

Supporting Information

“HFP” Fluorinated Cationic Lipids for Enhanced Lipoplex Stability and Gene Delivery

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Characterization of compounds. Thin layer chromatography (TLC) was performed on precoated plates (0.25 mm Silica Gel 60, F₂₅₄, Merck, Darmstadt, Germany). NMR spectra were recorded on Bruker 200 MHz and 300 MHz Avance DPX instruments. ¹H-, ¹³C-, ¹⁹F-, and ³¹P-NMR chemical shifts δ are reported in ppm relative to their standard reference (¹H: CHCl₃ at 7.27 ppm, H₂O at 4.63 ppm, CD₂HOD at 3.31 ppm, DMSO-*D*₆ at 2.50 ppm; ¹³C: CDCl₃ at 77.0 ppm, CD₃OD at 49.00 ppm, DMSO-*D*₆ at 39.52 ppm; ¹⁹F: CF₃CH₂OH external at -76.99 ppm; ³¹P: H₃PO₄ external at 0.00 ppm). IR spectra were recorded on a FT-IR Nicolet 380 spectrometer in the ATR mode and absorptions values ν are in wave numbers (cm⁻¹). Mass Spectra (MS) were recorded on a Waters Micromass ZQ instrument, using electrospray ionization (ESI) mode. Mass data are reported in mass units (m/z). High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics MicrOTOF-Q spectrometer in ESI mode. Abbreviations: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; b, broad; app., apparent.

2,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorotetradecanoyloxy)-propyl-1-trimethylammonium chloride (1a). TLC *R*_f 0.5 (CHCl₃/MeOH/H₂O 10:6:1). ¹H-NMR (CDCl₃/CD₃OD 1:1, 300 MHz) δ 5.73-5.65 (m, 1 H, COOCH); 4.79-4.65 (m, 1 H, COOCHH); 4.33-4.08 (m, 1 H, COOCHH); 3.80-3.60 (m, 6 H, 2 CF₂CH₂COO, CH₂NMe₃⁺); 3.24 (s, 9 H, NMe₃⁺); 2.15-1.90 (m, 4 H, 2 CF₂CH₂CH₂); 1.57-1.42 (m, 4 H, 2 CF₂CH₂CH₂); 1.31-1.14 (m, 12 H, 2 MeC₇H₁₄); 0.82 (t, *J* = 6.2 Hz, 6H, 2 CH₃CH₂). ¹³C-NMR (CDCl₃/CD₃OD 1:1, 50 MHz) δ 163.81 and 163.40 (2 C=O); 120.0-104.0 (12 CF₂); 67.53 (NCH₂CH); 65.40 (NCH₂CH); 64.02 (NCH₂CHCH₂); 54.28 (3 NCH₃); 36.70 (m, 2 CF₂CH₂CH₂); 31.20 (2 EtCH₂); 30.71 (t, *J* = 22.0 Hz, 2 CF₂CH₂CH₂); 28.58 (2 PrCH₂); 22.21 (2 MeCH₂); 19.86 (2 CF₂CH₂CH₂); 13.56 (2 CH₃CH₂). ¹⁹F-NMR (CDCl₃/CD₃OD 1:1, 188 MHz) δ -105.6 (m, 4 F, 2 CF₂CH₂COO); -108.4 (m, 4 F, 2 CF₂CH₂CH₂); -115.7 (m, 8 F, 2 C₂F₄CF₂CF₂C₂F₄); -116.8 (m, 4 F, 2 CF₂CF₂CH₂COO); -117.5 (m, 4 F, 2 CF₂CF₂CH₂CH₂). IR (film) ν 3377; 2958, 2931; 2873; 1750.

2,3-Bis(3,3,4,4,5,5,6,6-octafluorohexadecanoyloxy)-propyl-1-trimethylammonium chloride (1b). TLC *R*_f 0.5 (CHCl₃/MeOH/H₂O 10:6:1). ¹H-NMR (CDCl₃/CD₃OD 1:1, 300 MHz) δ 5.79-5.57 (m, 1 H, COOCH); 4.76-4.60 (m, 1 H, COOCHH); 4.33-3.60 (m, 7 H, COOCHH, 2 CF₂CH₂COO, CH₂NMe₃⁺); 3.24 (s, 9 H, NMe₃⁺); 2.05-1.79 (m, 4 H, 2 CF₂CH₂CH₂); 1.57-1.41 (m, 4 H, 2 CF₂CH₂CH₂); 1.25-1.11 (m, 28 H, 2 MeC₇H₁₄); 0.79 (t, *J* = 6.2 Hz, 6H, 2 CH₃CH₂). ¹³C-NMR (CDCl₃, 75 MHz) δ 163.74 and 163.37 (2 C=O); 120.0-107.0 (8 CF₂); 67.58 (NCH₂CH); 66.54 (NCH₂CH); 64.92 (NCH₂CHCH₂); 56.01 (3 NCH₃); 37.37 (m, 2 CF₂CH₂CH₂); 31.43 (2 EtCH₂); 30.50 (t, *J* = 20.7 Hz, 2 CF₂CH₂CH₂); 29.24, 29.08, 28.97, 28.84, and 28.72 (2 PrC₅H₁₀); 22.21 (2 MeCH₂); 19.69 (2 CF₂CH₂CH₂); 13.60 (2 CH₃CH₂). ¹⁹F-NMR (CDCl₃/CD₃OD 1:1, 188 MHz) δ -105.7 (m, 4 F, 2 CF₂CH₂COO); -108.4 (m, 4 F, 2 CF₂CH₂CH₂); -117.1 (m, 8 F, 2 C₂F₄CF₂CF₂C₂F₄). IR (film) ν 3388; 2955; 2922; 2854; 1750.

2,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorooctadecanoyloxy)-propyl-1-trimethylammonium chloride (1c). TLC *R*_f 0.5 (CHCl₃/MeOH/H₂O 10:6:1). ¹H-NMR (DMSO-*D*₆, 300 MHz) δ 5.67-5.62 (m, 1 H, COOCH); 4.54 (A part of ABX syst., dd, *J* = 3.2, 12.2 Hz, 1 H, CO₂CHH); 4.23 (B part of ABX syst., dd, *J* = 6.5, 12.2 Hz, 1 H, CO₂CHH); 3.65-3.49 (m, 2 H, CH₂NMe₃⁺); 3.33 (t, *J* = 17.0 Hz, 4 H, OCOCH₂); 3.14 (s, 9 H, NMe₃⁺); 2.27-2.07 (m, 4 H, 2 CF₂CH₂CH₂); 1.53-1.46 (m, 4 H, 2 CF₂CH₂CH₂); 1.27-1.22 (m, 28 H, 2 MeC₇H₁₄); 0.85 (t, *J* = 6.3 Hz, 6H, 2 CH₃CH₂). ¹³C-NMR (CDCl₃, 75 MHz) δ 163.67 and 163.25 (2 C=O); 122.0-107.0 (12 CF₂);

67.40 (NCH₂CH); 65.58 (NCH₂CH); 64.13 (NCH₂CHCH₂); 54.49 (3 NCH₃); 36.73 (m, 2 CF₂CH₂CH₂); 31.54 (2 EtCH₂); 30.53 (t, $J = 22.2$ Hz, 2 CF₂CH₂CH₂); 29.18, 29.07, 28.94, and 28.79 (2 PrC₅H₁₀); 22.32 (2 MeCH₂); 19.75 (2 CF₂CH₂CH₂); 13.64 (2 CH₃CH₂). ¹⁹F-NMR (CDCl₃, 188 MHz) δ -110.0 (m, 4 F, 2 CF₂CH₂COO); -112.7 (m, 4 F, 2 CF₂CH₂CH₂); -119.9 (m, 8 F, 2 C₂F₄CF₂CF₂C₂F₄); -121.3 (m, 4 F, 2 CF₂CF₂CH₂COO); -121.8 (m, 4 F, 2 CF₂CF₂CH₂CH₂). IR (film) ν 3349; 2921; 2853; 1754; 1167; 1136.

2,3-Bis(3,4,4,5,5,6,6,7,7,8,8-undecafluorotetradecen-2-oyloxy)-propyl-1-trimethylammonium chloride (2a). TLC R_f 0.5 (CHCl₃/MeOH/H₂O 10:6:1). ¹H-NMR (CDCl₃/CD₃OD 1:1, 300 MHz) δ 6.10 and 6.04 (2d, $J = 29.4$ Hz, 2 H, 2 CF=CHCOO); 5.77-5.68 (m, 1 H, CHCH₂NMe₃⁺); 4.74 (A part of ABX syst., dd, $J = 3.0, 12.3$ Hz, 1 H, CO₂CHH); 4.28 (B part of ABX syst., dd, $J = 5.1, 12.3$ Hz, 1 H, CO₂CHH); 4.16-3.82 (m, 2 H, COOCH₂); 3.24 (s, 9 H, NMe₃⁺); 1.99 (tt, $J = 8.4, 18.6$ Hz, 4 H, 2 CF₂CH₂); 1.56-1.50 (m, 4 H, 2 CF₂CH₂CH₂); 1.42-1.17 (m, 12 H, 2 MeC₃H₆); 0.84 (t, $J = 6.6$ Hz, 6 H; 2 CH₂CH₃). IR (film) ν 3367, 2959, 2929, 2861, 1737. ESI-HRMS for C₃₄H₄₂ClF₂₂NO₄: calcd. 946.2757 [M-Cl]⁺, found 946.2737.

2,3-Bis(3,4,4,5,5,6,6-heptafluorohexadecen-2-oyloxy)-propyl-1-trimethylammonium chloride (2b). TLC R_f 0.5 (CHCl₃/MeOH/H₂O 10:6:1). ¹H-NMR (CDCl₃/CD₃OD 1:1, 300 MHz) δ 6.02 and 5.98 (2d, $J = 29.7$ Hz, 2 H, 2 CF=CHCOO); 5.74 (m, 1 H, CHCH₂NMe₃⁺); 4.72 (A part of ABX syst., dd, $J = 3.3, 12.3$ Hz, 1 H, CO₂CHH); 4.30 (B part of ABX syst., dd, $J = 5.1, 12.3$ Hz, 1 H, CO₂CHH); 4.19 (A part of ABX syst., bd, $J = 14.4$ Hz, 1 H, CHHNMe₃⁺); 3.80 (B part of ABX syst., dd, $J = 8.4, 14.1$ Hz, 1 H, CHHNMe₃⁺); 3.26 (s, 9 H, NMe₃⁺); 2.01 (tt, $J = 8.3, 18.4$ Hz, 4 H, 2 CF₂CH₂); 1.57-1.51 (m, 4 H, 2 CF₂CH₂CH₂); 1.35-1.20 (m, 28 H, 2 MeC₇H₁₄); 0.84 (t, $J = 6.6$ Hz, 6 H; 2 CH₂CH₃). ¹³C-NMR (CDCl₃/CD₃OD 1:1, 75 MHz) δ 161.81 (2 COO); 157.58-153.54 (m, 2 CF=CH); 122.20-105.30 (m, 6 CF₂); 104.76 (m, 2 CF=CH); 69.06 (CH₂NMe₃⁺); 66.48 (CHCH₂NMe₃⁺); 63.68 (CH₂CHCH₂NMe₃⁺); 54.49 (3 NCH₃⁺); 31.64 (2 EtCH₂); 30.55 (t, $J = 22.2$ Hz, 2 CF₂CH₂); 29.27, 29.14, 29.04, 28.99, and 28.87 (2 PrC₅H₁₀); 22.43 (2 MeCH₂); 19.84 (2 CF₂CH₂CH₂); 13.83 (2 CH₃CH₂). ¹⁹F-NMR (CDCl₃, 188 MHz) δ -103.9 (m, 2 F, 2 CH=CF); -112.0 (m, 4 F, CF₂CH₂); -116.7 (m, 4 F, 2 CH=CFCE₂); -122.8 (m, 4 F, CF₂CF₂CH₂). IR (film) ν 3390; 2926; 2856; 1735. ESI-HRMS for C₃₈H₅₈ClF₁₄NO₄: calcd. 858.4137 [M-Cl]⁺, found 858.4170.

2,3-Bis(3,4,4,5,5,6,6,7,7,8,8-undecafluorooctadecen-2-oyloxy)-propyl-1-trimethylammonium chloride (2c). TLC R_f 0.5 (CHCl₃/MeOH/H₂O 10:6:1). ¹H-NMR (CDCl₃/CD₃OD 1:1, 300 MHz) δ 6.09 and 6.04 (2d, $J = 29.4$ Hz, 2 H, 2 CF=CHCOO); 5.78-5.70 (m, 1 H, CHCH₂NMe₃⁺); 4.74 (A part of ABX syst., dd, $J = 3.3, 12.3$ Hz, 1 H, CO₂CHH); 4.28 (B part of ABX syst., dd, $J = 5.0, 12.1$ Hz, 1 H, CO₂CHH); 4.12 (A part of ABX syst., bd, $J = 13.8$ Hz, 1 H, CHHNMe₃⁺); 3.73 (B part of ABX syst., m, 1 H, CHHNMe₃⁺); 3.23 (s, 9 H, NMe₃⁺); 1.99 (m, 4 H, 2 CF₂CH₂); 1.59-1.39 (m, 4 H, 2 CF₂CH₂CH₂); 1.30-1.23 (m, 28 H, 2 MeC₇H₁₄); 0.83 (t, $J = 6.5$ Hz, 6 H, 2 CH₂CH₃). ¹³C-NMR (CDCl₃, 75 MHz) δ 163.95 (2 COO); 158.38-153.77 (m, CH=CF); 122.17-105.68 (m, 10 CF₂); 105.28 and 105.00 (2 OCOCH=CF); 67.90, 65.25 and 64.40 (3 C, OCH₂CHCH₂N); 54.71 (3 C, NCH₃); 31.83 (EtCH₂); 30.77 (t, $J = 22.0$ Hz, C₉H₁₉CH₂); 29.48-29.10 (PrC₅H₁₀); 22.62 (MeCH₂); 20.02 (C₈H₁₇CH₂); 14.01 (CH₃). ¹⁹F-NMR (CDCl₃, 188 MHz) δ -106.2 (m, 2 F, 2 CH=CF); -112.8 (m, 4 F, 2 CF₂CH₂); -117.2 (m, 4 F, 2 CH₂C₃F₆CF₂); -120.1 (m, 4 F, 2 CH₂C₂F₄CF₂); -121.4 (m, 4 F, 2 CH=CFCE₂); -122.0 (m, 4 F, 2

CH₂CF₂CF₂). IR (film) ν 3392; 2954; 2924; 2855; 1739. ESI-HRMS for C₄₂H₅₈ClF₂₂NO₄: calcd. 1058.4009 [M-Cl]⁺, found 1058.3977.

1,2-Di[(Z)-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorohexadec-9-enoyl]-sn-glycero-3-phosphatidylethanolamine (3). TLC R_f 0.6 (CHCl₃/MeOH/H₂O 10/6/1). ¹H-NMR (CDCl₃/CD₃OD 1:1, 300 MHz) δ 6.43-6.29 (m, 2 H, *E*-CH=CHCF₂); 6.24-5.98 (m, 2 H, *Z*-CH=CHCF₂); 5.64-5.39 (m, 2 H, CH=CHCF₂); 5.38-5.29 (m, 1 H, POCH₂CHCH₂); 4.66-4.33 (m, 2 H, POCH₂CHO); 4.08-3.96 (m, 4 H, CH₂CH₂NH₃⁺, POCH₂CHCH₂); 3.22 (t, J = 17.7 Hz, 4 H, 2 CH₂CO₂); 2.42-2.25 (m, 4 H, 2 CH=CHCH₂); 1.50-1.22 (m, 16 H, H_{Alk}); 0.89 (m, J = 6.3 Hz, 6 H, 2 CH₃). ¹³C-NMR (CDCl₃/CD₃OD 1:1, 75 MHz) δ 164.65 and 164.42 (2 C=O); 146.16 (2 CH=CHCF₂); 119.2-103.2 (12 CF₂); 116.54 (t, J = 23.1 Hz, 2 CH=CHCF₂); 72.32 (CH₂CHOCH₂); 63.96 and 63.79 (CO₂CH₂CHOCH₂); 62.14 (CH₂CH₂NH₃⁺); 41.08 (CH₂CH₂NH₃⁺); 37.08 (m, 2 CH₂COO); 32.09 (2 EtCH₂); 29.53, 29.33, and 29.10 (2 EtCH₂CH₂CH₂); 20.03 (2 MeCH₂); 14.20 (2 CH₃). ¹⁹F-NMR (CDCl₃/CD₃OD 1:1, 188 MHz) δ -104.7 (m, 4 F, 2 *Z*-CF₂CH=CH); -109.4 (m, 4 F, 2 *E*-CF₂CH=CH); -110.0 (m, 4 F, 2 CF₂CH₂); -119.8 (m, 8 F, C₂F₄CF₂CF₂C₂F₄); -121.3 (m, 4 F, CF₂CF₂CH₂); -121.9 (m, 4 F, CF₂CF₂CH=CH). ³¹P-NMR (CDCl₃/CD₃OD 1:1, 121 MHz) δ 1.14. IR (film) ν 3377; 2959; 2929; 2858; 1751; 1194; 1140; 1092.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,10-diiodotetradecyl benzoate (4a). TLC R_f 0.6 (*n*-C₆H₁₄/CH₂Cl₂ 8:2). ¹H-NMR (CDCl₃, 300 MHz) δ 8.06 (d, J = 7.2 Hz, 2 H, 2 *o*-H_{Ar}); 7.63 (t, J = 7.5 Hz, 1 H, *p*-H_{Ar}); 7.48 (t, J = 7.6 Hz, 2 H, 2 *m*-H_{Ar}); 7.36 (dd, J = 2.4, 10.5 Hz, 1 H, COOCH₂); 4.37-4.32 (m, 1 H, C₄H₉CH₂); 3.65-3.10 (m, 2 H, COOCH₂CH₂); 3.02-2.65 (m, 2 H, C₄H₉CH₂CH₂); 1.89-1.74 (m, 2 H, PrCH₂); 1.43-1.27 (m, 4 H, MeCH₂CH₂); 0.94 (t, J = 7.2 Hz, 3 H, CH₃). ¹³C-NMR (CDCl₃, 75 MHz) δ 163.43 (C=O); 134.09 (*p*-C_{Ar}); 130.02 (2 *o*-C_{Ar}); 128.60 (2 *m*-C_{Ar}); 128.32 (C_{Ar}COO); 121-106 (6 CF₂); 43.85 (t, J = 21.0 Hz, COOCH₂CH₂); 41.67 (t, J = 20.7 Hz, BuCH₂CH₂); 40.89 (COOCH₂); 39.99 (BuCH₂); 31.60 (EtCH₂); 21.60 (MeCH₂); 20.92 (PrCH₂); 13.79 (CH₃). ¹⁹F-NMR (CDCl₃, 188 MHz) δ -111.9 (AB syst., δ_A = -110.3, δ_B = -113.4, J = 282 Hz, 2 F, CF₂CH₂CH₂IOCO); -111.1 (AB syst., δ_A = -108.3, δ_B = -111.9, J = 270 Hz, 2 F, CF₂CH₂CH₂CH₂C₈H₁₇); -119.5 (m, 4 F, 2 CH₂CF₂CF₂); 121.5 (m, 4 F, C₂F₄C₂CF₂C₂F₄). IR (film) ν 2927; 2856; 1745.

3,3,4,4,5,5,6,6-Octafluoro-1,8-diiodohexadecyl benzoate (4b). TLC R_f 0.6 (*n*-C₆H₁₄/CH₂Cl₂ 3:1). ¹H-NMR (CDCl₃, 200 MHz) δ 8.05 (d, J = 7.6 Hz, 2 H, 2 *o*-H_{Ar}); 7.64 (t, J = 7.0 Hz, 1 H, *p*-H_{Ar}); 7.49 (t, J = 7.4 Hz, 2 H, 2 *m*-H_{Ar}); 7.34 (d, J = 10.0 Hz, 1 H, COOCH₂); 4.41-4.26 (m, 1 H, C₈H₁₇CH₂); 3.53-2.71 (m, 4 H, 2CF₂CH₂); 1.79 (m, 2 H, C₇H₁₅CH₂); 1.60-1.20 (m, 12 H, MeC₆H₁₂); 0.90 (t, J = 6.0 Hz, 3 H, CH₃). ¹³C-NMR (CDCl₃, 50 MHz) δ 163.36 (C=O); 134.00 (*p*-C_{Ar}); 130.00 (2 *o*-C_{Ar}); 128.56 (2 *m*-C_{Ar}); 128.37 (C_{Ar}COO); 120-107 (4 CF₂); 43.93 (t, J = 20.5 Hz, COOCH₂CH₂); 41.72 (t, J = 20.8 Hz, C₈H₁₇CH₂CH₂); 41.19 (COOCH₂); 40.30 (C₈H₁₇CH₂); 31.76 (EtCH₂); 29.50, 29.28, 29.14, and 28.47 (PrC₄H₈); 22.60 (MeCH₂); 21.17 (C₇H₁₅CH₂); 14.04 (CH₃). ¹⁹F-NMR (CDCl₃, 188 MHz) δ -111.1 (AB syst., δ_A = -109.5, δ_B = -112.6, J = 282 Hz, 2 F, CF₂CH₂CH₂IOCO); -111.2 (AB syst., δ_A = -109.7, δ_B = -112.7, J = 270 Hz, 2 F, CF₂CH₂CH₂CH₂C₈H₁₇); -121.3 (m, 4 F, CF₂C₂F₄CF₂). IR (film) ν 2925; 2855; 1745.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,10-diiodooctadecyl benzoate (4c). TLC R_f 0.5 ($n\text{-C}_6\text{H}_{14}/\text{CH}_2\text{Cl}_2$ 1:1). ^1H -NMR (CDCl_3 , 300 MHz) δ 8.05 (d, $J = 7.2$ Hz, 2 H, $o\text{-H}_{\text{Ar}}$); 7.64 (t, $J = 7.1$ Hz, 1 H, $p\text{-H}_{\text{Ar}}$); 7.49 (t, $J = 7.6$ Hz, 2 H, $m\text{-H}_{\text{Ar}}$); 7.34 (dd, $J = 2.5, 10.5$ Hz, 1 H, COOCH); 4.37-4.31 (m, 1 H, $\text{C}_8\text{H}_{17}\text{CH}$); 3.60-3.44 and 3.37-3.09 (2 m, 2 H, COOCHICH_2); 3.02-2.67 (m, 2 H, $\text{C}_8\text{H}_{17}\text{CHICH}_2$); 1.74-1.82 (m, 2 H, $\text{C}_7\text{H}_{15}\text{CH}_2$); 1.60-1.26 (m, 12 H, $\text{MeC}_6\text{H}_{12}$); 0.89 (t, $J = 6.0$ Hz, CH_3). ^{13}C -NMR (CDCl_3 , 75 MHz) δ 163.51 (COO); 134.14 ($p\text{-C}_{\text{Ar}}$); 130.05 (2 $o\text{-C}_{\text{Ar}}$); 128.65 (2 $m\text{-C}_{\text{Ar}}$); 128.33 ($\text{C}_{\text{Ar}}\text{COO}$); 121-106 (6 CF_2); 43.88 (t, $J = 21.5$ Hz, COOCHICH_2); 41.70 (t, $J = 20.6$ Hz, $\text{C}_8\text{H}_{17}\text{CHICH}_2$); 40.89 (COOCH); 40.81 ($\text{C}_8\text{H}_{17}\text{CH}$); 31.79 (EtCH_2); 29.53, 29.31, 29.17, and 28.49 (PrC_4H_8); 22.63 (MeCH_2); 21.07 ($\text{C}_7\text{H}_{15}\text{CH}_2$); 14.07 (CH_3). ^{19}F -NMR (CDCl_3 , 188 MHz) δ -111.0 (AB syst., $\delta_A = -112.5$, $\delta_B = -119.4$, $J = 263$ Hz, 2 F, $\text{CF}_2\text{CH}_2\text{CHIOCO}$); -111.1 (AB syst., $\delta_A = -108.3$, $\delta_B = -113.9$, $J = 282$ Hz, 2 F, $\text{CF}_2\text{CH}_2\text{CHIC}_8\text{H}_{17}$); -119.6 (m, 4 F, 2 $\text{CH}_2\text{CF}_2\text{CF}_2$); 121.5 (m, 4 F, $\text{C}_2\text{F}_4\text{C}_2\text{F}_4\text{C}_2\text{F}_4$). IR (film) ν 2926; 2855; 1744.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluorotetradecyl benzoate (5a). TLC R_f 0.3 ($n\text{-C}_6\text{H}_{14}/\text{CH}_2\text{Cl}_2$ 6:4). ^1H -NMR (CDCl_3 , 300 MHz) δ 8.06 (d, $J = 7.2$ Hz, 2 H, $o\text{-H}_{\text{Ar}}$); 7.58 (t, $J = 7.8$ Hz, 1 H, $p\text{-H}_{\text{Ar}}$); 7.45 (dd, $J = 7.2, 7.8$ Hz, 2 H, $m\text{-H}_{\text{Ar}}$); 4.64 (t, $J = 6.3$ Hz, 2 H, COOCH_2); 2.61 (tt, $J = 6.3, 18.3$ Hz, 2 H, $\text{COOCH}_2\text{CH}_2$); 2.10-2.01 (m, 2 H, $\text{C}_5\text{H}_{11}\text{CH}_2$); 1.64-1.56 (m, 2 H, BuCH_2); 1.44-1.33 (m, 6 H, MeC_2H_6); 0.89 (t, $J = 6.0$ Hz, 3 H, CH_3). ^{13}C -NMR (CDCl_3 , 75 MHz) δ 166.08 (COO); 133.22 ($p\text{-C}_{\text{Ar}}$); 129.65 (3 C, $\text{C}_{\text{Ar}}\text{COO}$, 2 $o\text{-C}_{\text{Ar}}$); 128.40 (2 C, 2 $m\text{-C}_{\text{Ar}}$); 125.00-110.00 (6 CF_2); 56.86 (COOCH_2); 31.38 (EtCH_2); 30.94 (t, $J = 17.2$ Hz, $\text{COOCH}_2\text{CH}_2$); 30.71 (t, $J = 21.4$ Hz, $\text{C}_5\text{H}_{11}\text{CH}_2$); 28.76 (PrCH_2); 22.39 (MeCH_2); 16.35 (BuCH_2); 13.84 (CH_3). ^{19}F -NMR (CDCl_3 , 188 MHz) δ -111.6 (m, 2 F, $\text{OC}_2\text{H}_4\text{CF}_2$); -112.4 (m, 2 F, $\text{C}_6\text{H}_{13}\text{CF}_2$); -119.8 (m, 4 F, 2 $\text{CH}_2\text{CF}_2\text{CF}_2$); -121.7 (m, 4 F, 2 $\text{CH}_2\text{C}_2\text{F}_4\text{CF}_2$). IR (film) ν 2959; 2859; 1727.

3,3,4,4,5,5,6,6-Octafluorohexadecyl benzoate (5b). TLC R_f 0.5 ($n\text{-C}_6\text{H}_{14}/\text{CH}_2\text{Cl}_2$ 3:1). ^1H -NMR (CDCl_3 , 200 MHz) δ 8.06 (d, $J = 7.8$ Hz, 2 H, $o\text{-H}_{\text{Ar}}$); 7.58 (t, $J = 7.0$ Hz, 1 H, $p\text{-H}_{\text{Ar}}$); 7.45 (dd, $J = 7.0, 7.6$ Hz, 2 H, $m\text{-H}_{\text{Ar}}$); 4.63 (t, $J = 6.6$ Hz, 2 H, CH_2OCO); 2.60 (tt, $J = 6.4, 18.2$ Hz, 2 H, $\text{CH}_2\text{CH}_2\text{OCO}$); 2.19-1.94 (m, 2 H, $\text{C}_9\text{H}_{19}\text{CH}_2$); 1.70-1.53 (m, 2 H, $\text{C}_8\text{H}_{17}\text{CH}_2$); 1.45-1.20 (m, 14 H, $\text{MeC}_7\text{H}_{14}$); 0.91 (t, $J = 7.4$ Hz, 3 H, CH_3). ^{13}C -NMR (CDCl_3 , 75 MHz) δ 166.08 (COO); 133.17 ($p\text{-C}_{\text{Ar}}$); 129.64 (3 C, $\text{C}_{\text{Ar}}\text{COO}$, 2 $o\text{-C}_{\text{Ar}}$); 128.37 (2 C, 2 $m\text{-C}_{\text{Ar}}$); 57.01 (COOCH_2); 31.87 (EtCH_2); 30.96 (t, $J = 22.5$ Hz, $\text{COOCH}_2\text{CH}_2$); 30.76 (t, $J = 21.5$ Hz, $\text{C}_9\text{H}_{19}\text{CH}_2$); 29.51-29.13 (5 C, $\text{PrC}_5\text{H}_{10}$); 22.66 (MeCH_2); 20.13 ($\text{C}_8\text{H}_{17}\text{CH}_2$); 14.02 (CH_3). ^{19}F -NMR (CDCl_3 , 188 MHz) δ -111.6 (m, 2 F, $\text{COOC}_2\text{H}_4\text{CF}_2$); -112.5 (m, 2 F, $\text{C}_{10}\text{H}_{21}\text{CF}_2$); -121.4 (m, 2 F, $\text{COOC}_2\text{H}_4\text{CF}_2\text{CF}_2$); -121.7 (m, 2 F, $\text{C}_{10}\text{H}_{21}\text{CF}_2\text{CF}_2$). IR (film) ν 2925; 2855; 1726.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluorooctadecyl benzoate (5c). TLC R_f 0.4 ($n\text{-C}_6\text{H}_{14}/\text{CH}_2\text{Cl}_2$ 7:3). ^1H -NMR (CDCl_3 , 300 MHz) δ 8.06 (d, $J = 7.8$ Hz, 2 H, $o\text{-H}_{\text{Ar}}$); 7.59 (t, $J = 7.5$ Hz, 1 H, $p\text{-H}_{\text{Ar}}$); 7.46 (t, $J = 7.5$ Hz, 2 H, $m\text{-H}_{\text{Ar}}$); 4.64 (t, $J = 6.6$ Hz, 2 H, COOCH_2); 2.62 (tt, $J = 6.3, 18.3$ Hz, 2 H, $\text{COOCH}_2\text{CH}_2$); 2.15-1.97 (m, 2 H, $\text{C}_9\text{H}_{19}\text{CH}_2$); 1.67-1.59 (m, 2 H, $\text{C}_8\text{H}_{17}\text{CH}_2$); 1.45-1.29 (m, 14 H, $\text{MeC}_7\text{H}_{14}$); 0.90 (t, $J = 7.2$ Hz, 3 H, CH_3). ^{13}C -NMR (CDCl_3 , 75 MHz) δ 166.09 (COO); 132.24 ($p\text{-C}_{\text{Ar}}$); 129.66 (2 C, 2 $o\text{-C}_{\text{Ar}}$); 129.57 ($\text{C}_{\text{Ar}}\text{COO}$); 128.41 (2 C, 2 $m\text{-C}_{\text{Ar}}$); 110.00-125.00 (m, 6 CF_2); 56.88 (COOCH_2); 31.88 (EtCH_2); 30.95 (t, $J = 22.1$ Hz, $\text{COOCH}_2\text{CH}_2$); 30.73 (t, $J = 21.6$ Hz, $\text{C}_9\text{H}_{19}\text{CH}_2$); 29.52, 29.40, 29.29, 29.24 and 29.13 (5 C, $\text{PrC}_5\text{H}_{10}$); 22.67

(MeCH₂); 20.11 (C₈H₁₇CH₂); 14.03 (CH₃). ¹⁹F-NMR (CDCl₃, 188 MHz) δ -111.4 (m, 2 F, OC₂H₄CF₂); -112.3 (m, 2 F, C₆H₁₃CF₂); -119.7 (m, 4 F, 2 CH₂CF₂CF₂); -121.6 (m, 4 F, 2 CH₂C₂F₄CF₂). IR (film) ν 2959; 2860; 1727.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluorotetradecanol (6a). TLC *R_f* 0.15 (*n*-C₆H₁₄/CH₂Cl₂ 1:1). ¹H-NMR (CDCl₃, 200 MHz) δ 3.93 (t, *J* = 6.0 Hz, 2 H, CH₂OH); 2.35 (tt, *J* = 6.2, 18.8 Hz, 2H, CH₂CH₂OH); 2.18-1.90 (m, 2 H, C₅H₁₁CH₂); 1.63-1.56 (m, 2 H, C₄H₉CH₂); 1.50-1.29 (m, 6 H, MeC₃H₆); 0.91 (t, *J* = 6.6 Hz, 3 H, CH₃). ¹³C-NMR (CDCl₃, 50 MHz) δ 124.00-105.00 (6 CF₂); 54.92 (CH₂OH); 33.90 (t, *J* = 21.1 Hz, CH₂CH₂OH); 31.50 (EtCH₂); 31.01 (t, *J* = 22.3 Hz, C₅H₁₁CH₂); 28.88 (PrCH₂); 22.46 (MeCH₂); 20.14 (BuCH₂); 13.70 (CH₃). ¹⁹F-NMR (CDCl₃, 188 MHz) δ -111.6 (m, 2 F, CF₂C₂H₄OH); -112.5 (m, 2 F, C₆H₁₂CF₂); -119.9 (m, 4 F, C₂F₄C₂F₄C₂F₄); -121.7 (m, 2F, CF₂CF₂C₂H₄OH); -122.0 (m, 2 F, C₆H₁₂CF₂CF₂). IR (film) ν 3353; 2958.

3,3,4,4,5,5,6,6-Octafluorohexadecanol (6b). TLC *R_f* 0.6 (*n*-C₆H₁₄/CH₂Cl₂ 6:4). ¹H-NMR (CDCl₃, 300 MHz) δ 3.93 (t, *J* = 6.3 Hz, 2 H, CH₂OH); 2.35 (tt, *J* = 6.0, 25.6 Hz, 2 H, CH₂CH₂OH); 2.08-1.98 (m, 2 H, CH₂C₉H₁₉); 1.65-1.53 (m, 2 H, CH₂C₈H₁₇); 1.30-1.21 (m, 14 H, C₇H₁₄Me); 0.89 (t, *J* = 6.3 Hz, 3 H, CH₃). ¹³C-NMR (CDCl₃, 50 MHz) δ 55.00 (CH₂OH); 33.98 (t, *J* = 21.0 Hz, CH₂CH₂OH); 31.96 (EtCH₂); 31.02 (t, *J* = 22.4 Hz, CH₂C₉H₁₉); 29.61-29.23 (5 C, PrC₅H₁₀); 22.71 (MeCH₂); 20.20 (C₈H₁₇CH₂); 13.95 (CH₃). ¹⁹F-NMR (CDCl₃, 188 MHz) δ -111.6 (m, 2 F, CF₂C₂H₄OH); -112.5 (m, 2 F, CF₂C₁₀H₂₁); -121.6 (m, 2 F, CF₂CF₂C₂H₄OH); -122.0 (m, 2 F, CF₂CF₂C₁₀H₂₁). IR (film) ν 3356; 2925; 2856.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluorooctadecanol (6c). TLC *R_f* 0.15 (*n*-C₆H₁₄/CH₂Cl₂ 6:4). ¹H-NMR (CDCl₃, 300 MHz) δ 4.00 (t, *J* = 6.3 Hz, 2 H, CH₂OH); 2.40 (tt, *J* = 6.3, 25.5 Hz, 2 H, CH₂CH₂OH); 2.15-1.96 (m, 2 H, CH₂C₉H₁₉); 1.66-1.54 (m, 2 H, CH₂C₈H₁₇); 1.38-1.27 (m, 14 H, C₇H₁₄Me); 0.89 (t, *J* = 6.9 Hz, 3 H, CH₃). ¹³C-NMR (CDCl₃, 50 MHz) δ 55.18 (CH₂OH); 33.93 (t, *J* = 21.2 Hz, CH₂CH₂OH); 31.90 (EtCH₂); 30.95 (t, *J* = 22.3 Hz, CH₂C₉H₁₉); 29.54-29.15 (5 C, PrC₅H₁₀); 22.68 (MeCH₂); 20.12 (C₈H₁₇CH₂); 14.02 (CH₃). ¹⁹F-NMR (CDCl₃, 188 MHz) δ -111.4 (m, 2 F, CF₂C₂H₄OH); -112.4 (m, 2 F, CF₂C₁₀H₂₁); -119.8 (m, 4 F, CF₂CF₂C₂H₄OH, CF₂CF₂C₁₀H₂₁); -121.7 (m, 4 F, C₂F₄C₂F₄C₂F₄). IR (film) ν 3335; 2922; 2854.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluorotetradecanoic acid (7a). TLC *R_f* 0.2 (AcOEt/CHCl₃ 2:8). ¹H-NMR (CDCl₃, 300 MHz) δ 3.22 (t, *J* = 17.4 Hz, 2 H, CH₂COOH); 2.06 (tt, *J* = 7.5, 12.6 Hz, 2 H, CF₂CH₂CH₂); 1.60 (m, 2 H, CF₂CH₂CH₂); 1.43-1.27 (m, 6 H, MeC₃H₆); 0.91 (t, *J* = 6.6 Hz, 3 H, CH₃). ¹³C-NMR (CDCl₃, 75 MHz) δ 170.08 (COOH); 118.60-102.10 (m, 6 CF₂); 36.71 (t, *J* = 22.0 Hz, CH₂COOH); 31.39 (EtCH₂); 30.94 (t, *J* = 22.4 Hz, C₅H₁₁CH₂); 27.78 (EtCH₂); 22.41 (MeCH₂); 20.07 (BuCH₂); 13.93 (CH₃). ¹⁹F-NMR (CDCl₃, 188 MHz) δ -109.9 (m, 2 F, CF₂CH₂COOH); -112.3 (m, 2 F, C₆H₁₃CF₂); -119.7 (m, 4 F, C₂F₄C₂F₄C₂F₄); 121.0 (m, 2 F, CF₂CF₂CH₂COOH); 121.5 (m, 2 F, CF₂CF₂C₆H₁₃). IR (film) ν 2955; 2871; 1716.

3,3,4,4,5,5,6,6-Octafluorohexadecanoic acid (7b). TLC *R_f* 0.2 (CHCl₃/AcOEt 7:3). ¹H-NMR (CDCl₃, 300 MHz) δ 3.20 (t, *J* = 17.1 Hz, 2 H, CH₂COOH); 2.15-1.98 (m, 2 H, CF₂CH₂CH₂); 1.60 (m, 2 H, CF₂CH₂CH₂); 1.35-1.25

(m, 14 H, MeC₇H₁₄); 0.89 (t, $J = 6.0$ Hz, 3 H, CH₃). ¹³C-NMR (CDCl₃, 75 MHz) δ 161.89 (COOH); 121.10-107.80 (m, 4 CF₂); 35.96 (t, $J = 21.1$ Hz, CH₂COOH); 31.90 (EtCH₂); 30.94 (t, $J = 22.2$ Hz, C₉H₁₉CH₂); 29.53, 29.42, 29.31, 29.26, and 29.15 (PrC₅H₁₀); 22.68 (CH₃CH₂); 20.13 (CF₂CH₂CH₂); 14.01 (CH₃). ¹⁹F-NMR (CDCl₃, 188 MHz) δ -110.2 (m, 2 F, CF₂CH₂COOH); -112.4 (m, 2 F, C₁₀H₂₁CF₂); -119.7 (m, 4 F, CF₂C₂F₄CF₂). IR (film) ν 2919; 2851; 1716.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluorooctadecanoic acid (7c). TLC R_f 0.2 (AcOEt/CH₂Cl₂ 1:3). ¹H-NMR (CDCl₃, 300 MHz) δ 3.21 (t, $J = 17.4$ Hz, 2 H, CH₂COOH); 2.14-1.96 (m, 2 H, CF₂CH₂CH₂); 1.60 (m, 2 H, CF₂CH₂CH₂); 1.28 (m, 14 H, MeC₇H₁₄); 0.89 (t, $J = 6.0$ Hz, 3 H, CH₃). ¹³C-NMR (CDCl₃, 75 MHz) δ 169.37 (COOH); 125.02-105.18 (m, 6 CF₂); 36.63 (t, $J = 22.8$ Hz, CH₂COOH); 31.87 (EtCH₂); 30.94 (t, $J = 22.0$ Hz, C₉H₁₉CH₂); 29.50, 29.38, 29.27, 29.22, and 29.11 (PrC₅H₁₀); 22.67 (CH₃CH₂); 20.10 (CF₂CH₂CH₂); 14.09 (CH₃). ¹⁹F-NMR (CDCl₃, 188 MHz) δ -109.9 (m, 2 F, CF₂CH₂COOH); -112.3 (m, 2 F, C₁₀H₂₁CF₂); -119.7 (m, 4 F, C₂F₄C₂F₄C₂F₄); -121.0 (m, 2 F, CF₂CF₂CH₂COOH); -121.5 (s, 2 F, C₁₀H₂₁CF₂CF₂). IR (film) ν 2920; 2855; 1716.

N-[1-(2,3-Dihydroxy)propyl]-N,N,N-trimethylammonium chloride (8). ¹H-NMR (D₂O, 300 MHz) δ 4.19-4.12 (m, 1 H, CHOH); 3.46 (d, $J = 5.4$ Hz, 2 H, CH₂OH); 3.39-3.26 (m, 2 H, CH₂NMe₃⁺); 3.11 (s, 9 H, 3 CH₃). ¹³C-NMR (D₂O, 75 MHz) δ 68.60 (CH₂NMe₃⁺); 66.81 (CHOH); 64.05 (CH₂OH); 54.65 (3 CH₃). IR (film) ν 3390; 2478.

Benzyl 2-bromoethyl phosphite (9). TLC R_f 0.4 (*n*-C₆H₁₄/AcOEt 4:6). ¹H-NMR (CDCl₃, 300 MHz) δ 7.42-7.35 (m, 5 H, H_{Ar}); 6.97 (d, $J = 713.1$ Hz, 1 H, PH); 5.15 (d, $J = 9.6$ Hz, 2 H, PhCH₂); 4.34-4.25 (m, 2 H, BrCH₂CH₂); 3.48 (t, $J = 6.0$ Hz, 2 H, BrCH₂). ¹³C-NMR (CDCl₃, 75 MHz) δ 135.14 (d, $J = 5.7$ Hz, POCH₂C_{Ar}); 128.61 (*p*-C_{Ar}); 128.55 (2 *m*-C_{Ar}); 127.89 (2 *o*-C_{Ar}); 67.35 (PhCH₂); 64.74 (POCH₂CH₂); 29.60 (BrCH₂). ³¹P-NMR (CDCl₃, 81 MHz) δ 8.37 (s). IR (film) ν 3033; 2961; 1253; 1080; 948.

Benzyl 2-bromoethyl (2,2-dimethyl-1,3-dioxolan-4-yl)methyl phosphate (10). TLC R_f 0.3 (*n*-C₆H₁₄/AcOEt 3:1). ¹H-NMR (CDCl₃, 300 MHz) δ 7.36-7.31 (m, 5 H, H_{Ar}); 5.08 (d, $J = 8.7$ Hz, 2 H, CH₂Ph); 4.37-4.19 (m, 3 H, BrCH₂CH₂, POCH₂CHO); 4.03-3.96 (m, 3 H, POCH₂CHO, OCH₂HCHO); 3.75-3.72 (m, 1 H, OCH₂HCHO); 3.44 (t, $J = 6.3$ Hz, 2 H, BrCH₂); 1.37 (s, 3 H, CH₃); 1.31 (s, 3 H, CH₃). ¹³C-NMR (CDCl₃, 75 MHz) δ 135.71 (POCH₂C_{Ar}); 128.92 (*p*-C_{Ar}); 128.83 (2 *m*-C_{Ar}); 128.25 (2 *o*-C_{Ar}); 110.04 (CMe₂); 74.14 (POCH₂CH); 69.94 (PhCH₂); 67.91, 66.88 and 66.12 (BrCH₂CH₂, POCH₂CH, CH₂OCMe₂); 29.53 (BrCH₂); 26.88 (CH₃); 25.40 (CH₃). ³¹P-NMR (CDCl₃, 121 MHz) δ -0.90. IR (film) ν 2985; 2935; 2893.

2-Azidoethyl benzyl (2,2-dimethyl-1,3-dioxolan-4-yl)methyl phosphate (11). TLC R_f 0.3 (*n*-C₆H₁₄/AcOEt 6:4). ¹H-NMR (CDCl₃, 300 MHz) δ 7.40-7.35 (m, 5 H, H_{Ar}); 5.11 (d, $J = 8.7$ Hz, 2 H, PhCH₂); 4.25-3.70 (m, 7 H, N₃CH₂CH₂, POCH₂CH₂CH₂); 3.43 (t, $J = 4.6$ Hz, 2 H, N₃CH₂); 1.39 (s, 3 H, CH₃); 1.32 (s, 3 H, CH₃). ¹³C-NMR (CDCl₃, 75 MHz) δ 135.44 (POCH₂C_{Ar}); 128.64 (*p*-C_{Ar}); 128.55 (2 *m*-C_{Ar}); 127.98 (2 *o*-C_{Ar}); 109.79 (CMe₂);

73.81 (POCH₂CH); 69.62 (PhCH₂); 67.60 (CH₂OCMe₂); 66.14 (POCH₂CH); 65.89 (N₃CH₂CH₂); 50.66 (N₃CH₂CH₂); 26.58 (CH₃); 25.12 (CH₃). ³²P-NMR (CDCl₃, 121 MHz) δ -0.63. IR (film) ν 2102.

2-Azidoethyl benzyl 2,3-dihydroxypropyl phosphate (12). TLC *R*_f 0.1 (*n*-C₆H₁₄/AcOEt 4:6). ¹H-NMR (CDCl₃, 300 MHz) δ 7.37 (m, 5 H, H_{Ar}); 5.11 (d, *J* = 8.7 Hz, 2 H, PhCH₂); 4.18-4.07 (m, 4 H, N₃CH₂CH₂ and POCH₂CHOH); 3.88-3.72 (m, 2 H, CH₂OH); 3.70-3.55 (m, 1 H, POCH₂CHOH); 3.43 (t, *J* = 5.0 Hz, 2 H, N₃CH₂). ¹³C-NMR (CDCl₃, 75 MHz) δ 135.28 (C_{Ar}CH₂OP); 128.80 (*p*-C_{Ar}); 128.65 (2 C, *m*-C_{Ar}); 128.07 (2 C, *o*-C_{Ar}); 70.49 (C₆); 69.93; 68.83; 66.44; 62.65; 50.68 (N₃CH₂). RMN ³²P (CDCl₃, 121 MHz) δ 0.46. IR (film) ν 3385; 2957; 2926; 2857; 2360; 2109; 1728.

(Z)-3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluorohexadec-9-enoic acid (13). TLC *R*_f 0.2 (AcOEt/CH₂Cl₂ 1:3). ¹H-NMR (CDCl₃, 300 MHz) δ 6.45-6.36 (m, 1 H, *E*-CF₂CH=C); 6.14-6.08 (m, 1 H, *Z*-CF₂CH=C); 5.74-5.41 (m, 1 H, CF₂CH=CH); 3.21 (t, *J* = 17.4 Hz, 2 H, CH₂COOH); 2.35-2.28 (m, 2 H, C=CHCH₂); 1.47-1.21 (m, 8 H, MeC₄H₈); 0.89 (t, *J* = 7.7 Hz, 3 H, CH₃). ¹³C-NMR (CDCl₃, 75 MHz) δ 169.28 (COOH); 145.45 (*Z*-C=CHCF₂); 143.15 (*E*-C=CHCF₂); 120.0-107.0 (6 CF₂); 116.10 (t, *J* = 23.4 Hz, C=CHCF₂); 36.63 (t, *J* = 22.6 Hz, CH₂COOH); 31.53 (EtCH₂); 29.01, 28.79, and 28.55 (PrC₃H₆); 22.52 (MeCH₂); 14.00 (CH₃). ¹⁹F-NMR (CDCl₃, 188 MHz) δ -104.5 (m, 2 F, *Z*-CF₂CH=CH); -109.1 (m, 2 F, *E*-CF₂CH=CH); -109.9 (m, 2 F, CF₂CH₂COOH); -119.5 (m, 4 F); -121.0 (m, 2 F); -121.7 (m, 2 F). IR (film) ν 2930; 2860; 1732.

2-Azidoethyl benzyl 3-{1,2-di[(Z)-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorohexadec-9-enoyl]-sn-glycero} phosphate (14). TLC *R*_f 0.4 (*n*-C₆H₁₄/AcOEt/CH₂Cl₂ 2:1:1). ¹H-NMR (CDCl₃, 300 MHz) δ 7.45-6.32 (m, 5 H, 5 H_{Ar}); 6.53-6.31 (m, 2 H, 2 *E*-CF₂CH=C); 6.18-6.01 (m, 2 H, 2 *Z*-CF₂CH=C); 5.59-5.27 (m, 3 H, 2 CF₂CH=CH and POCH₂CHO); 5.13-5.08 (m, 2 H, PhCH₂); 4.50-4.03 (m, 6 H, N₃CH₂CH₂, POCH₂CHO, CO₂CH₂); 3.43 (m, 2 H, N₃CH₂); 3.14 (q, *J* = 17.4 Hz, 4 H, 2 CH₂CO₂); 2.32-2.25 (m, 4 H, 2 CH=CHCH₂); 1.31-1.25 (m, 16 H, 2 MeC₄H₈); 0.88 (t, *J* = 5.6 Hz, 6 H, 2 CH₃). ¹³C-NMR (CDCl₃, 50 MHz) δ 163.44 and 163.16 (2 COO); 145.42 (2 CH=CHCF₂); 135.25 (POCH₂C_{Ar}); 128.87 (*p*-C_{Ar}); 128.68 (*m*-C_{Ar}); 128.10 (*o*-C_{Ar}); 125.0-102.0 (12 CF₂); 116.00 (t, *J* = 23.1 Hz, 2 CH=CHCF₂); 70.67 (POCH₂CHO); 69.95 (PhCH₂); 66.48, 64.75 and 62.55 (CO₂CH₂CHOCH₂, N₃CH₂CH₂); 50.66 (N₃CH₂); 36.70 (t, *J* = 22.5 Hz, 2 CH₂COO); 31.48, 28.95, 28.73, and 28.49 (2 EtCH₂CH₂CH₂CH₂); 22.46 (2 MeCH₂); 13.89 (2 CH₃). ¹⁹F-NMR (CDCl₃, 188 MHz) δ -104.6 (m, 4 F, *E*-CF₂CH=C); -109.7 (m, 4 F, *Z*-CF₂CH=C); -110.3 (m, 4 F); -119.6 (m, 8 F); -121.1 (m, 4 F); -121.8 (m, 4 F). ³¹P-NMR (CDCl₃, 121 MHz) δ -0.65.

2-Azidoethyl 3-{1,2-di[(Z)-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorohexadec-9-enoyl]-sn-glycero} hydrogen phosphate (15). TLC *R*_f 0.6 (CHCl₃/MeOH/H₂O 10:6:1). ¹H-NMR (CDCl₃, 300 MHz) δ 6.40-6.31 (m, 2 H, 2 *E*-CF₂CH=C); 6.09-6.02 (m, 2 H, 2 *Z*-CF₂CH=C); 5.56-5.38 (m, 3 H, 2 CF₂CH=CH and POCH₂CHO); 4.65-3.92 (m, 6 H, N₃CH₂CH₂, POCH₂CHO, CO₂CH₂); 3.47 (m, 2 H, N₃CH₂); 3.18 (q, *J* = 18.0 Hz, 4 H, 2 CH₂CO₂); 2.30-2.18 (m, 4 H, 2 CH=CHCH₂); 1.40-1.27 (m, 16 H, 2 MeC₄H₈); 0.88 (t, *J* = 6.0 Hz, 6 H, 2 CH₃). ¹³C-NMR (CDCl₃, 75 MHz) δ 163.57 (2 COO); 145.07 (2 CH=CHCF₂); 125.0-102.0 (12 CF₂); 116.14 (t, *J* = 23.2 Hz, 2 CH=CHCF₂); 71.99 (POCH₂CHO); 64.73 (N₃CH₂CH₂); 63.75-63.68 (CO₂CH₂CHOCH₂); 51.31 (N₃CH₂);

36.50-36.10 (m, 2 CH_2COO); 31.53, 28.62, 28.39 and 27.90 (2 $\text{EtCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$); 22.46 (2 MeCH_2); 13.87 (2 CH_3). IR (film) ν 2958; 2930; 2860, 2114; 1751.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,10-diiodotetradec-9-enyl benzoate (16). TLC R_f 0.5 ($n\text{-C}_6\text{H}_{14}/\text{CH}_2\text{Cl}_2$ 75:25). $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 8.06 (m, 2 H; $o\text{-H}_{\text{Ar}}$); 7.64 (tt, $J = 6.4, 1.4$ Hz, 1 H, $p\text{-H}_{\text{Ar}}$); 7.49 (m, 2 H, $m\text{-H}_{\text{Ar}}$); 7.35 (dd, $J = 10.4, 2.4$ Hz, 1 H, CHI-OCO); 6.32 (t, $J = 14.4$ Hz, 1 H, $\text{CF}_2\text{CH}=\text{C}$); 3.69-3.10 (m, 2 H, CF_2CH_2); 2.63 (t, $J = 7.3$ Hz, 2 H, $\text{CH}_2\text{CI}=\text{C}$); 1.64-1.51 (m, 2 H, $\text{CH}=\text{CICH}_2$); 1.45-1.21 (m, 6 H); 0.90 (t, $J = 6.5$ Hz, 3 H, CH_3). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ 163.51 (CO); 134.14 ($p\text{-C}_{\text{Ar}}$); 130.05 (2 $o\text{-C}_{\text{Ar}}$); 128.65 (2 $m\text{-C}_{\text{Ar}}$); 128.34 (C_{ArCO}); 126.54 (t, $J = 23.9$ Hz, $\text{CF}_2\text{CH}=\text{C}$); 122.99 (m, $\text{CF}_2\text{CH}=\text{C}$); 120.00-105.00 (m, 6 CF_2); 43.90 (t, $J = 20.9$ Hz, CF_2CH_2); 41.09 ($\text{CH}_2\text{CI}=\text{C}$); 40.89 (CHI); 31.42 (CH_2Et); 29.97 (CH_2Pr); 28.06 (*homoallyl*- CH_2); 22.44 (CH_2Me); 13.97 (CH_3). $^{19}\text{F-NMR}$ (CDCl_3 , 188 MHz) δ -103.3 (m, 2 F, $E\text{-CF}_2\text{CH}=\text{C}$); -106.4 (m, 2 F, $Z\text{-CF}_2\text{CH}=\text{C}$); -111.7 (app. AB syst., 2 F, $\delta_A = -113.2$, $\delta_B = -110.2$, $J = 338.4$ Hz); -109.5 (m, 4 F); -121.3 (m, 4 F). IR (film) ν 2958; 2932; 2860; 1745.

(Z)-3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluorohexadec-9-enyl alcohol (17). TLC R_f 0.3 ($n\text{-C}_6\text{H}_{14}/\text{CH}_2\text{Cl}_2$ 2:8). $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 6.43-6.33 (m, 0.12 H, $E\text{-CH}=\text{CHCF}_2$); 6.18-6.03 (m, 0.88 H, $Z\text{-CH}=\text{CHCF}_2$); 5.63-5.41 (m, 1 H, $\text{CH}=\text{CHCF}_2$); 3.99 (t, $J = 6.4$ Hz, 2 H, CH_2OH); 2.46-2.19 (m, 4 H, $\text{CH}=\text{CHCH}_2$, CH_2CF_2); 1.44-1.29 (m, 8 H, 2 MeC_4H_8); 0.90 (t, $J = 6.7$ Hz, 3 H, CH_3). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ 145.30 ($\text{CH}=\text{CHCF}_2$, *Z*-isomer); 143.01 ($\text{CH}=\text{CHCF}_2$, *E*-isomer); 117.29-110.51 (m, 6 CF_2); 116.20 (t, $J = 23.2$ Hz, $\text{CH}=\text{CHCF}_2$); 55.34 (CH_2OH); 34.00 (t, $J = 21.4$ Hz, CF_2CH_2); 31.53 (EtCH_2); 29.01, 28.79, and 28.54 (3 CH_2); 22.51 (MeCH_2); 13.97 (CH_3). $^{19}\text{F-NMR}$ (CDCl_3 , 188 MHz) δ -104.6 (m, 2 F, $Z\text{-C}=\text{CHCF}_2$); -109.1 (m, 2 F, $E\text{-C}=\text{CHCF}_2$); -111.4 (m, 2 F, CF_2CH_2); -119.6 (m, 4 F); -121.8 (m, 4 F). IR (film) ν 3365; 2959; 2930; 2860; 1190; 1139.

Figure 1. Isothermal pressure-area curves obtained with **1c** (heavy black line), **2a** (dashed line), **2b** (dotted line), **2c** (black line), and DOTAP (heavy grey line).

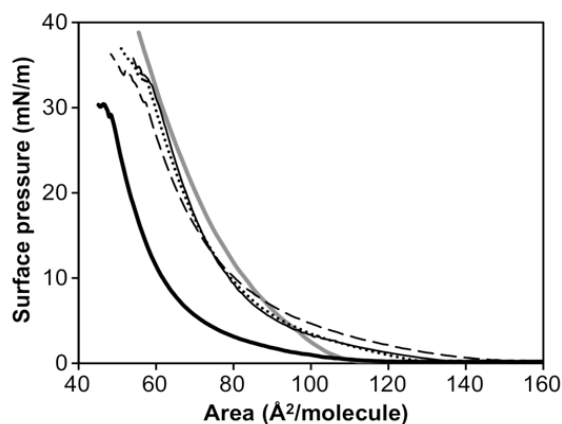


Table 1. Monolayer parameters for DOTAP, and compounds **1c** and **2a-c**.

Compound	A_s ($\text{\AA}^2/\text{molecule}$)	A_{lo} ($\text{\AA}^2/\text{molecule}$)	π_c (mN/m)
DOTAP	50.5	113	45
1c	51.0	124	27
2a	57.4	174	31
2b	58.8	138	33
2c	59.2	155	33

The error is estimated to be ± 5 % on surface and ± 10 % on collapse pressure values.

Figure 2. Cytotoxicity of DOTAP/DOPE, **1c**/DOPE, and **2c**/DOPE lipoplexes as a function of charge ratio (N/P 3: white; N/P 5: grey; N/P 6: black). BHK-21 cells were treated with lipoplexes containing 2 μg of plasmid DNA in culture medium supplemented with 10 % FCS.

