General Chemistry. ¹H NMR spectra were recorded on a Varian XL-300 spectrometer. Chemical shifts for ¹H NMR spectra are reported (in parts per million) relative to internal tetramethylsilane (Me₄Si, $\delta = 0.00$ ppm) with CDCl₃ as solvent. ¹³C NMR spectra were recorded at 75 MHz. Chemical shifts for ¹³C NMR spectra are reported (in parts per million) relative to CDCl₃ ($\delta = 77.0$ ppm) or C₆D₆ ($\delta = 128.5$ ppm). ³¹P NMR spectra were recorded at 121 MHz, and chemical shifts reported (in parts per million) relative to external 85% phosphoric acid ($\delta = 0.0$ ppm). Radial chromatography was carried out with a Harrison Associates Chromatotron using 1, 2, or 4 mm layers of silica gel 60 PF_{254} containing gypsum (E. Merck). Silica gel (200-300 mesh, Natland International Corporation) was used for flash chromatography. Ethyl acetate/hexanes mixtures were used as the eluent for chromatographic purifications. TLC plates were visualized by immersion in anisaldehyde stain (by volume: 93% ethanol, 3.5% sulfuric acid, 1% acetic acid, and 2.5% anisaldehyde) followed by heating. Organic solutions of products were dried over MgSO₄. Reagents were used as received. Reagent grade toluene was used as the solvent throughout this study, and was not dried. CAUTION! Tetramethyl orthosilicate (MeO)₄Si may cause blindness. Wear appropriate protection.

Selective Esterification: Competition Experiment. A mixture of phenyl phosphinic acid (0.709 g, 5 mmol), phenyl phosphonic acid (0.792 g, 5 mmol), diphenyl phosphinic acid (1.089 g, 5 mmol), and (EtO)₄Si (1.010 g, 4.9 mmol) in toluene (45 mL) was refluxed under N₂. The white suspension transiently became homogeneous, then milky. After 24 h, the milky reaction mixture was analyzed by ³¹P-NMR, and the only detectable new compound formed was ethyl phenylphosphinate (88%, δ 22.8, J_{PH} = 563 Hz). The reaction mixture was concentrated in vacuo, and the resulting white residue was partitioned between EtOAc and aq. NaHCO₃. The organic layer was washed with aq. NaHCO₃ (1 X), and brine (2 x). Drying over MgSO₄ and concentration afforded a clear, slightly yellow oil (0.633 g). This oil was dissolved in toluene, and ³¹P-NMR analysis showed ethyl phenylphosphinate (δ 22.3, J_{PH} = 562 Hz) as the only product. (¹H & ¹³C NMR spectra in CDCl₃ unambiguously confirmed this assignment.)

Ethyl phenylphosphinate. References: (a) Liu, L.; Li, G.; Huang, M. *Phosphorus, Sulfur, and Silicon* **1992**, *69*, 1; (b) Dahn, H.; Toan, V. V.; Ung-Truong, M. N. *Magn. Reson. Chem.* **1992**, *30*, 1089. ³¹P NMR (toluene) δ 23.1.

Methyl phenylphosphinate. References: (a) Liu, L.; Li, G.; Huang, M. *Phosphorus, Sulfur, and Silicon* **1992**, *69*, 1; (b) Dahn, H.; Toan, V. V.; Ung-Truong, M. N. *Magn. Reson. Chem.* **1992**, *30*, 1089. ¹H NMR (CDCl₃) δ 7.7-7.9 (m, 2 H), 7.45-7.65 (m, 3 H), 7.56 (d, *J* = 566 Hz, 1 H); 3.79 (d, *J* = 12 Hz); ¹³C NMR (CDCl₃) δ 133.0 (d, *J*_{PCCCC} = 3 Hz), 130.7 (d, *J*_{PCCC} = 12 Hz), 129.1 (d, *J*_{PC} = 131 Hz), 128.5 (d, *J*_{PCC} = 14 Hz), 51.9 (d, *J*_{POC} = 6 Hz);); ³¹P NMR (CDCl₃) δ 27.6.

Butyl phenylphosphinate. Reference: Dahn, H.; Toan, V. V.; Ung-Truong, M. N. *Magn. Reson. Chem.* **1992**, *30*, 1089. ¹H NMR (CDCl₃) δ 7.81 (d, *J* = 7 Hz, 1 H), 7.76 (*J* = 7 Hz, 1 H), 7.58 (d, *J* = 562 Hz, 1 H), 7.55-7.6 (m, 1 H), 7.45-7.55 (m, 2 H), 3.95-4.15 (m, 2 H), 1.6-1.8 (m, 2 H), 1.35-1.5 (m, 2 H), 0.92 (t, *J* = 7 Hz, 3 H); ¹³C NMR (CDCl₃) δ

132.4 (d, J_{PCCCC} = 3 Hz), 130.3 (d, J_{PCCC} = 12 Hz), 129.4 (d, J_{PC} = 132 Hz), 128.1 (d, J_{PCC} = 14 Hz), 65.1 (d, J_{POC} = 7 Hz), 31.8 (J_{POCC} = 6 Hz), 18.2, 12.9; ³¹P NMR (toluene) δ 22.8.

Allyl phenylphosphinate. Reference: Pudovik, A. N.; Pudovik, M. A. *Zh. Obshch. Khim.* **1966**, *36*, 1467. ¹H NMR (CDCl₃) δ 7.83 (d, *J* = 8 Hz, 1 H), 7.79 (d, *J* = 8 Hz, 1 H), 7.64 (d, *J* = 566 Hz, 1 H), 7.4-7.65 (m, 3 H), 5.85-6.1 (m, 2 H), 5.40 (d, *J* = 17 Hz, 1 H), 5.29 (d, *J* = 10 Hz, 1 H), 4.45-4.7 (m, 2 H); ¹³C NMR (CDCl₃) δ 132.6 (d, *J*_{PCCC} = 3 Hz), 131.8 (d, *J*_{POCC} = 7 Hz), 130.3 (d, *J*_{PCCC} = 12 Hz), 129.0 (d, *J*_{PC} = 137 Hz), 128.2 (d, *J*_{PCC} = 14 Hz), 118.0, 65.6 (d, *J*_{POC} = 6 Hz); ³¹P NMR (toluene) δ 23.8.

Methyl (4-phenylbutyl) phosphinate. ¹H NMR (CDCl₃) δ 7.02 (dt, J = 530, 2 Hz, 1 H), 7.1-7.3 (m, 5 H), 3.75 (d, J = 12 Hz, 3 H), 2.63 (t, J = 7 Hz, 2 H), 1.55-1.85 (m, 6 H); ¹³C NMR (CDCl₃) δ 141.4, 128.2, 128.1, 125.7, 52.6 (d, $J_{POC} = 7$ Hz), 35.2, 31.9 (d, $J_{PCC} = 15$ Hz), 28.2 (d, $J_{PC} = 93$ Hz), 20.1(d, $J_{PCC} = 3$ Hz); ³¹P NMR (CDCl₃) δ 42.2.

Ethyl (4-phenylbutyl) phosphinate. References: (a) Karanewsky, D. S.; Badia, M. C. *Tetrahedron Lett.* **1986**, *27*, 1751; (b) Thottathil, J. K.; Przybyla, C. A.; Moniot, J. *Tetrahedron Lett.* **1984**, *25*, 4737. ¹H NMR (CDCl₃) δ 7.06 (d, *J* = 530 Hz, 1H), 7.05-7.30 (m, 5 H), 3.9-4.2 (m, 2 H), 2.62 (t, *J* = 7 Hz, 2 H), 1.55-1.83 (m, 6 H), 1.34 (t, *J* = 7 Hz, 3 H); ¹³C NMR (CDCl₃) δ 141.3, 128.0, 125.6, 62.0 (d, *J*_{POC} = 7 Hz), 35.1, 31.9 (d, *J*_{PCC} = 15 Hz), 28.3 (d, *J*_{PC} = 94 Hz), 20.1 (d, *J*_{PCCC} = 3 Hz), 16.0 (d, *J*_{POCC} = 6 Hz); ³¹P NMR (neat) δ 39.0.

Butyl (4-phenylbutyl) phosphinate. ¹H NMR (CDCl₃) δ 7.06 (d, J = 530 Hz, 1H), 7.1-7.3 (m, 5 H), 3.9-4.15 (m, 2 H), 2.63 (t, J = 15 Hz, 2 H), 1.55-1.85 (m, 8 H), 1.3-1.45 (2 H), 0.94 (t, J = 7 Hz, 3 H); ¹³C NMR (CDCl₃) δ 141.5, 128.2, 125.7, 65.9 (d, $J_{POC} = 7$ Hz), 35.2, 32.2 (d, $J_{POCC} = 6$ Hz), 32.0 (d, $J_{PCC} = 16$ Hz), 28.5 (d, $J_{PC} = 94$ Hz), 20.2 (d, $J_{PCCC} = 3$ Hz), 18.6, 13.4.

Allyl (4-phenylbutyl) phosphinate. ¹H NMR (CDCl₃) δ 7.11 (d, J = 530 Hz, 1 H), 7.05-7.35 (m, 5 H), 5.85-6.0 (m, 1 H), 5.37 (d, J = 17 Hz, 1 H), 5.27 (d, J = 10 Hz, 1 H), 4.4-4.65 (m, 2 H), 2.63 (t, J = 7 Hz, 2 H), 1.5-1.9 (m, 6 H); ¹³C NMR (CDCl₃) δ 141.5, 132.3 (d, $J_{POCC} = 6$ Hz), 128.3, 125.8, 118.6, 66.4 (d, $J_{POC} = 7$ Hz), 35.3, 32.1 (d, $J_{PCC} = 16$ Hz), 28.6 (d, $J_{PC} = 93$ Hz), 20.2 (d, $J_{PCCC} = 3$ Hz); ³¹P NMR (CDCl₃) δ 39.5.

Allyl octylphosphinate. ¹H NMR (CDCl₃) δ 7.12 (d, J = 530 Hz, 1 H), 5.85-6.05 (m, 1 H), 5.39 (d, J = 16 Hz, 1 H), 5.29 (d, J = 10 Hz, 1 H), 4.45-4.7 (m, 2 H), 1.7-1.9 (m, 2 H), 1.5-1.7 (m, 2 H), 1.2-1.5 (s, 10 H), 0.89 (t, J = 5 Hz, 3 H); ¹³C NMR (CDCl₃) δ 132.4 (d, $J_{POCC} = 6$ Hz), 118.5, 66.4 (d, $J_{POC} = 7$ Hz), 31.6, 30.2 (d, $J_{PCC} = 16$ Hz), 29.6 (d, $J_{PC} = 92$ Hz), 28.9 (2), 22.5, 20.5 (d, $J_{PCCC} = 8$ Hz), 14.0; ³¹P NMR (CDCl₃) δ 40.1.

Butyl (1-hydroxydecyl)phosphinate (1:1 mixture of diastereoisomers).

¹H NMR (CDCl₃) δ 6.95 (d, *J* = 540 Hz, 1 H), 6.86 (d, *J* = 540 Hz, 1 H), 4.65 (br, 1 H), 4.50 (br, 1H), 4.0-4.25 (m, 4 H), 3.7-3.9 (m, 2 H), 1.5-1.8 (m, 8 H), 1.2-1.5 (m, 32 H), 0.80-1.0 (m, 12 H); ¹³C NMR (CDCl₃) δ 69.0 (d, *J*_{PC} = 110 Hz), 68.5 (d, *J*_{PC} = 110 Hz),

66.9 (d, $J_{POC} = 8$ Hz), 66.8 (d, $J_{POC} = 8$ Hz), 32.3 (3), 31.8, 29.8 (d, $J_{PCCC} = 5$ Hz), 29.5, 29.4, 29.2, 25.3 (d, $J_{PCC} = 13$ Hz), 22.6, 18.7, 14.0, 13.5; ³¹P NMR (CDCl₃) δ 39.5, 38.0.

Benzyl phenylphosphinate. Reference: Karanewsky, D. S.; Badia, M. C. *Tetrahedron Lett.* **1986**, 27, 1751. ¹H NMR (CDCl₃) δ 7.78 (d, J = 7 Hz, 1 H), 7.73 (d, J = 7 Hz, 1 H), 7.62 (d, J = 566 Hz, 1 H), 7.25-7.6 (m, 8 H), 4.7-5.15 (m, 2 H); ¹³C NMR (CDCl₃) δ 135.2 (d, $J_{POCC} = 7$ Hz), 132.8 (d, $J_{PCCCC} = 3$ Hz), 130.6 (d, $J_{PCCC} = 12$ Hz), 129.0 (d, $J_{PC} = 132$ Hz), 128.4 (d, $J_{PCC} = 15$ Hz), 128.35, 128.25, 127.7, 66.9 (d, $J_{POC} = 6$ Hz); ³¹P NMR (CDCl₃) δ 25.6.

i-Propyl phenylphosphinate. Reference: Houalla, D.; Marty, R.; Wolf, R. Z. *Naturforsch. B Anorg. Chem. Org. Chem. Biochem. Biochem. Biophys. Biol.* 1970, 25, 451. ¹H NMR (CDCl₃) δ 7.80 (d, J = 7 Hz, 1 H), 7.76 (d, J = 7 Hz, 1 H), 7.61 (d, J = 559 Hz, 1 H), 7.40-7.65 (m, 3 H), 4.65-4.75 (m, 1 H), 1.41 (d, J = 6 Hz, 3 H), 1.33 (d, J = 6 Hz, 3 H); ¹³C NMR (CDCl₃) δ 132.3 (d, $J_{PCCC} = 3$ Hz), 130.2 (d, $J_{PCCC} = 12$ Hz), 129.3 (d, $J_{PC} = 132$ Hz), 128.0 (d, $J_{PCC} = 14$ Hz), 70.6 (d, $J_{POC} = 6$ Hz), 23.5 (d, $J_{POCC} = 5$ Hz), 23.2 (d, $J_{POCC} = 4$ Hz); ³¹P NMR (toluene) δ 20.2.

Phenyl phenylphosphinate. References: (a) Johnson, M. K. *Biochem. Pharmacol.* **1988**, *37*, 4095; Kovaleva, T. V.; Feshchenko, N. G. *Zh. Obshch. Khim.* **1986**, *56*, 1777; (b) Yamashita, M., Long, P. T.; Shibata, M. *Carbohydr. Res.* **1980**, *84*, 35. Crude containing phenol ¹H NMR (C_6D_6) δ 7.59 (d, *J* = 7 Hz, 1 H), 7.54 (d, *J* = 7 Hz, 1 H), 7.32 (d, *J* = 587 Hz, 1 H), 6.75-7-2 (m, 8 H); ¹³C NMR (C_6D_6) δ 151.0 (d, *J*_{POC} = 9 Hz), 133.8 (d, *J*_{PCCCC} = 3 Hz), 131.2 (d, *J*_{PCCC} = 12 Hz), 130.2, 129.8 (d, *J*_{PC} = 173 Hz), 129.0 (d, *J*_{PCC} = 14 Hz), 125.7, 120.6 (d, *J*_{POCC} = 5 Hz); ³¹P NMR (toluene) δ 25.2. An authentic sample prepared from dichlorophenylphosphine and phenol afforded the same NMR data as above.

Phenyl octylphosphinate. Crude containing phenol ¹H NMR (C_6D_6) δ 6.7-7-7.15 (m, 5 H), 6.86 (d, J = 555 Hz, 1 H), 1.05-1.5 (m, 14 H), 0.86 (t, J = 7 Hz, 3 H); ¹³C NMR (C_6D_6) δ 151.4 (d, $J_{POC} = 9$ Hz), 130.3, 125.6, 120.3 (d, $J_{POCC} = 5$ Hz), 32.1, 30.4 (d, $J_{PCC} = 16$ Hz), 29.3, 29.2, 28.1 (d, $J_{PC} = 91$ Hz), 23.0, 20.7 (d, $J_{PCCC} = 3$ Hz), 14.3; ³¹P NMR (toluene) δ 39.5.

3-Aminopropyltrimethoxysilane hydrochloride (3).

To a solution of 3-aminopropyl trimethoxysilane (26.9 g, 150 mmol) in toluene (200 ml) was added NH₄Cl (16.0 g, 300 mmol) at room temperature, under nitrogen, and with vigorous stirring. The mixture refluxed for 48 hours. Filtration of the hot suspension removed excess NH₄Cl, and the filtrate was concentrated in vacuo to afford 3 as a white powder (92% crude yield). This material was used in the esterification reaction, without further purification. ¹H NMR (CDCl₃) δ 7.85 (br, 3 H), 3.58 (s, 9 H), 3.03 (t, *J* = 7 Hz, 2 H), 1.8-2.0 (m, 2 H), 0.75 (t, *J* = 8 Hz, 2 H); ¹³C NMR (CDCl₃) δ 50.4, 41.9, 20.8, 6.1.









RB-37 PPOBU





and a second s ţ Allyl phenylphosphinate 0: I











RB-67 PUMP





























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