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Ambidextrous 'hybrid' fluorinated zwitterionic geminis: self-assembly in both organic and aqueous media

Andrey Peresypkin,* Caroline Clavel and Fredric M. Menger

Experimental

General. ^{1}H NMR,^{13}C NMR spectra were recorded on Varian Inova 400 (400 MHz ^{1}H, 101 MHz ^{13}C) spectrometer in deutero chloroform ($CDCl_3$) with chloroform (7.27 ppm ^{1}H, 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 (0.0 ppm ^{31}P) as an external reference. ^{19}F NMR spectra were recorded on Varian Inova 400 (376 MHz ^{19}F) with trifluorotoluene in deuterobenzene (-63.7 ppm ^{19}F) as an external reference. Data are reported in the following order: chemical shifts are given (δ); multiplicities are indicated s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants, *J*, are reported (Hz). Infrared spectra were recorded on 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 spectra were performed by Mass Spectrometry Center in Emory University. Solvents for extraction were reagent grade and used as received. 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 nitrogen or argon atmosphere.

Starting Materials. Long-chain alcohols, 2-chloro-1,3,2-dioxaphospholane-2-oxide, 4-phenylbenzyl alcohol, triphenylphosphine, carbon tetrabromide, *N*,*N*-dimethyloctylamine

and *N*,*N*-dimethyldodecylamine, 1-bromodocosane and 1-bromoeicosane were purchased from Aldrich. *N*,*N*-dimethyldecylamine, *N*,*N*-dimethyltetradecylamine, *N*,*N*-dimethylhexadecylamine, and *N*,*N*-dimethyloctadecylamine were purchased from Pfaltz & Bauer. Dimethylamine (~5.6 M in ethanol) was purchased from Fluka. All purchased reagents were used without further purification.

Phase-Contrast and Fluorescent microscopy. Optical images were recorded on Nikon Diaphot TMD microscope. The microscope slides were prepared by affixing the Kalrez o-ring (Chemglass) on the microscope slide (Fisher Scientific) using Sealit (Fisher Scientific).

"Normal" vesicles were prepared by two methods: a) smeared solid was hydrated for *ca.* 10 min with water under the microscope slide, and b) electroformation method: 1 μL droplets of a gemini solution (0.25- 1.00 mg/mL in $CHCl_3$/methanol (9/1, v/v) were placed on Pt wires spaced 5 mm apart. The films were subsequently dried under a stream of nitrogen for 30 minutes. After adding 1.5 mL of Milli-Q purified water to the sample chamber, the films were subjected to an alternating current (10 Hz, 700 mV-2V) for 2-3 hours. Spherical, primarily unilamellar liposomes 20-100 μm formed, and were loosened from the Pt wire by progressive reduction in frequency over 20-30 minutes.

"Reversed" vesicles for fluorescent microscopy were prepared as follows: a small amount of sample (10 mg) was mixed with a fluorescent dye in methanol, to produce 0.5 wt. % of the dye relative to the compound. The mixture was dried under vacuum, then prehydrated with a mist of water (or exposing the films to high (> 70%) relative humidity) and the resulting material was applied on the microscope slide followed by addition of organic solvent. The images were taken with Optronix DEI-750TD three-chip color camera. Two organic dyes investigated: water-soluble Lucifer Yellow CH, lithium salt (Molecular Probes) and lipophilic "DiI"-(Molecular Probes). "Reversed" vesicles for phase-contrast microscopy were prepared similar to the precedure described above for fluorescent microscopy without addition of dye.

General procedure for the synthesis of long chain (C_{20} and C_{22}) dimethylamines and *N*,*N*-dimethyl(4-phenylbenzyl)amine. A mixture of a corresponding bromide (46 mmol,

1.0 equiv.) and a 5.6 M ethanolic solution of dimethylamine (460 mmol, 10.0 equiv.) was heated at 70-75 °C in a sealed tube under N_2 atmosphere for 24 h. The reaction was cooled to room temperature, the solvent was evaporated and the resulting solid was dried *in vacuo*. Hexanes (100 mL) and 1N NaOH (50 mL) were added and the resulting mixture was stirred for 30 min. The organic layer was separated, dried over $MgSO_4$ in the presence of charcoal for 1 hr, filtered through celite and evaporated to dryness to give a colorless oily residue which was dried under vacuum to give analytically pure compounds.

General Procedures for the Preparation of Compounds F_xC_y-C_z. A solution of 2-chloro-1,3,2-dioxaphospholane-2-oxide (35.09 mmol., 1.2 equiv.) in 10 mL of anhydrous THF-Et_2O (1:1) was slowly (10 min) added at 0 °C to a stirred mixture of a long-chain alcohol (29.24 mmol., 1.0 equiv.) and Et_3N (35.09 mmol., 1.2 equiv.) in 40 mL of anhydrous THF-Et_2O (1:1) under N_2 atmosphere. After the addition was complete, the reaction was allowed to stir for additional 3 hours at room temperature. After adding hexanes (5 mL) the reaction mixture was allowed to stir for additional 10 min, filtered through celite, washed with 50 mL of THF-Et_2O (1:1) and evaporated to give an oily residue which was dissolved in 60 mL of dry CH_3CN[1] and reacted with a corresponding long-chain dimethylamine (9.75 mmol., 2.0 equiv.)[2] at 65-70 °C for 48 h under N_2 atmosphere. The reactions were allowed to cool to ambient temperature for 24 hours to afford white crystals which were filtered, washed with CH_3CN, dried, washed with hexanes, and then subsequently recrystallized from CH_3CN to give compounds of the general formula F_xC_y-C_z in 0.5-56% yield as white, hygroscopic powders soluble in chloroform and ethanol.

4-phenylbenzylbromide. A solution of PPh_3 (48.16 g, 183.6 mmol, 1.5 equiv.) in dry CH_2Cl_2 (60 mL) was slowly added dropwise over 40-60 min to a solution of 4-

[1] In the cases of F_6C_2-C_{20} and F_6C_2-C_{22} the reactions with amines were conducted in dry DMF and the products were subsequently recrystallized from CH_3CN.

[2] In the second step of reactions with *N*,*N*-Dimethyleicosylamine and *N*,*N*-Dimethyldocosylamine only 1.2 equiv. of amines were used.

phenylbenzyl alcohol (22.55 g, 122.4 mmol, 1 equiv.) and CBr_4 (81.20 g, 244.8 mmol, 2 equiv.) in dry CH_2Cl_2 (120 mL) at 0 °C under Ar. The reaction was allowed to stir at ambient temperature for 24 h. The reaction was monitored by TLC (hexanes/EtOAc, 2:1). The reaction mixture was evaporated, dried under vacuum and the resulting brown residue was dissolved in small amount of CH_2Cl_2 and passed through the plug of SiO_2 (eluent: hexanes/EA, 10:1). The filtrate was evaporated, dried in vacuum, and recrystallized from CH_3CN to give 12.5 g of product as white, crystalline, and analytically pure solid. Yield: 40%; M.p. 82.5 °C (Lit[3]. m.p. 82 °C) ; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.57-7.62 (m, 4H), 7.44-7.51 (m, 4H), 7.38 (tt, ^3J(H,H)=7.2 Hz, ^4J(H,H)=1.6 Hz, 1H), 4.57 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 141.3, 140.4, 136.7, 129.5, 128.8, 127.5, 127.1, 33.4; Anal. Calcd for $C_{13}H_{11}Br$: C, 63.18; H, 4.49; Br, 32.33. Found: C, 63.11; H, 4.48, N, 32.25.

***N,N*-Dimethyleicosylamine**.[4] Yield: 89%; M.p. 32 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.20 (s, 6H), 1.44 (tt, ^3J(H,H)=7.2 Hz, 2H), 1.21-1.33 (m, 36H), 0.87 (t, ^3J(H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 60.0, 45.5, 31.9, 29.7, 29.6, 29.4, 27.8, 27.5, 22.7, 14.1. IR (CH_2Cl_2, KCl): ν = 2999 (s, C-H), 1475 (m, C-H); HRMS (FAB) calcd for $C_{22}H_{48}N$ (MH^+) 326.3787, found 326.3795; Anal. Calcd for $C_{22}H_{47}N$: C, 81.15; H, 14.55; N, 4.30. Found: C, 81.28; H, 14.67, N, 4.32.

***N,N*-Dimethyldocosylamine.** Yield: 79%; M.p. 40 °C (Lit[5]. m.p. 41 °C) ; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 2.21 (s, 6H), 1.44 (tt, ^3J(H,H)=6.8 Hz, 2H), 1.21-1.34 (m, 40H), 0.88 (t, ^3J(H,H)=6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 60.0, 45.5, 31.9, 29.7, 29.6, 29.4, 27.8, 27.5, 22.7, 14.1; Anal. Calcd for $C_{24}H_{51}N$: C, 81.50; H, 14.53; N, 3.96. Found: C, 81.63; H, 14.64, N, 3.82.

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***N*,*N*-dimethyl(4-phenylbenzyl)amine**.[6] Yield: 93%; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.60-7.68 (m, 4H), 7.43-7.50 (m, 4H), 7.37-7.40 (m, 1H), 3.52 (s, 2H), 2.33 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 140.9, 139.9, 137.9, 129.4, 128.6, 127.1, 126.9, 64.0, 45.3; Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.00; H, 8.17, N, 6.69.

Octanaminium,*N*-ethyl-2-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_6C_2-C_8) Yield: 29%; M.p. 210-212 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.32-4.38 (m, 2H), 4.19 (q, ^{3}J(H,H)=6.8 Hz, ^{3}J(H,P)=6.8 Hz, 2H), 3.79-3.84 (m, 2H), 3.42-3.46 (m, 2H), 3.31 (s, 6H), 2.50 (tt, ^{3}J(H,H)=6.6 Hz, ^{3}J(H,F)=18.8 Hz, 2H), 1.67-1.77 (br m, 2H), 1.20-1.36 (m, 10H), 0.88 (t, ^{3}J (H,H)=7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 65.8, 64.3, 59.2, 57.6, 51.8, 32.4, 31.8, 29.4, 29.2, 26.5, 23.0, 22.7, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.38 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -115.0 (2F), -123.4 (2F), -124.3 (2F), -125.1 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2945 (s, C-H), 1475 (m, C-H), 1245 (s, P=O), 1148 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{20}H_{32}F_{13}NO_4P$ (MH^+) 628.1861, found 628.1870; Anal. Calcd for $C_{20}H_{31}F_{13}NO_4P$: C, 38.29; H, 4.98; N, 2.23. Found: C, 38.41; H, 5.12, N, 2.33.

Decanaminium,*N*-ethyl-2-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_6C_2-C_{10}) Yield: 15%; M.p. 216 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.32-4.39 (m, 2H), 4.18 (q, ^{3}J(H,H)=6.8 Hz, ^{3}J(H,P)=6.8 Hz, 2H), 3.80-3.86 (m, 2H), 3.41-3.46 (m, 2H), 3.32 (s, 6H), 2.50 (tt, ^{3}J(H,H)=6.6 Hz, ^{3}J(H,F)=19.2 Hz, 2H), 1.68-1.78 (br m, 2H), 1.20-1.38 (m, 14H), 0.88 (t, ^{3}J (H,H)=7.0Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 65.7, 64.2, 59.2, 57.5, 51.8, 32.3, 32.0, 29.6, 29.4, 26.5, 23.0, 22.8, 14.1; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.38 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -115.0 (2F), -123.4 (2F), -124.4 (2F), -125.1 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2940 (s, C-H), 1475 (m, C-H), 1230 (s, P=O), 1148 cm^{-1} (s, C-F); HRMS

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(FAB) calcd for $C_{22}H_{36}F_{13}NO_4P$ (MH^+) 656.2174, found 656.2195; Anal. Calcd for $C_{22}H_{35}F_{13}NO_4P$: C, 40.31; H, 5.38; N, 2.14. Found: C, 40.53; H, 5.31, N, 2.26.

Dodecanaminium,*N*-ethyl-2-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_6C_2-C_{12}) Yield: 19%; M.p. 214 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.32-4.39 (m, 2H), 4.18 (q, ^3J(H,H)=6.8 Hz, ^3J(H,P)=6.8 Hz, 2H), 3.80-3.84 (m, 2H), 3.41-3.45 (m, 2H), 3.32 (s, 6H), 2.50 (tt, ^3J(H,H)=6.4 Hz, ^3J(H,F)=19.0 Hz, 2H), 1.68-1.76 (br m, 2H), 1.20-1.38 (m, 18H), 0.88 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 65.8, 64.1, 59.1, 57.5, 51.8, 32.40, 32.0, 29.8, 29.5, 26.5, 23.0, 22.8, 14.2; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.41 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -115.0 (2F), -123.3 (2F), -124.3 (2F), -125.1 (2F), -127.5 (2F); IR (CH_2Cl_2, KCl): ν = 2940 (s, C-H), 1475 (m, C-H), 1235 (s, P=O), 1181 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{24}H_{40}F_{13}NO_4P$ (MH^+) 684.2487, found 684.2478; Anal. Calcd for $C_{24}H_{39}F_{13}NO_4P$: C, 42.17; H, 5.75; N, 2.05. Found: C, 42.23; H, 5.77, N, 2.15.

Tetradecanaminium,*N*-ethyl-2-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_6C_2-C_{14}) Yield: 26%; M.p. 196 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.29-4.36 (m, 2H), 4.17 (q, ^3J(H,H)=6.8 Hz, ^3J(H,P)=6.8 Hz, 2H), 3.76-3.82 (m, 2H), 3.40-3.45 (m, 2H), 3.31 (s, 6H), 2.49 (tt, ^3J(H,H)=6.4 Hz, ^3J(H,F)=18.8 Hz, 2H), 1.66-1.76 (br m, 2H), 1.20-1.38 (m, 22H), 0.88 (t, ^3J (H,H)=7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 65.7, 64.2, 59.2, 57.5, 51.8, 32.4, 32.0, 29.8, 29.5, 26.5, 23.0, 22.8, 14.2; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.36 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -115.0 (2F), -123.4 (2F), -124.3 (2F), -125.1 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2940 (s, C-H), 1470 (m, C-H), 1235 (s, P=O), 1143 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{26}H_{44}F_{13}NO_4P$ (MH^+) 712.2800, found 712.2804; Anal. Calcd for $C_{26}H_{43}F_{13}NO_4P$: C, 43.89; H, 6.09; N, 1.97. Found: C, 43.88; H, 6.10, N, 1.96.

Hexadecanaminium,*N*-ethyl-2-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_6C_2-

C_{16}) Yield: 22%; M.p. 180-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.38-4.46 (m, 2H), 4.23 (q, ^{3}J(H,H)=6.8 Hz, ^{3}J(H,P)=6.8 Hz, 2H), 3.86-3.92 (m, 2H), 3.43-3.46 (m, 2H), 3.34 (s, 6H), 2.51 (tt, ^{3}J(H,F)=19.0 Hz, 2H), 1.68-1.78 (br m, 2H), 1.20-1.38 (m, 26H), 0.88 (t, ^{3}J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 65.9, 64.3, 59.2, 57.6, 51.9, 32.4, 32.0, 29.9, 29.5, 26.5, 23.0, 22.9, 14.3; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.37 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -115.0 (2F), -123.3 (2F), -124.3 (2F), -125.1 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2935 (s, C-H), 1460 (m, C-H), 1240 (s, P=O), 1143 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{28}H_{48}F_{13}NO_4P$ (MH^+) 740.3113, found 740.3118; Anal. Calcd for $C_{28}H_{47}F_{13}NO_4P$: C, 45.47; H, 6.40; N, 1.89. Found: C, 45.45; H, 6.40, N, 1.99.

Octadecanaminium,*N*-ethyl-2-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_6C_2-C_{18}) Yield: 18%; M.p. 174-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.32-4.39 (m, 2H), 4.19 (q, ^{3}J(H,H)=6.8 Hz, ^{3}J(H,P)=6.8 Hz, 2H), 3.79-3.83 (m, 2H), 3.40-3.45 (m, 2H), 3.32 (s, 6H), 2.50 (tt, ^{3}J(H,H)=6.8 Hz, ^{3}J(H,F)=19.0 Hz, 2H), 1.66-1.76 (br m, 2H), 1.20-1.38 (m, 30H), 0.88 (t, ^{3}J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 65.9, 64.2, 59.2, 57.5, 51.9, 32.1, 29.9, 29.5, 26.5, 23.0, 22.9, 14.3; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, 85 % H_3PO_4): δ = -0.358 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -115.0 (2F), -123.4 (2F), -124.3 (2F), -125.1 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2935 (s, C-H), 1460 (m, C-H), 1245 (s, P=O), 1142 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{30}H_{52}F_{13}NO_4P$ (MH^+) 768.3426, found 768.3433; Anal. Calcd for $C_{30}H_{51}F_{13}NO_4P$: C, 46.94; H, 6.70; N, 1.82. Found: C, 47.05; H, 6.82, N, 1.84.

Eicosanaminium,*N*-ethyl-2-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_6C_2-C_{20}) Yield: 34%; M.p. 175-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.30-4.35 (m, 2H), 4.18 (q, ^{3}J(H,H)=6.8 Hz, ^{3}J(H,P)=6.8 Hz, 2H), 3.79-3.82 (m, 2H), 3.40-3.46 (m, 2H), 3.33 (s, 6H), 2.50 (tt, ^{3}J(H,H)=6.8 Hz, ^{3}J(H,F)=19.0 Hz, 2H), 1.66-1.76 (br m, 2H), 1.20-1.38 (m, 34H), 0.88 (t, ^{3}J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 65.8, 64.0, 58.9, 57.3, 51.6, 31.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.3, 22.8, 22.7,

14.1; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.23 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -115.0 (2F), -123.3 (2F), -124.3 (2F), -125.1 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2928 (s, C-H), 1465 (m, C-H), 1250 (s, P=O), 1147 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{32}H_{56}F_{13}NO_4P$ (MH^+) 796.3739, found 796.3736; Anal. Calcd for $C_{32}H_{55}F_{13}NO_4P$: C, 48.30; H, 6.97; N, 1.76. Found: C, 48.54; H, 7.11, N, 1.81.

Docosanaminium,*N*-ethyl-2-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_6C_2-C_{22}) Yield: 33%; M.p. 162-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.32-4.39 (m, 2H), 4.19 (q, ^3J(H,H)=6.8 Hz, ^3J(H,P)=6.8 Hz, 2H), 3.79-3.82 (m, 2H), 3.41-3.47 (m, 2H), 3.34 (s, 6H), 2.50 (tt, ^3J(H,H)=6.8 Hz, ^3J(H,F)=19.0 Hz, 2H), 1.66-1.76 (br m, 2H), 1.20-1.38 (m, 38H), 0.88 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 65.8, 64.1, 58.9, 57.3, 51.6, 31.9, 29.7, 29.6, 29.5, 29.4, 29.2, 26.3, 22.8, 22.7, 14.1; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.27 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -115.0 (2F), -123.3 (2F), -124.3 (2F), -125.1 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2930 (s, C-H), 1475 (m, C-H), 1244 (s, P=O), 1147 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{34}H_{60}F_{13}NO_4P$ (MH^+) 824.4052, found 824.4062; Anal. Calcd for $C_{34}H_{59}F_{13}NO_4P$: C, 49.57; H, 7.22; N, 1.70. Found: C, 49.53; H, 7.24, N, 1.84.

Octanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_7C_1-C_8) Yield: 56%; M.p. 240 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.32-4.44 (m, 4H), 3.78-3.82 (m, 2H), 3.39-3.43 (m, 2H), 3.29 (s, 6H), 1.66-1.77 (br m, 2H), 1.20-1.36 (m, 10H), 0.87 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 66.1, 64.4, 62.2, 59.4, 51.8, 31.8, 29.3, 29.2, 26.4, 23.0, 29.2, 26.4, 23.0, 22.7, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -1.05 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -122.4 (2F), -123.5 (4F), -124.2 (2F), -124.7 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2945 (s, C-H), 1470 (m, C-H), 1250 (s, P=O), 1153 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{20}H_{29}F_{16}NO_4P$ (MH^+) 664.1673, found 664.1683; Anal. Calcd for $C_{20}H_{29}F_{15}NO_4P$: C, 36.21; H, 4.41; N, 2.11. Found: C, 36.47; H, 4.36, N, 2.12.

Decanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_7C_1-C_{10}) Yield: 41%; M.p. 236 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.32-4.44 (m, 4H), 3.78-3.82 (m, 2H), 3.39-3.43 (m, 2H), 3.29 (s, 6H), 1.66-1.76 (br m, 2H), 1.20-1.38 (m, 14H), 0.87 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 67.0, 66.0, 64.3, 59.5, 51.8, 32.0, 29.6, 29.4, 26.4, 23.0, 22.8, 14.2; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -1.08 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -122.3 (2F), -123.5 (4F), -124.2 (2F), -124.7 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2930 (s, C-H), 1445 (m, C-H), 1255 (s, P=O), 1143 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{22}H_{34}F_{15}NO_4P$ (MH^+) 692.1986, found 692.1986; Anal. Calcd for $C_{22}H_{33}F_{15}NO_4P$: C, 38.21; H, 4.81; N, 2.03. Found: C, 38.26; H, 4.72, N, 2.09.

Dodecanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_7C_1-C_{12}) Yield: 55%; M.p. 234 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.29-4.42 (m, 4H), 3.78-3.82 (m, 2H), 3.36-3.46 (m, 2H), 3.29 (s, 6H), 1.66-1.76 (br m, 2H), 1.20-1.36 (m, 18H), 0.88 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 66.1, 64.3, 62.2, 59.5, 51.7, 32.0, 29.8, 29.4, 26.5, 23.0, 22.8, 14.2; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.95 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -122.3 (2F), -123.5 (4F), -124.2 (2F), -124.7 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2925 (s, C-H), 1486 (m, C-H), 1250 (s, P=O), 1204 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{24}H_{36}F_{15}NO_4P$ (MH^+) 720.2299, found 720.2291; Anal. Calcd for $C_{24}H_{35}F_{15}NO_4P$: C, 40.06; H, 5.18; N, 1.95. Found: C, 40.10; H, 5.08, N, 1.99.

Tetradecanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_7C_1-C_{14}) Yield: 50%; M.p. 204 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.30-4.42 (m, 4H), 3.78-3.82 (m, 2H), 3.38-3.42 (m, 2H), 3.29 (s, 6H), 1.66-1.76 (br m, 2H), 1.20-1.36 (m, 22H), 0.88 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ =

66.0, 64.2, 62.1, 59.4, 51.7, 32.0, 29.8, 29.4, 26.4, 23.0, 22.8, 14.2; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -1.01 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -122.3 (2F), -123.5 (4F), -124.2 (2F), -124.7 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2935 (s, C-H), 1470 (m, C-H), 1250 (s, P=O), 1158 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{26}H_{42}F_{15}NO_4P$ (MH^+) 720.2299, found 720.2291; Anal. Calcd for $C_{26}H_{41}F_{15}NO_4P$: C, 41.77; H, 5.53; N, 1.87. Found: C, 41.91; H, 5.45, N, 1.93.

Hexadecanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_7C_1-C_{16}) Yield: 47%; M.p. 202 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.30-4.44 (m, 4H), 3.78-3.82 (m, 2H), 3.39-3.43 (m, 2H), 3.29 (s, 6H), 1.66-1.76 (br m, 2H), 1.20-1.36 (m, 26H), 0.88 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 66.0, 64.3, 62.1, 59.5, 51.7, 32.0, 29.9, 29.4, 26.5, 23.0, 22.9, 14.3; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.95 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -122.3 (2F), -123.5 (4F), -124.2 (2F), -124.7 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2919 (s, C-H), 1460 (m, C-H), 1255 (s, P=O), 1199 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{28}H_{46}F_{15}NO_4P$ (MH^+) 776.2925, found 776.2941; Anal. Calcd for $C_{28}H_{45}F_{15}NO_4P$: C, 43.36; H, 5.85; N, 1.81. Found: C, 43.31; H, 5.74, N, 1.82.

Octadecanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_7C_1-C_{18}) Yield: 38%; M.p. 198 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.32-4.44 (m, 4H), 3.79-3.83 (m, 2H), 3.38-3.43 (m, 2H), 3.30 (s, 6H), 1.66-1.76 (br m, 2H), 1.20-1.36 (m, 30H), 0.88 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 66.0, 64.3, 62.1, 59.4, 51.7, 32.1, 29.9, 29.4, 26.5, 23.0, 22.8, 14.3; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.86 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -122.3 (2F), -123.5 (4F), -124.2 (2F), -124.7 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2919 (s, C-H), 1481 (m, C-H), 1250 (s, P=O), 1148 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{30}H_{50}F_{15}NO_4P$ (MH^+) 804.3238, found 804.3234; Anal. Calcd for $C_{30}H_{49}F_{15}NO_4P$: C, 44.83; H, 6.15; N, 1.74. Found: C, 44.80; H, 6.00, N, 1.79.

Docosanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_7C_1-C_{22}) Yield: 51%; M.p. 196-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.32-4.44 (m, 4H), 3.81-3.87 (m, 2H), 3.38-3.45 (m, 2H), 3.31 (s, 6H), 1.66-1.76 (br m, 2H), 1.20-1.36 (m, 38H), 0.88 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 66.0, 64.1, 62.1, 59.3, 51.6, 31.9, 30.0, 29.6, 29.5, 29.4, 29.2, 26.2, 22.8, 22.7, 14.1; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -1.03 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -122.3 (2F), -123.4 (4F), -124.2 (2F), -124.7 (2F), -127.5 (2F); IR (CH_2Cl_2, KCl): ν = 2990 (s, C-H), 1429 (m, C-H), 1270 (s, P=O), 1148 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{34}H_{58}F_{15}NO_4P$ (MH^+) 860.3824, found 860.3864; Anal. Calcd for $C_{34}H_{57}F_{15}NO_4P$: C, 47.50; H, 6.68; N, 1.63. Found: C, 47.62; H, 6.76, N, 1.64.

Octanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (HF_6C_1-C_8) Yield: 2.5%; M.p. 156 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.07 (tt, ^2J(H,F)=52.0 Hz, ^3J(H,F)=5.2 Hz, 1H), 4.28-4.44 (m, 4H), 3.77-3.81 (m, 2H), 3.39-3.43 (m, 2H), 3.29 (s, 6H), 1.66-1.76 (m, 2H), 1.20-1.36 (m, 10H), 0.88 (t, ^3J (H,H)=6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 66.1, 64.3, 62.2, 59.5, 51.8, 31.8, 29.3, 29.2, 26.4, 23.0, 22.7, 14.1; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -1.09 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -122.3 (2F), -123.6 (2F), -124.9 (4F), -130.9 (2F), -138.4 (2F); IR (CH_2Cl_2, KCl): ν = 2935 (s, C-H), 1475 (m, C-H), 1260 (s, P=O), 1184 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{19}H_{31}F_{12}NO_4P$ (MH^+) 596.1799, found 596.1777; Anal. Calcd for $C_{19}H_{30}F_{12}NO_4P$: C, 38.33; H, 5.08; N, 2.35. Found: C, 38.60; H, 5.00, N, 2.34.

Decanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (HF_6C_1-C_{10}) Yield: 4.8%; M.p. 152 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.07 (tt, ^2J(H,F)=54.0 Hz, ^3J(H,F)=5.2 Hz, 1H), 4.32-4.44 (m, 4H), 3.78-3.82 (m, 2H), 3.38-3.43 (m, 2H), 3.29 (s, 6H), 1.66-1.76 (m, 2H), 1.20-1.36 (m, 14H), 0.88 (t, ^3J (H,H)=6.8 Hz,

3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 66.0, 64.3, 62.2, 59.5, 51.8, 32.0, 29.6, 29.4, 26.4, 23.0, 22.8, 14.2; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -1.06 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -122.3 (2F), -123.6 (2F), -124.9 (4F), -130.9 (2F), -138.5 (2F); IR (CH_2Cl_2, KCl): ν = 2925 (s, C-H), 1475 (m, C-H), 1276 (s, P=O), 1194 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{21}H_{35}F_{12}NO_4P$ (MH^+) 624.2112, found 624.2108; Anal. Calcd for $C_{21}H_{34}F_{12}NO_4P$: C, 40.46; H, 5.50; N, 2.25. Found: C, 40.50; H, 5.50, N, 2.20.

Dodecanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (HF_6C_1-C_{12}) Yield: 20.3%; M.p. 155 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.07 (tt, ^2J(H,F)=52.0 Hz, ^3J(H,F)=5.2 Hz, 1H), 4.32-4.42 (m, 4H), 3.78-3.82 (m, 2H), 3.38-3.43 (m, 2H), 3.29 (s, 6H), 1.66-1.76 (m, 2H), 1.20-1.36 (m, 18H), 0.88 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 66.0, 64.2, 62.2, 59.4, 51.7, 32.0, 29.8, 29.4, 26.5, 23.0, 22.8, 14.2; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -1.03 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -122.3 (2F), -123.6 (2F), -124.9 (4F), -130.9 (2F), -138.5 (2F); IR (CH_2Cl_2, KCl): ν = 2935 (s, C-H), 1470 (m, C-H), 1260 (s, P=O), 1204 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{23}H_{39}F_{12}NO_4P$ (MH^+) 624.2112, found 624.2108; Anal. Calcd for $C_{23}H_{38}F_{12}NO_4P$: C, 42.40; H, 5.88; N, 2.15. Found: C, 42.63; H, 5.92, N, 2.16.

Tetradecanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl) oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (HF_6C_1-C_{14}) Yield: 9.8%; M.p. 146 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.07 (tt, ^2J(H,F)=52.0 Hz, ^3J(H,F)=5.2 Hz, 1H), 4.28-4.42 (m, 4H), 3.78-3.82 (m, 2H), 3.37-3.42 (m, 2H), 3.29 (s, 6H), 1.66-1.76 (m, 2H), 1.20-1.36 (m, 22H), 0.88 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 66.0, 64.3, 62.2, 59.4, 51.7, 32.0, 29.8, 29.4, 26.5, 23.0, 22.9, 14.3; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.91 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -122.3 (2F), -123.6 (2F), -124.9 (4F), -130.9 (2F), -138.5 (2F); IR (CH_2Cl_2, KCl): ν = 2930 (s, C-H), 1475 (m, C-H), 1276 (s, P=O), 1199 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{25}H_{43}F_{12}NO_4P$ (MH^+) 680.2738, found 680.2706.

Hexadecanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl) oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (HF_6C_1-C_{16}) Yield: 10.5%; M.p. 148 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.07 (tt, ^2J(H,F)=52.0 Hz, ^3J(H,F)=5.2 Hz, 1H), 4.30-4.42 (m, 4H), 3.77-3.81 (m, 2H), 3.37-3.41 (m, 2H), 3.29 (s, 6H), 1.66-1.76 (m, 2H), 1.20-1.36 (m, 26H), 0.88 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 66.0, 64.3, 62.2, 59.5, 51.7, 32.1, 29.9, 29.4, 26.5, 23.0, 22.9, 14.3; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.96 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -122.3 (2F), -123.6 (2F), -124.8 (4F), -130.9 (2F), -138.5 (2F); IR (CH_2Cl_2, KCl): ν = 2930 (s, C-H), 1470 (m, C-H), 1276 (s, P=O), 1199 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{27}H_{47}F_{12}NO_4P$ (MH^+) 708.3051, found 708.3047.

Octadecanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (HF_6C_1-C_{18}) Yield: 26.3%; M.p. 154 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.07 (tt, ^2J(H,F)=52.0 Hz, ^3J(H,F)=5.2 Hz, 1H), 4.30-4.42 (m, 4H), 3.78-3.82 (m, 2H), 3.38-3.42 (m, 2H), 3.29 (s, 6H), 1.66-1.76 (m, 2H), 1.20-1.36 (m, 30H), 0.88 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 66.0, 64.3, 62.2, 59.4, 51.7, 32.1, 29.9, 29.4, 26.5, 23.0, 22.9, 14.3; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.94 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -122.3 (2F), -123.6 (2F), -124.9 (4F), -130.9 (2F), -138.5 (2F); IR (CH_2Cl_2, KCl): ν = 2930 (s, C-H), 1475 (m, C-H), 1281 (s, P=O), 1194 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{29}H_{51}F_{12}NO_4P$ (MH^+) 736.3364, found 736.3367.

Docosanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (HF_6C_1-C_{22}) Yield: 20%; M.p. 175-177 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.06 (tt, ^2J(H,F)=52.0 Hz, ^3J(H,F)=5.2 Hz, 1H), 4.30-4.42 (m, 4H), 3.78-3.82 (m, 2H), 3.38-3.42 (m, 2H), 3.30 (s, 6H), 1.66-1.76 (m, 2H), 1.20-1.36 (m, 38H), 0.88 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 65.8, 64.0, 61.9, 59.2, 51.4, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.2, 22.7, 22.6, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$, 25

°C): δ = -0.95 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -122.3 (2F), -123.7 (2F), -124.9 (4F), -130.9 (2F), -138.5 (2F); IR (CH_2Cl_2, KCl): ν = 2925 (s, C-H), 1470 (m, C-H), 1275 (s, P=O), 1190 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{33}H_{59}F_{12}NO_4P$ (MH^+) 792.3990, found 792.4026; Anal. Calcd for $C_{33}H_{58}F_{12}NO_4P$: C, 50.06; H, 7.38; N, 1.77. Found: C, 50.35; H, 7.48, N, 1.90.

Tetradecanaminium,*N*-ethyl-2-[[[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_8C_2-C_{14}) Yield: 19.8%; M.p. 200 °C (decomp.) ; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.30-4.38 (m, 2H), 4.18 (q, ^3J(H,H)=6.6 Hz, ^3J(H,P)=6.6 Hz, 2H), 3.77-3.82 (m, 2H), 3.42-3.46 (m, 2H), 3.31 (s, 6H), 2.49 (tt, ^3J(H,H)=6.8 Hz, ^3J(H,F)=19.0 Hz, 2H), 1.66-1.76 (br m, 2H), 1.20-1.36 (m, 22H), 0.88 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 65.8, 64.2, 59.2, 57.6, 51.9, 32.0, 29.8, 29.5, 26.5, 23.0, 22.8, 14.2; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.28 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -115.1 (2F), -123.2 (2F), -123.4 (4F), -124.2 (2F), -125.1 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2930 (s, C-H), 1660 (m, C-H), 1235 (s, P=O), 1176 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{28}H_{44}F_{17}NO_4P$ (MH^+) 812.2733, found 812.2737; Anal. Calcd for $C_{28}H_{43}F_{17}NO_4P$: C, 41.44; H, 5.34; N, 1.73. Found: C, 41.68; H, 5.55, N, 1.73.

Hexadecanaminium,*N*-ethyl-2-[[[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_8C_2-C_{16}) Yield: 19.0%; M.p. 188-190 °C ; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.28-4.36 (m, 2H), 4.17 (q, ^3J(H,H)=6.8 Hz, ^3J(H,P)=6.8 Hz, 2H), 3.77-3.81 (m, 2H), 3.39-3.45 (m, 2H), 3.31 (s, 6H), 2.49 (tt, ^3J(H,H)=6.2 Hz, ^3J(H,F)=19.0 Hz, 2H), 1.66-1.76 (br m, 2H), 1.20-1.36 (m, 26H), 0.88 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 65.8, 64.3, 59.2, 57.6, 51.8, 32.1, 29.9, 29.5, 26.5, 23.0, 22.9, 14.2; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.26 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -115.0 (2F), -123.2 (2F), -123.4 (4F), -124.2 (2F), -125.0 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2930 (s, C-H), 1465 (m, C-H), 1240 (s, P=O), 1219 cm^{-1} (s, C-F);

HRMS (FAB) calcd for $C_{30}H_{48}F_{17}NO_4P$ (MH^+) 840.3050, found 840.3085; Anal. Calcd for $C_{30}H_{47}F_{17}NO_4P$: C, 42.91; H, 5.64; N, 1.67. Found: C, 42.86; H, 5.59, N, 1.63.

Octadecanaminium,*N*-ethyl-2-[[[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_8C_2-C_{18}) Yield: 6.2%; M.p. 186-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.28-4.36 (m, 2H), 4.18 (q, ^3J(H,H)=6.8 Hz, ^3J(H,P)=6.8 Hz, 2H), 3.77-3.82 (m, 2H), 3.40-3.44 (m, 2H), 3.31 (s, 6H), 2.49 (tt, ^3J(H,H)=6.4 Hz, ^3J(H,F)=18.8 Hz, 2H), 1.66-1.76 (br m, 2H), 1.20-1.36 (m, 30H), 0.88 (t, ^3J (H,H)=7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 65.9, 64.3, 59.2, 57.6, 51.9, 32.1, 29.9, 29.5, 26.5, 23.0, 22.9, 14.3; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.34 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -115.0 (2F), -123.1 (2F), -123.4 (4F), -124.2 (2F), -125.1 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2935 (s, C-H), 1465 (m, C-H), 1250 (s, P=O), 1230 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{32}H_{52}F_{17}NO_4P$ (MH^+) 868.3363, found 868.3372; Anal. Calcd for $C_{32}H_{51}F_{17}NO_4P$: C, 44.29; H, 5.92; N, 1.61. Found: C, 44.22; H, 5.85, N, 1.58.

Docosanaminium,*N*-ethyl-2-[[[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_8C_2-C_{22}) Yield: 20%; M.p. 175-177 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.28-4.36 (m, 2H), 4.18 (q, ^3J(H,H)=6.8 Hz, ^3J(H,P)=6.8 Hz, 2H), 3.77-3.82 (m, 2H), 3.40-3.47 (m, 2H), 3.33 (s, 6H), 2.50 (tt, ^3J(H,H)=6.4 Hz, ^3J(H,F)=19.2 Hz, 2H), 1.66-1.76 (br m, 2H), 1.20-1.38 (m, 38H), 0.88 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 65.8, 64.1, 58.9, 57.3, 51.7, 32.0, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.3, 22.8, 14.1; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = 0.04 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -115.0 (2F), -123.1 (2F), -123.4 (4F), -124.2 (2F), -125.1 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2924 (s, C-H), 1465 (m, C-H), 1245 (s, P=O), 1230 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{36}H_{60}F_{17}NO_4P$ (MH^+) 924.3989, found 924.3994; Anal. Calcd for $C_{36}H_{59}F_{17}NO_4P$: C, 46.80; H, 6.44; N, 1.52. Found: C, 46.70; H, 6.32, N, 1.43.

Dodecanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,5-nonafluoropentyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (HF_4C_1-

C_{12}) Yield: 2.5%; M.p. 142-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.12 (tt, ^{2}J(H,F)=52.0 Hz, ^{3}J(H,F)=5.5 Hz, 1H), 4.32-4.42 (m, 4H), 3.76-3.81 (m, 2H), 3.37-3.42 (m, 2H), 3.29 (s, 6H), 1.66-1.76 (m, 2H), 1.20-1.36 (m, 18H), 0.88 (t, ^{3}J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 66.2, 64.3, 62.0, 59.4, 51.8, 32.0, 29.8, 29.4, 26.4, 23.0, 22.9, 14.3; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.94 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -122.3 (2F), -126.9 (2F), -131.6 (4F), -138.7 (2F); IR (CH_2Cl_2, KCl): ν = 2930 (s, C-H), 1475 (m, C-H), 1276 (s, P=O), 1196 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{21}H_{39}F_8NO_4P$ (MH^+) 552.2489, found 552.2487.

Tetradecanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,5-nonafluoropentyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (HF_4C_1-C_{14}) Yield: 12.3%; M.p. 146 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.12 (tt, ^{2}J(H,F)=52.0 Hz, ^{3}J(H,F)=5.6 Hz, 1H), 4.28-4.42 (m, 4H), 3.77-3.81 (m, 2H), 3.37-3.42 (m, 2H), 3.29 (s, 6H), 1.65-1.77 (m, 2H), 1.20-1.36 (m, 22H), 0.88 (t, ^{3}J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 66.0, 64.3, 62.0, 59.4, 51.7, 32.0, 29.8, 29.4, 26.5, 23.0, 22.9, 14.3; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -1.02 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -122.3 (2F), -126.9 (2F), -131.6 (4F), -138.7 (2F); IR (CH_2Cl_2, KCl): ν = 2930 (s, C-H), 1470 (m, C-H), 1276 (s, P=O), 1178 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{23}H_{43}F_8NO_4P$ (MH^+) 580.2802 found 580.2791; Anal. Calcd for $C_{23}H_{42}F_8NO_4P$: C, 47.67; H, 7.30; N, 2.42. Found: C, 47.89; H, 7.40, N, 2.38.

Hexadecanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,5-nonafluoropentyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (HF_4C_1-C_{16}) Yield: 4.8%; M.p. 140 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.12 (tt, ^{2}J(H,F)=52.0 Hz, ^{3}J(H,F)=5.6 Hz, 1H), 4.32-4.44 (m, 4H), 3.76-3.80 (m, 2H), 3.37-3.42 (m, 2H), 3.29 (s, 6H), 1.66-1.76 (m, 2H), 1.20-1.36 (m, 26H), 0.88 (t, ^{3}J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 66.0, 64.3, 62.0, 59.4, 51.7, 32.1, 29.9, 29.4, 26.4, 23.0, 22.9, 14.3; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.95 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -122.3 (2F), -126.9 (2F), -131.6 (4F), -138.7 (2F); IR

(CH_2Cl_2, KCl): ν = 2930 (s, C-H), 1475 (m, C-H), 1276 (s, P=O), 1173 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{25}H_{47}F_8NO_4P$ (MH^+) 608.3115 found 608.3105.

Octadecanaminium,*N*-ethyl-2-[[[(2,2,3,3,4,4,5,5,5-nonafluoropentyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (HF_4C_1-C_{18}) Yield: 0.5%; M.p. 138 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.11 (tt, ^2J(H,F)=51.8 Hz, ^3J(H,F)=5.6 Hz, 1H), 4.32-4.44 (m, 4H), 3.76-3.80 (m, 2H), 3.37-3.42 (m, 2H), 3.29 (s, 6H), 1.66-1.76 (m, 2H), 1.20-1.36 (m, 30H), 0.88 (t, ^3J (H,H)=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 66.3, 64.5, 62.1, 59.5, 51.9, 32.1, 29.9, 29.4, 26.4, 23.0, 22.9, 14.3; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -1.10 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -122.3 (2F), -126.8 (2F), -131.5 (4F), -138.7 (2F); IR (CH_2Cl_2, KCl): ν = 2945 (s, C-H), 1465 (m, C-H), 1286 (s, P=O), 1173 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{27}H_{51}F_8NO_4P$ (MH^+) 636.3428 found 636.3428.

4-Phenylbenzaminium,*N*-ethyl-2-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy]hydroxyphosphinyl]oxy]-*N*,*N*-dimethyl-, inner salt. (F_6C_2-biphenyl) Yield: 18%; M.p. 224 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.37-7.65 (m, 9H), 4.91 (s, 2H), 4.45-4.51 (m, 2H), 4.23 (q, ^3J(H,H)=6.8 Hz, ^3J(H,P)=6.8 Hz, 2H), 3.90-3.93 (m, 2H), 3.31 (s, 6H), 2.50 (tt, ^3J(H,H)=6.6 Hz, ^3J(H,F)=18.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 143.6, 139.5, 133.7, 128.9, 128.1, 127.7, 127.1, 126.0, 68.8, 64.3, 59.4, 57.7, 50.4, 32.1; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -0.62 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -82.2 (3F), -115.0 (2F), -123.3 (2F), -124.3 (2F), -125.1 (2F), -127.6 (2F); IR (CH_2Cl_2, KCl): ν = 2945 (s, C-H), 1475 (m, C-H), 1245 (s, P=O), 1148 cm^{-1} (s, C-F); HRMS (FAB) calcd for $C_{25}H_{26}F_{13}NO_4P$ (MH^+) 682.1378, found 682.1392; Anal. Calcd for $C_{25}H_{25}F_{13}NO_4P$: C, 44.06; H, 3.70; N, 2.06. Found: C, 43.80; H, 3.79, N, 2.20.