

## Supporting Information:

### Synthesis of Migration-Resistant Hydroxyethoxy Analogs of Lysophosphatidic Acid

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**General Procedures.** Chemicals were purchased from Aldrich and Acros Chemical Corporation and used without prior purification. Solvents were reagent-grade and distilled before use: CH<sub>2</sub>Cl<sub>2</sub> was distilled from CaH<sub>2</sub> and THF was distilled from sodium wire. TLC: precoated silica gel aluminum sheets (EM Science silica gel 60F<sub>254</sub>). Flash chromatography (FC): Silica gel Whatman 230~400 mesh ASTM. NMR spectra were recorded on a Varian INOVA 400 at 400 MHz (<sup>1</sup>H), 101 MHz (<sup>13</sup>C), 162 MHz (<sup>31</sup>P) at 25 °C. Chemical shifts are given in ppm with TMS as internal standard ( $\delta$  = 0.00); <sup>31</sup>P, 85% H<sub>3</sub>PO<sub>4</sub> ( $\delta$  = 0.00).

**3-*O*-Methoxybenzyl-2(S)-glycerol (1).** To a solution of *p*-methoxybenzyl alcohol (9.8 g, 70 mmol) in 25 mL anhydrous CH<sub>2</sub>Cl<sub>2</sub> in an ice bath, 1.0 M DIBAL-H in hexane (30 mL) was added. The reaction mixture was warmed to rt and stirred for 0.5 h. (S)-Glycidol (2 mL, 30 mmol) was added to the reaction mixture, which was then stirred at rt for 70 h. Sodium potassium tartrate (6.3 g, 30 mmol) in a minimum amount of water was then

added to the mixture and stirring continued for 0.5 h. The solvent was evaporated and the mixture was extracted with ethyl acetate, washed with water, dried over sodium sulfate, and concentrated. The crude product was purified by flash chromatography (EtOAc) to afford 3.3 g of a colorless oil (51%).  $R_f$  0.28 (EtOAc);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.517 (m, 2H), 3.599 (dd, 1H,  $J = 11.2, 5.4$  Hz), 3.5678 (dd, 1H,  $J = 11.2, 3.4$  Hz), 3.798 (s, 3H), 3.862 (m, 1H), 4.472 (s, 2H), 6.878 (dd,  $J = 8.4, 2.0$  Hz), 7.242 (dd,  $J = 8.0, 2.4$  Hz);  $^{13}\text{C-NMR}$ ,  $\delta$  55.253, 64.054, 70.574, 71.474, 73.220, 113.875, 129.440, 129.722, 159.372; MS (FAB)  $m/z$  235 ( $\text{M}^+ + \text{Na}$ , 24). HRMS,  $\text{M}^+ + \text{Na}$ , Found: 235.0939, Calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_4\text{Na}$ , 235.0946.

**3-*O-tert*-Butyl-dimethysilyl-1-*O*-methoxybenzyl-2(S)-glycerol (2).** A mixture of **1** (950 mg, 4.48 mmol), *tert*-butyldimethylsilyl chloride (810 mg, 5.4 mmol), TEA (546 mg, 5.4 mmol) and DMAP (55 mg, 0.448 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (15 mL) under an argon atmosphere was stirred at rt for 18 h. The reaction mixture was washed with NaCl saturated solution, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated. FC (EtOAc/hexane, 1/4, v/v) gave **2** as a colorless oil (980 mg, 78%).  $R_f$  0.31 (EtOAc/hexane 1/4);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.0 (s, 6H), 0.828 (s, 9H), 3.430 (m, 2H), 3.579 (m, 2H), 3.737 (s, 3H), 3.782 (m, 1H), 4.417 (s, 2H), 6.815 (dd,  $J = 8.8, 2.0$  Hz), 7.192 (dd,  $J = 8.8, 2.0$  Hz);  $^{13}\text{C-NMR}$ ,  $\delta$  -5.457, 18.237, 25.825, 55.208, 63.993, 70.628, 70.643, 73.045, 113.761, 129.333, 130.126, 159.228; MS (FAB)  $m/z$  325 ( $\text{M}^+ + \text{H}$ , 7). HRMS,  $\text{M}^+ + \text{H}$ , Found: 325.1831, Calcd for  $\text{C}_{17}\text{H}_{29}\text{O}_4\text{Si}$ , 325.1835.

**3-*O*-*tert*-Butyl-dimethylsilyl-1-*O*-methoxybenzyl-2(S)-*O*-(tetrahydro-pyran-2-yloxy)ethyl-*sn*-glycerol (3).** To a solution of **2** (900 mg, 2.76 mmol) in dry DMF (25 mL) was added 60% NaH in oil dispersion (375 mg, 9.4 mmol). The mixture was stirred at rt for 0.5 h. The 2-(2-bromoethoxy)tetrahydro-2H-pyran (1.25 mL, 8.28 mmol) and TBAI (1 g, 2.76 mmol) was added to the reaction. The mixture was stirred at rt for 18 h. After adding 5 mL H<sub>2</sub>O, the solvent was evaporated. The mixture was extracted with EtOAc (20 mL × 3). The extract was washed with NaCl saturated solution, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. FC (EtOAc/hexane, 1/4, v/v) gave **3** as a colorless oil (700 mg, 56%). *R*<sub>f</sub> 0.35 (EtOAc/hexane 1/4); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 0.004 (s, 6H), 0.841 (s, 9H), 1.513 (m, 4H), 1.718 (m, 2H), 3.450 (m, 2H), 3.531 (m, 2H), 3.624 (m, 2H), 3.724~3.754 (m, 1H), 3.759 (s, 3H), 3.802 (m, 2H), 4.44 (d, 2H, *J* = 2.4 Hz), 4.586 (t, 1H, *J* = 3.6 Hz), 6.824 (dd, *J* = 8.4, 1.6 Hz), 7.195 (dd, *J* = 8.4, 1.6 Hz); <sup>13</sup>C-NMR δ -5.423, -5.377, 18.264, 19.431, 25.455, 25.875, 30.572, 55.258, 62.083, 62.114, 62.579 (d, *J* = 7.68 Hz), 66.956 (d, *J* = 7.68 Hz), 69.809 (d, *J* = 6.16 Hz), 80.149 (d, *J* = 7.68 Hz), 98.856 (d, *J* = 7.68 Hz), 113.704, 113.818, 129.215, 129.360, 130.558, 159.102; MS (FAB) *m/z* 477 (M<sup>+</sup>+Na, 17). HRMS, M<sup>+</sup>+Na, Found: 477.2629, Calcd for C<sub>24</sub>H<sub>42</sub>O<sub>6</sub>NaSi, 477.2648.

**3-*O*-Methoxybenzyl-2(S)-*O*-(tetrahydro-pyran-2-yloxy)ethyl-*sn*-glycerol (4).** To a solution of **3** (330 mg, 0.726 mmol) in THF (5 mL) was added 1 M TBAF in THF (1.45 mL). The reaction mixture was stirred at rt for 3 h. The mixture was washed with NaCl saturated solution, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. FC (EtOAc/Hexane, 3/1, v/v) gave **4** as a colorless oil (241 mg, 95%). *R*<sub>f</sub> 0.22 (EtOAc/Hexane 3/2); <sup>1</sup>H-NMR

(CDCl<sub>3</sub>)  $\delta$  1.550 (m, 4H), 1.762 (m, 2H), 2.5 (br, 1H), 3.474~3.743 (m, 7H), 3.805 (s, 3H), 3.858 (m, 2H), 4.464 (s, 2H), 4.637 (m, 1H), 6.876 (dd,  $J$  = 7.6, 2.0 Hz), 7.251 (dd,  $J$  = 7.6, 2.0 Hz); <sup>13</sup>C-NMR 19.393 (d,  $J$  = 3.13 Hz), 25.287, 30.466 (d,  $J$  = 7.78 Hz), 55.243, 62.335 (d,  $J$  = 4.65 Hz), 62.838 (d,  $J$  = 12.32 Hz), 67.132 (d,  $J$  = 18.48 Hz), 69.824, 69.9 (d,  $J$  = 4.65 Hz), 73.118, 79.745, 99.013 (d,  $J$  = 10 Hz), 113.78, 129.254, 129.383, 130.115, 159.224; MS (FAB)  $m/z$  363 (M<sup>+</sup>+Na, 33). HRMS, M<sup>+</sup>+Na, Found: 363.1769, Calcd for C<sub>18</sub>H<sub>28</sub>O<sub>6</sub>Na, 363.1784.

**1-*O*-Methoxybenzyl-3-*O*-Oleoyl-2(S)-*O*-(tetrahydro-pyran-2-yloxy)ethyl-*sn*-glycerol**

**(5a).** A solution of **4** (240 mg, 0.705 mmol), oleic acid (319 mg, 1.13mmol), DCC (233 mg, 1.13mmol), DMAP (40 mg, 0.141 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was stirred at rt for 18 h, filtered through Celite, and concentrated. FC (EtOAc/hexane, 1/4, v/v) gave **5a** as a colorless oil (350 mg, 82%).  $R_f$  0.26 (EtOAc/Hexane 1/4); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  0.874 (t,  $J$  = 6.8 Hz, 3H), 1.275 (m, 20H), 1.4~1.8 (m, 8H), 2.002 (m, 2H), 2.284 (t,  $J$  = 7.6 Hz, 2H), 3.45~3.85 (m, 7H), 3.796 (s, 3H), 4.2 (m, 2H), 4.472 (s, 2H), 4.619 (m, 1H), 5.336 (m, 2H), 6.854 (dd,  $J$  = 8.8, 2.0 Hz), 7.237 (dd,  $J$  = 8.8, 2.0 Hz); MS (FAB)  $m/z$  627 (M<sup>+</sup>+Na, 43). HRMS, M<sup>+</sup>+Na, Found: 627.4203, Calcd for C<sub>36</sub>H<sub>60</sub>O<sub>7</sub>Na, 627.4237.

**3-*O*-Oleoyl-2(S)-*O*-(tetrahydro-pyran-2-yloxy)ethyl-*sn*-glycerol (6a).** A solution of **5a** (340 mg, 0.562 mmol), DDQ (128 mg, 0.562 mmol) in wet CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was stirred at rt for 8 h. After filtration, the filtrate was washed with NaCl saturated solution, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. FC (EtOAc/hexane, 2/3, v/v) gave **6a** as a colorless oil (180 mg, 66%).  $R_f$  0.36 (EtOAc/hexane 1/1); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  0.877 (t,  $J$  = 7.2 Hz,

3H), 1.273 (m, 20H), 1.52~1.804 (m, 8H), 2.006 (m, 2H), 2.319 (t,  $J = 7.2$  Hz, 2H), 3.50~3.76 (m, 6H), 3.92 (m, 3H), 4.13 (m, 2H), 4.65 (m, 1H), 5.34 (m, 2H); MS (FAB)  $m/z$  507 ( $M^+ + Na$ , 95). HRMS,  $M^+ + Na$ , Found: 507.3665, Calcd for  $C_{28}H_{52}O_6Na$ , 507.3662.

**3-*O*-Dimethylphosphoryl-1-*O*-oleoyl-2(S)-*O*-(tetrahydro-pyran-2-yloxy)ethyl-*sn*-glycerol (7a).** To a solution of **6a** (55 mg, 0.113 mmol) in  $CH_2Cl_2$  (5 mL) in an ice bath was added  $(OMe)_2P(O)Cl$  (20 mg, 0.136 mmol), and *t*-BuOK (19 mg, 0.17 mmol). The reaction mixture was stirred at rt for 2 h.  $NH_4Cl$  saturated solution (2 mL) was added and the mixture was stirred for 10 min. The reaction mixture was extracted with  $CH_2Cl_2$ , the extract was washed with NaCl saturated solution, dried over  $Na_2SO_4$ , and concentrated. FC (EtOAc/hexane, 2/1, v/v) gave **7a** as a colorless oil (50 mg, 75%).  $R_f$  0.26 (EtOAc/hexane 2/1);  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  0.875 (t,  $J = 6.8$  Hz, 3H), 1.280 (m, 20H), 1.499~1.819 (m, 8H), 2.004 (m, 2H), 2.32 (t,  $J = 8$  Hz, 2H), 3.529 (m, 2H), 3.71~3.872 (m, 11H), 4.128 (m, 2H), 4.247 (m, 2H), 4.62 (t,  $J = 4.4$  Hz, 1H), 5.34 (m, 2 H); MS (FAB)  $m/z$  615 ( $M^+ + Na$ , 100). HRMS,  $M^+ + Na$ , Found: 615.3646, Calcd for  $C_{30}H_{57}O_9NaP$ , 615.3638.

**2(S)-*O*-Hydroxyethyl-1-*O*-oleoyl-3-*O*-phosphoryl-*sn*-glycerol (8a).** A solution of **7a** (35 mg, 0.069 mmol), TMSBr (37 mg, 0.24 mmol) in  $CH_2Cl_2$  (1 mL) was stirred at rt for 5 h. The solvent was evaporated and the residue was dissolved in 95% methanol (1 mL) while stirring at rt for 1h. Reconcentration of the solvent gave **8a** as a colorless oil (32 mg, 95%).  $R_f$  0.36 ( $CH_2Cl_2/MeOH/H_2O$ , 20/10/1);  $^1H$ -NMR ( $CD_3OD$ )  $\delta$  0.893 (t,

$J = 7.2$  Hz, 3H), 1.304 (m, 20H), 1.609 (m, 2H), 2.024 (m, 4H), 2.341 (t,  $J = 7.6$  Hz, 2H), 3.667 (m, 4H), 3.787 (m, 1H), 4.049 (m, 2H), 4.2 (m, 2H), 5.336 (m, 2H);  $^{13}\text{C}$ -NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  14.452, 23.74, 25.990, 28.125, 30.192, 30.299, 30.337, 30.444, 30.611, 30.81, 30.840, 33.059, 34.912, 62.42, 63.914, 66.56 (d,  $J = 5.35$  Hz), 72.974, 77.985 (d,  $J = 7.78$  Hz), 130.795, 130.894, 175.163;  $^{31}\text{P}$ -NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  1.078 (s); MS (MALDI)  $m/z$  503 ( $\text{M}^+ + \text{Na}$ ). HRMS,  $\text{M}^+ + \text{Na}$ , Found: 503.2763, Calcd for  $\text{C}_{23}\text{H}_{45}\text{NaO}_8\text{P}$ , 503.2750.

**2(S)-O-Hydroxyethyl-1-O-palmitoyl-3-O-phosphoryl-*sn*-glycerol (8b).**  $R_f$  0.36 ( $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{H}_2\text{O}$ , 20/10/1);  $^1\text{H}$ -NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  0.891 (t,  $J = 7.2$  Hz, 3H), 1.281 (s, 24H), 1.608 (m, 2H), 2.34 (t,  $J = 7.2$  Hz, 2H), 3.670 (m, 4H), 3.799 (m, 1H), 4.054 (m, 2H), 4.2 (m, 2H);  $^{31}\text{P}$ -NMR  $\delta$  1.078 (s); MS (MALDI)  $m/z$  477 ( $\text{M}^+ + \text{Na}$ ). HRMS,  $\text{M}^+ + \text{Na}$ , Found: 477.2582, Calcd for  $\text{C}_{21}\text{H}_{43}\text{NaO}_8\text{P}$ , 477.2593.

**3-O-(Tetrahydro-pyran-2-yloxy)ethyl-2(S)-glycerol (9).**  $R_f$  0.25 (EtOAc);  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  1.521 (m, 4H), 1.78 (m, 2H), 2.710 (s, 1H), 3.332 (s, 1H), 3.51 (m, 2H), 3.56~3.70 (m, 6H), 3.857 (m, 3H), 4.610 (t,  $J = 4$  Hz, 1H);  $^{13}\text{C}$ -NMR,  $\delta$  19.508 (d,  $J = 1.15$  Hz), 25.299, 30.523, 62.503 (d,  $J = 3.8$  Hz), 63.975 (d,  $J = 2.2$  Hz), 66.732 (d,  $J = 4.6$  Hz), 70.423 (d,  $J = 3.0$  Hz), 70.846 (d,  $J = 5.4$  Hz), 73.016 (d,  $J = 7.6$  Hz), 99.166 (d,  $J = 4.5$  Hz); MS (CI)  $m/z$  221.1 ( $\text{M}^+ + \text{H}$ ). HRMS,  $\text{M}^+ + \text{H}$ , Found: 221.1375, Calcd for  $\text{C}_{10}\text{H}_{21}\text{O}_5$ , 221.1389.

**1,2(S)-Di-O-*tert*-butyl-dimethylsilyl-3-O-(tetrahydropyran-2-yloxy)ethyl-*sn*-glycerol (10).** A mixture of **9** (400 mg, 1.8 mmol), TBDMS chloride (663 mg, 4.4 mmol) and

imidazole (272 mg, 4 mmol) in anhydrous DMF (6 mL) under an argon atmosphere was stirred at rt for 20 h. The reaction mixture was diluted with H<sub>2</sub>O (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. FC (EtOAc/hexane, 1/8, v/v) gave **10** as a colorless oil (730 mg, 91%). R<sub>f</sub> 0.43 (EtOAc/hexane 1/8); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 0.068 (m, 12H), 0.883 (m, 18H), 1.483~1.856 (m, 6H), 3.423 (m, 2H), 3.48~3.65 (m, 6H), 3.839 (m, 3H), 4.632 (t, *J* = 3.6 Hz, 1H); <sup>13</sup>C-NMR, δ -5.436, -5.375, -4.681, -4.635, 18.190, 18.335, 19.319, 19.380, 25.458, 25.831, 25.862, 25.946, 30.545 (d, *J* = 1.5 Hz), 62.010 (d, *J* = 9.1 Hz), 65.167, 65.949 (d, *J* = 4.6 Hz), 70.745 (d, *J* = 5.4 Hz), 72.709, 73.334 (d, *J* = 3.0 Hz), 98.866 (d, *J* = 12.2 Hz); MS (CI) *m/z* 449.3 (M<sup>+</sup>+H). HRMS, M<sup>+</sup>+H, Found: 449.3121, Calcd for C<sub>22</sub>H<sub>49</sub>O<sub>5</sub>Si<sub>2</sub>, 449.3119.

**2(S)-O-tert-Butyl-dimethylsilyl-3-O-(tetrahydro-pyran-2-yloxy)ethyl-sn-glycerol (11).**

The HF-pyridine complex (0.383 mL, 13.2 mmol) was added to a mixture of **10** (1.0 g, 2.2 mmol) and pyridine (1.15 mL) in anhydrous THF (10 mL). After stirring 20 h at rt, the solution was diluted with EtOAc (50 mL), washed with 0.5M HCl (2 × 10 mL) and satd. CuSO<sub>4</sub> solution (10 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. FC (EtOAc/hexane, 1/2, v/v) gave **11** as a colorless oil (450 mg, 58%). R<sub>f</sub> 0.35 (EtOAc/hexane 1/2); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 0.078 (s, 6H), 0.876 (s, 9H), 1.474~1.848 (m, 6H), 2.321 (t, *J* = 3.6 Hz, 1H), 3.455~3.645 (m, 8H), 3.872 (m, 3H), 4.609 (t, *J* = 3.2 Hz, 1H); <sup>13</sup>C-NMR, δ -4.901, -4.665, 18.076, 19.319, 19.365, 25.367, 25.763, 30.468, 62.125 (d, *J* = 6.1 Hz), 65.041 (d, *J* = 3.8 Hz), 66.510 (d, *J* = 6.1 Hz), 70.711 (d, *J* = 4.6

Hz), 71.039 (d,  $J = 3.0$  Hz), 73.194 (d,  $J = 8.3$  Hz), 98.905 (d,  $J = 10.7$  Hz); MS (CI)  $m/z$  335.2 ( $M^+ + H$ ). HRMS,  $M^+ + H$ , Found: 335.2253, Calcd for  $C_{16}H_{35}O_5Si$ , 335.2254.

**1-*O*-(Tetrahydro-pyran-2-yloxy)ethyl-2(S)-*O*-*tert*-butyldimethylsilyl-3-*O*-dimethylphosphoryl-*sn*-glycerol (12).** Colorless oil.  $R_f$  0.35 (EtOAc/hexane 2/1);  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  0.073 (d,  $J = 2.4$  Hz, 6H), 0.866 (s, 9H), 1.478~1.829 (m, 6H), 3.542 (m, 4H), 3.62 (m, 2H), 3.733 (s, 3H), 3.764 (s, 3H), 3.835 (m, 2H), 3.967 (m, 2H), 4.077 (m, 1H), 4.601 (t,  $J = 4.0$  Hz, 1H);  $^{13}C$ -NMR  $\delta$  -4.874, -4.820, 18.058, 19.347, 19.385, 25.379, 25.684, 30.496, 54.183, 54.244, 62.103 (d,  $J = 5.3$  Hz), 65.610 (d,  $J = 2.3$  Hz), 69.008 (d,  $J = 6.1$  Hz), 70.761 (dd,  $J = 8.4, 2.3$  Hz), 70.850 (d,  $J = 2.3$  Hz), 72.264 (d,  $J = 4.6$  Hz), 98.906 (d,  $J = 6.9$  Hz);  $^{31}P$ -NMR  $\delta$  2.379 (s); MS (CI)  $m/z$  443.3 ( $M^+ + H$ ). HRMS,  $M^+ + H$ , Found: 443.2238, Calcd for  $C_{18}H_{40}O_8PSi$ , 443.2230.

**3-*O*-Dimethylphosphoryl-(2S)-*O*-oleoyl-1-*O*-(tetrahydro-pyran-2-yloxy)ethyl-*sn*-glycerol (14a).**  $R_f$  0.50 (EtOAc);  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  0.871 (t,  $J = 6.8$  Hz, 3H), 1.275 (m, 20H), 1.494~1.832 (m, 8H), 2.004 (m, 2H), 2.328 (t,  $J = 7.2$  Hz, 2H), 3.542 (m, 4H), 3.579 (m, 2H), 3.664 (m, 6H), 3.858 (m, 2H), 4.223 (m, 2H), 4.611 (t,  $J = 4.0$  Hz, 1H), 5.171 (m, 1H), 5.334 (m, 2H);  $^{13}C$ -NMR  $\delta$  14.083, 19.406, 22.655, 24.836, 25.393, 27.147, 27.193, 29.053, 29.091, 29.168, 29.297, 29.496, 29.686, 29.740, 30.525, 31.875, 34.231, 54.326, 54.387, 62.158, 65.983 (d,  $J = 5.3$  Hz), 66.551, 68.808, 70.486, 70.562, 70.882, 98.912 (d,  $J = 3.8$  Hz), 129.695, 129.992;  $^{31}P$ -NMR  $\delta$  2.258 (s); MS (MALDI)  $m/z$  615 ( $M^+ + Na$ ). HRMS,  $M^+ + Na$ , Found: 615.3617, Calcd for  $C_{30}H_{57}NaO_9P$ , 615.3638.



**1-*O*-Hydroxyethyl-2(S)-*O*-oleoyl-3-*O*-phosphoryl-*sn*-glycerol (15a).**  $R_f$  0.35 ( $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{H}_2\text{O}$ , 20/10/1);  $^1\text{H-NMR}$  ( $\text{CD}_3\text{OD}$ )  $\delta$  0.893 (t,  $J = 6.8$  Hz, 3H), 1.305 (m, 20H), 1.614 (t,  $J = 6.8$  Hz, 2H), 2.024 (m, 4H), 2.347 (t,  $J = 5.6$  Hz), 3.555 (m, 2H), 3.645 (t,  $J = 4.4$  Hz, 2H), 3.708 (m, 2H), 4.14 (m, 2H), 5.145 (m, 1H), 5.337 (t,  $J = 4.8$  Hz, 2H);  $^{13}\text{C-NMR}$   $\delta$  13.260, 22.548, 24.775, 26.993, 28.954, 29.000, 29.153, 29.252, 29.419, 29.633, 29.656, 31.867, 33.865, 60.968, 64.698, 68.762, 71.252 (d,  $J = 8.4$  Hz), 72.796, 72.850, 129.610, 129.694;  $^{31}\text{P-NMR}$   $\delta$  1.012 (s); MS (MALDI)  $m/z$  503 ( $\text{M}^+ + \text{Na}$ ). HRMS,  $\text{M}^+ + \text{Na}$ , Found: 503.2732, Calcd for  $\text{C}_{23}\text{H}_{45}\text{NaO}_8\text{P}$ , 503.2750

**1-*O*-Hydroxyethyl-2(S)-*O*-palmitoyl-3-*O*-phosphoryl-*sn*-glycerol (15b).**  $R_f$  0.35 ( $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{H}_2\text{O}$ , 20/10/1);  $^1\text{H-NMR}$  ( $\text{CD}_3\text{OD}$ )  $\delta$  0.890 (t,  $J = 6.8$  Hz, 3H), 1.280 (s, 24H), 1.601 (m, 2H), 2.346 (t,  $J = 7.6$  Hz, 2H), 2.567 (m, 2H), 3.634 (m, 2H), 3.717 (m, 2H), 4.143 (m, 2H), 5.147 (m, 1H);  $^{13}\text{C-NMR}$   $\delta$  14.431, 23.727, 25.969, 26.023, 30.156, 30.362, 30.423, 30.469, 30.560, 30.598, 30.675, 30.751, 30.781, 62.155, 65.937, 70.048, 72.801, 73.853, 74.010 (d,  $J = 5.3$  Hz);  $^{31}\text{P-NMR}$ ,  $\delta$  0.957 (s); MS (MALDI)  $m/z$  477 ( $\text{M}^+ + \text{Na}$ ). HRMS,  $\text{M}^+ + \text{Na}$ , Found: 477.2595, Calcd for  $\text{C}_{21}\text{H}_{43}\text{NaO}_8\text{P}$ , 477.2593.

*Ca<sup>2+</sup> measurements* - Sf9 cells were infected with human EDG7 baculovirus with a multiplicity of infection (MOI) of 10. The cells were harvested two days after baculovirus infection, washed gently with HBS buffer (20 mM Hepes, pH 7.4, containing 120 mM NaCl, 4.7 mM KCl, 1.2 mM  $\text{MgCl}_2$ , 1.25 mM  $\text{CaCl}_2$ , 1.2 mM  $\text{KH}_2\text{PO}_4$  and 10 mM glucose) and loaded with 2 mM Fura-2 acetoxymethyl ester (Fura-2 AM; Molecular Probes Inc.) for 30 min. Free Fura-2 AM was washed out and the cells were resuspended

in HBS buffer to produce a concentration of 1,000,000 cells/mL. Agonist-induced Fura-2 AM fluorescence was measured in quartz cuvettes kept at 27 °C by monitoring at excitation wavelengths of 340 and 380 nm and an emission wavelength of 300 nm using a CAF-110 spectrofluorimeter (Japan Spectroscopy, Inc., Tokyo, Japan). Fluorescence was recorded before and after addition of LPA and other phospholipids, dissolved in phosphate buffered saline with 0.01 % (w/v) of fatty acid-free bovine serum albumin (Sigma).