

Supplementary Data

Formation and transformations of oxidatively
truncated ether phospholipids in small
unilamellar vesicles

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1-O-Hexadecyl-2-(4-pentenoyl)-*sn*-glycero-3-phosphatidylcholine (8a). 1-O-Hexadecyl-2-lyso-*sn*-glycero-3-phosphatidylcholine (15 mg, 0.03 mmol), that was dried on a vacuum pump equipped with a dry ice-acetone trap overnight at room temperature, was dissolved in freshly distilled CHCl_3 (2 mL). 4-pentenoic acid (12.5 mg, 0.12 mmol), dicyclohexylcarbodiimide (DCC, 37.1 mg, 0.18 mmol) and N,N-dimethylaminopyridine (DMAP, 3.7 mg, 0.03 mmol) were added. The mixture was stirred at room temperature for 96 h under argon. The solvent was then removed by rotary evaporation, and the residue was purified by flash chromatography on silica with $\text{CHCl}_3/\text{MeOH}/\text{H}_2\text{O}$ (16/9/1, TLC: $R_f = 0.42$) to give **8a** (12.1 mg, 70%). ^1H NMR ($\text{CDCl}_3/\text{CD}_3\text{OD} = 1/1$, 400 MHz): δ 5.73-5.86(1H), 5.09-5.16(1H), 4.94-5.07(2H), 4.19-4.31 (2H), 3.93-4.07(2H), 3.58-3.64(4H), 3.39-3.52(2H), 3.22(9H), 2.46(t, $J = 7.0$ Hz, 2H), 2.38(t, $J = 6.9$ Hz, 2H), 1.50-1.60(2H), 1.16-1.35(26H), 0.89(t, $J = 6.8$ Hz, 3H). HRMS (FAB): m/z calcd for $\text{C}_{29}\text{H}_{59}\text{NO}_7\text{P}^+$ (MH^+) 564.4029, found 564.4010.

1-O-Hexadecyl-2-(5-hexenoyl)-*sn*-glycero-3-phosphatidylcholine (8b). A procedure analogous to that described above for **8a** was used to convert 5-hexenoic acid into **8b** (71%) TLC: $R_f = 0.17$ in $\text{CHCl}_3/\text{MeOH}/\text{H}_2\text{O}$ (16/9/1): ^1H NMR ($\text{CDCl}_3/\text{CD}_3\text{OD} = 1/1$, 400 MHz): δ 5.69-5.80(1H), 5.08-5.18(1H), 4.96-5.06(2H), 4.19-4.29(2H), 3.92-4.06(2H), 3.56-3.65(4H), 3.39-3.52(2H), 3.22(s, 9H), 2.37(t, $J = 7.5$ Hz, 3H), 2.11(td, $J = 7.7$ Hz, 6.8 Hz, 2H), 1.65-1.78(2H), 1.49-1.60(2H), 1.19-1.34(26H), 0.88(t, $J = 6.8$ Hz, 3H). HRMS (FAB): m/z calcd for $\text{C}_{30}\text{H}_{61}\text{NO}_7\text{P}^+$ (MH^+) 578.4186, found 578.4196.

1-O-Hexadecyl-2-(9-decenoyl)-sn-glycero-3-phosphatidylcholine (8c). A procedure analogous to that described above for **8a** was used to convert 9-decenoic acid into **8c** (79%) TLC: $R_f = 0.29$ CHCl₃/MeOH/H₂O (16/9/1): ¹H NMR (CDCl₃/CD₃OD = 1/1, 400 MHz): δ 5.69-5.82(1H), 5.16(m,1H), 4.96-5.02(2H), 4.17-4.27(2H), 3.92-4.05(2H), 3.56-3.65(4H), 3.38-3.52(2H), 3.23(s, 9H), 2.35(t, J = 7.5 Hz, 2H), 2.04(td, J = 7.8 Hz, 6.7 Hz, 2H), 1.54-1.63(2H), 1.46-1.54(2H), 1.17-1.39(34H), 0.89(t, J = 6.6 Hz, 3H). HRMS (FAB): m/z calcd for C₃₄H₆₉NO₇P⁺ (MH⁺) 634.4811, found 634.4813.

1-O-Hexadecyl-2-(4-oxobutyryl)-sn-glycero-3-phosphatidylcholine (OB-PAF, 2a). A solution of the compound **8a** (12.1 mg, 0.021 mmol) in 2 mL of a 2:1 mixture of MeOH/CH₂Cl₂ was cooled to -78 °C with magnetic stirring. Ozone was bubbled through the solution until a blue color appeared and persisted for another 20 min. The solution was purged with N₂ to remove the excess ozone. While still at -78 °C, Me₂S (17 μ L) was added, and the solution was then allowed to warm to room temperature. The solvents were removed by rotary evaporation with heptane (3 \times 5 mL) to afford aldehyde phospholipid **2a** (7.6 mg, 63%). ¹H NMR (CDCl₃/CD₃OD = 1/1, 400 MHz): δ 9.77(1H), 5.12-5.22(1H), 4.21-4.33(2H), 3.93-4.09(2H), 3.57-3.65(4H), 3.41-3.50(2H), 3.22(s, 9H), 2.56-2.92(2H), 2.42-2.54(1H), 1.79-2.00(1H), 1.55(t, J = 6.5 Hz, 2H), 1.24-1.36(26H), 0.89(t, J = 6.7 Hz, 3H). HRMS (FAB): m/z calcd for C₂₈H₅₇NO₈P⁺ (MH⁺) 566.3822, found 566.3830.

1-O-Hexadecyl-2-(5-oxovaleroyl)-sn-glycero-3-phosphatidylcholine (OV-PAF, 2b). This phospholipid was prepared similarly to **2a** using the

compound **8b** (17mg, 0.029 mmol) and Me₂S (22 μL) to give **2b** (14.7 mg, 87%). ¹H NMR (CDCl₃, 400 MHz): δ 9.69-9.71(s, 1H), 5.04-5.18(1H), 4.23(s, 2H), 3.81-4.04(2H), 3.68-3.79(2H), 3.40-3.56(2H), 3.25-3.33(11H), 2.49(t, J = 7.0, 2H), 2.22-2.41(2H), 1.86(tt, J=7.0, 7.0, 2H), 1.44(t, J = 6.3 Hz, 2H), 1.11-1.31(26H), 0.81(t, J = 6.6 Hz, 3H). HRMS (FAB): m/z calcd for C₂₉H₅₉NO₈P⁺ (MH⁺) 580.3978, found 580.3944.

1-O-Hexadecyl-2-(9-oxononanoyl)-sn-glycero-3-phosphatidylcholine (ON-PAF, 2c). This aldehyde was prepared similarly to **2a** using the compound **8c** (35 mg, 0.055 mmol) and Me₂S (42 μL) to give **2c** (25 mg, 71%). ¹H NMR (CDCl₃, 400 MHz): δ 9.74(t, J = 1.75 Hz, 1H), 5.15(m, 1H), 4.23-4.33(2H), 3.89-4.01(2H), 3.74-3.81(2H), 3.49-3.65(2H), 3.43-3.49(2H), 3.39(s, 9H), 2.45(td, J = 7.3, 1.75 Hz, 2H), 2.33(t, J = 7.4 Hz, 2H), 1.63-1.65(4H), 1.53(t, J = 6.8 Hz, 2H), 1.23-1.38(32H), 0.90(t, J = 6.8 Hz, 3H). HRMS (FAB): m/z calcd for C₃₃H₆₇NO₈P⁺ (MH⁺) 636.4604, found 636.4529.

1-O-Hexadecyl-2-succinoyl-sn-glycero-3-phosphatidylcholine (S-PAF, 3a). A mixture of lyso-PAF (15 mg, 0.031 mmol) and succinic anhydride (22 mg, 0.22 mmol), that was dried on a vacuum pump overnight at room temperature, was dissolved in dry CHCl₃ (1.5 mL). DMAP (12 mg, 0.098 mmol) was added to the solution. The mixture was then stirred at room temperature under argon for 96 h. The mixture was concentrated, and the residue was chromatographed on silica with CHCl₃/MeOH/H₂O (16/9/1, TLC: R_f = 0.05) to give **3a** (10 mg, 55%). ¹H

NMR (CDCl₃/CD₃OD = 1:1, 400 MHz): δ 5.17(m, 1H), 4.26(s, 2H), 3.92-4.10(2H), 3.54-3.60(4H), 3.37-3.52(2H), 3.22(s, 9H), 2.50-2.70(4H), 1.55(t, J = 6.9 Hz, 2H), 1.21-1.27(26H), 0.89(t, J = 6.8 Hz, 3H). HRMS (FAB): m/z calcd for C₂₈H₅₇NO₉P⁺ (MH⁺) 582.3771, found 582.3771.

1-O-Hexadecyl-2-glutaroyl-*sn*-glycero-3-phosphatidylcholine (G-PAF, 3b). This acid phospholipid was prepared similarly to **3a** using lyso-PAF (20mg, 0.042 mmol), glutaric anhydride (38.3 mg, 0.34 mmol) and DMAP (5.1 mg, 0.042 mmol) in dry CHCl₃ (2 mL). The crude product was purified by flash chromatography on a silica gel column with CHCl₃/MeOH/H₂O (15/9/1, TLC: R_f = 0.21) to afford **3b** (12.4 mg, 50%). ¹H NMR (CDCl₃/CD₃OD = 1:1, 400 MHz): δ 5.18(m, 1H), 4.18-4.25(s, 2H), 3.94-4.08 (2H), 3.58-3.64(4H), 3.39-3.52(2H), 3.22(s, 9H), 2.36-2.48(4H), 1.94(tt, J = 7.0 Hz, 7.0 Hz, 2H), 1.55(t, J = 6.4 Hz, 2H), 1.21-1.31(26H), 0.89(t, J = 6.8Hz, 3H). HRMS (FAB): m/z calcd for C₂₉H₅₉NO₉P⁺ (MH⁺) 596.3927, found 596.3916.

1-O-Hexadecyl-2-azelayl-*sn*-glycero-3-phosphatidylcholine (A-PAF, 3c). To a magnetic stirred solution of ON-PAF (**2c**) (15.2 mg, 0.024 mmol) in t-BuOH-H₂O (5:1, v/v, 0.4 mL) was added solution containing NaH₂PO₄ (4.78 mg, 0.035 mmol), 2-methyl-2-butene(136 μ L, 0.27 mmol, 2M solution in THF), and NaClO₂ (7.23 mg, 0.08 mmol) in t-BuOH-H₂O (5:1, v/v, 0.4 mL). The resulting mixture was stirred for 2 h at room temperature under Argon. The crude product was purified by flash chromatography on a silica gel column (CHCl₃/MeOH/H₂O, 15/9/1, TLC: R_f= 0.17) to give A-PAF (**3c**, 9.9 mg, 64%). ¹H NMR (CDCl₃/CD₃OD = 1:1, 400 MHz): δ 5.12 (m, 1H), 4.21(s, 2H), 3.88-4.04(2H),

3.53-3.62(4H), 3.35-3.49(2H), 3.19(s, 9H), 2.31(t, J = 7.4 Hz, 4H), 1.64-1.46(6H), 1.35-1.20(32H), 0.85(t, J = 6.8 Hz, 3H). HRMS (FAB): m/z calcd for C₃₃H₆₇NO₉P⁺ (MH⁺) 652.4553, found 652.4550.

1-O-Hexadecyl-2-[3-(2-furyl)propanoyl]-sn-glycero-3-phosphatidylcholine (12a). A mixture of 3-(2-furyl)propionic acid (23 mg, 0.16 mmol) and lyso-PAF (30 mg, 0.062 mmol), that was dried on a vacuum pump equipped with dry ice-acetone trap for 10 h at room temperature, was dissolved in dry CHCl₃ (2 mL, shaken with P₂O₅ for 0.5 h and distilled). DCC (137 mg, 0.66 mmol) and DMAP (13.7 mg, 0.11 mmol) were added. The mixture was stirred for 48 h under argon. The mixture was then concentrated, and the residue was purified by flash chromatography on silica (CHCl₃/MeOH/H₂O, 16:9:1, TLC: R_f = 0.36) to afford the furyl phospholipid **12a** (32.4 mg, 86%). ¹H NMR (CDCl₃, 200 MHz): δ 7.28-7.30(1H), 6.26(dd, J = 3.1 Hz, 1.8 Hz, 1H), 6.02(d, J = 3.1 Hz, 1H), 5.15(m, 1H), 4.26(s, 2H), 3.85-3.98(2H), 3.70-3.85(2H), 3.61(s, 2H), 3.50-3.58(2H), 3.33(s, 9H), 2.94(t, J = 7.4 Hz, 2H), 2.66(t, J = 7.7 Hz, 2H), 1.50(2H), 1.20-1.28(22H), 0.87(t, J = 6.6 Hz, 3H). HRMS (FAB): m/z calcd for C₃₁H₅₉NO₈P⁺ (MH⁺) 604.3978, found 604.3960.

1-O-Hexadecyl-2-[4-(2-furyl)butanoyl]-sn-glycero-3-phosphatidylcholine (12b). A procedure analogous to that described above for **12a** was used to convert 4-(2-furyl)butanoic acid into **12b** (85%) TLC: R_f = 0.40 (CHCl₃/MeOH/H₂O, 16:9:1). ¹H NMR (CDCl₃/CD₃OD = 1/1, 400 MHz): δ 7.28(d, J = 1.8 Hz, 1H), 6.24(dd, J = 3.1 Hz, 1.8 Hz, 1H), 5.99(d, J = 3.1 Hz, 1H), 5.14(m, 1H), 4.21(bs, 2H), 3.89-4.02(2H),

3.51-3.62(4H), 3.35-3.49(2H), 3.18(bs, 9H), 2.65(t, J = 7.4 Hz, 2H), 2.36(t, J = 7.4 Hz, 2H), 1.93(tt, J = 7.4 Hz, 7.4 Hz, 2H), 1.45-1.56(2H), 1.2-1.3(26H), 0.85(t, J = 6.8 Hz, 3H). HRMS (FAB): m/z calcd for C₃₂H₆₁NO₈P⁺ (MH⁺) 618.4135, found 618.4140.

1-O-Hexadecyl-2-[8-(2-furyl)octanoyl]-sn-glycero-3-phosphatidylcholine (12c). A procedure analogous to that described above for **12a** was used to convert 8-(2-furyl)octanoic acid into **12c** (79%) TLC: R_f = 0.39 (CHCl₃/MeOH/H₂O, 16:9:1). ¹H NMR (CDCl₃/CD₃OD = 1/1, 300 MHz): δ 7.27(dd, J = 1.86 Hz, 0.82 Hz, 1H), 6.24(dd, J = 3.12 Hz, 1.84 Hz, 1H), 5.94(dd, J = 3.12 Hz, 0.86 Hz, 1H), 5.14(m, 1H), 4.14-4.30(2H), 3.90-4.02(2H), 3.50-3.62(4H), 3.49-3.37(2H), 3.20(bs, 9H), 2.59(t, J = 7.4 Hz, 2H), 2.33(t, J = 7.3 Hz, 2H), 1.40-1.70(6H), 1.20-1.34(32H), 0.86(t, J = 6.6 Hz, 3H). HRMS (FAB): m/z calcd for C₃₆H₆₉NO₈P⁺ (MH⁺) 674.4761, found 674.4762.

1-O-Hexadecyl-2-(4-oxo-7-oxohept-5-enoyl)-sn-glycero-3-phosphatidylcholine (KOHA-PAF, 6a). N-Bromosuccinimide (NBS, 28.7 mg, 0.16 mmol) and pyridine (18.6 μL, 0.22 mmol) were sequentially added to a solution of furyl phosphatidylcholine **12a** (64.9 mg, 0.11 mmol) in THF/acetone/water (5/4/2) at -20 °C. The resulting mixture was stirred for 1 h at this temperature, and kept at room temperature for 6 h. The solvent was then removed quickly, and the residue was purified on a silica gel column (CHCl₃/MeOH/H₂O, 16:9:1, TLC: R_f = 0.13) affording KOHA-PAF (52.8 mg, 79%). ¹H NMR (CDCl₃, 400 MHz): δ 9.78(d, J = 7.3 Hz, 1H), 6.97(d, J = 16.2 Hz, 1H), 6.79(dd, J = 16.2 Hz, 7.3 Hz, 1H), 5.09(m, 1H), 4.26(bs, 2H), 3.83-3.99(2H), 3.78(bs, 2H), 3.47-3.51(2H), 3.25-3.42(11H), 2.91-3.11(2H), 2.58-2.79(2H), 1.47(t, J = 6.2 Hz, 2H),

1.14-1.32(26H), 0.83(t, J = 6.8 Hz, 3H). HRMS (FAB): m/z calcd for C₃₁H₅₉NO₉P⁺ (MH⁺) 620.3922, found 620.3914.

1-O-Hexadecyl-2-(5-oxo-8-oxooct-6-enoyl)-sn-glycero-3-phosphatidylcholine (KOOA-PAF, 6b). A procedure analogous to that described above for **6a** was used to convert **12b** into KOOA-PAF (**6b**, 68%): TLC R_f = 0.20(CHCl₃/MeOH/H₂O, 16:9:1). ¹H NMR (CDCl₃, 200 MHz): δ 9.80(d, J = 7.0 Hz, 1H), 6.97(d, J = 16.1 Hz, 1H), 6.82(dd, J = 16.2 Hz, 6.9 Hz, 1H), 5.16(m, 1H), 4.32(bs, 2H), 3.90(bs, 4H), 3.42-3.60(2H), 3.39(11H), 2.87(t, J = 7.0 Hz, 2H), 2.21-2.60(2H), 1.95(t, J = 6.7Hz, 2H), 1.51(2H), 1.10-1.30(26H), 0.88(t, J = 6.7 Hz, 3H). HRMS (FAB): m/z calcd for C₃₂H₆₁NO₉P⁺ (MH⁺) 634.4078, found 634.4063.

1-O-Hexadecyl-2-(9-oxo-12-oxododec-10-enoyl)-sn-glycero-3-phosphatidylcholine (KODA-PAF, 6c). A procedure analogous to that described above for **6a** was used to convert **12c** into **6c** (KODA-PAF, 70%) TLC: R_f = 0.17 (CHCl₃/MeOH/H₂O, 16:9:1). ¹H NMR (CDCl₃ + CD₃OD, 300 MHz): δ 9.72 (1H), 6.28-7.04 (2H), 5.13(m, 1H), 4.20(bs, 2H), 3.92(2H), 3.50-3.70(4H), 3.32-3.50(2H), 3.15(9H), 2.65-2.80 (1H), 2.50-2.65(1H), 2.20-2.40(2H), 1.40-1.70(6H), 1.10-1.40(32H), 0.86(3H). HRMS (FAB): m/z calcd for C₃₆H₆₉NO₉P⁺ (MH⁺) 690.4704, found 690.4704.

1-O-Hexadecyl-2-(7-carboxy-4-oxohep-5-enoyl)-sn-glycero-3-phosphatidylcholine (KHdiA-PAF, 7a). To a magnetically stirred solution of KOHA-PAF (**6a**) (11.9 mg, 0.019 mmol) in t-BuOH-H₂O (5:1, v/v, 1mL) were added NaH₂PO₄ (3.97 mg, 0.029 mmol), 2-methyl-2-butene (95.8

μL , 0.19 mmol, 2 M solution in THF), and NaClO_2 (5.27 mg, 0.059 mmol). The resulting mixture was stirred for 2 h at room temperature under Ar. The solvent was removed. The residue was purified by the flash chromatography on a silica gel column ($\text{CHCl}_3/\text{MeOH}/\text{H}_2\text{O}$, 16:9:1, TLC: $R_f = 0.12$) to give KHdiA-PAF (7.2 mg, 60%). $^1\text{H NMR}$ ($\text{CDCl}_3/\text{CD}_3\text{OD} = 1/1$, 400 MHz): δ 6.68-6.75(2H), 5.08(m, 1H), 4.12-4.24(2H), 3.87-4.03(2H), 3.50-3.60(4H), 3.32-3.46(2H), 3.16(bs, 9H), 2.95-3.06(1H), 2.81-2.91(1H), 2.61-2.73(1H), 2.50-2.61(1H), 1.48(t, $J = 7.1$ Hz, 2H), 1.15-1.30(26H), 0.82(t, $J = 6.7$ Hz, 3H). HRMS (FAB): m/z calcd for $\text{C}_{31}\text{H}_{59}\text{NO}_{10}\text{P}^+$ (MH^+) 636.3871, found 636.3875.

1-O-Hexadecyl-2-(8-carboxy-5-oxooct-6-enoyl)-sn-glycero-3-phosphatidylcholine (KOdiA-PAF, 7b). A procedure analogous to that described above for **7a** was used to convert KOOA-PAF (**6b**) into KOdiA-PAF (**7b**, 62%) TLC: $R_f = 0.12$ ($\text{CHCl}_3/\text{MeOH}/\text{H}_2\text{O}$, 16:9:1). $^1\text{H NMR}$ ($\text{CDCl}_3/\text{CD}_3\text{OD} = 1/1$, 200 MHz): δ 6.76(s, 1H), 6.75(s, 1H), 5.15(m, 1H), 4.24(bs, 2H), 3.92-4.10(2H), 3.50-3.65(4H), 3.35-3.50(2H), 3.21(bs, 9H), 2.74(t, $J = 7.0$ Hz, 2H), 2.39(t, $J = 7.4$ Hz, 2H), 1.80-2.00(2H), 1.40-1.65(2H), 1.10-1.40(26H), 0.86(t, $J = 6.5$ Hz, 3H). HRMS (FAB): m/z calcd for $\text{C}_{32}\text{H}_{61}\text{NO}_{10}\text{P}^+$ (MH^+) 650.4028, found 650.4023.

1-O-Hexadecyl-2-(12-carboxy-9-oxodec-10-enoyl)-sn-glycero-3-phosphatidylcholine (KDdiA-PAF, 7c). A procedure analogous to that described above for **7a** was used to convert KODA-PAF (**6c**) into KDdiA-PAF (**7c**, 42%) TLC: $R_f = 0.14$ ($\text{CHCl}_3/\text{MeOH}/\text{H}_2\text{O}$, 15:9:1). $^1\text{H NMR}$ ($\text{CDCl}_3/\text{CD}_3\text{OD} = 1/1$, 400 MHz): δ 6.75(2H), 5.13(m, 1H), 4.23(2H), 3.89-4.04(2H), 3.52-3.65(4H), 3.38-3.51(2H), 3.20(bs, 9H), 2.63(t, $J = 7.3$

Hz, 2H), 2.32(t, J = 7.3 Hz, 2H), 1.55-1.67(4H), 1.46-1.55(2H), 1.16-1.38(32H), 0.86(t, J = 6.6 Hz, 3H). HRMS (FAB): m/z calcd for $C_{36}H_{69}NO_{10}P^+$ (MH^+) 706.4654, found 706.4640.

1-O-Hexadecyl-2-[6-(2, 2-dimethyl-1, 3-dioxolan-4-yl)-4-(tetrahydro-2H-pyran-2-yloxy)hex-5-enoyl]-sn-glycero-3-phosphatidylcholine

(10a). A mixture of 4-(2-oxanyloxy)-6-(3,3-dimethyl-2,4-dioxolanyl)hex-5-enoic acid (62 mg, 0.20 mmol) and lyso-PAF (32 mg, 0.067 mmol), that was dried on a vacuum pump equipped with dry ice-acetone trap for 10 h at room temperature, was dissolved in dry $CHCl_3$ (2 mL, shaken with P_2O_5 for 0.5 h and distilled). DCC (81.7 mg, 0.39 mmol) and DMAP (8.06 mg, 0.067 mmol) were added. The mixture was stirred for 48 h under argon. The mixture was then concentrated by rotary evaporation, and the residue was purified by flash chromatography on silica ($CHCl_3/MeOH/H_2O$, 16:9:1, TLC: R_f = 0.14) to afford HOHA-PAF precursor **10a** (38.4 mg, 75%). 1H NMR ($CDCl_3/CD_3OD$ = 1/1, 400 MHz): δ 5.48-5.90(2H), 5.12(m, 1H), 4.47-4.55(1H), 4.21(2H), 4.04-4.17(2H), 3.89-4.02(2H), 3.77-3.88(1H), 3.52-3.62(5H), 3.35-3.51(4H), 3.15-3.23(9H), 2.33-2.54(2H), 1.74-1.96(3H), 1.62-1.74(2H), 1.45-1.62(5H), 1.39(s, 3H), 1.35(s, 3H), 1.20-1.35(26H), 0.85(t, J = 6.8 Hz, 3H). HRMS (FAB): m/z calcd for $C_{40}H_{76}NNaO_{11}P^+$ (MNa^+) 800.5048, found 800.5048.

1-O-Hexadecyl-2-[7-(2, 2-dimethyl-1, 3-dioxolan-4-yl)-5-(tetrahydro-2H-pyran-2-yloxy)hept-6-enoyl]-sn-glycero-3-phosphatidylcholine

(10b). A procedure analogous to that described above for **10a** was used to convert

5-(2-oxanyloxy)-7-(3,3-dimethyl-2,4-dioxolanyl)hept-6-enoic acid into the HOOA-PAF precursor **10b** (79%) TLC: $R_f = 0.28$ ($\text{CHCl}_3/\text{MeOH}/\text{H}_2\text{O}$, 16:9:1). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 5.51-5.85(2H), 5.10(m, 1H), 4.53-4.67(1H), 4.45-4.53(1H), 4.28(bs, 2H), 4.00-4.14(2H), 3.86-3.98(2H), 3.73-3.86(3H), 3.49-3.61(3H), 3.38-3.49(3H), 3.36(bs, 9H), 2.24-2.36(t, $J = 7.7$ Hz, 2H), 1.43-1.87(12H), 1.39(s, 3H), 1.36(s, 3H), 1.20-1.36(26H), 0.85(t, $J = 6.8$ Hz, 3H). HRMS (FAB): m/z calcd for $\text{C}_{41}\text{H}_{79}\text{NO}_{11}\text{P}^+$ (MH^+) 792.5385, found 792.5386.

1-O-Hexadecyl-2-[11-(2, 2-dimethyl-1,

3-dioxolan-4-yl)-9-(tetrahydro-2H-pyran-2-yloxy)-undec-10-enoyl]-*sn*-glycero-3-phosphatidylcholine (10c). A procedure analogous to that described above for **10a** was used to convert 9-(2-oxanyloxy)-11-(3,3-dimethyl-2,4-dioxolanyl)undec-10-enoic acid into the HODA-PAF precursor **10c** (67%) TLC: $R_f = 0.28$ ($\text{CHCl}_3/\text{MeOH}/\text{H}_2\text{O}$, 16:9:1). $^1\text{H NMR}$ ($\text{CDCl}_3/\text{CD}_3\text{OD} = 1/1$, 400 MHz): δ 5.45-5.78(2H), 5.05(m, 1H), 4.45(dd, $J = 13.6$ Hz, 6.2 Hz, 1H), 4.10-4.19(2H), 3.82-4.06(4H), 3.73-3.82(1H), 3.45-3.55(5H), 3.27-3.45(4H), 3.12(s, 9H), 2.24(t, $J = 7.5$ Hz, 2H), 1.68-1.82(1H), 1.36-1.67(11H), 1.32(s, 3H), 1.29(s, 3H), 1.13-1.26(34H), 0.79(t, $J = 6.8$ Hz, 3H). HRMS (FAB): m/z calcd for $\text{C}_{45}\text{H}_{86}\text{NNaO}_{11}\text{P}^+$ (MNa^+) 870.5831, found 870.5838.

1-O-Hexadecyl-2-(4-hydroxy-7-oxohept-5-enoyl)-*sn*-glycero-3-phosphatidylcholine (HOHA-PAF, 4a). A solution of the compound **10a**

(38.4 mg, 0.05mmol) in acetic acid/water (2:1, v/v, 2.2 mL) was stirred magnetically for 4 h at 40 °C, and then the solvent was removed by

rotary evaporation under reduced pressure. The last traces of HOAc were removed by azeotropic distillation with *n*-heptane (3 × 2 mL) under high vacuum. Dry methylene chloride (2 mL) and Na₂CO₃ (10.4 mg, 0.098 mmol) were added to the residue. The solution was stirred magnetically at -78 °C under an argon atmosphere, and Pb(OAc)₄ (24 mg, 0.058 mmol) was added. The resulting solution was stirred for 30 min, then the solvent was removed, and the residue was purified by flash chromatography on silica (CHCl₃/MeOH/H₂O, 15:9:1, TLC: R_f = 0.32) to give HOHA-PAF (**4a**, 23.8 mg, 77%). ¹H NMR (CDCl₃/CD₃OD = 1/1, 400 MHz): δ 9.53(d, J = 8.0 Hz, 1H), 6.92(dd, J = 15.6 Hz, 4.4 Hz, 1H), 6.29(dd, J = 15.6 Hz, 8.1 Hz, 1H), 5.14(m, 1H), 4.39-4.47(1H), 4.21(bs, 2H), 3.90-4.06(2H), 3.54-3.60(4H), 3.35-3.48(2H), 3.19(9H), 2.39-2.61(2H), 1.93-2.05(1H), 1.72-1.88(1H), 1.51(t, J = 6.1 Hz, 2H), 1.19-1.30(26H), 0.85(t, J = 6.6 Hz, 3H). HRMS (FAB): m/z calcd for C₃₁H₆₁NO₉P⁺ (MH⁺) 622.4084, found 622.4088.

1-O-Hexadecyl-2-(5-hydroxy-8-oxooct-6-enoyl)-sn-glycero-3-phosphatidylcholine (HOOA-PAF, 4b). A procedure analogous to that described above for **4a** was used to convert **10b** into (CHCl₃/MeOH/H₂O, 16:9:1, TLC: R_f = 0.18) to give HOOA-PAF (**4b**, 80%). ¹H NMR (CDCl₃/CD₃OD = 1/1, 400 MHz): δ 9.52(d, J = 8.0 Hz, 1H), 6.92(ddd, J = 15.5 Hz, 4.4 Hz, 1.2 Hz, 1H), 6.28(ddd, J = 15.5 Hz, 8.0 Hz, 1.4 Hz, 1H), 5.14(m, 1H), 4.33-4.39(1H), 4.20(bs, 2H), 3.88-4.05(2H), 3.53-3.60(4H), 3.33-3.48(2H), 3.18(9H), 2.31-2.45(2H), 1.55-1.83(4H), 1.46-1.55(2H), 1.19-1.30(26H), 0.85(t, J = 6.7 Hz, 3H). HRMS (FAB): m/z calcd for C₃₂H₆₃NO₉P⁺ (MH⁺) 636.4240, found 636.4236.

1-O-Hexadecyl-2-(9-hydroxy-12-oxododec-10-enoyl)-sn-glycero-3-phosphatidylcholine (HODA-PAF, 4c). A procedure analogous to that described above for **4a** was used to convert **10c** into HODA-PAF (**4c**, 86%) TLC: $R_f = 0.26$ ($\text{CHCl}_3/\text{MeOH}/\text{H}_2\text{O}$, 15:9:1). ^1H NMR ($\text{CDCl}_3/\text{CD}_3\text{OD} = 1/1$, 400 MHz): δ 9.52(d, $J = 8.0$ Hz, 1H), 6.91(dd, $J = 15.6$ Hz, 4.6 Hz, 1H), 6.26(ddd, $J = 15.6$ Hz, 8.0 Hz, 1.3 Hz, 1H), 5.12(m, 1H), 4.30-4.37(1H), 4.21(bs, 2H), 3.88-4.02(2H), 3.53-3.62(4H), 3.35-3.49(2H), 3.18(9H), 2.31(t, $J = 7.5$ Hz, 2H), 1.44-1.71(6H), 1.12-1.44(34H), 0.85(t, $J = 6.6$ Hz, 3H). HRMS (FAB): m/z calcd for $\text{C}_{36}\text{H}_{71}\text{NO}_9\text{P}^+$ (MH^+) 692.4866, found 692.4829.

1-O-Hexadecyl-2-(4-hydroxy-7-carboxyhept-5-enoyl)-sn-glycero-3-phosphatidylcholine (HHdiA-PAF, 5a). A procedure analogous to that described above for **7a** was used to convert **4a** into HHdiA-PAF (**5a**, 60%) TLC: $R_f = 0.09$ ($\text{CHCl}_3/\text{MeOH}/\text{H}_2\text{O}$, 15:9:1). ^1H NMR ($\text{CDCl}_3/\text{CD}_3\text{OD} = 1/1$, 400 MHz): δ 6.75(ddd, $J = 15.7$ Hz, 5.1 Hz, 2.2 Hz, 1H), 5.98(dd, $J = 15.6$ Hz, 1.6 Hz, 1H), 5.13(m, 1H), 4.24-4.31(1H), 4.21(bs, 2H), 3.90-4.05(2H), 3.53-3.61(4H), 3.35-3.48(2H), 3.18(9H), 2.36-2.53(2H), 1.85-1.96(1H), 1.72-1.85(1H), 1.51(t, $J = 7.0$ Hz, 2H), 1.21-1.28(26H), 0.85(t, $J = 6.8$ Hz, 3H). HRMS (FAB): m/z calcd for $\text{C}_{31}\text{H}_{61}\text{NO}_{10}\text{P}^+$ (MH^+) 638.4033, found 638.4003.

1-O-Hexadecyl-2-(5-hydroxy-8-carboxyoct-6-enoyl)-sn-glycero-3-phosphatidylcholine (HOdiA-PAF, 5b). A procedure analogous to that described above for **7a** was used to convert **4b** into HOdiA-PAF (**5b**, 65%) TLC: $R_f = 0.22$ ($\text{CHCl}_3/\text{MeOH}/\text{H}_2\text{O}$, 12:9:1.5). ^1H NMR ($\text{CDCl}_3/\text{CD}_3\text{OD} = 1/1$, 400 MHz): δ 6.51(ddd, $J = 15.7$ Hz, 5.9 Hz, 1.0 Hz, 1H), 5.94(dd, $J = 15.5$ Hz, 1.2 Hz, 1H), 5.14(m, 1H), 4.09-4.27(3H),

3.88-4.05(2H), 3.52-3.63(4H), 3.35-3.48(2H), 3.18(9H), 2.32-2.41(2H), 1.60-1.77(2H), 1.44-1.60(4H), 1.19-1.29(26H), 0.85(t, J = 7.0 Hz, 3H).

HRMS (FAB): m/z calcd for $C_{32}H_{62}NO_{10}P^+$ (MH^+) 652.4190, found 652.4172.

1-O-Hexadecyl-2-(9-hydroxy-12-carboxydodec-10-enoyl)-sn-glycero-3-phosphatidylcholine (HDdiA-PAF, 5c). A procedure analogous to that described above for **7a** was used to convert **4c** into HDdiA-PAF (**5c**, 61%) TLC: $R_f = 0.13$ ($CHCl_3/MeOH/H_2O$, 15:9:1). 1H NMR ($CDCl_3/CD_3OD = 1/1$, 400 MHz): δ 6.77(dd, J = 15.6 Hz, 5.4 Hz, 1H), 5.93(dd, J = 15.7 Hz, 1.4 Hz, 1H), 5.10(m, 1H), 4.12-4.25(3H), 3.87-4.01(2H), 3.50-3.61(4H), 3.34-3.48(2H), 3.17(9H), 2.30(t, J = 7.4 Hz, 2H), 1.57(t, J = 7.5 Hz, 2H), 1.46-1.54(4H), 1.18-1.33(34H), 0.84(t, J = 6.8 Hz, 3H). HRMS (FAB): m/z calcd for $C_{36}H_{71}NO_{10}P^+$ (MH^+) 708.4816, found 708.4792.

1-O-Hexadecyl-2-tridecanoyl-sn-glycero-3-phosphatidylcholine (C₁₃-PAF). 1-O-Hexadecyl-2-lyso-*sn*-glycero-3-phosphatidylcholine (16 mg, 0.03 mmol), which was dried on a vacuum pump equipped with a dry ice-acetone trap overnight at room temperature, was dissolved in freshly distilled $CHCl_3$ (2 mL). Tridecanoic acid (72 mg, 0.33 mmol), DCC (40 mg, 0.19 mmol) and DMAP (4.0 mg, 0.033 mmol) were added. The mixture was stirred at room temperature for 96 h under argon. The solvent was then removed by rotary evaporation and the residue was purified by flash chromatography on silica with $CHCl_3/MeOH/H_2O$ (16/9/1, TLC: $R_f = 0.26$) to give C₁₃-PAF (13 mg, 58%). 1H NMR ($CDCl_3/CD_3OD = 1/1$, 400 MHz): δ 5.12(m, 1H), 4.17-4.24(2H), 3.89-4.01(2H), 3.55-3.69(4H), 3.33-3.49(2H), 3.18(9H), 2.28-2.34(2H), 1.59(t, J = 7.11 Hz, 2H),

1.51(t, J = 7.11 Hz, 2H), 1.21-1.29(44H), 0.85(t, J = 6.70 Hz, 6H). HRMS (FAB): m/z calcd for C₃₇H₇₇NO₇P⁺ (MH⁺) 678.5438, found 678.5423.

1-O-Hexadecyl-2-linoleoyl-*sn*-glycero-3-phosphatidylcholine (LA-PAF). 1-O-Hexadecyl-2-lyso-*sn*-glycero-3-phosphatidylcholine (25 mg, 0.052 mmol), which was dried on a vacuum pump equipped with a dry ice-acetone trap overnight at room temperature, was dissolved in freshly distilled CHCl₃ (2 mL). Linoleic acid (145.6 mg, 0.52 mmol), DCC (62.4 mg, 0.30 mmol) and DMAP (6.24 mg, 0.051 mmol) were added. The mixture was stirred at room temperature for 96 h under argon. The solvent was then removed by rotary evaporation and the residue was purified by flash chromatography on silica with CHCl₃/MeOH/H₂O (16/9/1, TLC: R_f = 0.29) to give LA-PAF (25.5 mg, 66%). H NMR (CDCl₃/CD₃OD = 1/1, 400 MHz): δ 5.23-5.38(4H), 5.12(m, 1H), 4.21(2H), 3.88-4.02(2H), 3.53-3.60(4H), 3.35-3.49(2H), 3.18(bs, 9H), 2.74(t, J = 6.18 Hz, 2H), 2.31(td, J = 7.4 Hz, 1.8 Hz, 2H), 1.98-2.07(4H), 1.59(t, J = 6.5 Hz, 1H), 1.51(t, J = 6.5 Hz, 1H), 1.20-1.37(40H), 0.79-0.90(6H). HRMS (FAB): m/z calcd for C₄₂H₈₃NO₇P⁺ (MH⁺) 744.5907, found 744.5907.

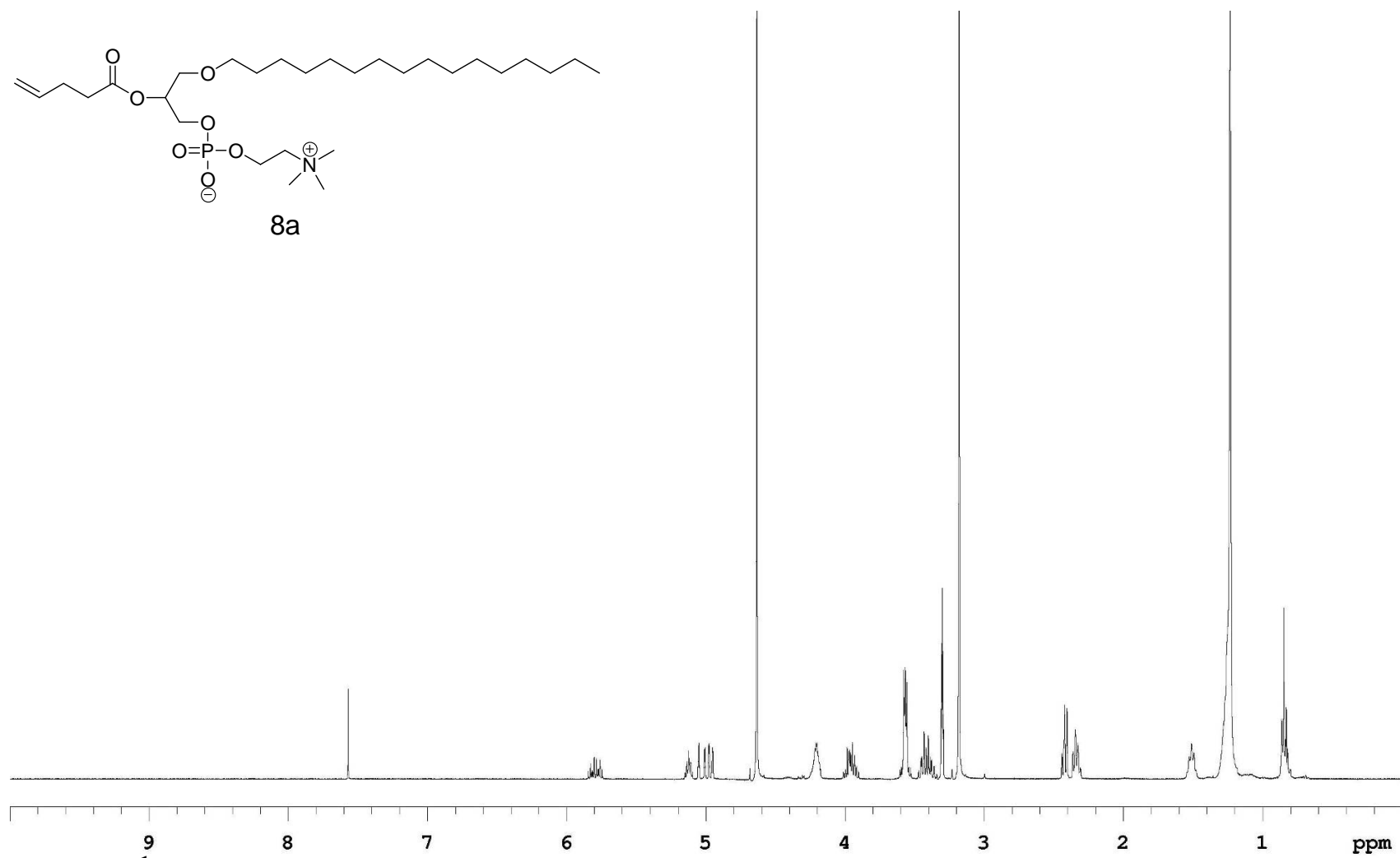
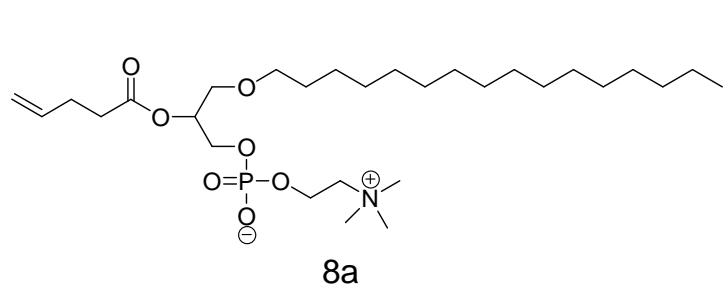


Figure S1. $^1\text{H-NMR}$ (400 M, $\text{CDCl}_3+\text{CD}_3\text{OD}$) of 1-O-Hexadecyl-2-(4-pentenoyl)-sn-glycero-3-phosphatidylcholine (8a).

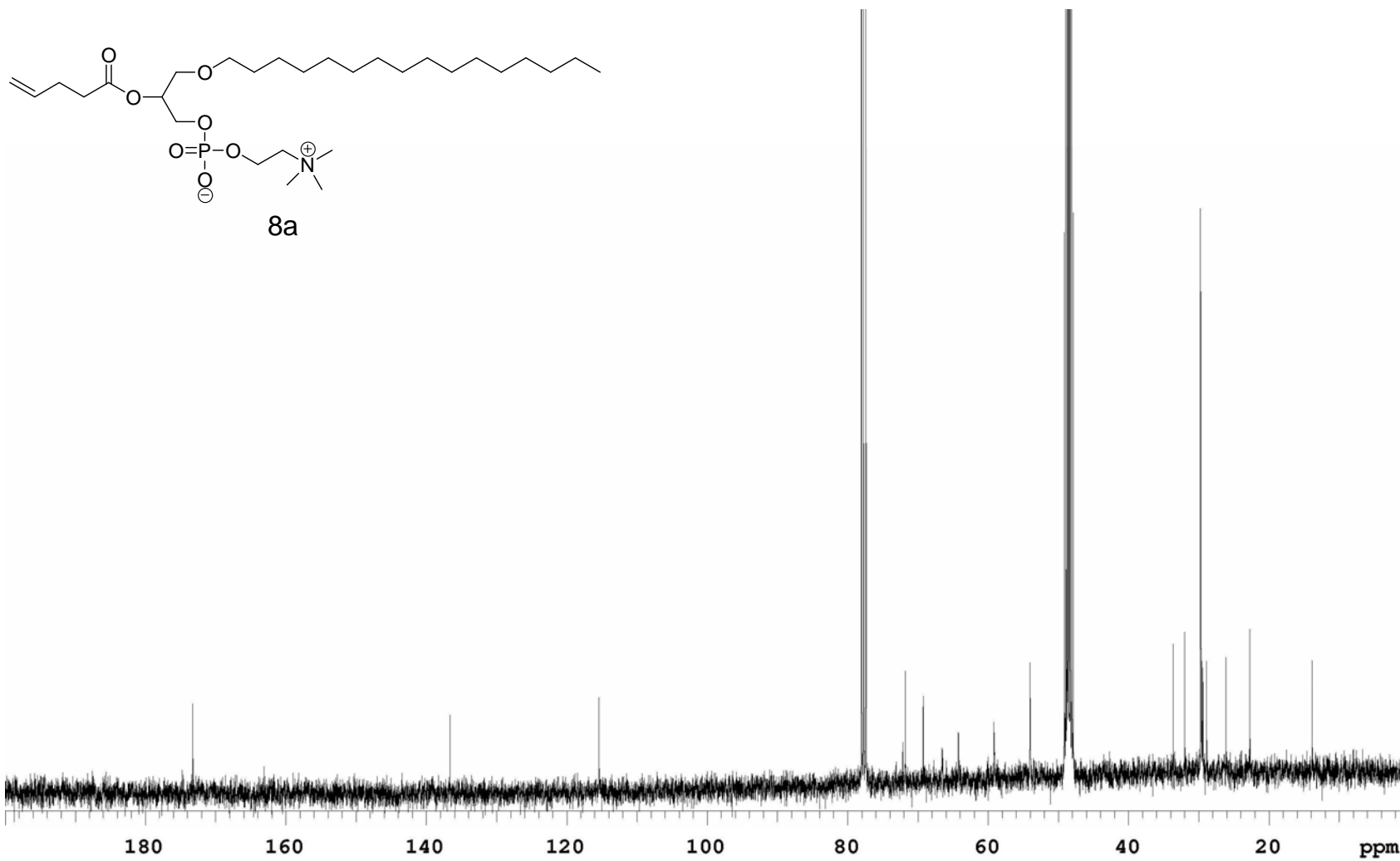


Figure S2. ¹³C-NMR (100 M, CDCl₃+CD₃OD) of 1-O-Hexadecyl-2-(4-pentenoyl)-sn-glycero-3-phosphatidylcholine (8a).

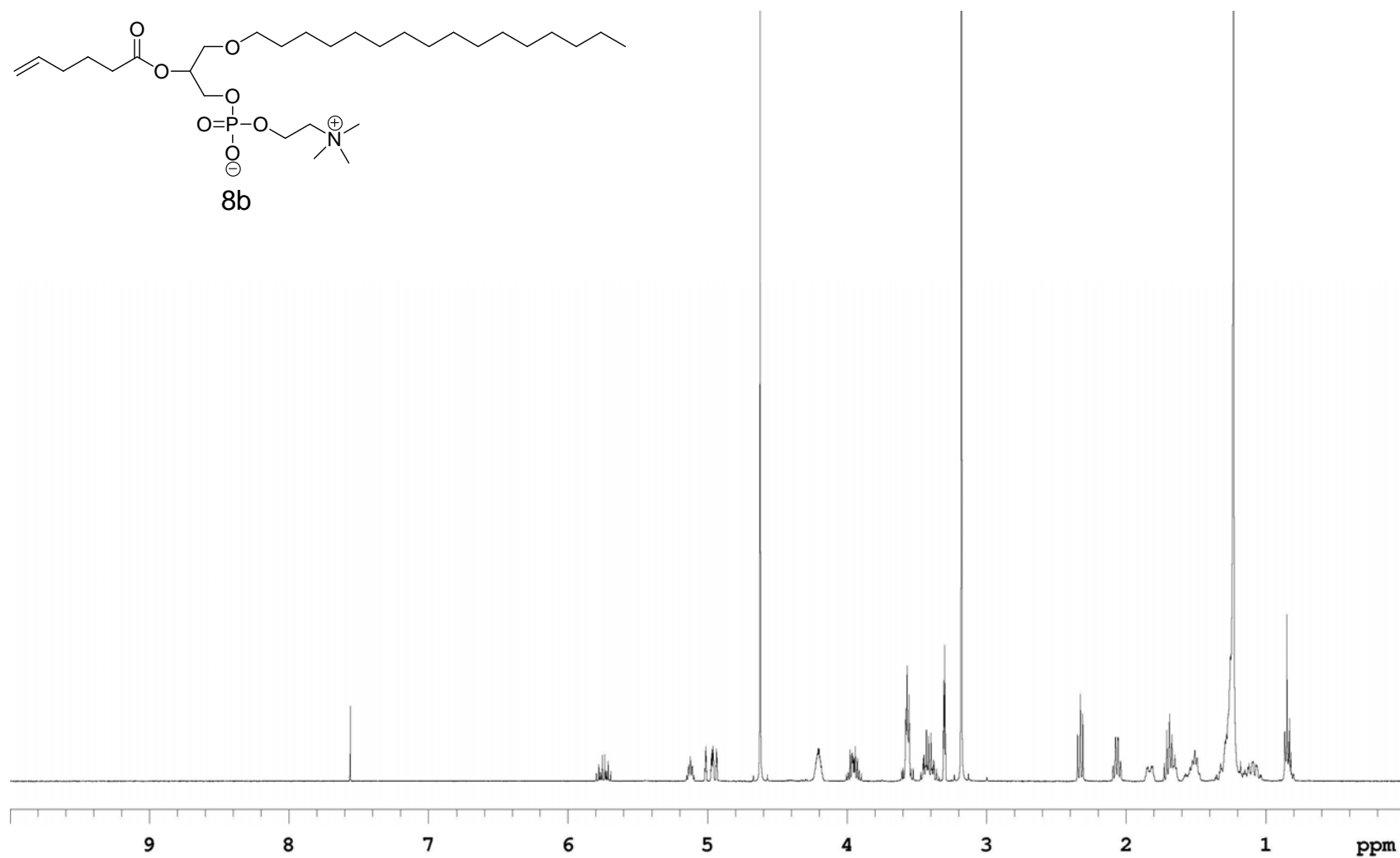
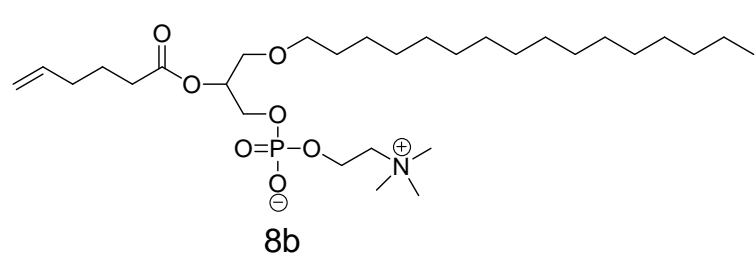


Figure S3. $^1\text{H-NMR}$ (400 M, $\text{CDCl}_3+\text{CD}_3\text{OD}$) of 1-O-Hexadecyl-2-(5-hexenoyl)-sn-glycero-3-phosphatidylcholine (8b).

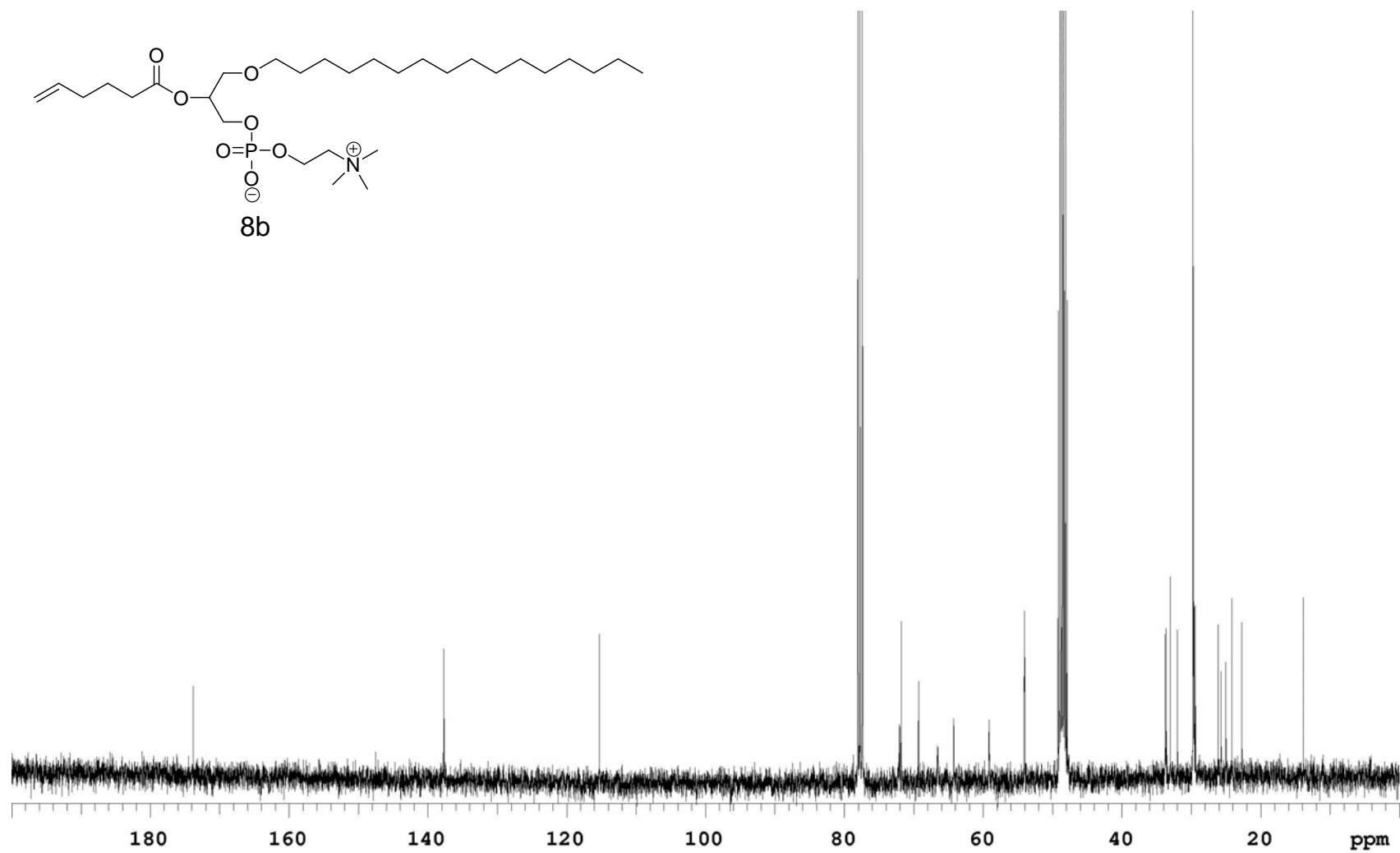
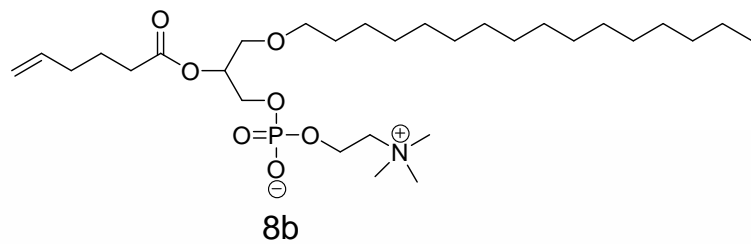


Figure S4. ¹³C-NMR (100 M, CDCl₃+CD₃OD) of 1-O-Hexadecyl-2-(5-hexenoyl)-sn-glycero-3-phosphatidylcholine (8b).

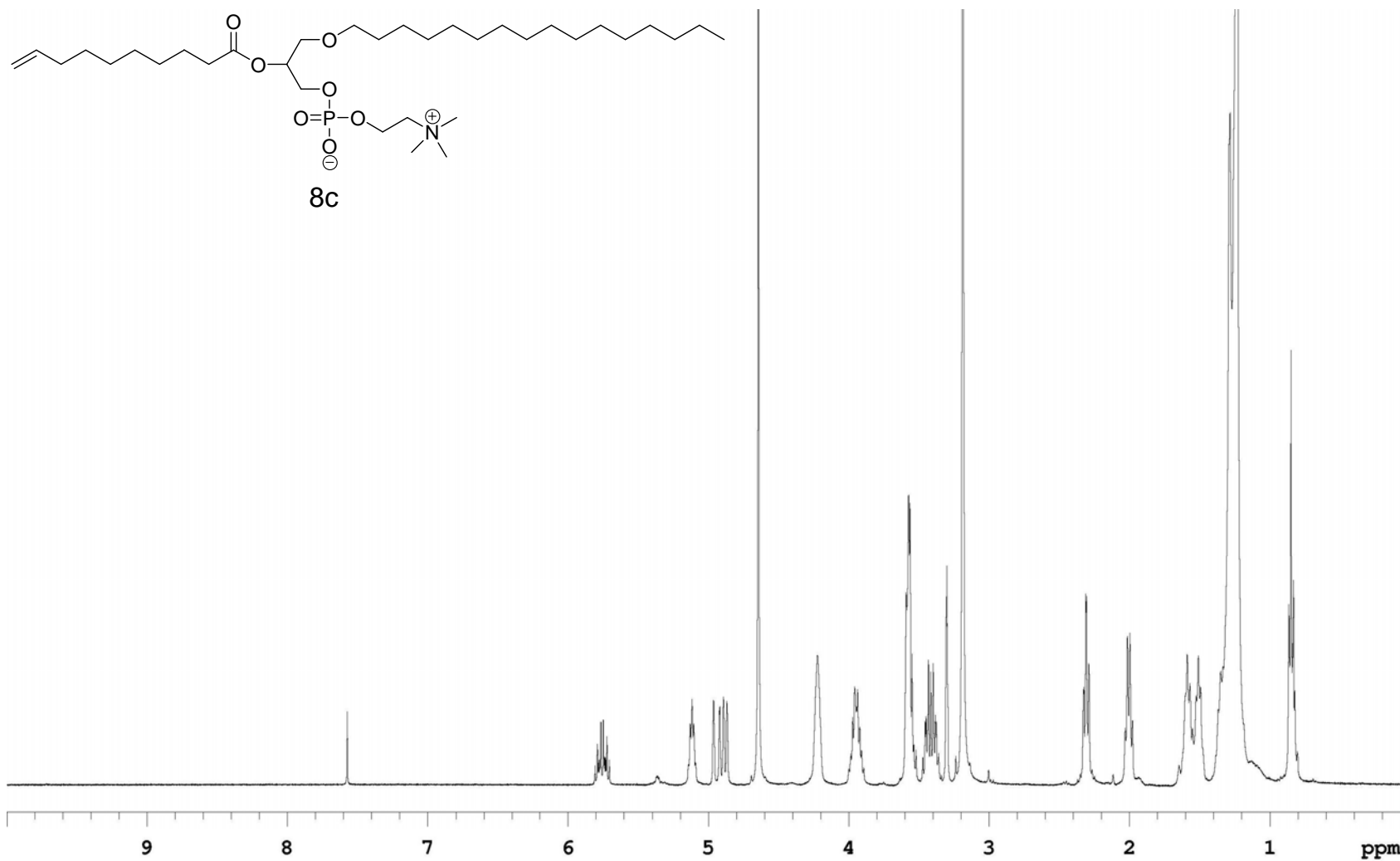


Figure S5. ¹H-NMR (400 M, CDCl₃+CD₃OD) of 1-O-Hexadecyl-2-(9-decenoyl)-sn-glycero-3-phosphatidylcholine (8c).

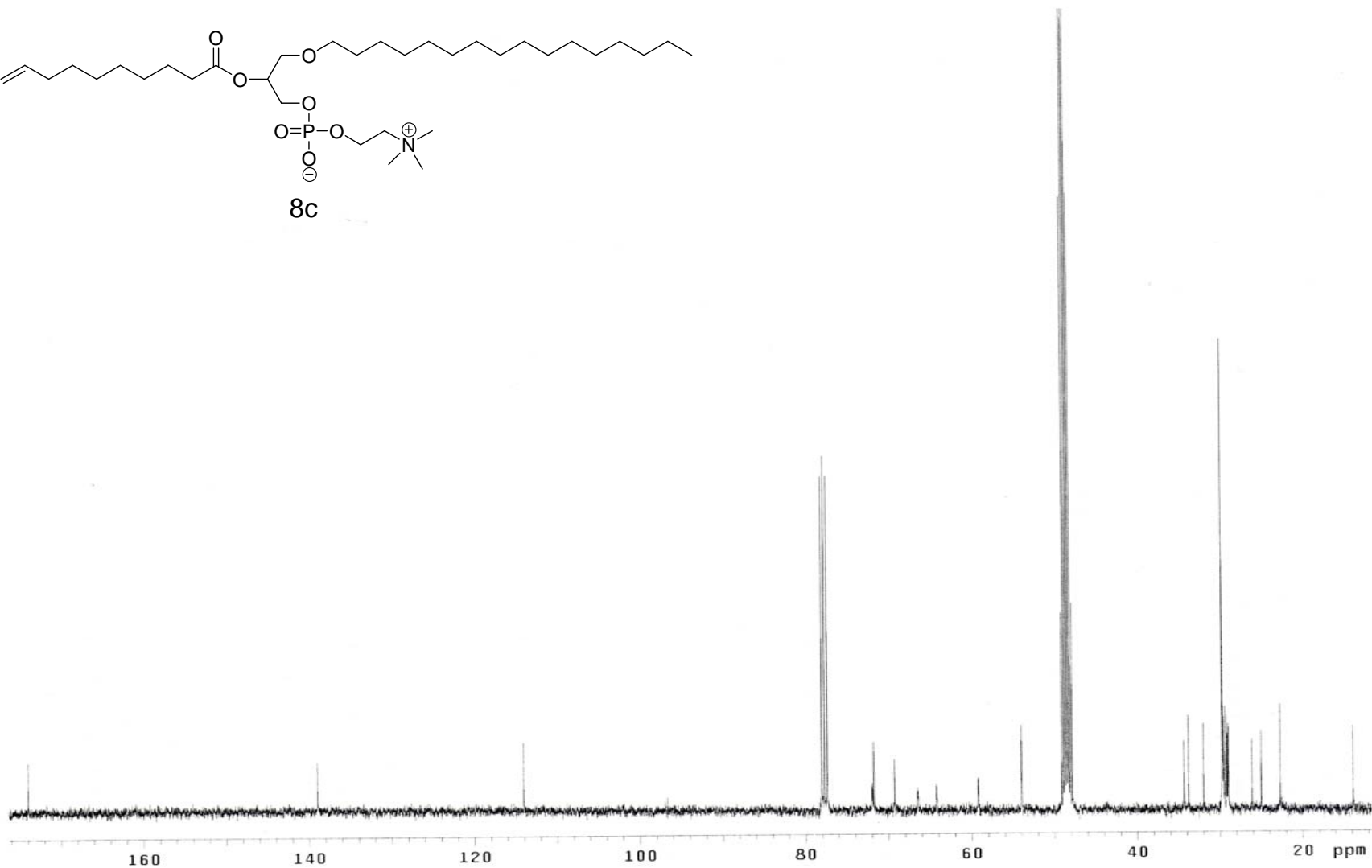
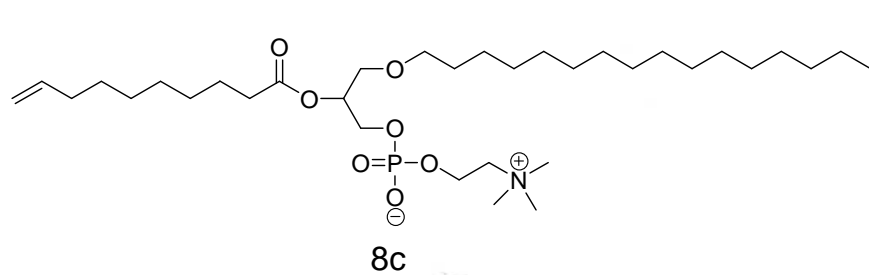
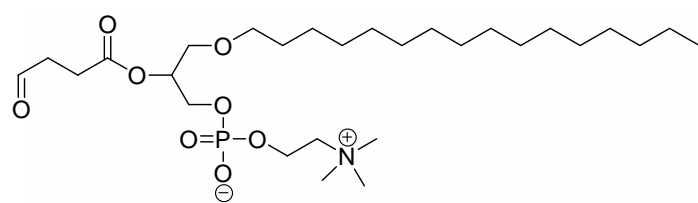


Figure S6. ^{13}C -NMR (100 M, $\text{CDCl}_3+\text{CD}_3\text{OD}$) of 1-O-Hexadecyl-2-(9-decenoyl)-sn-glycero-3-phosphatidylcholine (8c).



OB-PAF 2a

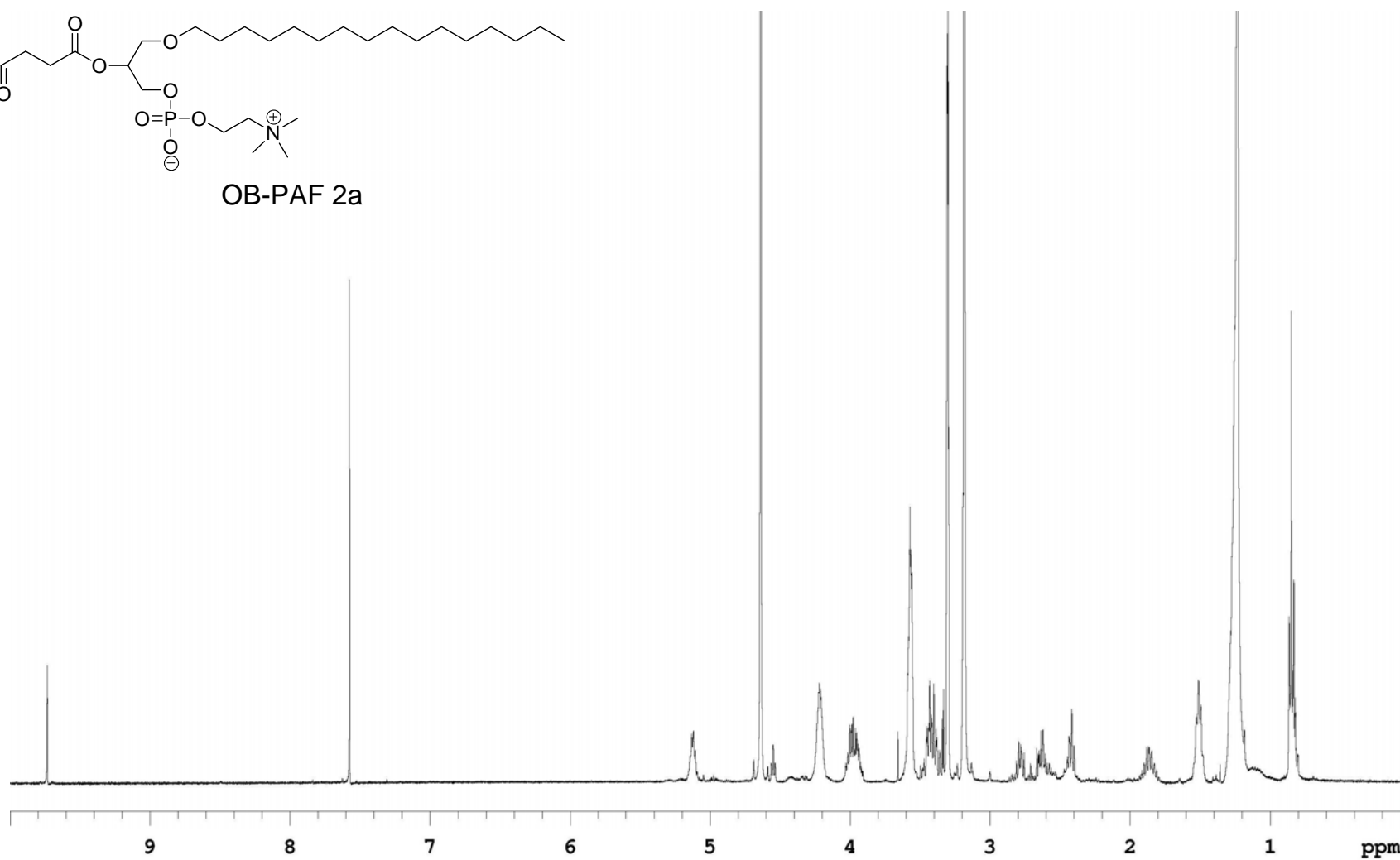


Figure S7. ¹H-NMR (400 M, CDCl₃+CD₃OD) of OB-PAF (2a).

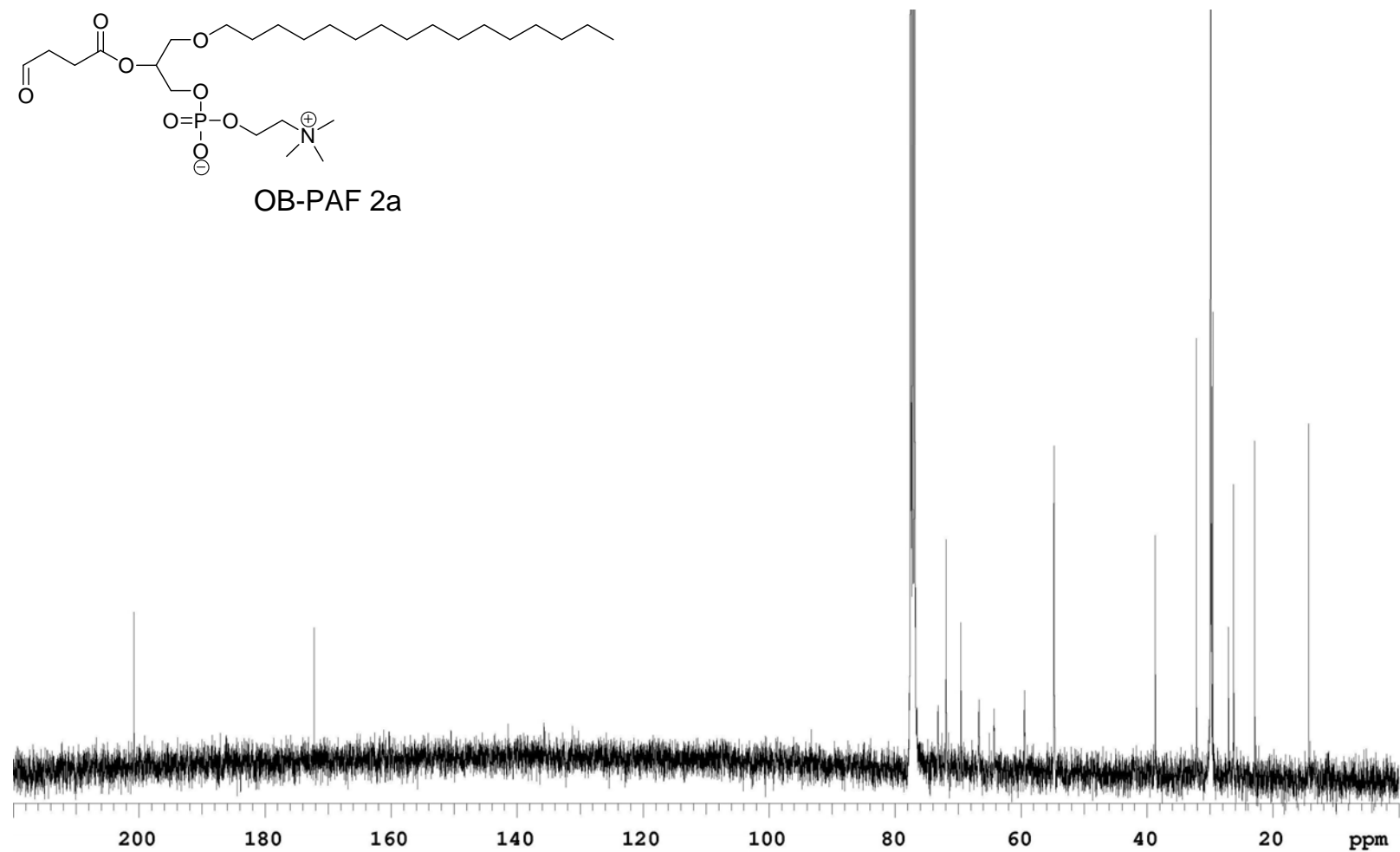
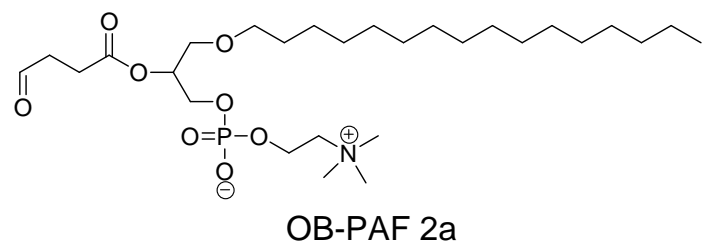


Figure S8. ^{13}C -NMR (75 M, CDCl_3) of OB-PAF (2a).

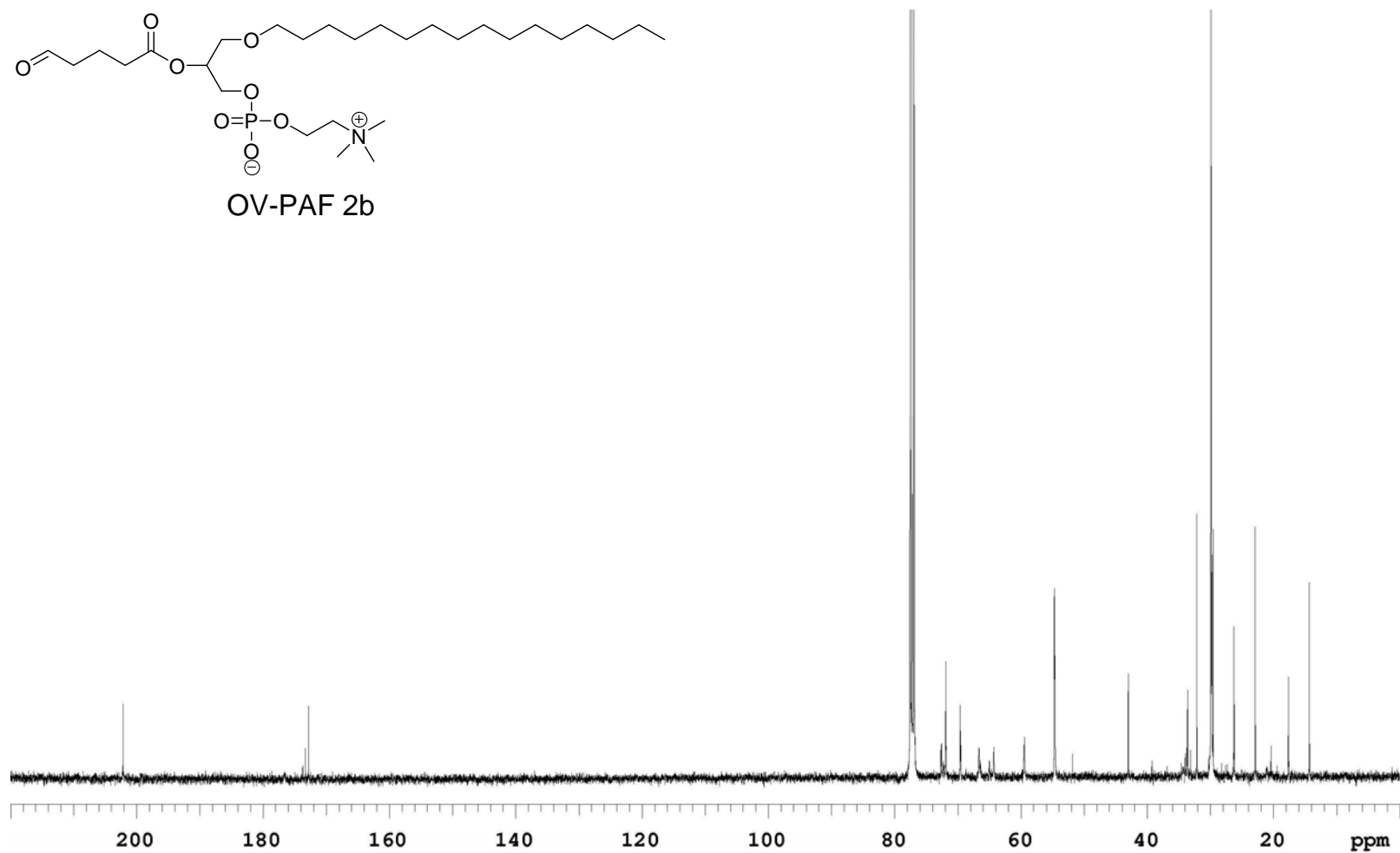
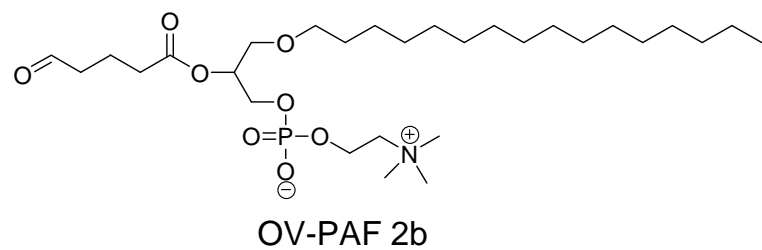


Figure S10. ¹³C-NMR (75 M, CDCl₃) of OV-PAF (2b).

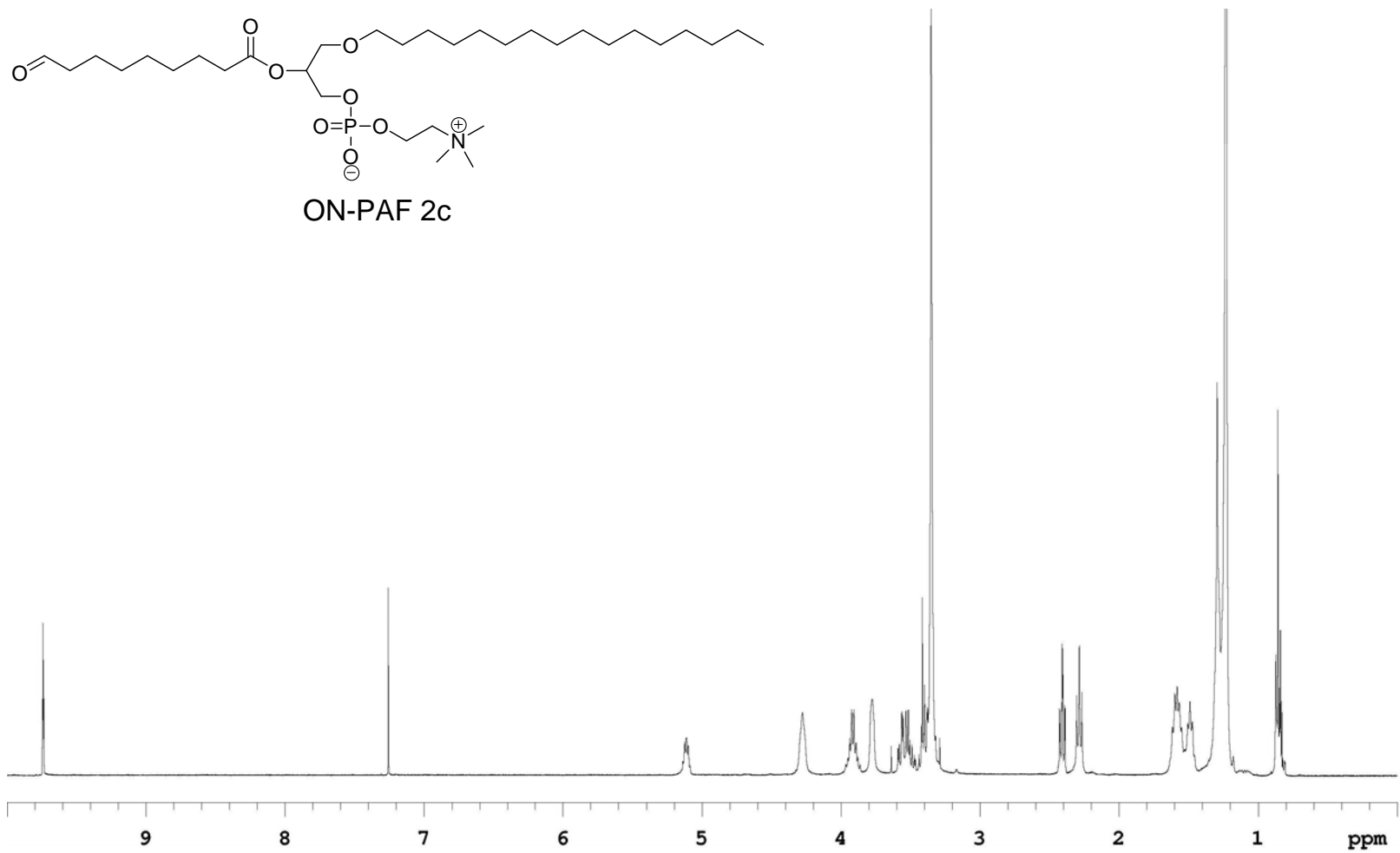


Figure S11. ¹H-NMR (400 M, CDCl₃+CD₃OD) of ON-PAF (2c).

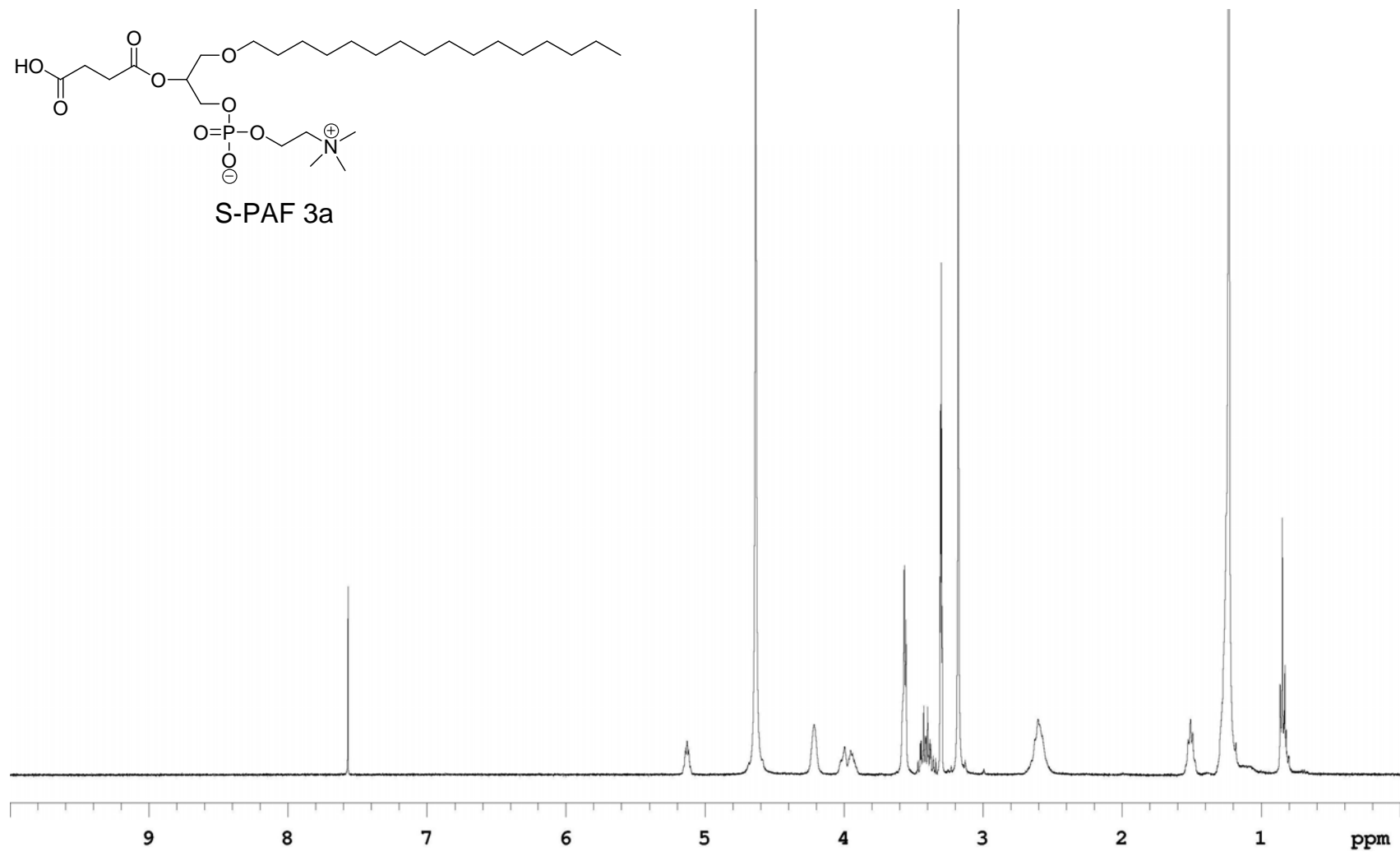
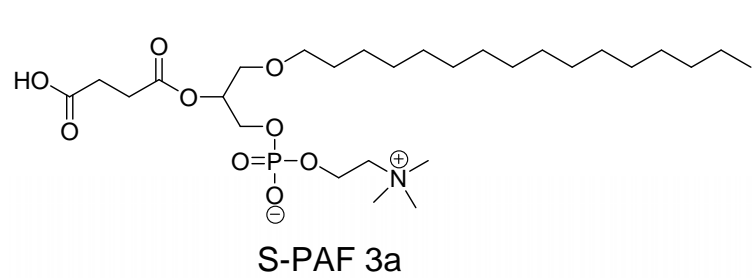


Figure S13. ¹H-NMR (400 M, CDCl₃+CD₃OD) of S-PAF (3a).

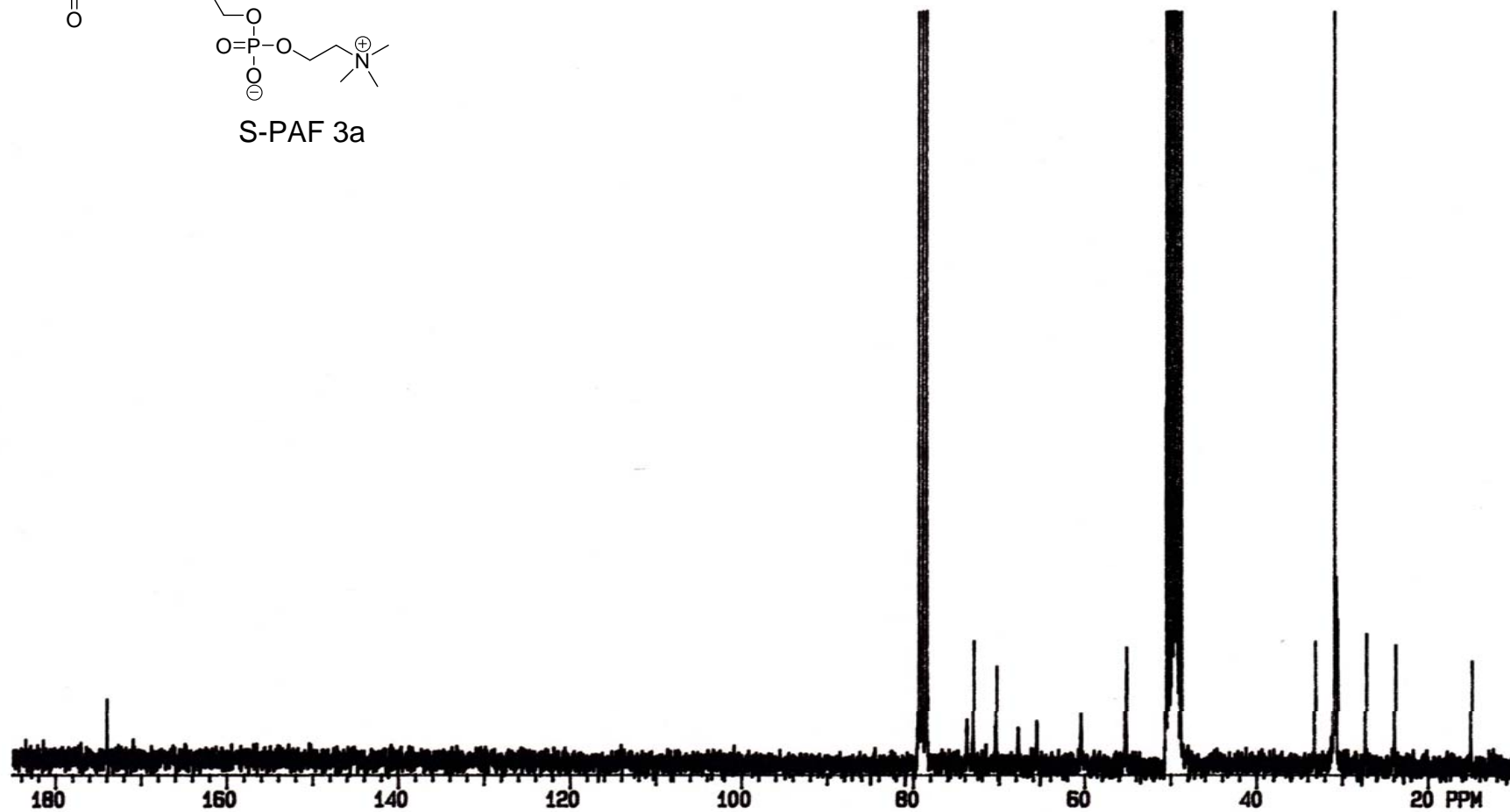
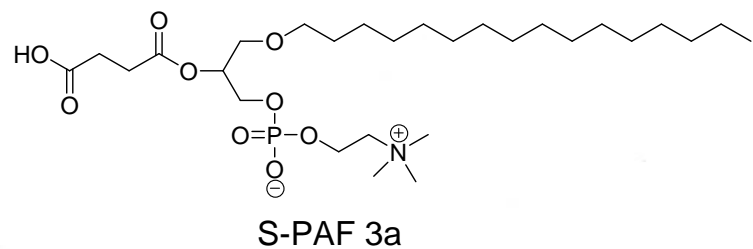


Figure S14. ¹³C-NMR (75 M, CDCl₃+CD₃OD) of S-PAF (3a).

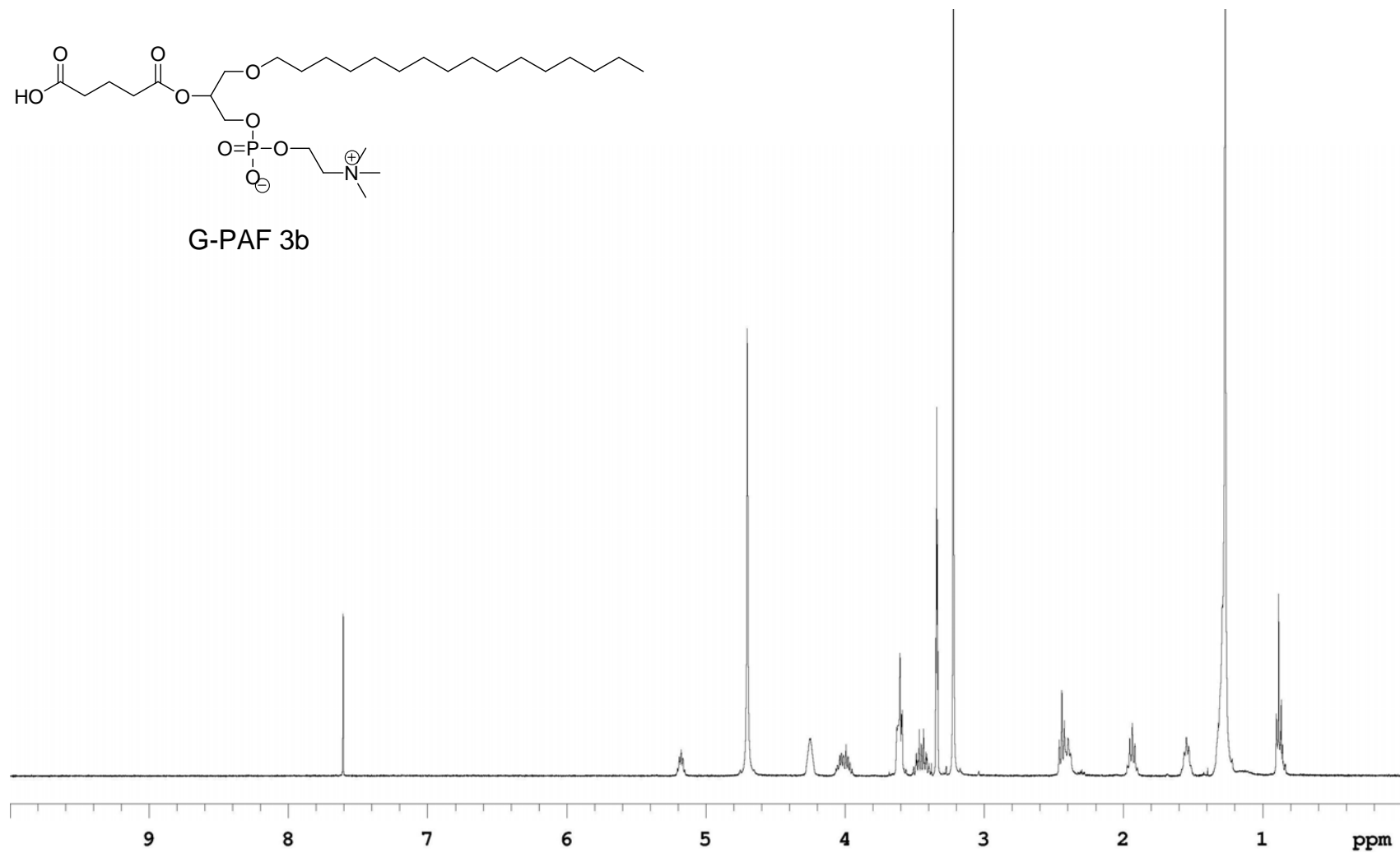
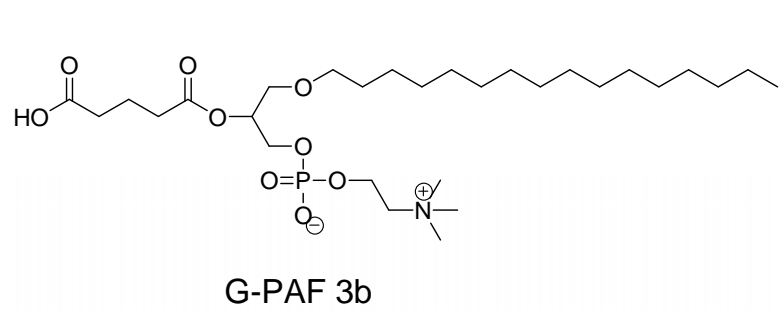
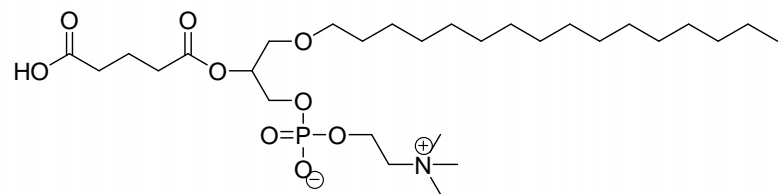


Figure S15. ¹H-NMR (400 M, CDCl₃+CD₃OD) of G-PAF (3b).



G-PAF 3b

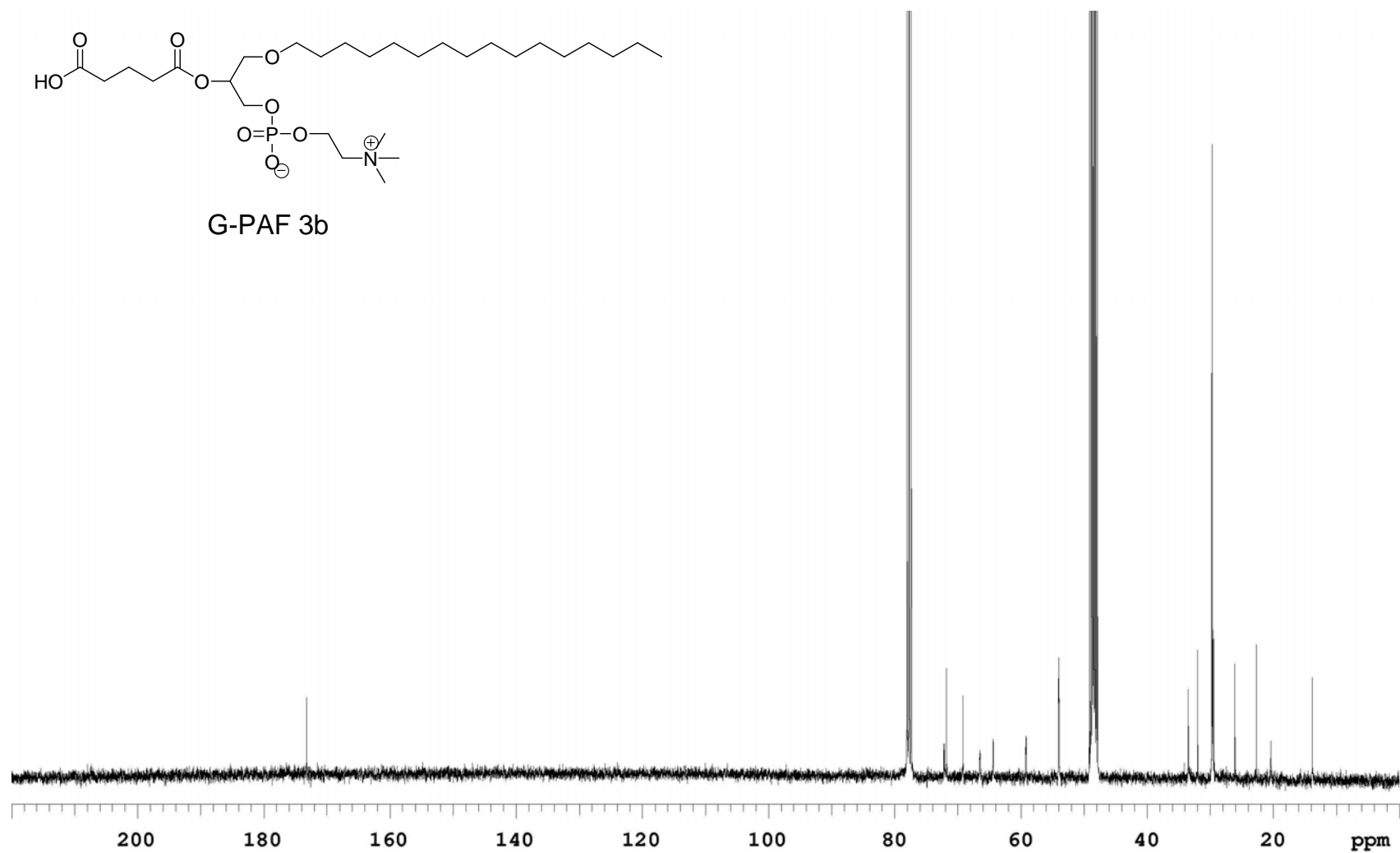


Figure S16. ¹³C-NMR (100 M, CDCl₃+CD₃OD) of G-PAF (3b).

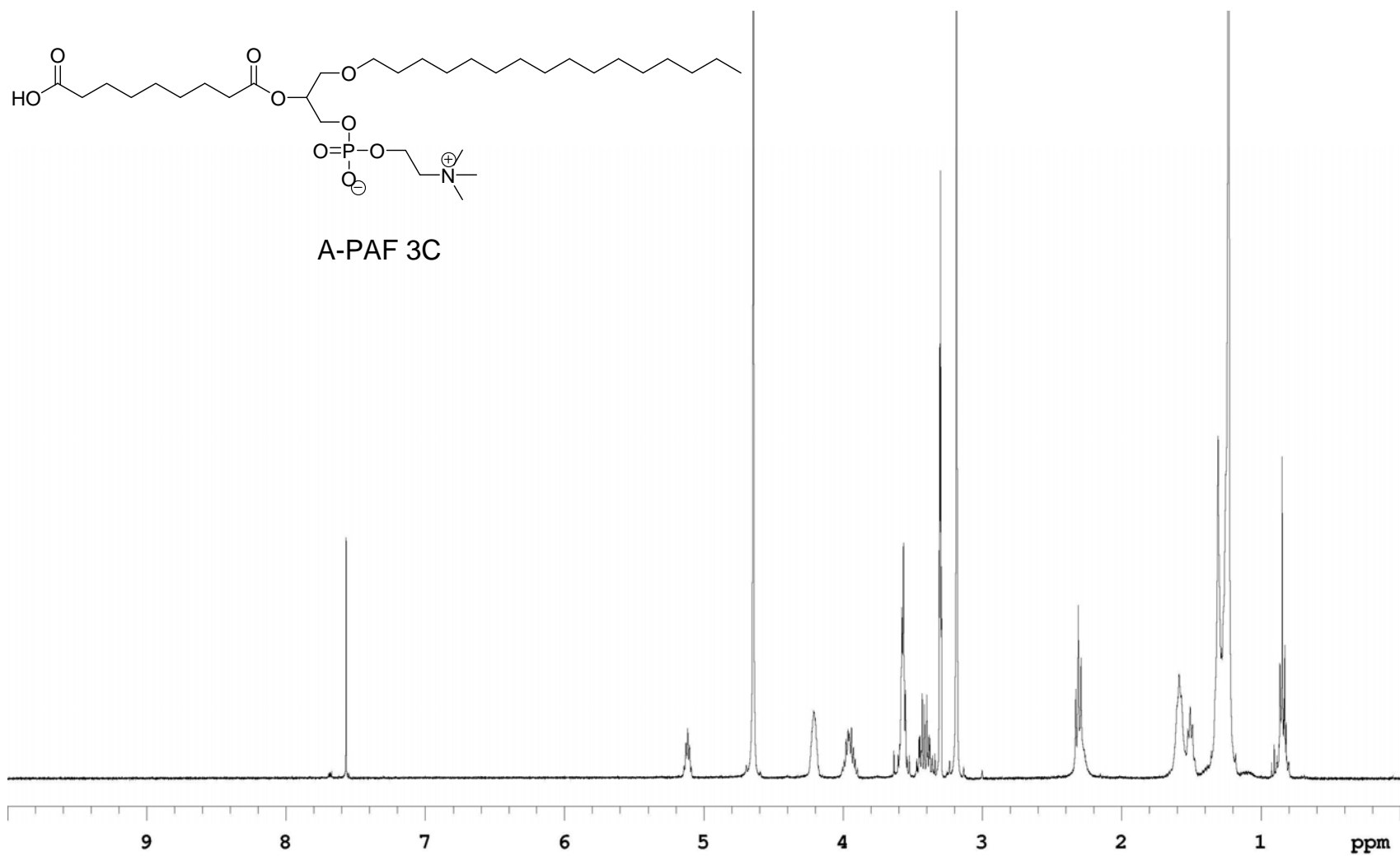
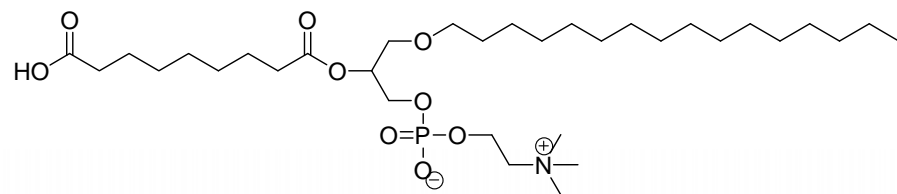


Figure S17. ¹H-NMR (400 M, CDCl₃+CD₃OD) of A-PAF (3c).



A-PAF 3C

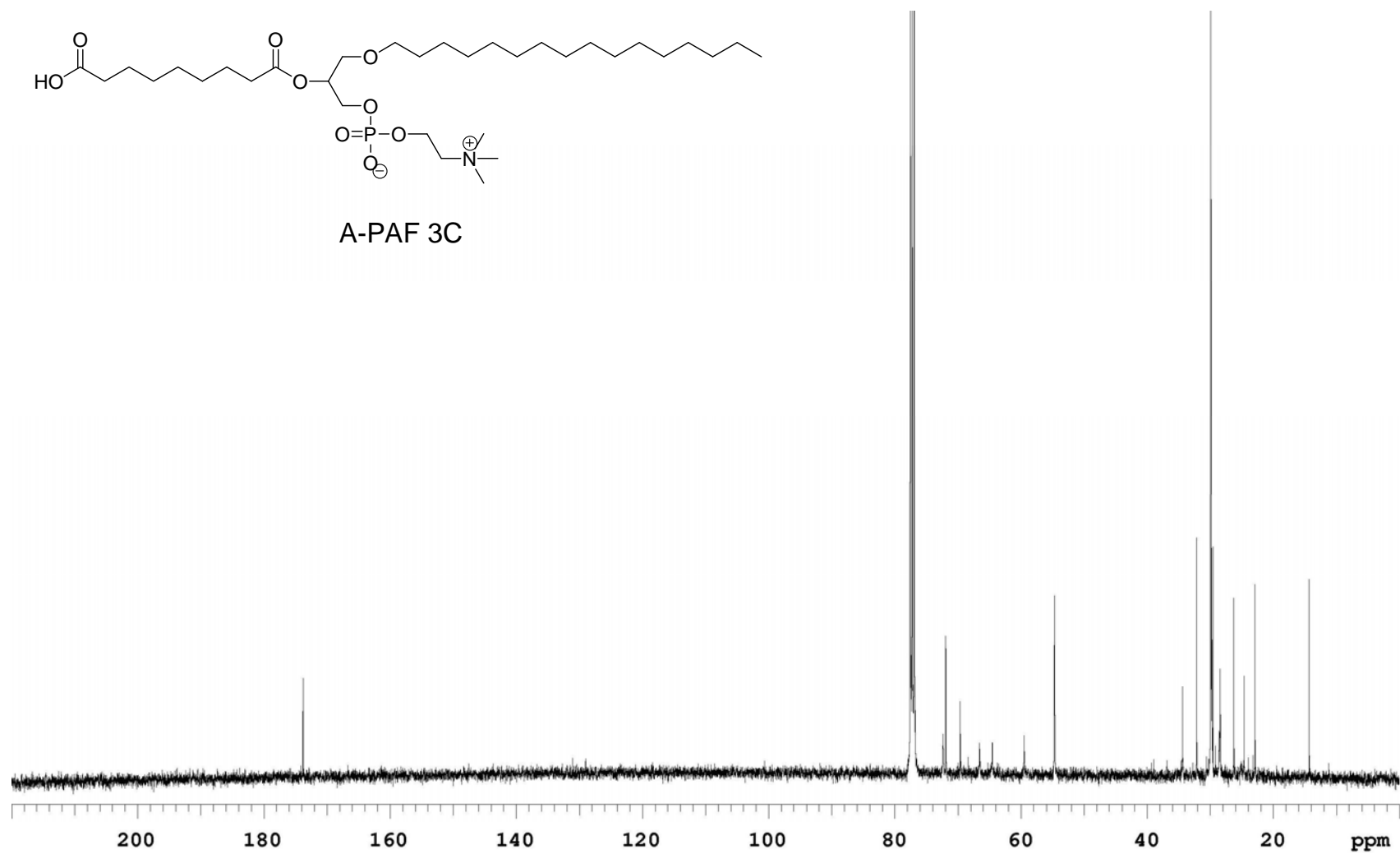
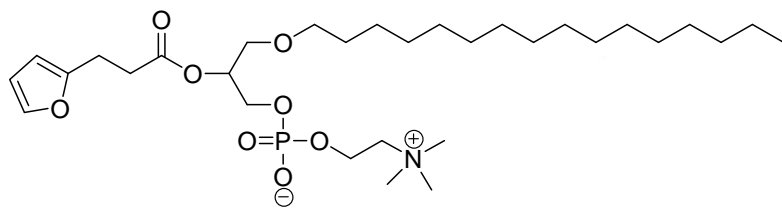


Figure S18. ¹³C-NMR (100 M, CDCl₃+CD₃OD) of A-PAF (3c).



12a

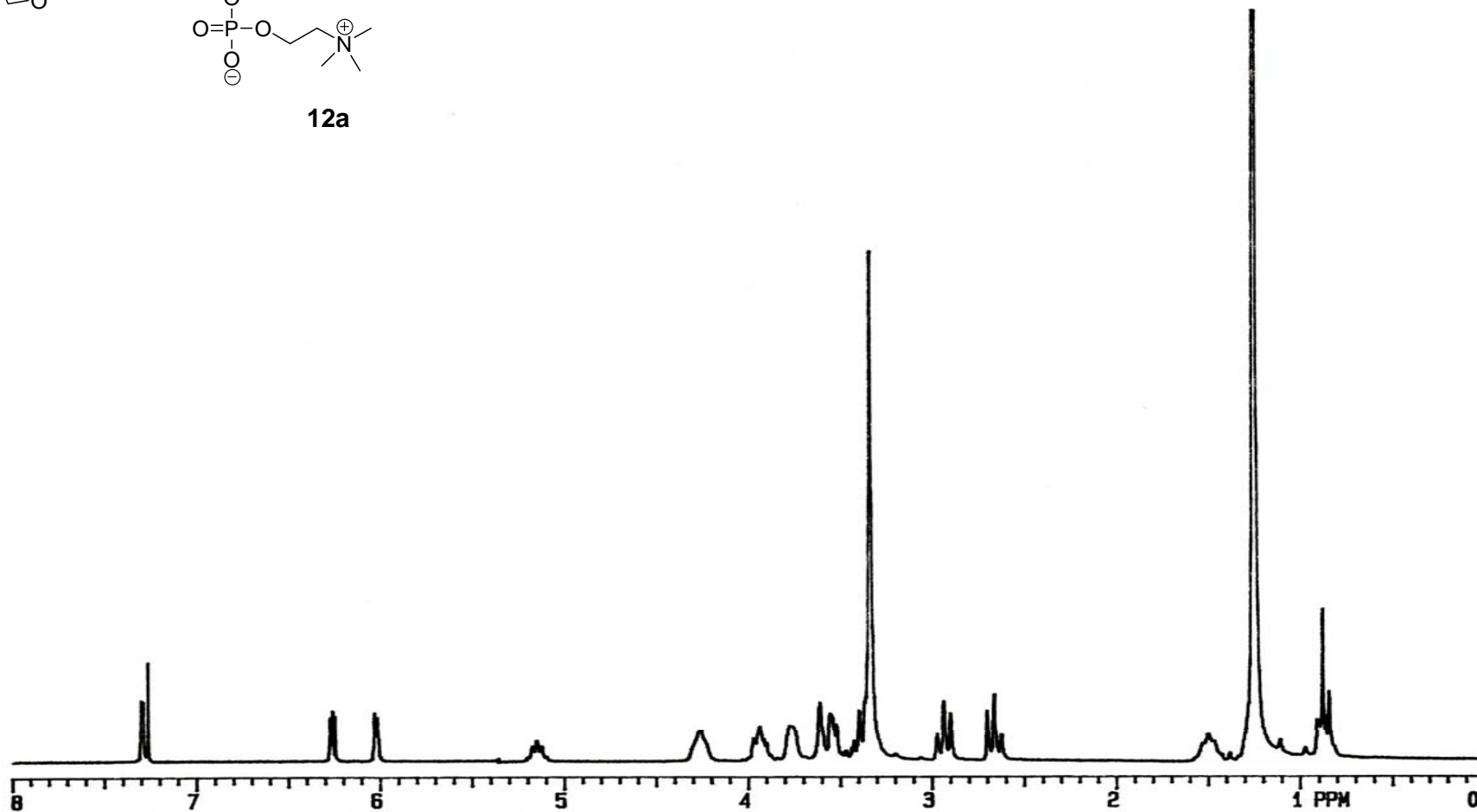
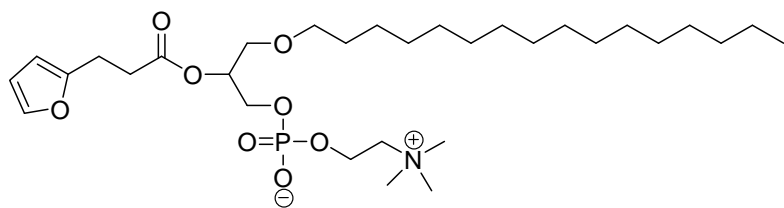


Figure S19. $^1\text{H-NMR}$ (200 M, CDCl_3) of 1-O-Hexadecyl-2-[3-(2-furyl)propanoyl]-sn-glycero-3-phosphatidylcholine



12a

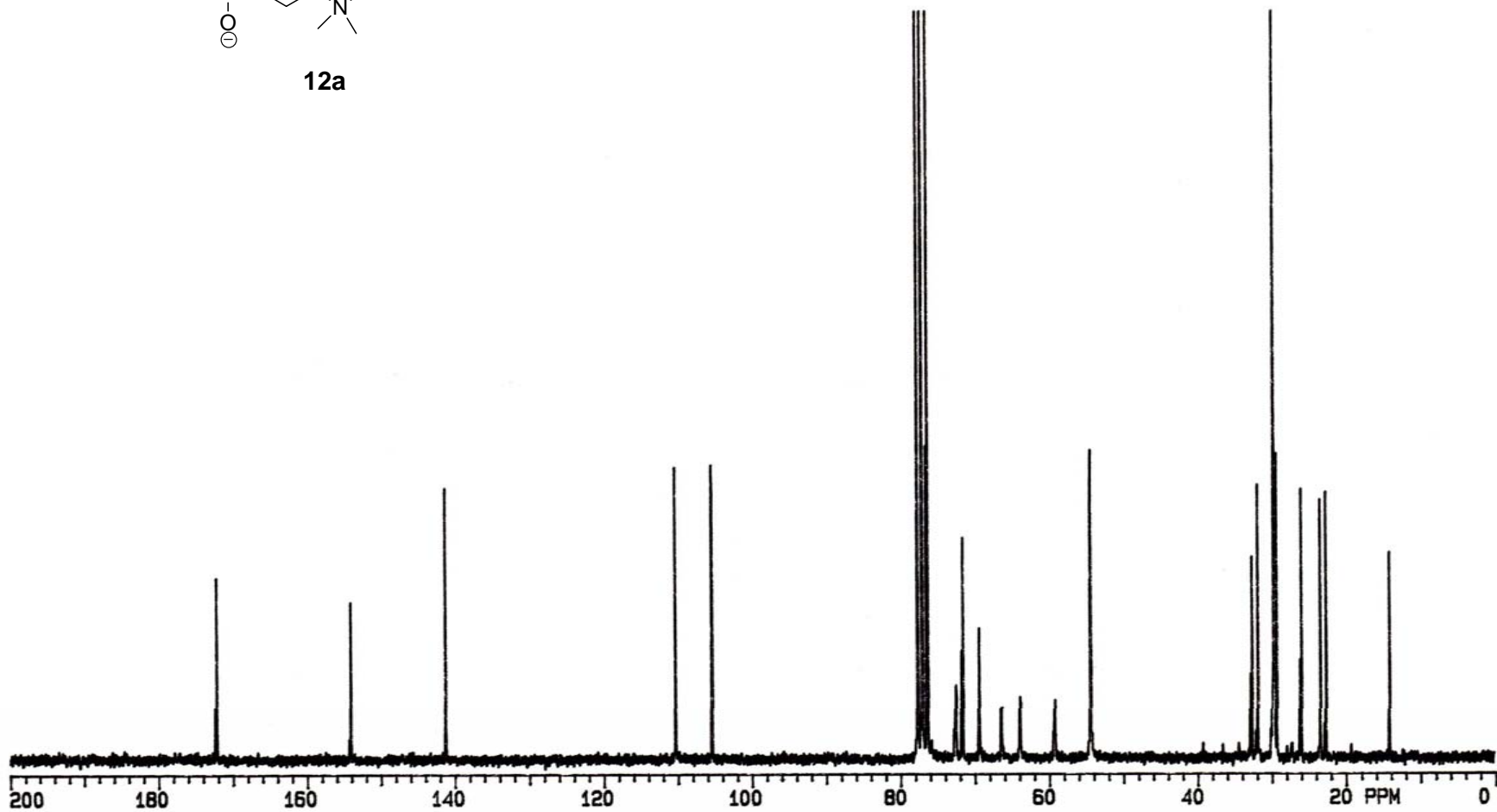


Figure S20. ^{13}C -NMR (50 M, CDCl_3) of 1-O-Hexadecyl-2-[3-(2-furyl)propanoyl]-sn-glycero-3-phosphatidylcholine

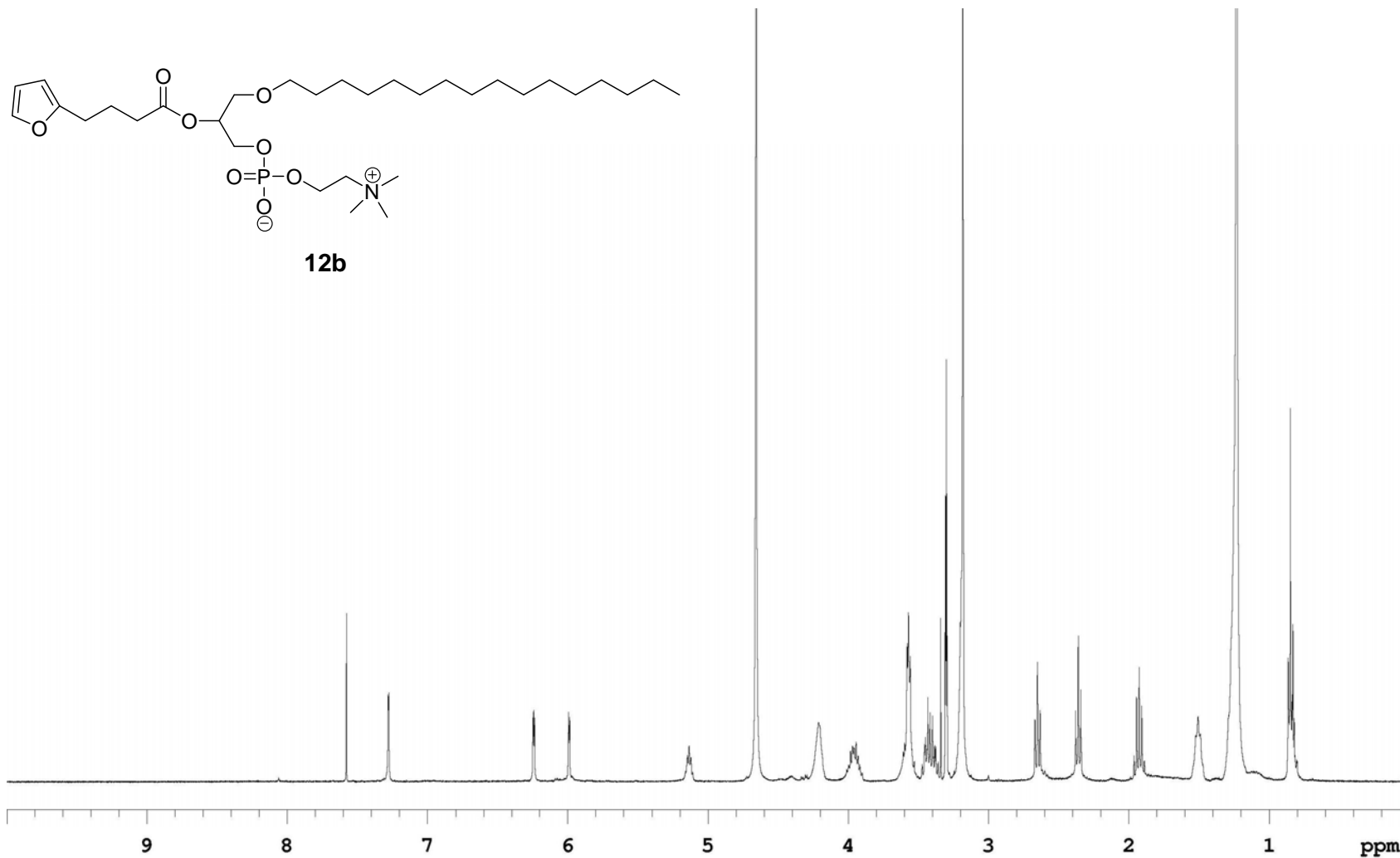


Figure S21. ¹H-NMR (400 M, CDCl₃+CD₃OD) of 1-O-Hexadecyl-2-[4-(2-furyl)butanoyl]-sn-glycero-3-phosphatidylcholine (12b).

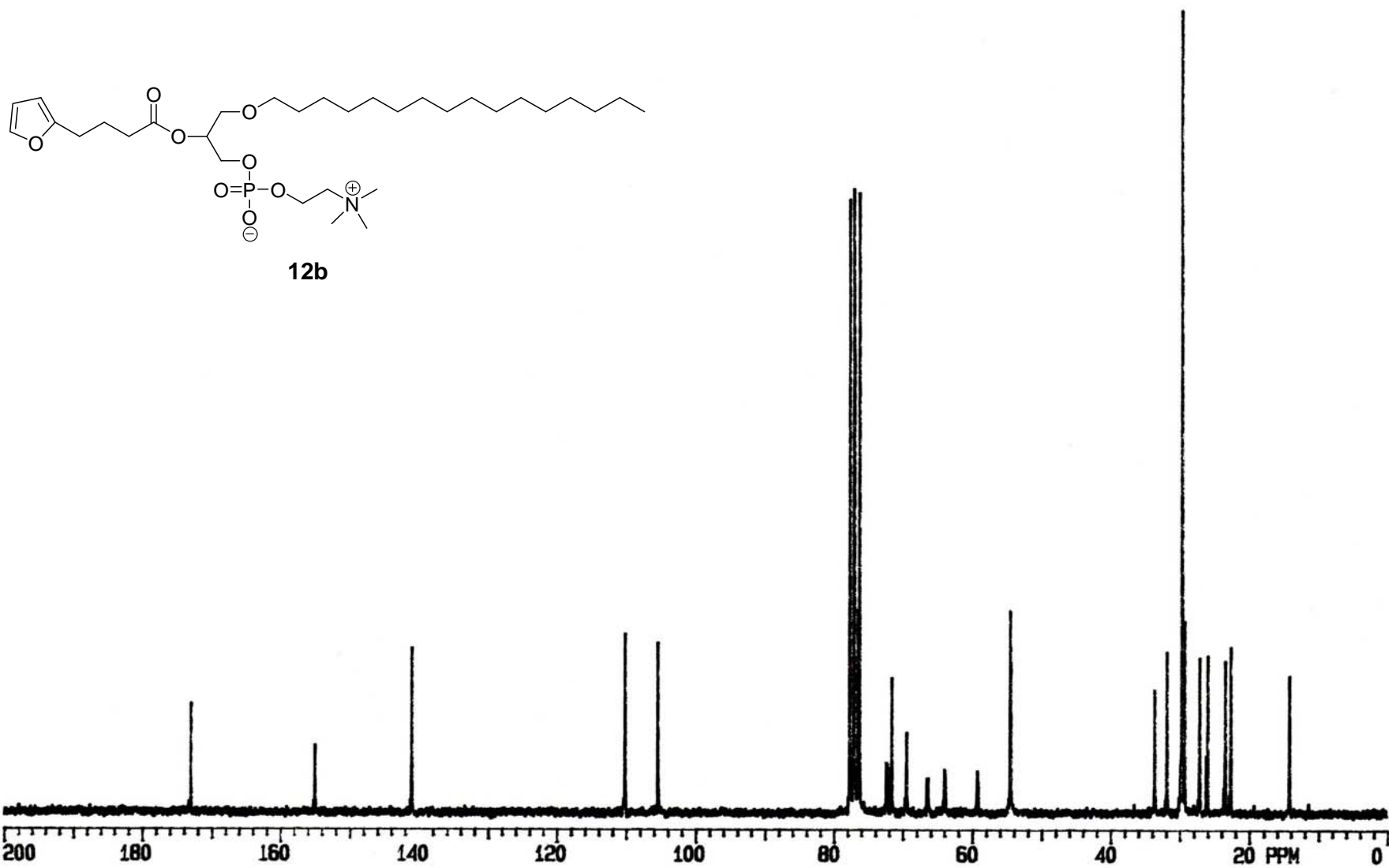
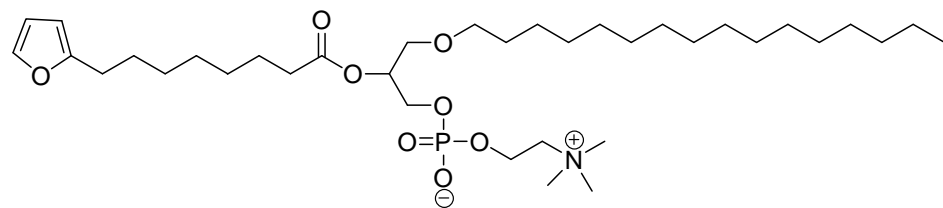


Figure S22. ¹³C-NMR (50 M, CDCl₃) of 1-O-Hexadecyl-2-[4-(2-furyl)butanoyl]-sn-glycerophosphatidylcholine (12b).



12c

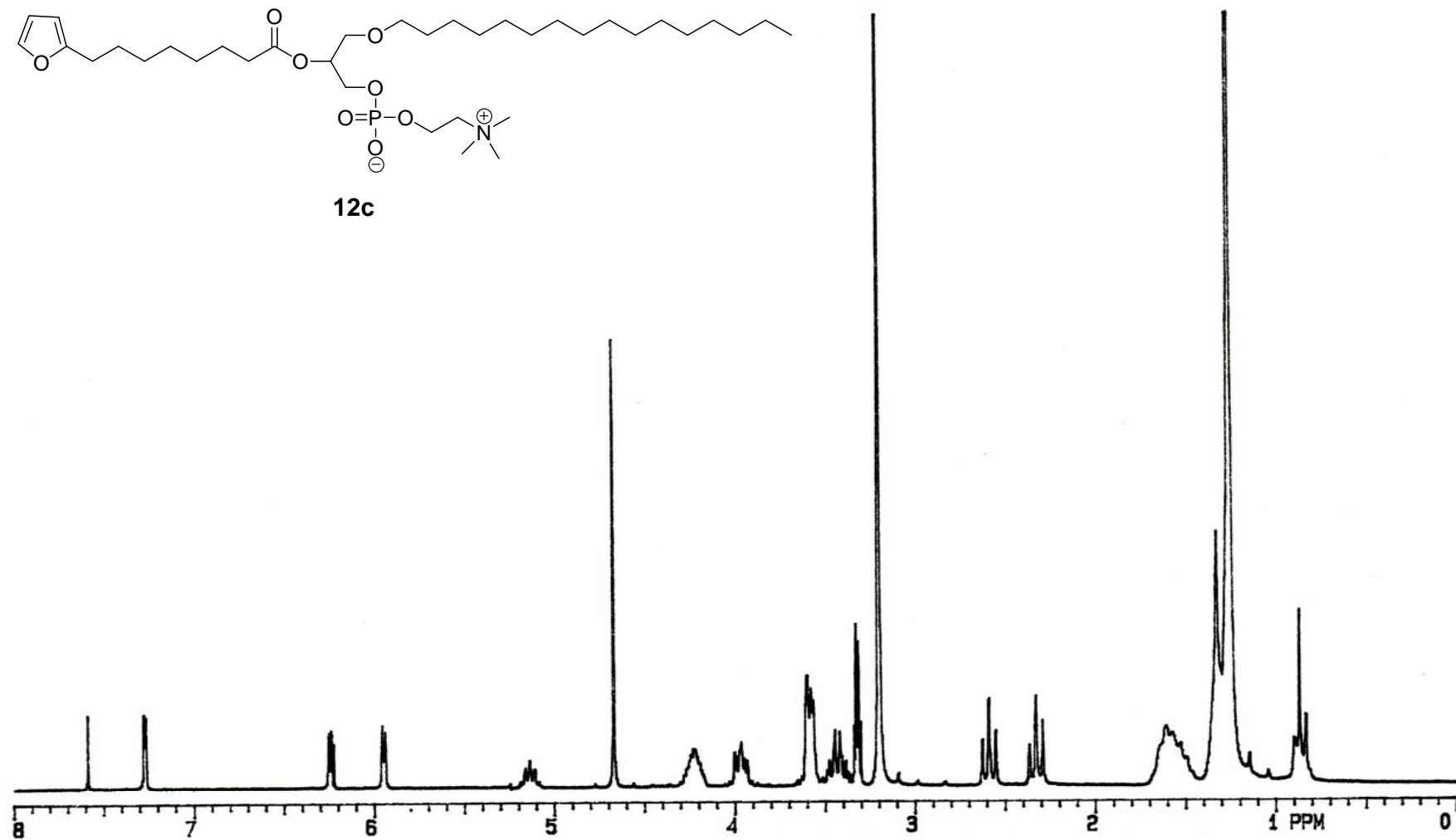


Figure S23. $^1\text{H-NMR}$ (200 M, $\text{CDCl}_3+\text{CD}_3\text{OD}$) of 1-O-Hexadecyl-2-[8-(2-furyl)octanoyl]-sn-glycero-3-phosphatidylcholine

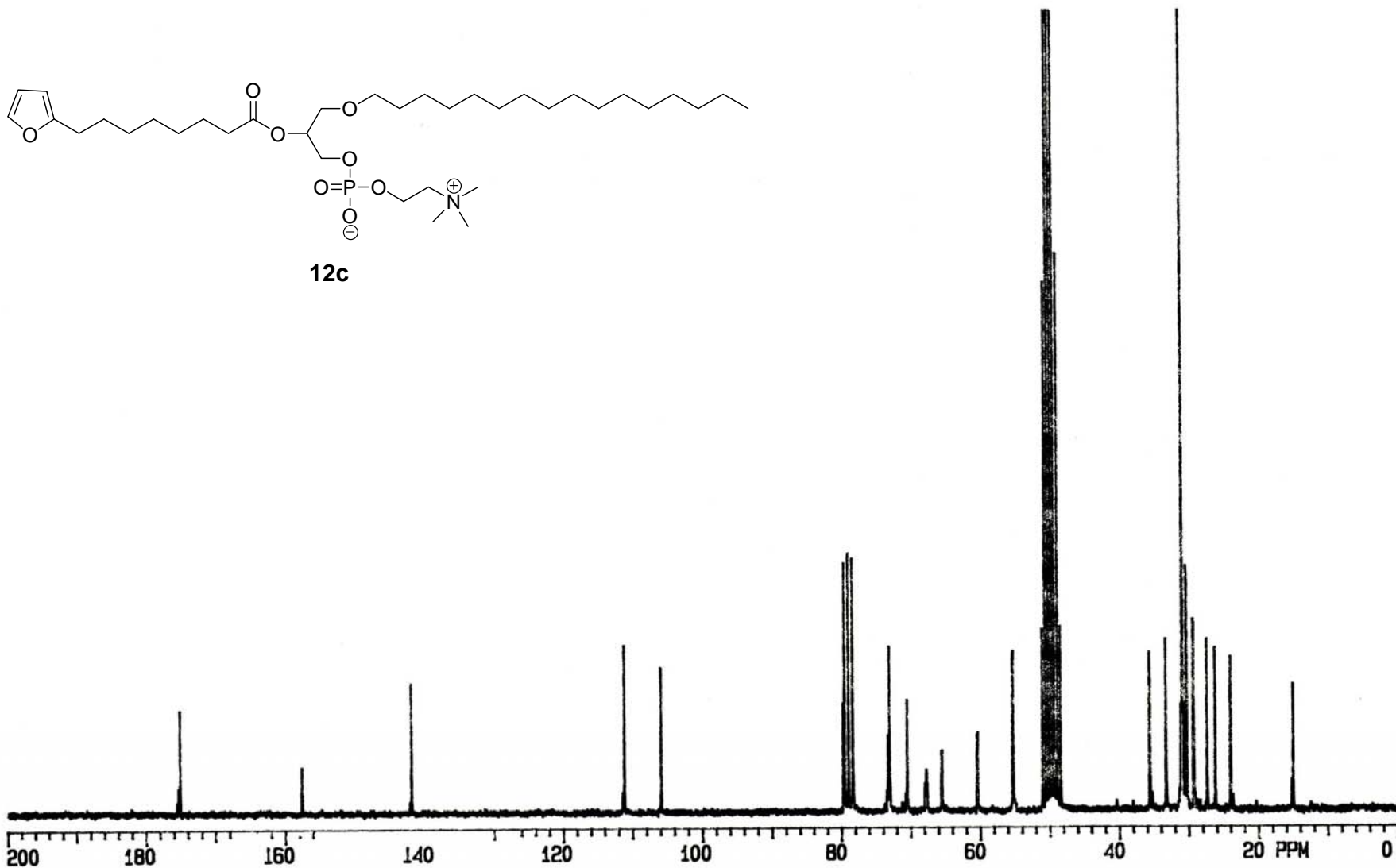


Figure S24. ¹³C-NMR (50 M, CDCl₃+CD₃OD) of 1-O-Hexadecyl-2-[8-(2-furyl)octanoyl]-sn-glycero-3-phosphatidylcholine

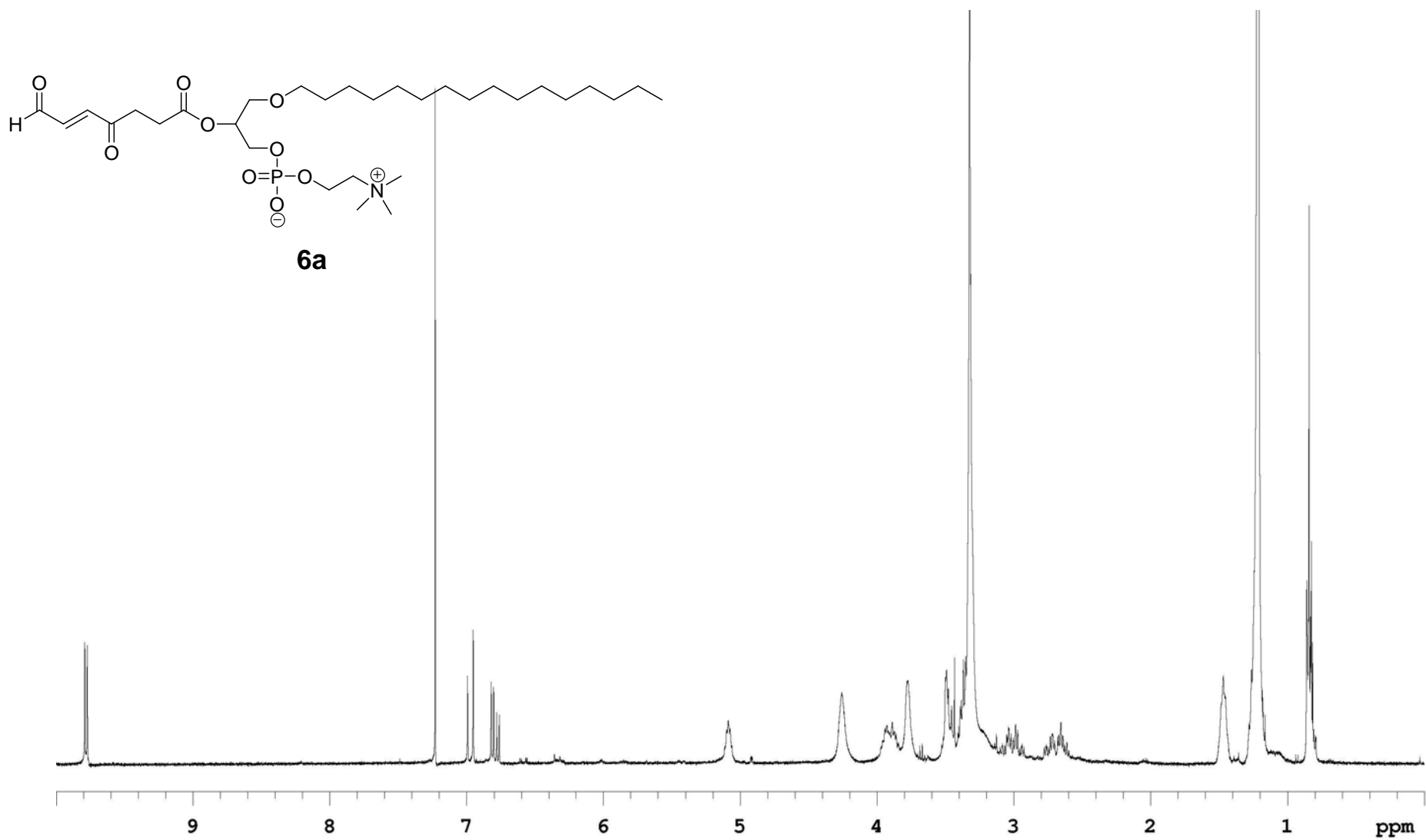


Figure S25. ¹H-NMR (400 M, CDCl₃) of KOHA-PAF (6a).

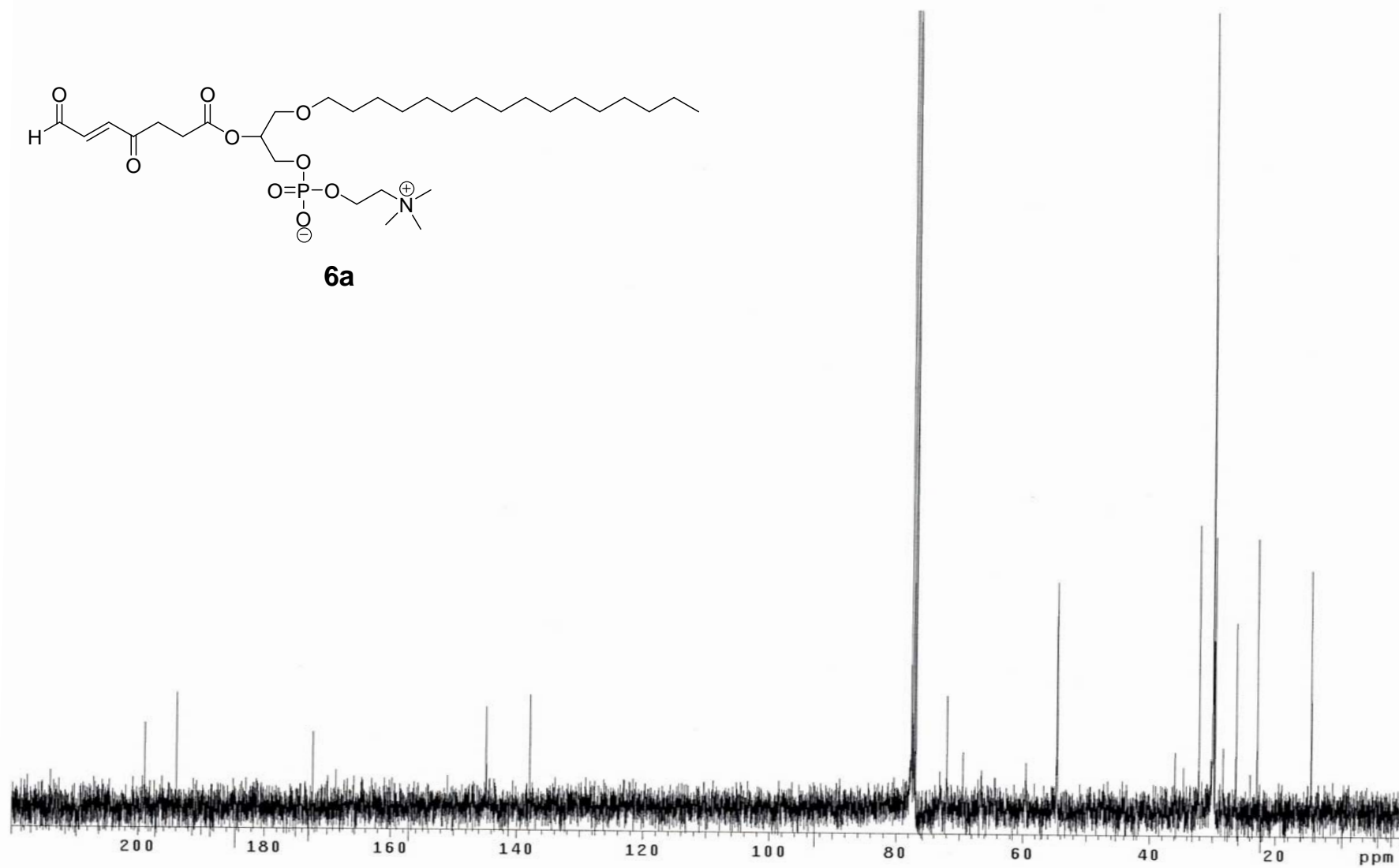


Figure S26. ¹³C-NMR (100 M, CDCl₃) of KOHA-PAF (6a).

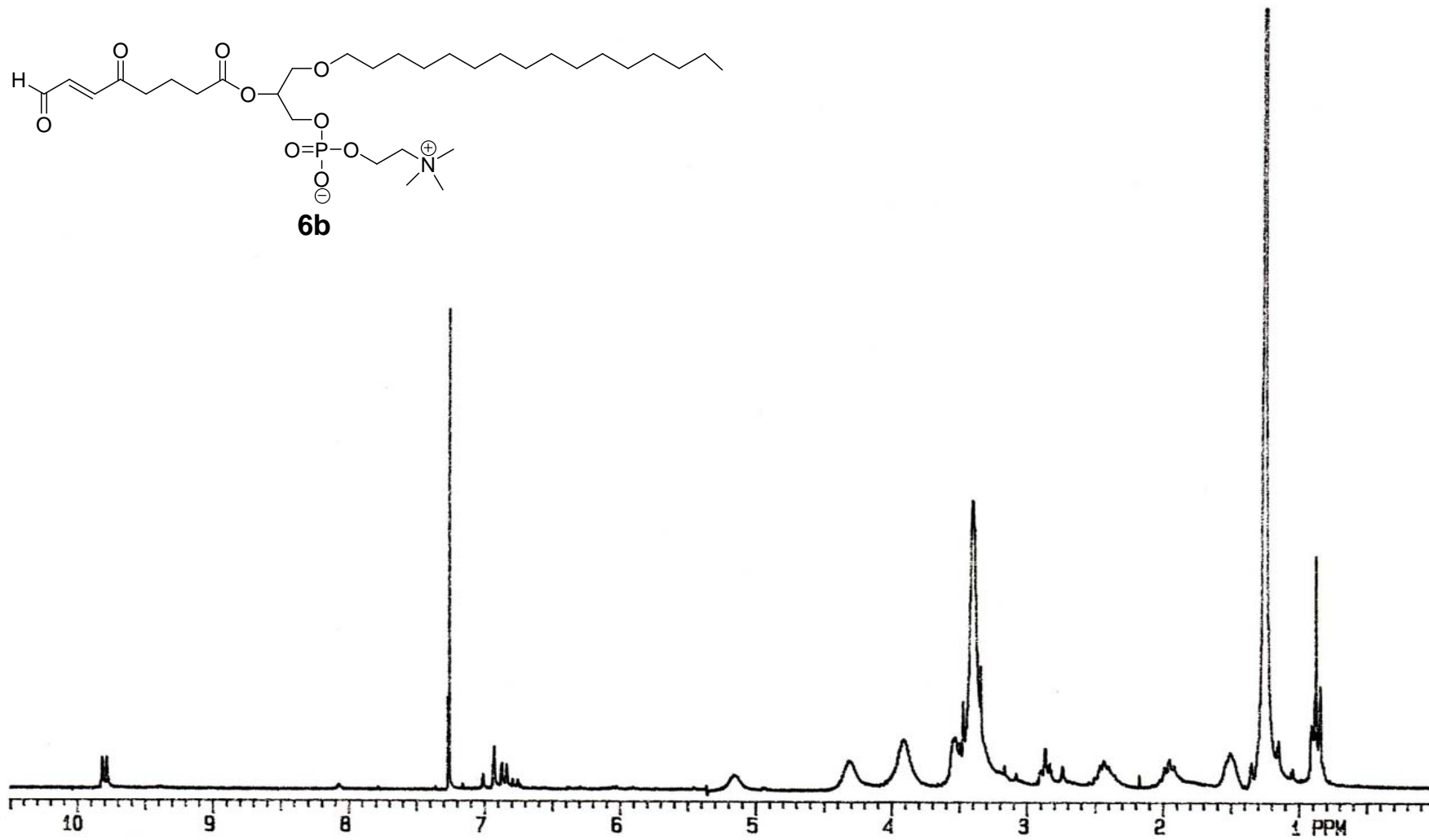
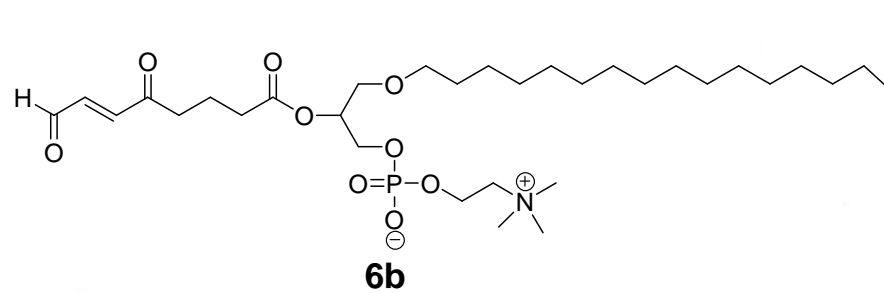


Figure S27. ¹H-NMR (200 M, CDCl₃) of KOOA-PAF (6b).

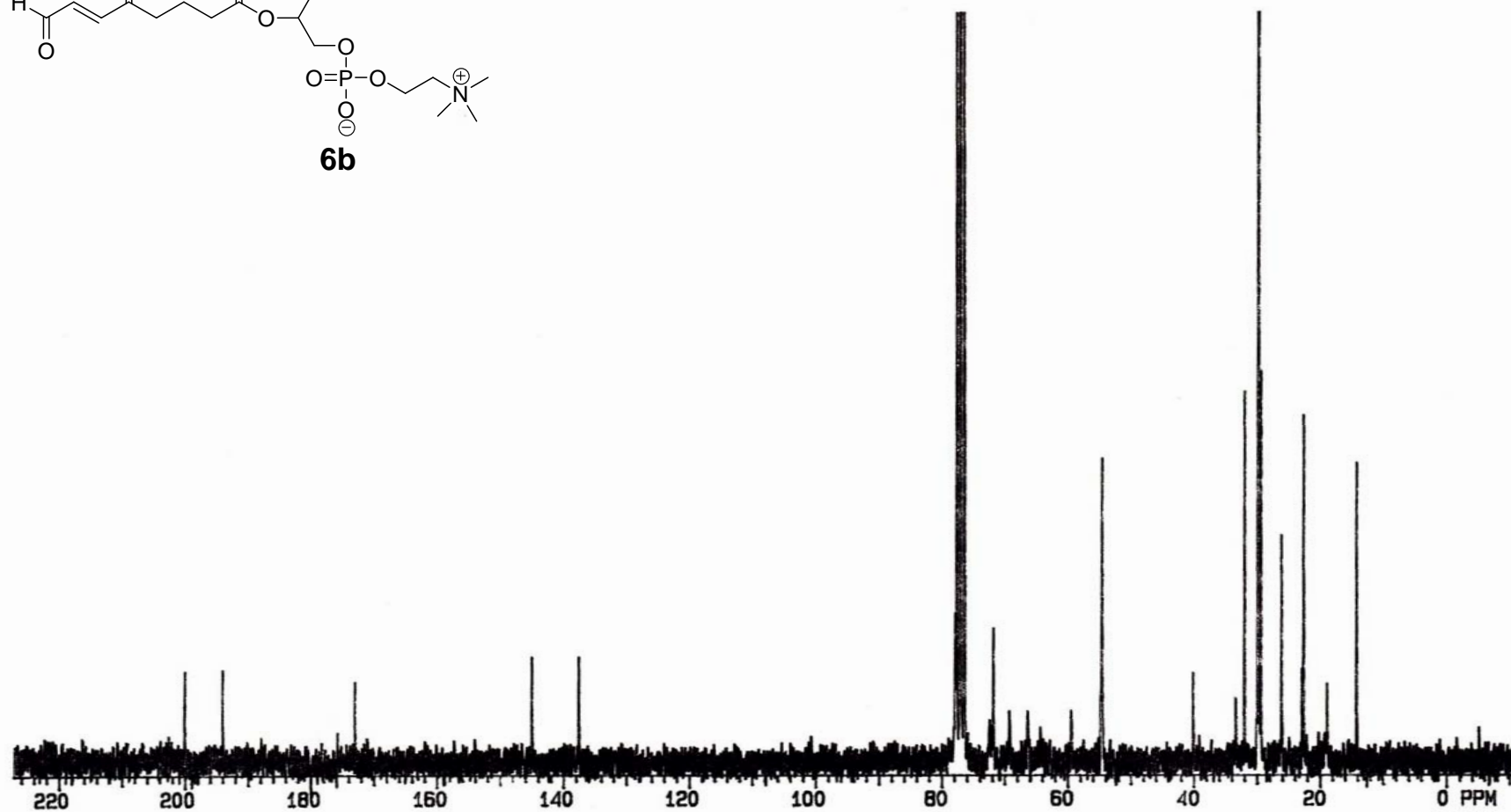
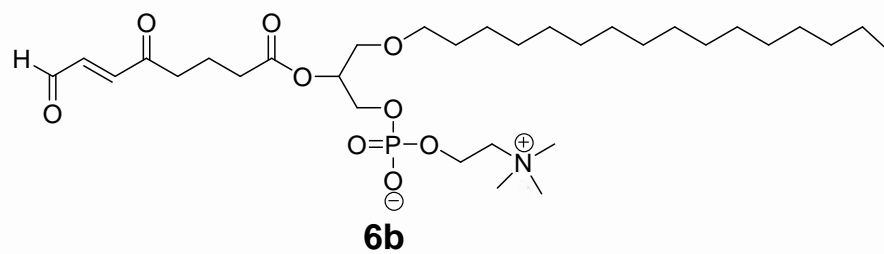


Figure S28. ^{13}C -NMR (50 M, CDCl_3) of KOOA-PAF (6b).

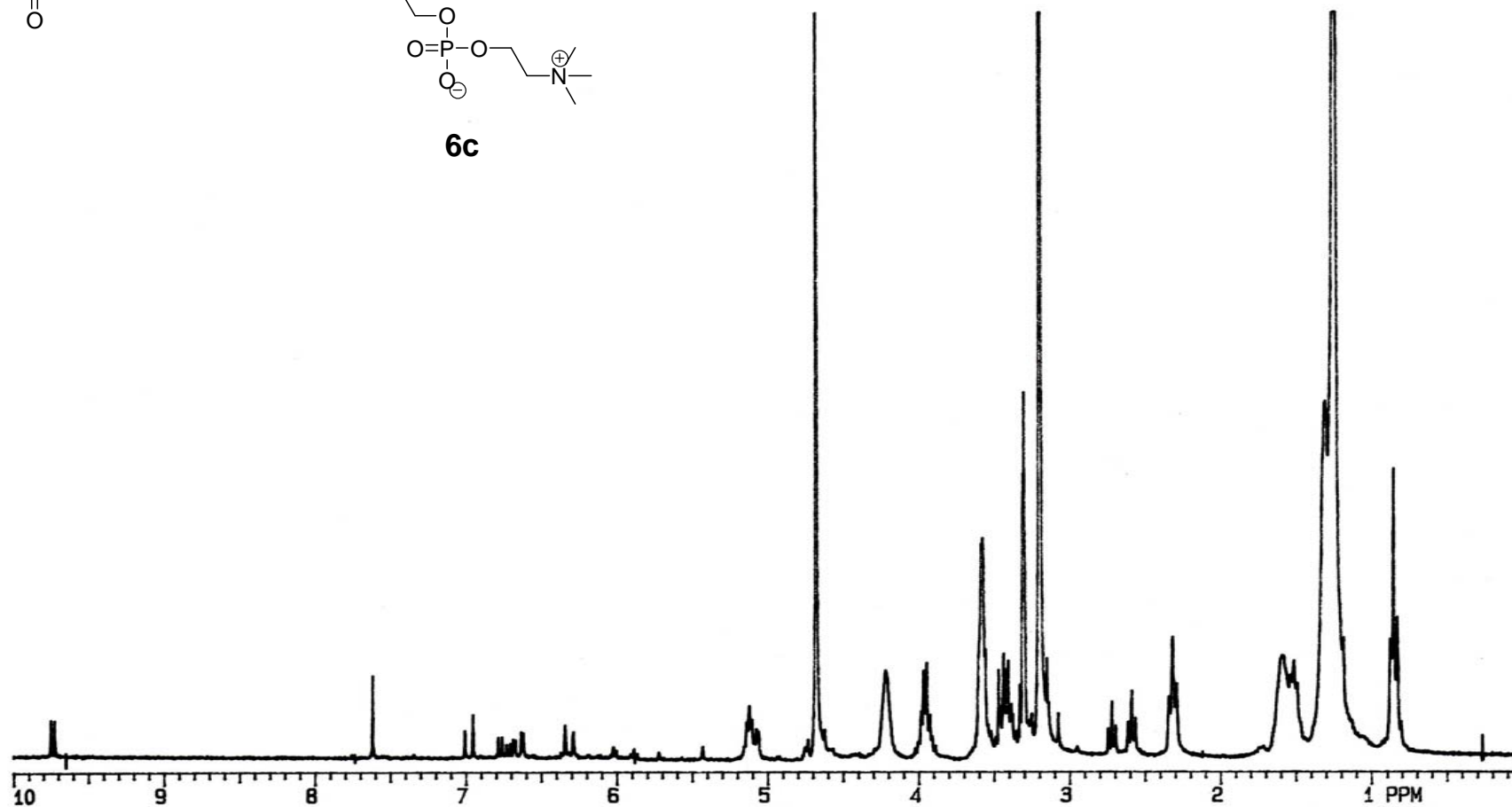
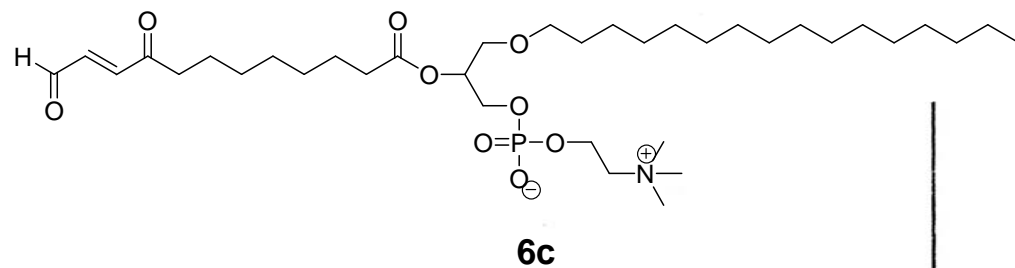


Figure S29. ¹H-NMR (300 M, CDCl₃+CD₃OD) of KODA-PAF (6c).

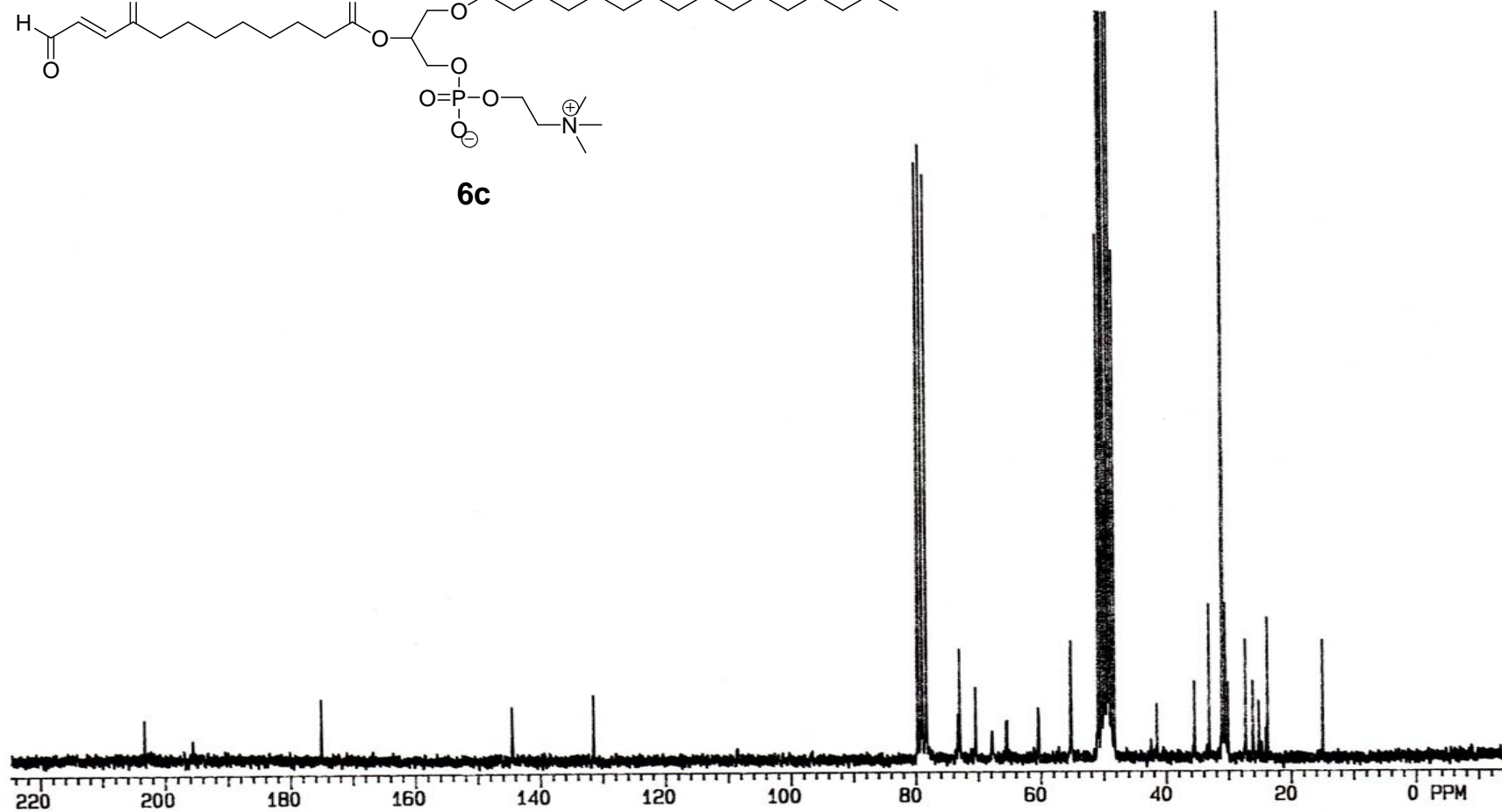
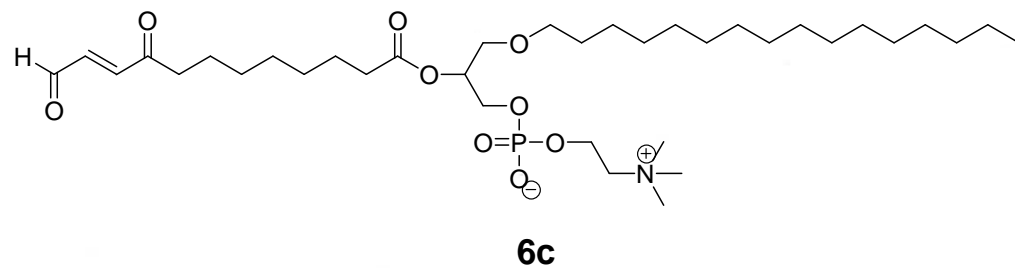


Figure S30. ^{13}C -NMR (50 M, $\text{CDCl}_3+\text{CD}_3\text{OD}$) of KODA-PAF (6c).

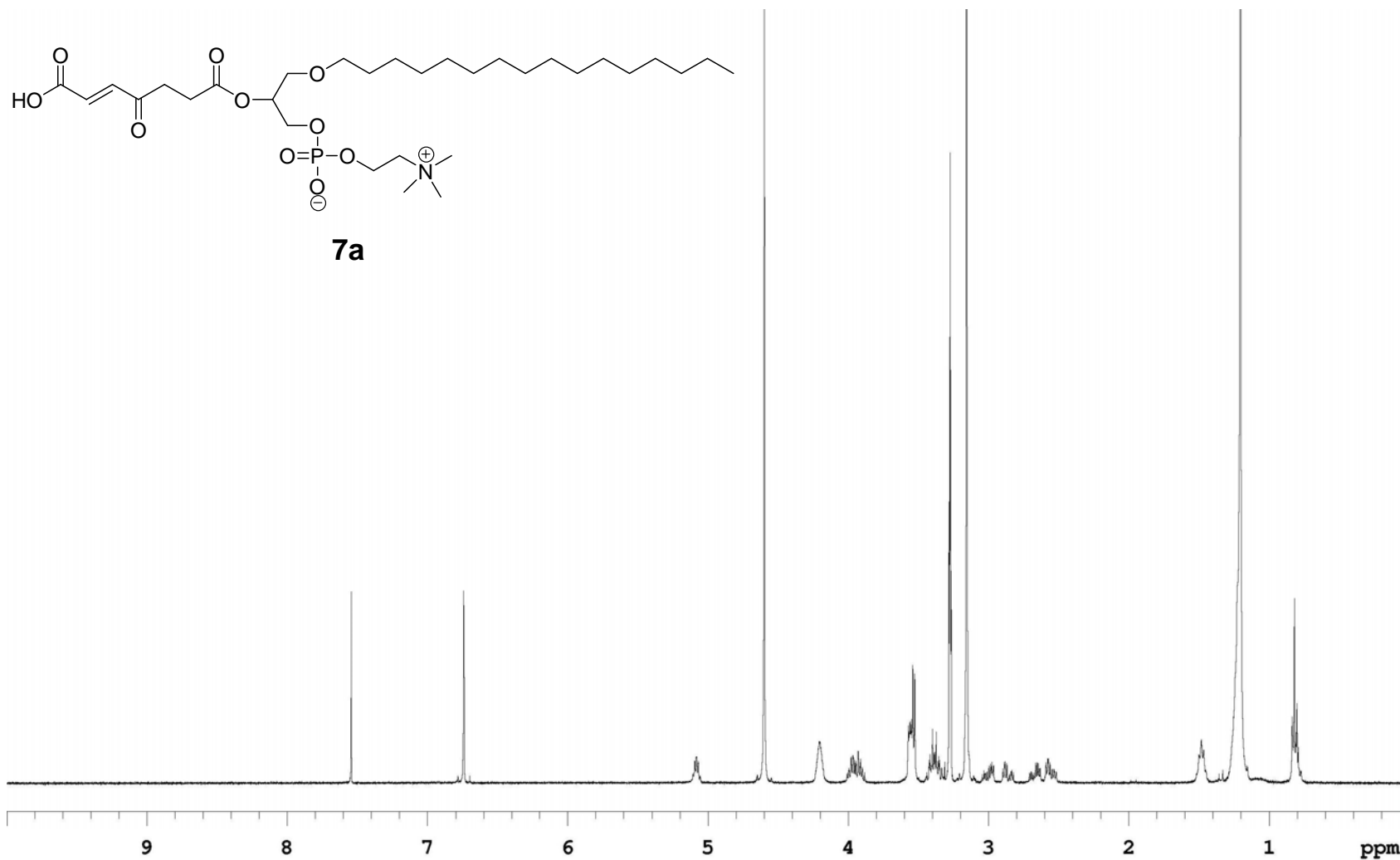
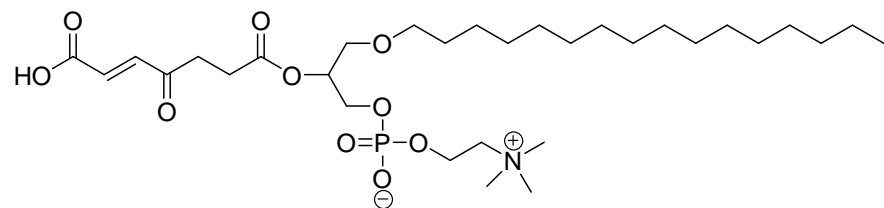


Figure S31. ¹H-NMR (400 M, CDCl₃+CD₃OD) of KHdiA-PAF (7a).



7a

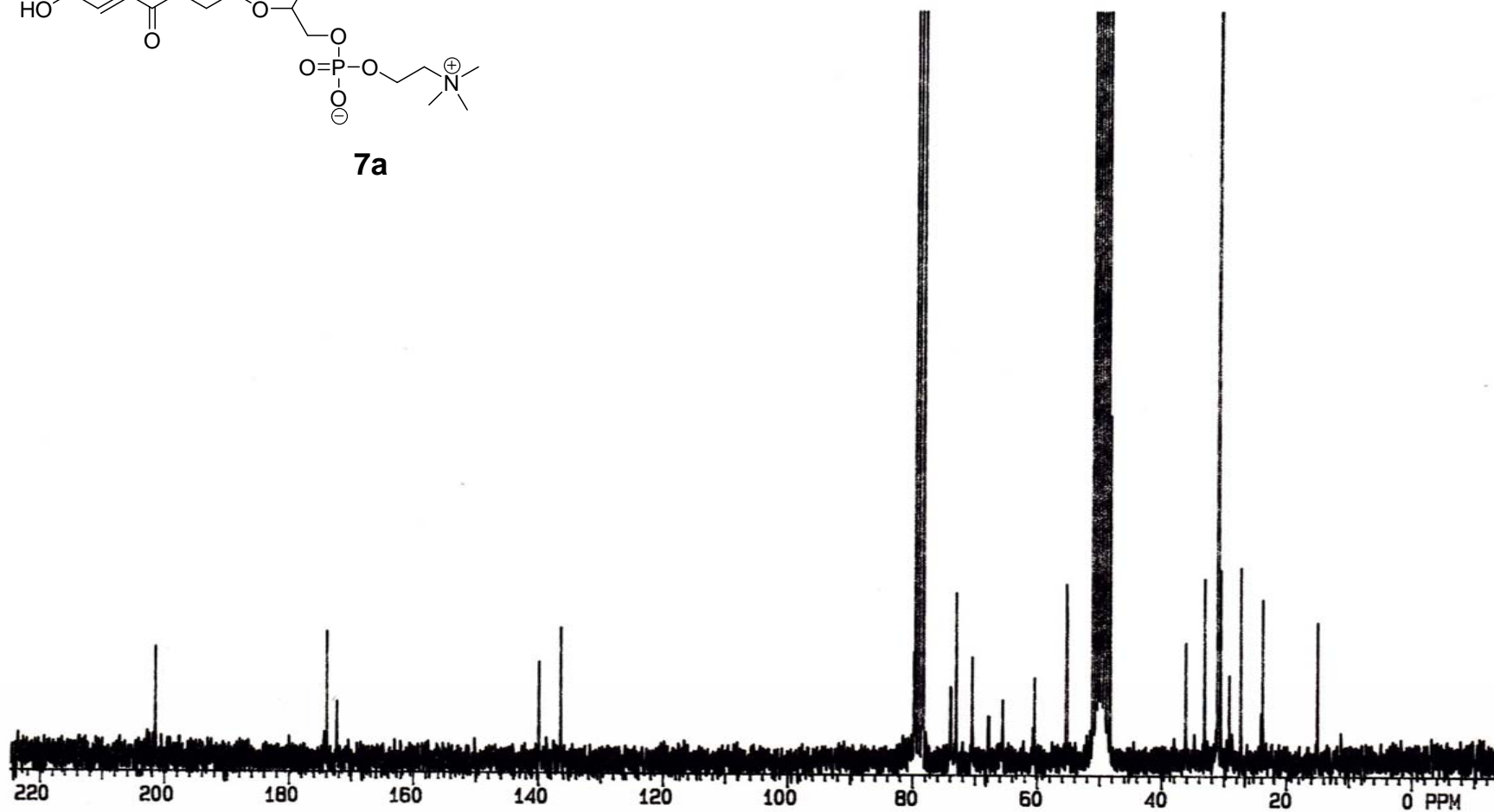
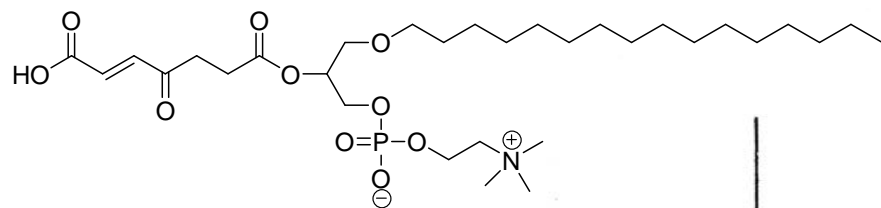


Figure S32. ¹³C-NMR (50 M, CDCl₃+CD₃OD) of KHdiA-PAF (7a).



7a

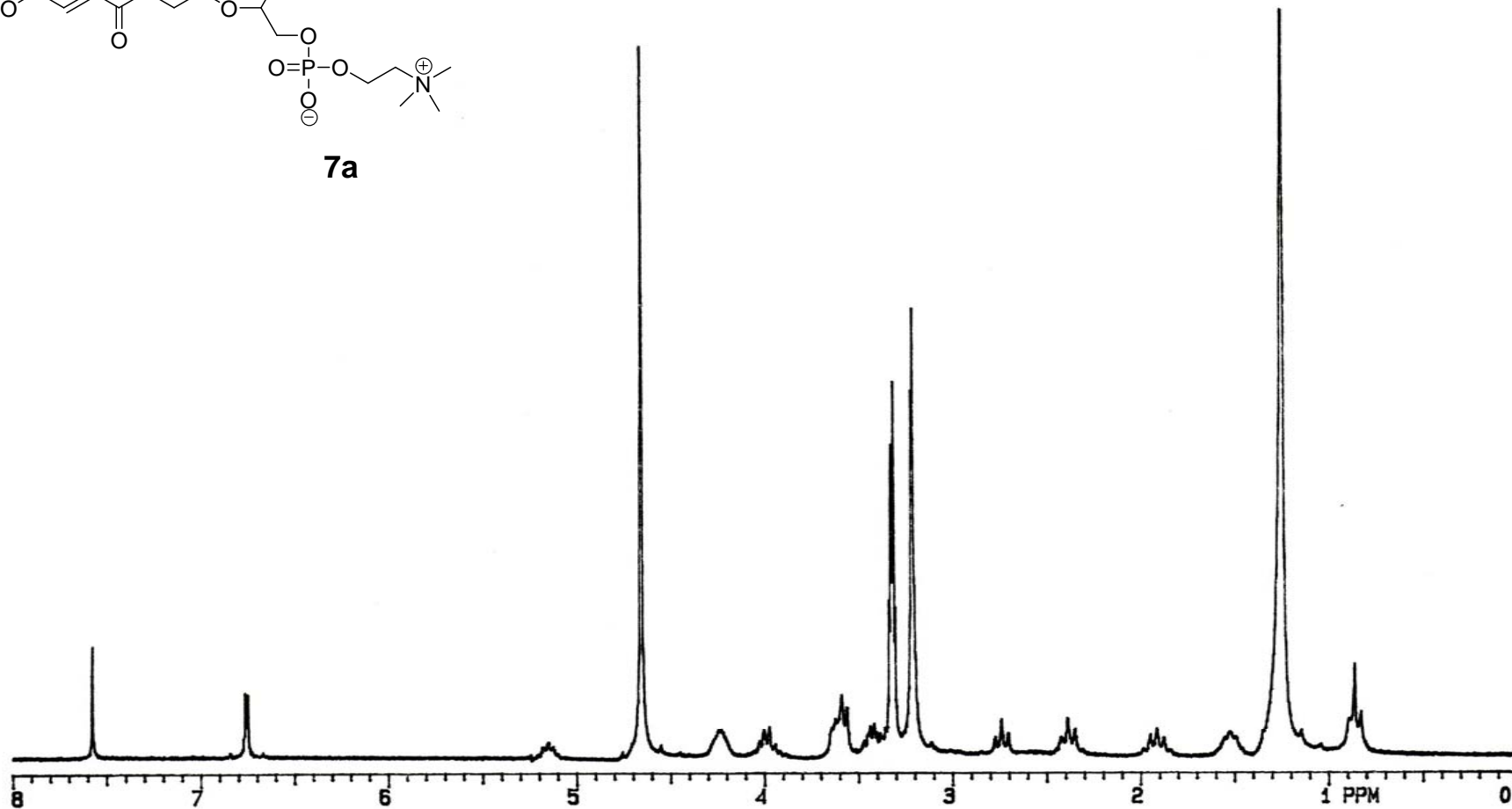


Figure S33. $^1\text{H-NMR}$ (200 M, $\text{CDCl}_3+\text{CD}_3\text{OD}$) of KODiA-PAF (7b).

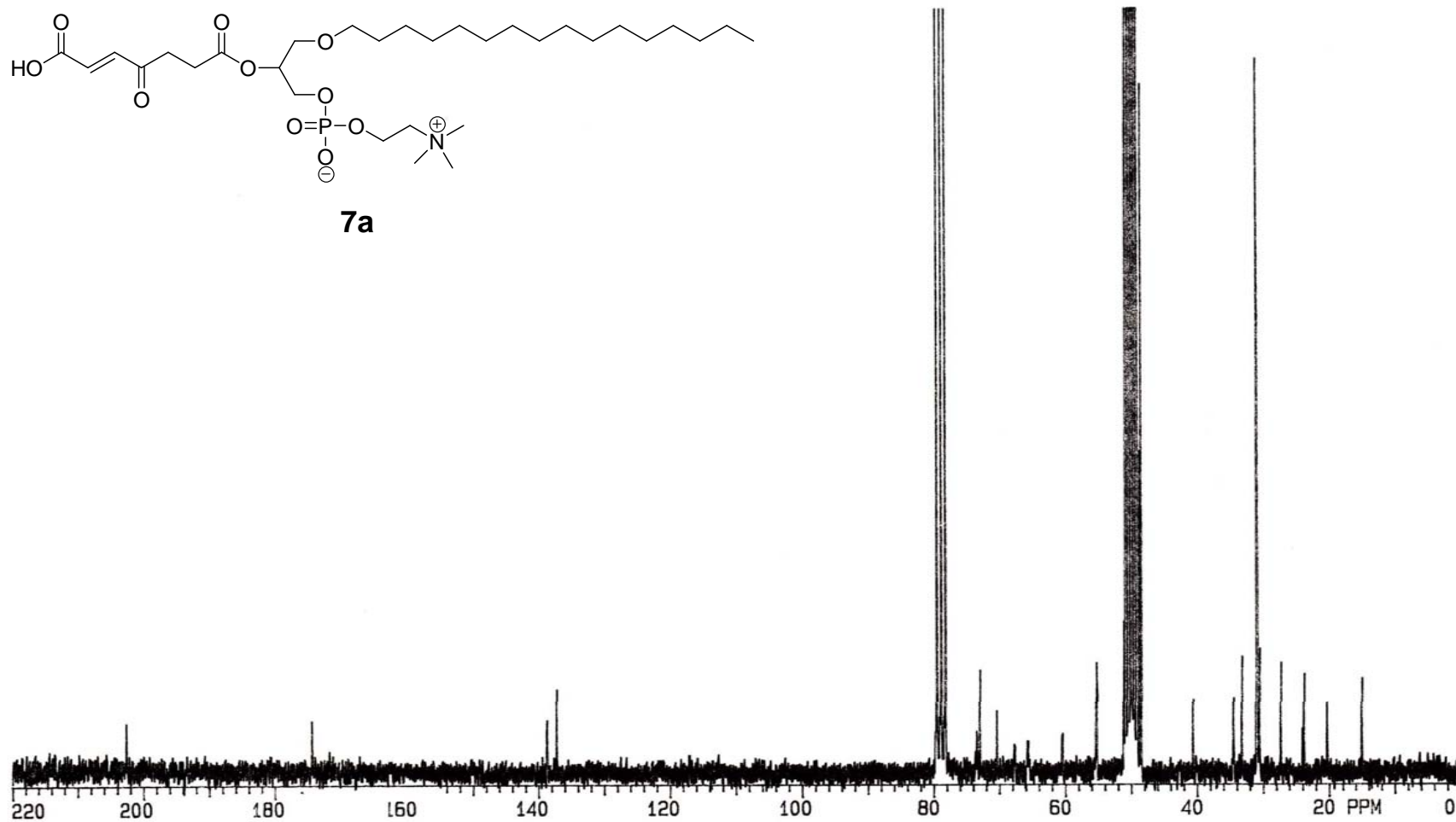
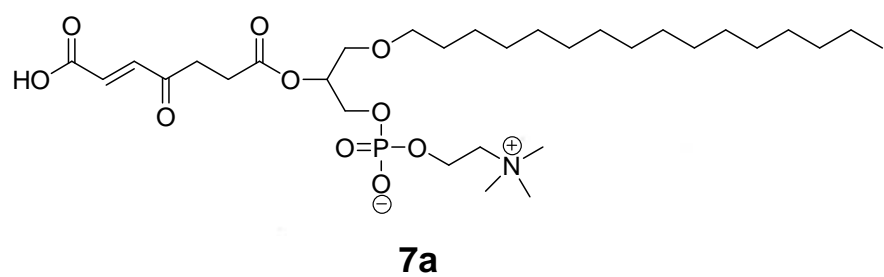


Figure S34. ^{13}C -NMR (50 M, $\text{CDCl}_3+\text{CD}_3\text{OD}$) of KODiA-PAF (7b).

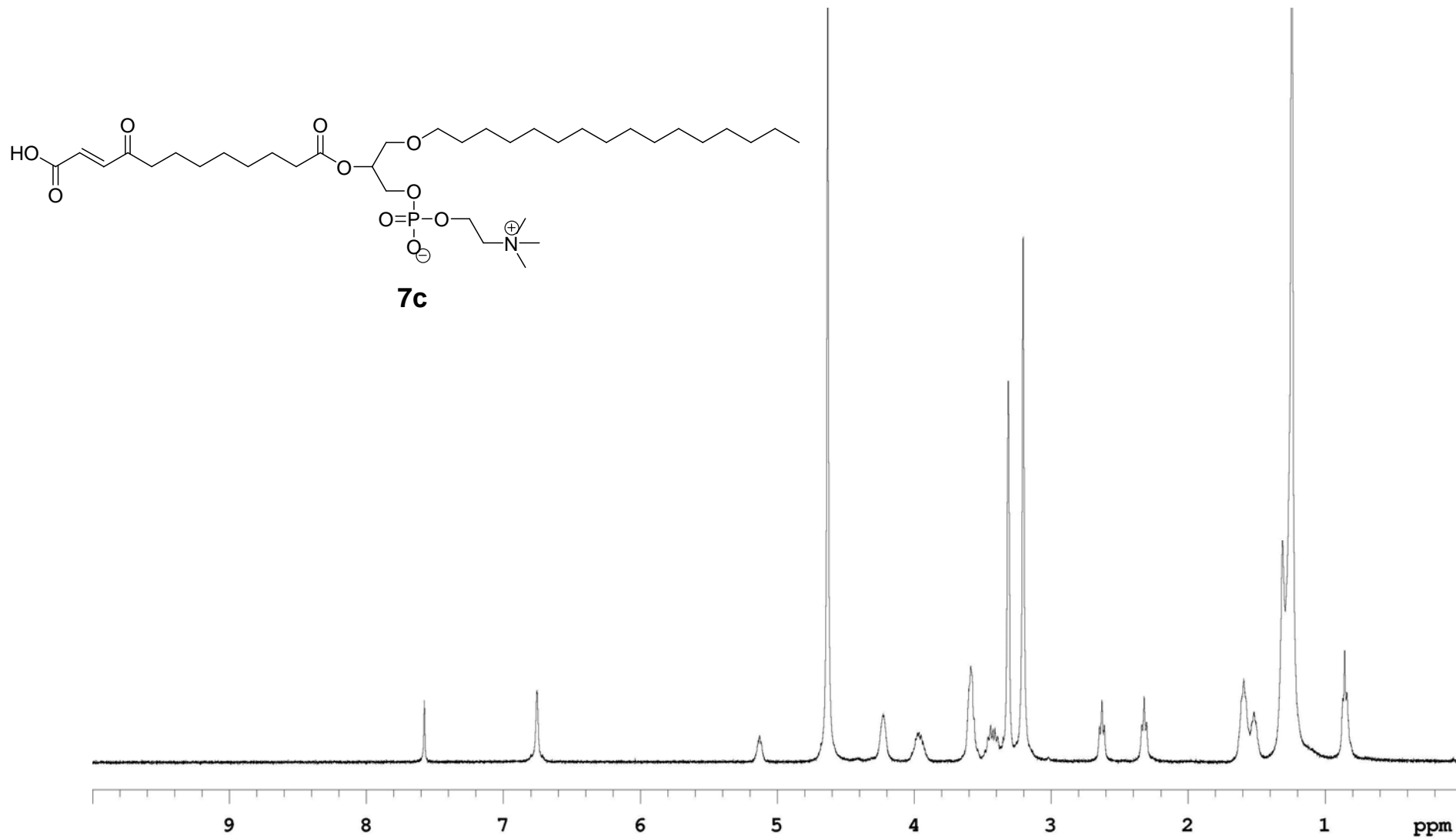


Figure S35. ¹H-NMR (400 M, CDCl₃+CD₃OD) of KDdiA-PAF (7c).

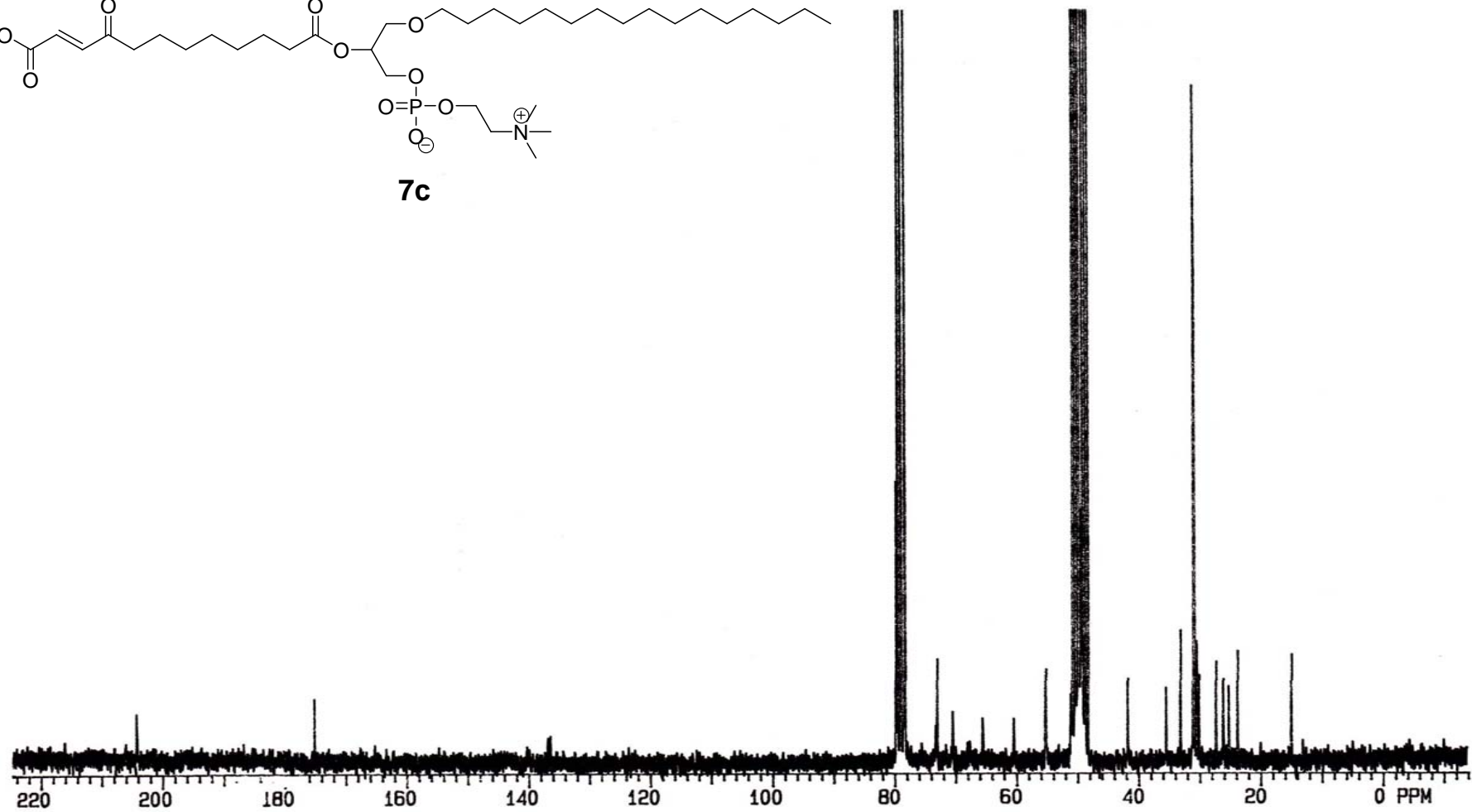
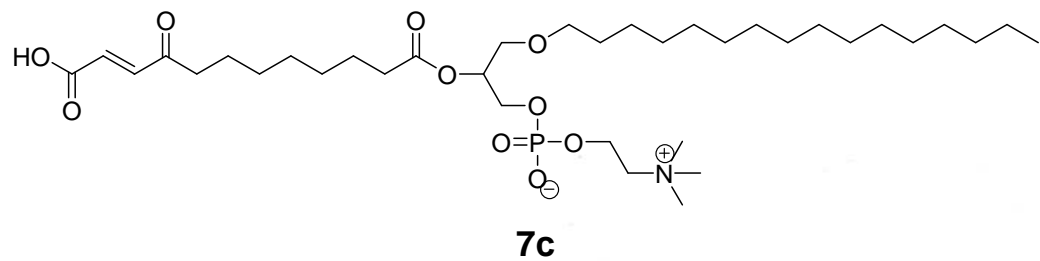


Figure S36. ^{13}C -NMR (50 M, $\text{CDCl}_3+\text{CD}_3\text{OD}$) of KDdiA-PAF (7c).

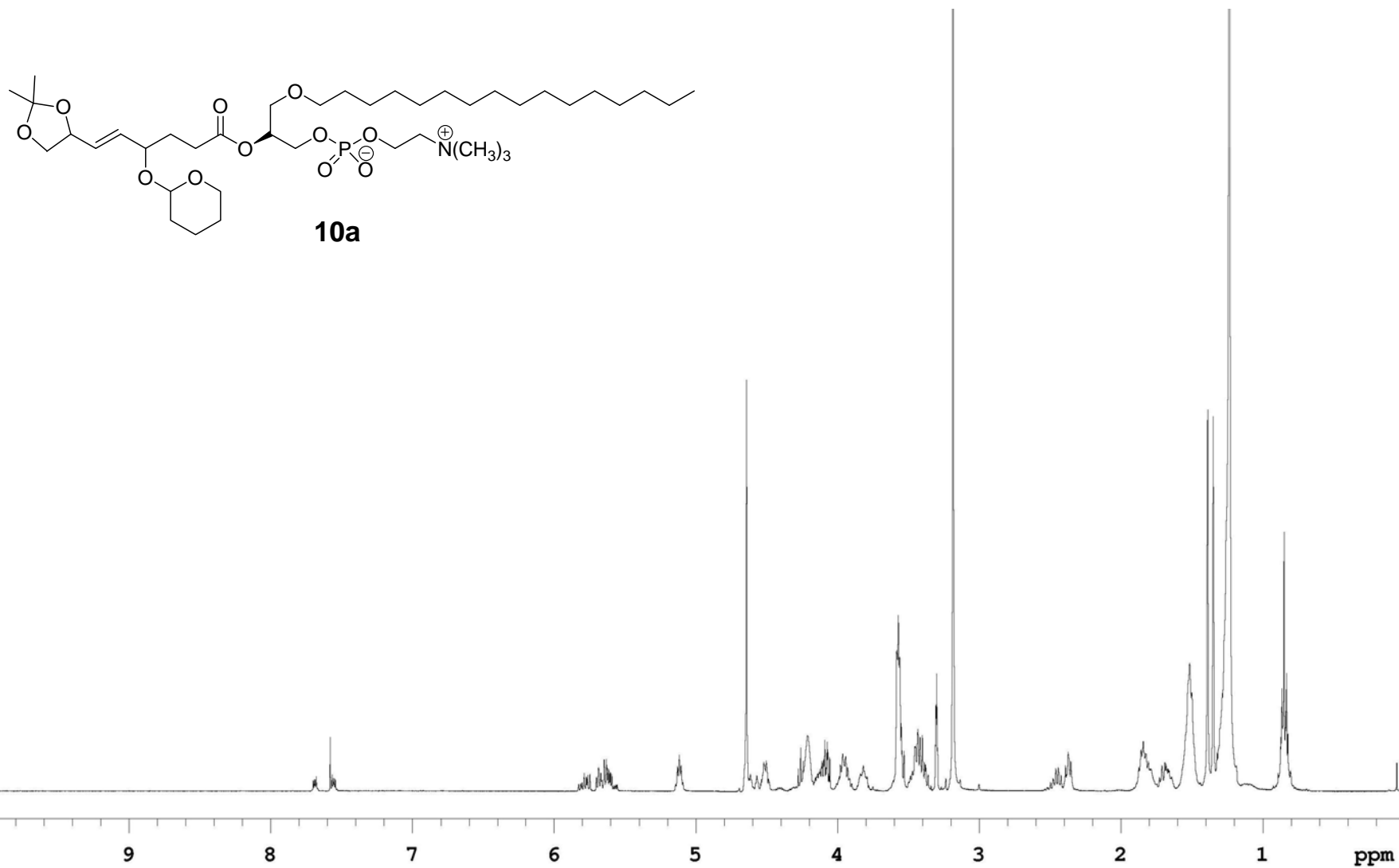


Figure S37. ¹H-NMR (400 M, CDCl₃+CD₃OD) of 1-O-Hexadecyl-2-[6-(2,2-dimethyl-1,3-dioxolan-4-yl)-4-(tetrahydro-2H-pyran-2-yloxy)hex-5-enoyl]-sn-glycero-3-phosphatidylcholine (10a).

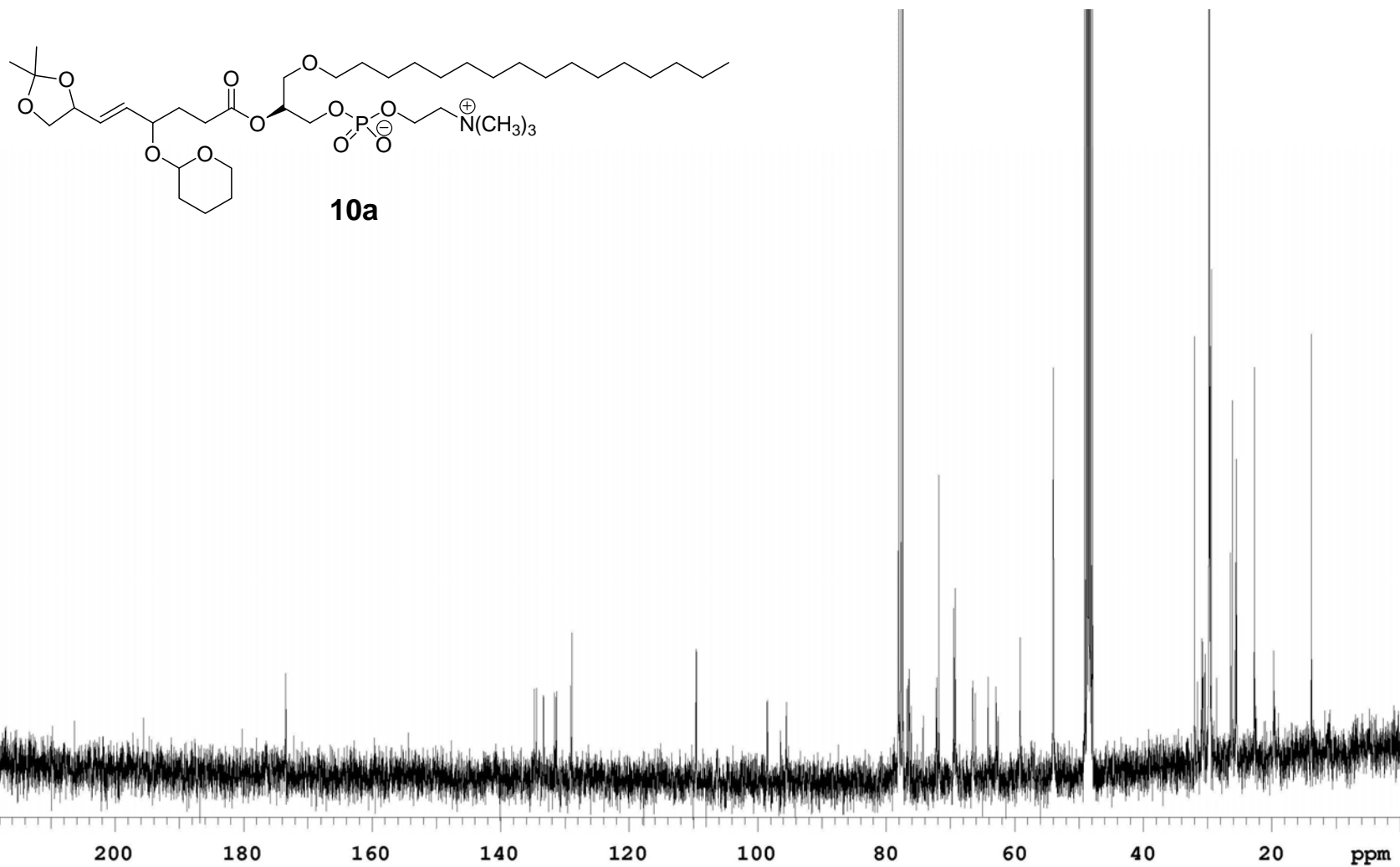


Figure S38. ¹³C-NMR (100 M, CDCl₃+CD₃OD) of 1-O-Hexadecyl-2-[6-(2, 2-dimethyl-1, 3-dioxolan-4-yl)-4-(tetrahydro-2H-pyran-2-yloxy)hex-5-enoyl]-sn-glycero-3-phosphatidylcholine (10a).

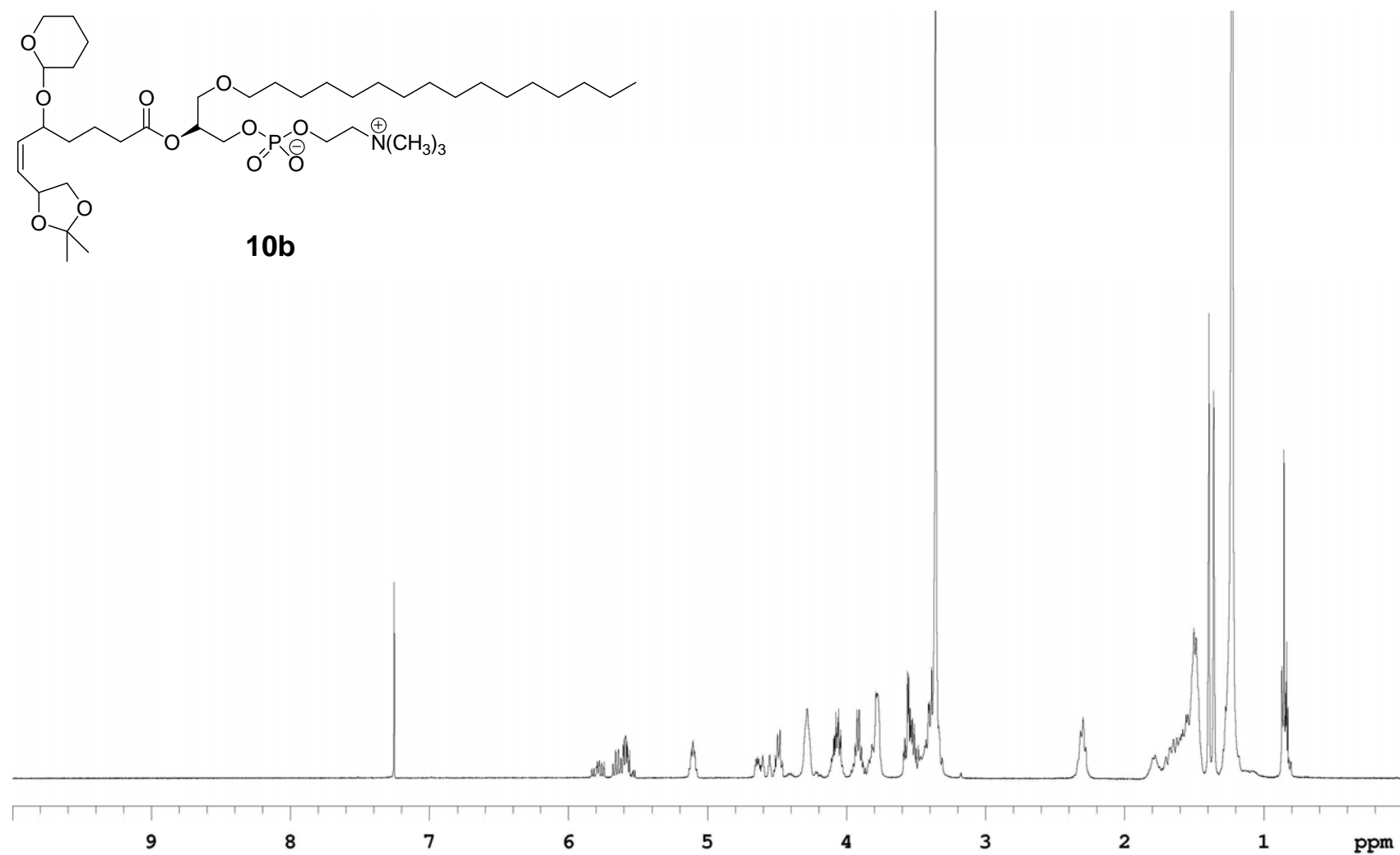
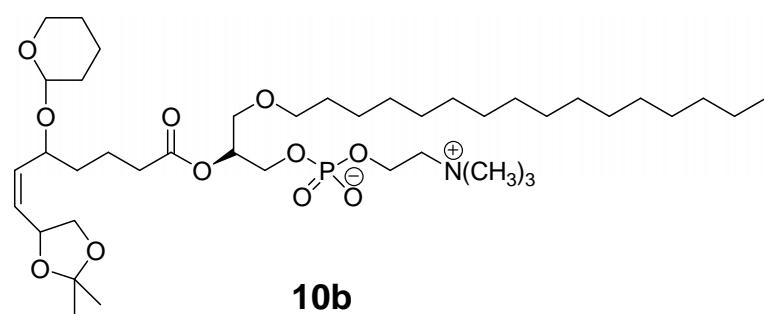


Figure S39. $^1\text{H-NMR}$ (400 M, $\text{CDCl}_3+\text{CD}_3\text{OD}$) of 1-O-Hexadecyl-2-[7-(2, 2-dimethyl-1, 3-dioxolan-4-yl)-5-(tetrahydro-2H-pyran-2-yloxy)hept-6-enoyl]-sn-glycero-3-phosphatidylcholine (10b).

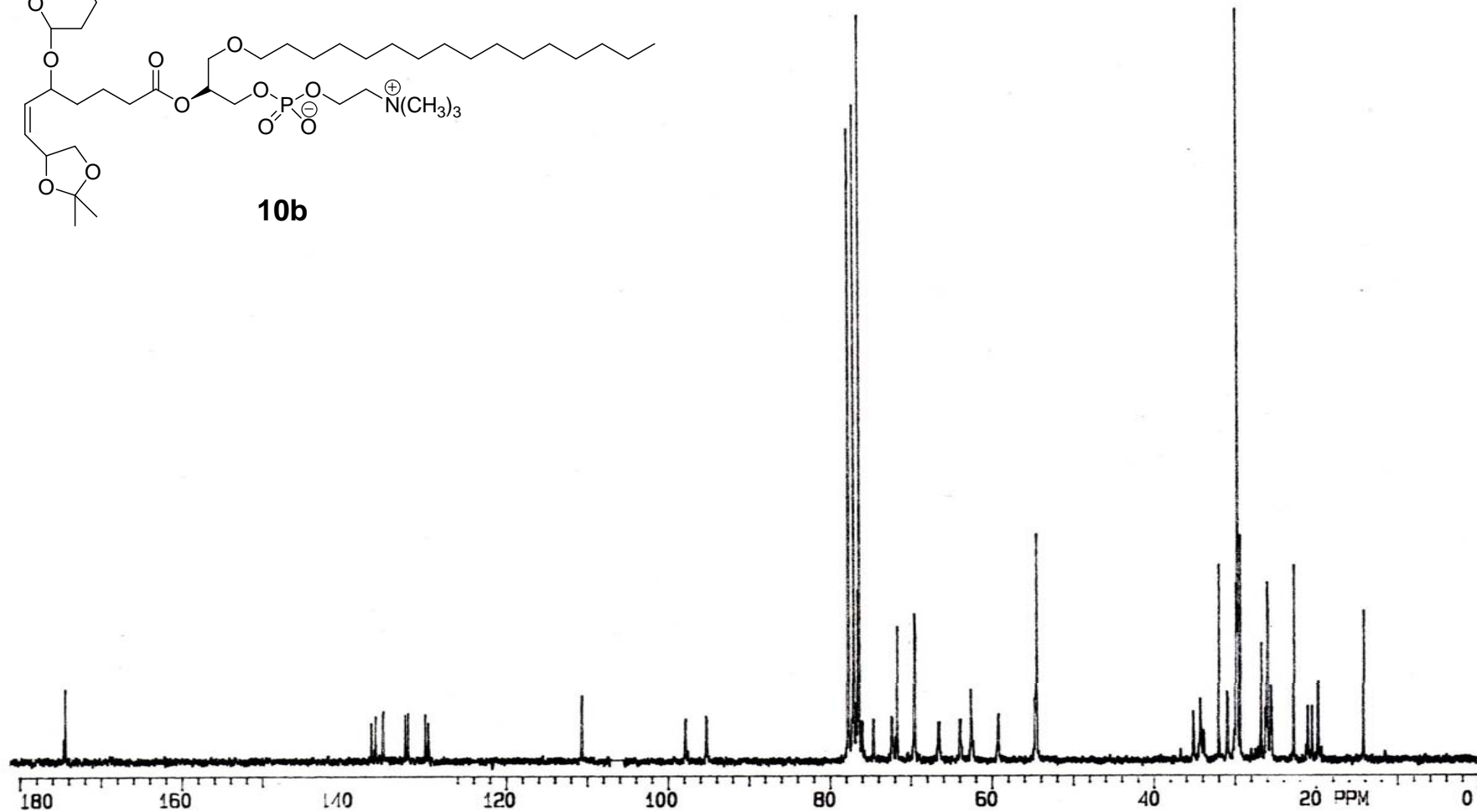
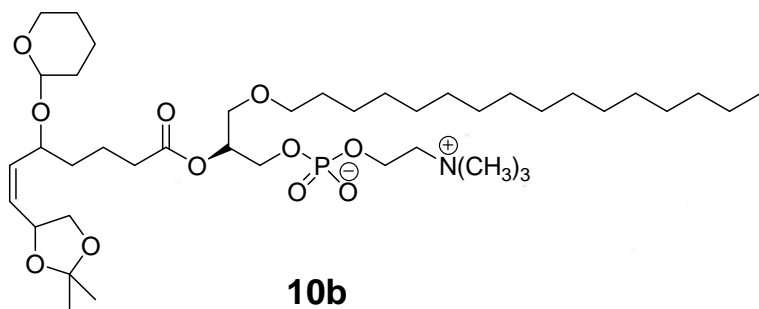


Figure S40. ¹³C-NMR (50 M, CDCl₃) of 1-O-Hexadecyl-2-[7-(2, 2-dimethyl-1, 3-dioxolan-4-yl)-5-(tetrahydro-2H-pyran-2-yloxy)hept-6-enoyl]-sn-glycero-3-phosphatidylcholine (10b).

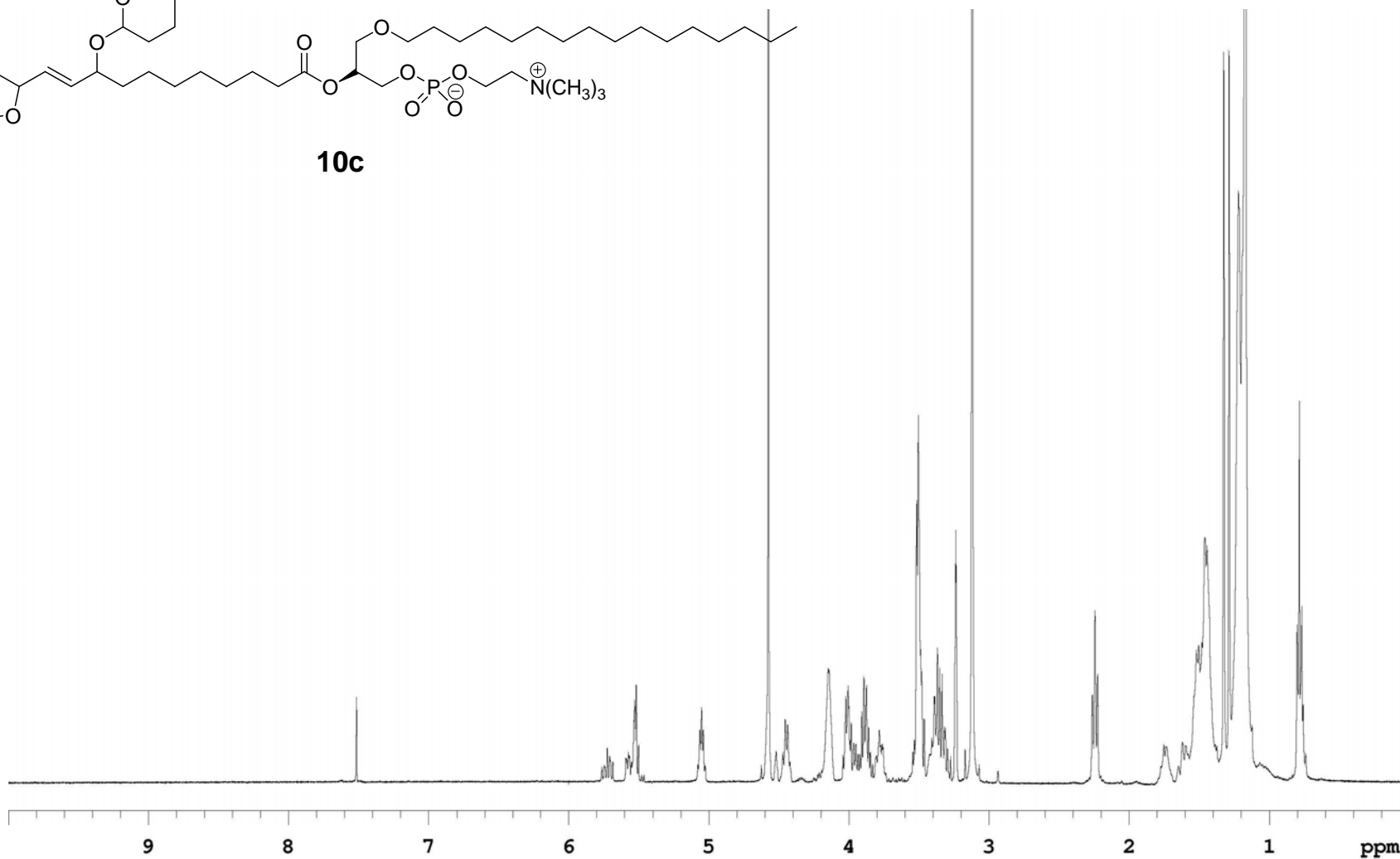
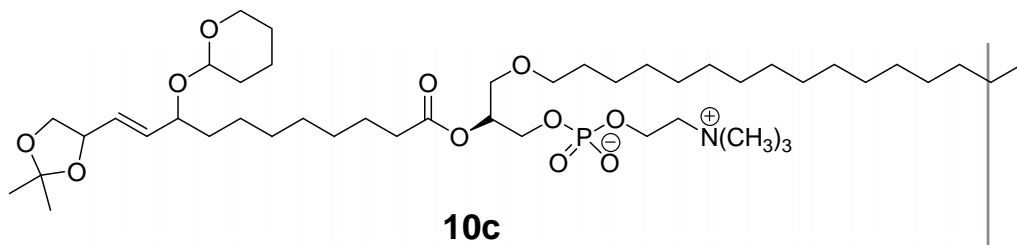


Figure S41. ¹H-NMR (400 M, CDCl₃+CD₃OD) of 1-O-Hexadecyl-2-[11-(2, 2-dimethyl-1, 3-dioxolan-4-yl)-9-(tetrahydro-2H-pyran-2-yloxy)-undec-10-enoyl]-sn-glycero-3-phosphatidylcholine (10c).

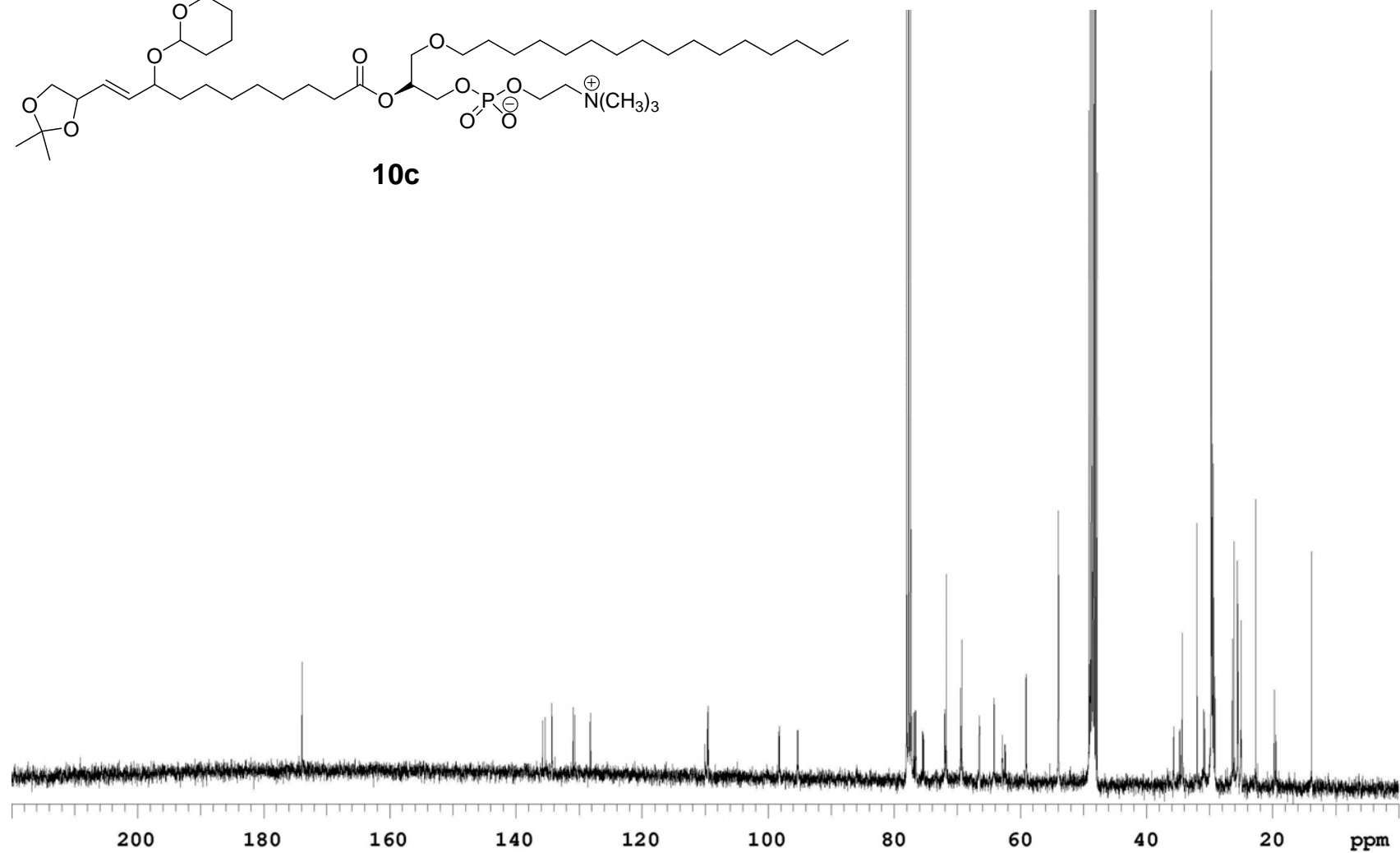
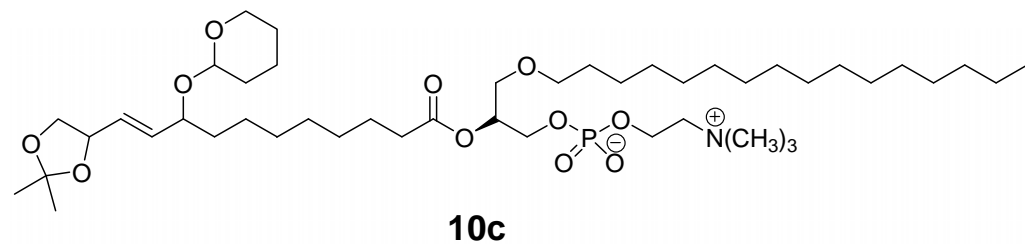


Figure S42. ^{13}C -NMR (100 M, $\text{CDCl}_3 + \text{CD}_3\text{OD}$) of 1-O-Hexadecyl-2-[11-(2, 2-dimethyl-1, 3-dioxolan-4-yl)-9-(tetrahydro-2H-pyran-2-yloxy)-undec-10-enoyl]-sn-glycero-3-phosphatidylcholine (10c).

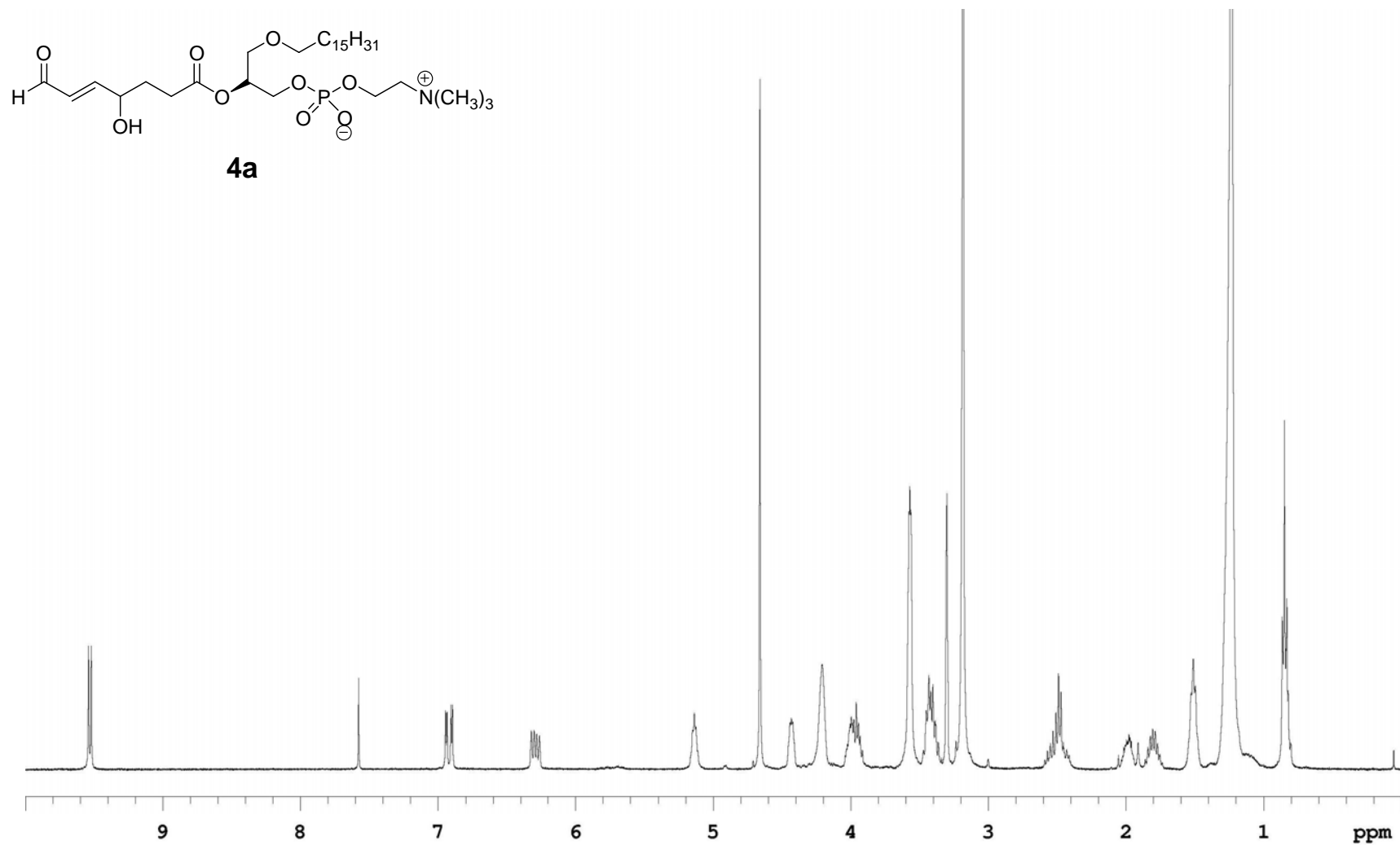
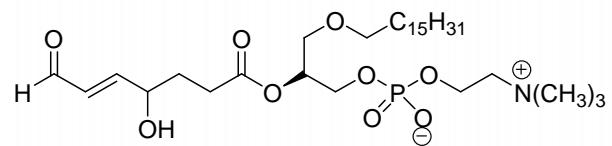


Figure S43. ¹H-NMR (400 M, CDCl₃+CD₃OD) of HOHA-PAF (4a).



4a

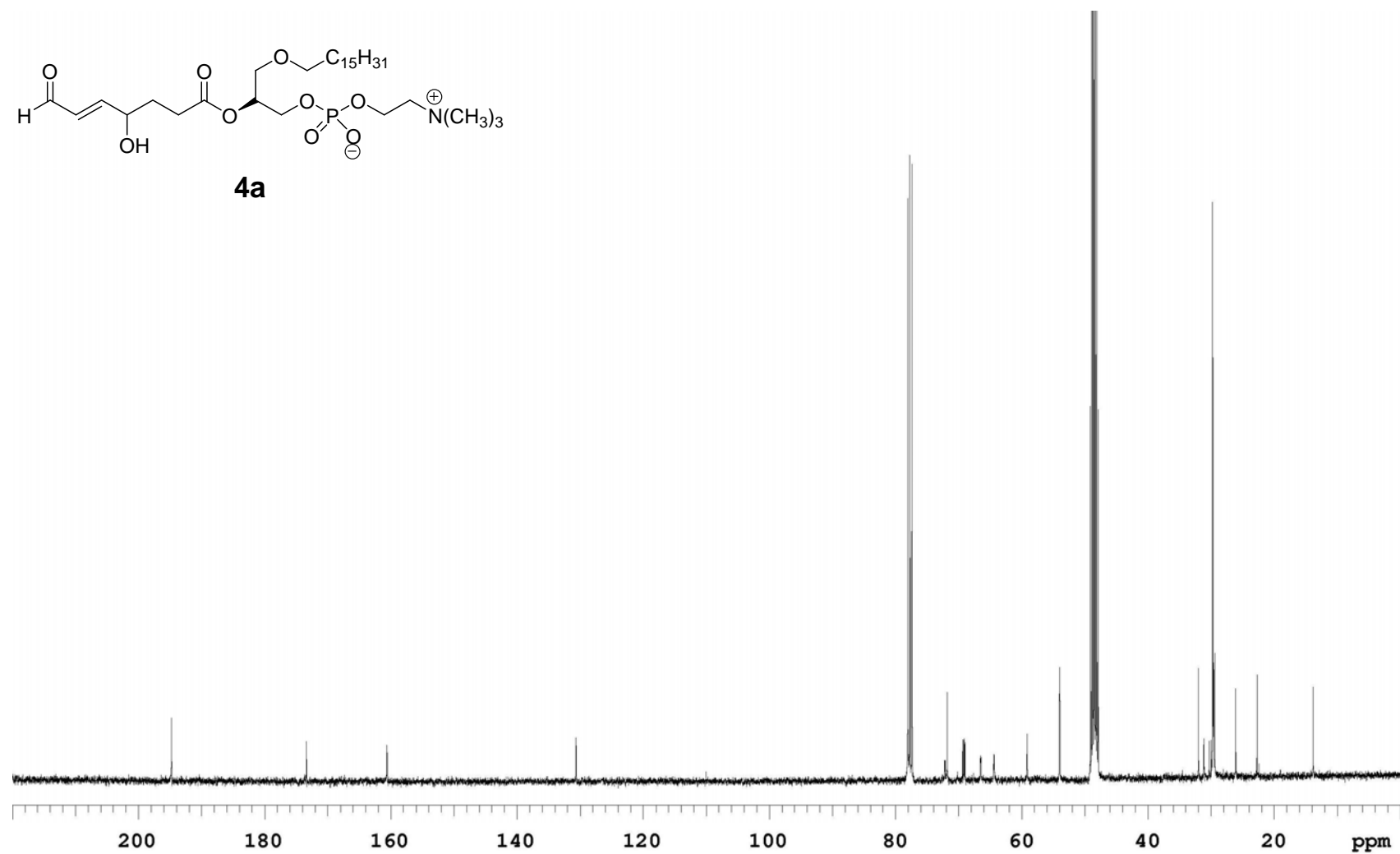


Figure S44. ¹³C-NMR (100 M, CDCl₃+CD₃OD) of HOHA-PAF (4a).

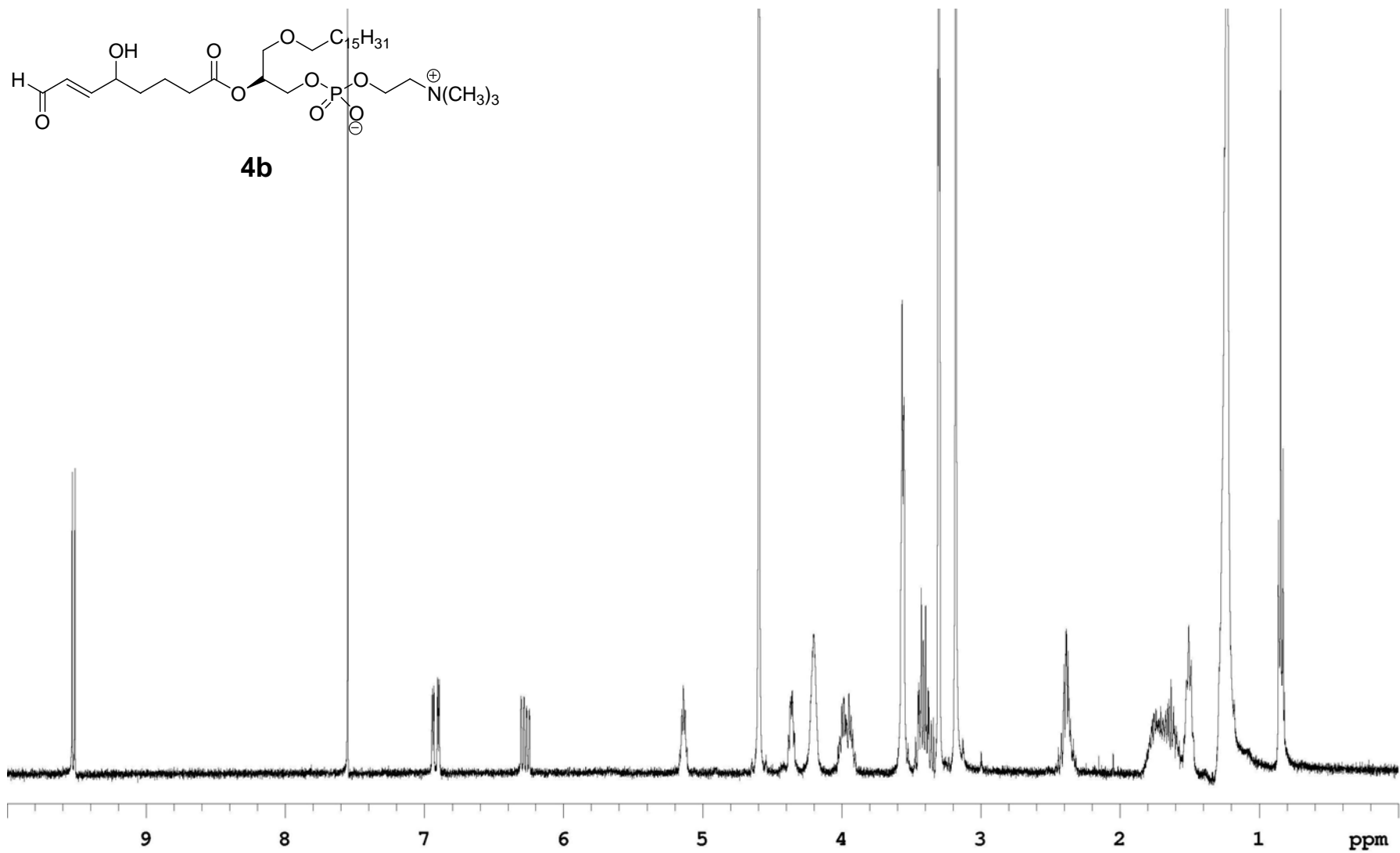
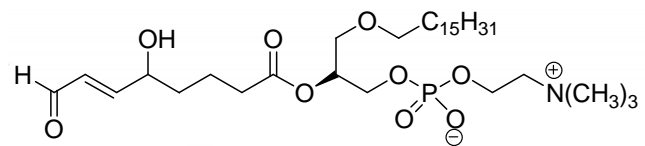


Figure S45. ¹H-NMR (400 M, CDCl₃+CD₃OD) of HOOA-PAF (4b).



4b

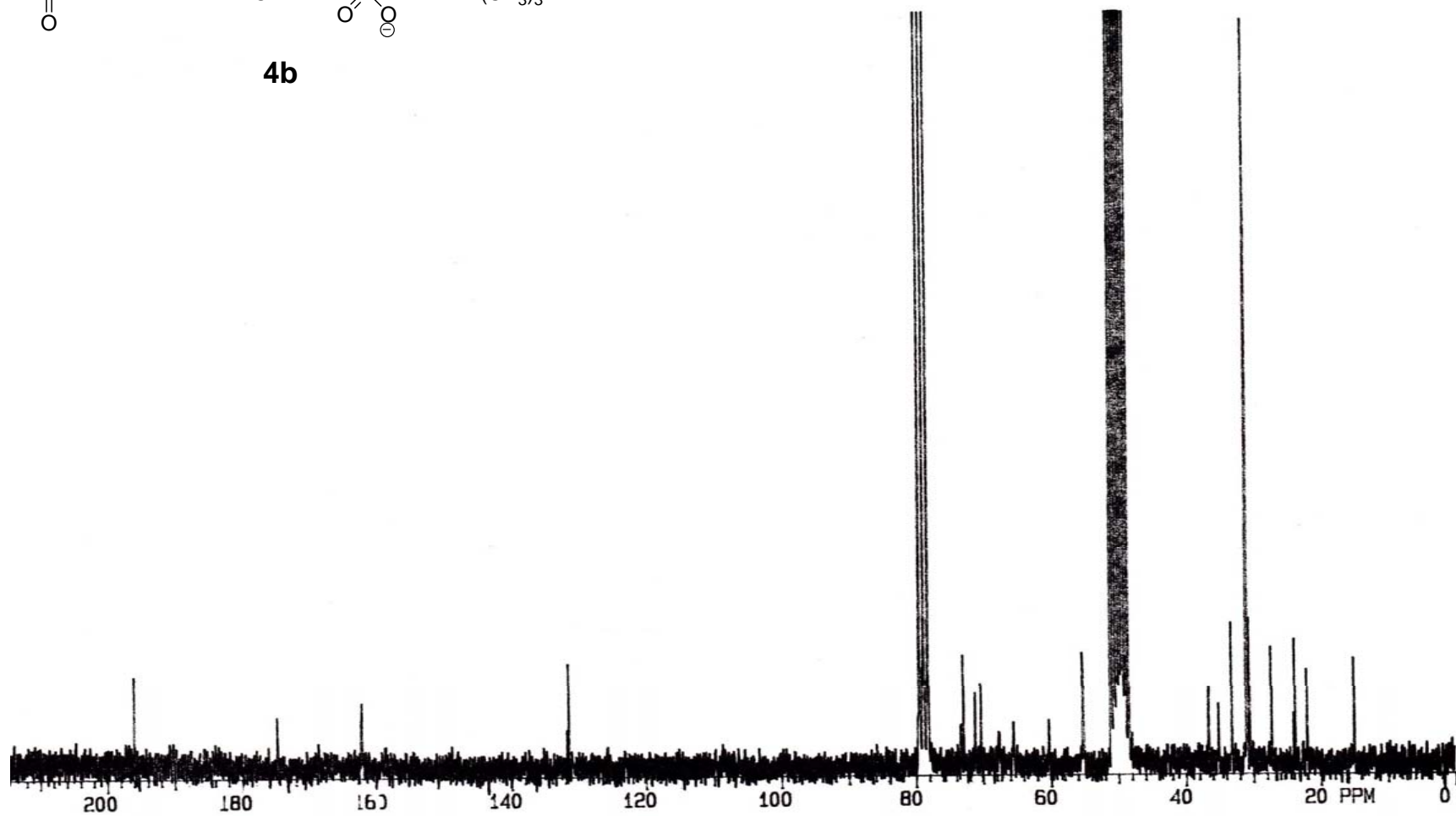


Figure S46. ¹³C-NMR (50 M, CDCl₃+CD₃OD) of HOOA-PAF (4b).

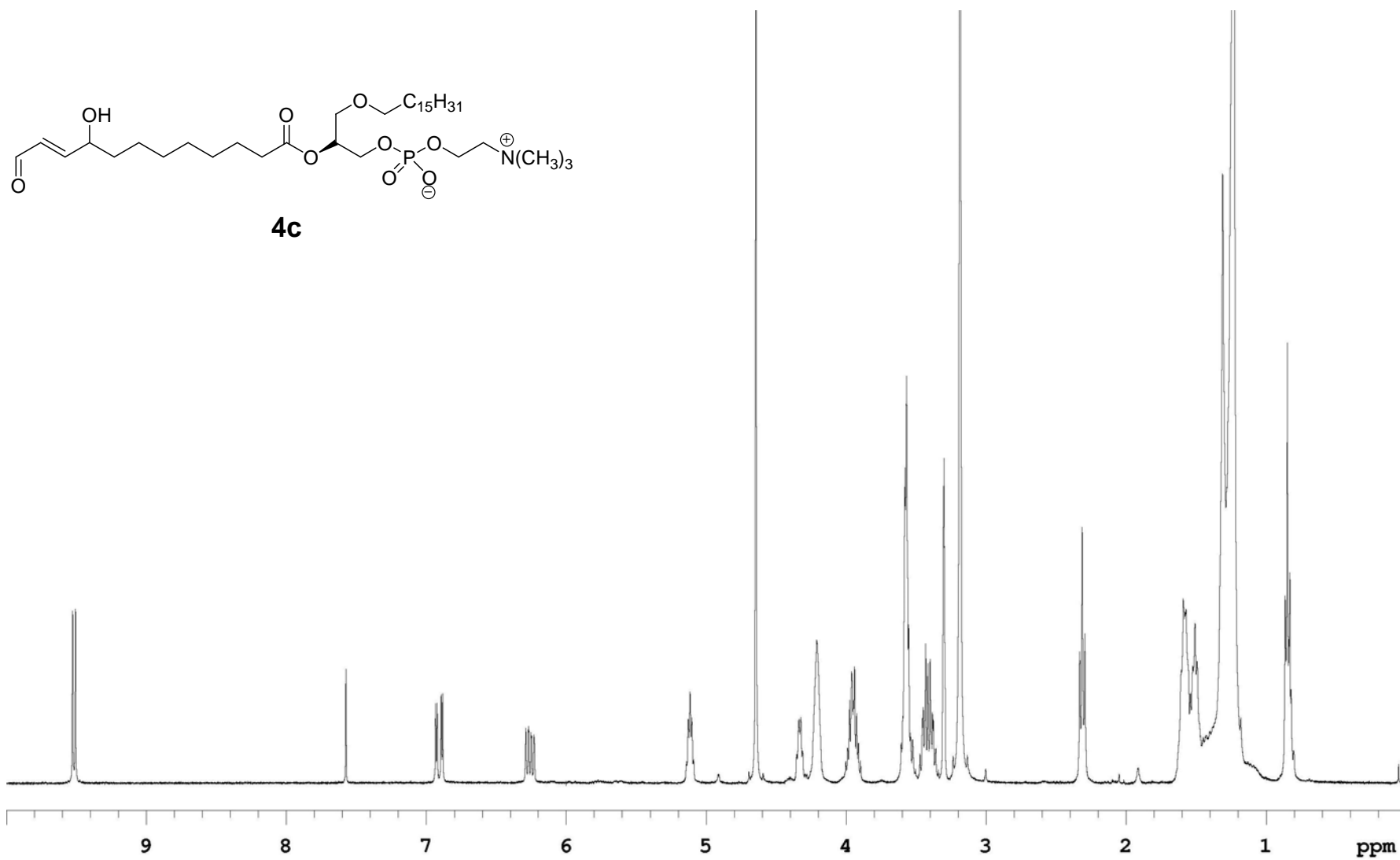


Figure S47. ¹H-NMR (400 M, CDCl₃+CD₃OD) of HODA-PAF (4c).

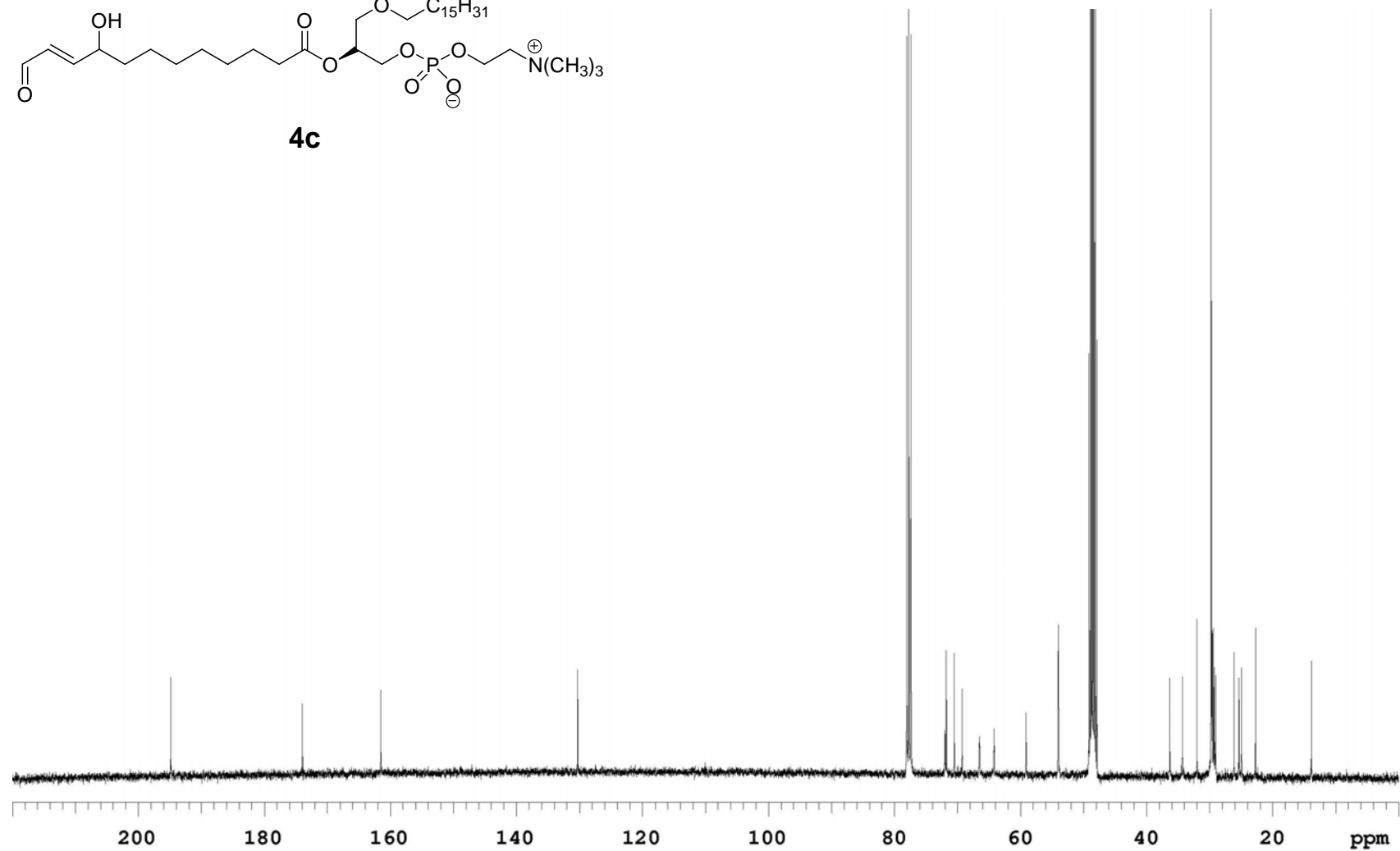
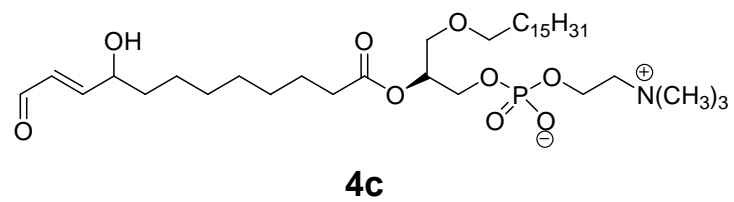


Figure S48. ^{13}C -NMR (100 M, $\text{CDCl}_3+\text{CD}_3\text{OD}$) of HODA-PAF (4c).

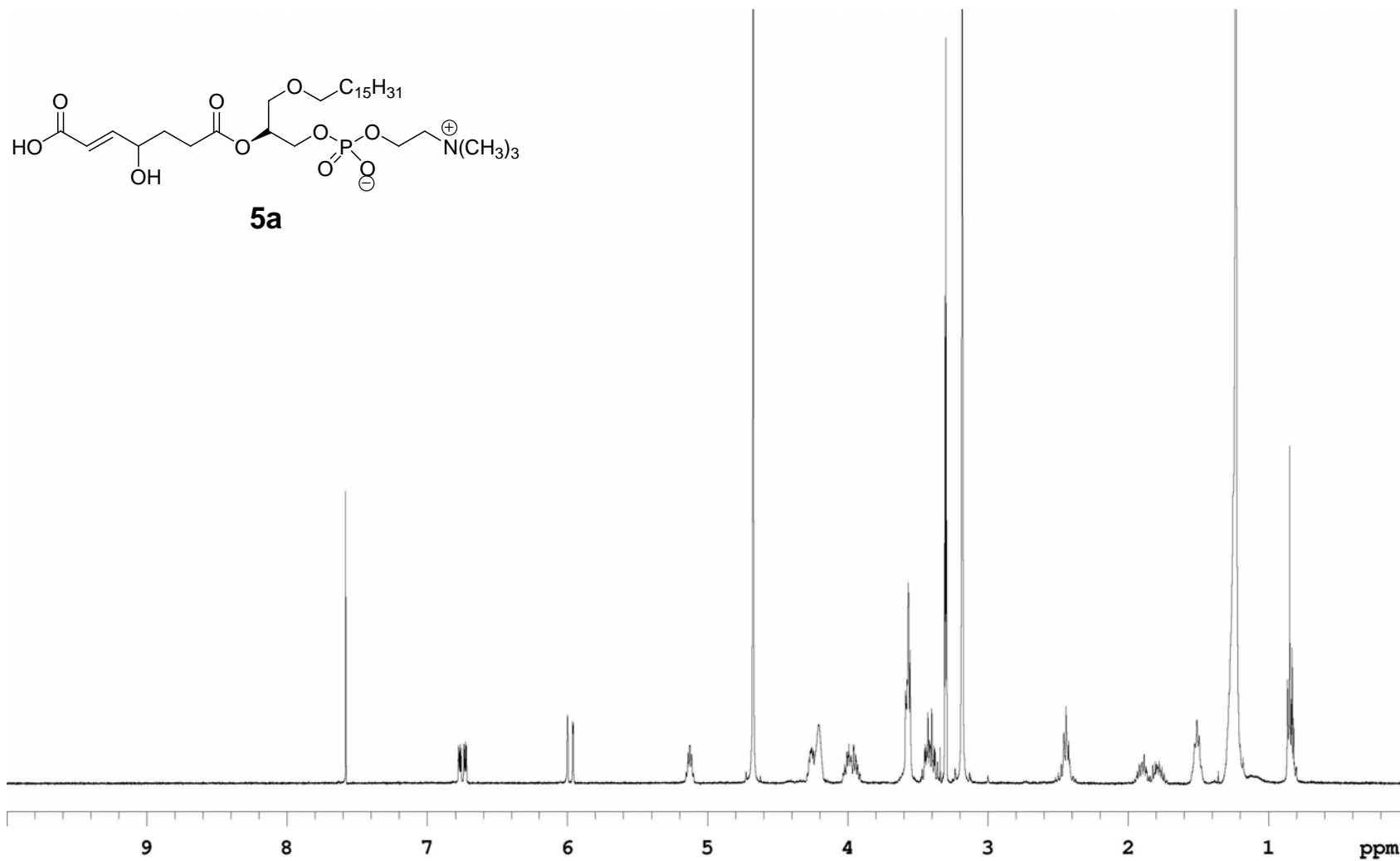
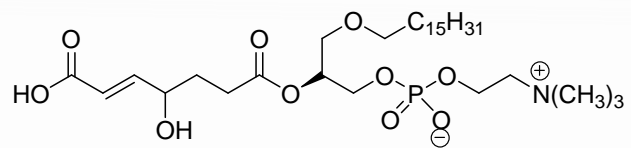


Figure S49. ¹H-NMR (400 M, CDCl₃+CD₃OD) of HHdiA-PAF (5a).



5a

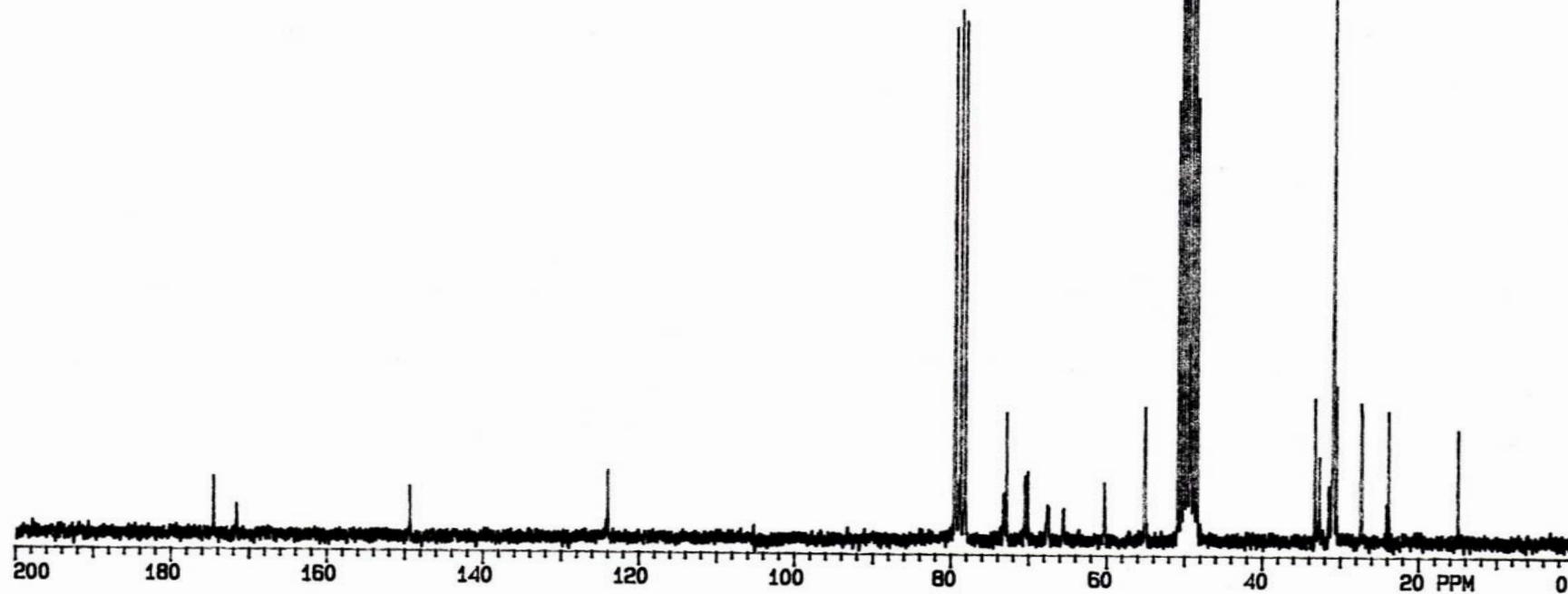
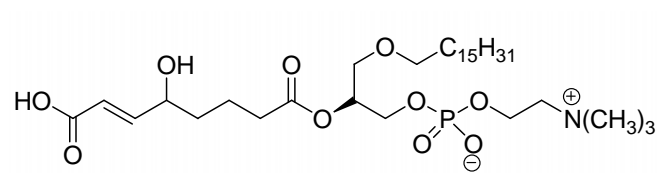


Figure S50. ¹³C-NMR (50 M, CDCl₃+CD₃OD) of HHdiA-PAF (5a).



5b

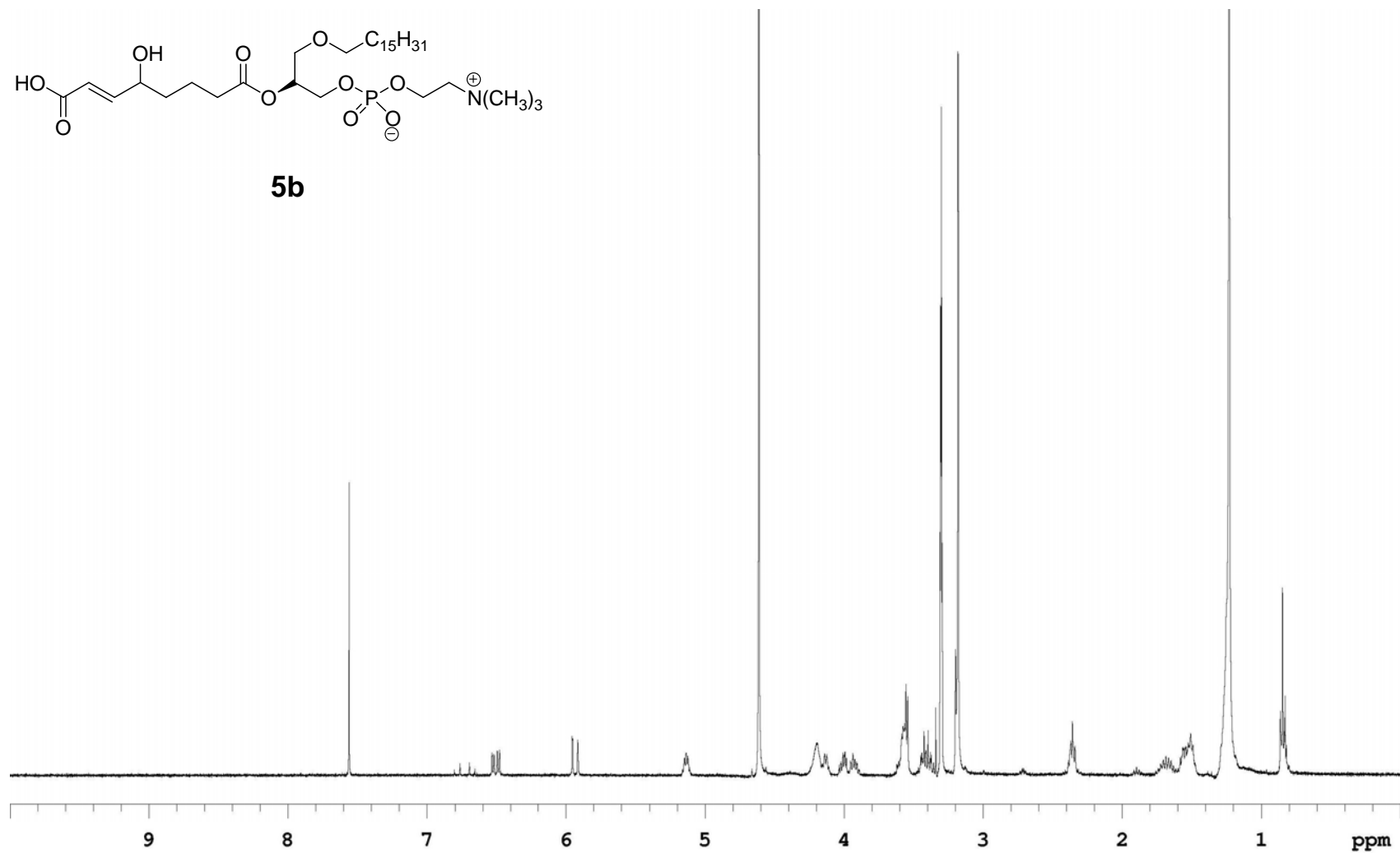


Figure S51. ¹H-NMR (400 M, CDCl₃+CD₃OD) of HOdiA-PAF (5b).

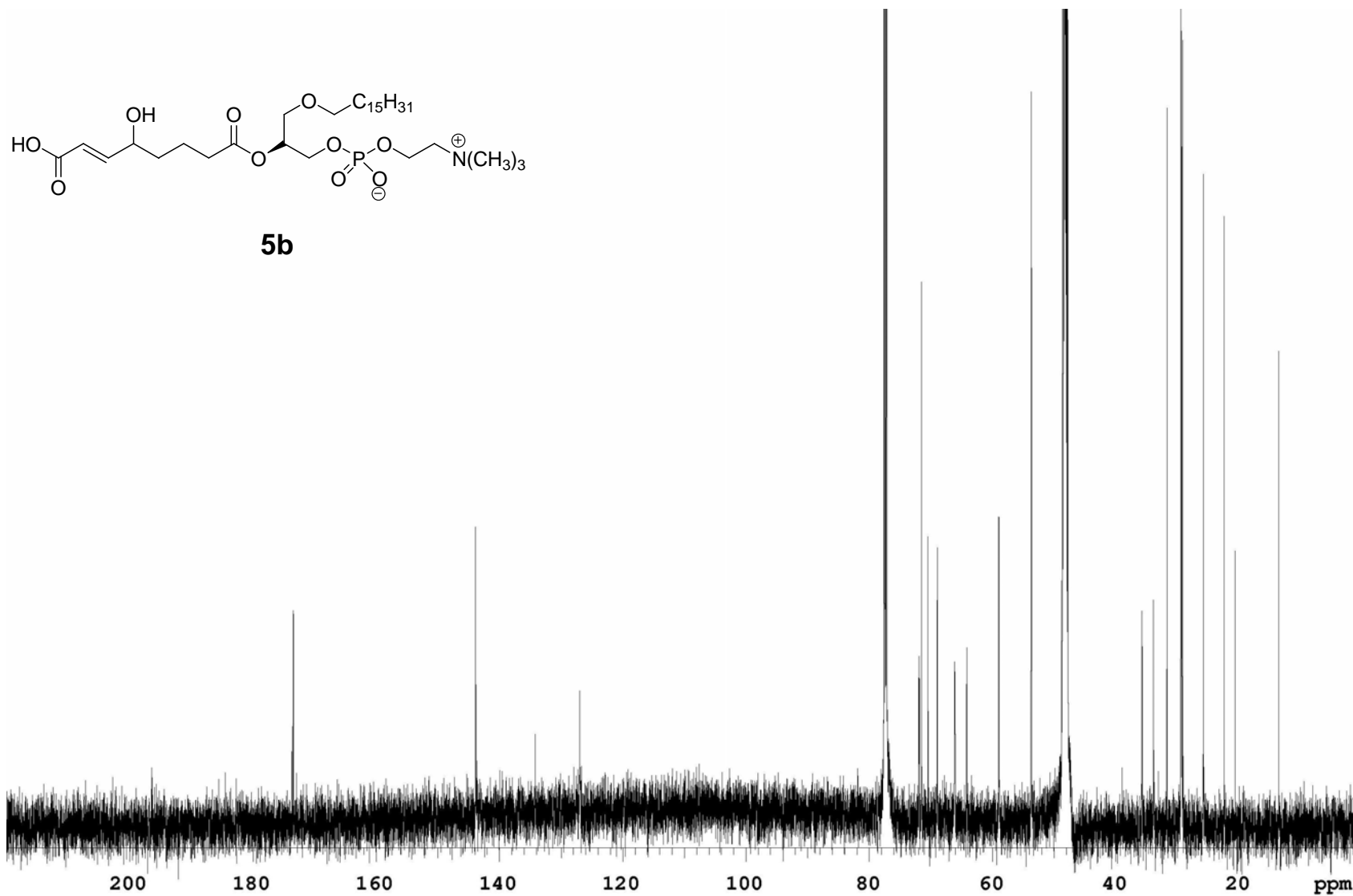


Figure S52. ¹³C-NMR (100 M, CDCl₃+CD₃OD) of HOdiA-PAF (5b).

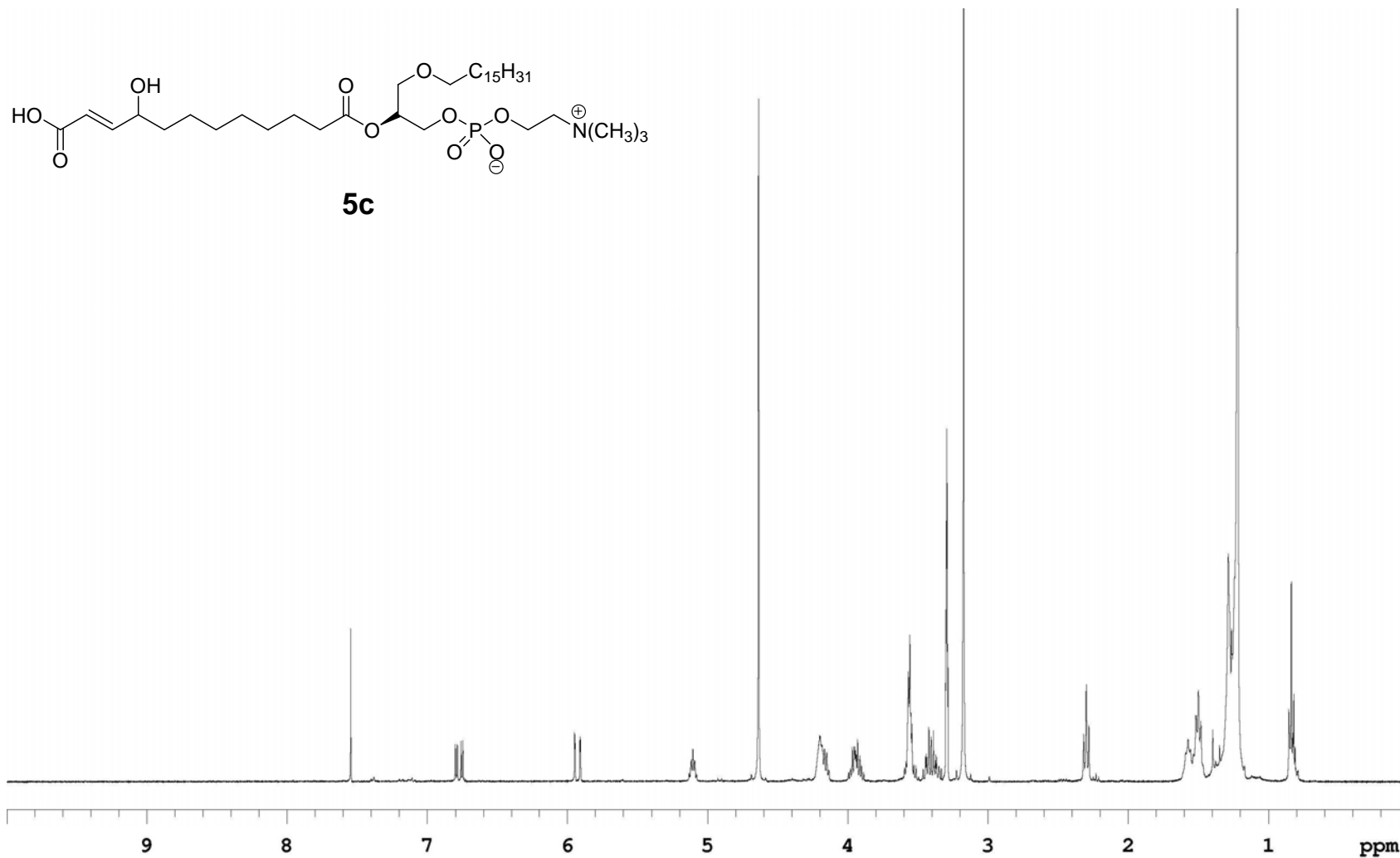


Figure S53. ¹H-NMR (400 M, CDCl₃+CD₃OD) of HDdiA-PAF (5c).

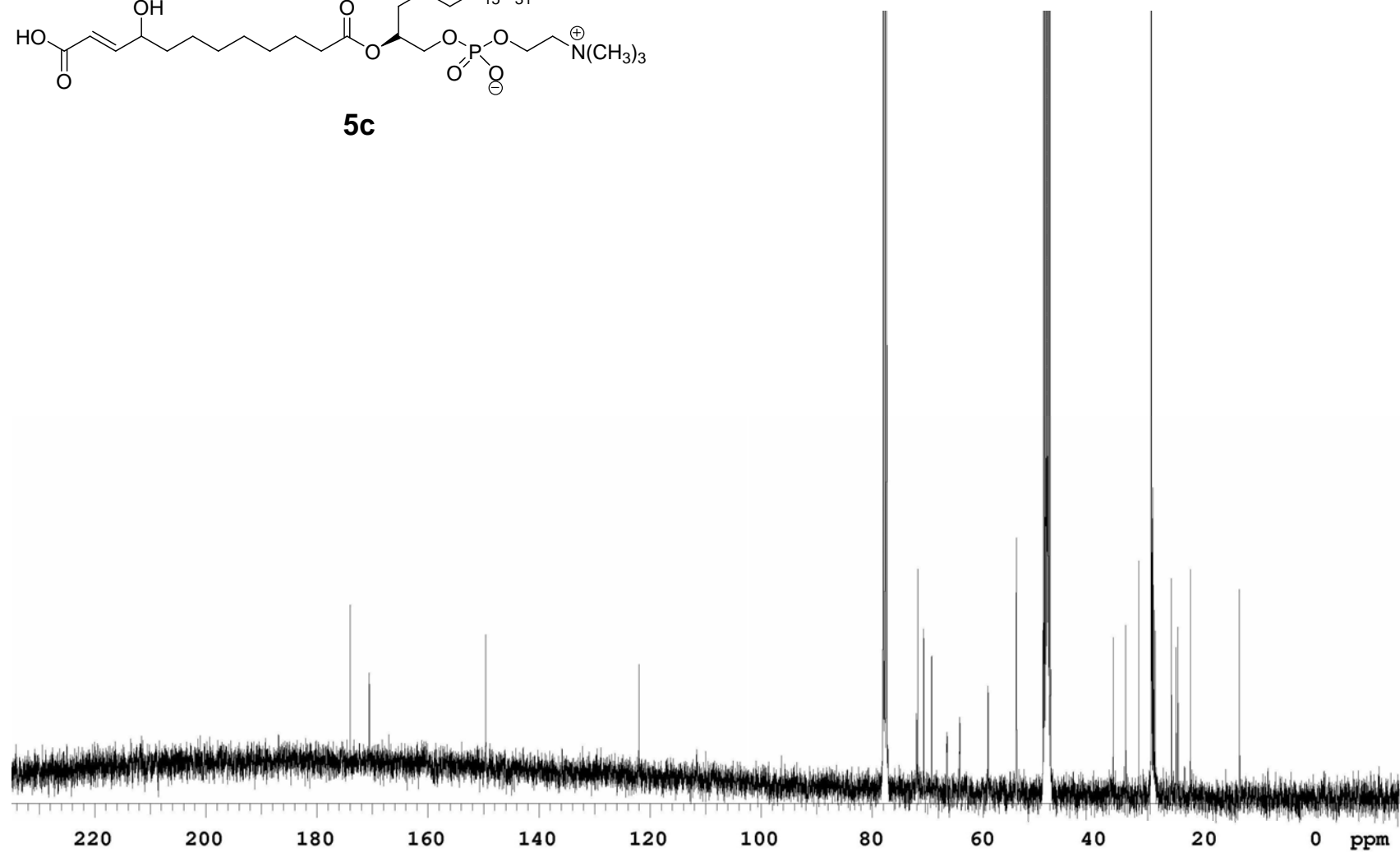
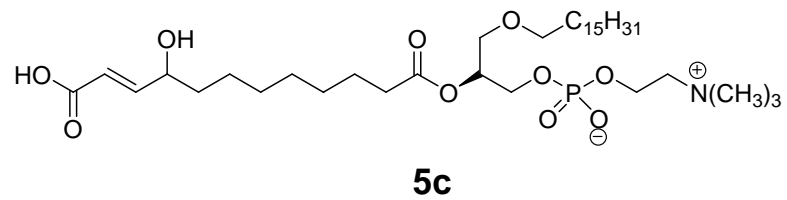


Figure S54. ^{13}C -NMR (100 M, $\text{CDCl}_3+\text{CD}_3\text{OD}$) of HDdiA-PAF (**5c**).

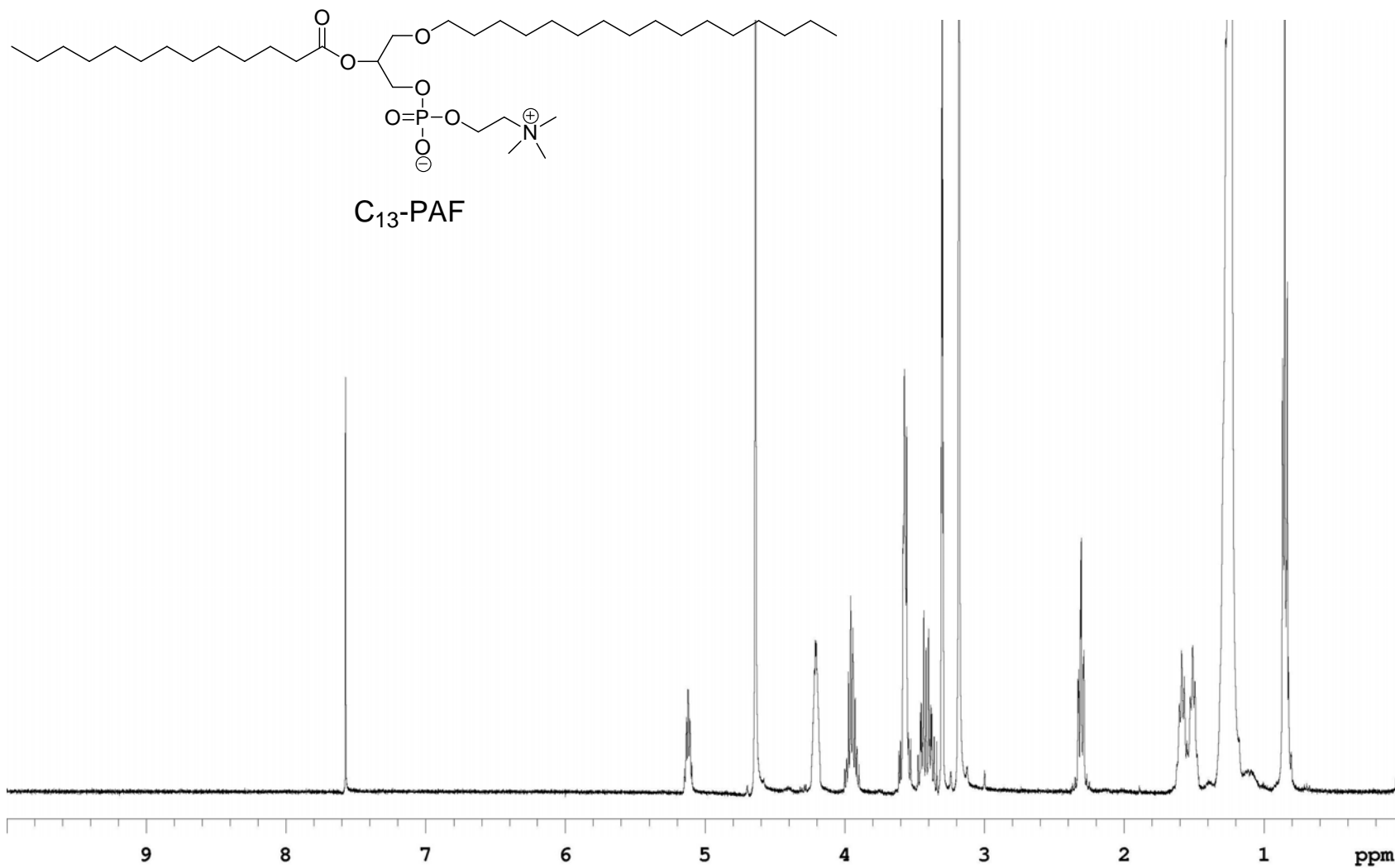
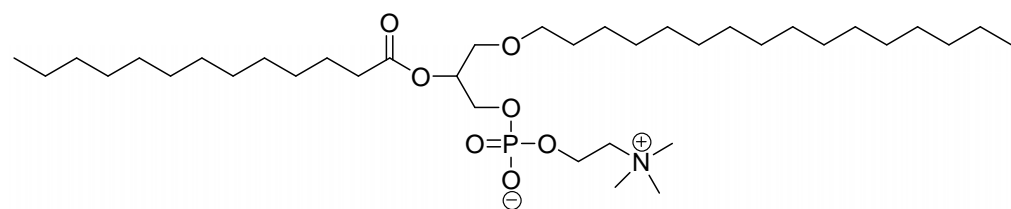


Figure S55. ¹H-NMR (400 M, CDCl₃+CD₃OD) of C₁₃-PAF.



C₁₃-PAF

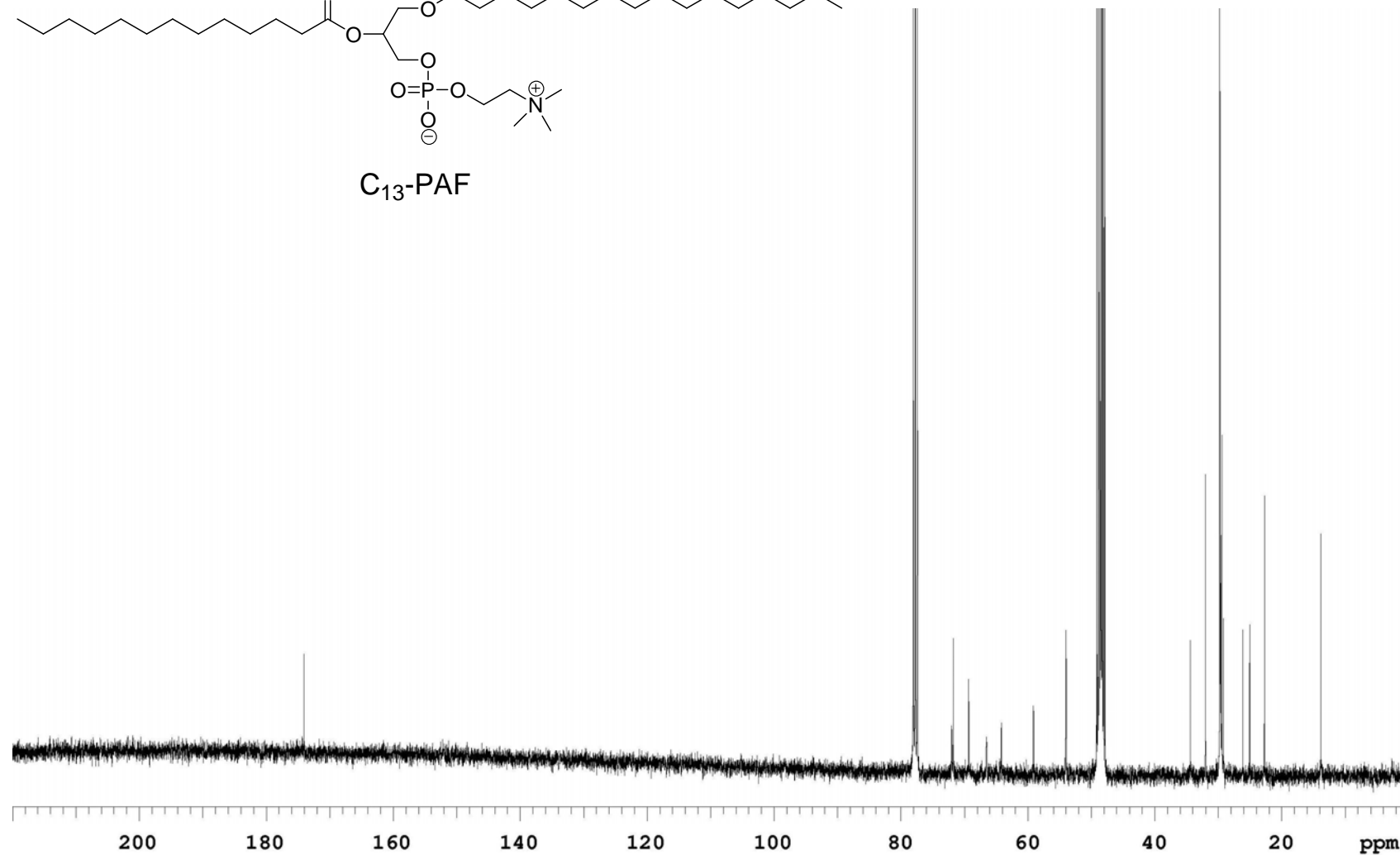


Figure S56. ¹³C-NMR (100 M, CDCl₃+CD₃OD) of C₁₃-PAF.

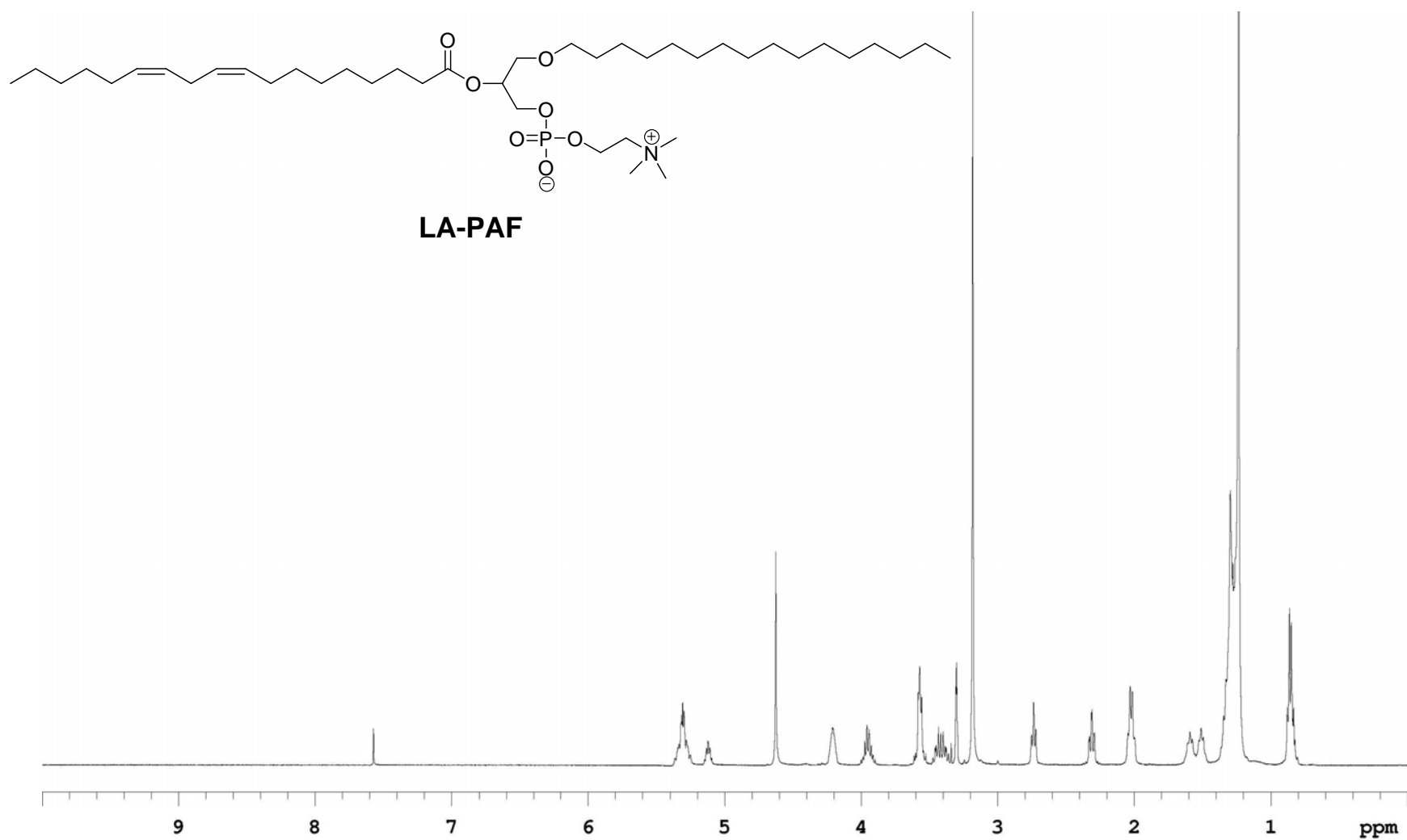


Figure S57. ¹H-NMR (400 M, CDCl₃+CD₃OD) of LA-PAF.

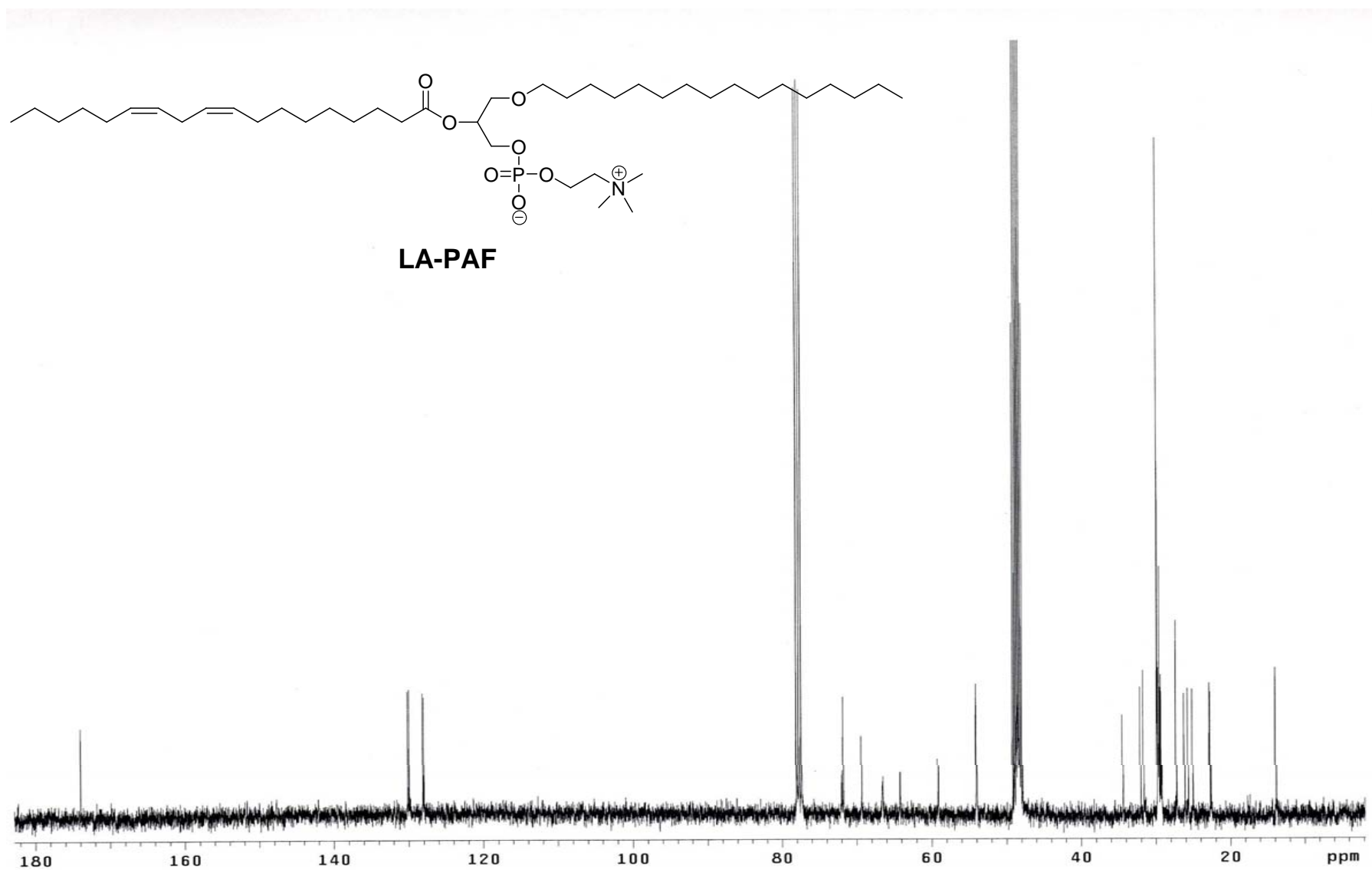


Figure S58. ¹³C-NMR (100 M, CDCl₃+CD₃OD) of LA-PAF.

Microphosphorus Assay. The amount of synthetic lipid was calibrated with a standard microphosphorus assay,³⁰ which was modified to measure phospholipids at the level of 10 to 20 g of phospholipids. Lipid (15 – 25 g) was digested with 0.2 mL of perchloric acid (72 %) in a glass 5-mL disposable cell culture tube, which was heated to boiling in a sand bath. A yellow color appeared and then disappeared during the process. Water (2.1 mL), 0.1 mL of aqueous ammonium molybdate (5 %) and 0.1 mL of aqueous amidol reagent containing 1 % amidol (2, 4-diaminophenol dihydrochloride) and sodium bisulfite (20 %) were sequentially added to the tube, which was vortexed after the addition. The tube was covered with a beaker, and heated in a boiling water bath for 7 min. Then the tube was cooled, and the absorbance of the stable blue color was measured with a UV-vis spectrometer at 830 nm in a 1 cm cuvette after 15 min. A standard calibration curve was obtained using 0 g P, 0.5 g P, 1 g P, 2 g P, 4 g P obtained from a stock solution of KH_2PO_4 (40 g P/ml).

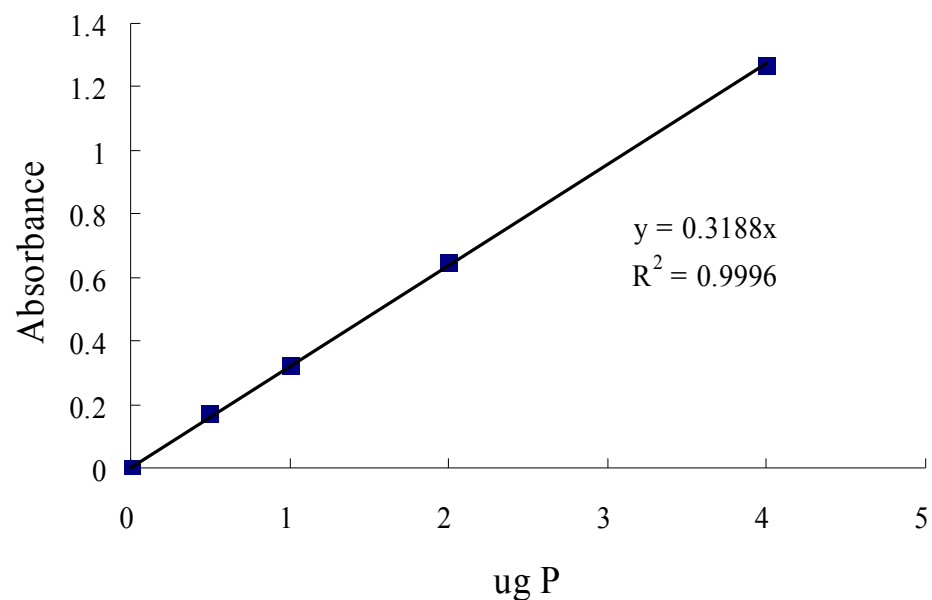


Figure S59. Calibration curve for microphosphorus assay.

Percent Polyunsaturated^a Lipids in Various Human Tissues

	PC ^a	PE ^a	PS ^a	PL ^a	L ^a
plasma	30(1)			47(2)	44±3(1), 45(3)
low-density lipoprotein	30(1)				50±1(1)
high-density lipoprotein	37(1)				47±1(1)
red blood cells	25(1),39(2)	49(2)		47(2),36(4)	32±4(1)
platelets	32(1)				41±1(1)
whole blood					36±5(1)
leukocytes				33(5)	
fibroblasts	25(6)	56(6)	38(6)	20(5) ^b , 30(5) ^c , 30(7),31(8)	28(9),46(8)
lymphocytes	22(10)	53(10)		39(10)	38(11),40(3)
PBMC				50(12), 36(13)	
monocyte					37(11)
brain—white matter	3(14),4(15), 3(16)	26(14),19(15), 29(16)	5(14),9(15)		14(15)
brain—frontal gray	4(16)	44(16)			
brain—hippocampus	4(16)	42(16)			
brain—pons	1(16)	25(16)			
brain—temporal cortex				31(17)	
spinal cord	4(18)	25(18)			
peripheral nerve	5(18)	24(18)			
myelin	4(19)	28(19)			
axolemma	8(19)	37(19)			
retina				22(20) ^j	
retinal pigment epithelium				14(20) ^j ,44(21)	
Bruch's membrane/choroid				18(20) ^j	
lipofuscin				33(21)	
rod outer segments				49(21)	
neural retina				36(21)	
lens epithelium	28(22)				
heart	38(23)	50(23)			
lung	30(24)				
bronchial epithelium				19(25)	
alveolar epithelium				20(25)	
LSA (from BALF)	3(26)				
liver					26(27)
liver microsomes	40(28)	51(28)			
spermatozoa				34±1(29) ^d ,26±1(29) ^e	
placenta	36(30) ^f ,37(30), 40±1(31)	51(30) ^f ,49(30) ^g , 51±1(31)	29(30) ^f ,37(30) ^g , 29±1(31)	39±1(31)	
skeletal muscle				53(32) ^h ,53(33),51(34), 48(35) ^l ,44(36) ^m	
vastus lateralis muscle				53(37) ^k	
prostasome	2(38)	13(38)	23(38)		
HUVEC	36(39)	61(39)	39(39)	10(40), 32(41), 43(39)	
intestinal mucosa				38(42)	
colonocyte epithelium				13(43)	
buccal cheek cell				24(44) ⁱ	

Abbreviations: FA , fatty acids; PC, phosphatidylcholine; PE, phosphatidylethanolamine; PS, phosphatidylserine; PL, phospholipids; L, lipids; HUVEC, human umbilical vein epithelial cells; PBMC, peripheral blood mononuclear cells; FBS, fetal bovine serum; HS, human serum; LSA, large surfactant aggregates; BALF, bronchoalveolar lavage fluid, ^a expressed as % of total or select FA detected, as specified in corresponding reference, ^bcell cultures supplemented with FBS, ^ccell cultures supplemented with HS, ^dfrom 47% Percoll, ^efrom 90% Percoll, ^ffrom early placentae, ^gfrom term placentae, ^han average from formula-fed, breast-fed, and non- or limited breast-fed infants, ⁱ an average of values for both 36- and 57-week infants, ^jan average of macula and periphery values, ^k an average of 8-, 14-, and 30-day untrained groups, ^l an average of 3 different age populations, ^mValues are an average of 4 different age populations .

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