ = 6.1 Hz, C-2), 70.28 (d, $^3J_{CP}$ = 8.6 Hz, *sn*-2), 69.89 (C-4), 63.55 (d, $^2J_{CP}$ = 5.7 Hz, *sn*-3), 62.55 (*sn*-1), 61.64 (C-6), 45.89 (N-(*C*H_2-CH_3)$_3$), 33.99, 33.83, 31.66, 29.43, 29.26, 29.09, 29.06, 28.88, 24.64, 24.60, 22.39, 13.66, 13.62 (FA), 8.20 (N-(CH_2-*C*H_3)$_3$); ^{31}P NMR (243 MHz, $CDCl_3$ / CD_3OD = 2 / 1) δ -2.90 ppm: ESI MS calcd for $[C_{41}H_{78}O_{13}P]^-$ requires *m/z* 809.52; found 809.59.; HRMS calcd for $[C_{41}H_{78}O_{13}P]^-$ requires *m/z* 809.5185; found 809.5203.

3-15-2. Using 1,2-di-*O*-palmitoyl-*sn*-glycerol-3-phosphate sodium salt.

1,2-di-*O*-palmitoyl-*sn*-glycerol-3-phosphate sodium salt (**13**, 1 mg, 1.2 μmol), D-glucose (0.65 mg, 3.6 μmol) and TEA (6 μL, 43 mmol) were suspended in propionitrile/H_2O (1/5, 18 μL), treated with DMC (1.8 mg, 11 μmol) at 0 °C and stirred at 4 °C for 1 h. The mixture was applied to silica gel column chromatography (Iatrobeads 6RS-8060 No.1104) and eluted with $CHCl_3$/MeOH/TEA (100/0/1 to 89/11/0.2, 80/20/0.2, *v/v*). All fractions containing **14** were collected and concentrated *in vacuo*. The residue was purified by gel permeation column chromatography (Sephadex LH20) with $CHCl_3$/MeOH/TEA (50/50/1, *v/v*) to give **14** (0.28 mg, 20%).

3-16. Synthesis of ^{13}C-labeled phosphatidyl glucoside (U-$^{13}C_6$): **15**



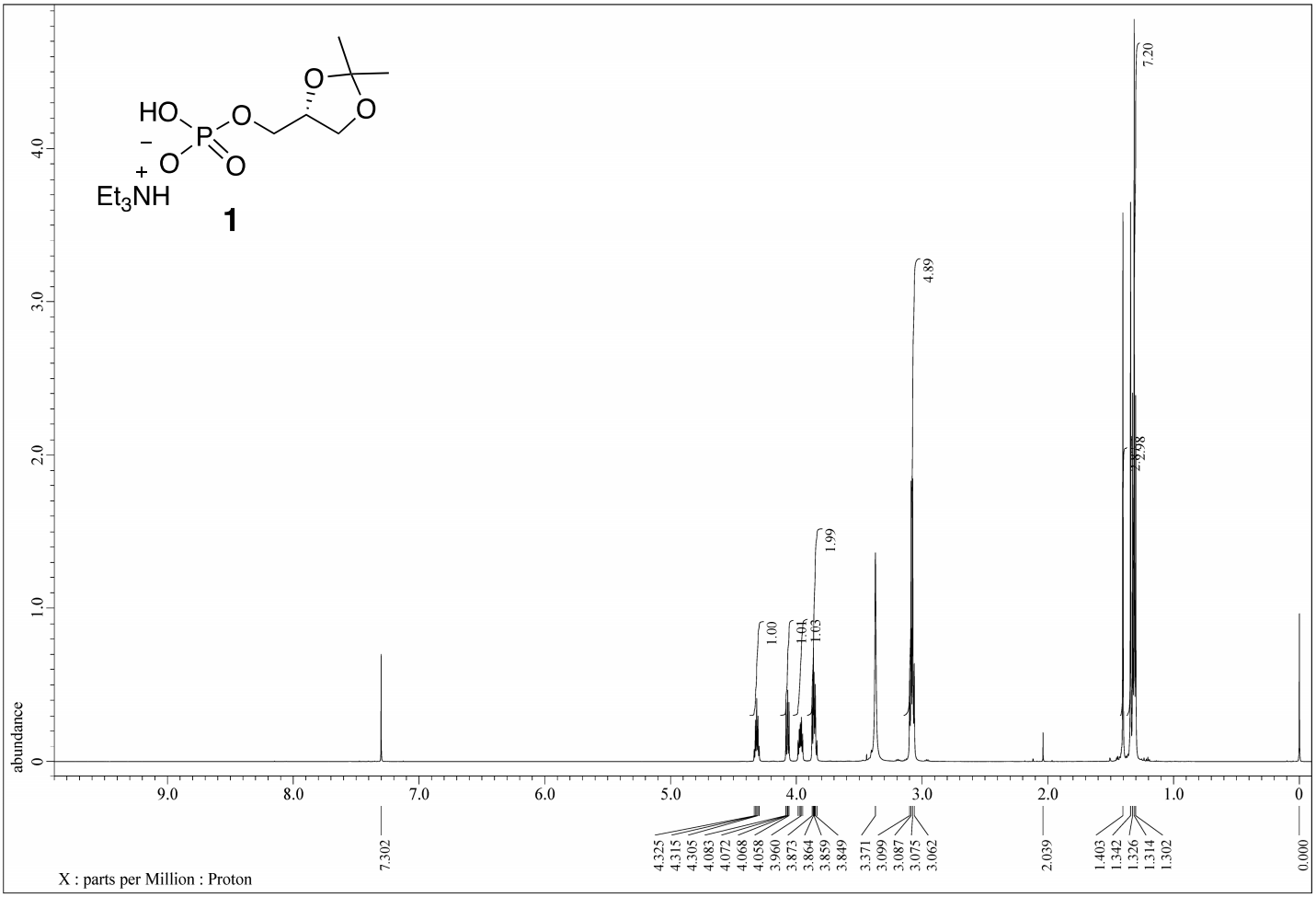
A mixture of PA(18:0/20:0) **3** (5.0 mg, 6 μmol), $^{13}C_6$-D-glucose (3.3 mg, 18 μmol) and TEA (30 μL, 215 mmol) in 90 μL of propionitrile/H_2O (1/5) was treated with DMC (9.1 mg, 55 μmol) at 0 °C. The reaction mixture was stirred at 4 °C for 1 h. The mixture was applied to silica gel column chromatography (Iatrobeads 6RS-8060 No.1104) and eluted with $CHCl_3$/MeOH/TEA (100/0/1 to 89/11/0.2, 80/20/0.2, *v/v*). The eluent was evaporated *in vacuo*. The residue was purified by gel permeation column chromatography (Sephadex LH20) with $CHCl_3$/MeOH/TEA (50/50/1, *v/v*) to give **15** (1.5 mg, 25%); ^{1}H NMR (600 MHz, $CDCl_3$ / CD_3OD = 2 / 1): δ 5.28-5.24 (m, 1H, *sn*-2), 4.82 (dt, 1H, $^1J_{CH}$ = 162.6 Hz, $^3J_{HP}$ = 7.8 Hz, *J* = 7.8 Hz, H-1), 4.42-4.40 (m, 1H, *sn*-1$_a$), 4.21-4.18 (m, 1H, *sn*-1$_b$), 4.09-4.02 (m, 3H, *sn*-3, H-6), 3.80-3.74 (m, 1H, H-6'), 3.56-3.39 (m, 2H, H-3, H-5), 3.32-3.25 (m, 2H, H-4, H-2), 3.17-3.14 (m, 6H, N-(CH_2-CH_3)$_3$), 2.34-2.30 (m, 4H, FA), 1.64-1.58 (m, 4H, FA), 1.35 (t, 9H, *J* = 7.2 Hz, *J* = 7.2 Hz, N-(CH_2-CH_3)$_3$), 1.33-1.27 (m, 60H, FA), 0.89 (m, 6H, *J* = 7.2 Hz, *J* = 7.2 Hz, FA); ^{13}C NMR (150 MHz, $CDCl_3$ / CD_3OD = 2 / 1): δ 97.77 (dd, *J* = 46.7 Hz, $^2J_{CP}$ = 4.4 Hz, 2.9 Hz, C-1), 76.79 (t, *J* = 43.1 Hz, *J* = 41.7 Hz, C-5), 75.89 (t, *J* = 38.7 Hz, *J* = 38.9 Hz, C-3), 73.87 (m, *J* = 42.5 Hz, *J* = 42.3 Hz, $^3J_{CP}$ = 7.2 Hz, 7.2 Hz, 5.7 Hz, 7.2 Hz, C-2), 69.92 (t, *J* = 38.7 Hz, *J* = 40.4 Hz, C-4), 61.53 (d, *J* = 43.2 Hz, C-6), 29.41 (FA); ^{31}P NMR (243 MHz, $CDCl_3$ / CD_3OD = 2 / 1) δ -2.33 ppm: ESI MS calcd for $[^{13}C_6C_{41}H_{90}O_{13}P]^-$ requires *m/z* 899.61; found 899.65, HRMS calcd for $[^{13}C_6C_{41}H_{90}O_{13}P]^-$ requires *m/z* 899.6325; found 899.6333.

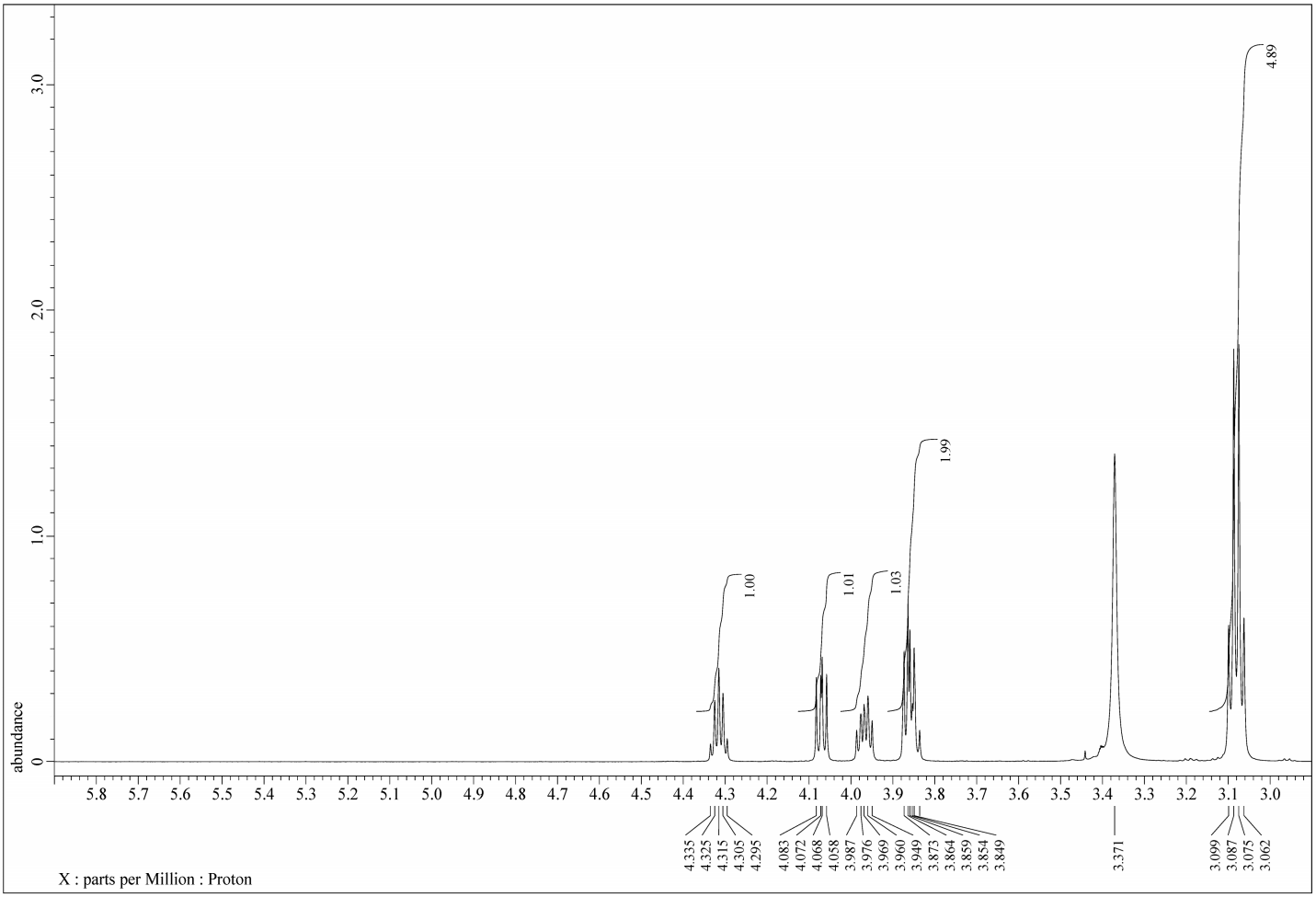
4. ^{1}H, ^{13}C, and ^{31}P NMR spectra of synthetic compounds:

PA derivatives (**1**, **5**, **7**, **9**, **11**, and **13**)

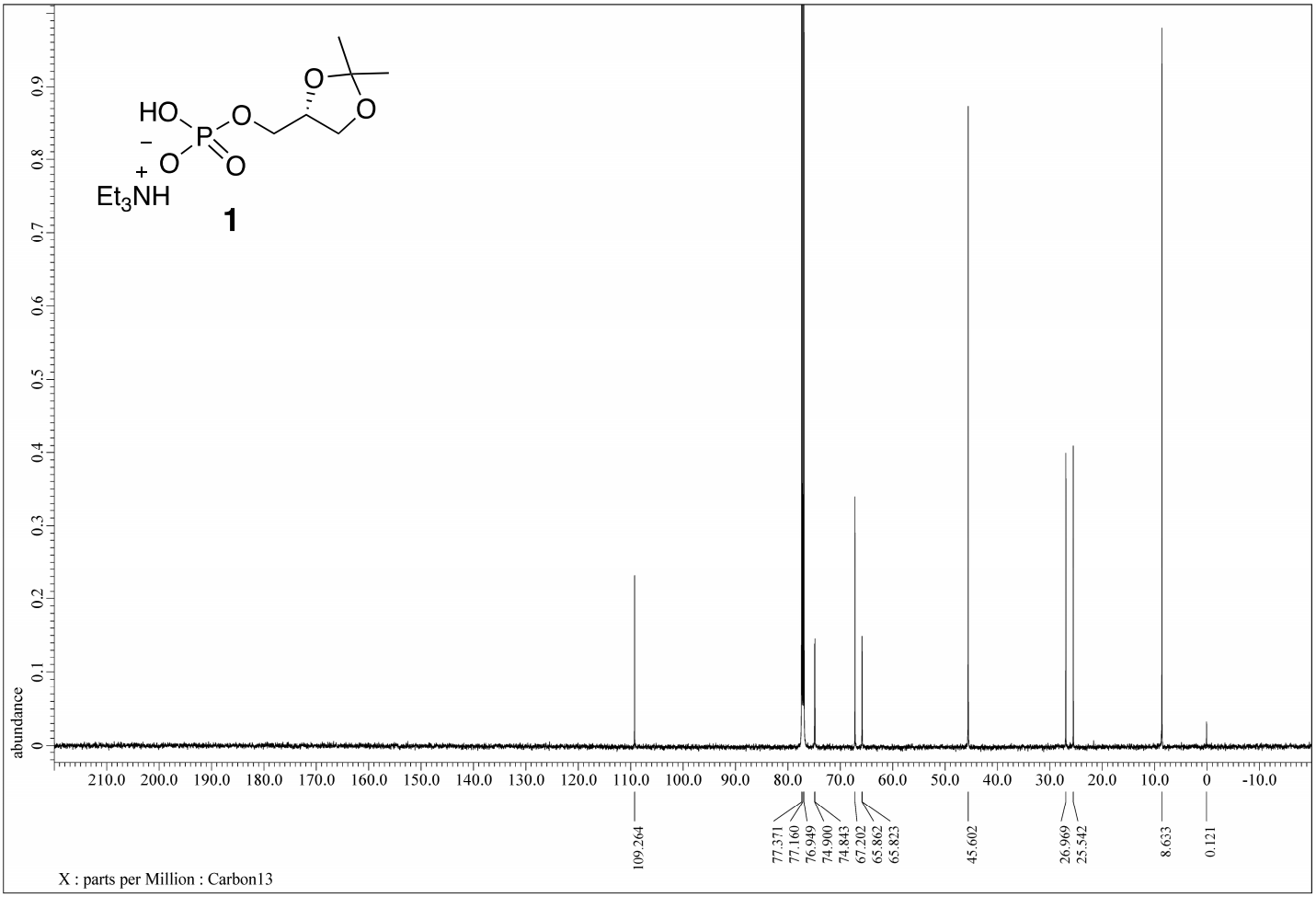
PtdGlc derivatives (**2**, **4, 6**, **8**, **10**, **12**, **14**, and **15**)

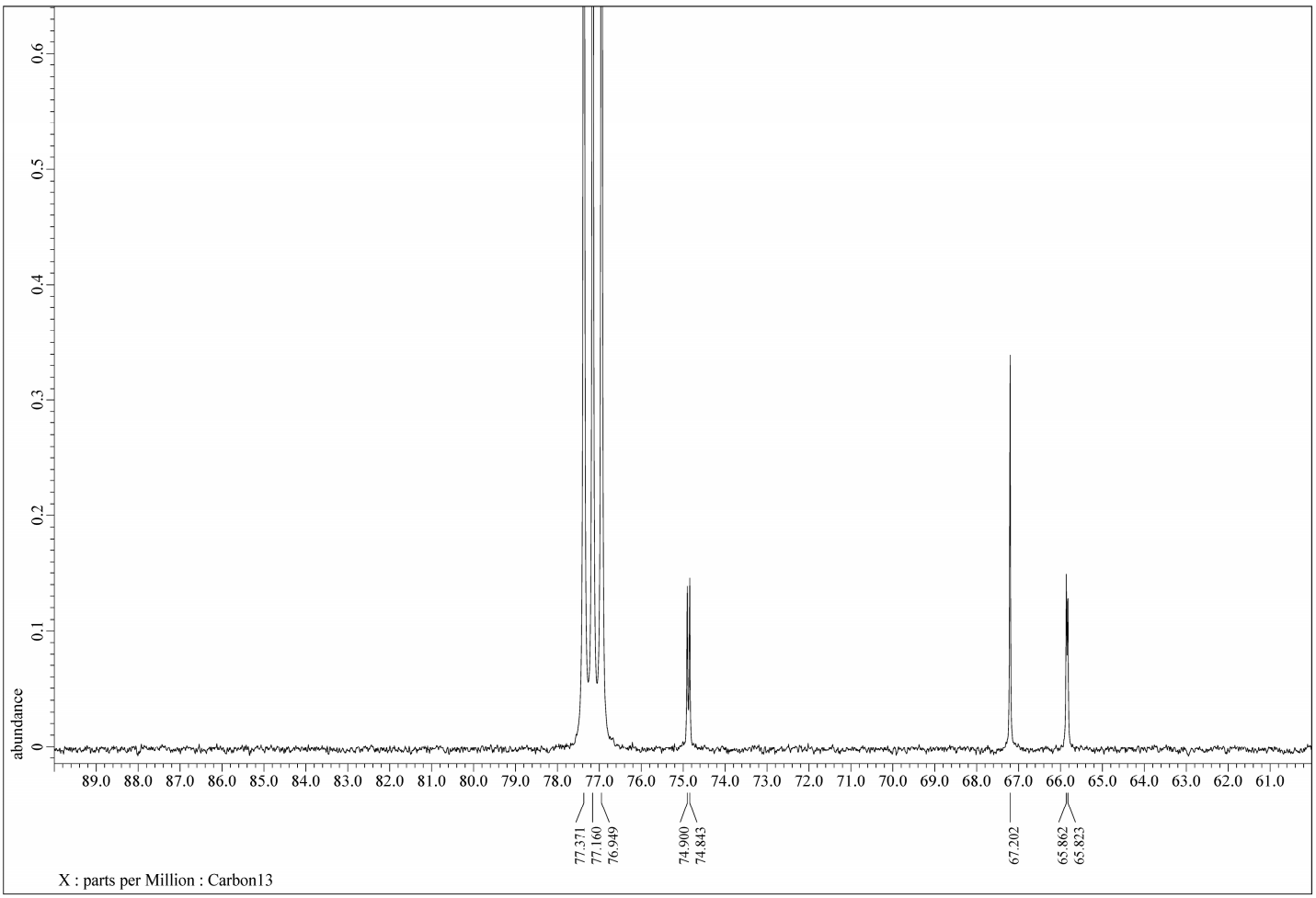
^{1}H-NMR data of (*R*)-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl hydrogen phosphate triethylammonium salt (**1**), 600 MHz, $CDCl_3$, CD_3OD 3%



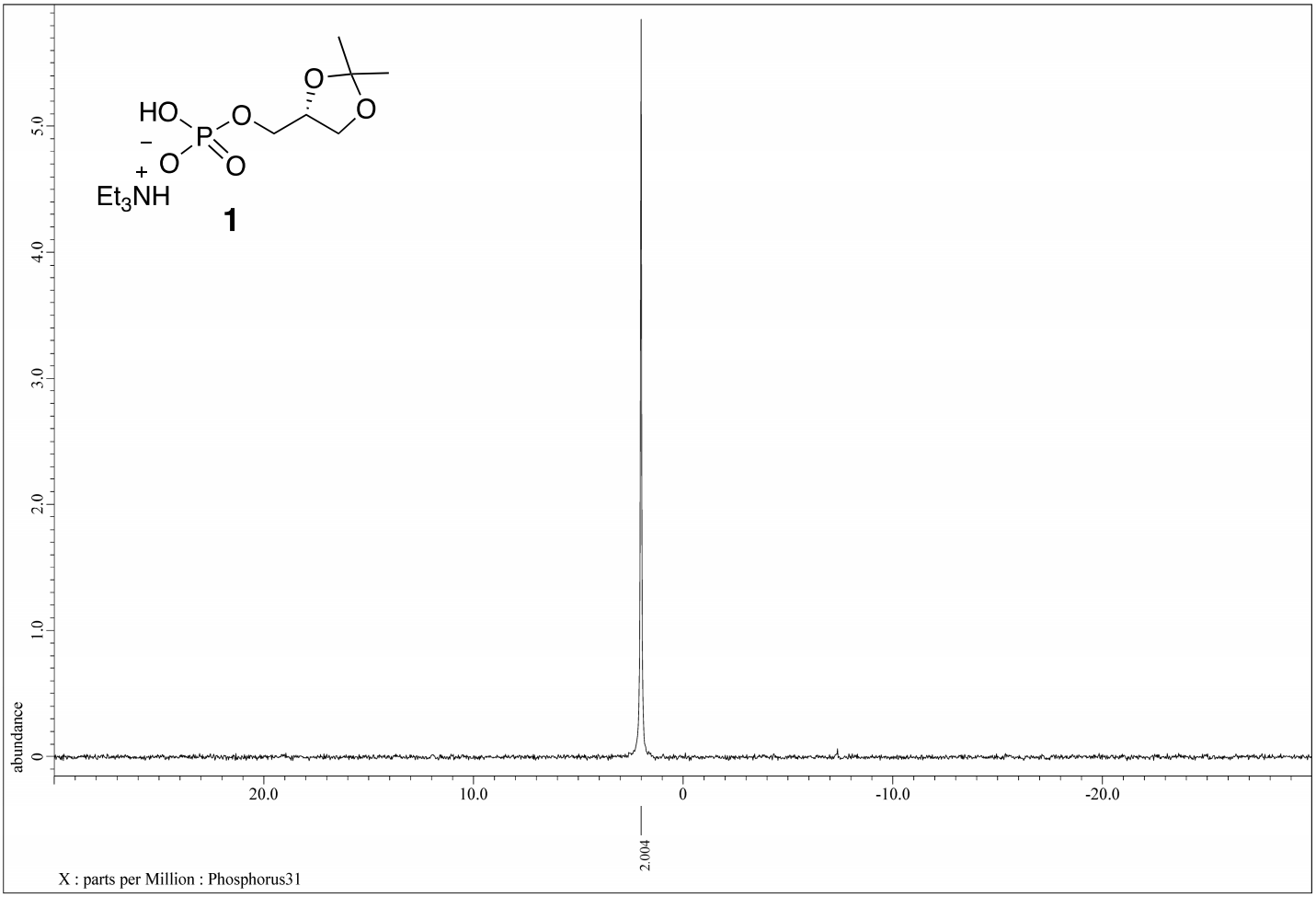


^{13}C-NMR data of (*R*)-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl hydrogen phosphate triethylammonium salt (**1**), 150 MHz, $CDCl_3$, CD_3OD 3%

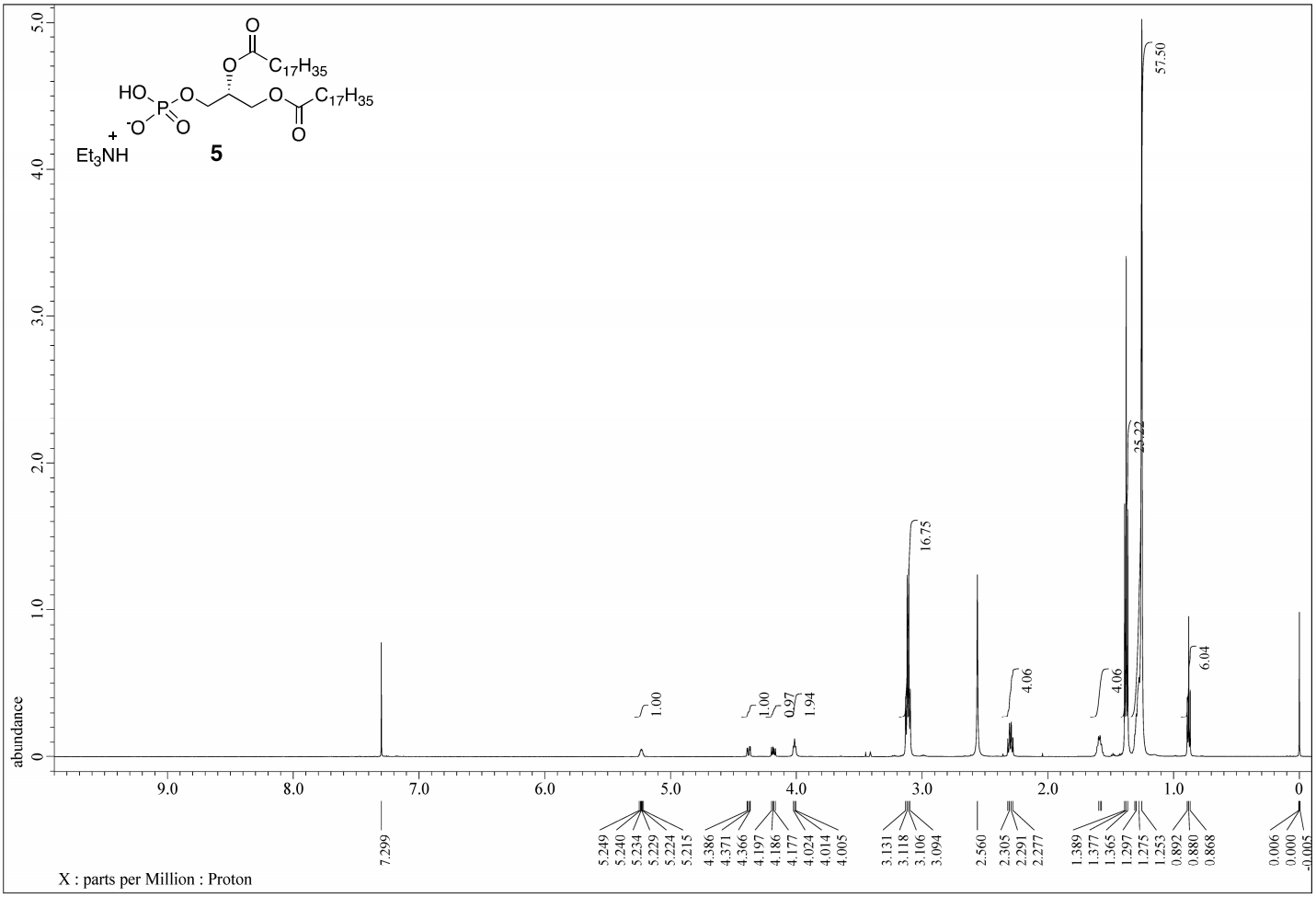


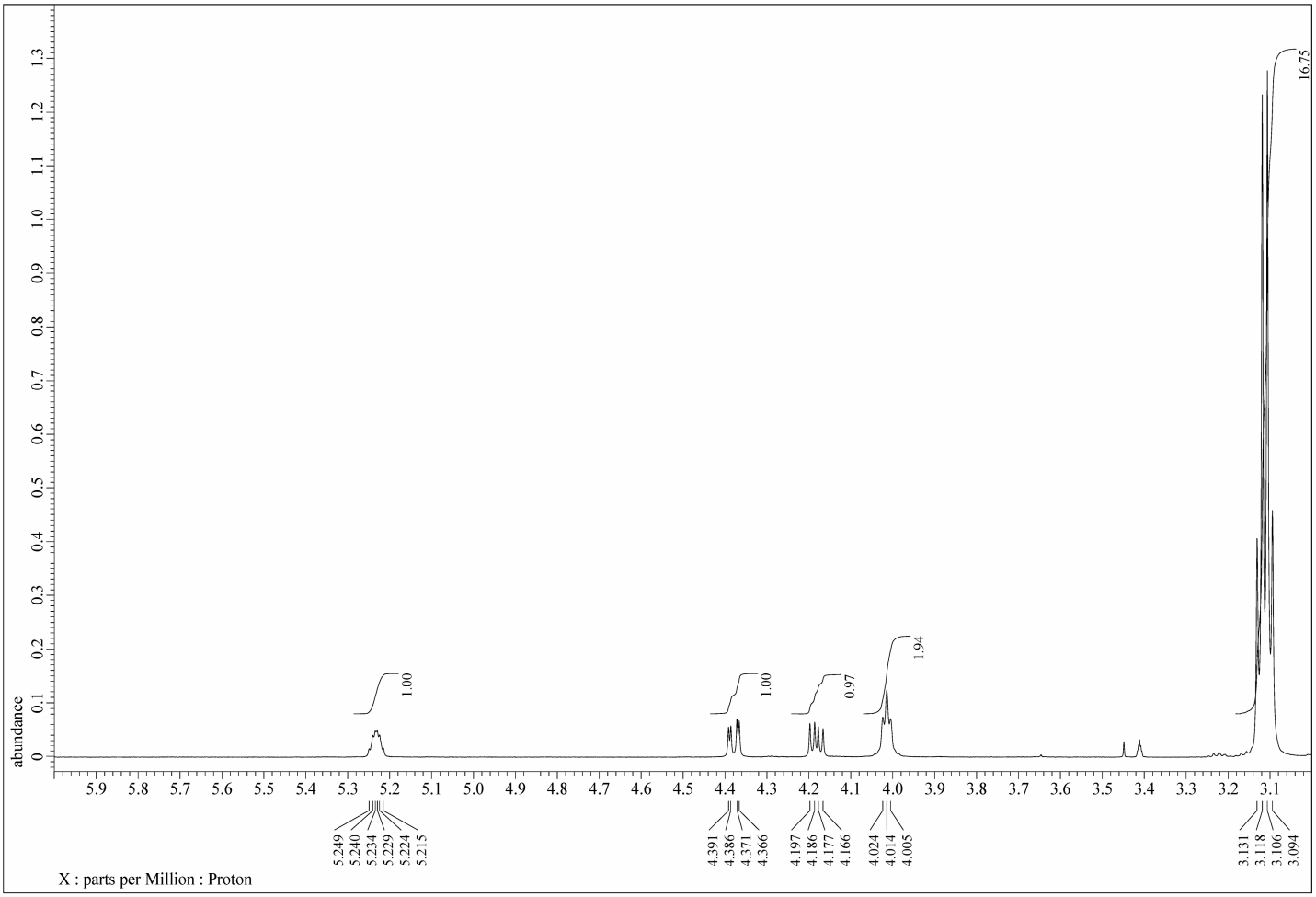


^{31}P-NMR data of (*R*)-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl hydrogen phosphate triethylammonium salt (**1**), 243 MHz, $CDCl_3$, CD_3OD 3%

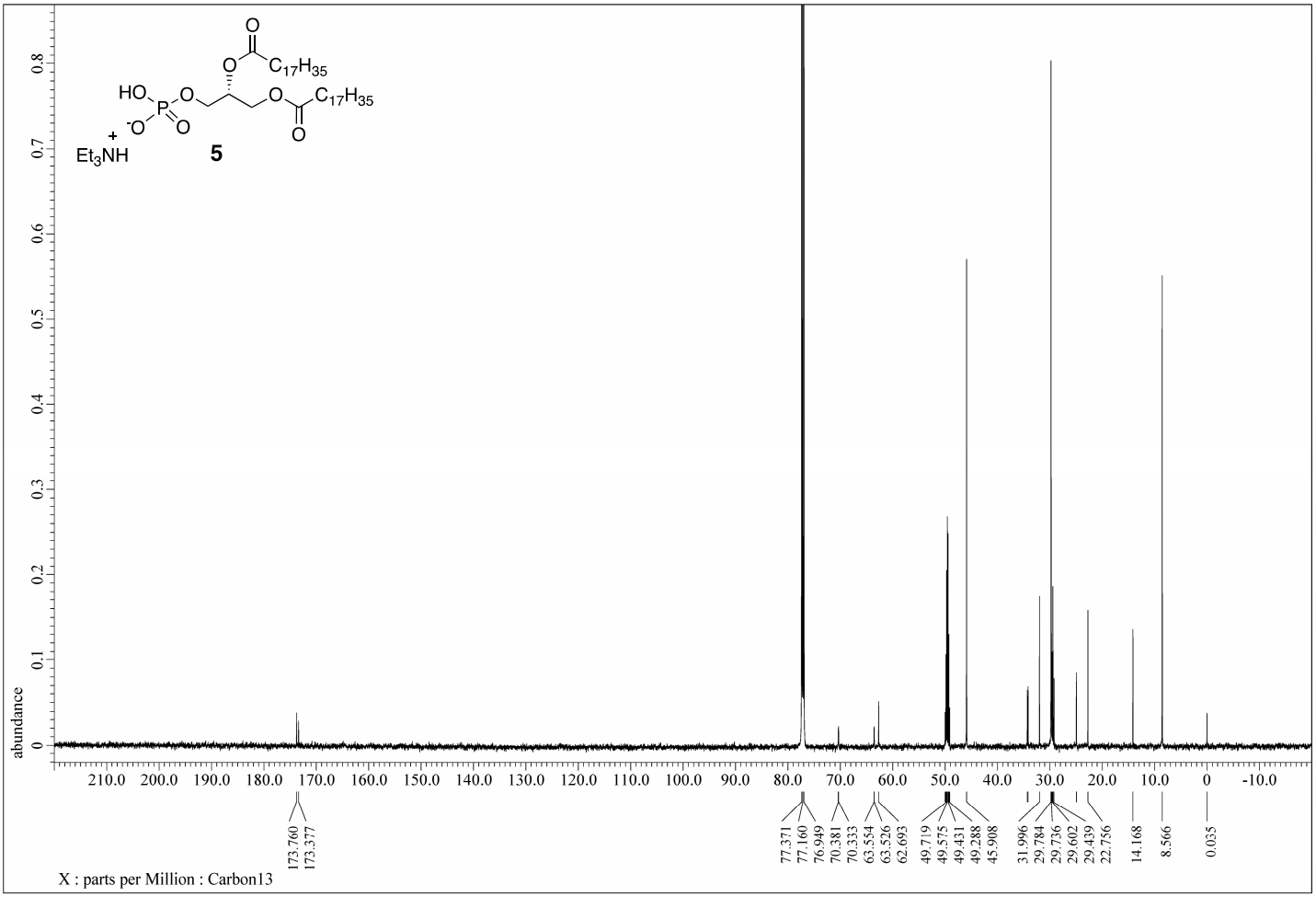


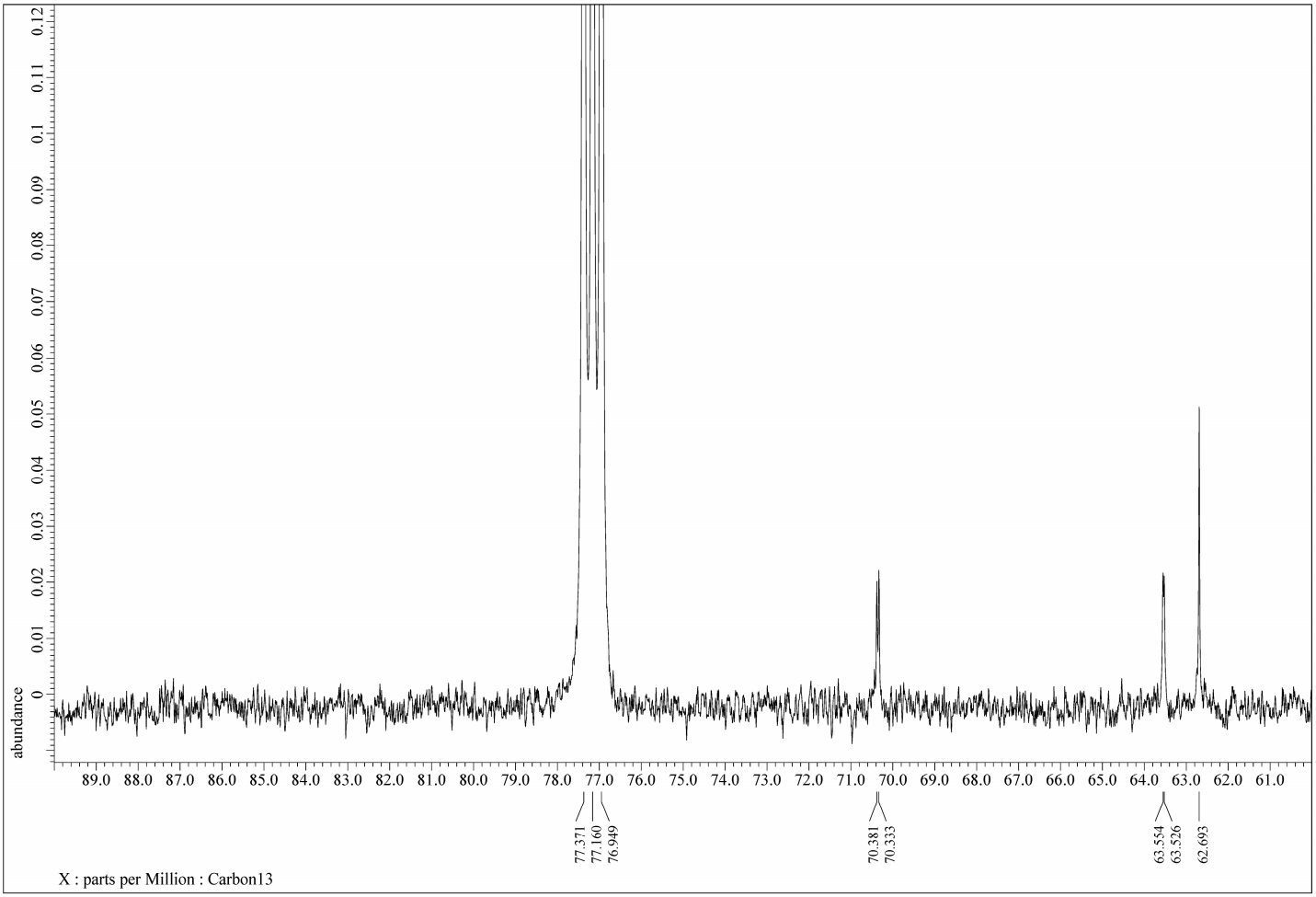
^{1}H-NMR data of PA (18:0/18:0): 1, 2-di-*O*-stearyl-*sn*-glycerol-3-phosphate triethylammonium salt (**5**), 600 MHz, $CDCl_3$, CD_3OD 3%



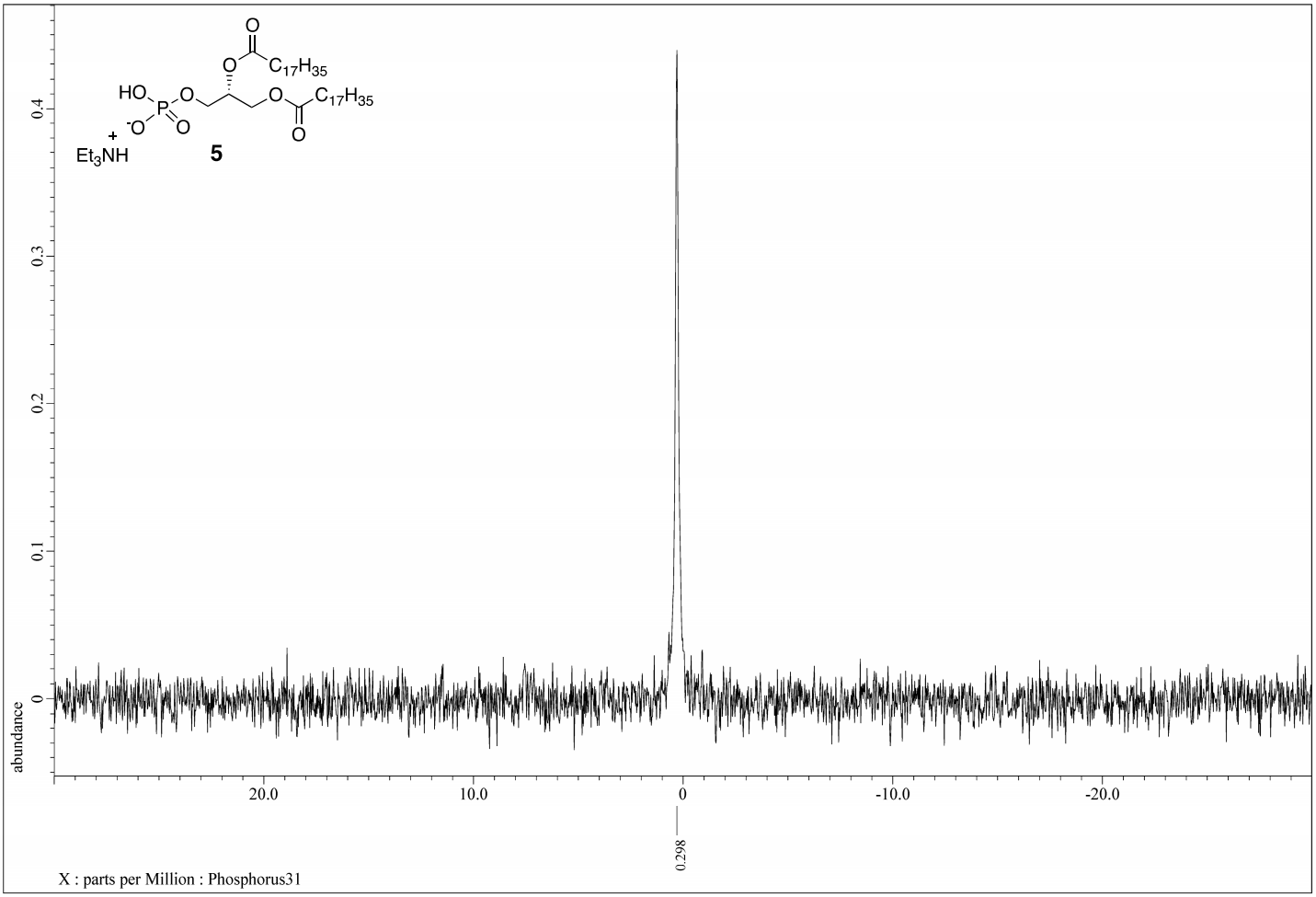


^{13}C-NMR data of PA (18:0/18:0): 1, 2-di-*O*-stearyl-*sn*-glycerol-3-phosphate triethylammonium salt (**5**), 150 MHz, $CDCl_3$, CD_3OD 3%

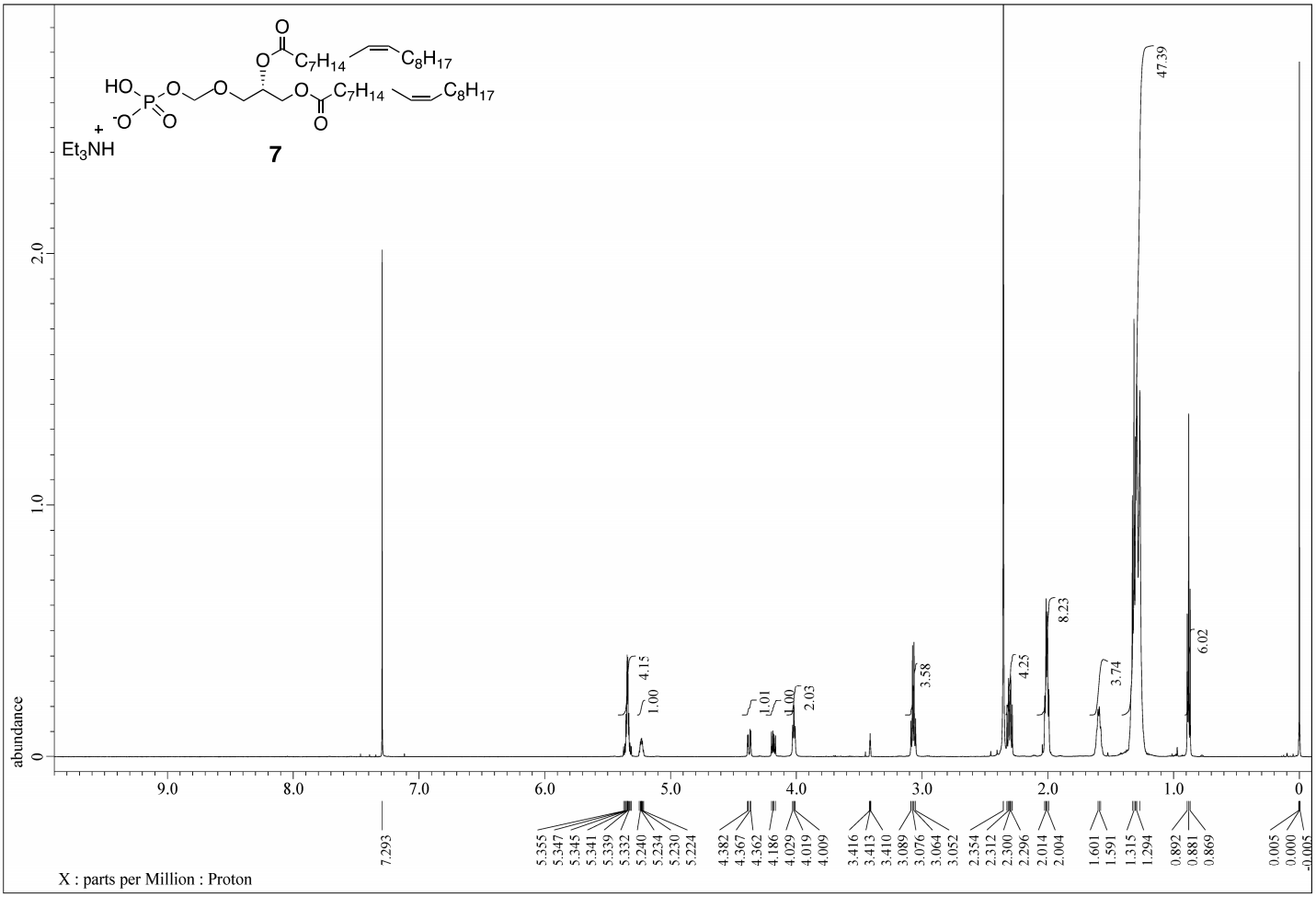


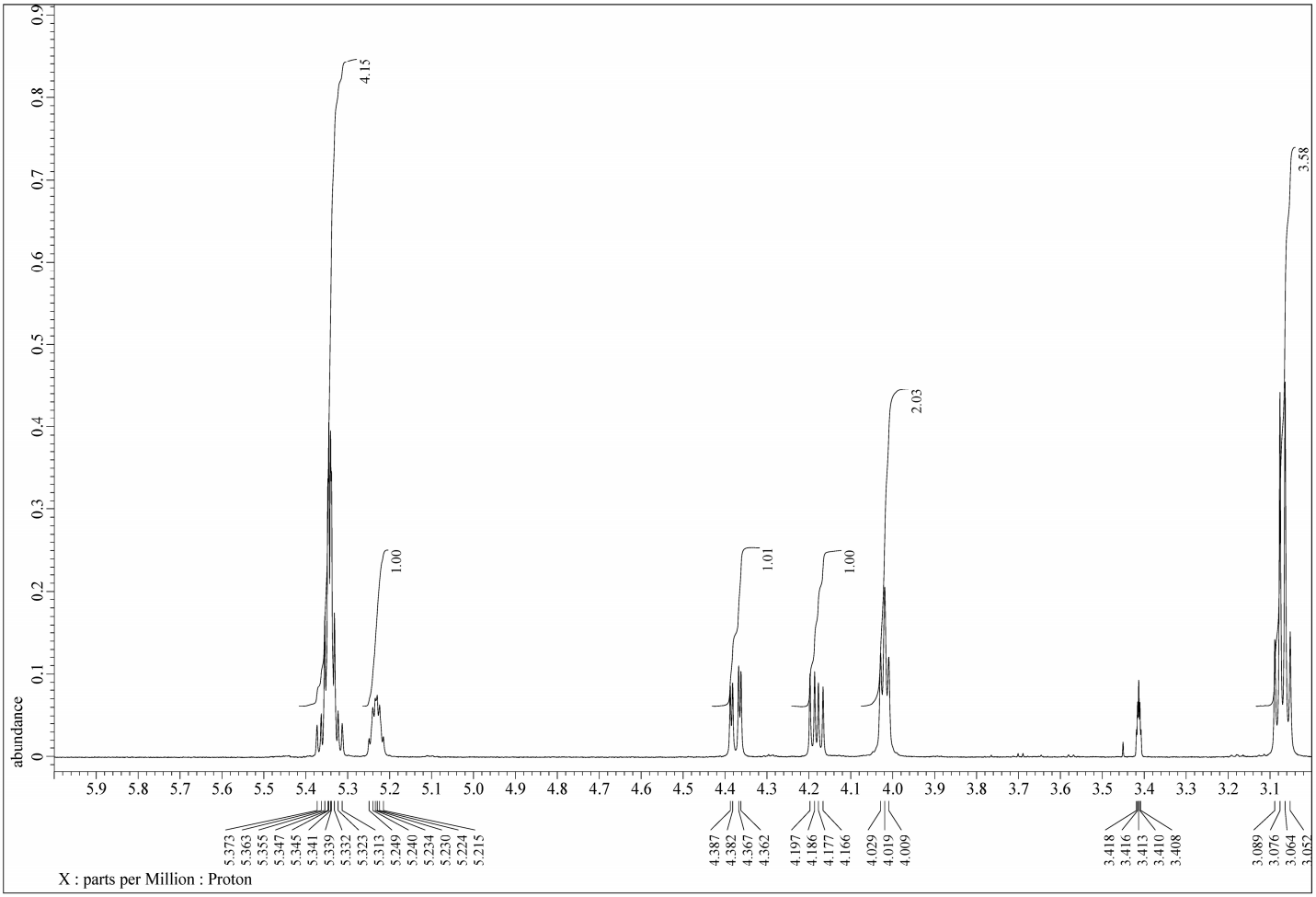


^{31}P-NMR data of PA (18:0/18:0): 1, 2-di-*O*-stearyl-*sn*-glycerol-3-phosphate triethylammonium salt (**5**), 243 MHz, $CDCl_3$, CD_3OD 3%

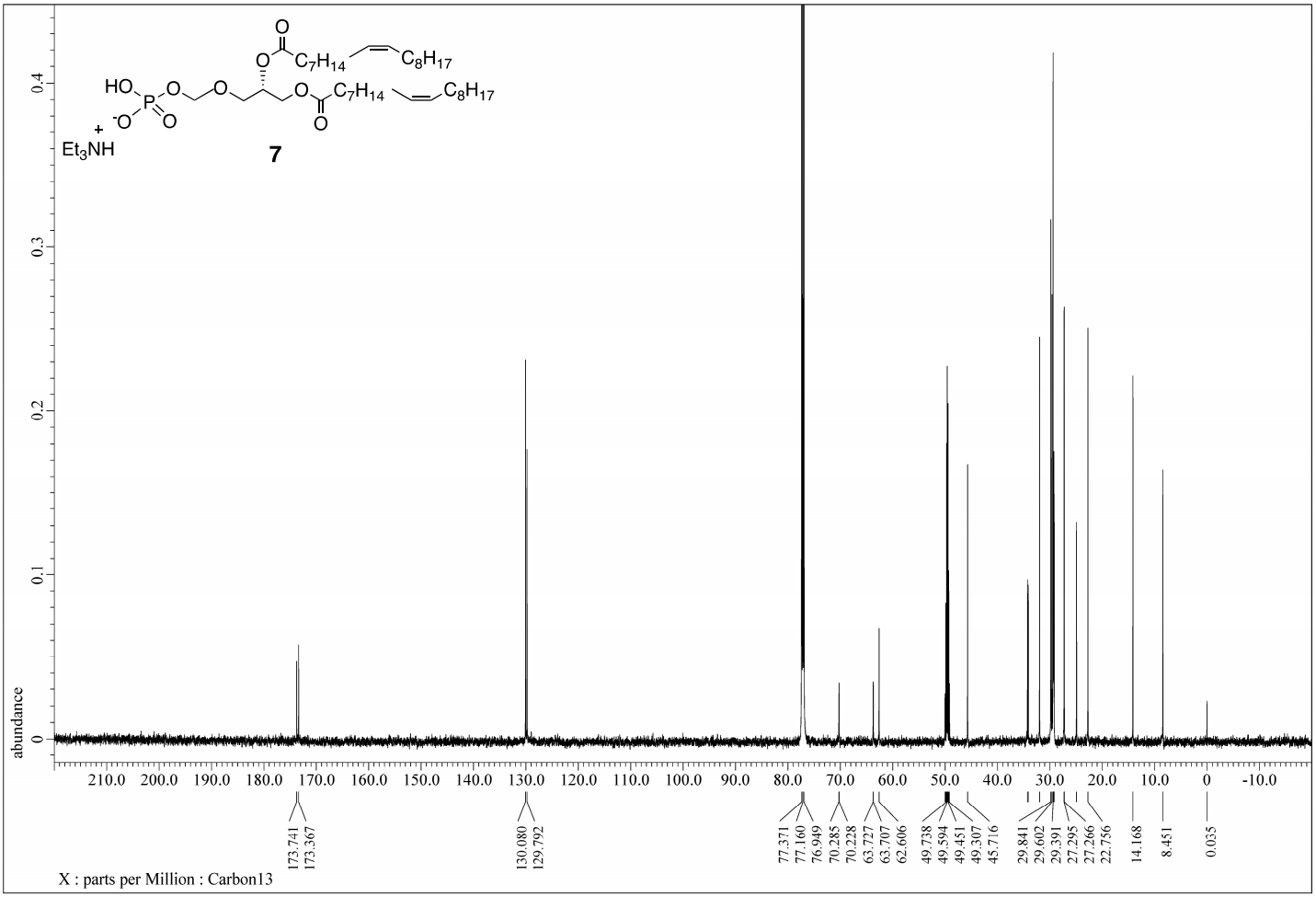


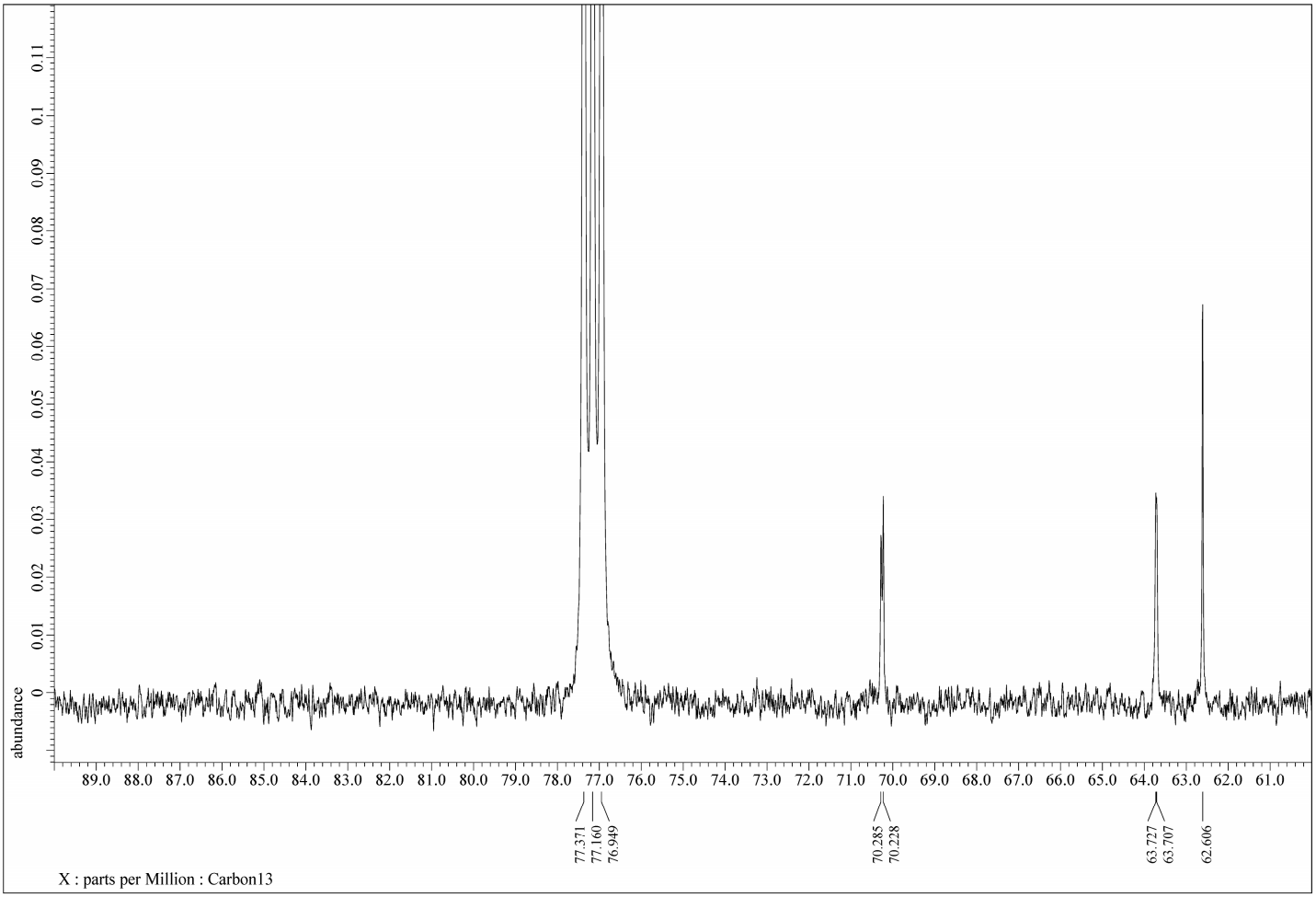
^{1}H-NMR data of PA (18:1/18:1): 1, 2-di-*O*-oleoyl-*sn*-glycerol-3-phosphate triethylammonium salt (**7**), 600 MHz, $CDCl_3$, CD_3OD 3%



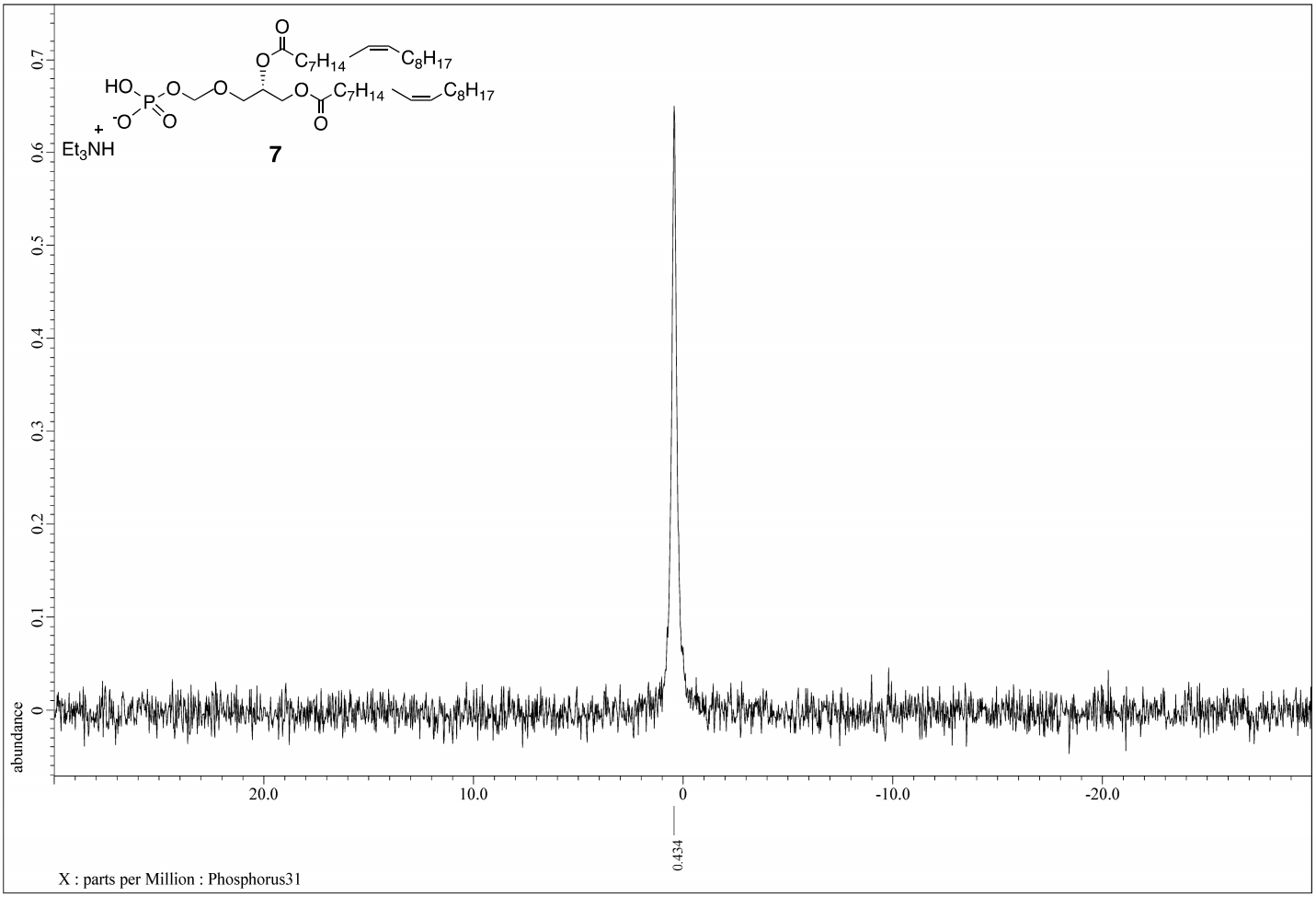


^{13}C-NMR data of PA (18:1/18:1): 1, 2-di-*O*-oleoyl-*sn*-glycerol-3-phosphate triethylammonium salt (**7**), 150 MHz, $CDCl_3$, CD_3OD 3%

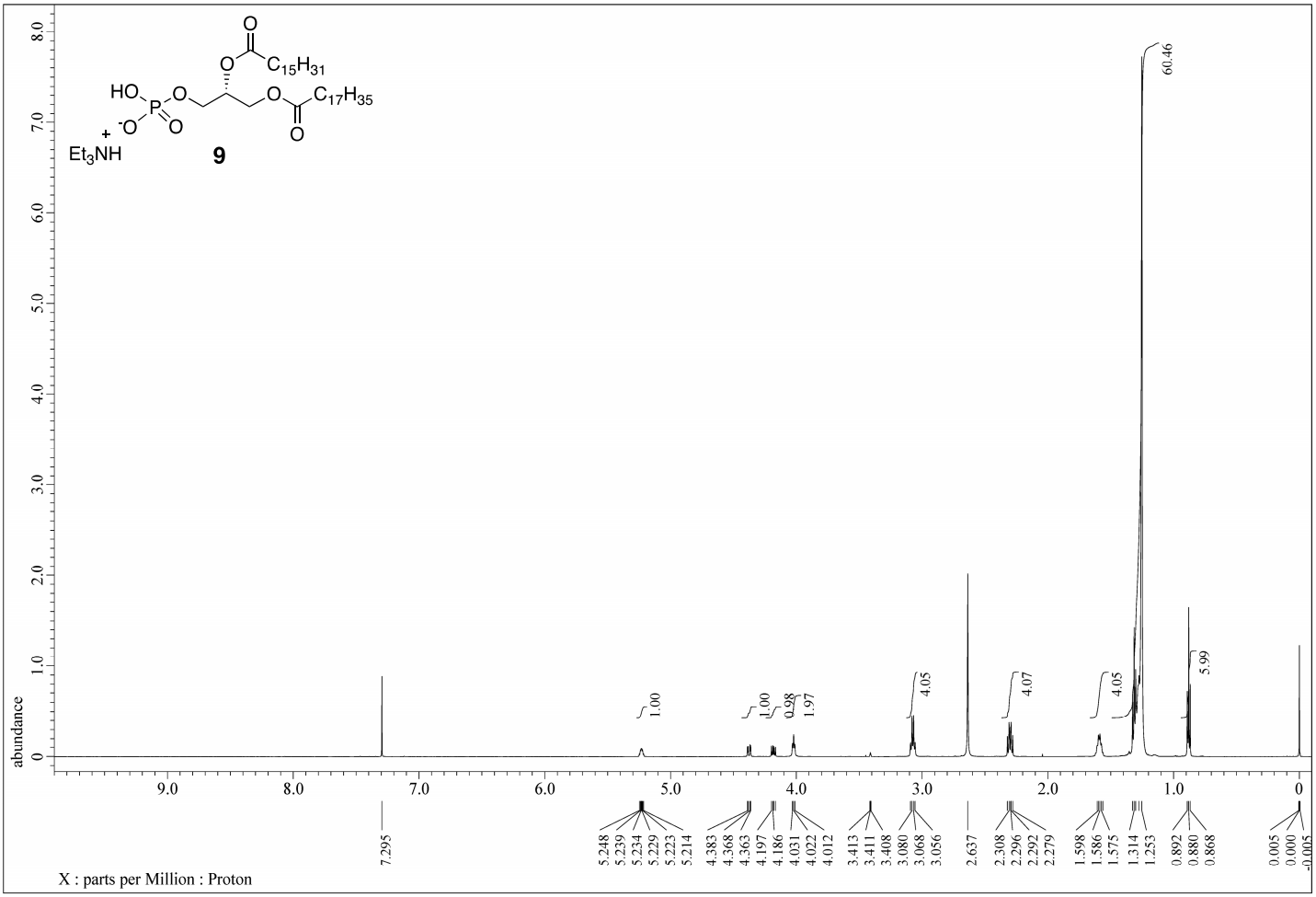


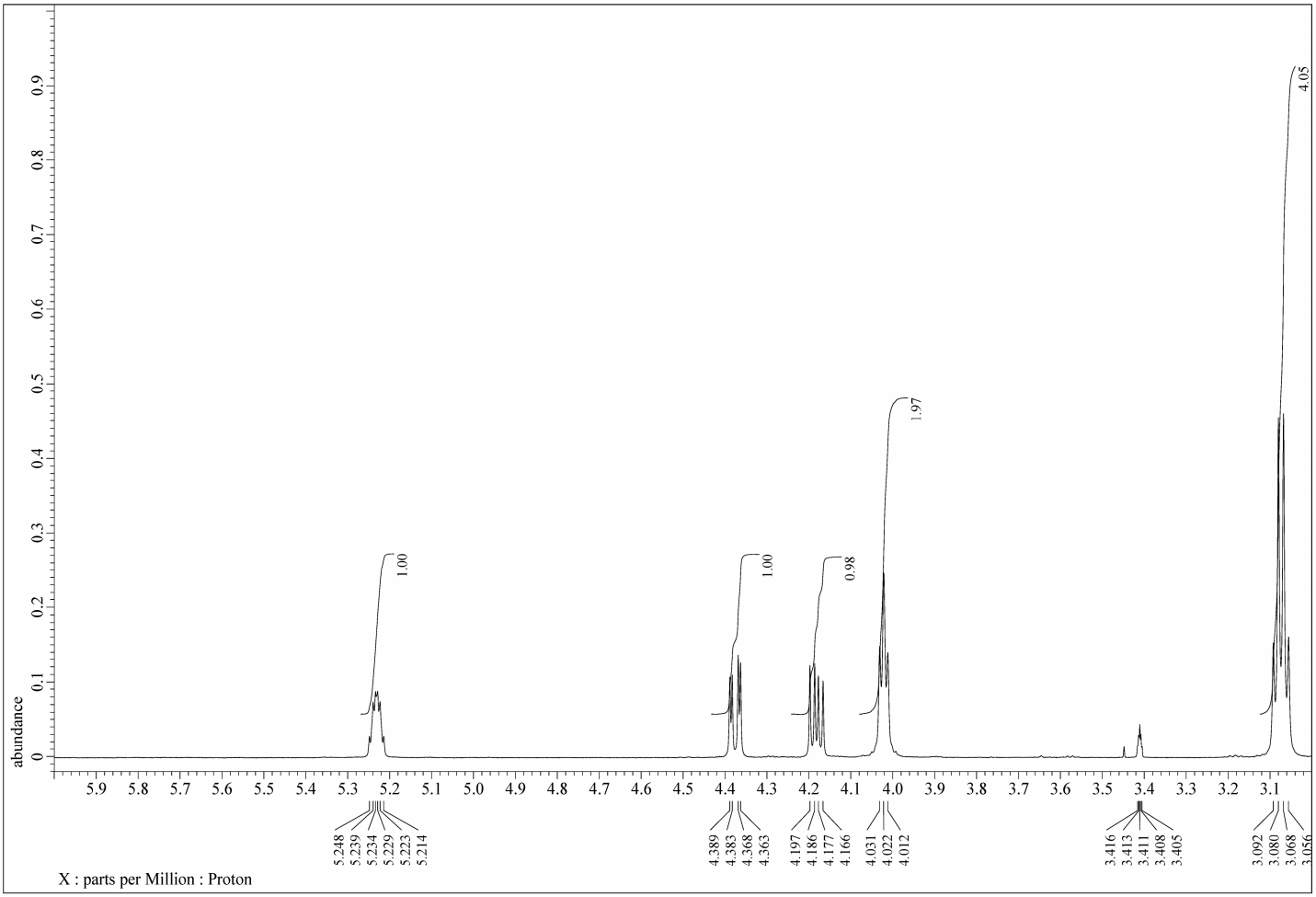


^{31}P-NMR data of PA (18:1/18:1): 1, 2-di-*O*-oleoyl-*sn*-glycerol-3-phosphate triethylammonium salt (**7**), 243 MHz, $CDCl_3$, CD_3OD 3%

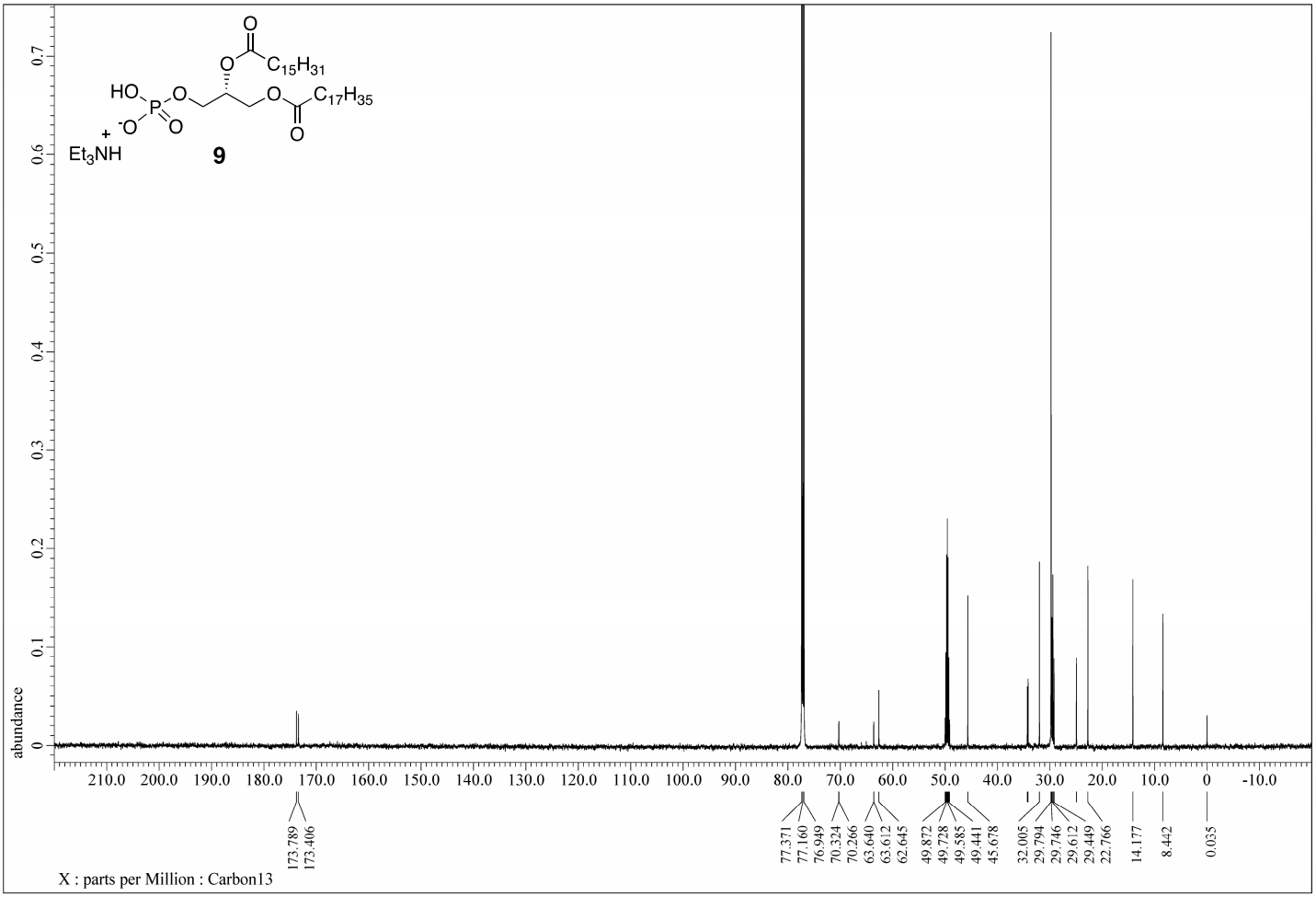


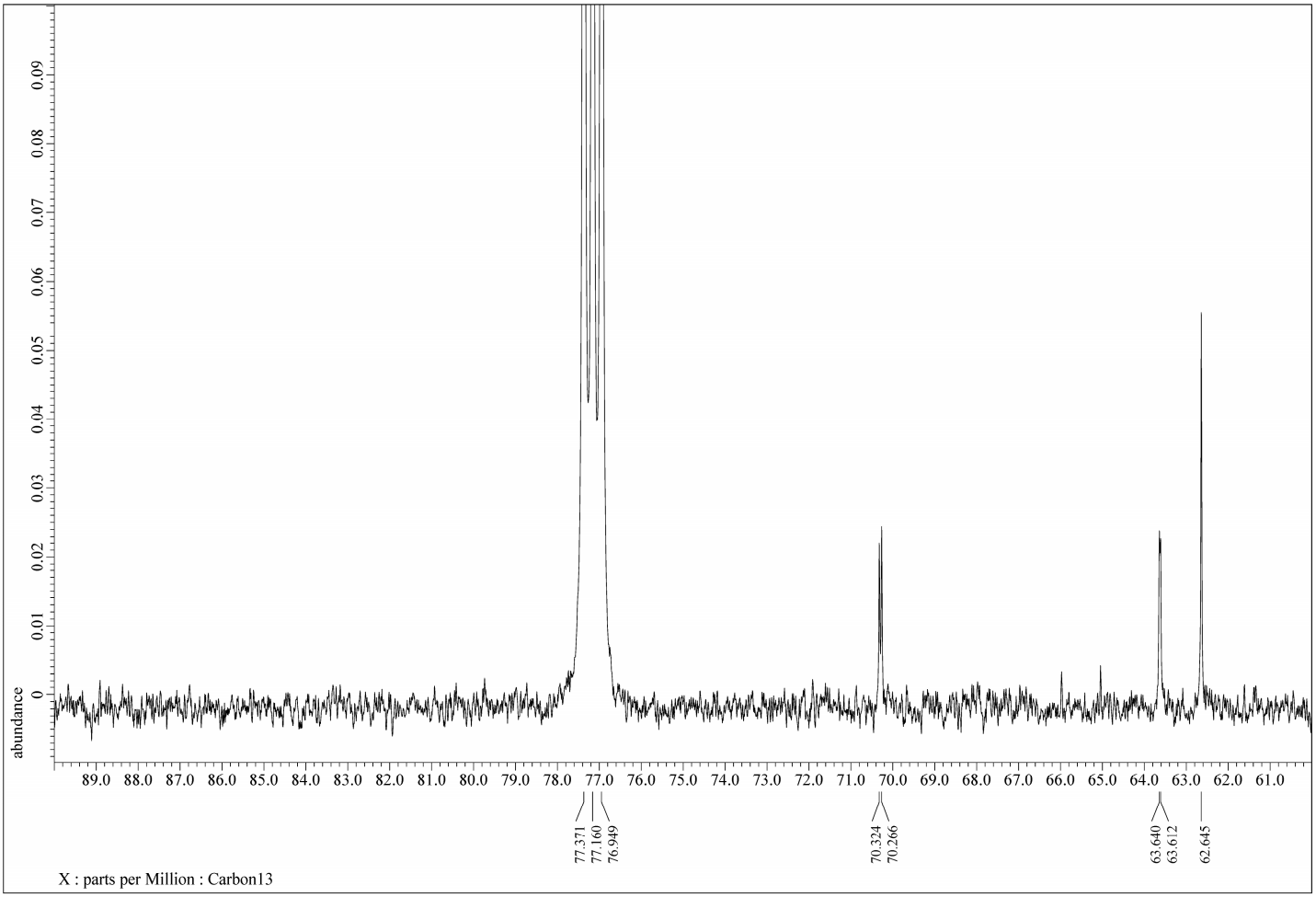
^{1}H-NMR data of PA (18:0/16:0): 1-*O*-stearoyl-2-*O*-palmityol-*sn*-glycerol-3-phosphate triethylammonium salt (**9**) , 600 MHz, $CDCl_3$, CD_3OD 3%



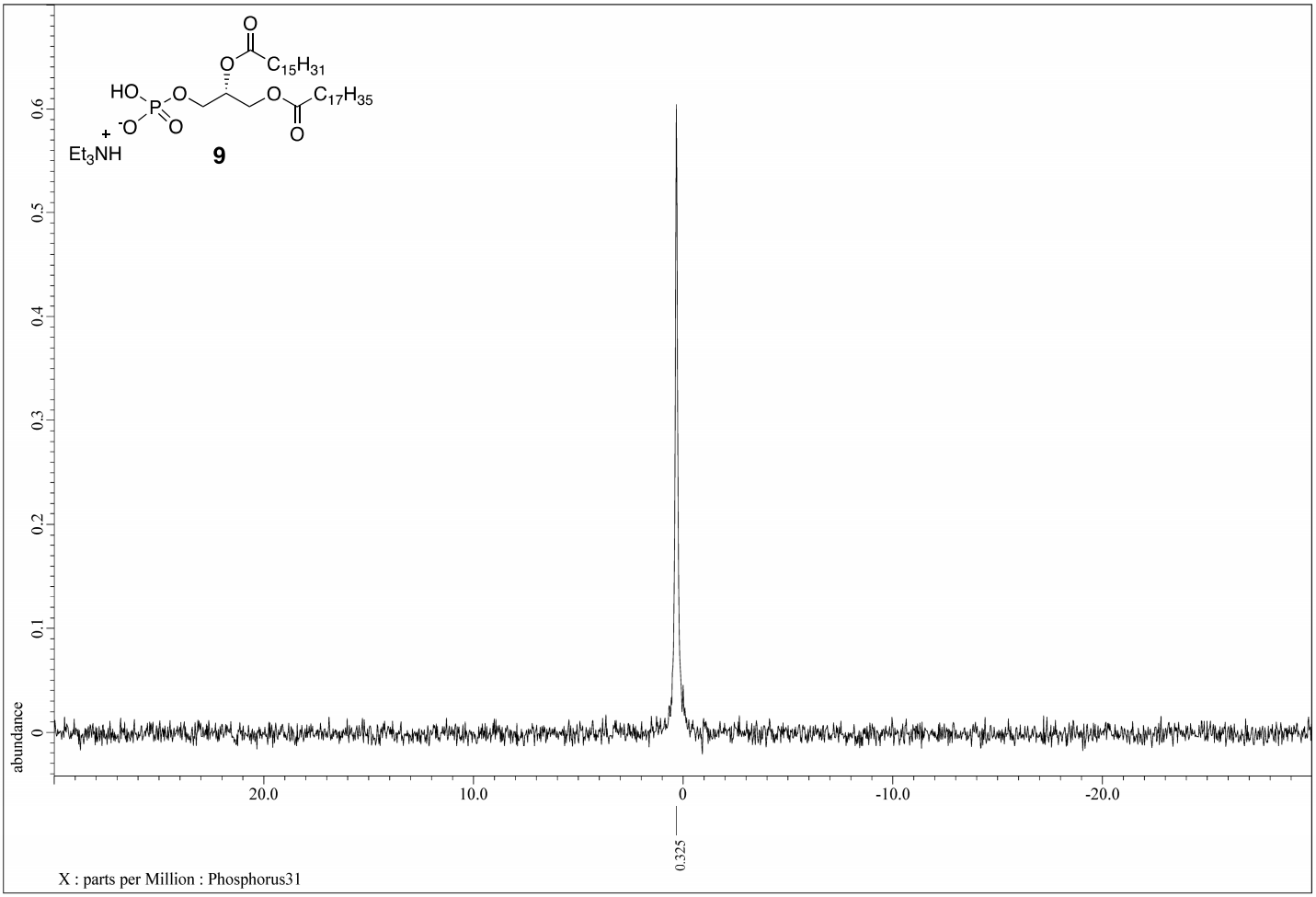


^{13}C-NMR data of PA (18:0/16:0): 1-*O*-stearoyl-2-*O*-palmityol-*sn*-glycerol-3-phosphate triethylammonium salt (**9**), 150 MHz, $CDCl_3$, CD_3OD 3%

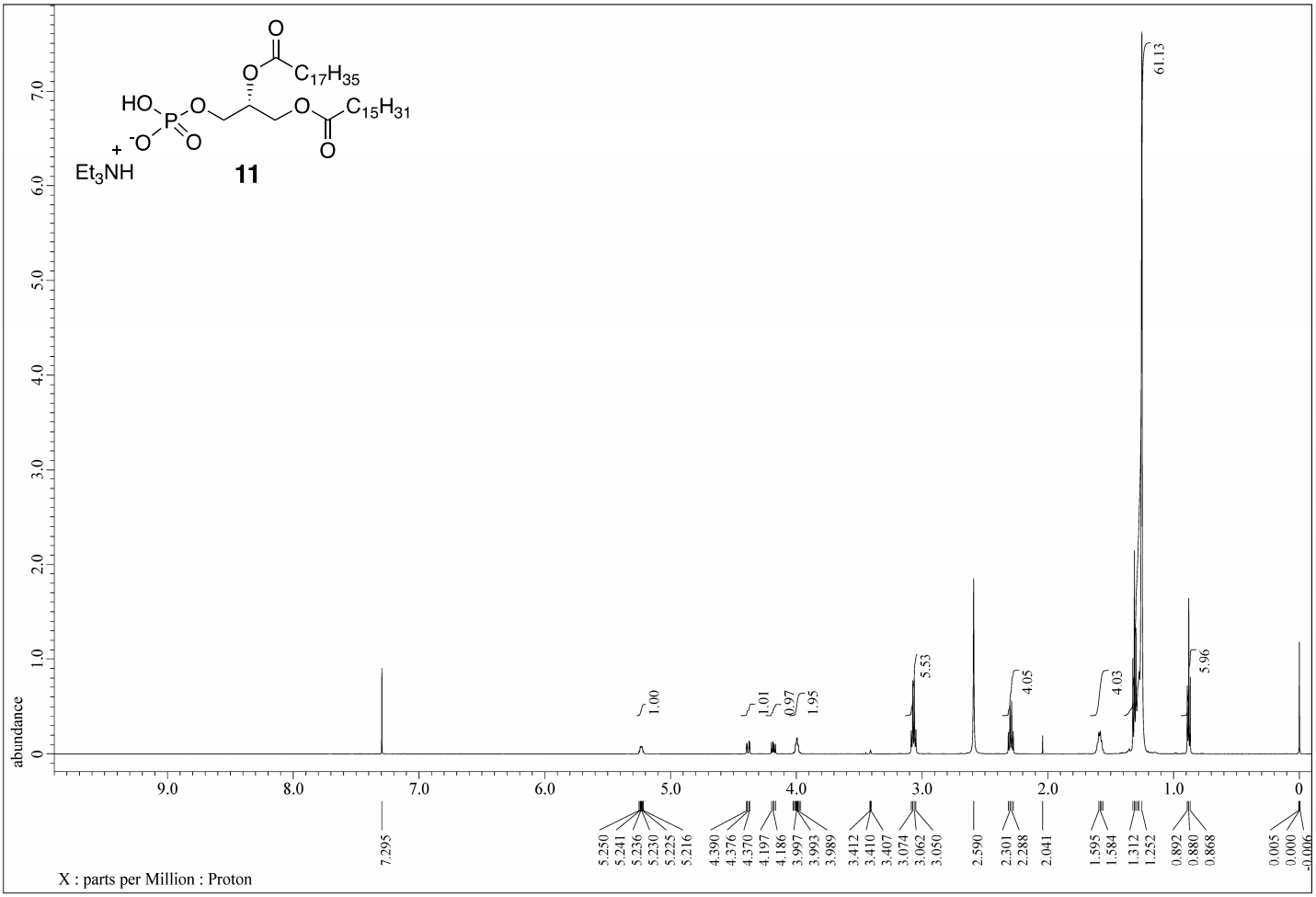


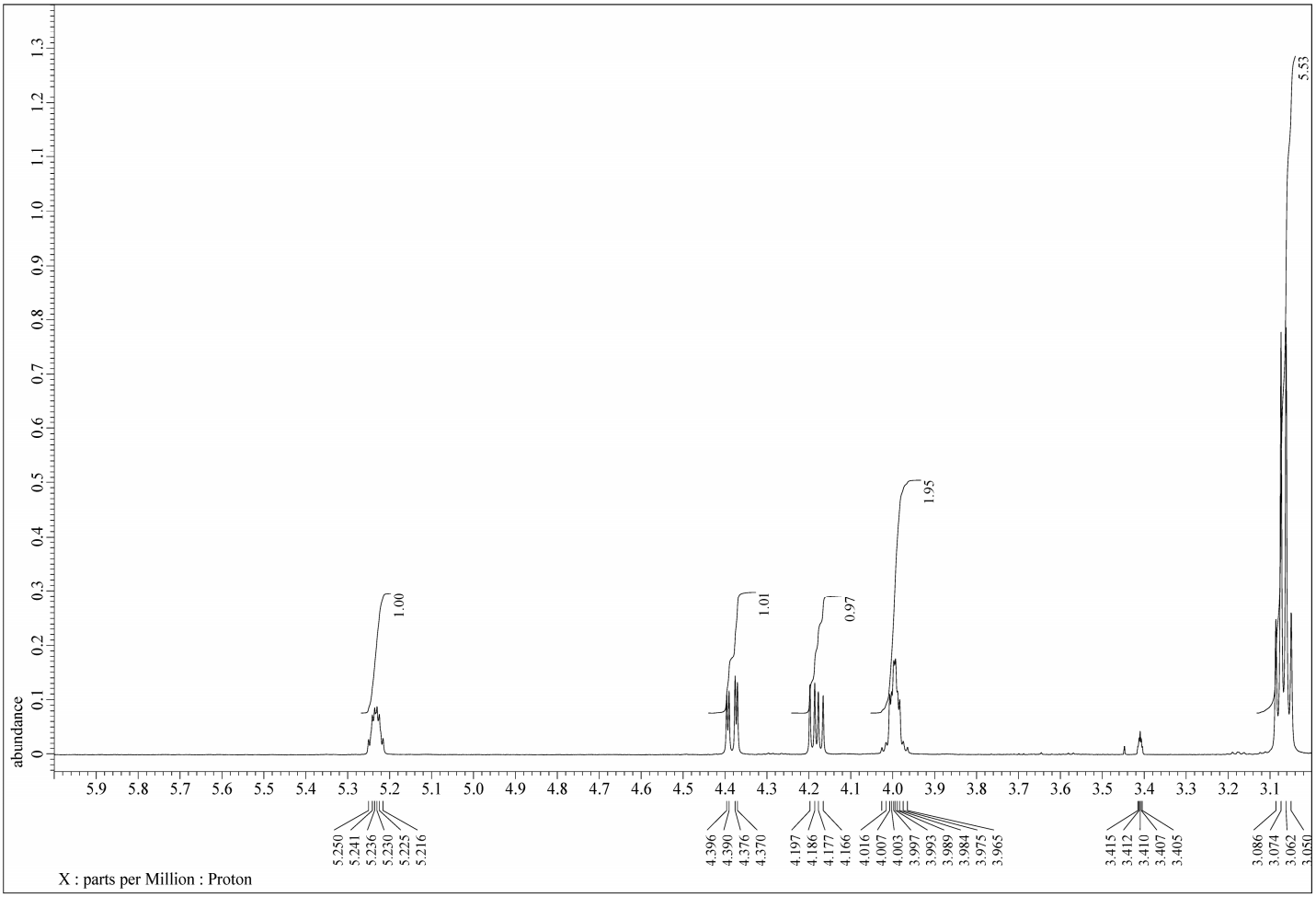


^{31}P-NMR data of PA (18:0/16:0): 1-*O*-stearoyl-2-*O*-palmityol-*sn*-glycerol-3-phosphate triethylammonium salt (**9**), 243 MHz, $CDCl_3$, CD_3OD 3%

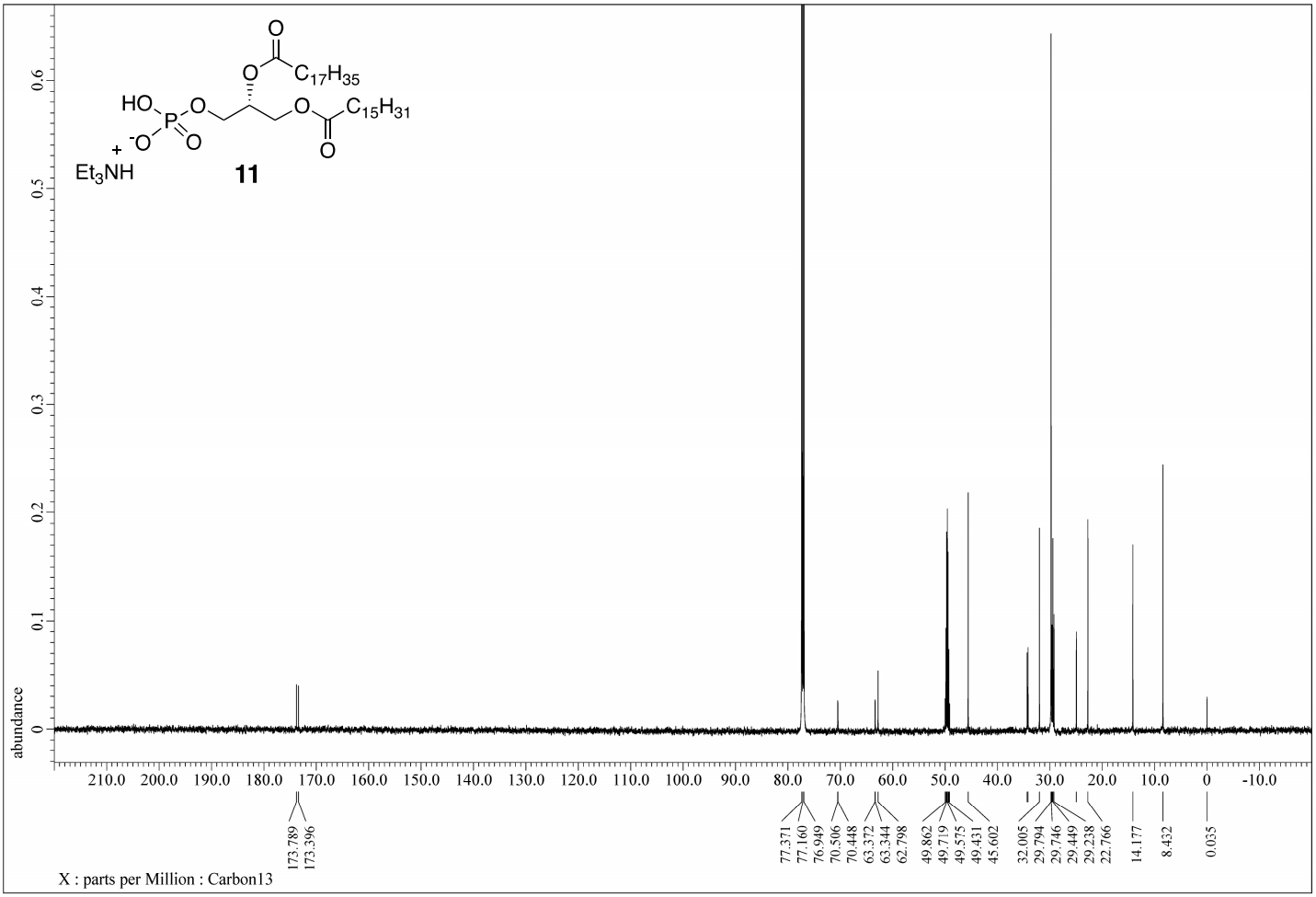


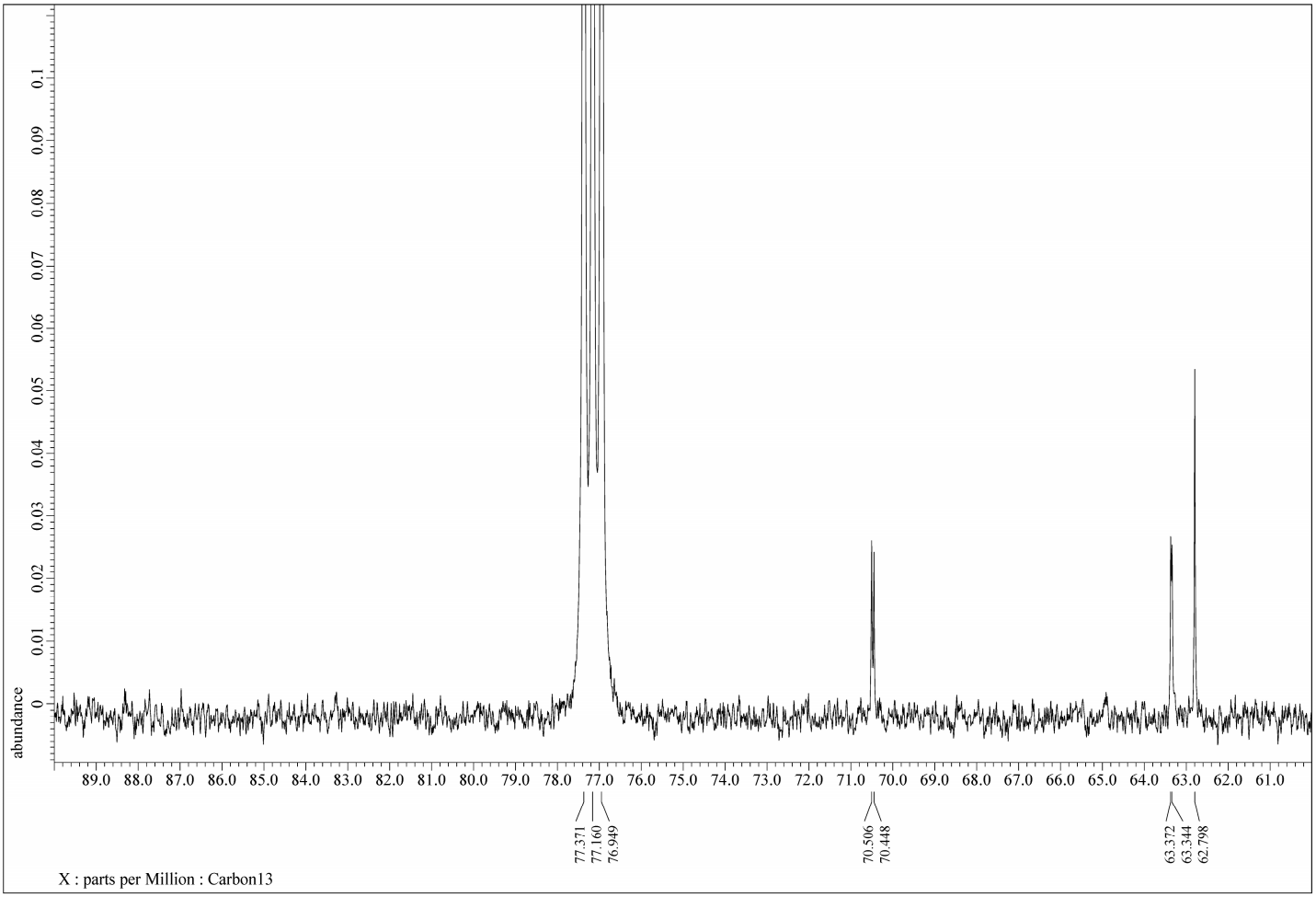
^{1}H-NMR data of PA (16:0/18:0): 1-*O*-palmitoyl-2-*O*-stearoyl-*sn*-glycerol-3-phosphate triethylammonium salt (**11**), 600 MHz, $CDCl_3$, CD_3OD 3%



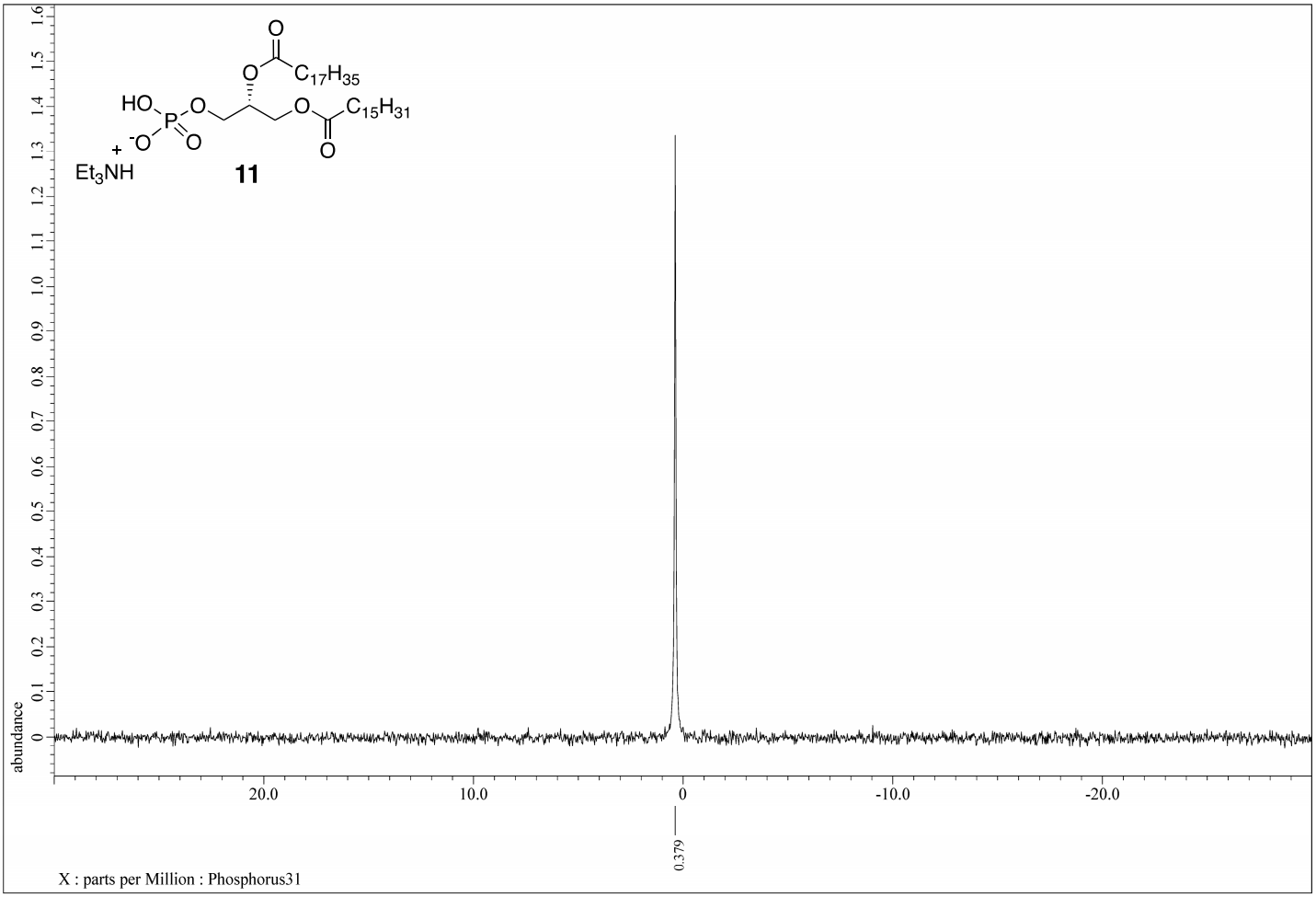


^{13}C-NMR data of PA (16:0/18:0): 1-*O*-palmitoyl-2-*O*-stearoyl-*sn*-glycerol-3-phosphate triethylammonium salt (**11**), 150 MHz, $CDCl_3$, CD_3OD 3%

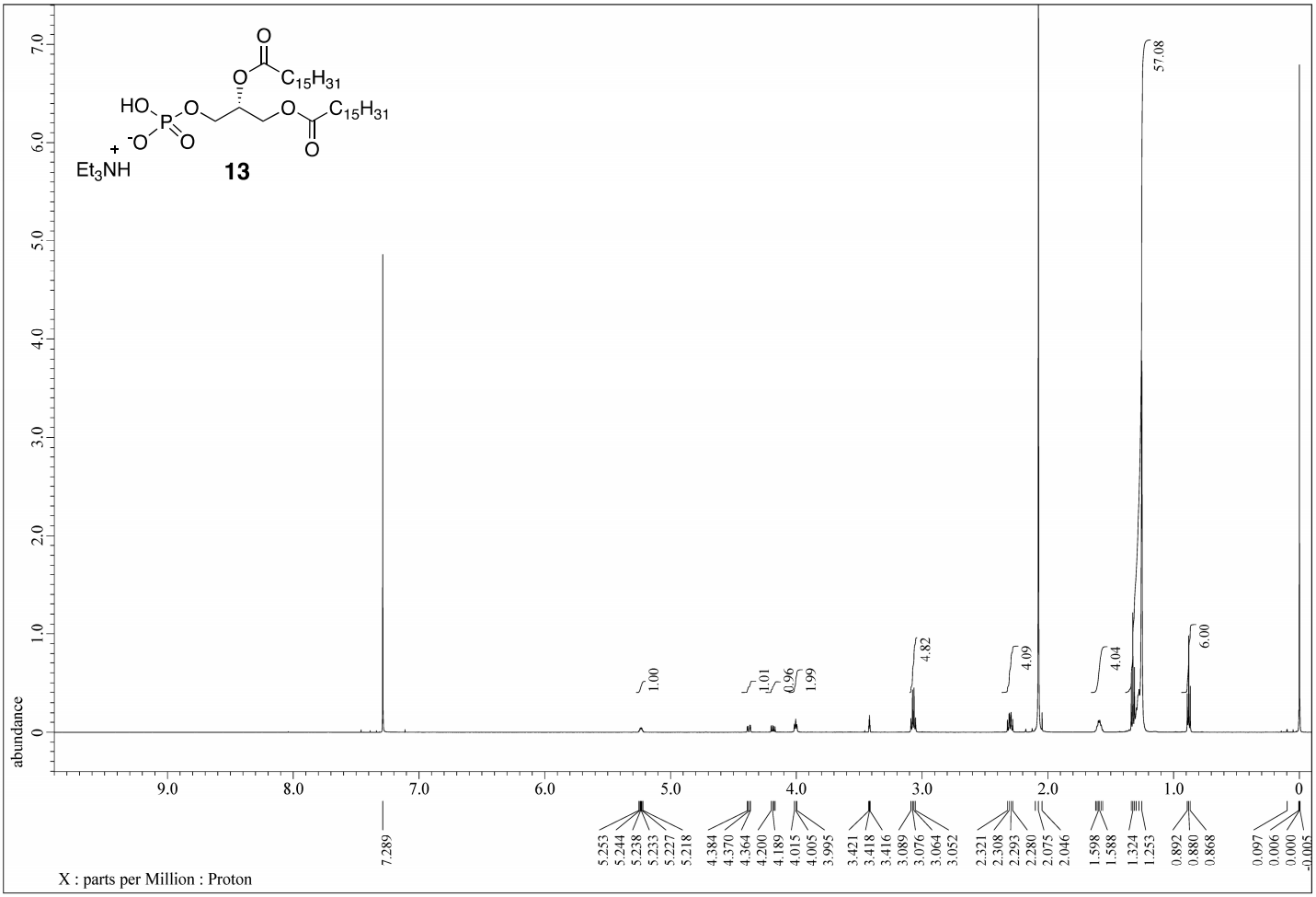


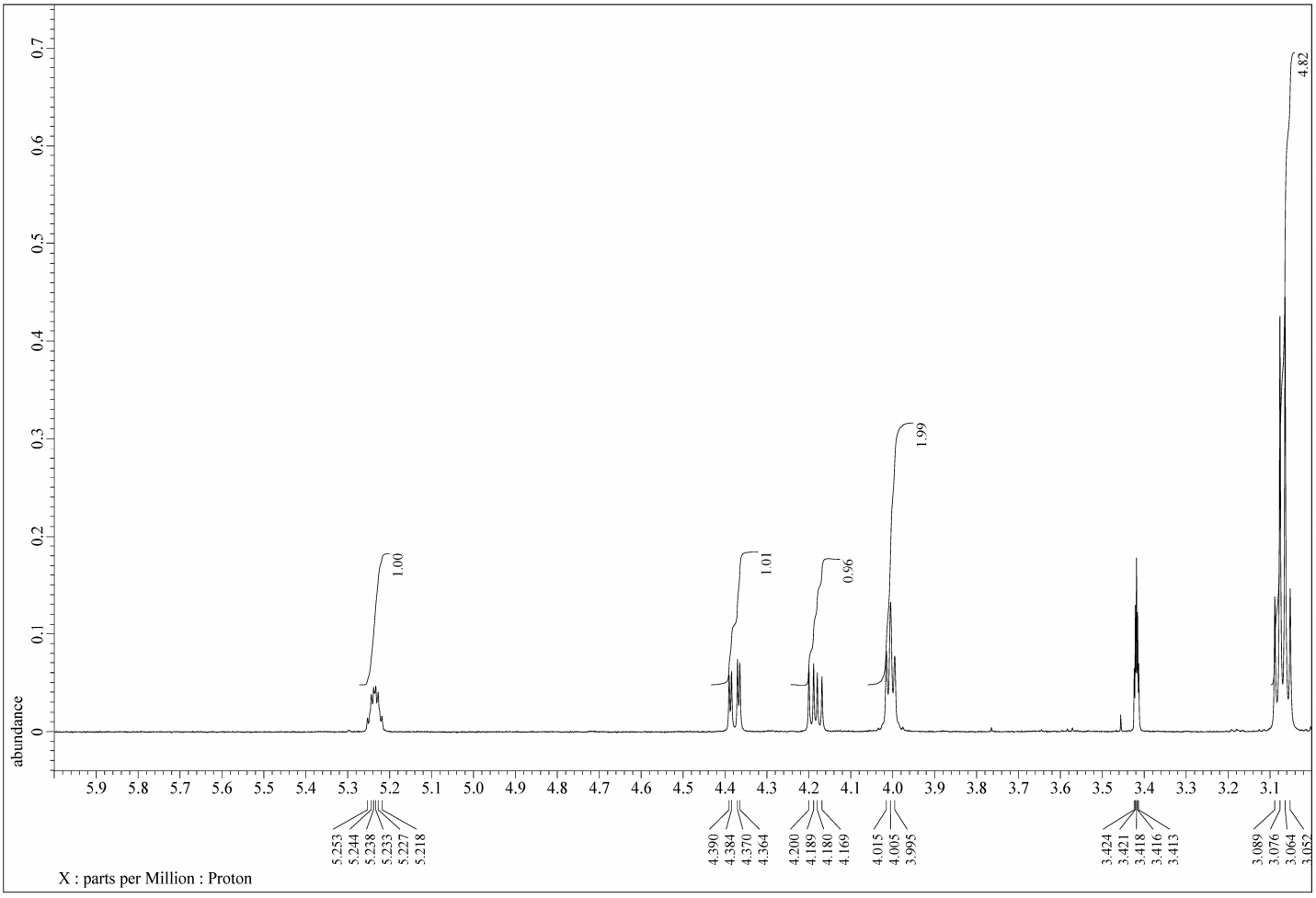


^{31}P-NMR data of PA (16:0/18:0): 1-*O*-palmitoyl-2-*O*-stearoyl-*sn*-glycerol-3-phosphate triethylammonium salt (**11**), 243 MHz, $CDCl_3$, CD_3OD 3%

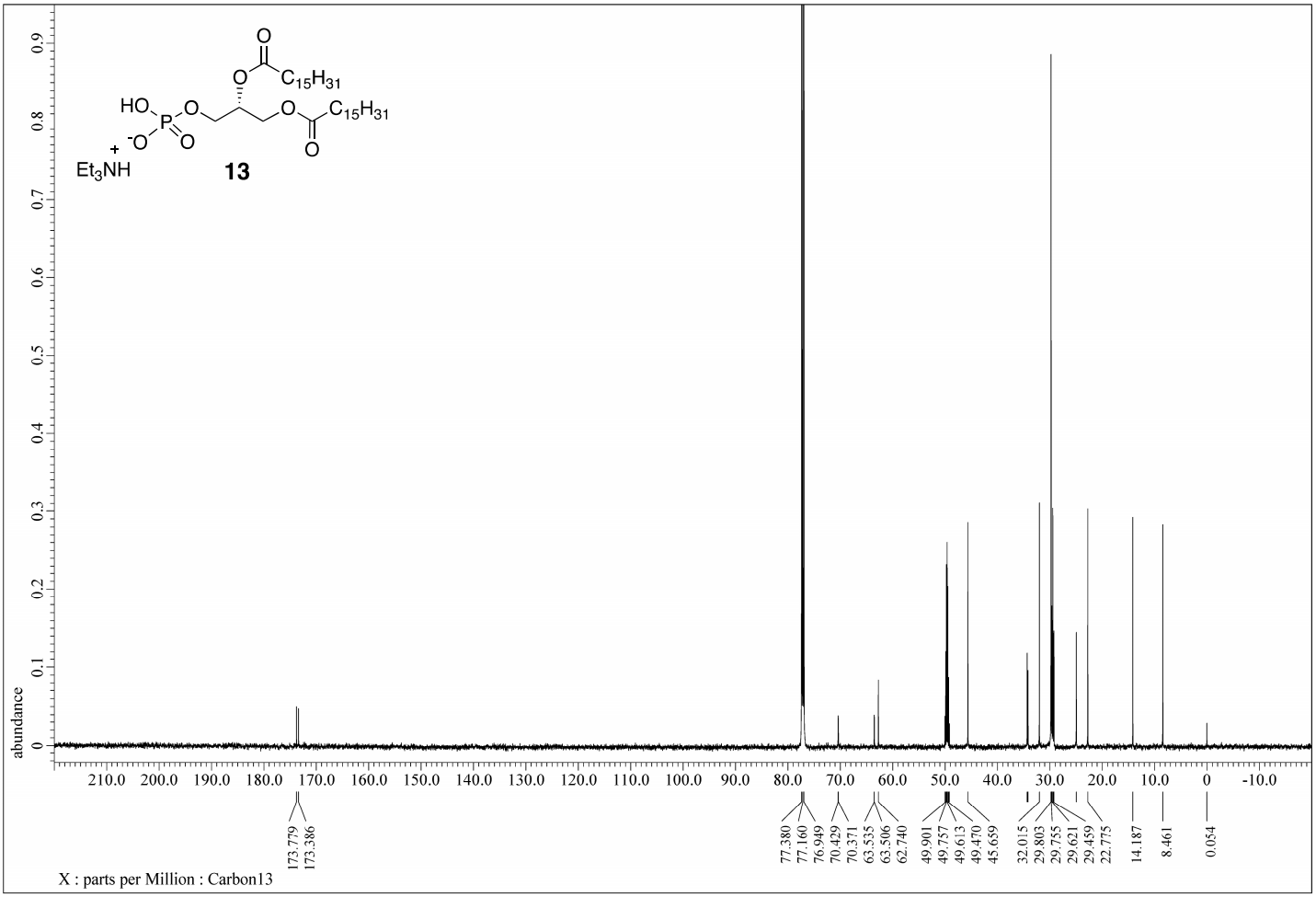


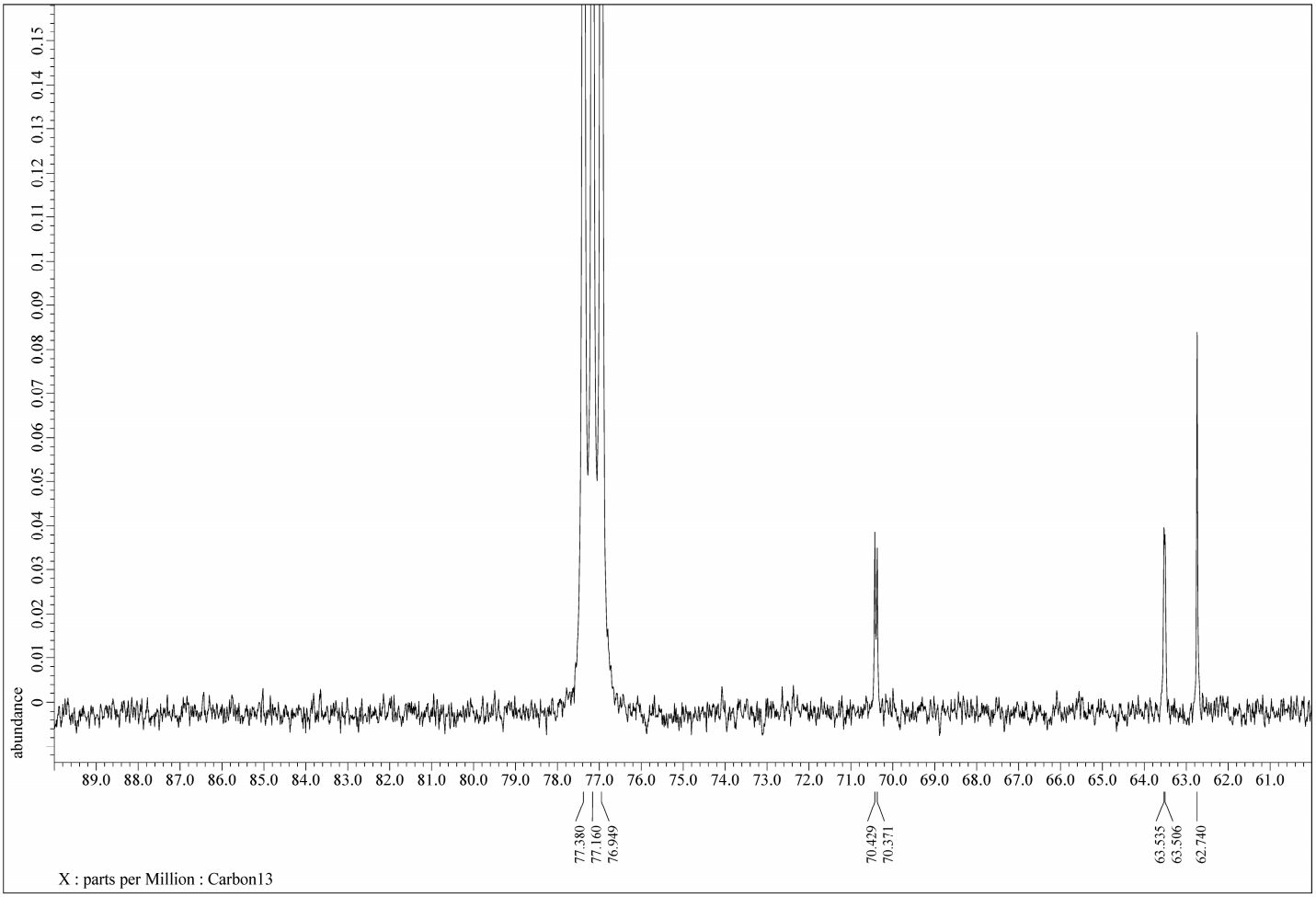
^{1}H-NMR data of PA (16:0/16:0): 1, 2-di-*O*-palmitoyl-*sn*-glycerol-3-phosphate triethylammonium salt (**13**), 600 MHz, $CDCl_3$, CD_3OD 3%



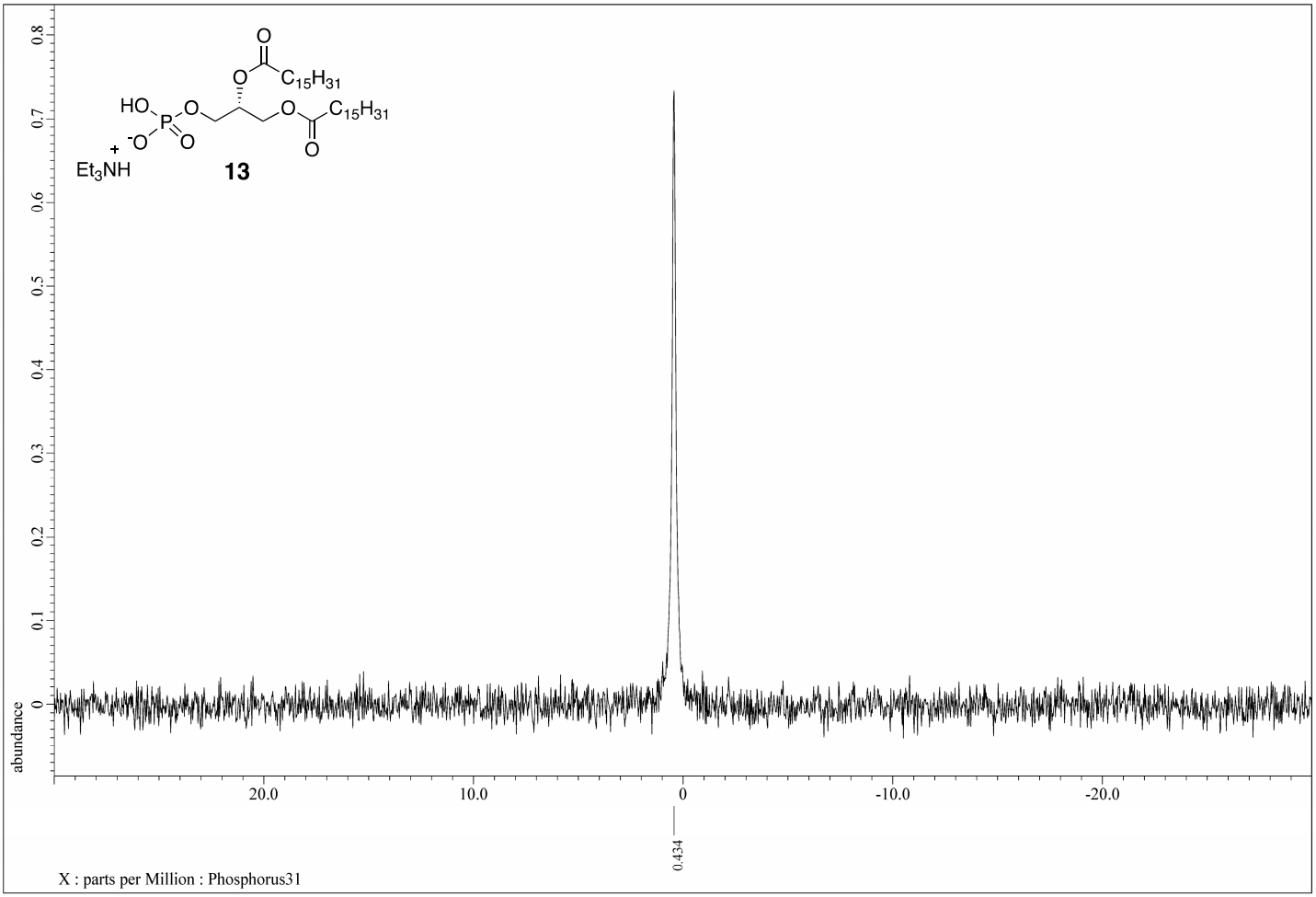


^{13}C-NMR data of PA (16:0/16:0): 1, 2-di-*O*-palmitoyl-*sn*-glycerol-3-phosphate triethylammonium salt (**13**), 150 MHz, $CDCl_3$, CD_3OD 3%

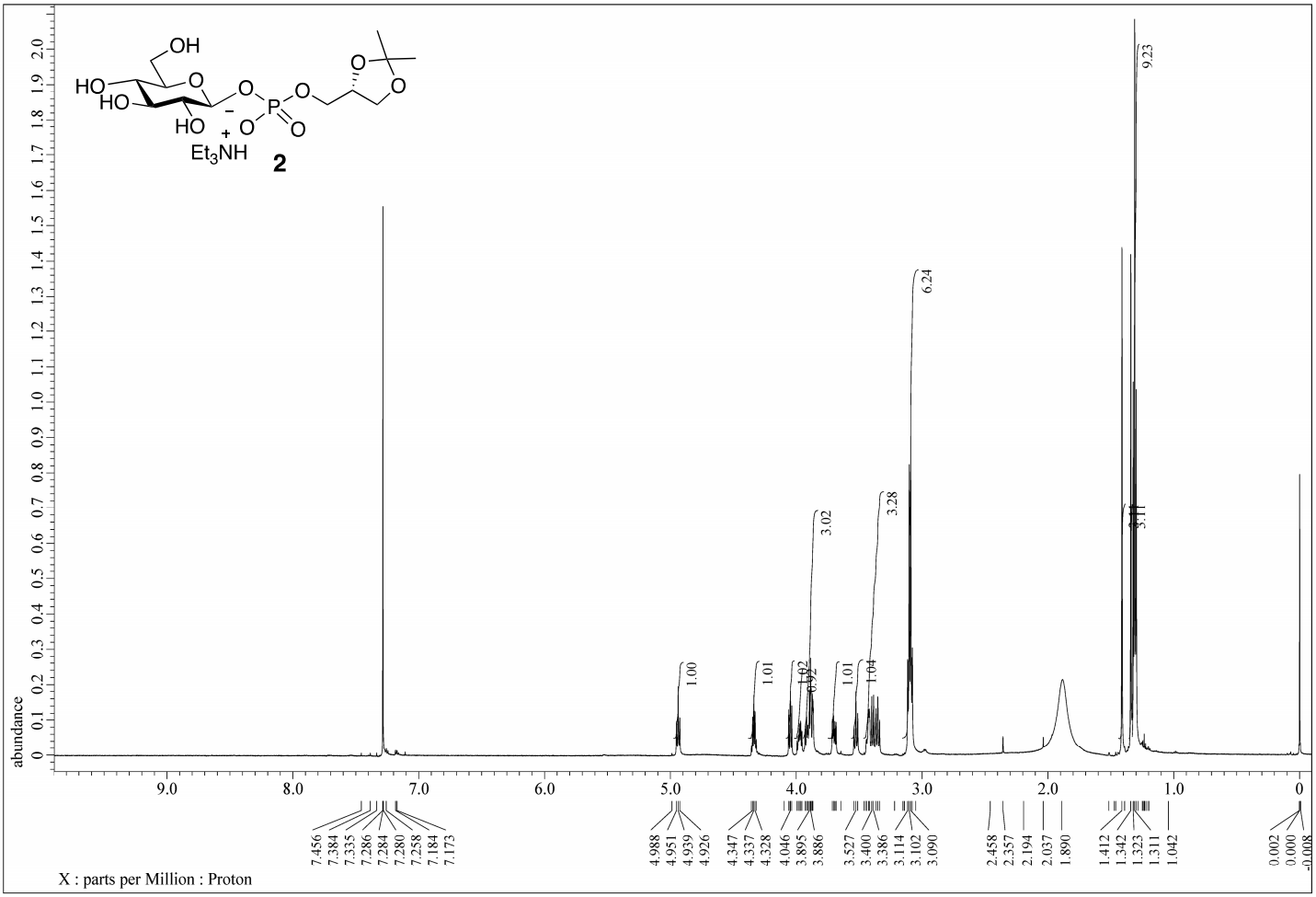


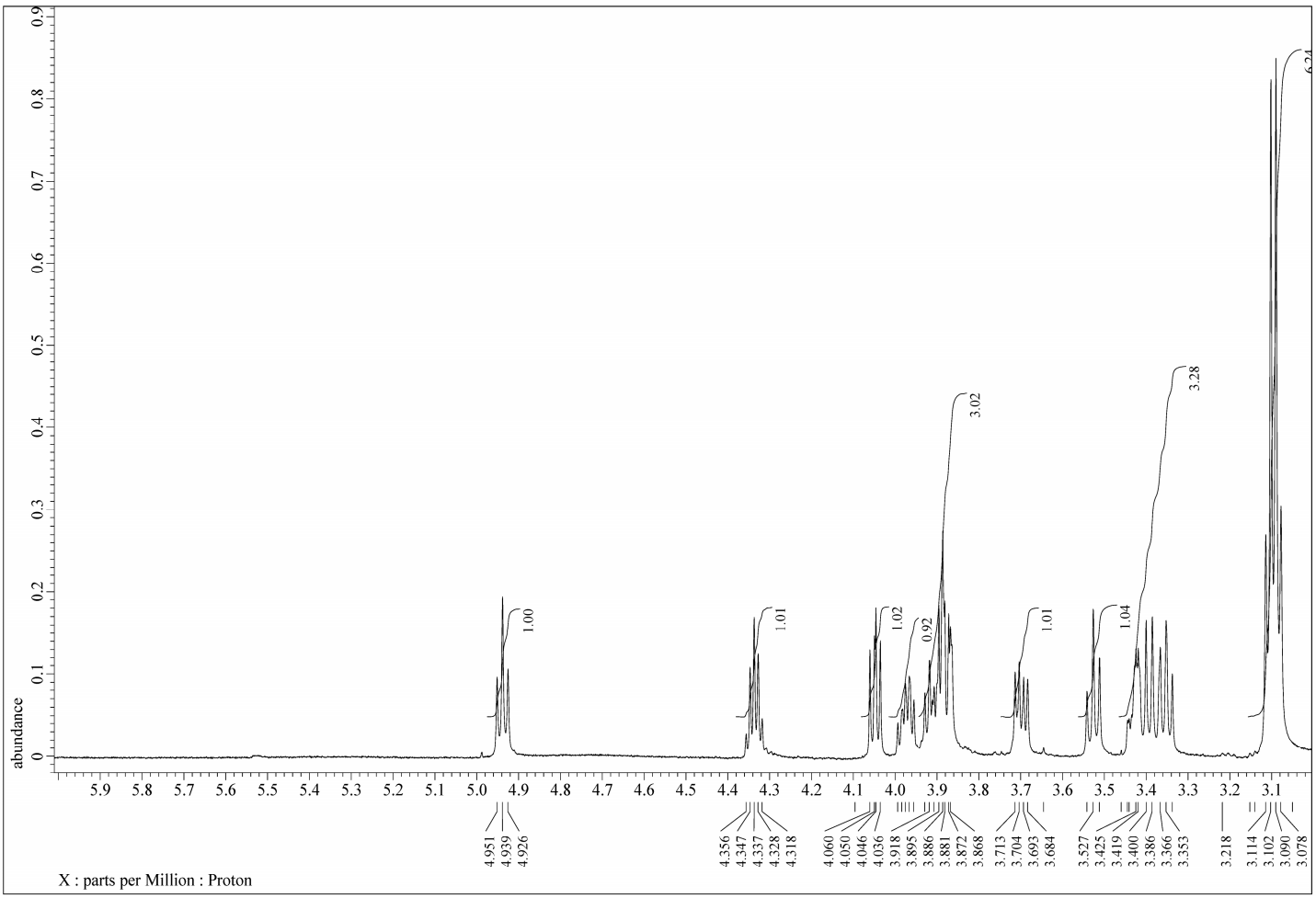


^{31}P-NMR data of PA (16:0/16:0): 1, 2-di-*O*-palmitoyl-*sn*-glycerol-3-phosphate triethylammonium salt (**13**), 243 MHz, $CDCl_3$, CD_3OD 3%

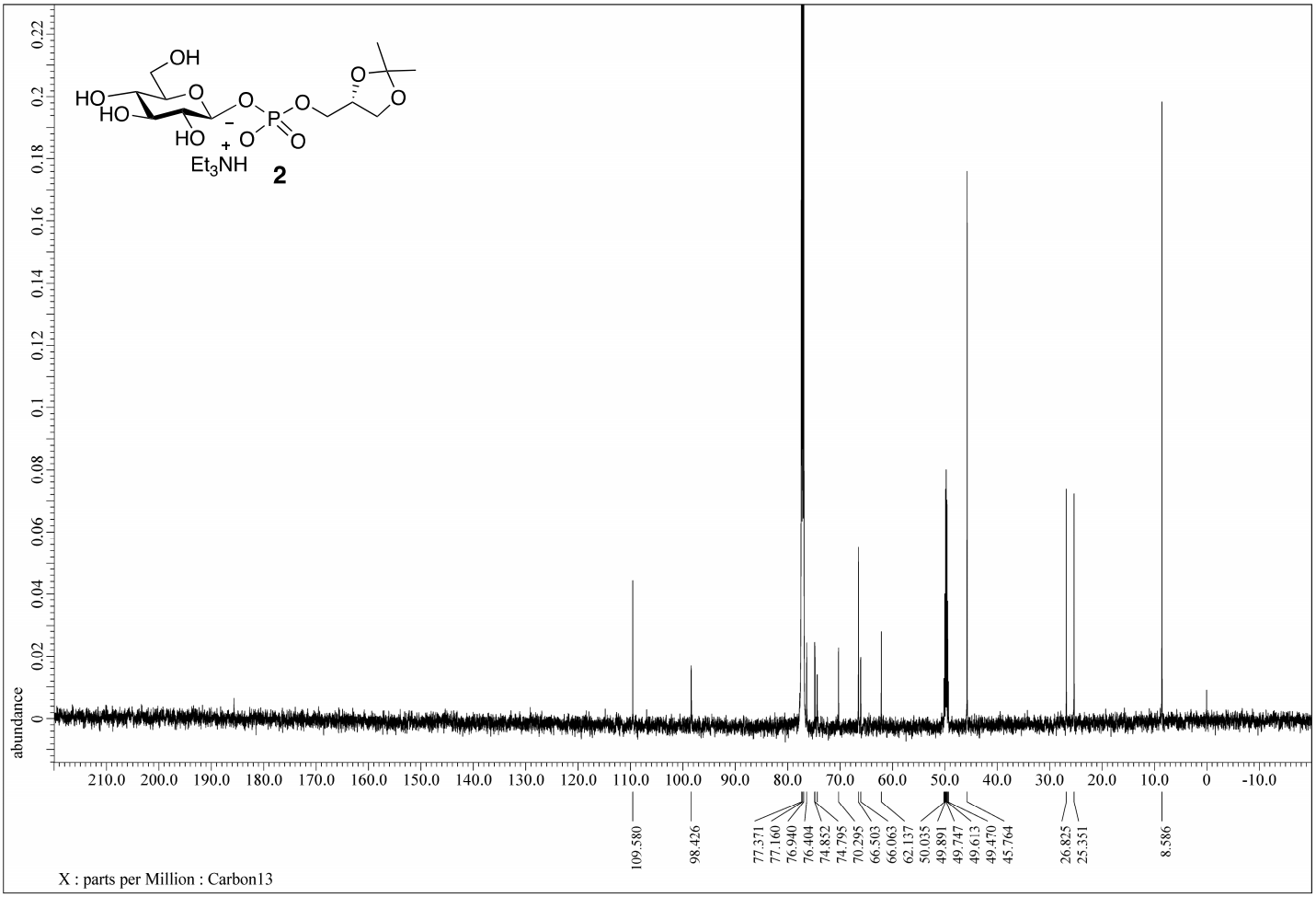


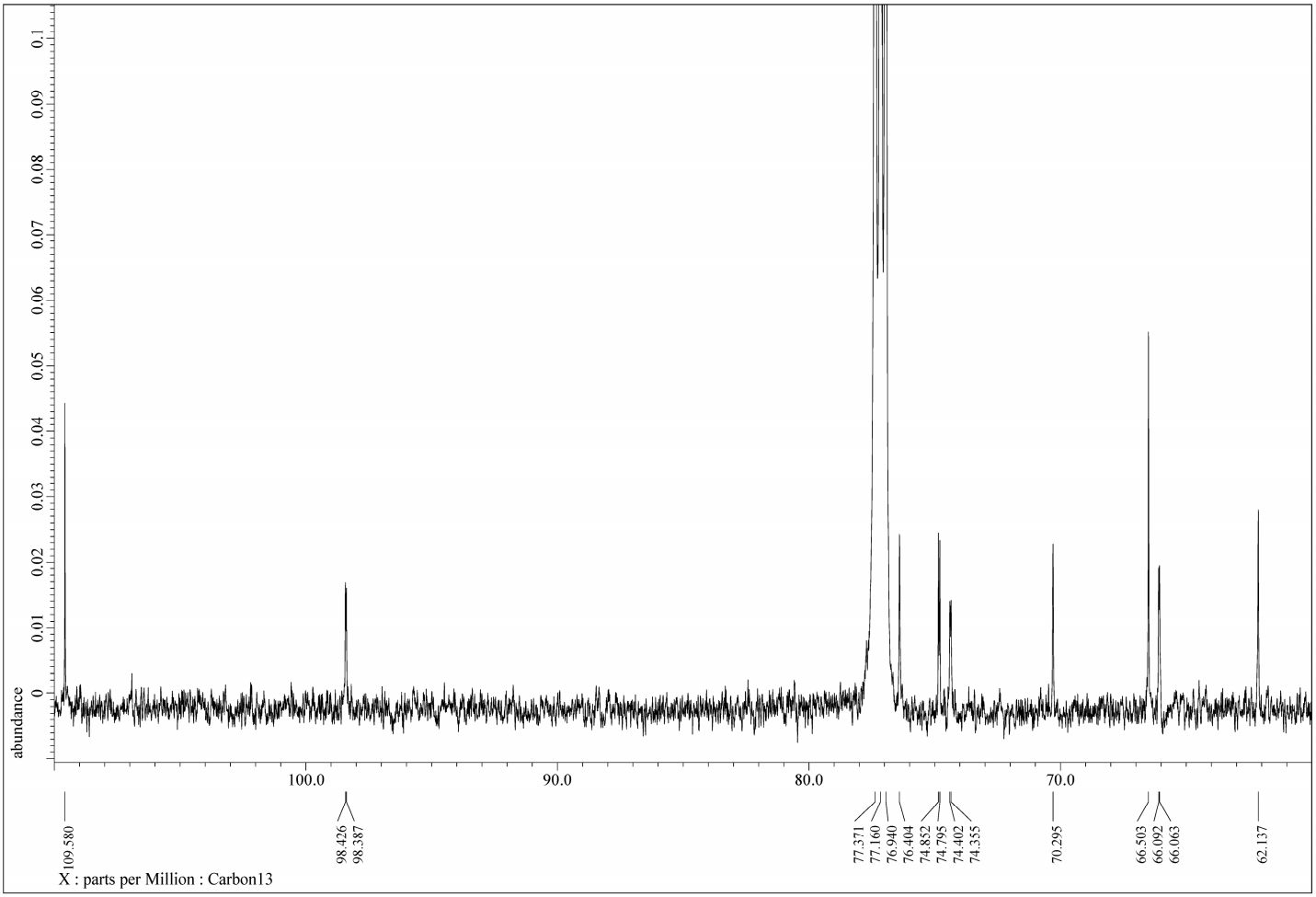
^{1}H-NMR data of 2,2-dimethyl-1,3-dioxolan-4-ylmethyl phosphatidyl glucoside (**2**), 600 MHz, $CDCl_3$, CD_3OD 3%



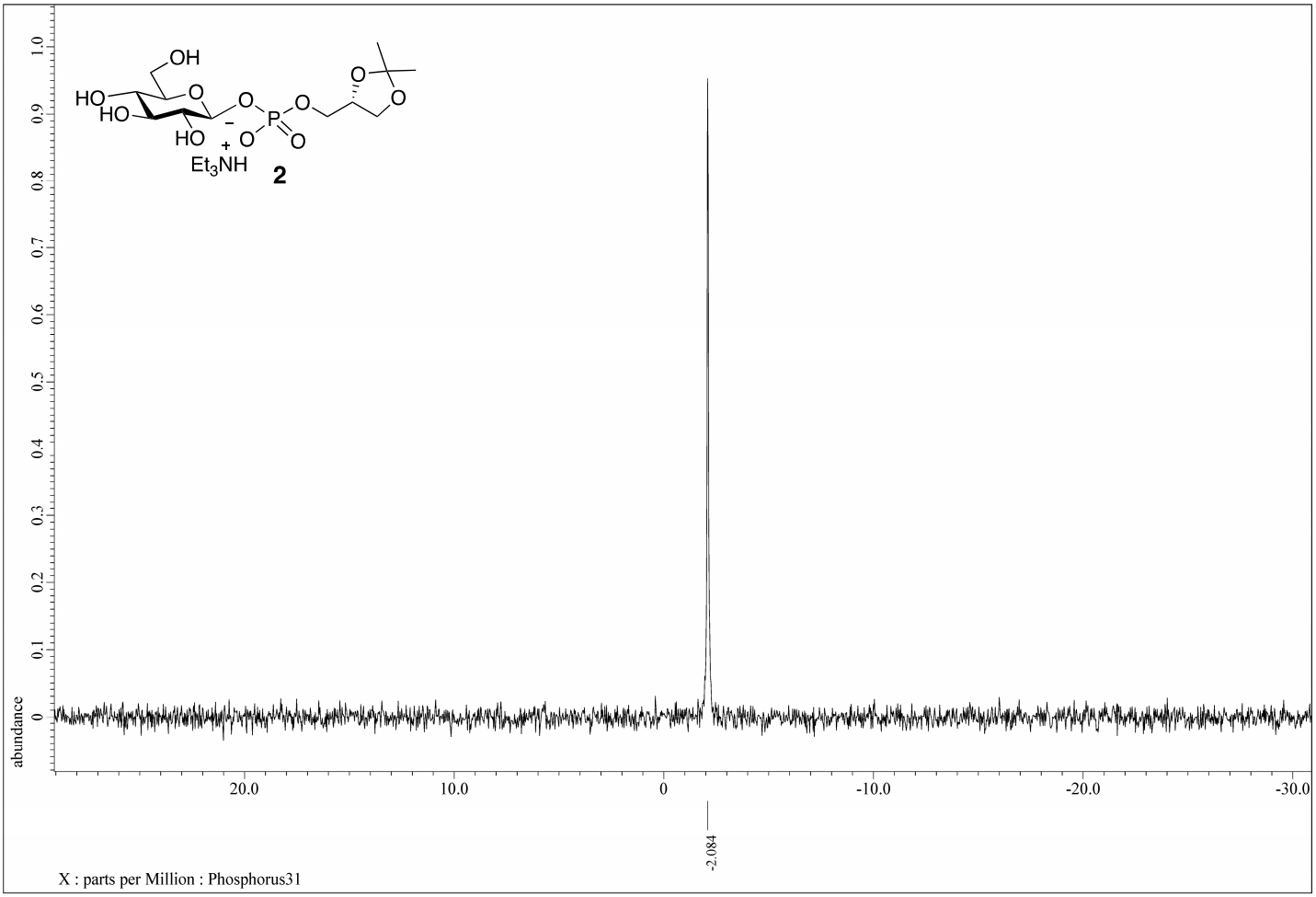


^{13}C-NMR data of 2,2-dimethyl-1,3-dioxolan-4-ylmethyl phosphatidyl glucoside (**2**), 150 MHz, $CDCl_3$, CD_3OD 3%

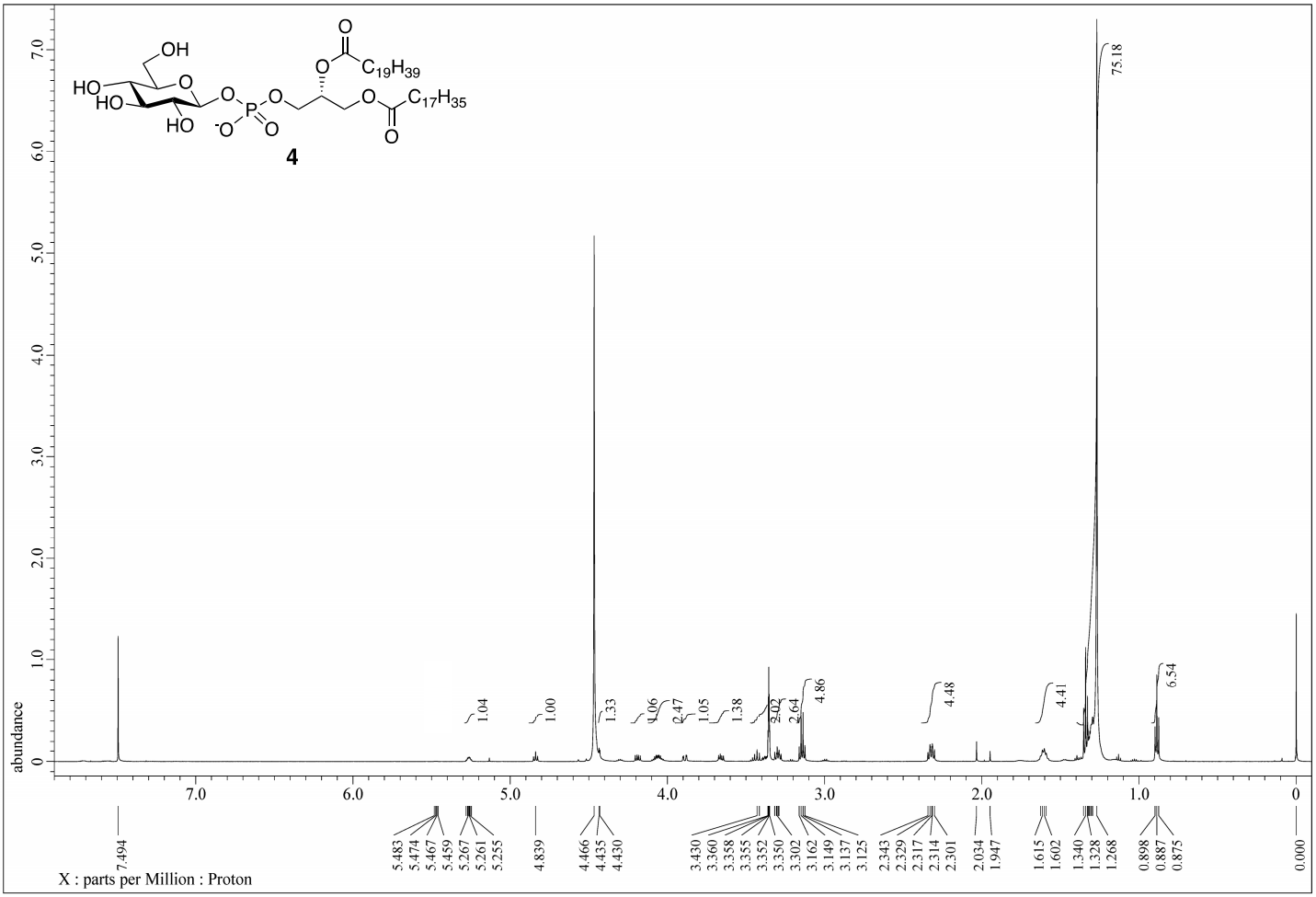


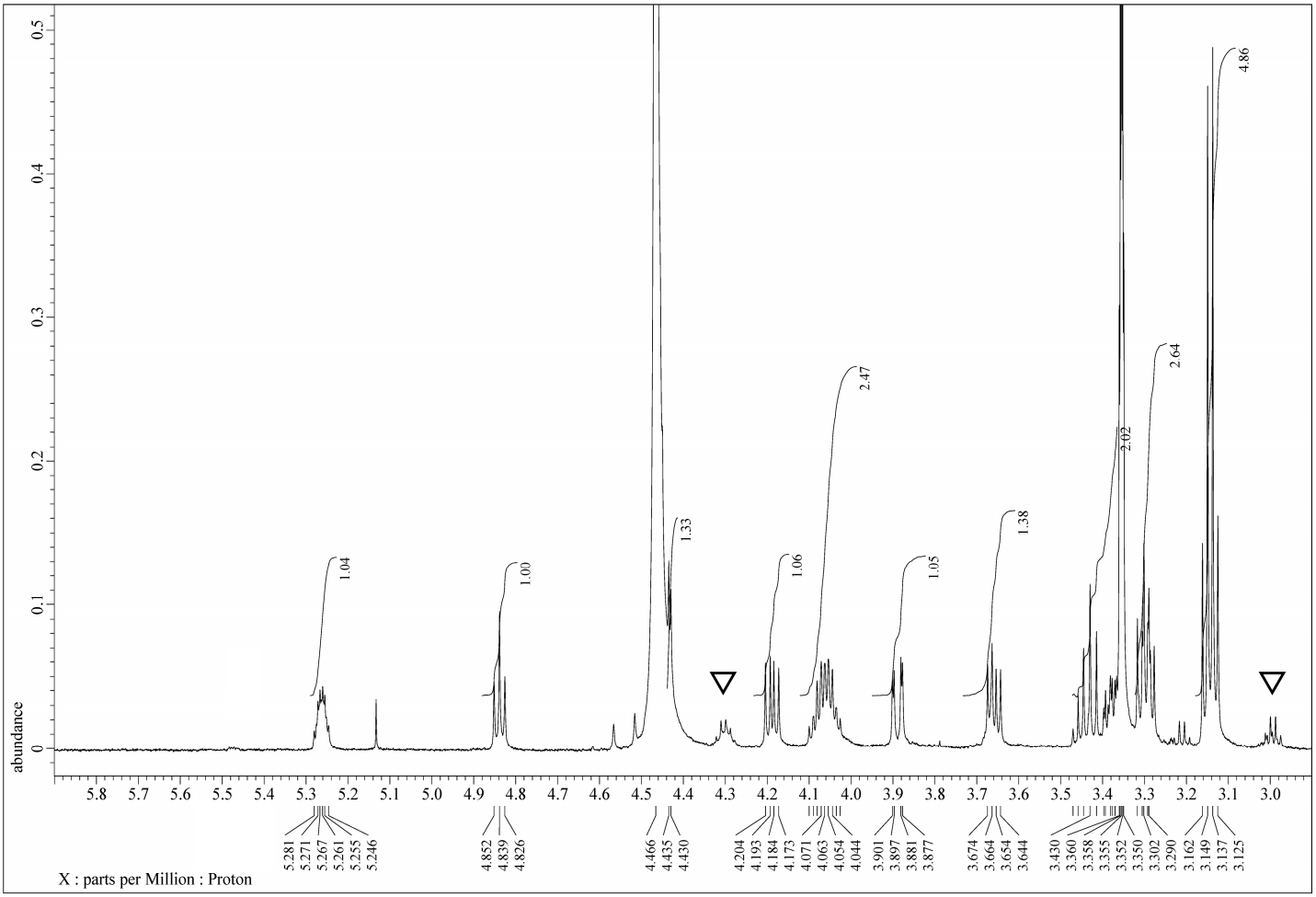


^{31}P-NMR data of 2,2-dimethyl-1,3-dioxolan-4-ylmethyl phosphatidyl glucoside (**2**), 243 MHz, $CDCl_3$, CD_3OD 3%

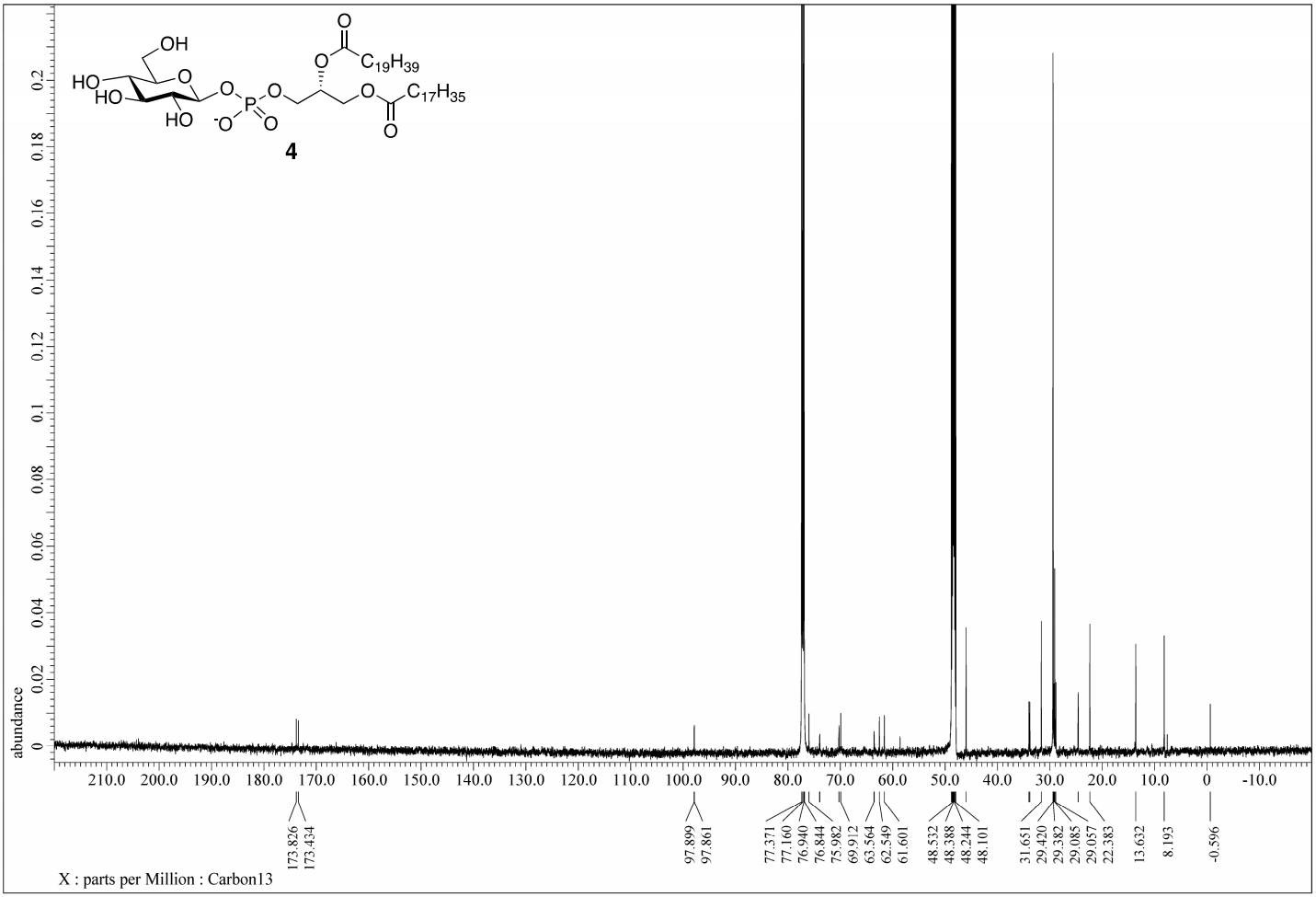


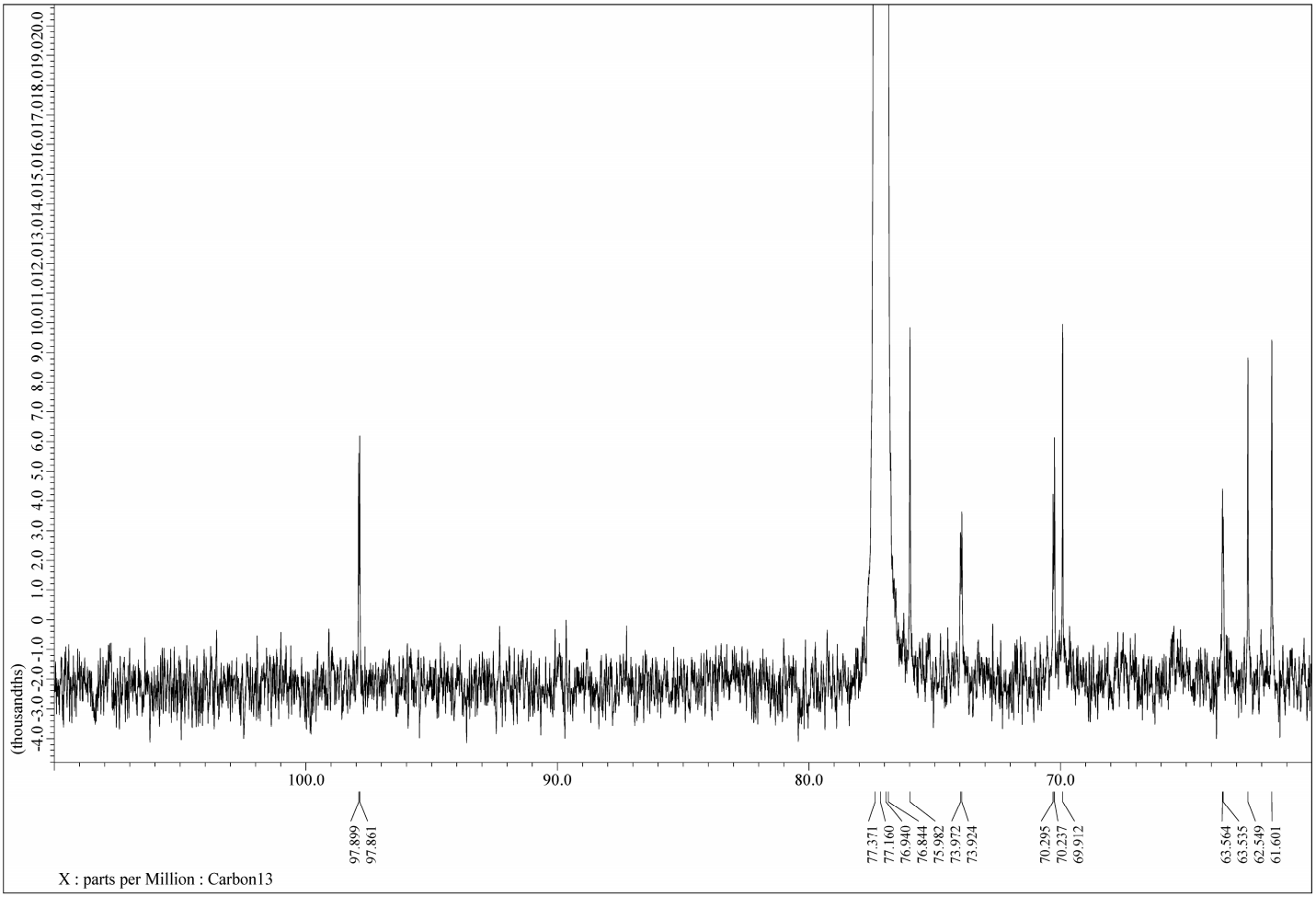
^{1}H-NMR data of phosphatidyl glucoside (PtdGlc) (18:0/20:0) (**4**), 600 MHz, $CDCl_3/CD_3OD$ = 2/1



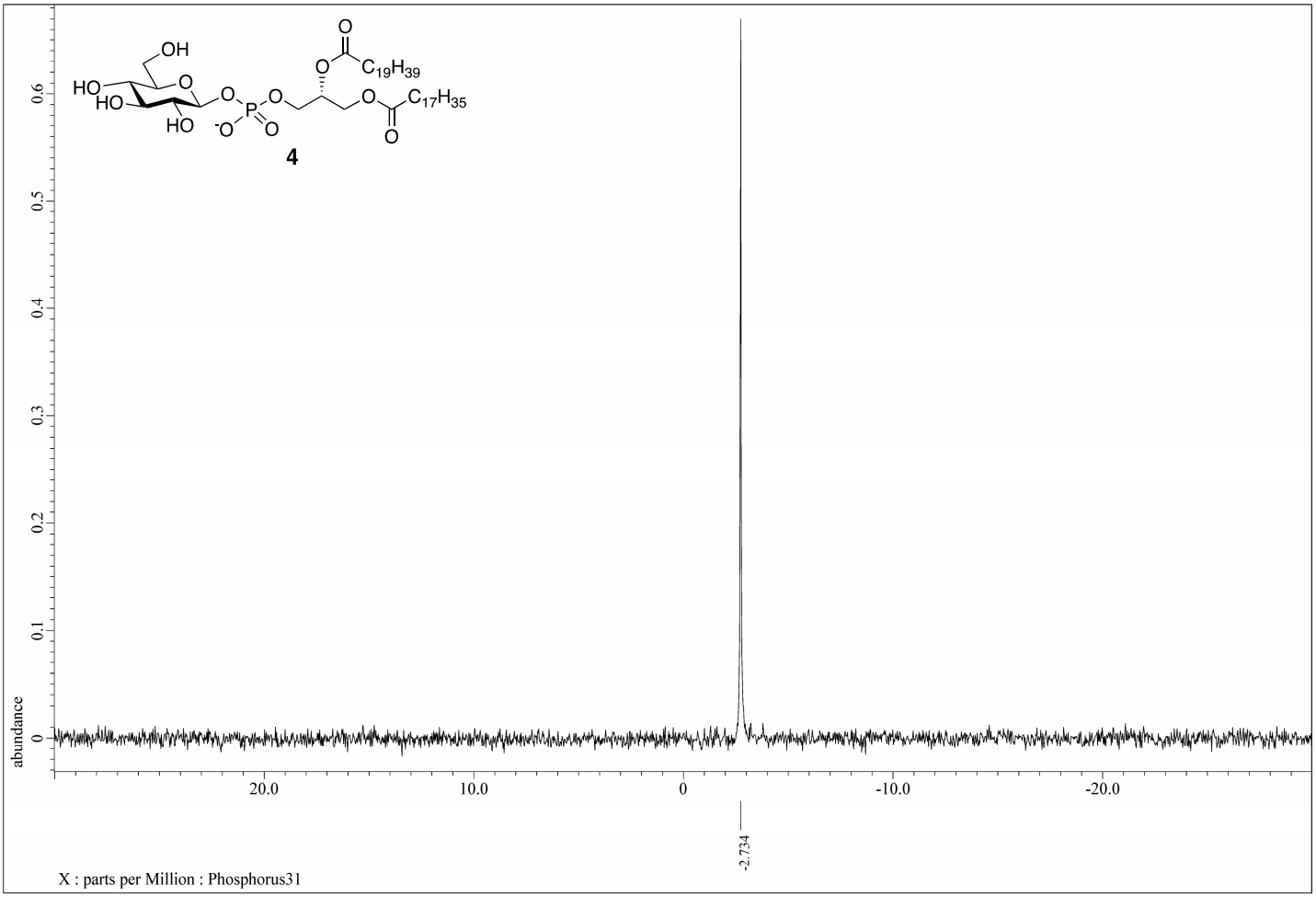


^{13}C-NMR data phosphatidyl glucoside (PtdGlc) (18:0/20:0) (**4**), 150 MHz, $CDCl_3/CD_3OD$ = 2/1

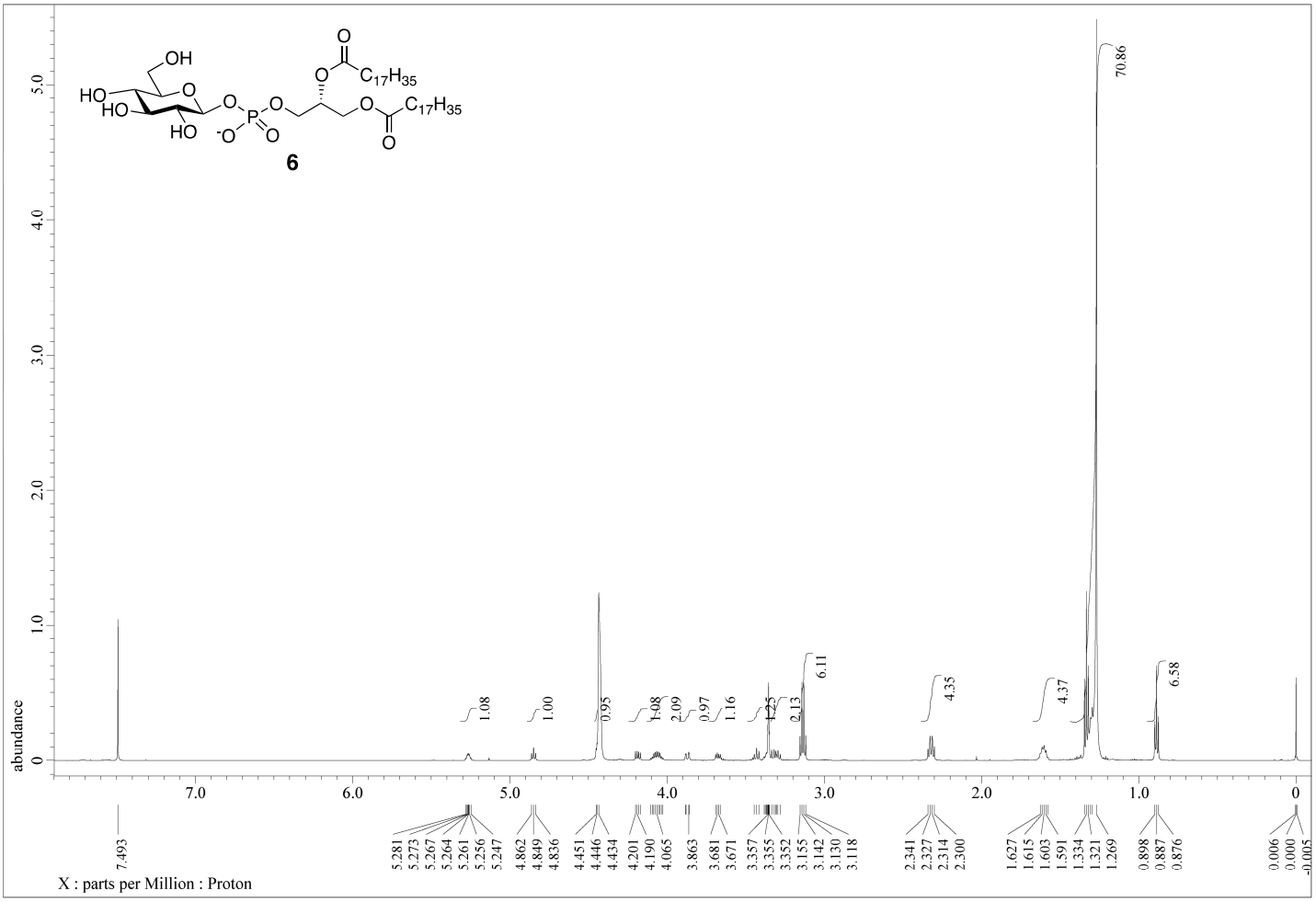


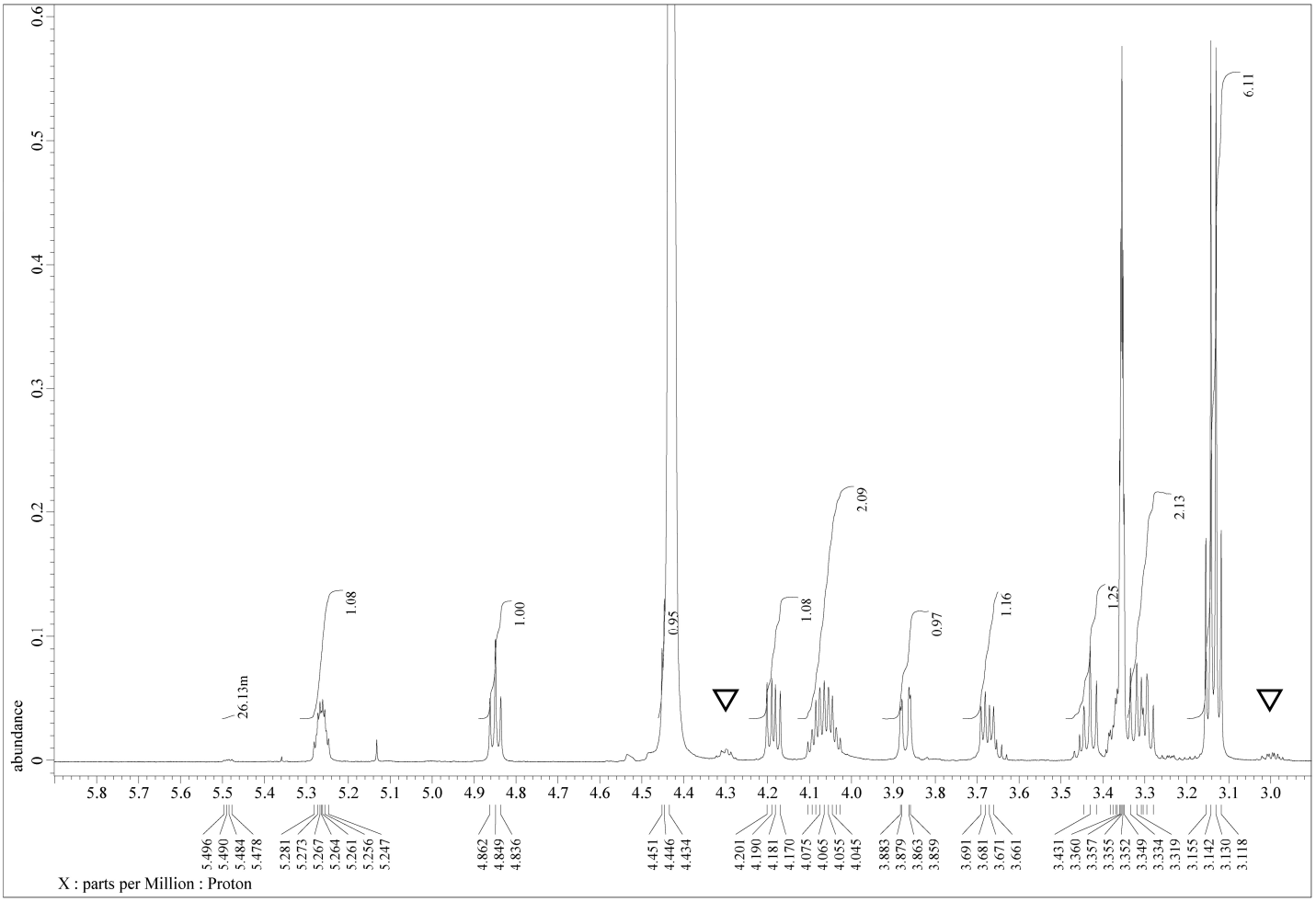


^{31}P-NMR data of phosphatidyl glucoside (PtdGlc) (18:0/20:0) (**4**), 243 MHz, $CDCl_3/CD_3OD$ = 2/1

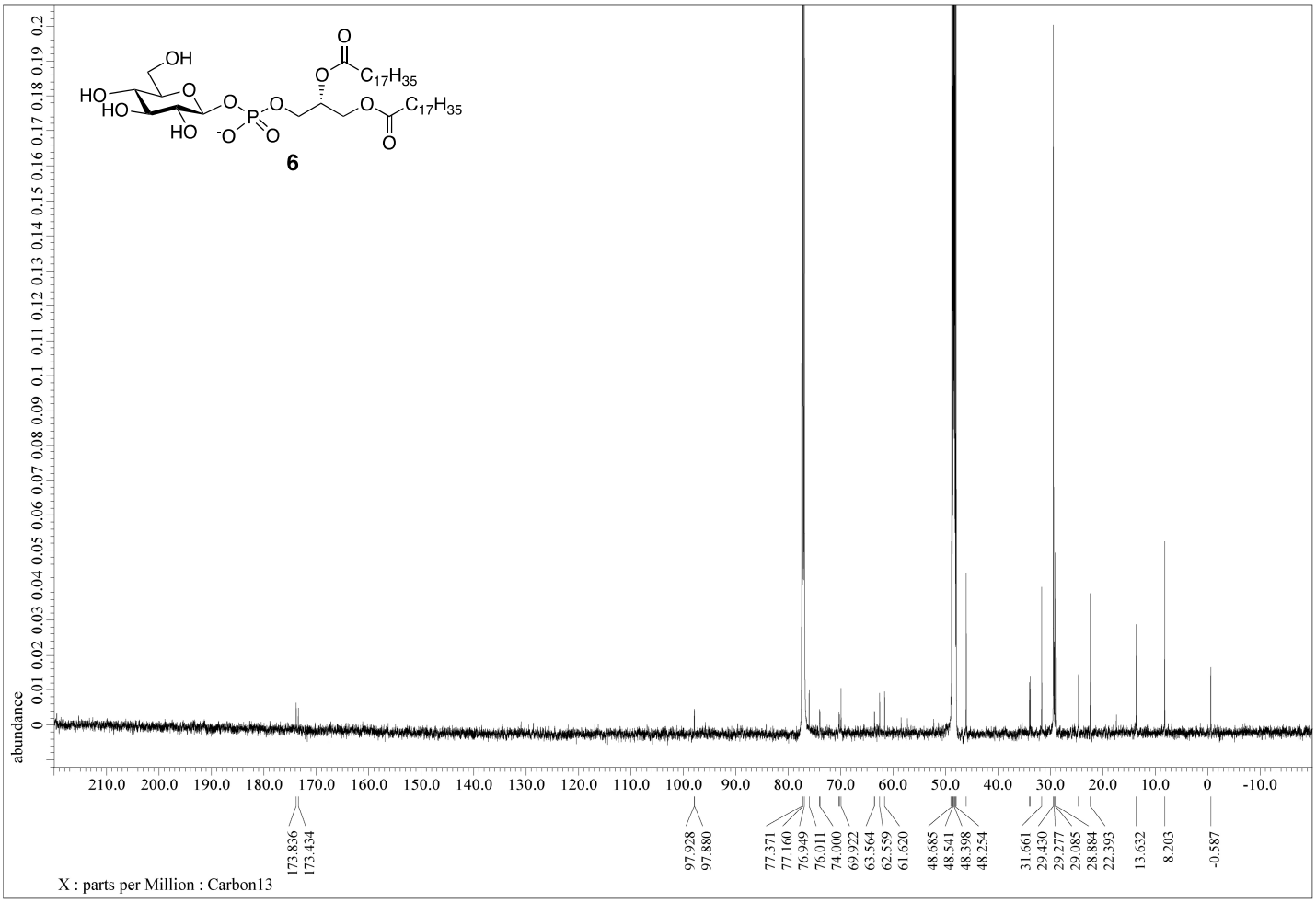


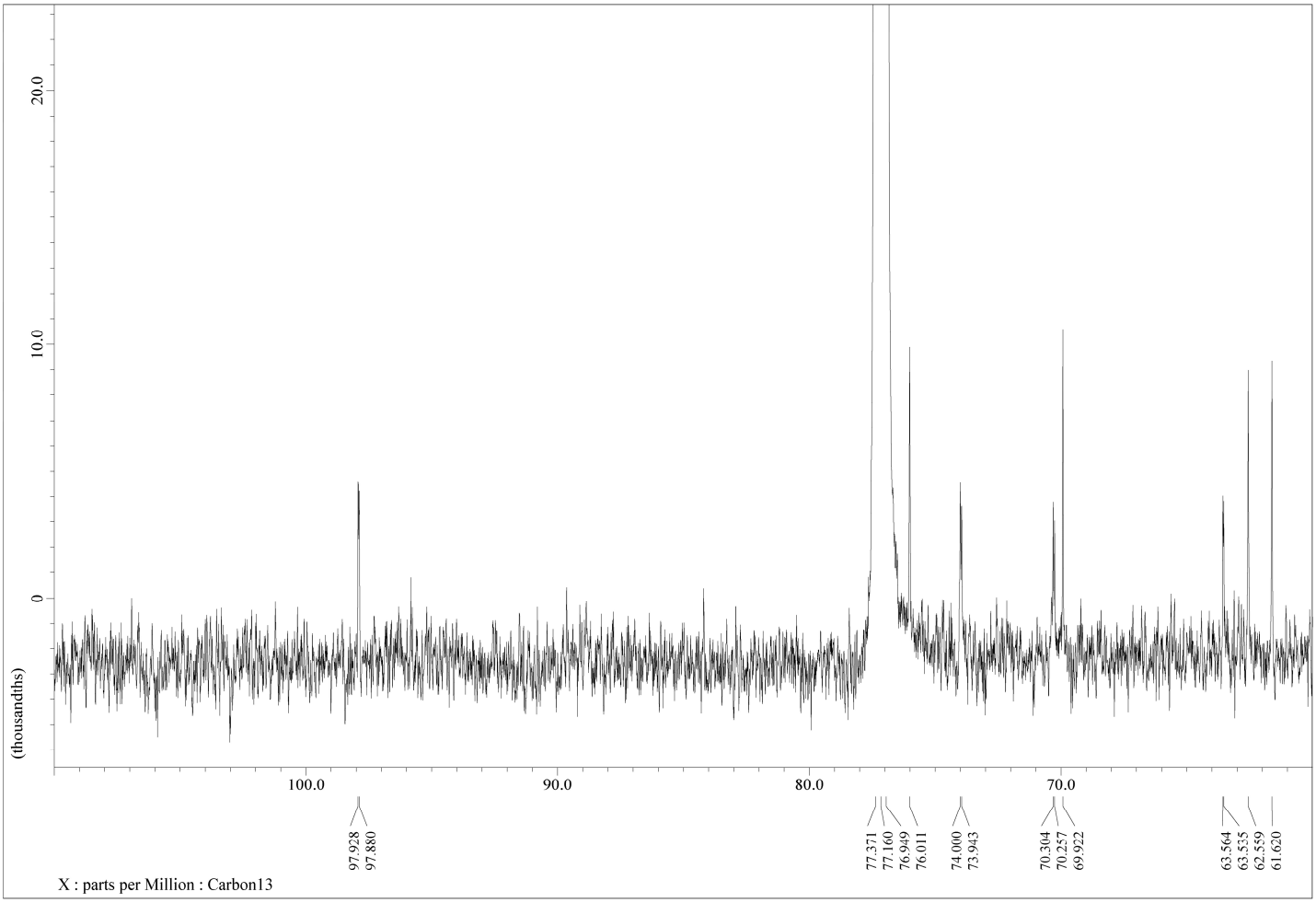
^{1}H-NMR data of PtdGlc (18:0/18:0) (**6**), 600 MHz, $CDCl_3/CD_3OD$ = 2/1



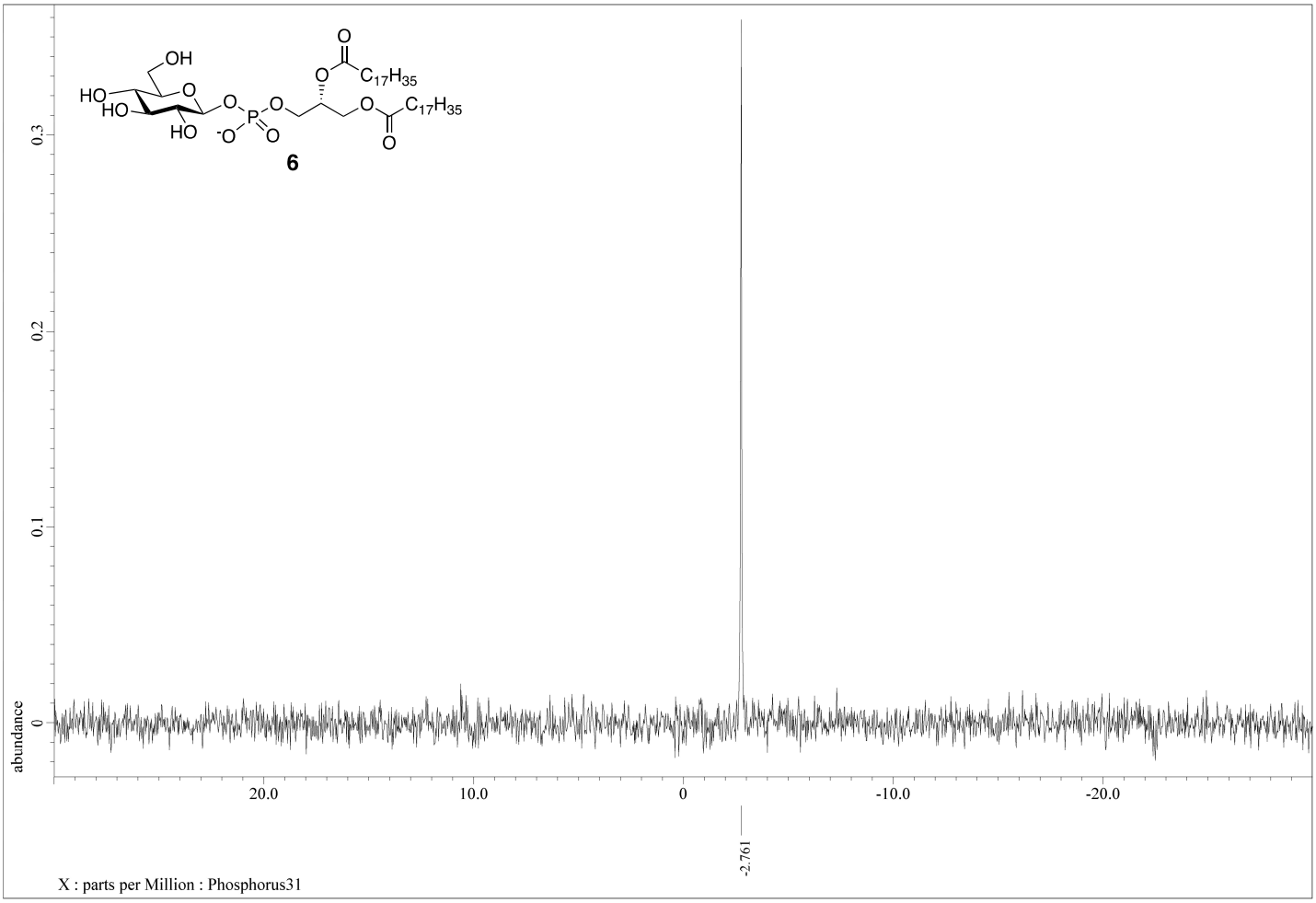


^{13}C-NMR data of PtdGlc (18:0/18:0) (**6**), 150 MHz, $CDCl_3/CD_3OD$ = 2/1

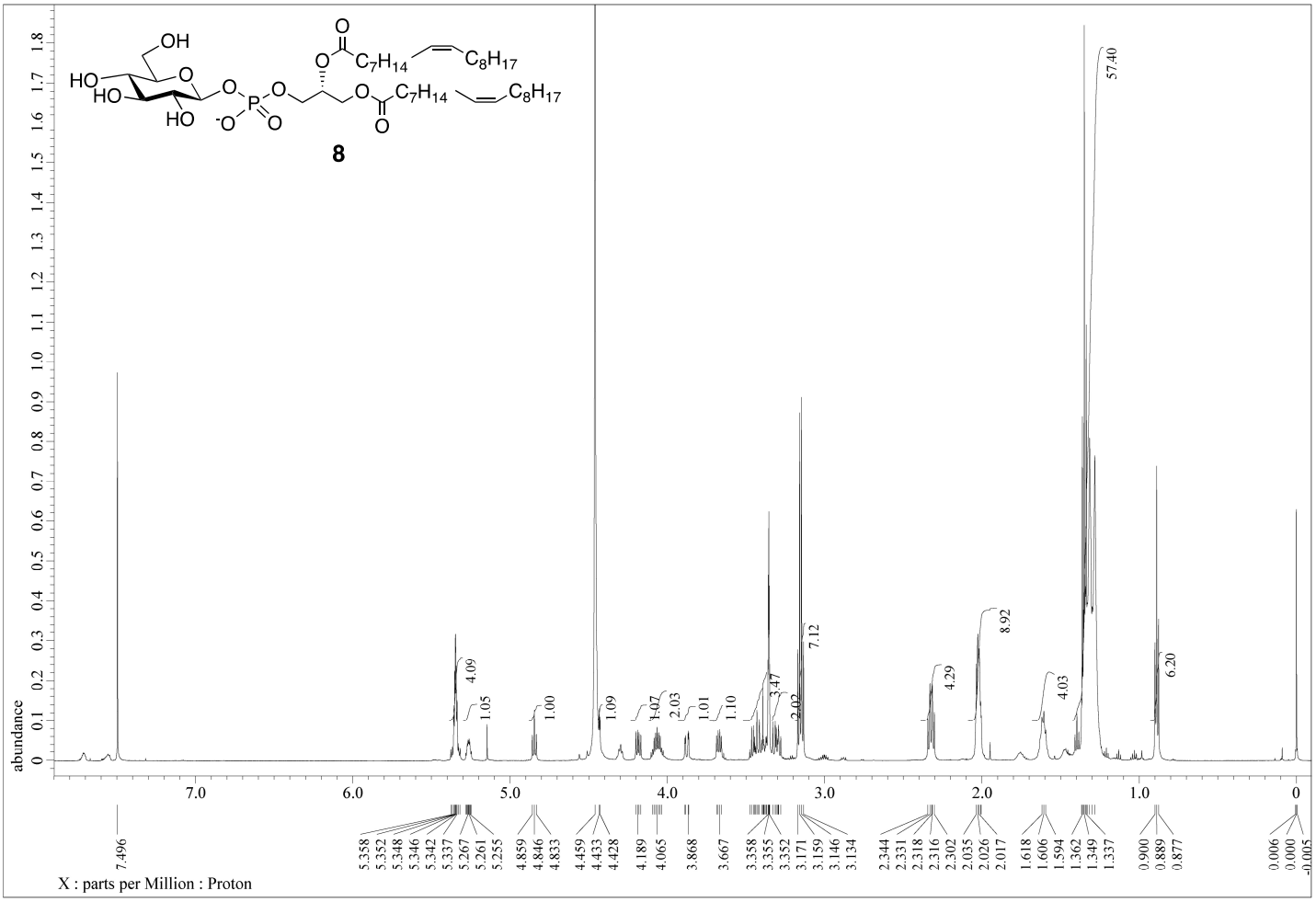


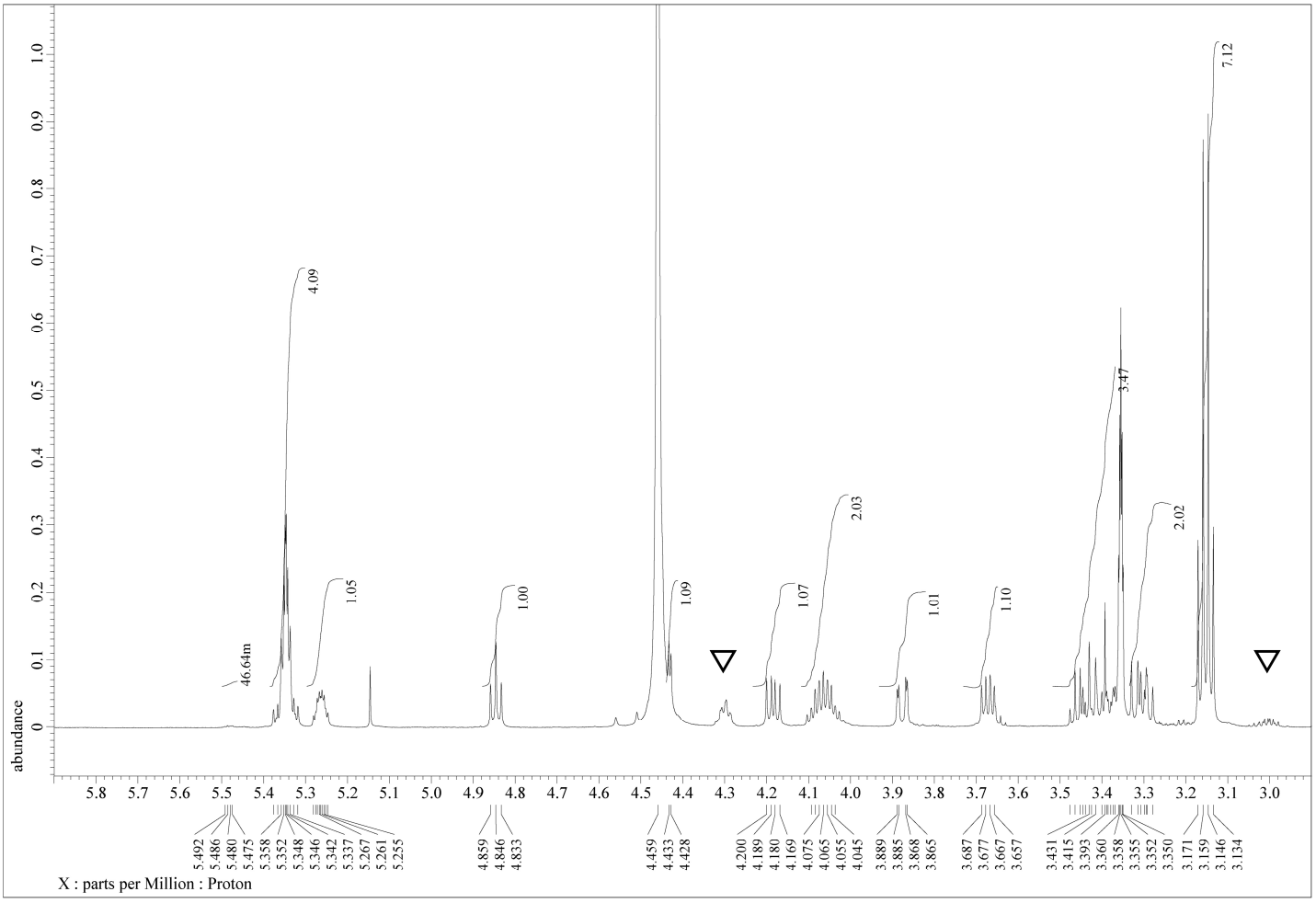


^{31}P-NMR data of PtdGlc (18:0/18:0) (**6**), 150 MHz, $CDCl_3/CD_3OD$ = 2/1

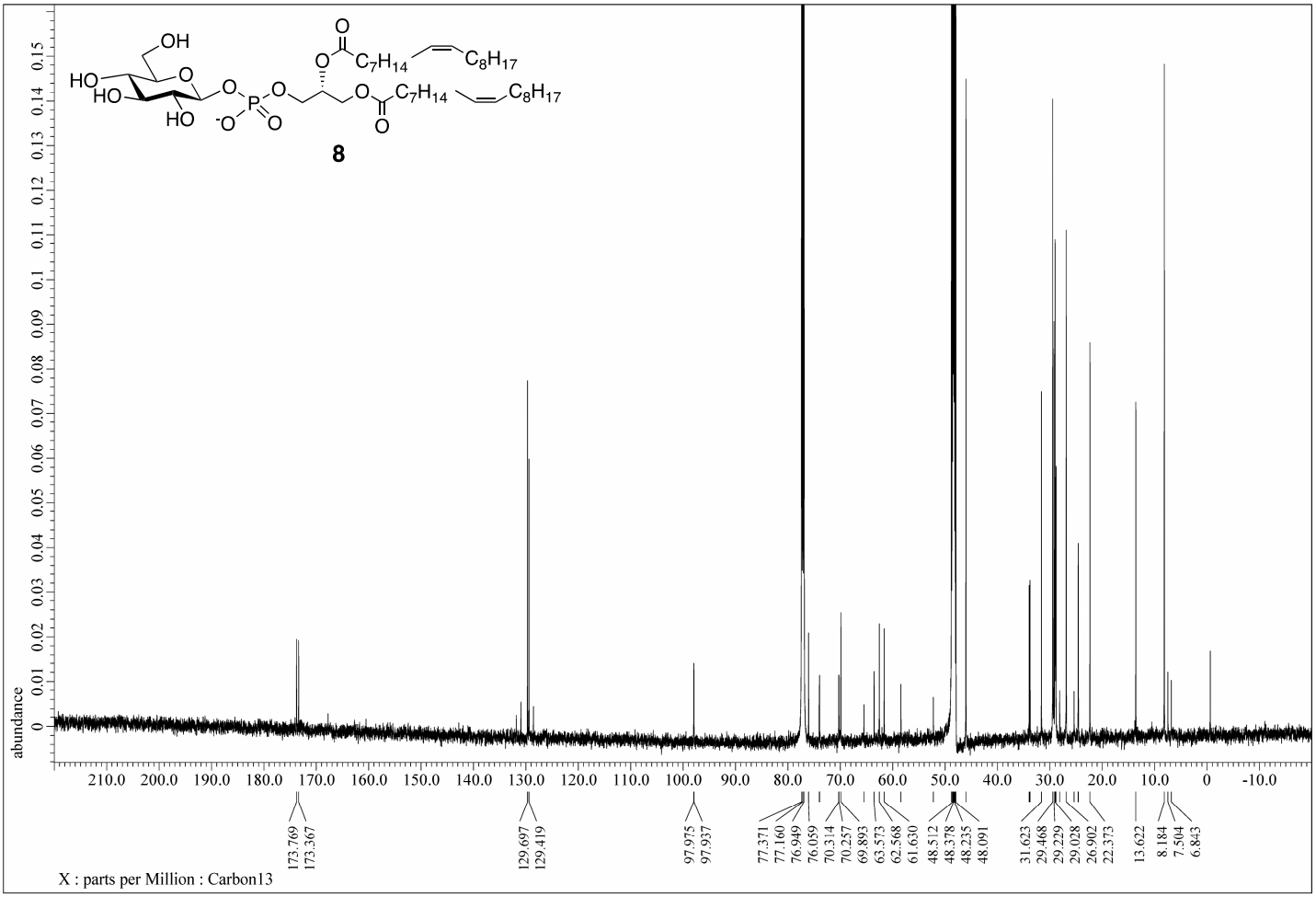


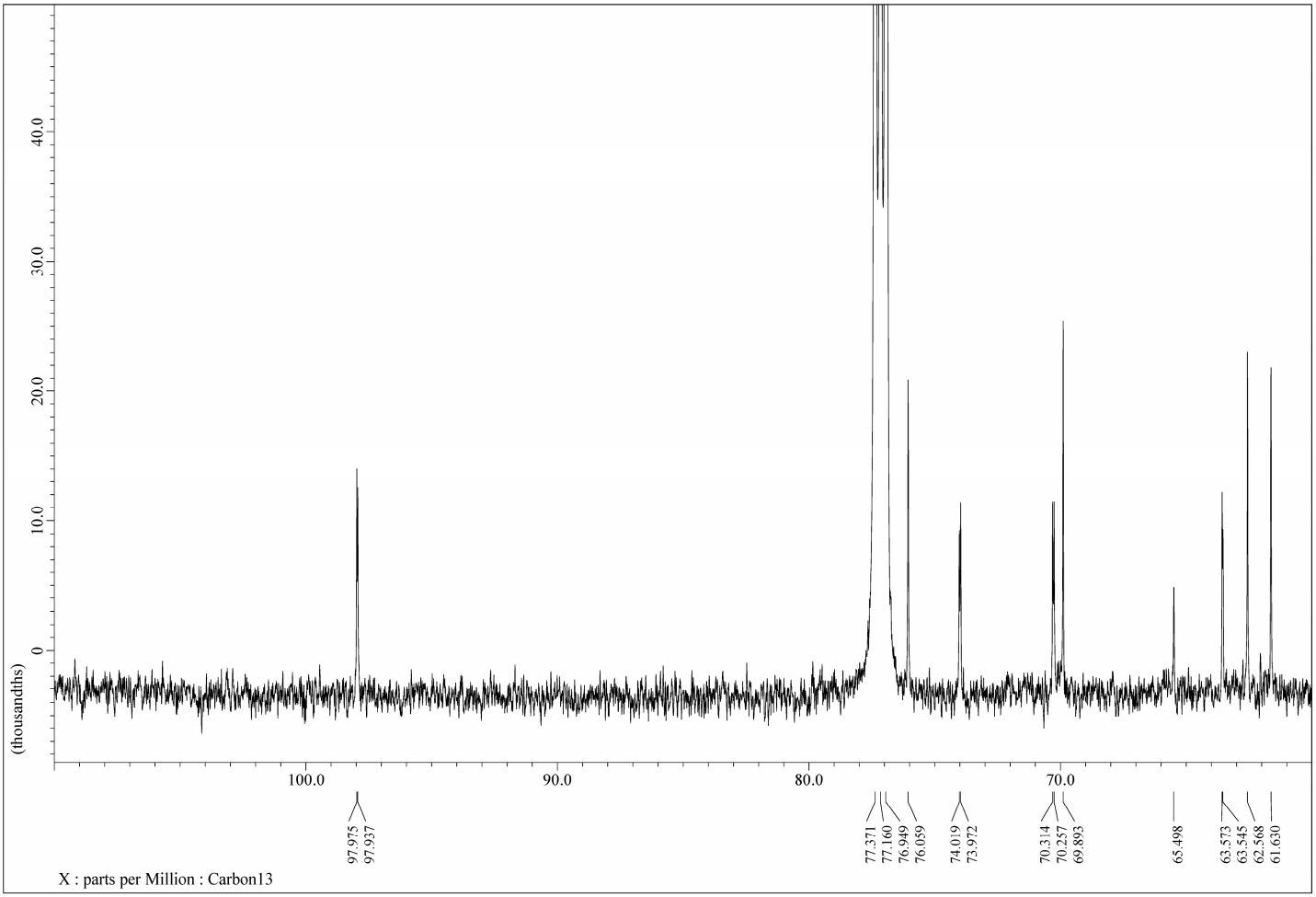
^{1}H-NMR data of PtdGlc (18:1/18:1) (**8**), 600 MHz, $CDCl_3/CD_3OD$ = 2/1



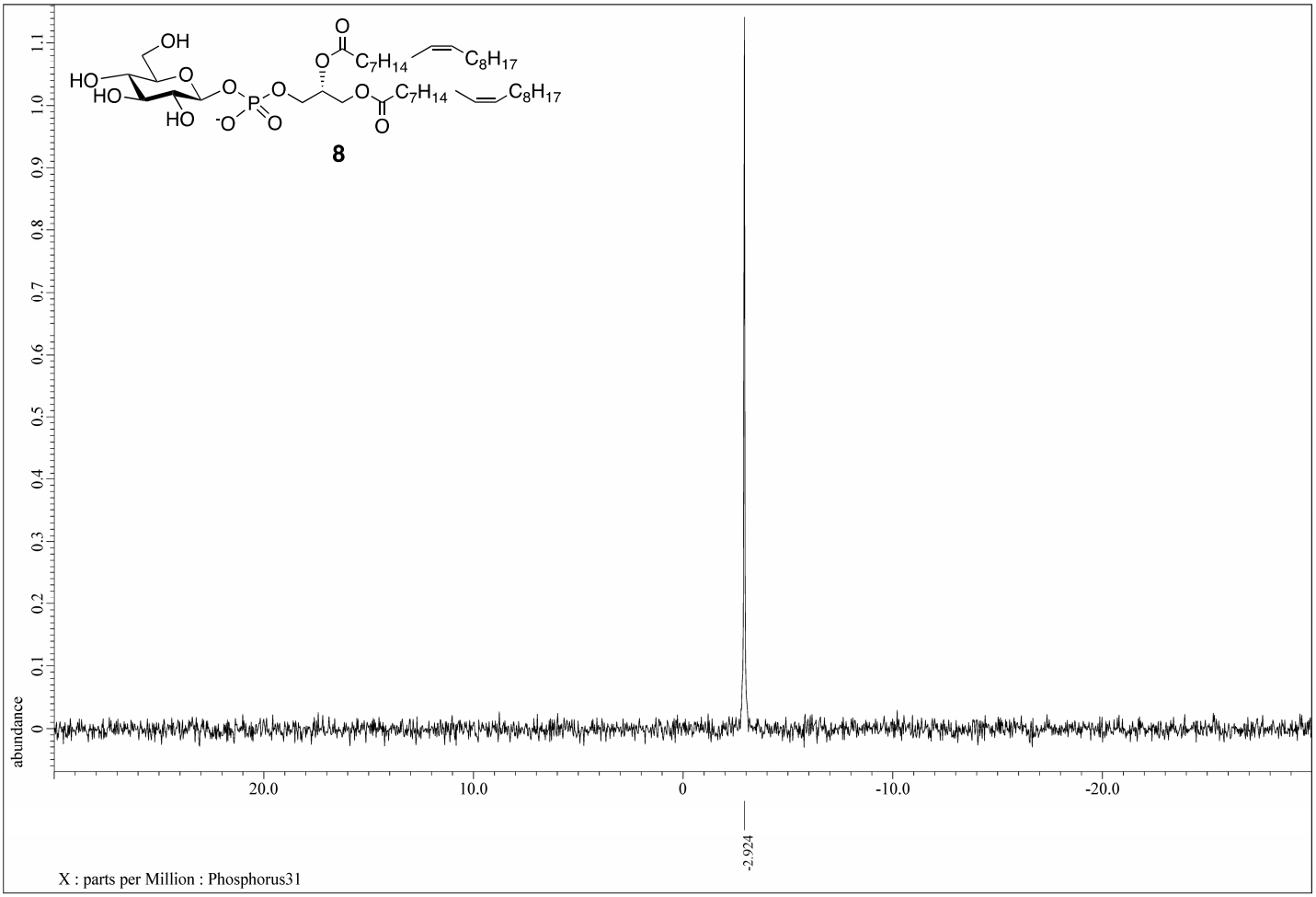


^{13}C-NMR data of PtdGlc (18:1/18:1) (**8**), 150 MHz, $CDCl_3/CD_3OD$ = 2/1

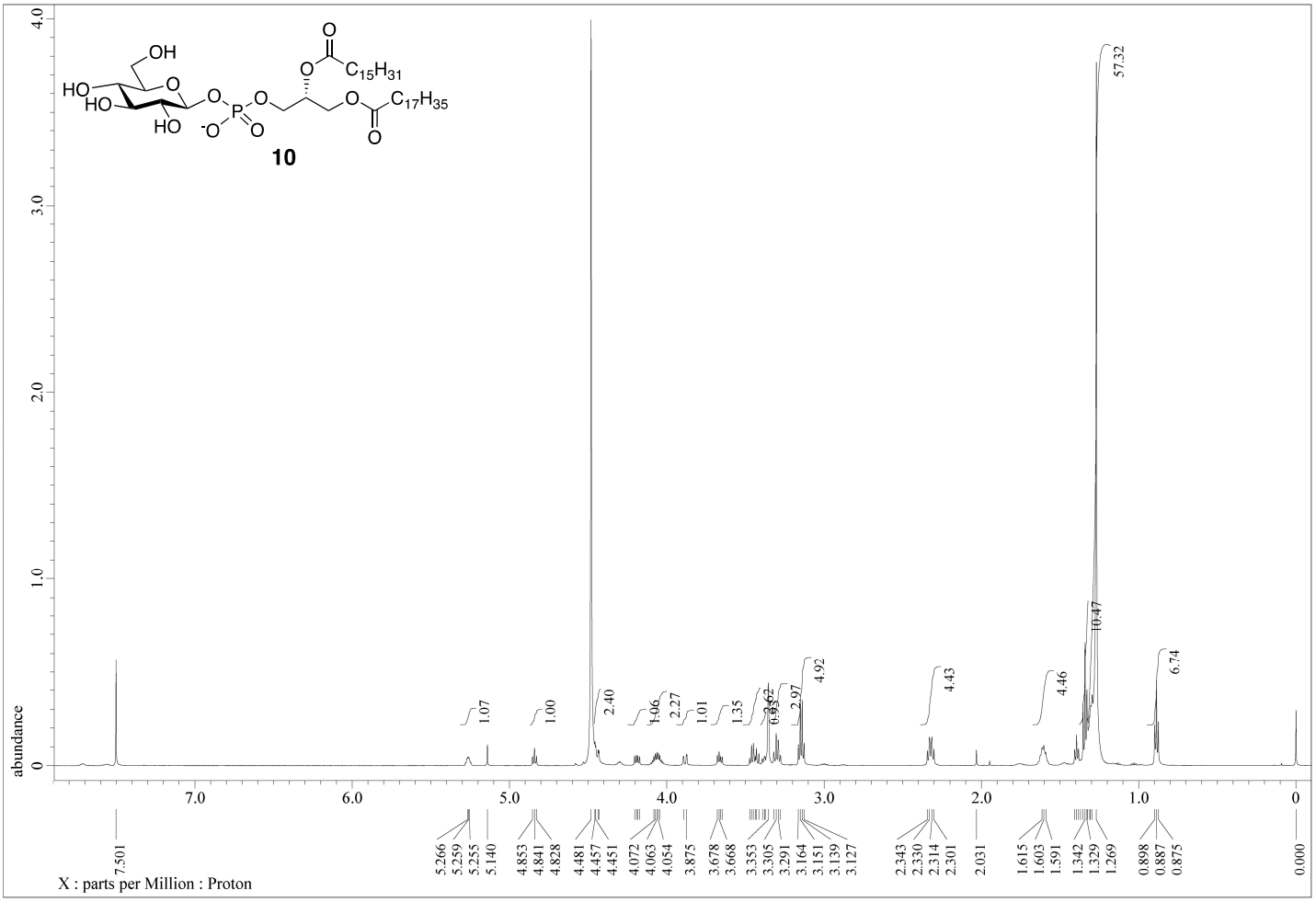


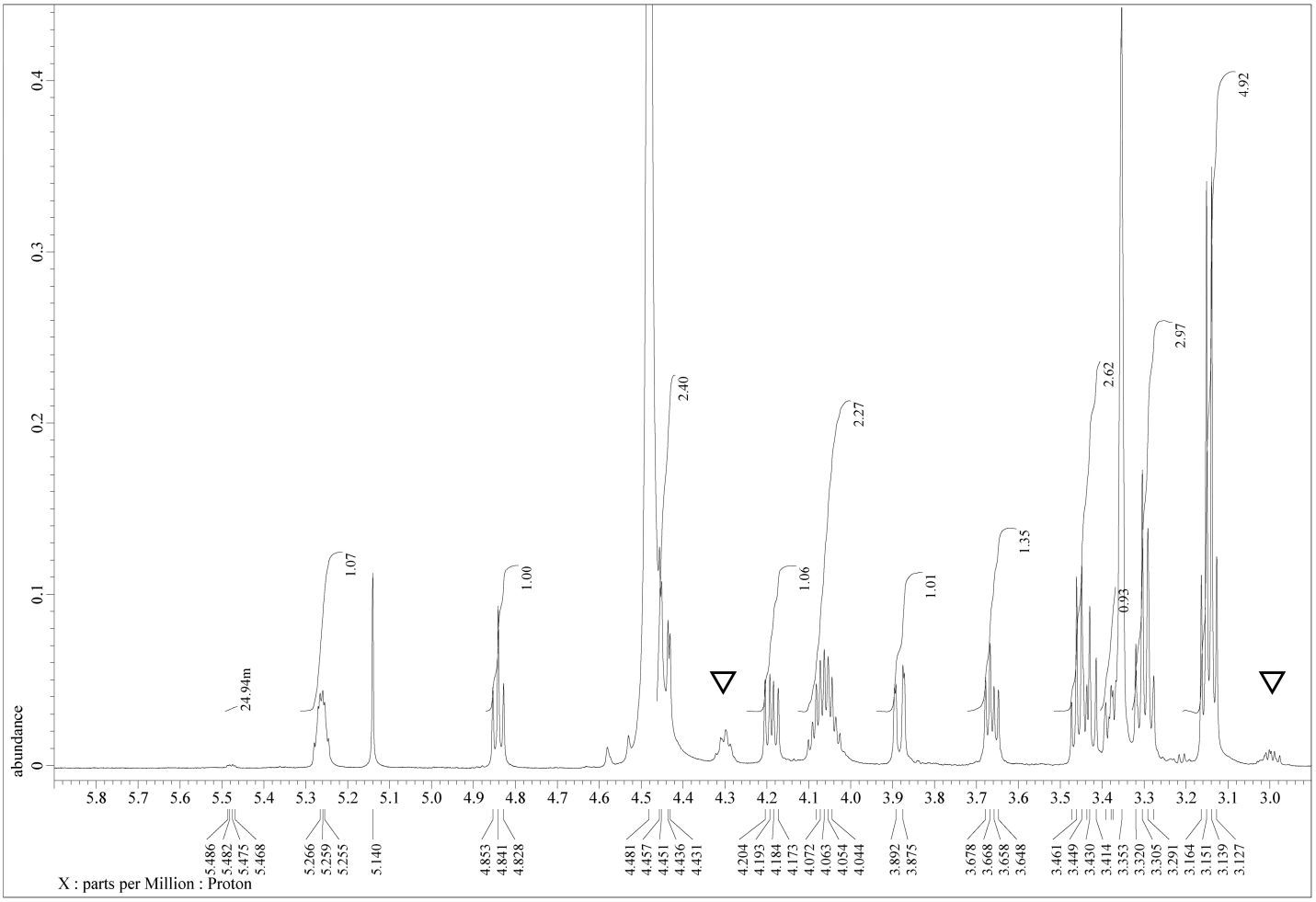


^{31}P-NMR data of PtdGlc (18:1/18:1) (**8**), 243 MHz, $CDCl_3/CD_3OD$ = 2/1

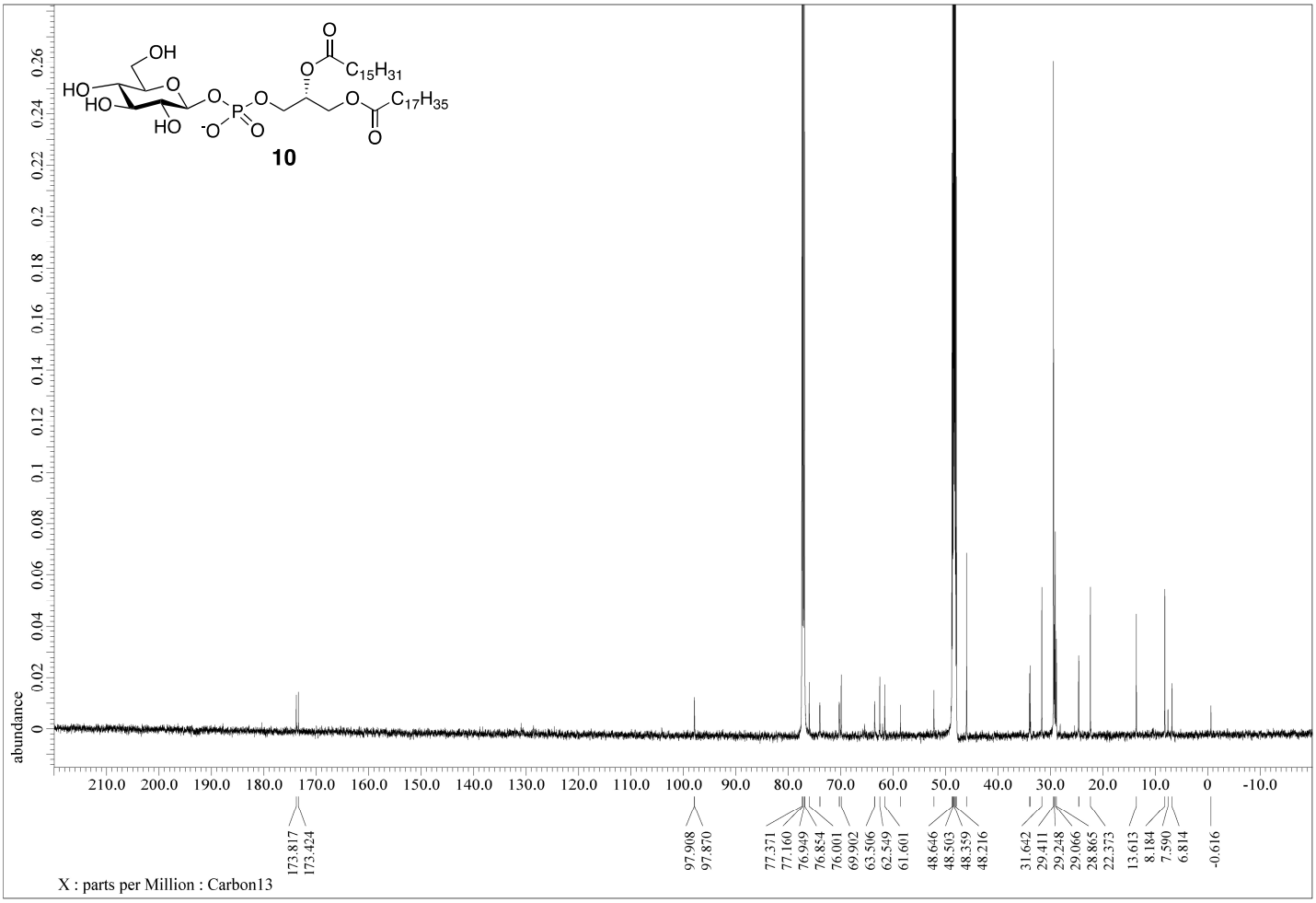


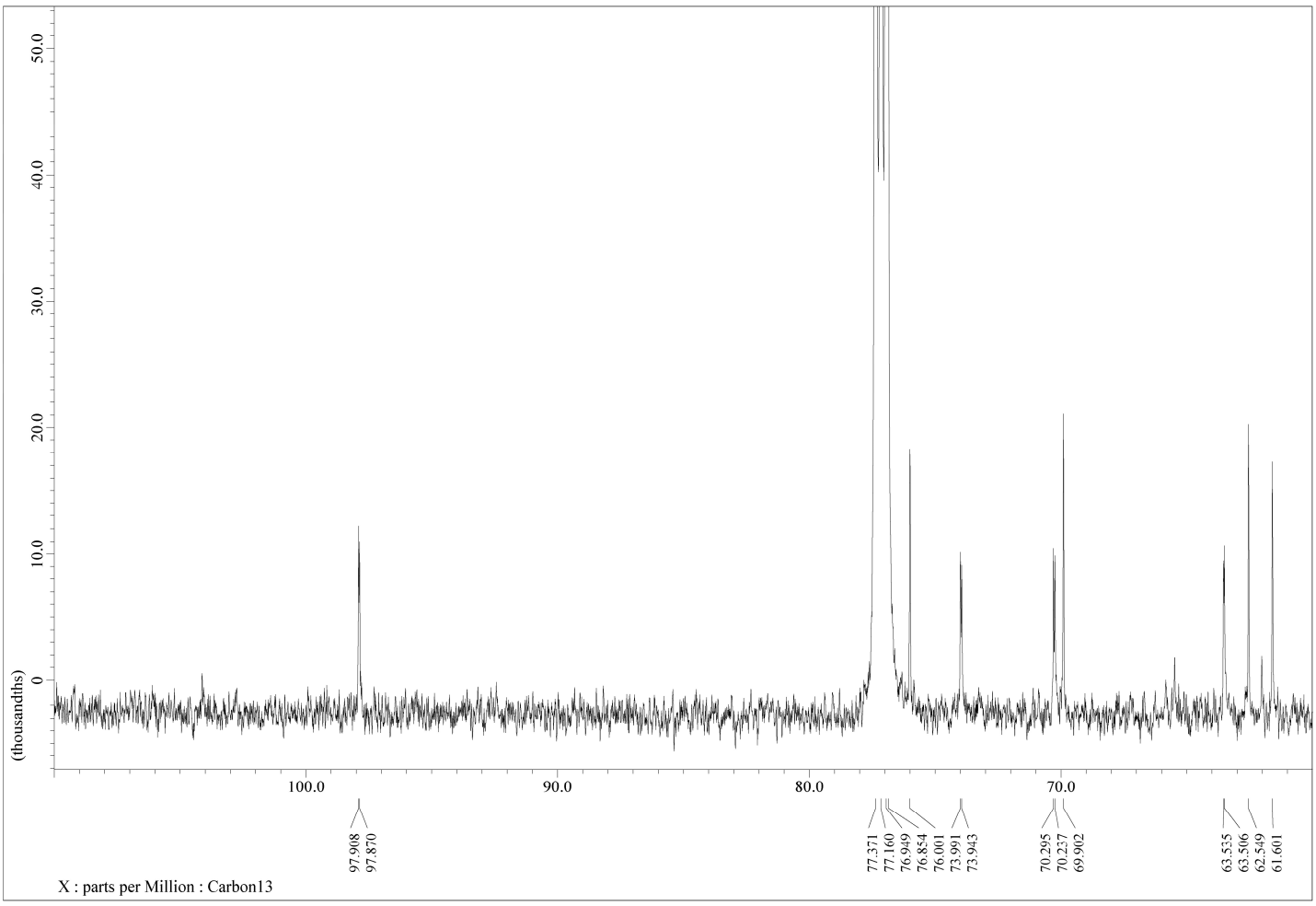
^{1}H-NMR data of PtdGlc (18:0/16:0) (**10**), 600 MHz, $CDCl_3/CD_3OD$ = 2/1



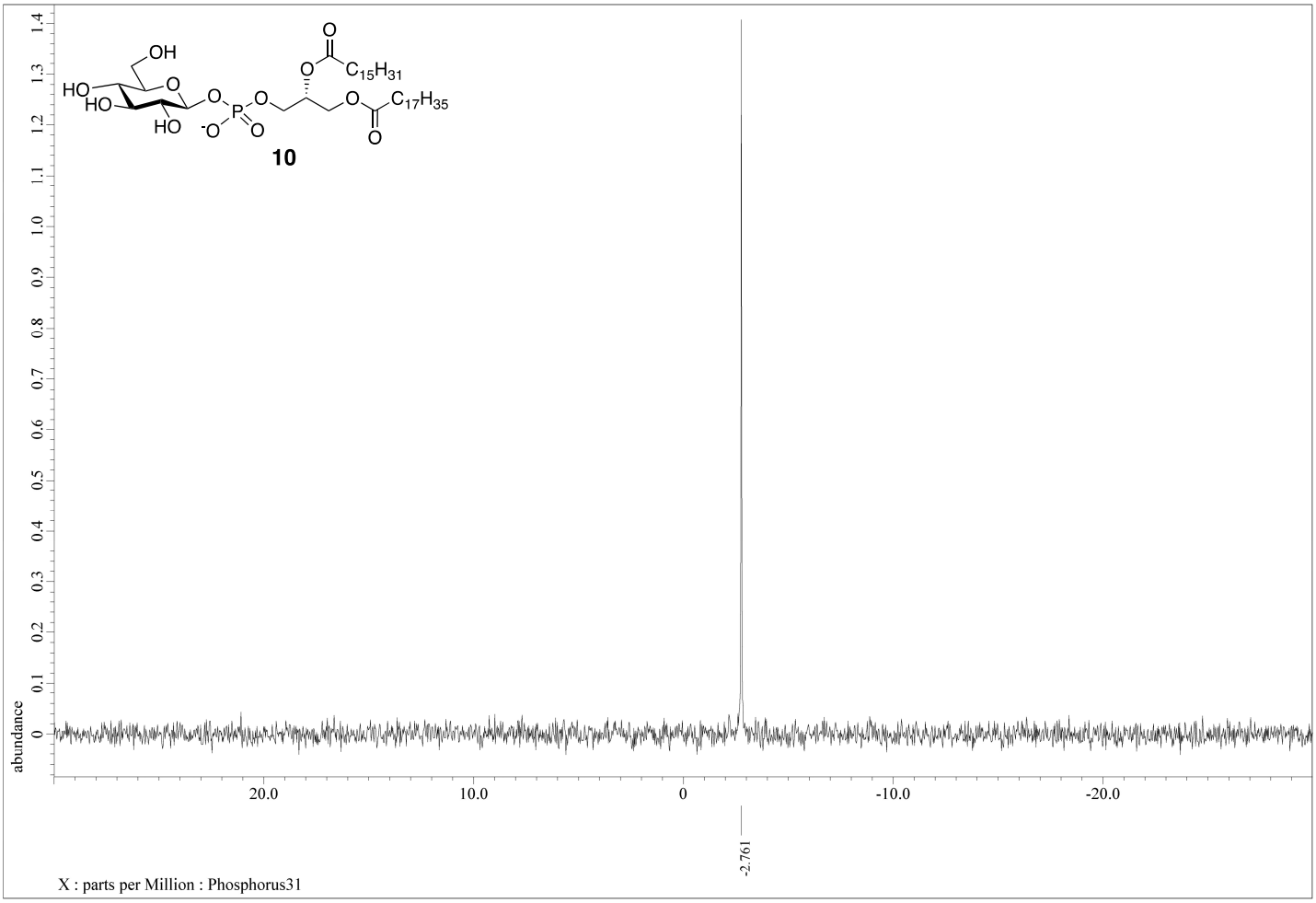


^{13}C-NMR data of PtdGlc (18:0/16:0) (**10**), 150 MHz, $CDCl_3/CD_3OD$ = 2/1

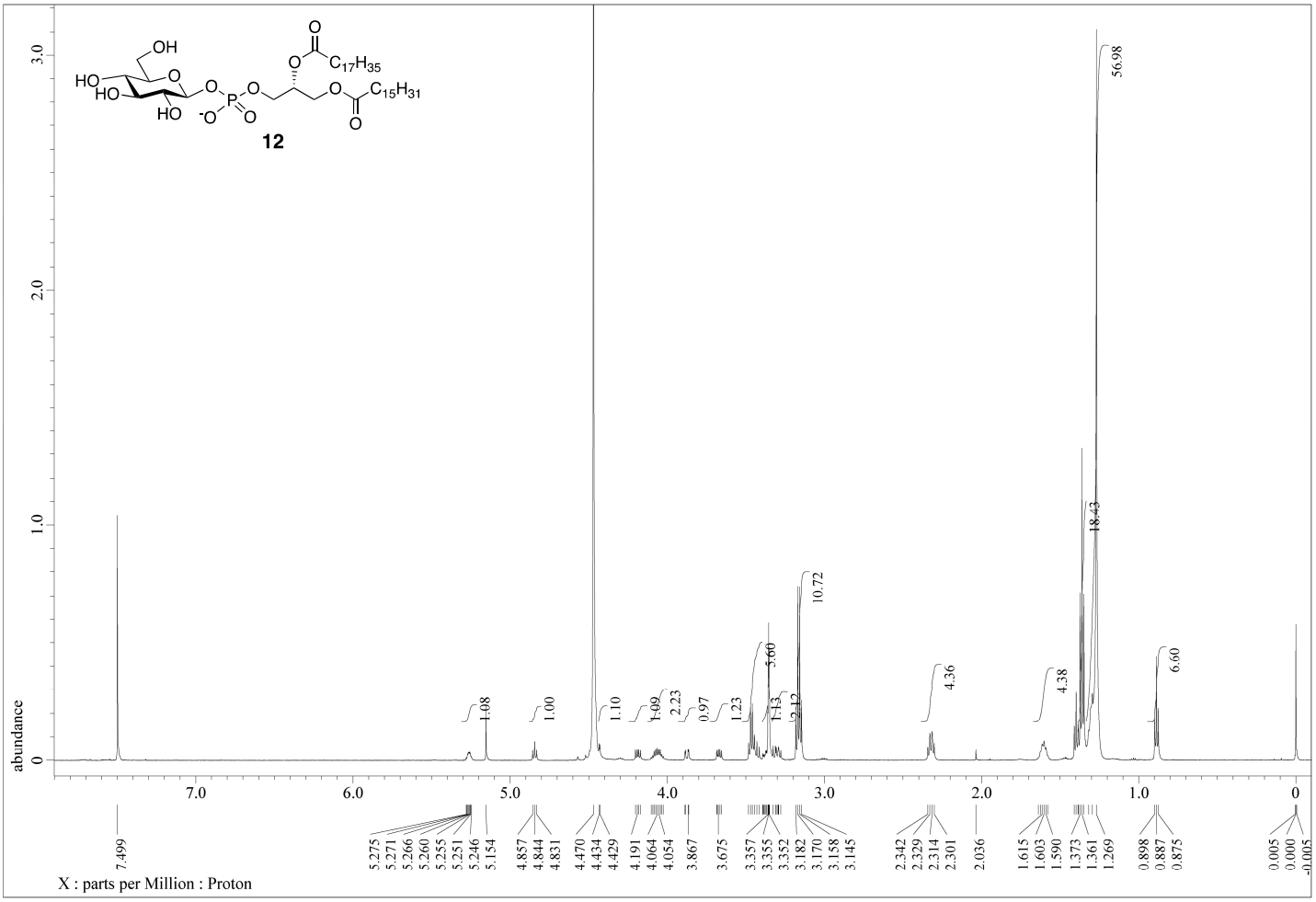


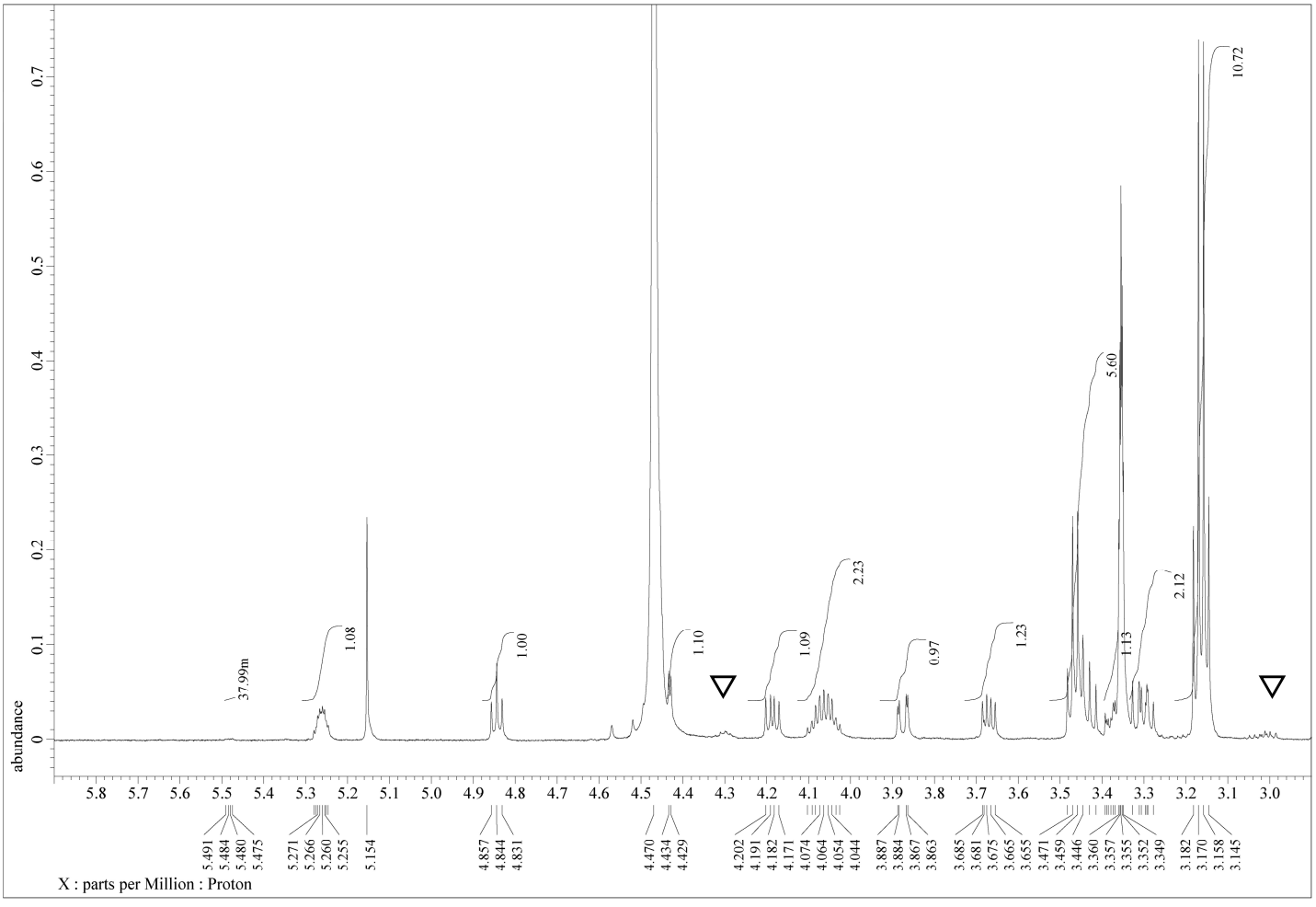


^{31}P-NMR data of PtdGlc (18:0/16:0) (**10**), 243 MHz, $CDCl_3/CD_3OD$ = 2/1

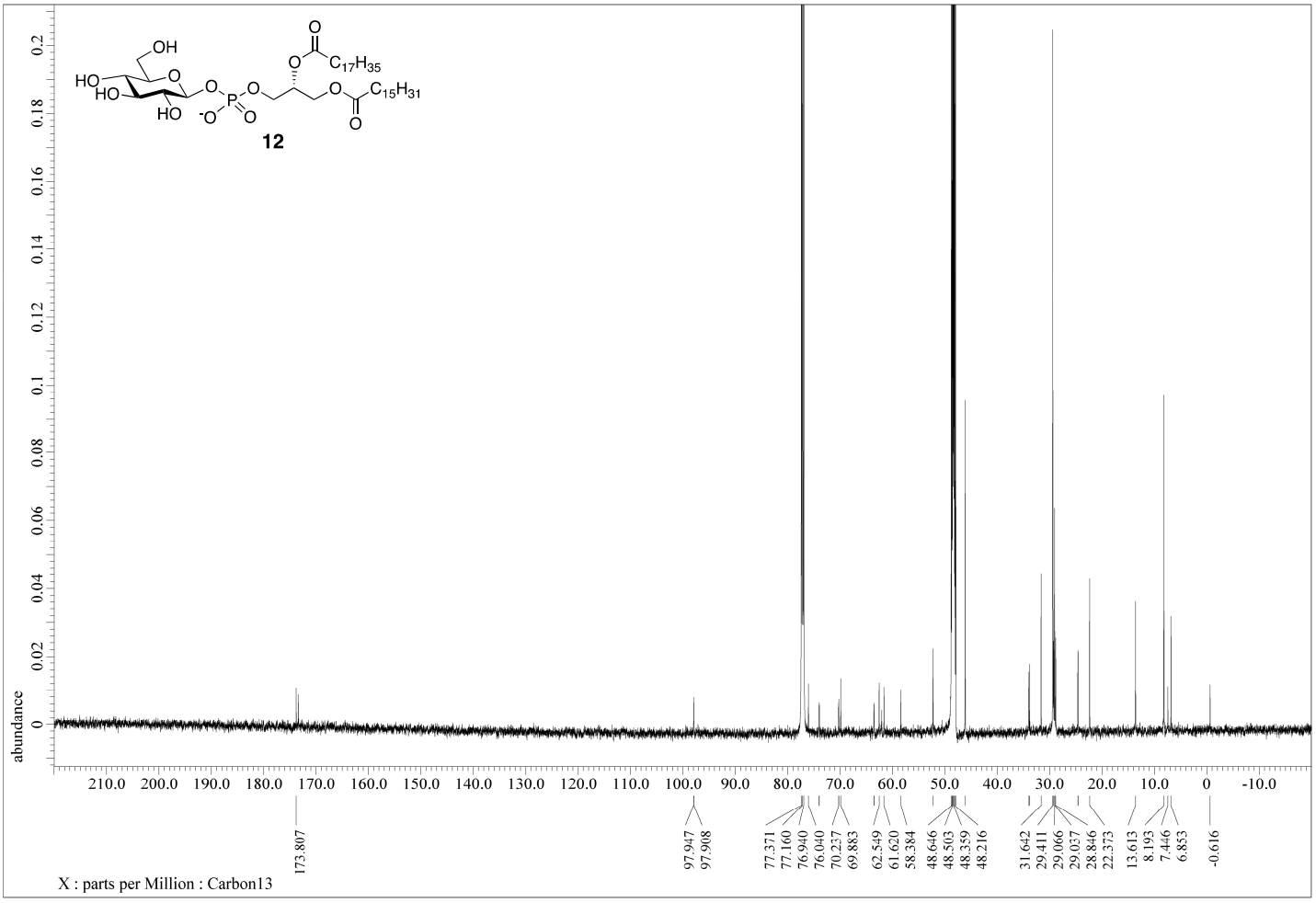


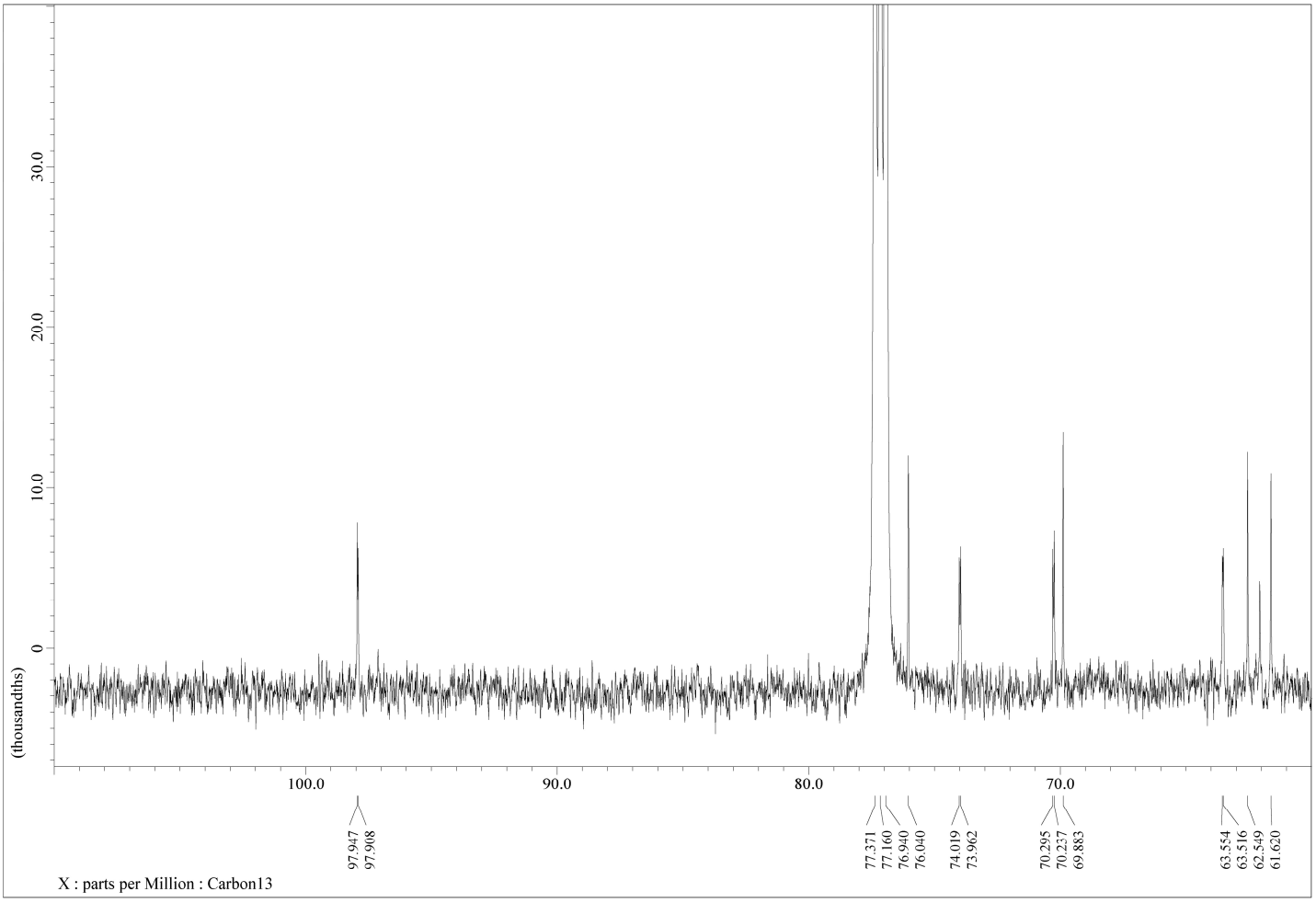
^{1}H-NMR data of PtdGlc (16:0/18:0) (**12**), 600 MHz, $CDCl_3/CD_3OD$ = 2/1



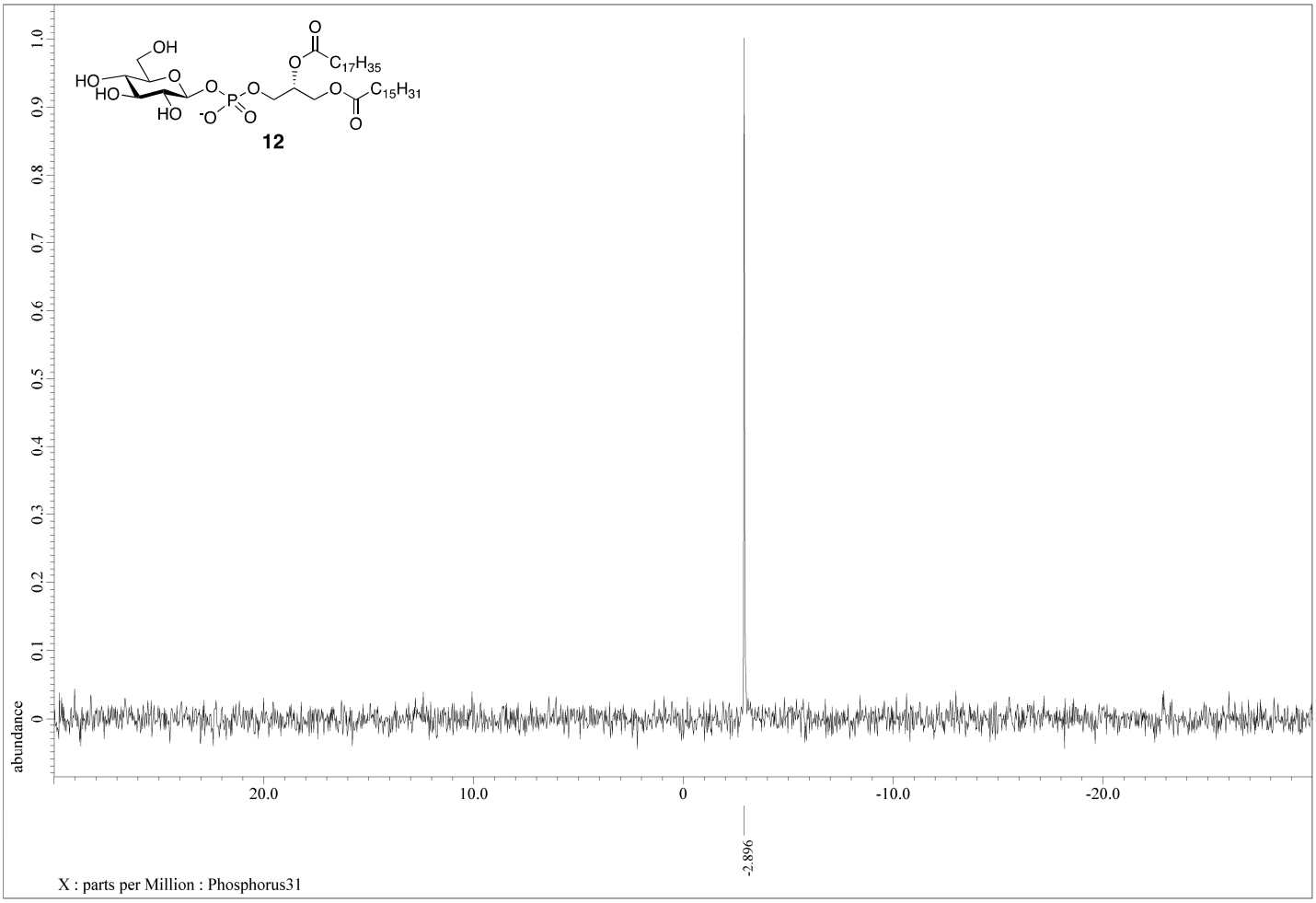


^{13}C-NMR data of PtdGlc (16:0/18:0) (**12**), 150 MHz, $CDCl_3/CD_3OD$ = 2/1

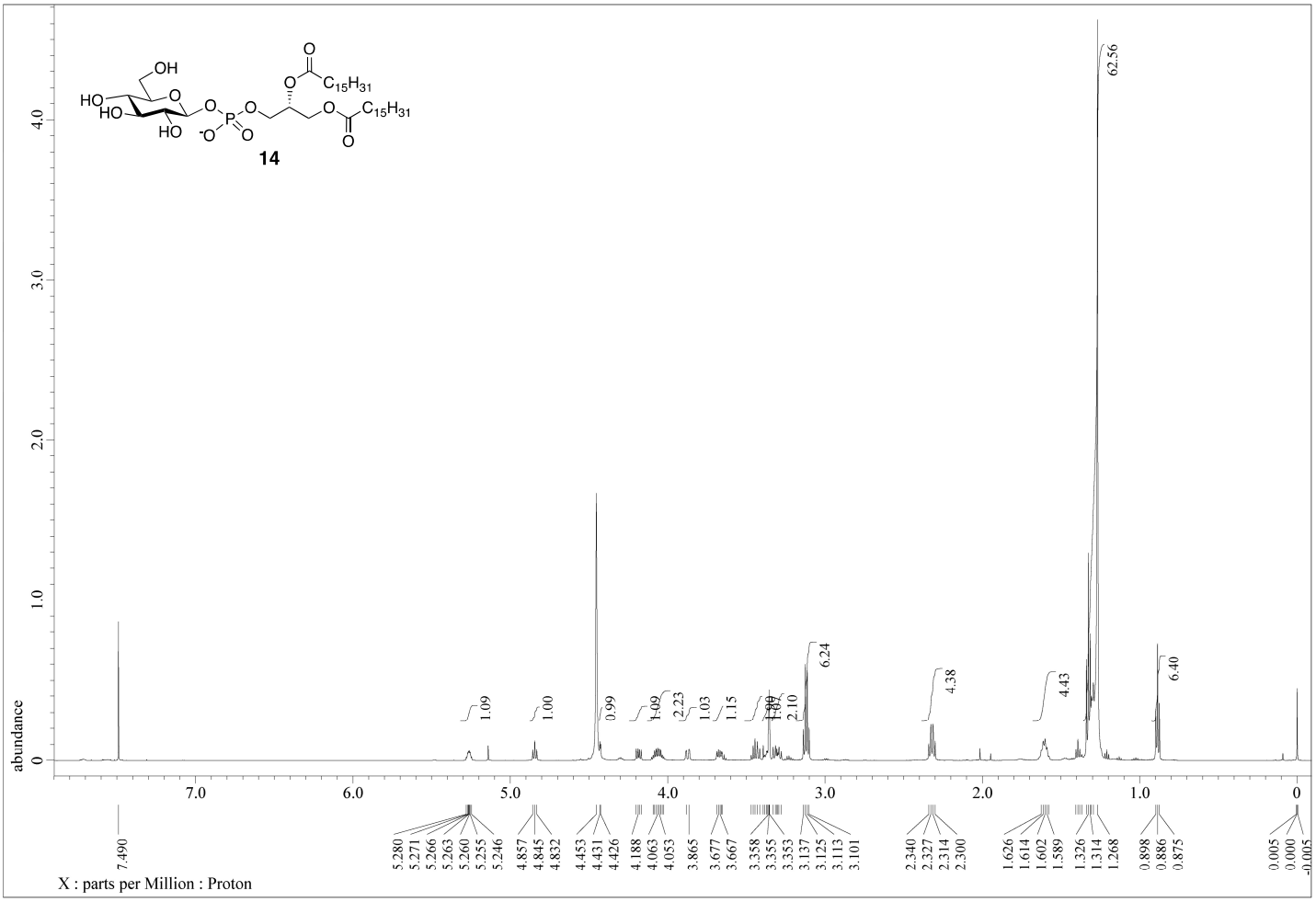


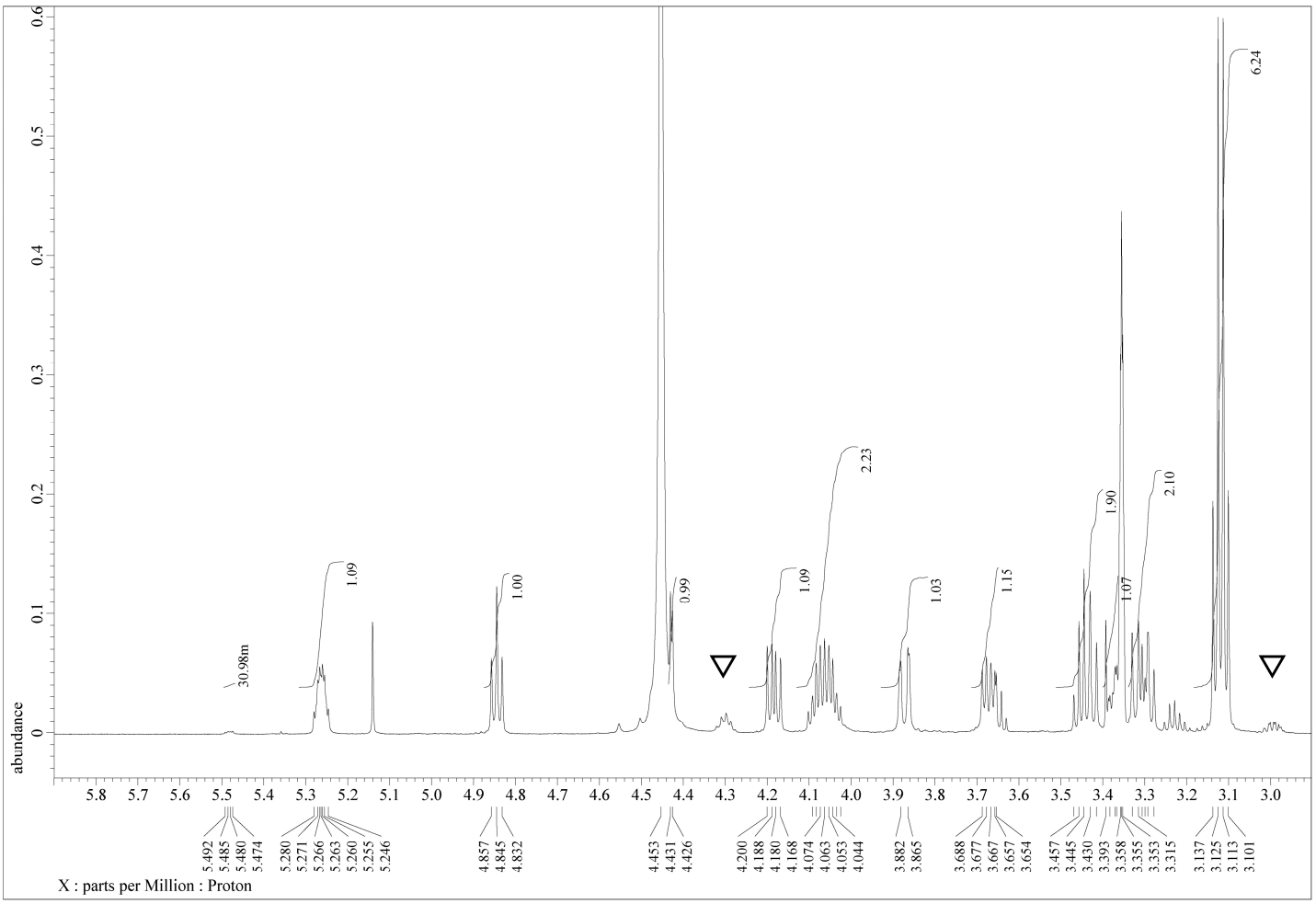


^{31}P-NMR data of PtdGlc (16:0/18:0) (**12**), 243 MHz, $CDCl_3/CD_3OD$ = 2/1

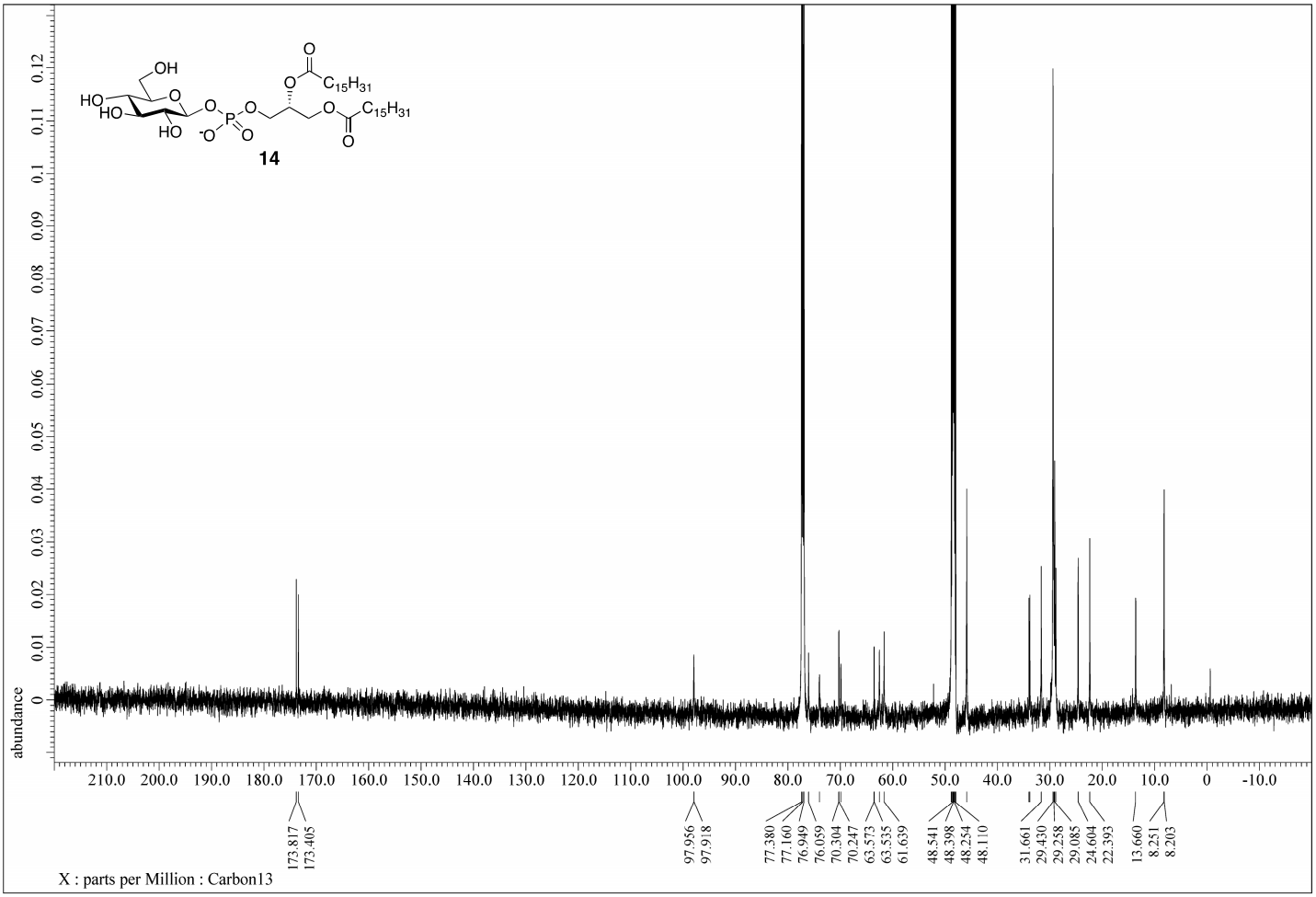


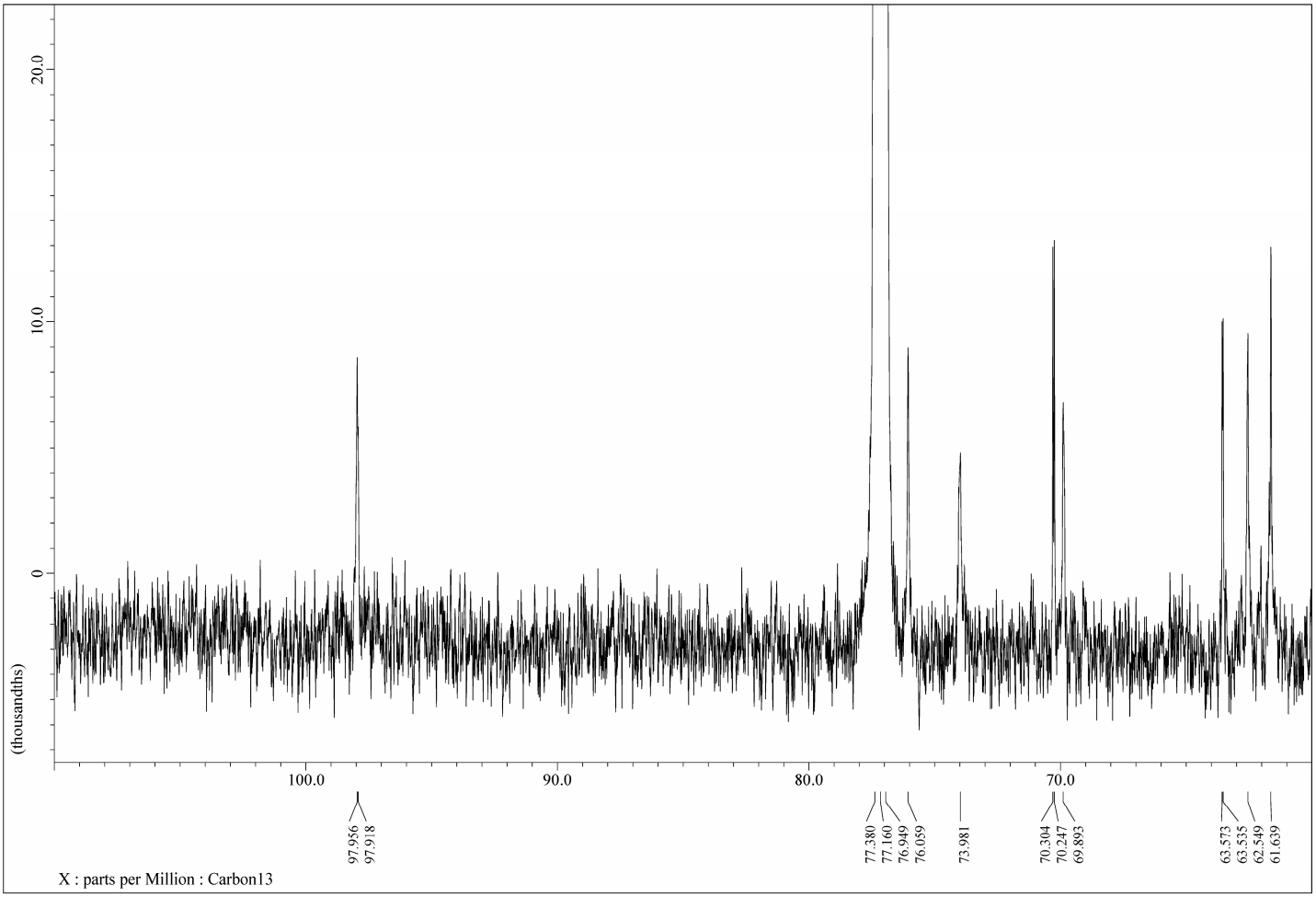
^{1}H-NMR data of PtdGlc (16:0/16:0) (**14**), 600 MHz, $CDCl_3/CD_3OD$ = 2/1



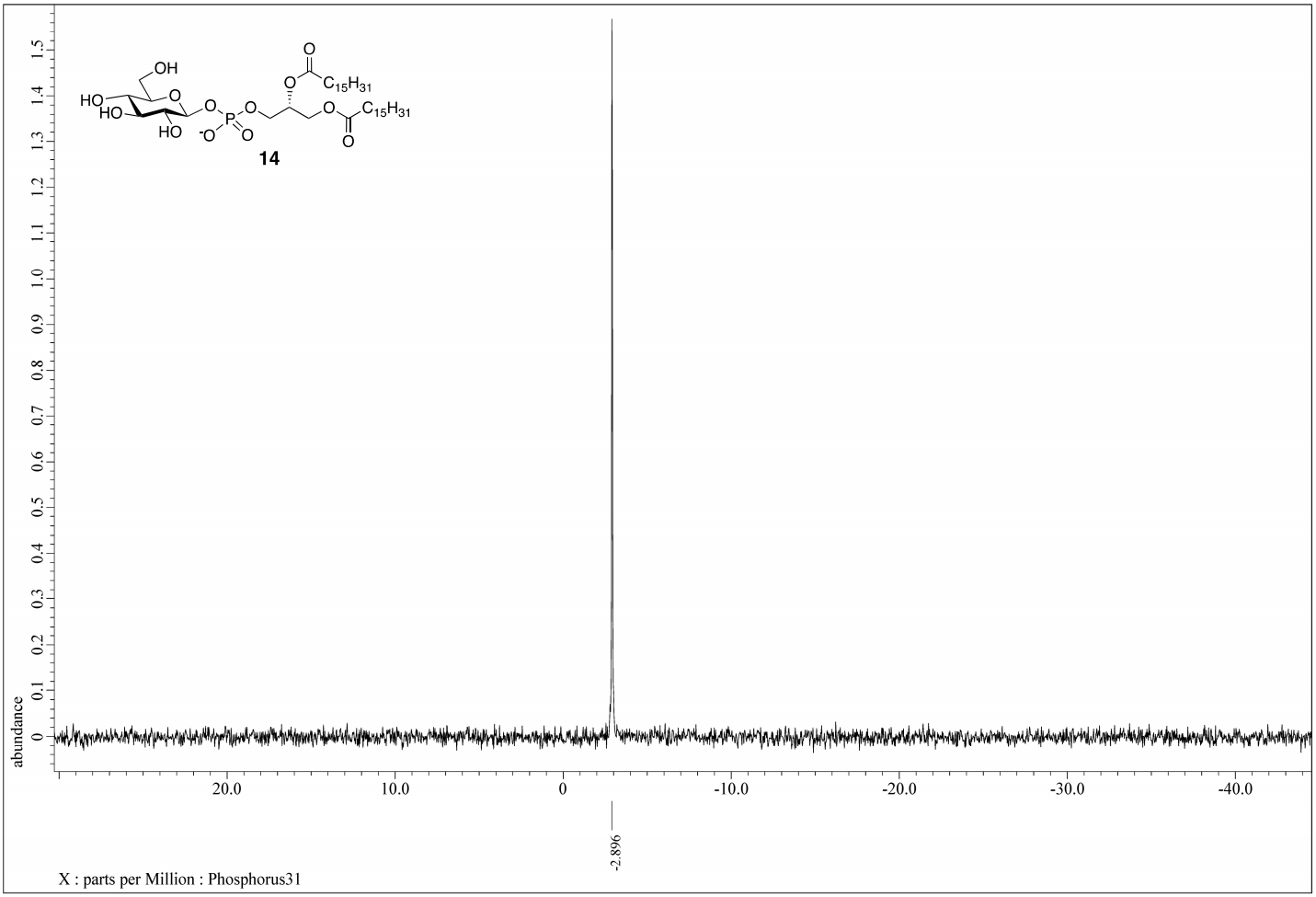


^{13}C-NMR data of PtdGlc (16:0/16:0) (**14**), 150 MHz, $CDCl_3/CD_3OD$ = 2/1

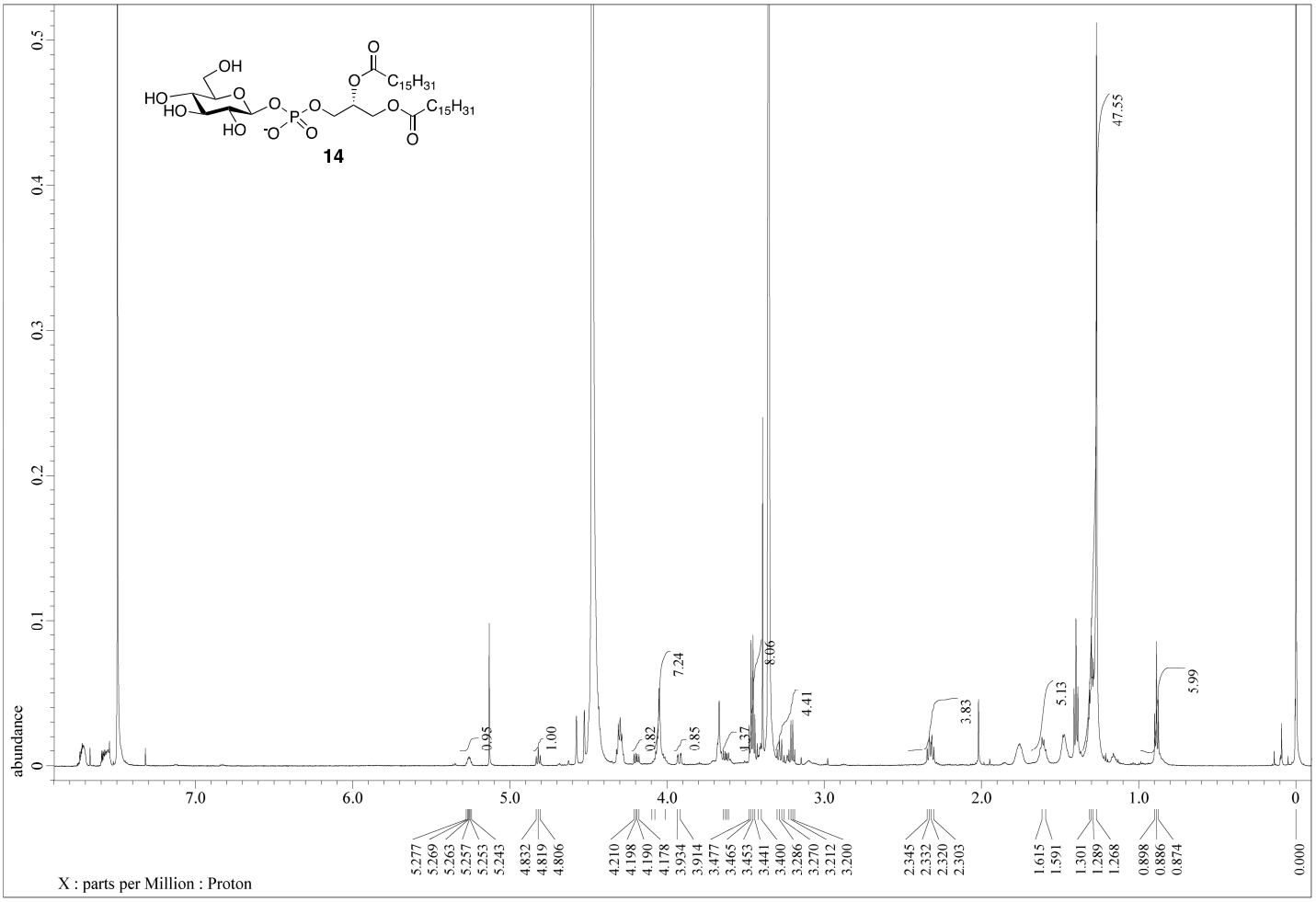


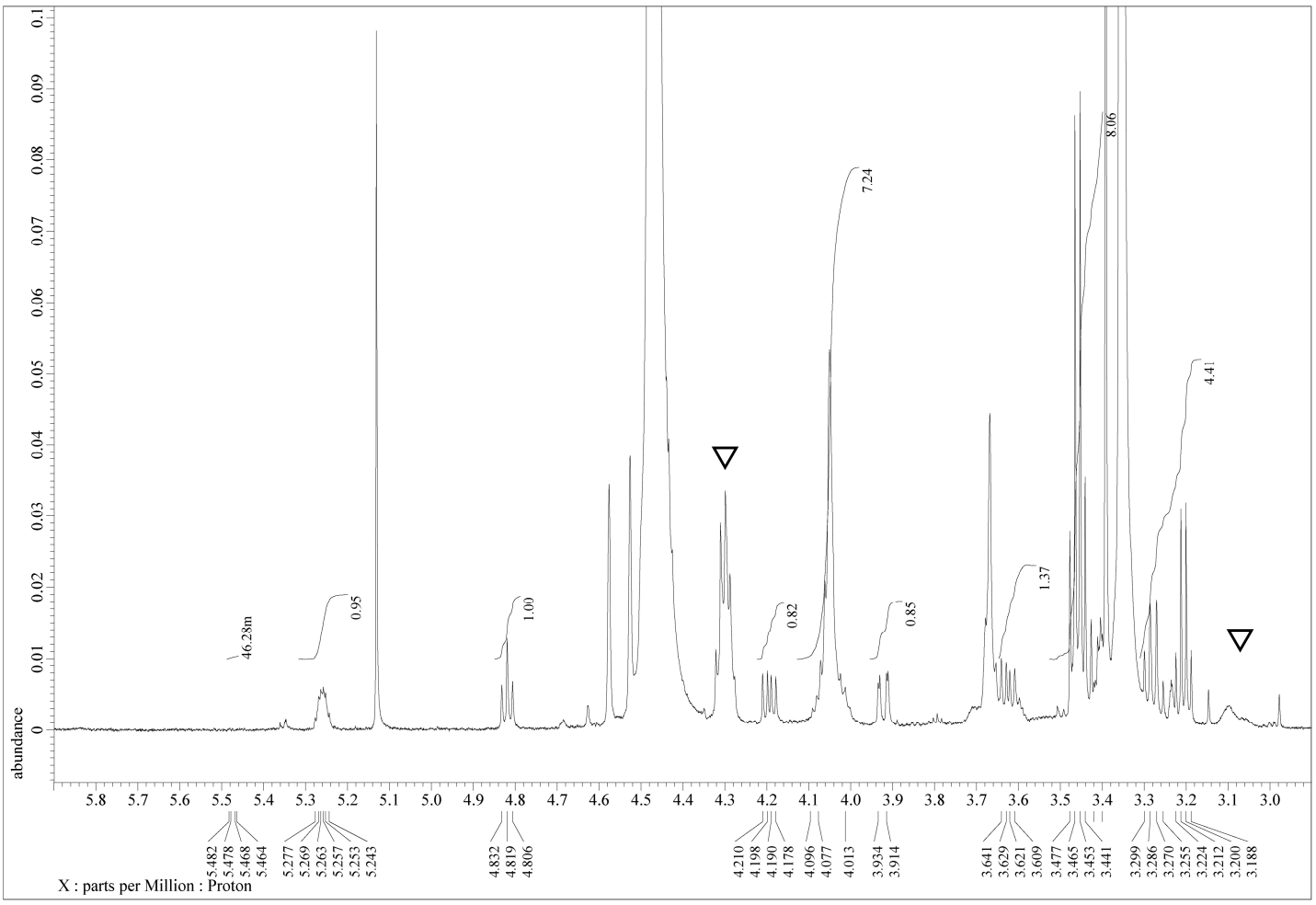


^{31}P-NMR data of PtdGlc (16:0/16:0) (**14**), 243 MHz, $CDCl_3/CD_3OD$ = 2/1

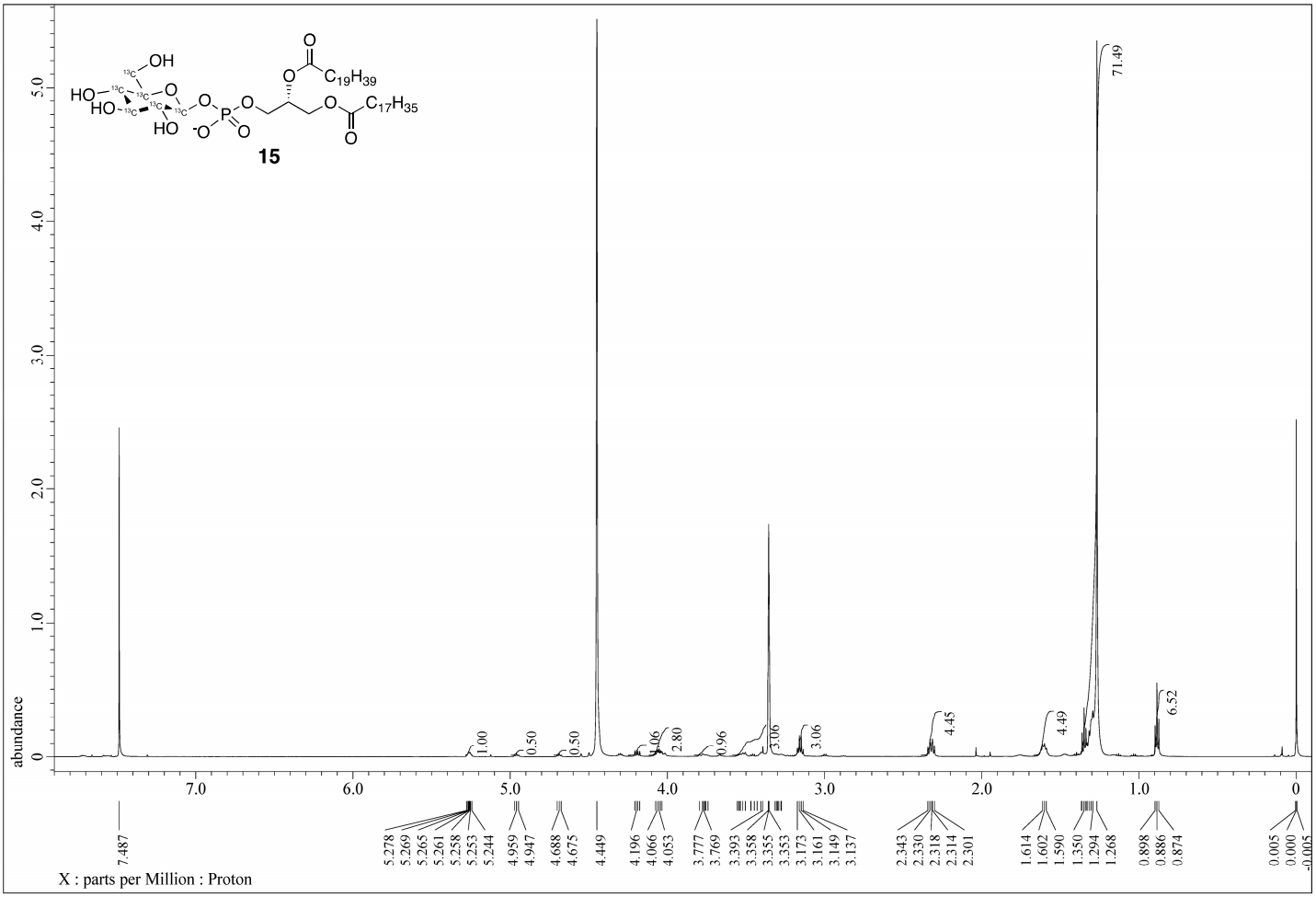


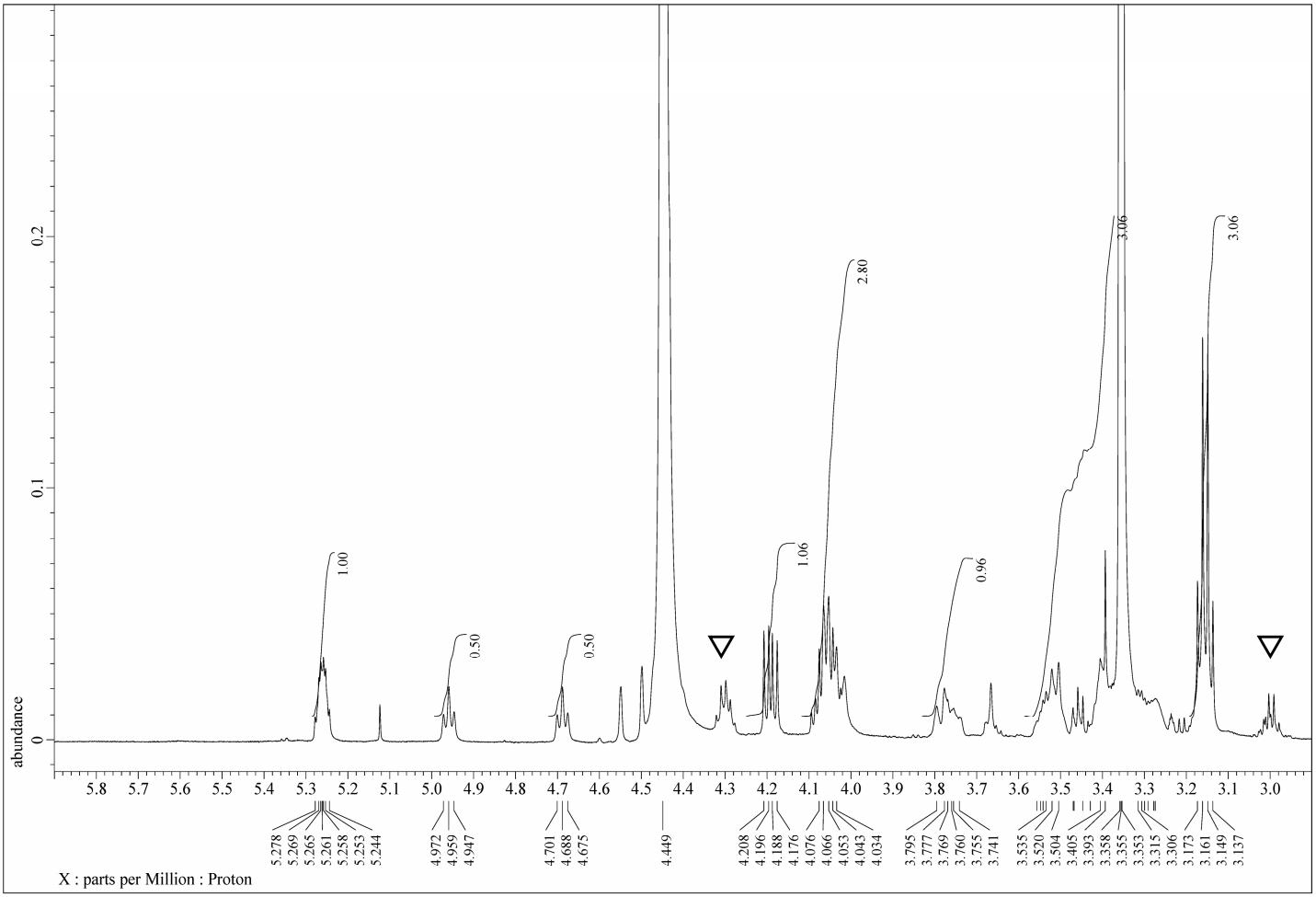
^{1}H-NMR data of PtdGlc (16:0/16:0) (**14**) from PA(16:0, 16:0) sodium salt (for Table 3, entry 6)
600 MHz, $CDCl_3/CD_3OD$ = 2/1



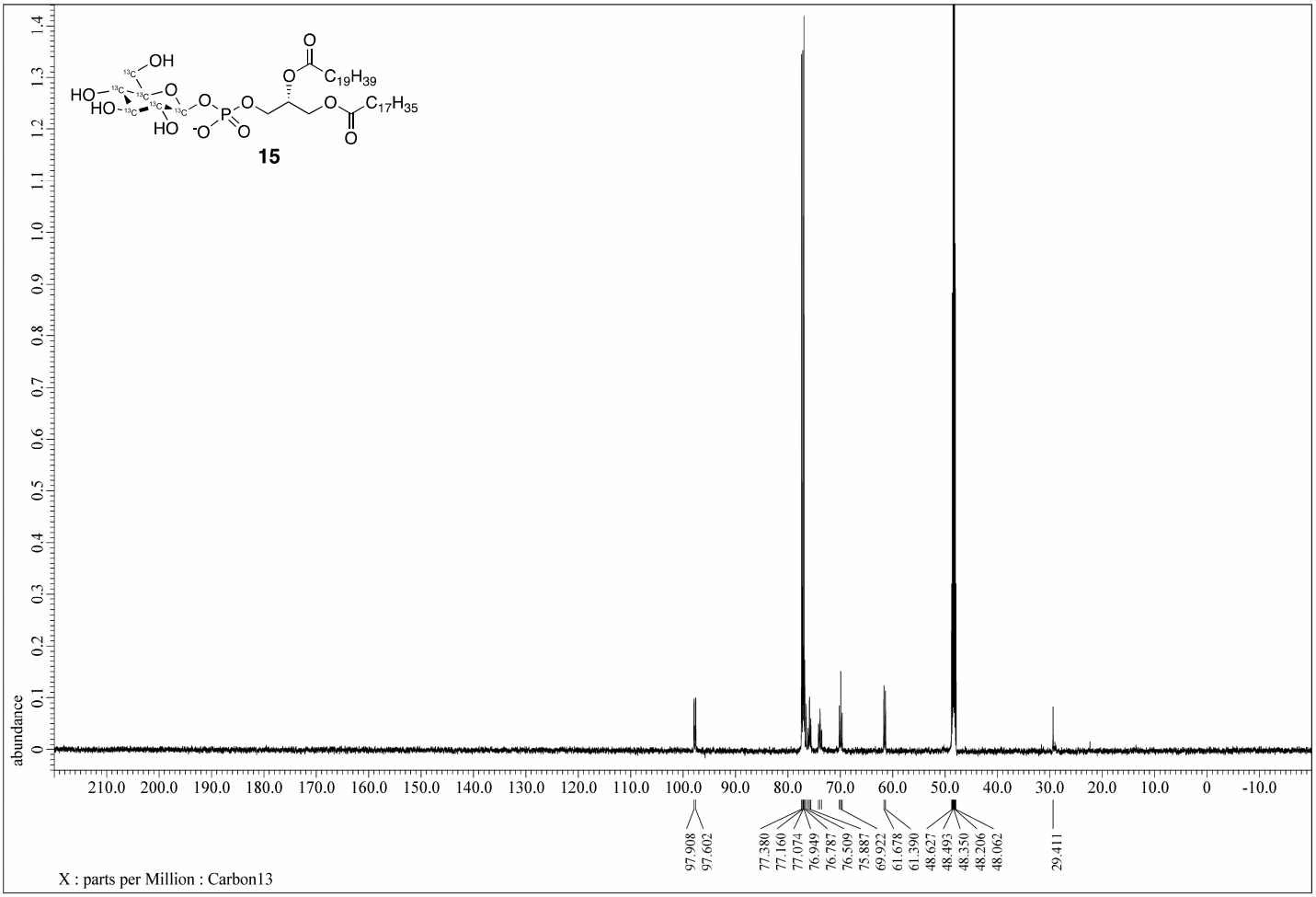


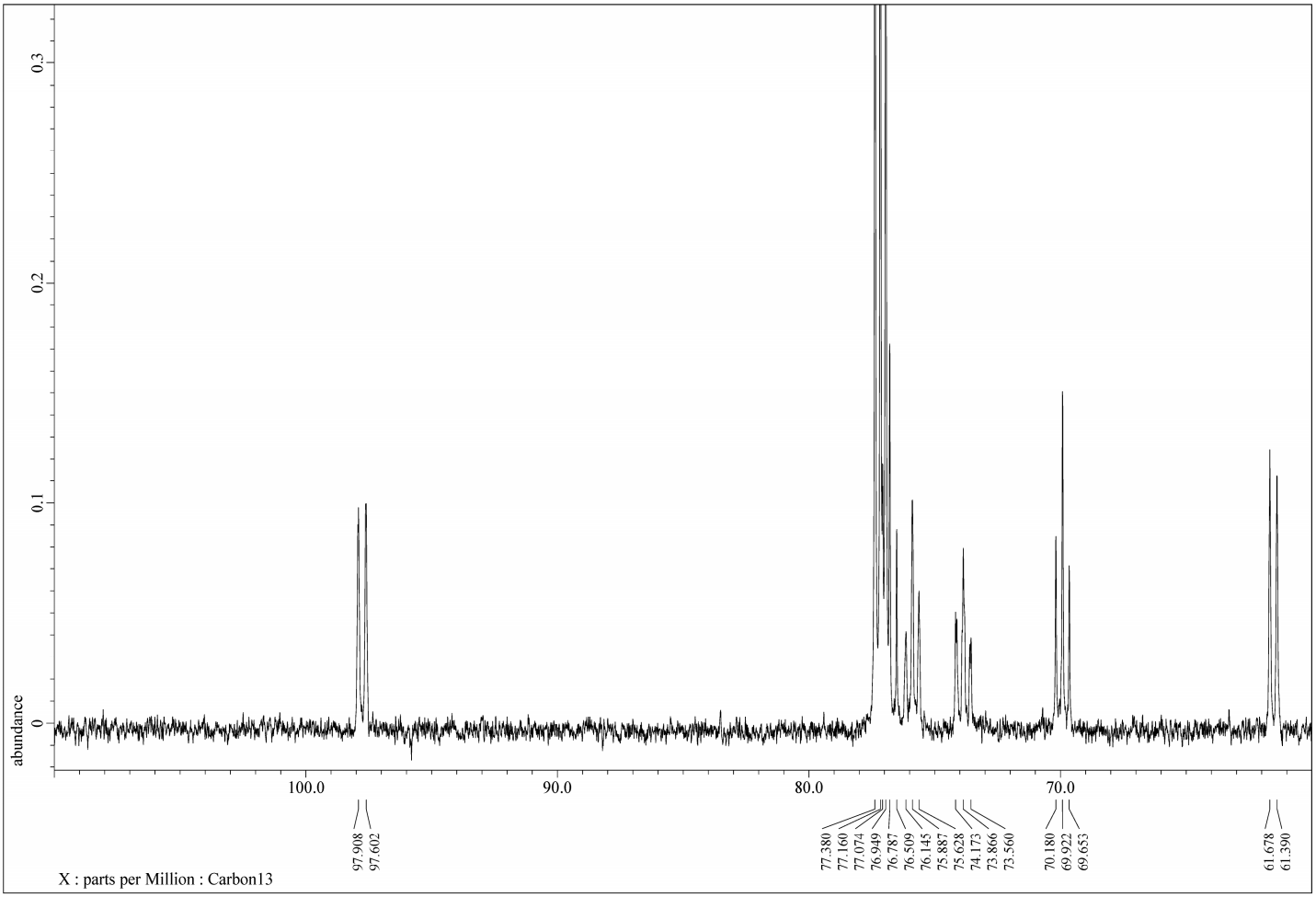
^{1}H-NMR data of ^{13}C-labeled phosphatidyl glucoside (U-$^{13}C_6$) (**15**), 600 MHz, $CDCl_3/CD_3OD$ = 2/1





^{13}C-NMR data of ^{13}C-labeled phosphatidyl glucoside (U-$^{13}C_6$) (**15**), 600 MHz, $CDCl_3/CD_3OD$ = 2/1





^{31}P-NMR data of ^{13}C-labeled phosphatidyl glucoside (U-$^{13}C_6$) (**15**), 243 MHz, $CDCl_3/CD_3OD$ = 2/1