

Supporting Information

General. ^1H NMR, ^{13}C NMR spectra were recorded on Varian Inova 400 (400MHz ^1H , 100 MHz ^{13}C) or Varian Mercury 300 (300 MHz ^1H , 75 MHz ^{13}C) spectrometers in deuterio chloroform (CDCl_3) with chloroform (7.27 ppm ^1H , 77.0 ppm ^{13}C) as an internal reference. ^{31}P NMR spectra were recorded on Varian Inova 400 (162 MHz ^{31}P) with 85 % H_3PO_4 (0 ppm ^{31}P) as an external reference. Data are reported in the following order: chemical shifts are given (δ); multiplicities are indicated br (broadened), s (singlet), d (doublet), t (triplet), m (multiplet), exch (exchangeable); coupling constants, J , are reported (Hz); integration is provided. Infrared spectra were recorded on a Perkin Elmer 983 IR spectrometer (KBr) and a Nicolet 510 FT-IR (CH_2Cl_2 , KCl) spectrometer. Peaks are reported (cm^{-1}) with the following relative intensities: s (strong, 67-100%), m (medium, 40-67%), w (weak, 20-40%), and br (broad). Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, Georgia. Uncorrected melting points were taken on a Thomas-Hoover melting point apparatus in open capillary tubes. MS was performed by the Mass Spectrometry Center of Emory University. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel plates with F-254 indicator. Visualization was accomplished by iodine or a 20 wt. % solution of phosphomolibdic acid in ethanol (Aldrich). Dried solvents used as reaction media were dried under 4Å molecular sieves and titrated for water level prior to use with a Fisher Coulomatic K-F titrator. All reactions were performed under a dry Ar atmosphere.

Surface Tension. The CMC measurements were performed by measuring the surface tension of aqueous solutions (in deionized Millipore Milli-Q[®] water (18 $\text{M}\Omega\cdot\text{cm}$)) of zwitterionic gemini surfactants with two methods:

1. Using a Kibron $\mu\text{TROUGH}^{\text{®}}$ monolayer apparatus as a tensiometer. The wire probe was used to measure the surface pressure (π) of 2 ml samples. After a set of readings at different concentrations the wire was washed with ethanol and dried in a flame. The corresponding surface tension (γ) was then deduced from the equation: $\gamma = \gamma_0 - \pi$, where γ_0 is a surface tension of pure water (72.8 mN m^{-1}). Surface tensions for aged samples were obtained by allowing the samples to stand covered and undisturbed for

24 hours. Care was taken not to agitate the samples prior and during the measurements.

2. Using a Model 21 Fisher Tensiomat utilizing the Du Nuoy ring method. The 6-cm platinum ring was raised and lowered manually. After a set of readings at a particular concentrations, the ring was rinsed with deionized water, 10 % HCl, and deionized water prior to drying in a flame. Only the first measurements were used for the CMC calculations, since further measurements resulted in a significant disturbance of the air/water interface thus causing a gradual increase of the surface tension.

All samples were dried in vacuum over P_2O_5 at 70 °C for 24 hrs prior to all CMC measurements which were taken at 23°C.

Dynamic Light Scattering (DLS). The DLS measurements were performed with an N4 PLUS Coulter particle sizer.

Electron Microscopy.

Cryo-HRSEM: Aqueous solutions of zwitterionic geminis were prepared using deionized Millipore Milli-Q® water (18 MΩ*cm). Then, several microliters of the prepared solutions were transferred to small gold planchets, which were rapidly frozen with liquid ethane. A specimen was fractured and then coated with a 1 nm thick layer of Cr. Afterwards, the specimen was finally transferred to the upper stage of the ISI DS-130F field emission scanning electron microscope. Transfer to the microscope resulted in some ice crystallization on the surface of the specimen. The ice was subsequently sublimed by raising the temperature from -160°C to -110°C at $< 2 \times 10^{-7}$ torr. All images presented in this paper were taken at -110°C .

TEM (uranium oxyacetate negative stain): Aqueous solutions of zwitterionic geminis were prepared using deionized Millipore Milli-Q® water (18 MΩ*cm). Then they were mixed (1:1) with a 2 % aqueous solution of uranium oxyacetate and a droplet was placed on a grid and allowed to settle for a minute, after which the bulk of the water was removed with filter paper. The grids were allowed to dry further under vacuum.

Starting Materials. Long-chain alcohols, 2-chloro-1,3,2-dioxaphospholane-2-oxide, N,N-dimethyloctyl amine and N,N-dimethyldecyl amine were purchased from Aldrich. N,N-dimethyldecyl amine, N,N-dimethyltetradecyl amine, N,N-

dimethylhexadecyl amine and N,N-dimethyloctadecyl amine were purchased from Pfaltz & Bauer. All reagents were used without further purification.

Light Microscopy. Optical images were taken on Nikon Diaphot TMD microscope.

General Procedures for the Preparation of Compounds C_x-C_y. A solution of 2-chloro-1,3,2-dioxaphospholane-2-oxide (11.5 mmol, 1.15 equiv.) in 5 mL of anhydrous THF-Et₂O (1:1) was slowly (10 min) added at -5°C to a stirred mixture of the corresponding long-chain alcohol (10.0 mmol, 1.00 equiv.) and Et₃N (11.5 mmol, 1.15 equiv.) in 25 mL of anhydrous THF-Et₂O (1:1) under Ar atmosphere. After the addition was complete, the reaction was allowed to stir for additional 4 hours at room temperature. After adding hexanes (3mL), the reaction mixture was filtered through celite, washed with 25 mL of THF-ether (1:1) and evaporated to give an oily residue which was dissolved in anhydrous CH₃CN (20 mL) and reacted with a corresponding long-chain dimethylamine (20.0 mmol, 2 equiv.) at 65-70 °C for 48 hours under Ar atmosphere. Then, the reaction was allowed to cool down to room temperature, poured into ether (200 mL), filtered, and thoroughly washed with ether to give the crude product as a white powder, which was subsequently recrystallized from CHCl₃-Et₂O to give compounds of the general formula C_x-C_y in 10-57 % overall yield as white, hygroscopic powders. No attempt was made to optimize yields.

Tetradecanaminium,N-ethyl-2-[[hydroxy(dodecyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. (C₁₂-C₁₄) Yield: 33 %; M.p. 196-197°C; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 4.27-4.32 (br m, 2H), 3.78-3.85 (br m, 4H), 3.43-3.50 (br m, 2H), 3.36 (br s, 6H), 1.65-1.75 (br m, 2H), 1.59 (tt, ³J(H,H)=7.2 Hz, 2H), 1.20-1.38 (m, 40H), 0.88 (t, ³J(H,H)=7.2Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 65.4, 63.9, 58.7, 51.7, 31.9, 31.1, 29.6, 29.5, 29.4, 29.3, 26.3, 25.9, 22.8, 22.6, 14.1; ³¹P NMR (162 MHz, CDCl₃, 25 °C, 85 % H₃PO₄): δ = 0.81 (s); IR (KBr): ν = 2955 (vs, C-H), 1468 (s, C-H), 1241 (vs, P=O), 1078 cm⁻¹ (vs, C-O); Anal. Calcd for C₃₀H₆₄NO₄P: C, 67.50; H, 12.08; N, 2.62. Found: C, 67.26; H, 11.94, N, 2.65.

Dodecanaminium,N-ethyl-2-[[hydroxy(dodecyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. (C₁₂-C₁₂) Yield: 57 %; M.p. 190.5-191.5°C; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 4.26-4.33 (br m, 2H), 3.78-3.88 (br m, 4H), 3.45-3.52 (br m, 2H), 3.37 (br s, 6H), 1.65-1.77 (br m, 2H), 1.60 (tt, ³J (H,H)=7.2 Hz, 2H), 1.20-1.38 (m, 36H), 0.88 (t, ³J (H,H)=6.6Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 65.4, 65.3, 63.8, 58.7, 51.5, 31.8, 31.1, 31.0, 29.6, 29.5, 29.4, 29.3, 29.2, 26.3, 25.9, 22.8, 22.6, 14.0; ³¹P NMR (162 MHz, CDCl₃, 25 °C, 85 % H₃PO₄): δ = 0.70 (s); IR (KBr): ν = 3010 (vs, C-H), 1427 (s, C-H), 1286 (vs, P=O), 1034 cm⁻¹ (vs, C-O); HRMS (FAB) calcd for C₂₈H₆₁NO₄P (MH⁺) 506.4338, found 506.4360; Anal. Calcd for C₂₈H₆₀NO₄P: C, 66.49; H, 11.96; N, 2.77. Found: C, 66.38; H, 12.03, N, 2.89.

Octanaminium,N-ethyl-2-[[hydroxy(dodecyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. (C₁₂-C₈) Yield: 33 %; M.p. 190.5-191.5°C; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 4.25-4.34 (br m, 2H), 3.78-3.88 (br m, 4H), 3.42-3.52 (br m, 2H), 3.37 (br s, 6H), 1.65-1.77 (br m, 2H), 1.59 (tt, ³J (H,H)=7.6 Hz, 2H), 1.18-1.38 (m, 28H), 0.88 (t, ³J (H,H)=8Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 65.3, 63.7, 58.7, 51.5, 31.8, 31.5, 31.0, 29.6, 29.5, 29.4, 29.2, 29.1, 29.0, 26.2, 25.8, 22.7, 22.5, 22.4, 14.0, 13.9; ³¹P NMR (162 MHz, CDCl₃, 25 °C, 85 % H₃PO₄): δ = 0.63 (s); IR (KBr): ν = 2925 (vs, C-H), 1467 (s, C-H), 1234 (vs, P=O), 1074 cm⁻¹ (vs, C-O); HRMS (FAB) calcd for C₂₄H₅₃NO₄P (MH⁺) 450.3712, found 450.3712; Anal. Calcd for C₂₄H₅₂NO₄P: C, 64.11; H, 11.66; N, 3.12. Found: C, 64.27; H, 11.72, N, 3.12.

Octanaminium,N-ethyl-2-[[hydroxy(decyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. (C₁₀-C₈) Yield: 32 %; M.p. 199-201°C; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 4.26-4.29 (br m, 2H), 3.77-3.85 (br m, 4H), 3.43-3.50 (br m, 2H), 3.35 (br s, 6H), 1.65-1.75 (br m, 2H), 1.58 (tt, ³J (H,H)=7.2 Hz, 2H), 1.20-1.38 (m, 24H), 0.87 (t, ³J (H,H)=7.2Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 65.4, 63.9, 58.7, 51.6, 31.8, 31.6, 31.1, 29.6, 29.5, 29.4, 29.2, 29.0, 26.3, 25.9, 22.8, 22.6, 22.5, 14.0; ³¹P NMR (162 MHz, CDCl₃, 25 °C, 85 % H₃PO₄): δ = 0.76 (s); IR (CH₂Cl₂, KCl): ν = 2934 (vs, C-H), 1465 (s, C-H), 1255 (vs, P=O), 1075 cm⁻¹ (vs, C-O); HRMS (FAB) calcd for

$C_{22}H_{49}NO_4P$ (MH^+) 422.3399, found 422.3399; Anal. Calcd for $C_{22}H_{48}NO_4P$: C, 62.68; H, 11.48; N, 3.32. Found: C, 62.41; H, 11.54, N, 3.40.

Decanaminium,N-ethyl-2-[[hydroxy(decyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. (C_{10} - C_{10}) Yield: 24 %; M.p. 198-200°C; 1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.28-4.33 (br m, 2H), 3.75-3.88 (br m, 4H), 3.43-3.50 (br m, 2H), 3.37 (br s, 6H), 1.65-1.75 (br m, 2H), 1.61 (tt, $^3J(H,H)=7.6$ Hz, 2H), 1.20-1.38 (m, 28H), 0.86-0.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 65.4, 63.8, 58.7, 51.6, 31.8, 31.1, 31.0, 29.6, 29.5, 29.4, 29.2, 26.3, 25.8, 22.8, 22.6, 22.5, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, 85 % H_3PO_4): δ = 0.88 (s); IR (CH_2Cl_2 , KCl): ν = 2917 (vs, C-H), 1468 (s, C-H), 1240 (vs, P=O), 1079 cm^{-1} (vs, C-O); HRMS (FAB) calcd for $C_{24}H_{53}NO_4P$ (MH^+) 450.3712, found 450.3714; Anal. Calcd for $C_{24}H_{52}NO_4P$: C, 64.11; H, 11.66; N, 3.12. Found: C, 63.86; H, 11.72, N, 3.19.

Dodecanaminium,N-ethyl-2-[[hydroxy(decyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. (C_{10} - C_{12}) Yield: 34 %; M.p. 189-190°C; 1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.26-4.33 (br m, 2H), 3.75-3.88 (br m, 4H), 3.43-3.50 (br m, 2H), 3.36 (br s, 6H), 1.65-1.75 (br m, 2H), 1.60 (tt, $^3J(H,H)=7.2$ Hz, 2H), 1.20-1.38 (m, 32H), 0.85-0.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 65.3, 63.8, 58.7, 51.5, 31.8, 31.1, 31.0, 29.6, 29.5, 29.4, 29.3, 29.2, 26.3, 25.8, 22.8, 22.5, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, 85 % H_3PO_4): δ = 0.79 (s); IR (CH_2Cl_2 , KCl): ν = 2924 (vs, C-H), 1430 (s, C-H), 1265 (vs, P=O), 1075 cm^{-1} (vs, C-O); HRMS (FAB) calcd for $C_{26}H_{57}NO_4P$ (MH^+) 478.4025, found 478.4022; Anal. Calcd for $C_{26}H_{56}NO_4P$: C, 65.37; H, 11.82; N, 2.93. Found: C, 65.58; H, 11.91, N, 2.96.

Tetradecanaminium,N-ethyl-2-[[hydroxy(decyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. (C_{10} - C_{14}) Yield: 43 %; M.p. 196-198°C; 1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.28-4.33 (br m, 2H), 3.75-3.88 (br m, 4H), 3.43-3.50 (br m, 2H), 3.36 (br s, 6H), 1.65-1.75 (br m, 2H), 1.60 (tt, $^3J(H,H)=7.2$ Hz, 2H), 1.20-1.38 (m, 36H), 0.88 (t, $^3J(H,H)=7.2$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 65.4, 63.9, 58.8, 51.6, 31.9, 31.1, 31.0, 29.6, 29.5, 29.4, 29.3, 26.3, 25.9, 22.8, 22.6, 22.5, 14.1; ^{31}P NMR

(162 MHz, CDCl₃, 25 °C, 85 % H₃PO₄): δ = 0.75 (s); IR (CH₂Cl₂, KCl): ν = 2935 (vs, C-H), 1424 (s, C-H), 1260 (vs, P=O), 1086 cm⁻¹ (vs, C-O); HRMS (FAB) calcd for C₂₈H₆₁NO₄P (MH⁺) 506.4338, found 506.4328; Anal. Calcd for C₂₈H₆₀NO₄P: C, 66.49; H, 11.96; N, 2.77. Found: C, 66.34; H, 11.97, N, 2.83.

Hexadecanaminium,N-ethyl-2-[[hydroxy(decyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. (C₁₀-C₁₆) Yield: 27 %; M.p. 195-197°C; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 4.28-4.33 (br m, 2H), 3.77-3.89 (br m, 4H), 3.43-3.50 (br m, 2H), 3.37 (br s, 6H), 1.65-1.75 (br m, 2H), 1.61 (tt, ³J(H,H)=7.2 Hz, 2H), 1.20-1.38 (m, 40H), 0.88 (t, ³J(H,H)=6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 65.5, 64.0, 58.8, 51.7, 31.9, 31.1, 31.0, 29.7, 29.6, 29.5, 29.3, 26.3, 25.9, 22.9, 22.7, 14.1; ³¹P NMR (162 MHz, CDCl₃, 25 °C, 85 % H₃PO₄): δ = 0.82 (s); IR (CH₂Cl₂, KCl): ν = 2919 (vs, C-H), 1429 (s, C-H), 1265 (vs, P=O), 1081 cm⁻¹ (vs, C-O); HRMS (FAB) calcd for C₃₀H₆₅NO₄P (MH⁺) 534.4651, found 534.4658; Anal. Calcd for C₃₀H₆₄NO₄P: C, 67.50; H, 12.08; N, 2.62. Found: C, 67.29; H, 12.09, N, 2.67.

Octanaminium,N-ethyl-2-[[hydroxy(octyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. (C₈-C₈) Yield: 12 %; M.p. 201-202°C; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 4.26-4.33 (br m, 2H), 3.78-3.87 (br m, 4H), 3.45-3.52 (br m, 2H), 3.36 (br s, 6H), 1.65-1.77 (br m, 2H), 1.60 (tt, ³J(H,H)=7.6 Hz, 2H), 1.20-1.39 (m, 20H), 0.83-0.92 (m, 6H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 65.5, 63.9, 58.8, 51.7, 31.8, 31.7, 31.6, 31.1, 31.0, 29.4, 29.3, 29.2, 29.1, 26.3, 25.9, 22.8, 22.6, 22.5, 14.1, 14.0; ³¹P NMR (162 MHz, CDCl₃, 25 °C, 85 % H₃PO₄): δ = 0.72 (s); IR (CH₂Cl₂, KCl): ν = 2929 (vs, C-H), 1470 (s, C-H), 1239 (vs, P=O), 1065 cm⁻¹ (vs, C-O); HRMS (FAB) calcd for C₂₀H₄₅NO₄P (MH⁺) 394.3086, found 394.3073.

Decanaminium,N-ethyl-2-[[hydroxy(octyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. (C₈-C₁₀) Yield: 25 %; M.p. 196-198°C; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 4.27-4.32 (br m, 2H), 3.76-3.88 (br m, 4H), 3.43-3.50 (br m, 2H), 3.36 (br s, 6H), 1.65-1.75 (br m, 2H), 1.60 (tt, ³J(H,H)=7.6 Hz, 2H), 1.20-1.38 (m, 24H), 0.83-0.90 (m, 6H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 65.5, 64.0, 58.8, 51.7, 31.8, 31.1, 29.7,

29.4, 29.3, 29.2, 26.3, 25.9, 22.8, 22.6, 14.1; ^{31}P NMR (162 MHz, CDCl_3 , 25 °C, 85 % H_3PO_4): δ = 0.77 (s); IR (CH_2Cl_2 , KCl): ν = 2929 (vs, C-H), 1428 (s, C-H), 1265 (vs, P=O), 1070 cm^{-1} (vs, C-O); HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{49}\text{NO}_4\text{P}$ (MH^+) 422.3399, found 422.3383; Anal. Calcd for $\text{C}_{22}\text{H}_{48}\text{NO}_4\text{P}$: C, 62.68; H, 11.48; N, 3.32. Found: C, 62.45; H, 11.30, N, 3.29.

Dodecanaminium,N-ethyl-2-[[hydroxy(octyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. ($\text{C}_8\text{-C}_{12}$) Yield: 35 %; M.p. 199-200°C; ^1H NMR (400 MHz, CDCl_3 , 25 °C): δ = 4.26-4.33 (br m, 2H), 3.78-3.88 (br m, 4H), 3.45-3.50 (br m, 2H), 3.37 (br s, 6H), 1.65-1.77 (br m, 2H), 1.60 (tt, $^3J(\text{H,H})=7.6$ Hz, 2H), 1.20-1.38 (m, 28H), 0.84-0.90 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): δ = 65.4, 65.3, 63.9, 58.7, 51.6, 31.8, 31.1, 31.0, 29.5, 29.4, 29.3, 29.2, 26.3, 25.9, 22.8, 22.6, 14.0; ^{31}P NMR (162 MHz, CDCl_3 , 25 °C, 85 % H_3PO_4): δ = 0.78 (s); IR (CH_2Cl_2 , KCl): ν = 2929 (vs, C-H), 1465 (s, C-H), 1260 (vs, P=O), 1081 cm^{-1} (vs, C-O); HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{53}\text{NO}_4\text{P}$ (MH^+) 450.3712, found 450.3708; Anal. Calcd for $\text{C}_{24}\text{H}_{52}\text{NO}_4\text{P}$: C, 64.11; H, 11.66; N, 3.12. Found: C, 63.85; H, 11.49, N, 3.12.

Tetradecanaminium,N-ethyl-2-[[hydroxy(octyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. ($\text{C}_8\text{-C}_{14}$) Yield: 16 %; M.p. 186-188°C; ^1H NMR (400 MHz, CDCl_3 , 25 °C): δ = 4.28-4.33 (br m, 2H), 3.76-3.88 (br m, 4H), 3.43-3.50 (br m, 2H), 3.36 (br s, 6H), 1.65-1.75 (br m, 2H), 1.60 (tt, $^3J(\text{H,H})=7.2$ Hz, 2H), 1.20-1.38 (m, 32H), 0.83-0.90 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): δ = 65.5, 65.4, 64.0, 58.8, 51.7, 31.9, 31.8, 31.1, 31.0, 29.6, 29.5, 29.4, 29.3, 26.3, 25.9, 22.8, 22.6, 14.1; ^{31}P NMR (162 MHz, CDCl_3 , 25 °C, 85 % H_3PO_4): δ = 0.80 (s); IR (CH_2Cl_2 , KCl): ν = 2930 (vs, C-H), 1460 (s, C-H), 1265 (vs, P=O), 1070 cm^{-1} (vs, C-O); Anal. Calcd for $\text{C}_{26}\text{H}_{56}\text{NO}_4\text{P}$: C, 65.37; H, 11.82; N, 2.93. Found: C, 65.08; H, 11.88, N, 2.94.

Octadecanaminium,N-ethyl-2-[[hydroxy(octyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. ($\text{C}_8\text{-C}_{18}$) Yield: 23 %; M.p. 195-197°C; ^1H NMR (400 MHz, CDCl_3 , 25 °C): δ = 4.27-4.34 (br m, 2H), 3.78-3.88 (br m, 4H), 3.45-3.50 (br m, 2H),

3.37 (br s, 6H), 1.65-1.77 (br m, 2H), 1.61 (tt, $^3J(\text{H,H})=7.2$ Hz, 2H), 1.20-1.38 (m, 40H), 0.88 (t, $^3J(\text{H,H})=6.6$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): δ = 65.6, 65.5, 65.4, 64.0, 58.8, 51.7, 31.9, 31.8, 31.1, 29.7, 29.6, 29.5, 29.4, 29.3, 26.3, 25.9, 22.9, 22.6, 14.1; ^{31}P NMR (162 MHz, CDCl_3 , 25 °C, 85 % H_3PO_4): δ = 0.79 (s); IR (CH_2Cl_2 , KCl): ν = 2930 (vs, C-H), 1465 (s, C-H), 1260 (vs, P=O), 1081 cm^{-1} (vs, C-O); HRMS (FAB) calcd for $\text{C}_{30}\text{H}_{65}\text{NO}_4\text{P}$ (MH^+) 534.4651, found 534.4628; Anal. Calcd for $\text{C}_{30}\text{H}_{64}\text{NO}_4\text{P}$: C, 67.50; H, 12.08; N, 2.62. Found: C, 67.25; H, 12.14, N, 2.67.

Octanaminium,N-ethyl-2-[[hydroxy(tetradecyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. ($\text{C}_{14}\text{-C}_8$) Yield: 15 %; M.p. 190-191°C; ^1H NMR (400 MHz, CDCl_3 , 25 °C): δ = 4.22-4.29 (br m, 2H), 3.78-3.83 (br m, 4H), 3.43-3.50 (br m, 2H), 3.34 (br s, 6H), 1.62-1.73 (br m, 2H), 1.56 (tt, $^3J(\text{H,H})=7.2$ Hz, 2H), 1.20-1.38 (m, 32H), 0.85 (t, $^3J(\text{H,H})=6.8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): δ = 65.5, 65.4, 63.8, 58.7, 51.6, 31.8, 31.6, 31.1, 31.0, 29.7, 29.6, 29.5, 29.3, 29.2, 29.0, 26.3, 25.9, 22.6, 22.5, 14.0; ^{31}P NMR (162 MHz, CDCl_3 , 25 °C, 85 % H_3PO_4): δ = 0.86 (s); IR (CH_2Cl_2 , KCl): ν = 2929 (vs, C-H), 1465 (s, C-H), 1260 (vs, P=O), 1080 cm^{-1} (vs, C-O); HRMS (FAB) calcd for $\text{C}_{26}\text{H}_{57}\text{NO}_4\text{P}$ (MH^+) 478.4025, found 478.4023; Anal. Calcd for $\text{C}_{26}\text{H}_{56}\text{NO}_4\text{P}$: C, 65.37; H, 11.82; N, 2.93. Found: C, 65.15; H, 11.71, N, 2.96.

Decanaminium,N-ethyl-2-[[hydroxy(tetradecyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. ($\text{C}_{14}\text{-C}_{10}$) Yield: 10 %; M.p. 197-198°C; ^1H NMR (400 MHz, CDCl_3 , 25 °C): δ = 4.22-4.29 (br m, 2H), 3.78-3.83 (br m, 4H), 3.43-3.50 (br m, 2H), 3.34 (br s, 6H), 1.62-1.73 (br m, 2H), 1.56 (tt, $^3J(\text{H,H})=7.2$ Hz, 2H), 1.20-1.38 (m, 36H), 0.85 (t, $^3J(\text{H,H})=6.8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): δ = 65.5, 65.4, 65.3, 63.9, 58.8, 51.6, 31.8, 31.1, 31.0, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.3, 25.8, 22.8, 22.6, 14.0; ^{31}P NMR (162 MHz, CDCl_3 , 25 °C, 85 % H_3PO_4): δ = 0.84 (s); IR (CH_2Cl_2 , KCl): ν = 2930 (vs, C-H), 1465 (s, C-H), 1265 (vs, P=O), 1076 cm^{-1} (vs, C-O); HRMS (FAB) calcd for $\text{C}_{28}\text{H}_{61}\text{NO}_4\text{P}$ (MH^+) 506.4338, found 506.4339; Anal. Calcd for $\text{C}_{28}\text{H}_{60}\text{NO}_4\text{P}$: C, 66.49; H, 11.96; N, 2.77. Found: C, 66.62; H, 12.08, N, 2.95

Dodecanaminium,N-ethyl-2-[[hydroxy(tetradecyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. (C₁₄-C₁₂) Yield: 16 %; M.p. 197-198°C; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 4.27-4.33 (br m, 2H), 3.78-3.88 (br m, 4H), 3.43-3.50 (br m, 2H), 3.37 (br s, 6H), 1.62-1.73 (br m, 2H), 1.61 (tt, ³J(H,H)=7.6 Hz, 2H), 1.20-1.38 (m, 40H), 0.88 (t, ³J(H,H)=6.6Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 65.6, 65.5, 65.4, 64.0, 58.8, 51.7, 31.9, 31.1, 29.7, 29.6, 29.5, 29.4, 29.3, 26.3, 25.9, 22.9, 22.7, 14.1; ³¹P NMR (162 MHz, CDCl₃, 25 °C, 85 % H₃PO₄): δ = 0.82 (s); IR (CH₂Cl₂, KCl): ν = 2925 (vs, C-H), 1445 (s, C-H), 1260 (vs, P=O), 1075 cm⁻¹ (vs, C-O); HRMS (FAB) calcd for C₃₀H₆₅NO₄P (MH⁺) 534.4651, found 534.4626; Anal. Calcd for C₃₀H₆₄NO₄P: C, 67.50; H, 12.08; N, 2.62. Found: C, 67.59; H, 12.18, N, 2.83.

Octanaminium,N-ethyl-2-[[hydroxy(octadecyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. (C₁₈-C₈) Yield: 19 %; M.p. 188.5-189.5°C; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 4.27-4.34 (br m, 2H), 3.78-3.88 (br m, 4H), 3.45-3.50 (br m, 2H), 3.37 (br s, 6H), 1.65-1.77 (br m, 2H), 1.61 (tt, ³J(H,H)=7.2 Hz, 2H), 1.20-1.38 (m, 40H), 0.88 (t, ³J(H,H)=6.9Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 65.6, 64.0, 58.9, 51.7, 31.9, 31.6, 31.0, 29.6, 29.5, 29.3, 29.2, 29.0, 26.3, 25.9, 22.8, 22.7, 14.1, 14.0; ³¹P NMR (162 MHz, CDCl₃, 25 °C, 85 % H₃PO₄): δ = 0.39 (s); IR (KBr): ν = 2923 (vs, C-H), 1467 (s, C-H), 1253 (vs, P=O), 1082 cm⁻¹ (vs, C-O); HRMS (FAB) calcd for C₃₀H₆₅NO₄P (MH⁺) 534.4651, found 534.4673.

Octadecanaminium,N-ethyl-2-[[hydroxy(octadecyloxy)phosphinyl]oxy]-N,N-dimethyl-, inner salt. (C₁₈-C₁₈) Yield: 12 %; M.p. 186.5-187.5°C; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 4.27-4.34 (br m, 2H), 3.78-3.88 (br m, 4H), 3.45-3.50 (br m, 2H), 3.36 (br s, 6H), 1.65-1.77 (br m, 2H), 1.61 (tt, ³J(H,H)=7.2 Hz, 2H), 1.20-1.38 (m, 60H), 0.88 (t, ³J(H,H)=6.9Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 65.5, 63.9, 58.8, 51.7, 31.8, 31.1, 31.0, 29.7, 29.5, 29.4, 29.3, 26.3, 25.9, 22.7, 14.1; ³¹P NMR (162 MHz, CDCl₃, 25 °C, 85 % H₃PO₄): δ = 0.58 (s); IR (KBr): ν = 3018 (vs, C-H), 1425 (s, C-H), 1285 (vs, P=O), 1167 cm⁻¹ (vs, C-O); HRMS (FAB) calcd for C₄₀H₈₅NO₄P (MH⁺) 674.6216, found 674.6209; Anal. Calcd for C₄₀H₈₄NO₄P: C, 71.27; H, 12.56; N, 2.08. Found: C, 71.02; H, 12.58, N, 2.21.