## SUPPLEMENTARY MATERIAL

**12, 12, 13, 13, 14, 14, 15, 15, 16, 16, 17, 17, 18, 18, 19, 19, 19-Heptadecafluoro-1-phosphononanadecane (1, $F_8H_{11}$ PA).** To a solution of 41.10 g (75 mmol) of perfluorooctyl iodide and 11.92 g (70 mmol) of 10-undecen-1-ol in a mixture of 100 mL of acetonitrile and 40 mL of water was added a mixture of 6.89 g (82 mmol) of $NaHCO_3$ and 13.58 g (78 mmol) of $Na_2S_2O_4$ in small portions with stirring. The reaction mixture was stirred at room temperature overnight and acidified with 1 N hydrochloric acid. The mixture was extracted with diethyl ether, and the combined organic phases were washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl and dried over $MgSO_4$. Concentration afforded 43.2 g of 12,12,13,13,14,14,15,15,16,16, 17,17,18,18,19,19,19-heptadecafluoro-10-iodo-1-nonadecanol as a white solid. A solution of the crude iodide in 50 mL of ethanol was filtered to remove a small amount of insoluble material, and the filtrate was added dropwise with stirring to a slurry of 19.6 g (300 mmol) of Zn powder in 150 mL of ethanol containing

4.0 g of acetic acid. The reaction mixture was heated at 50 °C for 4 h. The mixture was filtered, and concentration of the filtrate gave approximately 45 g of a soft white solid, 12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-heptadecafluoro-1-nonadecanol[42] as a mixture with some zinc salts, and this mixture was used in the next step without further purification. To a mixture of 40.0 g of the crude alcohol and 250 mL of 48 % hydrobromic acid was slowly added 25 mL of concentrated sulfuric acid. The reaction mixture was heated at 100 °C for 18 h and poured into 1 L of water. The mixture was extracted with hexanes, and the combined organic phases were washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. The solution was concentrated to an amber liquid, which was eluted through 3 inches of silica with hexanes. Concentration of the eluent yielded an iodine-colored solid. The crude product was redissolved in 250 mL of hexanes, and this solution was concentrated under reduced pressure. Dissolution in hexanes and concentration were repeated two times finally affording 20.20 g (50 % from 10-undecen-1-ol) of 12,12,13,13,14,14,15,15,16,16,17,17, 18,18,19,19,19-heptadecafluoro-1-bromononadecane[42] as a white solid. $^1$H NMR ($CDCl_3$) 1.23 (m, 14 H), 1.59 (m, 2 H), 1.82 (m, 2 H), 2.01 (tt, $J_{HH}$ = 8 Hz, $J_{HF}$ = 19 Hz, 2 H), 3.40 (t, J = 6 Hz, 2 H). A mixture of 5.23 g (8 mmol) of 12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-heptadecafluoro-1-bromononadecane and 4.2 g (25 mmol) triethyl phosphite was heated for 18 h at 150 °C. Diethyl ethylphosphonate and other volatiles were distilled, bp 30-50 °C at 0.05 mm Hg, and the $^1$H NMR spectrum of the concentrate indicated approximately 15 % of the starting bromide remaining. An additional 2.0 g (12 mmol) of triethyl phosphite was added and heating at 150 °C was continued for 6 h. Volatiles were again distilled under reduced pressure, affording 1-(diethylphosphono)-12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-heptadecafluorononadecane as a clear, pale yellowish liquid. To a solution of the crude diethyl phosphonate ester in 10 mL of dichloromethane was added 3.1 g (20 mmol) of bromotrimethylsilane. After 24 h at room temperature, the solution was concentrated to a nearly colorless liquid, and the intermediate silylphosphonate ester was dissolved in 200 mL of methanol. A precipitate quickly formed, and the mixture was stirred at room temperature for 3 h. The mixture was cooled to 0 °C, the precipitate was collected by filtration, and

recrystallization from methanol gave 2.72 g (52 % from the starting bromide) of 12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-heptadecafluoro-1-phosphononononadecane as white crystals, mp 115-117 °C. $^{1}$H NMR ($d_4$-methanol) 1.36 (m, 14 H), 1.44 (m, 2 H), 1.55-1.75 (m, 4 H), 2.15 (tt, $J_{HH}$ = 8 Hz, $J_{HF}$ = 19 Hz, 2 H); $^{13}$C NMR ($d_4$-methanol) 20.10, 22.72 ($J_{CP}$ = 6 Hz), 26.94 ($J_{CP}$ = 138 Hz), 28.91, 29.04, 29.10, 29.24, 29.26, 29.36, 30.52 ($J_{CP}$ = 17 Hz), 30.69 ($J_{CF}$ = 22 Hz); $^{19}$F NMR ($d_4$-methanol) –80.80 (3 F), -113.54 (2 F), -120.99 (2 F), -121.16 (4 F), -122.00 (2 F), -122.79 (2 F), -125.53 (2 F); $^{31}$P NMR ($d_4$-methanol) 32.67; high-resolution mass spectrum, calculated for $C_{19}H_{24}F_{17}O_3P$ 654.1192, measured 654.1210.

**1-Phosphonohexadecane (2, $H_{16}$ PA).** 1-Phosphonohexadecane (**2**) was purchased from Oryza Laboratories, and was received as a mixture with the corresponding monoethyl and diethyl esters. A mixture of 5.0 g (approximately 14 mmol) of this material and 40 ml concentrated HCl was heated at 100 °C for 12 hr. The mixture was diluted with 10 ml water, and the precipitated solid was collected by filtration. Recrystallization from heptane afforded 3.27 g (76 %) white crystals, mp 95-97 °C.

**1-Phosphonodocosane (3, $H_{22}$ PA).** A mixture of 19.48 g (50 mmol) of 1-bromodocosane and 25.0 g (150 mmol) triethyl phosphite was heated for 18 h at 150 °C. Diethyl ethylphosphonate and other volatiles were distilled, bp 30-50 °C at 0.05 mm Hg, leaving 1-(diethylphosphono)docosane as a waxy solid. The crude diethyl phosphonate ester was combined with 350 mL of concentrated hydrochloric acid, and this mixture was heated for 18 h at 100 °C. The mixture was cooled to room temperature, 100 mL of water was added, and precipitated solids were collected by filtration. Recrystallization from heptane yielded 11.77 g (60 % overall) of 1-phosphonodocosane as white crystals, mp 100-102 °C. $^{1}$H NMR ($d_8$-tetrahydrofuran) 0.92 (t, J = 7 Hz, 3 H), 1.31 (m, 36 H), 1.41 (m, 2 H), 1.61 (m, 4 H); $^{13}$C NMR ($d_8$-tetrahydrofuran) 19.09, 28.23, 28.45 ($J_{CP}$ = 5 Hz), 32.65 ($J_{CP}$ = 143 Hz), 34.95-35.33 (16 C), 36.33 ($J_{CP}$ = 16 Hz), 37.56; $^{31}$P NMR ($d_8$-tetrahydrofuran) 36.27; high-resolution mass spectrum, calculated for $C_{22}H_{47}O_3P$ 390.3263, measured 390.3243.

**1-Phosphonohexadecane-$d_{33}$.** A mixture of 1.05 g (3.1 mmol) of 1-bromohexadecane-$d_{33}$ and 2.0 g (12.0 mmol) triethyl phosphite was heated for 20 h at 150 °C. Diethyl ethylphosphonate and other

volatiles were distilled, bp 30-50 °C at 0.05 mm Hg, and bulb-to-bulb distillation of the concentrate gave 1.17 g (95 %) of 1-(diethylphosphono)hexadecane as a clear, colorless liquid, bp 180-190 °C at 0.05 mm. To a solution of 1.17 g (3.0 mmol) of the diethyl phosphonate ester in 8 mL of dichloromethane was added 1.18 g (7.7 mmol) of bromotrimethylsilane. After 24 h at room temperature, the solution was concentrated to a pale yellowish liquid, and the intermediate silylphosphonate ester was dissolved in 25 mL of methanol. The resultant solution was stirred at room temperature for 3 h and concentrated to 1.00 g of a white solid. Recrystallization from heptane afforded 0.74 g (73 %) of 1-phosphonohexadecane-$d_{33}$ as colorless leaves, mp 89-93 °C. $^{1}$H NMR ($d_8$-tetrahydrofuran) 9.97 (br s, 2 H); $^{2}$H NMR ($d_8$-tetrahydrofuran) 0.86 (m, 3 D), 1.27 (m, 28 D), 1.58 (m, 2 D); $^{31}$P NMR ($d_8$-tetrahydrofuran) 33.81; high-resolution mass spectrum, calculated for $C_{16}H_2D_{33}NaO_3P$ ($M+Na^+$) 362.4293, measured 362.4294.