Supporting Information:

Porphyrins Bearing Arylphosphonic Acid Tethers for Attachment to Oxide Surfaces

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I. Experimental Section

General. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in CDCl_3 unless noted otherwise. Mass spectra of porphyrinic compounds were obtained by FABMS, laser desorption mass spectrometry in the absence of a matrix (LDMS),⁴⁵ and/or MALDI-MS MS using the matrix 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP). Absorption and emission spectra were collected in toluene at room temperature unless noted otherwise. Melting points are uncorrected. Silica gel (40 μm average particle size) was used for column chromatography. Alumina activity grade I was deactivated to grade V for chromatography of magnesium-porphyrinic compounds.⁴⁰ Phosphoric acid (H_3PO_4) was used as external standard (referenced to δ 0.00 ppm) for ^{31}P NMR (161.98 MHz) spectroscopy. Preparative SEC was performed as described previously.⁴³ All Pd-mediated coupling reactions were carried out under argon using standard Schlenk techniques.⁴¹

Non-Commercial Compounds. Compounds **1**,²⁷ **5**,³⁴ **7-9**,³⁵ **13**,³⁷ **14**,³⁷ **19**,³⁸ **Zn22**,³⁹ **25**,³⁵ **26**,³⁴ **Zn28**,⁴² and 4-iodophenylferrocene⁴⁴ were synthesized according to literature procedures.

Solvents. Toluene and TEA were freshly distilled from CaH_2 and sparged of oxygen prior to use. THF was distilled from sodium. CH_3CN was distilled from CaH_2 and stored over molecular sieves. All other solvents were used as received. CHCl_3 stabilized with 0.8% ethanol was used for the porphyrin-forming reactions and chromatography procedures. CHCl_3 stabilized with amlenes (not ethanol) was used for the cleavage of dialkyl phosphonates.

4-(Di-*tert*-butyloxyphosphoryl)benzaldehyde dimethylacetal (2). Samples of **1** (5.0 g, 22 mmol) and di-*tert*-butylphosphite (5.1 g, 27 mmol) were coupled using $\text{Pd}(\text{PPh}_3)_4$ (1.3 g, 1.1 mmol) in toluene/TEA [10 mL, (1:1)] at 80 $^\circ\text{C}$ under argon for 20 h. A precipitate was formed during the course of the reaction. The reaction mixture was filtered and the filtrate was concentrated. Column chromatography [silica, hexanes/ethyl acetate (8:2) $\rightarrow$ ethyl acetate/MeOH (9:1)] afforded a yellow oil (4.00 g, 53%): bp 152 $^\circ\text{C}$; ^1H NMR δ 1.46 (s, 18 H), 3.34 (s, 6H), 5.41 (s, 1H), 7.48–7.52 (m, 2H), 7.76–7.83 (m, 2H); ^{13}C NMR δ 30.8, 30.9, 52.7, 82.3, 82.4, 103.4, 127.3, 127.4, 132.1, 132.2, 142.6, 142.7; ^{31}P NMR (THF- d_8) δ 10.6; Anal. Calcd for $\text{C}_{17}\text{H}_{29}\text{O}_5\text{P}$: C, 59.29; H, 8.49. Found: C, 59.18; H, 8.49.

5-[4-(Di-*tert*-butyloxyphosphoryl)phenyl]-10,15,20-trimesitylporphyrin (3a). Following a standard procedure³⁰ employing $\text{BF}_3\cdot\text{O}(\text{Et})_2$ –ethanol cocatalysis,³¹ a mixture of mesitaldehyde (1.34 g, 9.00 mmol), **2** (1.00 g, 3.00 mmol), and pyrrole (805 mg, 12.0 mmol) were condensed in CHCl_3 (1.2 L) containing ethanol as a stabilizer was treated with $\text{BF}_3\cdot\text{O}(\text{Et})_2$ (500 μL) at room temperature for 1.5 h. DDQ (2.04 g, 9.00 mmol) was added. After 1 h, TEA was added and the reaction mixture was concentrated. Column chromatography [silica, CHCl_3 /hexanes (1:1) $\rightarrow$ CHCl_3 /ethyl acetate (8:2); silica, CHCl_3 /ethyl acetate (8:2)] afforded a purple solid (255 mg, 6.8%): ^1H NMR δ –2.58 (br s, 2H), 1.65 (s, 18H), 1.84–1.85 (m, 18H), 2.62 (s, 9H), 7.27 (s, 6H), 8.14–8.27 (m, 4H), 8.64–8.73 (m, 8H); ^{31}P NMR (THF- d_8) δ 10.7; LDMS obsd 934.0, 877.2 [(M – *tert*-Bu)⁺]; 821.01 [(M – 2 x *tert*-Bu)⁺]; FABMS obsd 932.4788; calcd 932.4794 ($\text{C}_{61}\text{H}_{65}\text{N}_4\text{O}_3\text{P}$); λ_{abs} 420, 514, 547, 592, 650 nm; λ_{em} (λ_{ex} = 550) 650, 719 nm.

5-[4-Diethoxyphosphoryl)phenyl]-10,15,20-trimesitylporphyrin (3b). Following a standard procedure³⁰ employing $\text{BF}_3\cdot\text{O}(\text{Et})_2$ –ethanol cocatalysis,³¹ a mixture of mesitaldehyde (0.880 mL, 6.00 mmol), 4-(diethoxyphosphoryl)benzaldehyde⁴ (242 mg, 2.00 mmol) and pyrrole (0.550 mL, 8.00 mmol) in CHCl_3 (800 mL) containing ethanol as a stabilizer was treated

with $\text{BF}_3\cdot\text{O}(\text{Et})_2$ (0.330 mL, 2.64 mmol, 3.3 mM) at room temperature for 30 min. DDQ (1.36 g, 6.00 mmol) was added. After 1 h, the mixture was filtered through an alumina pad (eluted with 2% methanol in CH_2Cl_2) and the filtrate was concentrated. The residue obtained was chromatographed (silica, CHCl_3). The second slow moving band (purple) was collected and concentrated. The purple residue was chromatographed (alumina, CHCl_3) as eluant to afford a purple solid (190 mg, 11%): ^1H NMR δ -2.57 (brs, 2H), 1.52 (t, J = 7.6 Hz, 6H), 1.85 (s, 12H), 1.86 (s, 6H), 2.62 (s, 3H), 2.63 (s, 6 H), 4.34–4.42 (m, 4H), 7.28 (s, 6H), 8.18 (d, J = 7.6 Hz, 1H), 8.21 (d, J = 7.6 Hz, 1H), 8.32 (d, J = 4.4 Hz, 1H), 8.34 (d, J = 4.4 Hz, 1H), 8.65 (s, 4H), 8.68–8.74 (m, 4H); LDMS obsd 876.92; FABMS obsd 876.4158, calcd 876.4168 ($\text{C}_{57}\text{H}_{57}\text{N}_4\text{O}_3\text{P}$); λ_{abs} 417, 513, 547, 593, 648 nm.

Zn(II)-5-[4-(Di-*tert*-butyloxyphosphoryl)phenyl]-10,15-20-trimesitylporphyrin

(Zn3a). A solution of **3a** (0.210 g, 0.225 mmol) in CHCl_3 (50 mL) was treated overnight with $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ (0.250 g, 1.14 mmol) in methanol (5 mL) at room temperature. The reaction mixture was washed with water, dried (Na_2SO_4) and chromatographed [silica, CHCl_3 /ethyl acetate (9:1)] to afford a purple solid (163 mg, 73%): ^1H NMR δ 1.64 (s, 18H), 1.84 (s, 18H), 2.62 (s, 9H), 7.27 (s, 6H), 8.07–8.28 (m, 4H), 8.64–8.75 (m, 8H); ^{31}P NMR (THF-d_8) δ 11.1; LDMS obsd 993.5, 881.9 [(M – 2 x *tert*-Bu) $^+$]; FABMS obsd 994.3925; calcd 994.3929 ($\text{C}_{61}\text{H}_{63}\text{N}_4\text{O}_3\text{PZn}$); λ_{abs} 423, 550 nm; λ_{em} (λ_{ex} = 550 nm) 600, 649 nm.

Zinc(II)-5-[4-(Diethoxyphosphoryl)phenyl]-10,15,20-trimesitylporphyrin (Zn3b).

A solution of porphyrin **3b** (0.080 g, 0.090 mmol) in CHCl_3 /methanol (8:1) was treated overnight with $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ (0.099 g, 0.45 mmol). Standard workup including chromatography [silica, CHCl_3 /methanol (98:2)] afforded a purple solid (0.071 g, 85%): ^1H NMR δ 1.17 (t, J = 7.2 Hz, 6 H), δ 1.80–1.88 (m, 18H), 2.58–2.65 (m, 9H), 3.60–3.75 (m, 4H), 7.28 (s, 6H), 7.43–7.55 (m, 2H), 8.12–8.21 (m, 2H), 8.65–8.78 (m, 8H); LDMS obsd 937.9; FABMS obsd 938.3339, calcd 938.3303 ($\text{C}_{57}\text{H}_{55}\text{N}_4\text{O}_3\text{PZn}$); λ_{abs} 423, 549 nm.

Mg(II)-5-[4-(Di-*tert*-butyloxyphosphoryl)phenyl]-10,15-20-trimesitylporphyrin

(Mg3a). Following a known procedure,³³ a solution of **3a** (23 mg, 0.025 mmol) in CH_2Cl_2 (1 mL) was treated with the ethereal MgI_2 -DIEA reagent (7 mL, ~0.04 M solution of MgI_2) and the mixture was stirred at room temperature for 1 h. The mixture was diluted with CH_2Cl_2 and washed with aqueous 5% NaHCO_3 and water, dried (Na_2SO_4) and concentrated. Trituration with hexanes afforded a purple solid (17 mg, 71%): ^1H NMR (THF-d_8) δ 1.63 (s, 18H), 1.82–1.89 (m, 18H), 2.58–2.63 (s, 9H), 7.27 (s, 6H), 8.05–8.15 (m, 2H), 8.21–8.29 (m, 2H), 8.52–8.56 (m, 6H), 8.63–8.66 (m, 2H); ^{31}P NMR (THF-d_8) δ 11.31; LDMS obsd 956.3, 901.2 [(M – *tert*-Bu) $^+$], 843.8 [(M – 2 x *tert*-Bu) $^+$]; FABMS obsd 954.4443; calcd 954.4488 ($\text{C}_{61}\text{H}_{63}\text{MgN}_4\text{O}_3\text{P}$); λ_{abs} (THF) 431, 573, 614 nm.

5-(4-Dihydroxyphosphorylphenyl)-10,15,20-trimesitylporphyrin (4).

Following a general procedure,⁶ a sample of **Zn3b** (175 mg, 0.200 mmol) in CH_2Cl_2 (20 mL) was treated with 16 equiv of TMS-Br (0.420 mL, 3.20 mmol). The green mixture was stirred overnight at room temperature. The solvent was evaporated to afford a green residue. The green residue was suspended in water and the suspension was stirred at room temperature for 2 h. The mixture was extracted with CHCl_3 . The CHCl_3 layer was washed with saturated aqueous NaHCO_3 , water and dried (Na_2SO_4). The solution was concentrated. Chromatography [silica, CHCl_3 /MeOH (1:1)] afforded a purple solid (130 mg, 79%): ^1H NMR δ -2.74 (br s, 2H), 1.76 (s, 18H), 2.57 (s, 9H), 7.12 – 7.26 (m, 4H), 7.32 (s, 2H), 8.04 – 8.16 (m, 4H), 8.46 – 8.62 (m, 6H), 8.74 – 8.82 (m, 2H);

LD-MS obsd 820.9; FAB-MS obsd 820.3560, calcd 820.3542 (C₅₃H₄₉N₄O₃P); λ_{abs} (THF) 419, 515, 550, 592, 648 nm.

Zn(II)-5-[4-(Dihydroxyphosphoryl)phenyl]-10,15,20-trimesitylporphyrin (Zn4; from Zn3a). A mixture of **Zn3a** (150 mg, 0.150 mmol), TMS-Cl (287 μ L, 2.25 mmol) and TEA (300 μ L, 3 mmol) in CHCl₃ (15 mL) was stirred at reflux (~65 °C) under argon for 4 h. The reaction mixture was washed with water, dried (Na₂SO₄) and chromatographed [silica, CHCl₃/ethyl acetate (1:1) $\rightarrow$ CHCl₃/MeOH (1:1)] to afford a purple solid (118 mg, 89%): ¹H NMR δ 1.70–1.76 (m, 18H), 2.50–2.51 (m, 9H), 7.20–7.26 (m, 6H), 8.10–8.11 (m, 2H), 8.28–8.29 (m, 2H), 8.50–8.51 (m, 6H), 8.70–8.71 (m, 2H); ³¹P NMR (THF-d₈) δ 12.2; LDMS obsd 885.70; FABMS obsd 881.49; calcd 882.27 (C₅₃H₄₇N₄O₃PZn); λ_{abs} 420, 550 nm; λ_{em} 596, 645 nm.

Zn4 from Zn3b. A mixture of **Zn3b** (30 mg, 0.032 mmol), TMS-Br (66 μ L, 0.50 mmol) and TEA (66 μ L, 0.63 mmol) in CHCl₃ (4 mL) was stirred at reflux for 4 h. The reaction mixture was diluted with CH₂Cl₂ (100 mL), washed with water, dried (Na₂SO₄) and chromatographed [silica, CHCl₃/ethyl acetate (1:1) $\rightarrow$ CHCl₃/MeOH (1:1)] to afford a purple solid (23 mg, 81%). Characterization data were consistent with those reported above.

Zn4 by metalation of 4. A solution of porphyrin **4** (0.123 g, 0.150 mmol) in CHCl₃/methanol (15 mL, 2:1) was treated overnight with Zn(OAc)₂·2H₂O (0.329 g, 1.50 mmol). Standard workup including chromatography [silica, CHCl₃/MeOH (1:1)] afforded a purple solid (0.103 g, 77%). Characterization data were consistent with those reported above.

Mg(II)-5-[4-(Dihydroxyphosphoryl)phenyl]-10,15,20-trimesitylporphyrin (Mg4). A sample of **Mg3a** (14 mg, 0.015 mmol) in CHCl₃ (5 mL) was treated with TEA (0.041 mL, 0.30 mmol) and TMS-Br (0.030 mL, 0.23 mmol). The cloudy mixture was stirred at reflux for 4 h. Water was added and the mixture was extracted with CHCl₃. The organic layer was dried (Na₂SO₄) and concentrated. Trituration with hexanes afforded a purple solid (10 mg, 77%): ¹H NMR (THF-d₈) δ 1.75–1.90 (m, 18H), 2.50–2.70 (m, 9H), 7.15–7.35 (m, 6H), 8.10–8.35 (m, 4H), 8.45–8.62 (m, 6H), 8.68–8.82 (m, 2H); ³¹P NMR (THF-d₈) δ 14.37; MALDI-MS (POPOP) obsd 843.5, 821.5 [(M – Mg)⁺]; FABMS obsd 842.3239; calcd 842.3236 (C₅₃H₄₇MgN₄O₃P); λ_{abs} (THF) 431, 574, 614 nm.

5-[4-(Di-*tert*-butyloxyphosphoryl)phenyl]dipyrrromethane (6). Method A: Following a general procedure,³⁴ a solution of **2** (3.44 g, 10.0 mmol) and pyrrole (17.4 mL, 0.250 mol) in CH₂Cl₂ (20 mL) was treated with TFA (77 μ L, 1.0 mmol) under argon for 2 h at room temperature. Then 0.1 M NaOH was added. The mixture was poured into brine and ethyl acetate. The organic phase was isolated, washed with water, dried (Na₂SO₄) and concentrated. Column chromatography [silica, CH₂Cl₂/ethyl acetate (3:1)] afforded an orange oil. Recrystallization [ethanol/water (1:1)] afforded a pale brown powder (1.3 g, 31%): mp 138–139 °C; ¹H NMR δ 1.44 (s, 18H), 5.51 (s, 1H), 5.93 (s, 2H), 6.13–6.15 (m, 2H), 6.69–6.71 (m, 2H), 7.13–7.22 (m, 2H), 7.52–7.62 (m, 2H), 8.68 (br s, 2H); ¹³C NMR δ 30.46, 30.50, 43.9, 82.61, 82.68, 107.4, 107.9, 117.7, 128.1, 128.2, 130.2, 131.4, 131.5, 132.05, 132.11, 146.49, 146.52; ³¹P NMR δ 10.94; Anal. Calcd for C₂₃H₃₁N₂O₃P: C, 66.65; H, 7.54; N, 6.76. Found: C, 66.57; H, 7.41; N, 6.65.

Method B: Samples of **5** (1.0 g, 3.4 mmol) and Pd(PPh₃)₄ (200 mg, 0.17 mmol) in TEA (1 mL) and toluene (1 mL) was treated with di-*tert*-butylphosphite (740 mg, 3.8 mmol). The reaction mixture was stirred under argon at 85 °C for 20 h, then concentrated and

chromatographed [silica, CHCl₃/ethyl acetate (3:1)] to afford a light brown solid (600 mg, 43%). Characterization data were consistent with those described above.

5,15-Bis(pentafluorophenyl)-10-[4-(di-*tert*-butyloxyphosphoryl)phenyl]-20-(4-iodophenyl)porphyrin (10). Following a standard procedure,³⁶ a solution of **7** (888 mg, 1.21 mmol) in THF/methanol [55 mL (10:1)] was treated with NaBH₄ (915 mg, 24.2 mmol). The resulting dipyrromethane-dicarbinol (**7-diol**) was condensed with **6** (0.500 g, 1.21 mmol) in CH₂Cl₂ (484 mL) containing Yb(OTf)₃ (954 mg, 1.53 mmol, 3.2 mM). After 20 min, a sample of DDQ (824 mg, 3.63 mmol) was added. After 30 min, TEA was added followed by filtration through a silica pad [CH₂Cl₂/ethyl acetate (5:1)]. Column chromatography [silica, CHCl₃/MeOH (98:2)] followed by trituration with methanol afforded a purple solid (62 mg, 4.6%): ¹H NMR δ -2.88 (br s, 2H), 1.68 (s, 18H), 7.95 (d, *J* = 6.8 Hz, 2H), 8.13 (d, *J* = 6.8 Hz, 2H), 8.19–8.29 (m, 4H), 8.82–8.83 (m, 4H), 8.91 (d, *J* = 4.8 Hz, 2H), 8.94 (d, *J* = 4.8 Hz, 2H); LDMS obsd 1114.1, 1058.0 [(M - *tert*-Bu)⁺], 1000.9 [(M - 2 x *tert*-Bu)⁺]; FABMS obsd 1112.1429; calcd 1112.1410 (C₅₂H₃₆F₁₀N₄O₃P). λ_{abs} 419, 512, 544, 589, 643 nm; λ_{em} (λ_{ex} = 513 nm) 647, 715 nm.

5,15-Bis(pentafluorophenyl)-10-[4-(di-*tert*-butyloxyphosphoryl)phenyl]-20-[4-(2-(trimethylsilyl)ethynyl)phenyl]porphyrin (11). Following a standard procedure,³⁵ a solution of **8** (1.02 g, 1.45 mmol) in THF/methanol [55 mL (10:1)] was treated with NaBH₄ (1.10 g, 29.0 mmol). The resulting dipyrromethane-dicarbinol (**8-diol**) was condensed with **6** (600 mg, 1.45 mmol) in CH₃CN (580 mL) containing TFA (1.34 mL, 17.4 mmol, 30 mM). After 6 min, a sample of DDQ (824 mg, 3.63 mmol) was added. After 30 min, TEA was added and the mixture was filtered through a silica pad [CH₂Cl₂/ethyl acetate (5:1)]. The porphyrin-containing fractions (which contained a large amount of dipyrin) were combined and concentrated. Trituration with methanol followed by filtration afforded a purple solid (123 mg, 7.8%): ¹H NMR δ -2.86 (br s, 2H), 0.39 (s, 9H), 1.68 (s, 18H), 7.90 (d, *J* = 7.6 Hz, 2H), 8.17 (d, *J* = 7.6 Hz, 2H), 8.19–8.29 (m, 4H), 8.83–8.84 (m, 4H), 8.91–8.94 (m, 4H); ³¹P NMR δ 10.14; LDMS obsd 1083.7, 1027.7 [(M - *tert*-Bu)⁺], 971.4 [(M - 2 x *tert*-Bu)⁺]; FABMS obsd 1082.2810; calcd 1082.2839 (C₅₇H₄₅F₁₀N₄O₃PSi). λ_{abs} 419, 512, 545, 589, 644 nm; λ_{em} (λ_{ex} = 512 nm) 648, 715 nm.

Mg(II)-5,15-Bis(pentafluorophenyl)-10-[4-(di-*tert*-butyloxyphosphoryl)phenyl]-20-[4-[2-(trimethylsilyl)ethynyl]phenyl]porphyrin (Mg11). Samples of **Mg27** (184 mg, 177 μmol) and [Pd(PPh₃)₄] (21 mg, 18 μmol) were treated with toluene/TEA [7 mL, (5:1)] and di-*tert*-butylphosphite (354 μmol, 1.77 mmol) at 80 °C under argon for 16 h. The reaction mixture was concentrated. Column chromatography (silica, CHCl₃) followed by trituration with methanol (2x) and hexanes (1x) afforded a purple solid (124 mg, 63%): ¹H NMR (THF-d₈) δ 0.37 (s, 9H), 1.52 (s, 18H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.90–8.00 (m, 2H), 8.19 (d, *J* = 8.1 Hz, 2H), 8.23–8.26 (m, 2H), 8.82 (d, *J* = 4.4 Hz, 2H), 8.47 (d, *J* = 4.4 Hz, 2H), 8.89–8.91 (m, 4H); LDMS obsd 1104.2, 1048.1 [(M - *tert*-Bu)⁺], 991.2 [(M - 2 x *tert*-Bu)⁺]; FABMS obsd 1104.2496; calcd 1104.2533 (C₅₇H₄₃F₁₀MgN₄O₃PSi); λ_{abs} (toluene + 5% THF) = 429, 566, 614 nm; λ_{em} (toluene + 5% THF) (λ_{ex} = 566 nm) 610, 667 nm.

5-[4-(Di-*tert*-butyloxyphosphoryl)phenyl]-10-(4-iodophenyl)-15-mesityl-20-[4-(2-(trimethylsilyl)ethynyl)phenyl]porphyrin (12). Following a standard procedure,³⁵ a solution of **9** (0.347 g, 0.500 mmol) in THF/methanol [33 mL (10:1)] was treated with NaBH₄ (0.380 g, 10.0 mmol). The resulting dipyrromethane-dicarbinol (**9-diol**) was condensed with **6** (0.207 g, 0.500 mmol) in CH₃CN (200 mL) containing TFA (0.460 mL, 6.00 mmol, 30 mM). After 5 min, a sample of DDQ (0.340 mg, 1.50 mmol) was added. After 1 h, TEA was added and the mixture

was filtered through a silica pad [CHCl₃/ethyl acetate (95:5)]. The porphyrin-containing fractions were combined, concentrated and chromatographed [silica, CHCl₃/ethyl acetate (90:10)] to afford a purple solid (127 mg, 25%): ¹H NMR δ -2.73 (br s, 2H), 0.39 (s, 9H), 1.68 (s, 18H), 1.84 (s, 6H), 2.64 (s, 3H), 7.29 (s, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 2H), 8.09 (d, *J* = 8.4 Hz, 2H), 8.15 – 8.30 (m, 6H), 8.70 – 8.75 (m, 2H), 8.76 – 8.90 (m, 6H); ³¹P NMR δ 10.14; LDMS obsd 1072.2, 960.7 [(M – *tert*-Bu)⁺], 834.3 [(M – 2 x *tert*-Bu – I)⁺]; FABMS obsd 1070.3202; calcd 1070.3217 (C₆₀H₆₀IN₄O₃PSi). λ_{abs} 422, 515, 550, 592, 648 nm.

5-[4-(Di-*tert*-butyloxyphosphoryl)phenyl]-1-*p*-toluoyldipyrromethane (15).

Following a general procedure,³⁷ a solution of EtMgBr (5 mL, 5 mmol, 1.0 M in THF) was added to a solution of **6** (829 mg, 2.00 mmol) in THF (2 mL) under Ar. The mixture was stirred at room temperature for 10 min and then cooled to -78 °C. A solution of **13** (459 mg, 2.00 mmol) in THF (2 mL) was added over 1 min. The solution was maintained at -78 °C for 10 min, and then the cooling bath was removed. After 30 min, the reaction was quenched with saturated aqueous NH₄Cl. The mixture was allowed to warm to room temperature, poured into CH₂Cl₂, washed with water and then dried (Na₂SO₄). Column chromatography (silica, CH₂Cl₂/ethyl acetate (3:1)) afforded a pale yellow solid (512 mg, 48%): mp 97–99 °C; ¹H NMR δ 1.44 (s, 18H), 2.42 (s, 3H), 5.59 (s, 1H), 5.93 – 5.98 (m, 1H), 6.01 – 6.07 (m, 1H), 6.12 – 6.16 (m, 1H), 6.65 – 6.69 (m, 1H), 6.78 – 6.82 (m, 1H), 7.20 – 7.28 (m, 4H), 7.64 – 7.74 (m, 4H), 8.68 (br s, 1H), 9.97 (br s, 1H); ¹³C NMR δ 21.6, 30.39, 30.43, 44.0, 82.3, 82.4, 107.7, 108.0, 110.9, 118.1, 121.2, 127.9, 128.1, 129.0, 129.1, 130.6, 130.8, 131.2, 131.6, 131.7, 133.2, 135.6, 141.6, 142.4, 144.58, 144.61, 184.8; ³¹P NMR δ 10.30; Anal. Calcd for C₃₁H₃₇N₂O₄P: C, 69.91; H, 7.00; N, 5.26. Found: C, 69.91; H, 7.11; N, 5.15.

5-[4-(Di-*tert*-butyloxyphosphoryl)phenyl]-1-[4-[2-(trimethylsilyl)ethynyl]benzoyl]dipyrromethane (16). Following the procedure described for compound **15**, reaction of **6** (829 mg, 2.00 mmol) and **14** (623 mg, 2.00 mmol) followed by column chromatography [silica, CH₂Cl₂/ethyl acetate (3:1)] afforded a pale yellow solid (853 mg, 69%): mp 116–117 °C; ¹H NMR δ 0.26 (s, 9H), 1.45 (s, 18H), 5.58 (s, 1H), 5.93–5.99 (m, 1H), 6.03–6.09 (m, 1H), 6.12–6.18 (m, 1H), 6.70 (s, 1H), 6.73–6.80 (m, 1H), 7.19–7.27 (m, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.65–7.78 (m, 4H), 8.45 (br s, 1H), 9.82 (br s, 1H); ¹³C NMR δ -0.12, 30.43, 30.46, 44.0, 82.3, 82.42, 82.45, 82.49, 82.53, 97.3, 104.2, 107.8, 108.1, 111.2, 118.2, 121.5, 126.6, 127.9, 128.1, 128.8, 130.4, 130.6, 131.3, 131.6, 131.7, 131.8, 133.3, 137.9, 142.1, 144.49, 144.53, 183.9; ³¹P NMR δ 10.26; Anal. Calcd for C₃₅H₄₃N₂O₄PSi: C, 68.38; H, 7.05; N, 4.56. Found: C, 68.51; H, 7.12; N, 4.51.

5,15-Bis[4-(di-*tert*-butyloxyphosphoryl)phenyl]-10,20-di-*p*-tolylporphyrin (17).

Following a general procedure,³⁷ a solution of **15** (266 mg, 0.500 mmol) in THF/methanol [9 mL, (3:1)] was treated with NaBH₄ (475 mg, 12.5 mmol). The resulting carbinol (**15-OH**) was dissolved in CH₃CN (100 mL) and treated with TFA (230 μL, 3.0 mmol, 30 mM). After 5 min, a sample of DDQ (170 mg, 0.75 mmol) was added. After 1 h, TEA (420 μL, 3.0 mmol) was added. The mixture was concentrated and chromatographed [silica, CH₂Cl₂/ethyl acetate (3:1)], affording a purple solid (72 mg, 28%): ¹H NMR δ -2.78 (br s, 2H), 1.68 (s, 36H), 2.71 (s, 6H), 7.56 (d, *J* = 8.0 Hz, 4H), 8.10 (d, *J* = 8.0 Hz, 4H), 8.16–8.23 (m, 4H), 8.26–8.33 (m, 4H), 8.80 (d, *J* = 4.8 Hz, 4H), 8.91 (d, *J* = 4.8 Hz, 4H); ³¹P NMR δ 10.41; LDMS obsd 1027.6, 972.5 [(M – *tert*-Bu)⁺], 915.9 [(M – 2 x *tert*-Bu)⁺], 860.3 [(M – 3 x *tert*-Bu)⁺], 802.8 [(M – 4 x *tert*-Bu)⁺]; FABMS obsd 1026.4604; calcd 1026.4614 (C₆₂H₆₈N₄O₆P₂); λ_{abs} (THF) 418, 514, 548, 592, 647 nm.

1-Bromo-5-[4-(di-*tert*-butyloxyphosphoryl)phenyl]-9-*p*-toluoyldipyrromethane (18). Following a general procedure,³⁸ a solution of **15** (266 mg, 0.500 mmol) in THF (10 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ under Ar. A sample of NBS (89 mg, 0.50 mmol) was added and the reaction mixture was stirred for 1 h at $-78\text{ }^{\circ}\text{C}$. Hexanes (10 mL) and water (10 mL) were added and the mixture was allowed to warm to room temperature. The organic phase was extracted with CH_2Cl_2 , dried (Na_2SO_4) and concentrated under reduced pressure without heating. Column chromatography [silica, CH_2Cl_2 /ethyl acetate (3:1)] afforded a pale brown powder (239 mg, 78%): mp $132\text{--}134\text{ }^{\circ}\text{C}$ (dec.); ^1H NMR δ 1.44 (s, 18H), 2.42 (s, 3H), 5.55 (s, 1H), 5.85–5.90 (m, 1H), 6.00–6.06 (m, 1H), 6.07–6.09 (m, 1H), 6.70–6.81 (m, 1H), 7.10–7.26 (m, 4H), 7.60–7.70 (m, 4H), 9.20 (br s, 1H), 10.38 (br, 1H); ^{13}C NMR δ 30.66, 30.70, 44.3, 82.7, 82.8, 98.4, 109.9, 110.3, 111.4, 121.6, 128.1, 128.2, 129.2, 129.5, 131.2, 131.6, 131.9, 132.0, 132.3, 133.6, 135.7, 141.2, 142.7, 144.2, 144.3, 185.3; ^{31}P NMR δ 9.99; Anal. Calcd for $\text{C}_{31}\text{H}_{36}\text{BrN}_2\text{O}_4\text{P}$: C, 60.89; H, 5.93; N, 4.58. Found: C, 59.93; H, 6.07; N, 4.10.

Zn(II)-10-[4-(Di-*tert*-butyloxyphosphoryl)phenyl]-17,18-dihydro-18,18-dimethyl-5-*p*-tolylporphyrin (Zn20). Following a general procedure,³⁸ a solution of **18** (183 mg, 0.300 mmol) in THF/methanol [12.5 mL (4:1)] was treated with NaBH_4 (114 mg, 3.00 mmol). After 15 min, the reaction mixture was quenched with cold water and extracted with CH_2Cl_2 . The organic layer was dried (K_2CO_3) and concentrated under reduced pressure without heating to afford mono-carbinol **18-OH** as a foam. The latter was dissolved in CH_3CN (3 mL) and **19** (57 mg, 0.30 mmol) was added followed by TFA (23 μL , 0.30 mmol). The reaction mixture was stirred at room temperature for 30 min, and then diluted with 27 mL of CH_3CN . Samples of AgOTf (231 mg, 0.900 mmol), $\text{Zn}(\text{OAc})_2$ (826 mg, 4.50 mmol), and 2,2,6,6-tetramethylpiperidine (2.4 mL, 9.0 mmol) were added. The resulting mixture was refluxed for 18 h exposed to air. The mixture was concentrated. Column chromatography [silica, CH_2Cl_2 /ethyl acetate (3:1)] afforded a purple-green solid (39 mg, 17%): ^1H NMR (THF- d_8) δ 1.57 (s, 18H), 2.04 (s, 6H), 2.65 (s, 3H), 4.53 (s, 2H), 7.49 (d, $J = 7.6\text{ Hz}$, 2H), 7.93 (d, $J = 7.6\text{ Hz}$, 2H), 7.96 – 8.02 (m, 2H), 8.07 – 8.14 (m, 2H), 8.23 (d, $J = 4.4\text{ Hz}$, 1H), 8.31 (d, $J = 4.4\text{ Hz}$, 1H), 8.50 (d, $J = 4.4\text{ Hz}$, 1H), 8.55 – 8.65 (m, 5H); ^{31}P NMR δ 14.32; LDMS obsd 763.2, 700.1 [(M – *tert*-Bu)⁺], 648.8 [(M – 2 x *tert*-Bu)⁺], 586.6 [(M – (2 x *tert*-Bu) – Zn)⁺]; FABMS obsd 760.2548; calcd 760.2521 ($\text{C}_{43}\text{H}_{45}\text{N}_4\text{O}_3\text{PZn}$); λ_{abs} (THF) 412, 607 nm.

Zn(II)-17,18-Dihydro-10-[4-(dihydroxyphosphoryl)phenyl]-18,18-dimethyl-5-*p*-tolylporphyrin (Zn21). A solution of **Zn20** (20.0 mg, 26.0 μmol) in CHCl_3 (5 mL) was treated with TEA (0.073 mL, 0.52 mmol) and TMS-Cl (0.049 mL, 0.39 mmol). The cloudy mixture was stirred at reflux for 4 h, at which time TLC indicated the absence of starting material [R_f for **Zn20** = 1, R_f for **Zn21** = 0.1 ($\text{CHCl}_3/\text{MeOH}$, 1:1)]. Water was added and the organic phase was extracted with CHCl_3 , dried (Na_2SO_4) and concentrated. Trituration with hexanes afforded a purple solid (15 mg, 88%): The acquisition of ^1H and ^{31}P NMR in CDCl_3 , THF- d_8 , CD_3OD , or $\text{DMSO}-d_6$ did not show any clear indication of peaks; MALDI-MS (POPOP) obsd 648.5, calcd 648.1 ($\text{C}_{35}\text{H}_{29}\text{N}_4\text{O}_3\text{PZn}$); λ_{abs} (THF) 414, 608 nm. A FABMS spectrum gave very weak, uninformative signals.

Zn(II)-5-[4-(Di-*tert*-butyloxyphosphoryl)phenyl]-10,20-dimesityl-15-[4-[2-(trimethylsilyl)ethynyl]phenyl]porphyrin (Zn23). Samples of **Zn22** (191 mg, 194 μmol) and di-*tert*-butylphosphite (388 μmol , 1.94 mmol) were coupled using $[\text{Pd}(\text{PPh}_3)_4]$ (22 mg, 19 μmol) in toluene/TEA [6 mL, (5:1)] at $80\text{ }^{\circ}\text{C}$ under argon for 16 h. Column chromatography [silica, $\text{CHCl}_3 \rightarrow \text{CHCl}_3/\text{MeOH}$ (10:1); silica, $\text{CHCl}_3/\text{MeOH}$ (4:1)] followed by trituration with hexanes

afforded a purple solid (94 mg, 46%): ^1H NMR (THF- d_8) δ 0.36 (s, 9H), 1.63 (s, 18H), 1.84 (s, 12H), 2.61 (s, 6H), 7.30 (s, 4H), 7.81 (d, J = 8.0 Hz, 2H), 8.11–8.14 (m, 2H), 8.18 (d, J = 8.0 Hz, 2H), 8.24–8.27 (m, 2H), 8.66–8.68 (m, 4H), 8.75–8.78 (m, 4H); LDMS obsd 1050.5, 996.6 [(M – *tert*-Bu) $^+$], 935.6 [(M – 2 x *tert*-Bu) $^+$]; FABMS obsd 1048.3855; calcd 1048.3867 (C₆₃H₆₅N₄O₃PSiZn); λ_{abs} 424, 483, 514, 550, 590 nm; λ_{em} (λ_{ex} = 550 nm) 597, 646 nm.

Zn(II)-5-[4-(Di-*tert*-butyloxyphosphoryl)phenyl]-10,20-dimesityl-15-(4-ethynylphenyl)porphyrin (Zn24). A solution of **Zn23** (87 mg, 82 μmol) in CHCl₃/THF [10 mL, (3:1)] was treated with TBAF (99 μL , 99 μmol , 1.0 M in THF) at room temperature under argon for 1 h. Column chromatography [silica, CHCl₃/MeOH, (3:1)] afforded a purple solid (68 mg, 84%): ^1H NMR (THF- d_8) δ 1.64 (s, 18H), 1.84 (s, 12H), 2.61 (s, 6H), 3.78 (s, 1H), 7.30 (s, 4H), 7.84 (d, J = 8.0 Hz, 2H), 8.11–8.20 (m, 4H), 8.25–8.28 (m, 2H), 8.66–8.69 (m, 4H), 8.75 (d, J = 4.4 Hz, 2H), 8.78 (d, J = 4.4 Hz, 2H); LDMS obsd 975.1, 921.2 [(M – *tert*-Bu) $^+$], 863.3 [(M – 2 x *tert*-Bu) $^+$]; FABMS obsd 976.3447; calcd 976.3460 (C₆₀H₅₇N₄O₃PZn); λ_{abs} 423, 486, 514, 550, 591 nm; λ_{em} (λ_{ex} = 550 nm) 597, 646 nm.

5,15-Bis(pentafluorophenyl)-10-(4-iodophenyl)-20-[4-[2-(trimethylsilyl)ethynyl]phenyl]porphyrin (27). Following a general procedure,³⁵ a solution of **25** (1.02 g, 1.44 mmol) in dry THF/methanol [85 mL, (10:1)] was treated with NaBH₄ (1.09 g, 28.7 mmol) affording the corresponding dipyrromethane-dicarbinol (**25-diol**). The latter was condensed with **26** (500 mg, 1.44 mmol) in acetonitrile (580 mL) containing TFA (1.33 mL, 17.3 mmol). After 5 min, DDQ (0.980 g, 4.32 mmol) was added followed by TEA (2.41 mL, 17.3 mmol) and the mixture was stirred at room temperature for 1 h. The mixture was filtered through an alumina pad. Column chromatography [silica, CH₂Cl₂/hexanes (1:1)] afforded a purple solid (326 mg, 22%): ^1H NMR δ –2.83 (br s, 2H), 0.38 (s, 9H), 7.90 (d, J = 8.1 Hz, 2H), 7.95 (d, J = 8.1 Hz, 2H), 8.13 (d, J = 8.1 Hz, 2H), 8.17 (d, J = 8.1 Hz, 2H), 8.80–8.83 (m, 4H), 8.90–8.94 (m, 4H); LDMS obsd 1016.1; 998.0 [(M – F) $^+$]; FABMS obsd 1016.0920; calcd 1016.0890 (C₄₉H₂₇F₁₀IN₄Si); λ_{abs} 420, 512, 545, 589, 647 nm.

Mg(II)-5,15-Bis(pentafluorophenyl)-10-(4-iodophenyl)-20-[4-[2-(trimethylsilyl)ethynyl]phenyl]porphyrin (Mg27). Following a general procedure,³² a solution of **27** (200 mg, 197 μmol) in CH₂Cl₂ (16 mL) was treated with DIEA (1.37 mL, 7.87 mmol) and MgI₂ (1.09 g, 3.93 mmol). After 2 h, the mixture was washed with 5% NaHCO₃, dried (Na₂SO₄), and concentrated. Column chromatography [alumina, CH₂Cl₂/THF (10:1)] afforded a purple solid (204 mg, 99%): ^1H NMR δ (CDCl₃ + 10% THF- d_8) 0.23 (s, 9H), 7.70 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H), 8.62–8.63 (m, 4H), 8.71–8.74 (m, 4H); LDMS obsd 1038.5; 1020.4 [(M – F) $^+$]; FABMS obsd 1038.0564; calcd 1038.0584 (C₄₉H₂₅F₁₀IMgN₄Si); λ_{abs} 427, 522, 562, 605 nm; λ_{em} (λ_{ex} = 562 nm) 611, 665 nm.

4-(Ferrocenyl)phenylphosphonic acid (29). Samples of 4-iodophenylferrocene (300 mg, 0.773 mmol) and Pd(PPh₃)₄ (134 mg, 0.116 mmol) were treated with toluene/TEA [36 mL, (5:1)] and bis(trimethylsilyl)phosphite (2.20 mL, 0.012 mol) at 70 °C under argon for 18 h. The mixture was diluted with 50 mL of CH₂Cl₂ and extracted with saturated NaHCO₃ (3 x 20 mL). The aqueous layer was acidified with concentrated HCl and extracted with ether (3 x 50 mL). The combined organic layers were dried (Na₂SO₄) and filtered. Hexanes was added and the precipitate was collected to afford an orange solid (102 mg, 40% yield): mp > 235 °C (dec.); ^1H NMR (DMSO- d_6) δ 4.00 (s, 5H), 4.38 (s, 2H), 4.83 (s, 2H), 7.50–7.61 (m, 4H); FABMS obsd 342.0101; calcd 342.0108 (C₁₆H₁₅FeO₃P); Anal. Calcd for C₁₆H₁₅FeO₃P: C, 56.17; H, 4.42.

Found: C, 56.29; H, 4.48.

Dyad-1. Following a general procedure,⁴¹ samples of **Zn24** (49 mg, 0.050 mmol) and **Zn28** (47 mg, 0.050 mmol) were treated with Pd₂(dba)₃ (6.9 mg, 7.5 μmol) and P(*o*-tol)₃ (18 mg, 0.06 mmol) in toluene/TEA [18 mL, (5:1)] at 35 °C under argon. After 4 h, an identical batch of catalyst was added. The reaction was continued for another 7 h. Purification by a silica column [CHCl₃/MeOH (98:2)], a preparative SEC column (THF), and a short silica column [CHCl₃/MeOH (98:2)] afforded a brown-purple solid (48 mg, 54%): ¹H NMR (THF-d₈) δ 1.65 (s, 18H), 1.85–1.91 (m, 30H), 2.59–2.65 (m, 15H), 7.28–7.34 (m, 10H), 8.03–8.08 (m, 4H), 8.12–8.19 (m, 2H), 8.26–8.34 (m, 6H), 8.62–8.66 (m, 4H), 8.68–8.72 (m, 4H), 8.74 (d, *J* = 4.4 Hz, 2H), 8.78 (d, *J* = 4.4 Hz, 2H), 8.87 (d, *J* = 4.4 Hz, 2H), 8.90 (d, *J* = 4.4 Hz, 2H); ³¹P NMR δ 11.06; MALDI-MS (POPOP) obsd 1781.2, 1723.4 [(M – *tert*-Bu)⁺], 1667.0 [(M – 2 x *tert*-Bu)⁺]; FABMS obsd 1776.6273; calcd 1776.6317 (C₁₁₃H₁₀₁N₈O₃PZn₂); λ_{abs} 428, 551, 593 nm.

Dyad-2. A solution of **Dyad-1** (31 mg, 0.017 mmol) and TEA (47 μL, 0.34 mmol) in CHCl₃ (3.4 mL) was treated with TMS-Cl (33 μL, 0.26 mmol) at 65 °C under argon for 4 h. Water was added and the organic layer was dried (Na₂SO₄) and concentrated. Trituration with hexanes afforded a purple solid (23 mg, 82%): ¹H NMR (CD₃OD) δ 1.82–1.92 (m, 30H), 2.57–2.65 (m, 15H), 7.25–7.34 (m, 10H), 7.98–8.06 (m, 4H), 8.18–8.23 (m, 4H), 8.26–8.32 (m, 4H), 8.58–8.72 (m, 10H), 8.78–8.88 (m, 6H); ³¹P NMR δ (not observed); MALDI-MS (POPOP) obsd 1667.4; FABMS obsd 1664.5020; calcd 1664.5065 (C₁₀₅H₈₅N₈O₃PZn₂); λ_{abs} 428, 551, 591 nm.

Electrochemical Studies of Monolayers on SiO₂. Redox-active molecules bearing phosphonic acid groups were tethered to thin layers of SiO₂ grown on (100) p-type Si substrates with a doping density of 1 x 10¹⁸ cm⁻³ (obtained from MEMC, Inc.). A thin SiO₂ layer (4.5 nm) was obtained by thermal growth at 900 °C in O₂. This layer was then further thinned by subjecting the oxide layer to a slow etch in 1% HF solution for ~35 sec, affording a 1.3 nm layer of SiO₂ as determined by ellipsometry. A solution of the redox-active compound in DMF was added dropwise (8 drops) to the thin SiO₂ surface. After each drop, the substrate was heated to 170 °C for 10 min. The sample was then rinsed in CH₂Cl₂. The substrate was then placed on a probe station and the backside (working electrode) was contacted via the chuck. A solution of 1.0 M Bu₄NPF₆ in propylene carbonate was placed on top of the molecules and used as the conducting gate electrolyte. A silver gate electrode was immersed in the electrolyte and used as the reference electrode. Traditional cyclic voltammetry measurements were obtained using a custom program run using National Instruments LabVIEW.

II. Survey of Suitable Phosphonic Acid Masking Agents.

Screening Experiments. We screened the following masking agents for the protection of the phosphonic acid group: (1) 2-trimethylsilylethyl, (2) 2-cyanoethyl, (3) 2-chloroethyl, and (4) methyl groups. The reaction of 1-(1,3-dioxolan-2-yl)-4-(diethoxyphosphoryl)benzene (**S-1**)⁴ with TMS-Br in CH₂Cl₂ gave 4-(dihydroxyphosphoryl)benzaldehyde (**S-2**) (Scheme S-1). Compound **S-2** was subjected to condensation with 2-cyanoethanol, 2-trimethylsilylethanol or 2-chloroethanol in the presence of DCC in THF at room temperature. The condensation was successful only with 2-cyanoethanol, affording condensed product **S-3** in 66% yield after column chromatography. The condensation with 2-chloroethanol or 2-trimethylsilylethanol showed a new spot on TLC, but workup followed by purification by column chromatography failed to give the desired product.

Scheme S-1.

The cyanoethyl-protected phosphate group has been cleaved by treatment with primary, secondary or tertiary amines.⁴⁶ Our applications require Sonogashira reactions (warm, basic solvent containing a Pd catalyst) for the synthesis of multiporphyrin arrays. The basic conditions generally entail use of toluene/TEA (5:1). Therefore, we first tested the stability of compound **S-3** with toluene/TEA at room temperature. A solution of **S-3** in toluene was treated overnight with TEA (toluene/TEA = 5:1) at room temperature. TLC analysis showed a mixture **S-2** and **S-3** in a 4:1 ratio, indicating the inapplicability of cyanoethyl-protected phosphonates in our studies.

We have also tried to introduce a methyl-protected phosphonate to 4-bromobenzaldehyde dimethylacetal²⁷ (**S-6**). We carried out the Pd-mediated coupling of dimethylphosphite and **S-6** following conditions similar to those reported for the synthesis of compound **S-1** [Pd(PPh₃)₄, toluene/TEA (5:1), 80 °C]. The starting material disappeared but did not afford the desired product.

Stability of Metalloporphyrins to Cleavage Conditions. The stability of metalloporphyrins under the conditions for deprotecting the *tert*-butyl group from the phosphonate moiety using TMS-Cl/TEA²⁵ was first checked with **ZnTMP**⁴⁷ [Zn(II)-*meso*-tetramesitylporphyrin] and **MgTMP**³² [Mg(II)-*meso*-tetramesitylporphyrin]. Thus, **ZnTMP** or **MgTMP** was treated with 15 equiv of TMS-Cl and 20 equiv of TEA in CHCl₃ (stabilized with amylenes) at 65 °C for 4 h. UV-vis and fluorescence spectroscopy showed no detectable demetalation in either case.

4-(Dihydroxyphosphoryl)benzaldehyde (S-2). A solution of **S-1** (1.14 g, 4.00 mmol) in CH₂Cl₂ (8 mL) was treated with 4 equiv of TMS-Br (2.20 mL, 16.0 mmol). The solution was stirred overnight at room temperature. The solvent was evaporated and the residue was

suspended in water. The mixture was stirred at room temperature for 2 h. The mixture was extracted with ethyl acetate. The water layer was saturated with NaCl and extracted again with ethyl acetate. The combined extracts were dried (Na_2SO_4) and concentrated to afford a brown solid. The brown solid was suspended in CH_2Cl_2 and sonicated. Filtration afforded a yellow solid (220 mg, 30%): IR (neat) 2920, 1665 cm^{-1} ; ^1H NMR δ 7.78–8.10 (m, 4H), 10.06 (s, 1H).

4-[Bis-(2-cyanoethoxy)phosphoryl]benzaldehyde (S-3). A solution of **S-2** (73 mg, 0.39 mmol) in THF (4 mL) was treated with DCC (0.25 g, 1.2 mmol) and 2-cyanoethanol (0.059 mL, 0.86 mmol). The mixture was stirred overnight at room temperature. The mixture was directly chromatographed (silica, ethyl acetate) affording a colorless liquid (75 mg, 66%): ^1H NMR δ 2.70–2.90 (m, 4H), 4.20–4.50 (m, 4H), 7.95–8.10 (m, 4H), 10.10 (s, 1H).

References

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3a

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Zn3a

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843.464

821.469

Mg4

S31

INSTRUM TOP
OpId N. Sriinivasan
SMPNAM 010099
QDATE Mon Feb 3 13:41:01 2003
DATA /data/chemistry/LINDSEY/KUMAR
POLAP1 PGSA-Chemistry LINDSEY KUMAR
ADOP.m Reflecton
TD 40000
NSHOTS 51
SMONIM 0
SMOPTS1 0
SMOPTS2 0
SMOPTS3 0
DW 1.00 (ns)
DELAY 0 (ns)
Uis1 20.00 (kV)
Uis2 18.70 (kV)
Uref1 0.00 (kV)
Uref2 0.00 (kV)
Uens 16.20 (kV)
Urefull 0.00 (kV)
Udet1 1.50 (kV)
Udet2 1.50 (kV)
Udet3 2.00 (kV)
REPRZ 1.00 (Hz)
ATTEN 5000
ML1 2062844.837
ML2 333.982
ML3 0.000
HITURBC no
GDEON yes
GDELY short
REFRAN no
REFRND no
LINSBND no
UIS2BND no
DPCAL1 510.84
DPMAS 700.00 (Da)
RENOVAL 0.31
LENOVAL 0.31
SMOBY 0.01
CNT1 kpk-410 Mg-IMS .P-3HQ .par
CNT2 02.03.03

INSTRUM TOF
 OPID N. Srinivasan
 APPRAN 021245
 ACQUIRE DATE 23 12 07 06 2002
 PATH /data/chemistry/LINDSEY/LOEWE
 POLARI POS Reflector
 AQOP_m 40000
 TD 210
 NSHOTS 0
 SNOBOM 0
 SNOPT1 0
 SNOPT2 0
 SNOPT3 0
 DW 1.00 [ns]
 DELAY 0 [ns]
 Uis1 20.00 [KV]
 Uis2 18.70 [KV]
 Uref1 0.00 [KV]
 Uref2 7.50 [KV]
 Uinmass 10.00 [KV]
 RefPull 0.00 [KV]
 UdetL 1.50 [KV]
 UdetR 0.00 [KV]
 Udef1 2.00 [KV]
 UDEF2 2.00 [KV]
 ACQEN 29.00 [Hz]
 ML1 2067125.193
 ML2 333.982
 ML3 0.000
 HITURBO no
 GDEON yes
 DEELY Short
 DEELV no
 RENSND no
 LINSND no
 UIS2BND no
 DECAL1 510.84
 DPMAS 700.00 [Da]
 REMVAL 0.3
 IS2BNDV 0.91
 CMT1 RL001
 CMT2 no matrix

11

S37

12

INSTRUM TCF
 OPID N. Srinivasan
 SMPNAM 010066
 ACQDATE Thu Jan 23 12:07:19 2003
 ACQTIME 12:07:19
 PGM Data-Chemistry/LINDSEY KUMAR
 Reflct Reflector
 ACP_m 40060
 ID 34
 NoSHOTS 0
 SMOPT1 0
 SMOPT2 0
 SMOPT3 0
 DM 1.00 [ns]
 DELAY 0 [ns]
 U1s1 20.00 [Kv]
 U1s2 16.70 [Kv]
 Uref1 0.00 [Kv]
 U1ens 10.00 [Kv]
 U1ens2 10.00 [Kv]
 Uref2 16.00 [Kv]
 U1s3 1.50 [Kv]
 U1s4 1.55 [Kv]
 U1s5 2.00 [Kv]
 U1s6 1.00 [Hz]
 U1s7 207294.094
 U1s8 371.681
 ML3 0.000
 HITURBO no
 GDEON yes
 GDELY short
 DEFLCN no
 KINSENO no
 KINSENO no
 G1S2ND no
 DPCAL1 510.84
 DPMAS 760.00 [Da]
 REMVAL 0.13
 LENDVAL 0.28
 LENDV 0.28
 KMK-406 Reflct
 QMT1 KMK-406 Reflct
 QMT2 Sat=55, matrix

S42

16

16

0.000

16

10.258

ppm

-15

-10

-5

0

5

10

15

20

25

10.409

-25 ppm

-20

-15

-10

-5

0

5

10

15

20

25

30

9.994

30 25 20 15 10 5 0 -5 -10 -15 -20 -25 ppm

14.321

30 25 20 15 10 5 0 -5 -10 -15 -20 -25 ppm

INSTRUM TCF

Method file : STDEFMET.M (modified) Last update: Date
 02/03/03 Time 08:55:16
 Information : Default Method
 Data File : <untitled>

Overlaid Spectra:

#	Name	Peaks (nm)	Abs (AU)
1		414.0	1.24850
1		608.0	0.24670
1		511.0	0.15464

Report generated by :

Signature:

*** End Spectrum/Peak Report ***

/data/chemistry/LINDSEY/KUMAR/030104/3SRef/pdata/1 tof Mon Feb 3 15:31:08 2003

Zn23

Zn23

Zn24

Zn24

863.28

975.09

921.20

985.09

802.43

847.25

914.16

INSTRUM TQF
 ANALYST M. Srinivasan
 SAMPLE Zn24
 ACQ DATE Thu Oct 17 11:45:37 2002
 PATH /data/chemistry/LINDSEY LEWE
 PULPROG PDS
 A2 2.0 Reflecter
 TL 40000
 RESOLUTION 86
 SMOOTHING 0
 SPLIT 0
 DELAY 1.00 [ns]
 D0 0 [ns]
 U1 20.00 [KV]
 U2 18.70 [KV]
 U3 0 [KV]
 U4 0 [KV]
 U5 10.00 [KV]
 U6 10.00 [KV]
 RefPull 0.00 [KV]
 Udet1 1.50 [KV]
 Udet2 0.00 [KV]
 Udet3 2.00 [KV]
 Udet4 1.00 [KV]
 XRTN 23.00 [Hz]
 ML1 1062614.147
 ML2 316.110
 ML3 0.000
 HITUP no
 SDECN yes
 SDECN yes
 DEFCN yes
 BLINBND no
 BLINBND no
 BLINBND no
 BLINBND no
 BLINBND no
 DPCAL 510.64
 DPMAS 700.00 [Da]
 FWHM 0.22
 RESOLV 0.91
 QMT PSL133
 QMT2 no matrix

S63

27

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/data/chemistry/LINDSEY/LOEWE/020883/1SRef/pdata/1
...
tof Thu Jul 25 10:40:15 2002

```

Mg11

INSTRUM T1
 Q113 Q113
 SMPRSE 11.40.16
 DATE Thu Oct 17 11:40:16 2002
 FILENAME data/chemistry/LINDSEY/LOEWE
 POLARI 1000
 ACQVAL 4.10
 TO 4.10
 NSHETS 1
 SMOBUN 0
 SMOPTS1 0
 SMOPTS2 0
 SMOPTS3 0
 DN 1.00 [ns]
 DELAY 0.10 [ns]
 U1s1 20.00 [KV]
 U1s2 16.70 [KV]
 Uref1 0.00 [KV]
 Uref2 0.00 [KV]
 U1s3 10.00 [KV]
 RefPull 0.00 [KV]
 UdetL 1.50 [KV]
 UdetR 0.00 [KV]
 Udet1 2.00 [KV]
 REPH2 0.00 [Hz]
 REPH1 0.00 [Hz]
 ML1 320.14 147
 ML2 116.110
 ML3 0.000
 HITURBO no
 GUEON yes
 GUELY shift
 GUEON no
 RASSED no
 LINSERD no
 U1S2BND no
 DPCAL 510.84
 DPMAS 750.00 [Da]
 REMVAL 0.33
 LEGAL 0.06
 LEGNOV 0.01
 CMT1 RES16
 CMT2 NO MATTX

29

Dyad-1

S72

tof Sat Mar 29 15:38:44 2003

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INSTRUM  TOF
OPID      N_Srinivasan
SNNPNAME  030224
AQ DATE   Sat Mar 29 15:15:51 2003
PAPATH    /data/chemistry/LINSEY/PUMAR
POLARI     POS
REFLECTOR  Reflector
ID         ID40060
N3SHOTS   63
SNOMNUM    0
SMOPTS1    0
SMOPTS2    0
SMOPTS3    0
SMOPTS4    0
SMOPTS5    0
SMOPTS6    0
SMOPTS7    0
SMOPTS8    0
SMOPTS9    0
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SMOPTS410
```

INSTRUM	TOP
OPID	N. Srinivasan
SMPNAM	01CZ24
AQDATE	Sat Mar 29 15:16:02 2003
DATA PATH	/data/chemistry/LINDESEY/RUMAR
OS	LINUX
CARDR	0
Reflector	0
TID	4506CC
NSHOTS	100
SNUNUM	0
SMPTES1	0
SMPTES2	0
SMPTES3	0
DW	1.50 [ms]
DELAY	0 [ms]
U1s1	20.00 [kV]
U1s2	18.00 [kV]
U1s3	15.00 [kV]
U1s4	7.50 [kV]
U1s5	7.50 [kV]
Ultmass	10.50 [kV]
RefrFull	0.00 [kV]
UnderL1	1.50 [kV]
UnderL2	1.50 [kV]
UnderL3	2.00 [kV]
UnderL4	1.50 [kV]
REPHZ	1.00 [Hz]
ATTEN	46.0
M.M.1	2058470.669
M.L2	331.962
M.L3	0.000
HITRHO	no
GDCEN	yes
DEPLEN	short
DEPLEN	no
FLASND	no
FLASND	no
UISSBND	no
ppCAL1	510.64
PPMMASS	700.60 [Da]
RENVAL	0.31
RENVAL	0.31
LSRANDV	0.0
SWT1	kuk-432 di-OH-phos
SWT2	kuk-432 OI-CH-phos