Supporting Information

Versatile Synthesis of *meso*-Aryloxy- and Alkoxy-Substituted Porphyrins via Palladium-Catalyzed C–O Cross-Coupling Reactions

Guang-Yao Gao, Andrew J. Colvin, Ying Chen and X. Peter Zhang*

Department of Chemistry, University of Tennessee, Knoxville, TN 37996

Experimental Section

General Considerations. All reactions were carried out under a nitrogen atmosphere in oven-dried glassware following standard Schlenk techniques. Toluene was distilled under nitrogen from sodium benzophenone ketyl. All alcohols were purchased from Acros Organics or Aldrich Chemical Co. and used without further purification. Cesium carbonate was obtained as a gift from Chemetall Chemical Products, Inc. Palladium(II) acetate, tris(dibenzylideneacetone)dipalladium(0), bis(2-diphenylphosphinophenyl)ether (DPEphos) and 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (Xantphos) were purchased from Strem Chemical Co. All ligands, palladium precursors and bases were stored in desiccators filled with anhydrous calcium sulfate, and weighed in the air. All bromoporphyrins and their zinc complexes were prepared according to the method described in literatures.¹

General Procedures for Etheration of *meso*-Bromoporphyrin. An oven-dried Schlenk tube equipped with a stirring bar was degassed on vacuum line and purged with nitrogen. The tube was then charged with palladium precursor (5 mol %), phosphine ligand (10 mol %), bromoporphyrin (0.05 mmol) and base (2.0 equiv per Br). The tube was capped with a Teflon screwcap, evacuated and backfilled with nitrogen. After the Teflon screwcap was replaced with a rubber septum, solvent (3 mL) and alcohol (4.0 equiv per Br) were added via syringe successively, followed by additional solvent (2 mL) to wash down possible reactants on the tube wall. The tube was purged with nitrogen (1-2 min) and the septum was then replaced with the Teflon screwcap and sealed. The reaction mixture was heated in an oil bath with stirring and monitored by TLC. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate, washed with water (x3) and concentrated to dryness. The solid residue was purified by flash chromatography.

[5-Phenoxy-10,20-diphenylporphinato]Zinc(II) (Table 1, entry 1). The general procedure was used to couple [5-bromo-10,20-diphenylporphinato]Zinc(II) (30 mg, 0.05 mmol) with

phenol (17 mg, 0.018 mmol), by using Pd(OAc)₂ (1.1 mg, 0.005 mmol) and DPEphos (4.0 mg, 0.015 mmol) in the presence of Cs₂CO₃ (24 mg, 0.07 mmol). The reaction was conducted in toluene at 100 °C for 23 h. The title compound was isolated by flash chromatography (silica gel, THF:hexanes (v/v) = 1:8) to as a red solid (24 mg, 80%). ¹H NMR (300 MHz, CDCl₃): δ 10.13 (s, 1H), 9.39 (d, *J* = 4.5 Hz, 2H), 9.31 (d, *J* = 4.8 Hz, 2H), 9.09 (d, *J* = 4.5 Hz, 2H), 8.92 (d, *J* = 4.8 Hz, 2H), 8.19 (m, 4H), 7.74 (m, 6H), 7.23 (m, 2H), 7.02 (m, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 165.9, 150.3, 150.1, 149.7, 145.8, 142.3, 134.5, 132.9, 132.2, 131.8, 129.6, 128.0, 127.5, 126.6, 121.5, 120.7, 116.6, 107.7, 105.6. UV–vis (CHCl₃, λ_{max}, nm): 398(sh), 418, 510, 548, 590. HRMS-EI ([M]⁺): calcd for C₃₈H₂₄N₄OZn, 616.1242; found: 616.1250.

[5-(4'-Methylphenoxy)-10,20-diphenylporphinato]Zinc(II) (Table 1, entry 2). The general procedure was used to couple [5-bromo-10,20-diphenylporphinato]Zinc(II) (30 mg, 0.05 mmol) with 4-cresol (20 mg, 0.018 mmol), using Pd(OAc)₂ (1.1 mg, 0.005 mmol) and DPEphos (4.0 mg, 0.015 mmol) in the presence of Cs₂CO₃ (24 mg, 0.07 mmol). The reaction was conducted in toluene at 100 °C for 16 h. The title compound was isolated by flash chromatography (silica gel, toluene:hexanes (v/v) = 3:1) as a red solid (21 mg, 65%). ¹H NMR (300 MHz, CDCl₃): δ 9.97 (s, 1H), 9.30 (d, *J* = 4.5 Hz, 2H), 9.21 (d, *J* = 4.5 Hz, 2H), 8.92 (d, *J* = 4.5 Hz, 2H), 8.8 (d, *J* = 4.5 Hz, 2H), 8.13 (m, 4H), 8.13 (m, 6H), 6.97 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 2.2 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 150.3, 145.8, 143.4, 142.7, 134.6, 132.7, 132.0, 131.6, 130.4, 130.0, 128.9, 128.4, 127.9, 127.4, 126.5, 125.2, 120.3, 116.3, 105.2, 24.9. UV–vis (CHCl₃, λ_{max}, nm): 399 (sh), 418, 548, 589. HRMS-EI ([M]⁺): calcd for C₃₉H₂₆N₄OZn, 630.1398; found: 630.1394.

[5-(3'-Methylphenoxy)-10,20-diphenylporphinato]Zinc(II) (Table 1, entry 3). The general procedure was used to couple [5-bromo-10,20-diphenylporphinato]Zinc(II) (30 mg, 0.05 mmol) with 3-cresol (20 μL, 0.018 mmol), using Pd₂(dba)₃ (1.5 mg, 0.0075 mmol) and DPEphos (9.6 mg, 0.036 mmol) in the presence of Cs₂CO₃ (34 mg, 0.1mmol). The reaction was conducted in toluene at 100 °C for 16 h. The title compound was isolated by flash chromatography (silica gel, THF:hexanes (v/v) = 1:8) as a red solid (25 mg, 78%). ¹H NMR (300 MHz, CDCl₃): δ 10.03 (s, 1H), 9.36 (d, *J* = 4.5 Hz, 2H), 9.25 (d, *J* = 4.5 Hz, 2H), 9.00 (d, *J* = 4.2 Hz, 2H), 8.89 (d, *J* = 4.5 Hz, 2H), 8.2 (m, 4H), 7.76 (m, 6H), 7.10 (t, *J* = 7.5Hz, 1H), 6.80 (m, 3H), 2.15 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 166.1, 150.0, 150.2, 149.6, 145.8, 142.7, 139.7, 134.6, 132.7, 132.0, 131.6, 129.3, 127.9, 127.4, 126.5, 122.2, 120.3, 117.3, 113.7, 105.2, 21.4. UV–vis (CHCl₃, λ_{max}, nm): 399 (sh), 418, 548, 589. HRMS-EI ([M]⁺): calcd for C₃₉H₂₆N₄OZn, 630.1398; found: 630.1394.

[5-(2'-Methylphenoxy)-10,20-diphenylporphinato]Zinc(II) (Table 1, entry 4). The general procedure was used to couple [5-bromo-10,20-diphenylporphinato]Zinc(II) (30 mg, 0.05 mmol) with 2-cresol (20 μ L, 0.018 mmol), using Pd₂(dba)₃ (1.5 mg, 0.0075 mmol) and DPEphos (9.6 mg, 0.036 mmol) in the presence of Cs₂CO₃ (34 mg, 0.1 mmol). The reaction was conducted in toluene at 100 °C for 16 h. The title compound was isolated by flash chromatography (silica gel, THF:hexanes (v/v) = 1:8) as a red solid (27.8 mg, 89%). ¹H NMR (300 MHz, CDCl₃): δ 9.94 (s, 1H), 9.33 (d, *J* = 4.8 Hz, 2H), 9.19 (d, *J* = 4.5 Hz, 2H), 8.97 (d, *J* = 4.2 Hz, 2H), 8.90 (d, *J* = 4.8 Hz, 2H), 8.18 (m, 4H), 7.74 (m, 6H), 7.47 (d, *J* = 6.9 Hz, 1H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.68 (t, *J* = 7.2 Hz, 1H), 6.02 (d, *J* = 8.4 Hz, 1H), 3.10 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 150.1, 149.9, 149.6, 145.7, 142.3, 140.7, 140.6, 140.6, 140.5, 134.5, 132.8, 132.1, 131.6, 131.0, 127.8, 127.5, 126.8, 126.6, 121.1, 116.2, 105.3, 17.0. UV-vis (CHCl₃, λ_{max} , nm): 398 (sh), 418, 548, 589. HRMS-EI ([M]⁺): calcd for C₃₉H₂₆N₄OZn, 630.1398; found: 630.1394.

[5-(4'-*t*-Butylphenoxy)-10,20-diphenylporphinato]Zinc(II) (Table 1, entry 5). The general procedure was used to couple [5-bromo-10,20-diphenylporphinato]Zinc(II) (30 mg, 0.05 mmol) with 4-*t*-butylphenol (27 mg, 0.18 mmol), using Pd(OAc)₂ (1.1 mg, 0.005 mmol) and DPEphos (4.0 mg, 0.015 mmol) in the presence of Cs₂CO₃ (24 mg, 0.07 mmol). The reaction was conducted in toluene at 100 °C for 18 h. The title compound was isolated by flash chromatography (silica gel, THF:hexanes (v/v) = 1:8) as a red solid (23.8 mg, 73%). ¹H NMR (300 MHz, CDCl₃): δ 10.16 (s, 1H), 9.45 (d, *J* = 4.8 Hz, 2H), 9.34 (d, *J* = 4.2 Hz, 2H), 9.06 (d, *J* = 4.5 Hz, 2H), 8.93 (d, *J* = 4.8 Hz, 2H), 8.22 (m, 4H), 7.77 (m, 6H), 7.24 (d, *J* = 9.9 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 1.26 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 164.0, 159.9, 150.4, 150.1, 149.7, 146.0, 144.1, 142.4, 134.5, 132.9, 132.1, 131.7, 128.1, 127.5, 126.7, 126.3, 120.66, 115.9, 105.5, 31.5, 29.7. UV-vis (CHCl₃, λ_{max} , nm): 399 (sh), 419, 548, 589. HRMS-EI ([M]⁺): calcd for C₄₂H₃₂N₄OZn, 672.1868; found: 672.1860.

[5-(2'-Isopropylphenoxy)-10,20-diphenylporphinato]Zinc(II) (Table 1, entry 6). The general procedure was used to couple [5-bromo-10,20-diphenylporphinato]Zinc(II) (30 mg, 0.05 mmol) with 2-isopropylphenol (25 μ L, 0.018 mmol), using Pd(OAc)₂ (1.1 mg, 0.005 mmol) and DPEphos (4.0 mg, 0.015 mmol) in the presence of Cs₂CO₃ (24 mg, 0.07 mmol). The reaction was conducted in toluene at 100 °C for 17 h. The title compound was isolated by flash chromatography (silica gel, THF:hexanes (v/v) = 1:8) as a red solid (23 mg, 72%). ¹H NMR (300 MHz, CDCl₃): δ 10.05 (s, 1H), 9.33 (d, *J* = 4.8 Hz, 2H), 9.26 (d, *J* = 4.5 Hz, 2H), 9.01 (d, *J* = 4.8 Hz, 2H), 8.90 (d, *J* = 4.5 Hz, 2H), 8.19 (m, 4H), 7.75 (m, 6H), 7.60 (d, *J* = 7.8 Hz, 1H), 6.96 (t, *J*

= 7.5 Hz, 1H), 6.67 (t, J = 7.2 Hz, 1H), 6.02 (d, J = 8.1 Hz, 1H), 4.40 (m, 1H), 1.82 (d, J = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ 163.86, 150.3, 150.0, 149.6, 145.8, 142.5, 135.8, 134.5, 132.8, 132.1, 131.6, 127.9, 127.4, 126.6, 126.5, 121.3, 120.4, 116.4, 105.2, 28.0, 23.3. UV-vis (CHCl_3 , λ_{max} , nm): 398 (sh), 419, 547, 589. HRMS-EI ($[\text{M}]^+$): calcd for $\text{C}_{41}\text{H}_{30}\text{N}_4\text{OZn}$, 658.1711; found: 658.1702.

[5-(4'-Methoxyphenoxy)-10,20-diphenylporphinato]Zinc(II) (Table 1, entry 7). The general procedure was used to couple [5-bromo-10,20-diphenylporphinato]Zinc(II) (30 mg, 0.05 mmol) with 4-methoxyphenol (22 mg, 0.18 mmol), using $\text{Pd}(\text{OAc})_2$ (1.1 mg, 0.005 mmol) and DPEphos (4.0 mg, 0.015 mmol) in the presence of Cs_2CO_3 (24 mg, 0.07 mmol). The reaction was conducted in toluene at 100 °C for 17 h. The title compound was isolated by flash chromatography (silica gel, THF:hexanes (v/v) = 1:8) as a red solid (29.9 mg, 93%). ^1H NMR (300 MHz, CDCl_3): δ 10.02 (s, 1H), 9.35 (d, J = 4.2 Hz, 2H), 9.24 (d, J = 3.9 Hz, 2H), 8.98 (d, J = 4.2 Hz, 2H), 8.8 (d, J = 3.9 Hz, 2H), 8.18 (m, 4H), 7.75 (m, 6H), 6.92 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 8.4 Hz, 2H), 3.60 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 160.8, 153.9, 150.2, 150.0, 149.5, 145.9, 142.6, 134.6, 132.7, 132.1, 132.0, 131.6, 127.9, 127.4, 126.5, 120.4, 117.1, 114.6, 105.2, 55.6. UV-vis (CHCl_3 , λ_{max} , nm): 398 (sh), 419, 548, 590. HRMS-EI ($[\text{M}]^+$): calcd for $\text{C}_{39}\text{H}_{26}\text{N}_4\text{O}_2\text{Zn}$, 646.1347; found: 646.1369.

[5-(4'-Fluorophenoxy)-10,20-diphenylporphinato]Zinc(II) (Table 1, entry 8). The general procedure was used to couple [5-bromo-10,20-diphenylporphinato]Zinc(II) (30 mg, 0.05 mmol) with 4-fluorophenol (20 mg, 0.18 mmol), using $\text{Pd}(\text{OAc})_2$ (1.1 mg, 0.005 mmol) and DPEphos (4.0 mg, 0.015 mmol) in the presence of Cs_2CO_3 (24 mg, 0.07 mmol). The reaction was conducted in toluene at 100°C for 17 h. The title compound was isolated by flash chromatography (silica gel, THF:hexanes (v/v) = 1:8) as a red solid (25.4 mg, 78%). ^1H NMR (300 MHz, CDCl_3): δ 10.10 (s, 1H), 9.35 (d, J = 4.5 Hz, 2H), 9.29 (d, J = 4.2 Hz, 2H), 9.02 (d, J = 4.8 Hz, 2H), 8.91 (d, J = 4.8 Hz, 2H), 8.19 (m, 4H), 7.76 (m, 6H), 6.93 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3): δ 150.4, 150.2, 149.70, 145.4, 134.5, 132.9, 132.2, 131.8, 127.7, 127.5, 126.6, 120.6, 117.4, 117.2, 116.1, 115.8, 105.6. UV-vis (CHCl_3 , λ_{max} , nm): 399 (sh), 418, 547, 589. HRMS-EI ($[\text{M}]^+$): calcd for $\text{C}_{38}\text{H}_{23}\text{N}_4\text{OFZn}$, 634.1147; found: 634.1150.

[5,15-Diphenoxo-10,20-diphenylporphyrinato]Zinc(II) (Table 1 entry 9). The general procedure was used to couple [5,15-di-bromoporphyrinato]Zinc(II) (34.2 mg, 0.05 mmol) with phenol (34.0 mg, 0.36 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and DPEphos (13.5 mg, 0.025 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in

toluene at 80 °C for 5 h. The title compound was isolated by flash chromatography as red solid (15.4 mg, 43.4%). ¹H NMR (CDCl₃, 300 MHz) δ 9.23 (d, *J* = 4.8 Hz, 4H), 8.74 (d, *J* = 4.8 Hz, 4H), 8.14 (m, 4H), 7.74 (m, 6H), 7.23 (m, 4H), 7.00 (m, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ 160.8, 153.9, 150.2, 150.0, 149.5, 145.9, 142.6, 135.2, 132.9, 130.5, 128.4, 127.5, 117.1. UV–vis (CHCl₃, λ_{max}, nm): 420, 427, 518, 556. HRMS-EI ([M]⁺): calcd for C₄₄H₂₈N₄O₂Zn, 708.1504, found 708.1482.

[5,15-Bis(4'-methoxyphenoxy)-10,20-diphenylporphinato]Zinc(II) (Table 1, entry 10). The general procedure was used to couple [5,15-dibromo-10,20-diphenylporphinato]Zinc(II) (34 mg, 0.05 mmol) with 4-methoxyphenol (22 mg, 0.018 mmol), using Pd₂(dba)₃ (1.5 mg, 0.0075 mmol) and DPEphos (9.6 mg, 0.036 mmol) in the presence of Cs₂CO₃ (47 mg, 0.14 mmol). The reaction was conducted in toluene at 100°C for 18 h. The title compound was isolated by flash chromatography (silica gel, THF:hexanes (v/v) = 1:8) as a purple solid (26 mg, 68%). ¹H NMR (300 MHz, THF-*d*₈): δ 9.28 (m, 4H), 8.77 (m, 4H), 8.17 (m, 4H), 7.73 (m, 6H), 8.8 (d, *J* = 4.5 Hz, 2H), 8.13 (m, 4H), 7.73 (m, 6H), 6.95 (d, *J* = 9.3 Hz, 4H), 6.77 (d, *J* = 9.6 Hz, 4H), 3.67 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 155.4, 150.4, 147.8, 144.0, 135.3, 132.7, 128.4, 128.2, 127.2, 117.8, 115.3, 55.7. UV-vis (CHCl₃, λ_{max}, nm): 427, 557, 599. HRMS-EI ([M]⁺): calcd for C₄₆H₃₂N₄O₄Zn, 768.1715; found: 768.1710.

[5,15-Bis(4'-methoxybenzyloxy)-10,20-diphenylporphyrinato]Zinc(II) (Table 1, entry 11). The general procedure was used to couple [5,15-dibromo-10,20-diphenylporphinato]Zinc(II) (34 mg, 0.05 mmol) with 4-methoxybenzyl alcohol (50 mg, 0.36 mmol), using Pd₂(dba)₃ (4.6 mg, 0.005 mmol) and Xantphos (14.5 mg, 0.025 mmol) in the presence of Cs₂CO₃ (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 80 °C for 4.5 h. The title compound was isolated by flash chromatography (17.3 mg, 43.4 %). ¹H NMR (300 MHz, CDCl₃): δ 9.36 (d, *J* = 4.5 Hz, 4H), 8.86 (d, *J* = 4.5 Hz, 4H), 8.15 (dd, *J* = 1.8, 7.8 Hz, 4H), 7.75 (m, 6H), 7.58 (d, *J* = 8.7 Hz, 4H), 6.98 (d, *J* = 8.7 Hz, 4H), 5.86 (s, 4H), 3.85 (s, 6H). ¹³C NMR (CDCl₃, 75 MHz): δ 164.6, 149.4, 146.9, 142.5, 134.4, 131.9, 130.1, 129.7, 127.5, 126.6, 114.1, 85.5, 55.4. UV–vis (CHCl₃, λ_{max}, nm): 421, 424, 556.

[5,15-Dihexyloxy)-10,20-diphenylporphyrinato]Zinc(II) (Table 1, entry 12). The general procedure was used to couple [5,15-dibromo-10,20-diphenylporphinato]Zinc(II) (34.2 mg, 0.05 mmol) with 1-hexanol (50.2 μL, 0.4 mmol), using Pd₂(dba)₃ (4.6 mg, 0.005 mmol) and DPEphos (13.5 mg, 0.025 mmol) in the presence of Cs₂CO₃ (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 °C for 25 h. The title compound was isolated by flash

chromatography (19.6 mg, 54 %). ^1H NMR (300 MHz, CDCl_3): δ 9.36 (d, J = 4.8 Hz, 4H), 8.87 (d, J = 4.8 Hz, 4H), 8.14 (m, 4H), 7.74 (m, 6H), 4.86 (t, J = 6.6 Hz, 4H), 2.26 (m, 4H), 1.82 (m, 4H), 1.50 (m, 8H), 0.97 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ 149.2, 146.9, 142.6, 138.5, 134.4, 131.8, 127.4, 127.2, 126.6, 120.6, 84.6, 31.9, 31.0, 26.1, 22.8, 14.2. UV-vis (CHCl_3 , λ_{max} , nm): 401 (sh), 422, 526, 555. HRMS-MALDI ($[\text{M}]^+$): calcd for $\text{C}_{44}\text{H}_{44}\text{N}_4\text{O}_2\text{Zn}$, 724.2750, found 724.2769.

[5,15-Bis(2'-cyclohexylethoxy)-10,20-diphenylporphyrinato]Zinc(II) (Table 1, entry 13). The general procedure was used to couple [5,15-dibromo-10,20-diphenylporphinato]Zinc(II) (34.2 mg, 0.05 mmol) with 2-cyclohexylethanol (56.0 μL , 0.4 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and Xantphos (14.5 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 $^\circ\text{C}$ for 23 h. The title compound was isolated by flash chromatography (19.6 mg, 50.4 %). ^1H NMR (300 MHz, CDCl_3): δ 9.32 (d, J = 4.8 Hz, 4H), 8.86 (d, J = 4.8 Hz, 4H), 8.14 (m, 4H), 7.74 (m, 6H), 4.86 (m, 4H), 2.14 (m, 4H), 1.97 (m, 6H), 1.76 (m, 6H), 1.08-1.42 (m, 10H). ^{13}C NMR (75 MHz, CDCl_3): δ 149.2, 146.9, 142.6, 138.0, 134.4, 131.8, 127.4, 127.1, 126.6, 120.6, 82.6, 38.4, 34.8, 33.6, 26.6, 26.4. UV-vis (CHCl_3 , λ_{max} , nm): 400 (sh), 421, 424 (sh), 518, 555. HRMS-EI ($[\text{M}]^+$): calcd for $\text{C}_{48}\text{H}_{48}\text{N}_4\text{O}_2\text{Zn}$, 776.3069, found 776.3079.

[5,15-Bis(cyclopentyloxy)-10,20-diphenylporphyrinato]Zinc(II) (Table 1, entry 14). The general procedure was used to couple [5,15-dibromo-10,20-diphenylporphinato]Zinc(II) (34.2 mg, 0.05 mmol) with cyclopentanol (36.3 μL , 0.4 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and DPEphos (13.5 mg, 0.025 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 $^\circ\text{C}$ for 44 h. The title compound was isolated by flash chromatography (17.2 mg, 50%). ^1H NMR (300 MHz, CDCl_3): δ 9.46 (d, J = 4.8 Hz, 4H), 8.87 (d, J = 4.8 Hz, 4H), 8.18 (m, 4H), 7.75 (m, 6H), 5.69 (m, 2H), 2.53 (m, 4H), 2.32 (m, 4H), 1.80-1.95 (m, 8H). ^{13}C NMR (75 MHz, CDCl_3): δ 149.0, 147.5, 143.3, 142.7, 136.7, 134.4, 131.6, 130.5, 128.9, 128.4, 127.8, 127.4, 126.6, 125.2, 120.6, 95.3, 33.0, 23.9. UV-vis (CHCl_3 , λ_{max} , nm): 401 (sh), 421, 423 (sh), 521, 555.

5,15-Diphenoxy-10,20-diphenylporphyrin (Table 2 entry 1). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with phenol (19.0 mg, 0.2 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and DPEphos (5.4 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 $^\circ\text{C}$ for 4 h. The title compound was isolated by flash chromatography as a purple crystalline solid (19.1

mg, 58.8%). ^1H NMR (300 MHz, CDCl_3): δ 9.28 (d, J = 4.8 Hz, 4H), 8.78 (d, J = 4.8 Hz, 4H), 8.16 (m, 4H), 7.73 (m, 6H), 7.25 (m, 6H), 7.02 (d, J = 8.1 Hz, 4H), -2.47 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 165.8, 141.1, 134.6, 131.4, 129.7, 127.9, 126.9, 121.7, 116.5. UV-vis (CHCl_3 , λ_{max} , nm): 420, 424 (sh), 517, 555. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{44}\text{H}_{31}\text{N}_4\text{O}_2$, 647.2442, found 647.2431.

5,15-Bis(*p*-tolylloxy)-10,20-diphenylporphyrin (Table 2, entry 2). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with *p*-cresol (21.6 mg, 0.2 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and Xantphos (5.8 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 °C for 24 h. The title compound was isolated by flash chromatography as a purple crystalline solid (23.4 mg, 69.4%). ^1H NMR (300 MHz, CDCl_3): δ 9.28 (d, J = 4.8 Hz, 4H), 8.77 (d, J = 4.8 Hz, 4H), 8.15 (m, 4H), 7.72 (m, 6H), 7.03 (d, J = 8.7 Hz, 4H), 6.90 (d, J = 9.3 Hz, 4H), 2.26 (s, 6H), -2.47 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 164.1, 134.6, 132.0, 131.3, 131.0, 130.1, 127.8, 126.9, 116.3, 20.5. UV-vis (CHCl_3 , λ_{max} , nm): 400 (sh), 420, 518, 555. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{46}\text{H}_{35}\text{N}_4\text{O}_2$, 675.2755, found 675.2773.

5,15-Bis(*m*-tolylloxy)-10,20-diphenylporphyrin (Table 2, entry 3). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with *m*-cresol (21 μL , 0.2 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and Xantphos (5.8 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 °C for 23 h. The title compound was isolated by flash chromatography as a purple crystalline solid (20.4 mg, 60.5%). ^1H NMR (300 MHz, CDCl_3): δ 9.31 (d, J = 4.8 Hz, 4H), 8.82 (d, J = 4.8 Hz, 4H), 8.19 (m, 4H), 7.75 (m, 6H), 7.15 (m, 2H), 6.86 (m, 6H), 2.15 (s, 6H), -2.45 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 165.9, 141.1, 139.9, 134.6, 131.8, 131.3, 129.4, 127.8, 126.9, 122.6, 120.3, 117.3, 113.7, 21.4. UV-vis (CHCl_3 , λ_{max} , nm): 402 (sh), 419, 518, 555. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{46}\text{H}_{35}\text{N}_4\text{O}_2$, 675.2755, found 675.2753.

5,15-Bis(*o*-tolylloxy)-10,20-diphenylporphyrin (Table 2, entry 4). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with *o*-cresol (41.2 μL , 0.4 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and DPEphos (5.4 mg, 0.01 mmol) in the presence of Cs_2CO_3 (130.3 mg, 0.4 mmol). The reaction was conducted in toluene at 100 °C for 48 h. The title compound was isolated by flash chromatography as a purple crystalline solid (14.8 mg, 43.9%). ^1H NMR (300 MHz, CDCl_3): δ 9.22 (d, J = 4.8 Hz, 4H), 8.78 (d, J = 4.8 Hz, 4H), 8.17 (m, 4H), 7.74 (m, 6H), 7.47 (d, J = 7.2 Hz, 2H), 6.91 (t, J = 7.2 Hz, 2H), 6.7 (t, J = 7.2

Hz, 2H), 6.04 (d, $J = 8.1$ Hz, 2H), 3.08 (s, 6H) -2.41 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 164.5, 141.1, 134.6, 132.1, 131.3, 131.1, 127.8, 127.6, 126.9, 125.6, 121.4, 120.2, 116.2, 16.9. UV-vis (CHCl_3 , λ_{max} , nm): 402 (sh), 419, 518, 555. HRMS-MALDI ($[\text{M}]^+$): calcd for $\text{C}_{46}\text{H}_{34}\text{N}_4\text{O}_2$, 674.2676, found 674.2658.

5,15-Bis(4'-*tert*-butyl-phenoxy)-10,20-diphenylporphyrin (Table 2, entry 5). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with 4-*tert*-butylphenol (60.0 mg, 0.4 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and DPEphos (5.4 mg, 0.01 mmol) in the presence of Cs_2CO_3 (130.3 mg, 0.4 mmol). The reaction was conducted in toluene at 100 °C for 48 h. The title compound was isolated by flash chromatography as a purple crystalline solid (17 mg, 44.8%). ^1H NMR (300 MHz, CDCl_3): δ 9.31 (d, $J = 4.8$ Hz, 4H), 8.78 (d, $J = 4.8$ Hz, 4H), 8.16 (m, 4H), 7.73 (m, 6H), 7.24 (d, $J = 8.7$ Hz, 4H), 6.95 (d, $J = 9.0$ Hz, 4H), 1.26 (s, 18H), -2.46 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 163.8, 144.3, 141.2, 134.6, 132.0, 131.3, 127.9, 127.8, 126.9, 126.4, 120.2, 115.8, 34.1, 31.5. UV-vis (CHCl_3 , λ_{max} , nm): 402 (sh), 420, 518, 554. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{52}\text{H}_{47}\text{N}_4\text{O}_2$, 759.3694, found 759.3713.

5,15-Bis(2'-isopropylphenoxy)-10,20-diphenylporphyrin (Table 2, entry 6). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with 2-isopropylphenol (54 μL , 0.4 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and DPEphos (5.4 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 °C for 25 h. The title compound was isolated by flash chromatography as a purple crystalline solid (18.3 mg, 50.1%). ^1H NMR (300 MHz, CDCl_3): δ 9.22 (d, $J = 4.8$ Hz, 4H), 8.79 (d, $J = 4.8$ Hz, 4H), 8.18 (m, 4H), 7.74 (m, 6H), 7.56 (d, $J = 7.5$ Hz, 2H), 7.00 (t, $J = 7.5$ Hz, 2H), 6.71 (t, $J = 7.5$ Hz, 2H), 6.04 (d, $J = 8.4$ Hz, 2H), 4.37 (m, 2H), 1.81 (d, $J = 6.9$ Hz, 6H) - 2.37 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 163.6, 141.1, 135.8, 134.6, 132.1, 131.4, 131.1, 127.8, 127.7, 126.9, 126.7, 126.6, 121.6, 120.2, 116.4, 27.9, 23.4. UV-vis (CHCl_3 , λ_{max} , nm): 402 (sh), 421, 518, 555. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{50}\text{H}_{43}\text{N}_4\text{O}_2$, 731.3381; found 731.3395.

5,15-Bis(3',5'-dimethylphenoxy)-10,20-diphenylporphyrin (Table 2, entry 7). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with 3,5-dimethylphenol (48.9 mg, 0.4 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and DPEphos (13.5 mg, 0.025 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 °C for 21 h. The title compound was isolated by flash

chromatography as a purple crystalline solid (20.2 mg, 57.5%). ^1H NMR (300 MHz, CDCl_3): δ 9.30 (d, $J = 4.8$ Hz, 4H), 8.79 (d, $J = 4.8$ Hz, 4H), 8.18 (m, 4H), 7.73 (m, 6H), 6.64 (s, 2H), 6.63 (s, 4H), 2.11 (s, 12H), -2.46 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 166.0, 141.1, 139.5, 134.6, 131.3, 127.8, 126.9, 123.5, 114.5, 21.3. UV-vis (CHCl_3 , λ_{max} , nm): 401 (sh), 418, 518, 555. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{48}\text{H}_{39}\text{N}_4\text{O}_2$, 703.3068, found 703.3048.

5,15-Bis(2',4'-dimethylphenoxy)-10,20-Diphenylporphyrin (Table 2, entry 8). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with 2,4-dimethylphenol (48.9 μL , 0.4 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and DPEphos (13.5 mg, 0.025 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 $^\circ\text{C}$ for 21 h. The title compound was isolated by flash chromatography as a purple crystalline solid (21.6 mg, 61.5%). ^1H NMR (300 MHz, CDCl_3): δ 9.23 (d, $J = 4.8$ Hz, 4H), 8.78 (d, $J = 4.8$ Hz, 4H), 8.17 (m, 4H), 7.74 (m, 6H), 7.28 (d, $J = 1.8$ Hz, 2H), 6.52 (t, $J = 8.1, 1.5$ Hz, 2H), 5.93 (d, $J = 8.7$ Hz, 2H), 3.05 (s, 6H), 2.25 (s, 6H), -2.39 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 162.9, 141.2, 134.6, 132.5, 131.7, 131.3, 130.6, 127.8, 127.6, 127.2, 126.9, 125.2, 120.2, 116.0, 20.4, 16.8. UV-vis (CHCl_3 , λ_{max} , nm): 403 (sh), 419, 426 (sh), 518, 556. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{48}\text{H}_{39}\text{N}_4\text{O}_2$, 703.3068, found 703.3072.

5,15-Bis(4'-methoxyphenoxy)-10,20-diphenylporphyrin (Table 2, entry 10). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with 4-methoxyphenol (24.8 mg, 0.2 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and Xantphos (5.8 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol) and molecular sieves (32 mg). The reaction was conducted in toluene at 80 $^\circ\text{C}$ for 16 h. The title compound was isolated by flash chromatography as a purple crystalline solid (27.6 mg, 78.1 %). ^1H NMR (300 MHz, CDCl_3): δ 9.28 (d, $J = 4.8$ Hz, 4H), 8.77 (d, $J = 4.8$ Hz, 4H), 8.15 (m, 4H), 7.73 (m, 6H), 6.99 (d, $J = 9.0$ Hz, 4H), 6.76 (d, $J = 9.3$ Hz, 4H), 3.70 (s, 6H), -2.47 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 141.1, 139.7, 134.6, 127.8, 126.9, 117.1, 114.7, 89.8. UV-vis (CHCl_3 , λ_{max} , nm): 402 (sh), 421, 519, 556. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{46}\text{H}_{35}\text{N}_4\text{O}_4$, 707.2653, found 707.2644.

5,15-Bis[(3'-dimethylamino)phenoxy]-10,20-diphenylporphyrin (Table 2, entry 11). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with 3-dimethylaminophenol (27.4 mg, 0.2 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and Xantphos (5.8 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 80 $^\circ\text{C}$ for 18 h. The title compound was isolated by flash

chromatography as a purple solid (16.2 mg, 44.2%). ^1H NMR (300 MHz, CDCl_3): δ 9.32 (d, $J = 4.8$ Hz, 4H), 8.77 (d, $J = 4.8$ Hz, 4H), 8.16 (m, 4H), 7.74 (m, 6H), 7.00 (t, $J = 8.1$ Hz, 2H), 6.86 (m, 6H), 6.72 (d, $J = 2.1$ Hz, 2H), 6.38 (dd, $J = 8.1, 2.4$ Hz, 2H), 6.07 (dd, $J = 8.1, 2.4$ Hz, 2H), 2.83 (s, 12H), -2.47 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 167.4, 141.5, 134.6, 131.4, 130.1, 128.1, 128.0, 127.7, 126.9, 106.0, 105.3, 101.1, 40.4. UV-vis (CHCl_3 , λ_{max} , nm): 421, 519, 555. HRMS-EI ($[\text{M}]^+$): calcd for $\text{C}_{48}\text{H}_{41}\text{N}_6\text{O}_2$, 732.3213; found 732.3206.

5,15-Bis(4'-fluorophenoxy)-10,20-diphenylporphyrin (Table 2, entry 12). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with 4-fluorophenol (22.4 mg, 0.2 mmol), using $\text{Pd}(\text{OAc})_2$ (1.1 mg, 0.005 mmol) and DPEphos (5.4 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 80 °C for 4 h. The title compound was isolated by flash chromatography as a purple crystalline solid (18.6 mg, 54.5%). ^1H NMR (300 MHz, CDCl_3): δ 9.26 (d, $J = 4.8$ Hz, 4H), 8.80 (d, $J = 4.8$ Hz, 4H), 8.16 (m, 4H), 7.74 (m, 6H), 6.95 (m, 8H), -2.50 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 161.9, 159.2, 156.0, 140.9, 134.5, 131.8, 131.5, 127.9, 127.7, 126.9, 120.5, 117.4, 117.3, 116.3, 115.9. UV-vis (CHCl_3 , λ_{max} , nm): 420, 424 (sh), 517, 555. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{44}\text{H}_{29}\text{F}_2\text{N}_4\text{O}_2$, 683.2253, found 683.2212.

5,15-Bis(3'-nitrophenoxy)-10,20-bis(3',4',5'-trimethoxyphenyl)porphyrin (Table 2, entry 13). The general procedure was used to couple 5,15-dibromo-10,20-bis(3',4',5'-trimethoxyphenyl)porphyrin (40.0 mg, 0.05 mmol) with 4-nitrophenol (55.6 mg, 0.4 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and DPEphos (13.5 mg, 0.025 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 °C for 40 h. The title compound was isolated by flash chromatography as a brown-purple solid (20.6 mg, 44.9%). ^1H NMR (300 MHz, CDCl_3): δ 9.23 (d, $J = 4.8$ Hz, 4H), 8.93 (d, $J = 4.8$ Hz, 4H), 7.92 (m, 2H), 7.74 (m, 2H), 7.48 (m, 4H), 7.42 (s, 4H), 4.15 (s, 6H), 3.96 (s, 12H), -2.51 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 165.5, 151.6, 149.5, 136.2, 132.0, 130.6, 130.4, 127.4, 122.4, 117.0, 112.7, 111.4, 61.3, 56.4. UV-vis (CHCl_3 , λ_{max} , nm): 401 (sh), 422, 516, 554. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{50}\text{H}_{41}\text{N}_6\text{O}_{12}$, 917.2777, found 917.2770.

5,15-Bis(4'-nitrophenoxy)-10,20-bis(3',4',5'-trimethoxyphenyl)porphyrin (Table 2, entry 14). The general procedure was used to couple 5,15-dibromo-10,20-bis(3',4',5'-trimethoxyphenyl)porphyrin (40.0 mg, 0.05 mmol) with 4-nitrophenol (55.6 mg, 0.4 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and DPEphos (13.5 mg, 0.025 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 °C for 24 h. The title

compound was isolated by flash chromatography as a brown-purple solid (25.5 mg, 55.6 %). ^1H NMR (300 MHz, CDCl_3): δ 9.23 (d, J = 4.8 Hz, 4H), 8.93 (d, J = 4.8 Hz, 4H), 7.92 (m, 2H), 7.74 (m, 2H), 7.48 (m, 4H), 7.42 (s, 4H), 4.15 (s, 6H), 3.96 (s, 12H), -2.50 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 165.5, 151.6, 149.5, 136.2, 132.0, 130.4, 127.4, 122.4, 117.0, 112.7, 111.4, 61.3, 56.4. UV-vis (CHCl_3 , λ_{max} , nm): 403 (sh), 423, 517, 555. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{50}\text{H}_{41}\text{N}_6\text{O}_{12}$, 917.2777, found 917.2784.

5,15-Dibenzyloxy-10,20-diphenylporphyrin (Table 3, entry 1). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with benzyl alcohol (20.8 μL , 0.2 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and Xantphos (5.8 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 80 $^\circ\text{C}$ for 18 h. The title compound was isolated by flash chromatography as a purple solid (13.6 mg, 40.3%). ^1H NMR (300 MHz, CDCl_3): δ 9.43 (d, J = 4.8 Hz, 4H), 8.83 (d, J = 4.8 Hz, 4H), 8.20 (m, 4H), 7.76 (m, 10H), 7.51 (m, 6H), 6.06 (s, 4H), -2.63 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 141.5, 137.4, 137.2, 134.6, 131.0, 128.9, 128.6, 128.3, 127.7, 127.1, 119.8, 86.1. UV-vis (CHCl_3 , λ_{max} , nm): 402 (sh), 417, 518, 555. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{46}\text{H}_{35}\text{N}_4\text{O}_2$, 675.2755, found 675.2765.

5,15-Bis(4'-fluorobenzyloxy)-10,20-diphenylporphyrin (Table 3, entry 2). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with 4-fluorobenzyl alcohol (21.5 μL , 0.2 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and Xantphos (5.8 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 80 $^\circ\text{C}$ for 19.5 h. The title compound was isolated by flash chromatography as a purple solid (17.0 mg, 47.8%). ^1H NMR (300 MHz, CDCl_3): δ 9.41 (d, J = 4.8 Hz, 4H), 8.86 (d, J = 4.8 Hz, 4H), 8.24 (m, 4H), 7.82 (m, 4H), 7.74 (m, 6H), 7.24 (s, 4H), 6.04 (s, 4H), -2.61 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 141.4, 136.9, 134.6, 130.9, 130.4, 130.3, 127.8, 126.9, 119.9, 115.9, 115.6, 85.1. UV-vis (CHCl_3 , λ_{max} , nm): 400 (sh), 417, 518, 558. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{46}\text{H}_{33}\text{F}_2\text{N}_4\text{O}_2$, 711.2566, found 711.2593.

5,15-Bis(4'-methoxybenzyloxy)-10,20-diphenylporphyrin (Table 3, entry 3). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with 4-methoxybenzyl alcohol (50 mg, 0.36 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and Xantphos (14.5 mg, 0.025 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 80 $^\circ\text{C}$ for 4.5 h. The title compound was isolated by flash chromatography as a purple crystalline solid (15.0 mg, 40.8%). ^1H NMR (300 MHz, CDCl_3): δ

9.41 (d, $J = 4.8$ Hz, 4H), 8.82 (d, $J = 4.8$ Hz, 4H), 8.20 (m, 4H), 7.76 (m, 6H), 7.64 (d, $J = 8.7$ Hz, 4H, 4H), 7.00 (d, $J = 8.1$ Hz, 4H), 5.98 (s, 4H), 3.87 (s, 6H), -2.64 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 159.9, 141.5, 134.6, 130.8, 130.3, 129.6, 127.8, 127.7, 127.2, 126.9, 119.8, 114.2, 100.1, 85.8, 55.4. UV-vis (CHCl_3 , λ_{max} , nm): 401 (sh), 418, 518, 555. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{48}\text{H}_{39}\text{N}_4\text{O}_4$, 735.2966, found 735.2966.

5,15-Bis(3'-pyridylcarbinoxy)-10,20-diphenylporphyrine (Table 3, entry 4). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with 3-pyridyl carbinol (19.4 μL , 0.2 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and Xantphos (5.8 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 80 °C for 17 h. The title compound was isolated by flash chromatography as a purple solid (20.9 mg, 61.8%). ^1H NMR (300 MHz, CDCl_3): δ 9.39 (d, $J = 4.8$ Hz, 4H), 8.84 (d, $J = 4.8$ Hz, 4H), 8.73 (dd, $J = 4.8, 1.8$ Hz, 2H), 8.19 (m, 4H), 8.07 (m, 4H), 7.76 (m, 6H), 7.42 (dd, $J = 7.5, 2.4$ Hz, 2H), 6.06 (s, 4H), -2.66 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 150.0, 149.7, 141.3, 136.7, 136.0, 134.6, 132.8, 131.2, 127.9, 126.9, 123.7, 120.2, 83.1. UV-vis (CHCl_3 , λ_{max} , nm): 401 (sh), 417, 518, 554. HRMS-EI ($[\text{M}]^+$): calcd for $\text{C}_{44}\text{H}_{32}\text{N}_6\text{O}_2$, 676.2587; found 676.2311.

5,15-Dihexyloxy-10,20-diphenylporphyrin (Table 3, entry 5). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with 1-hexanol (25.1 μL , 0.2 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and Xantphos (5.8 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 80 °C for 17 h. The title compound was isolated by flash chromatography as a purple solid (17.0 mg, 51.3%). ^1H NMR (300 MHz, CDCl_3): δ 9.48 (d, $J = 4.8$ Hz, 4H), 8.87 (d, $J = 4.8$ Hz, 4H), 8.22 (m, 4H), 7.77 (m, 6H), 5.01 (t, $J = 6.6$ Hz, 4H), 2.38 (m, 4H), 1.91 (m, 4H), 1.54 (m, 8H), 1.02 (m, 4H), -2.59 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 141.6, 137.7, 134.6, 130.7, 127.7, 126.9, 119.6, 84.9, 31.9, 31.1, 26.2, 22.8, 14.2. UV-vis (CHCl_3 , λ_{max} , nm): 400 (sh), 416, 518, 555. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{44}\text{H}_{47}\text{N}_4\text{O}_2$, 663.3694, found 663.3727.

5,15-Dibutoxy-10,20-diphenylporphyrin (Table 3, entry 6). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with *n*-butanol (36.6 μL , 0.2 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and Xantphos (14.5 mg, 0.025 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 °C for 38.5 h. The title compound was isolated by flash chromatography as a purple solid (20.0 mg, 65.9%). ^1H NMR (300 MHz, CDCl_3): δ 9.45 (d, $J = 4.8$ Hz, 4H), 8.84 (d, $J = 4.8$ Hz,

4H), 8.20 (m, 4H), 7.76 (m, 6H), 4.99 (t, $J = 6.6$ Hz 4H), 2.35 (m, 4H), 1.92 (m, 4H), 1.18 (m, 4H), -2.63 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 141.6, 137.7, 134.6, 130.7, 127.7, 126.8, 119.6, 84.6, 33.1, 19.7, 14.2. UV-vis (CHCl_3 , λ_{max} , nm): 400 (sh), 416, 518, 555. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{40}\text{H}_{39}\text{N}_4\text{O}_2$, 607.3068, found 607.3063.

5,15-Diethoxy-10,20-diphenylporphyrin (Table 3, entry 7). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with anhydrous ethanol (23.5 μL , 0.2 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and DPEphos (13.5 mg, 0.025 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 $^\circ\text{C}$ for 47 h. The title compound was isolated by flash chromatography as a purple solid (13.6 mg, 49.4%). ^1H NMR (300 MHz, CDCl_3): δ 9.47 (d, $J = 4.8$ Hz, 4H), 8.85 (d, $J = 4.8$ Hz, 4H), 8.20 (m, 4H), 7.77 (m, 6H), 5.08 (m, 4H), 1.92 (m, 4H), -2.63 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 141.6, 137.4, 134.6, 130.7, 127.7, 127.0, 126.9, 119.6, 79.9, 16.5. UV-vis (CHCl_3 , λ_{max} , nm): 400 (sh), 416, 486, 518, 555. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{36}\text{H}_{31}\text{N}_4\text{O}_2$, 551.2442, found 551.2419.

5,15-Bis(1'-methylbutoxy)-10,20-diphenylporphyrin (Table 3, entry 8). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with dl-2-pentanol (43.4 μL , 0.2 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and Xantphos (14.5 mg, 0.025 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 $^\circ\text{C}$ for 38.5 h. The title compound was isolated by flash chromatography as a purple solid (9.6 mg, 30.2%). ^1H NMR (300 MHz, CDCl_3): δ 9.43 (d, $J = 4.8$ Hz, 4H), 8.80 (d, $J = 4.8$ Hz, 4H), 8.21 (m, 4H), 7.77 (m, 6H), 5.24 (dd, $J = 12.3, 6.3$ Hz, 2H), 2.27 (m, 2H), 2.11 (m, 2H), 1.76 (m, 4H), 1.47 (m, 6H), 1.05 (m, 6H), -2.53 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 141.8, 135.9, 134.6, 130.4, 127.6, 127.4, 126.8, 119.5, 88.7, 39.7, 20.5, 19.3, 14.4. UV-vis (CHCl_3 , λ_{max} , nm): 401 (sh), 418, 521, 558. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{40}\text{H}_{39}\text{N}_4\text{O}_2$, 607.3068, found 607.3063.

5,15-Bis(α,α,α -trifluoroethoxy)-10,20-diphenylporphyrin (Table 3, entry 9). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with α,α,α -trifluoroethanol (29.2 μL , 0.4 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and DPEphos (13.5 mg, 0.025 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 $^\circ\text{C}$ for 47 h. The title compound was isolated by flash chromatography as a purple solid (10.7 mg, 32.5%). ^1H NMR (300 MHz, CDCl_3): δ 9.48 (d, $J = 4.8$ Hz, 4H), 8.91 (d, $J = 4.8$ Hz, 4H), 8.20 (m, 4H), 7.78 (m, 6H), 5.34 (m, 2H), -2.78 (s, 2H).

^{13}C NMR (75 MHz, CDCl_3): δ 146.7, 141.0, 134.6, 131.9, 131.7, 128.0, 127.0, 126.6, 120.7, 120.2, 78.6, 78.2. UV-vis (CHCl_3 , λ_{max} , nm): 401 (sh), 414, 514, 550. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{36}\text{H}_{25}\text{F}_6\text{N}_4\text{O}_2$, 659.1876, found 659.1849.

5,15-Bis(2'-cyclohexylethoxy)-10,20-diphenylporphyrin (Table 3, entry 10). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with 2-cyclohexylethanol (28.0 μL , 0.2 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and Xantphos (5.8 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 80 $^\circ\text{C}$ for 17 h. The title compound was isolated by flash chromatography as a purple solid (22.5 mg, 62.9%). ^1H NMR (300 MHz, CDCl_3): δ 9.44 (d, $J = 4.8$ Hz, 4H), 8.85 (d, $J = 4.8$ Hz, 4H), 8.21 (m, 4H), 7.76 (m, 6H), 5.03 (t, $J = 6.5$ Hz, 4H), 2.27 (m, 4H), 2.01 (m, 6H), 1.80 (m, 6H), 1.13-1.51 (m, 10H), -2.63 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 141.6, 137.7, 134.6, 130.7, 127.7, 126.8, 119.6, 82.9, 38.5, 34.8, 33.6, 26.6, 26.4. UV-vis (CHCl_3 , λ_{max} , nm): 400 (sh), 416, 518, 555. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{48}\text{H}_{51}\text{N}_4\text{O}_2$, 715.4007, found 715.3977.

5,15-Dicyclopentyloxy-10,20-diphenylporphyrin (Table 3, entry 11). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31.0 mg, 0.05 mmol) with cyclopentanol (36.3 μL , 0.4 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and DPEphos (13.5 mg, 0.025 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 $^\circ\text{C}$ for 41 h. The title compound was isolated by flash chromatography as a purple solid (19.6 mg, 62.1 %). ^1H NMR (300 MHz, CDCl_3): δ 9.42 (d, $J = 4.8$ Hz, 4H), 8.81 (d, $J = 4.8$ Hz, 4H), 8.20 (m, 4H), 7.77 (m, 6H), 5.66 (m, 2H), 2.54 (m, 4H), 2.35 (m, 4H), 1.81 (m, 8H), -2.52 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 141.7, 136.7, 134.6, 130.5, 127.7, 127.4, 126.8, 119.6, 95.6, 32.9, 23.9. UV-vis (CHCl_3 , λ_{max} , nm): 400 (sh), 418, 521, 558. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{42}\text{H}_{39}\text{N}_4\text{O}_2$, 631.3068, found 631.3059.

5,15-Dihexyloxy-10,20-bis(3',4',5'-trimethoxyphenyl)porphyrin (Table 3, entry 12). The general procedure was used to couple 5,15-dibromo-10,20-bis(3',4',5'-trimethoxyphenyl)porphyrin (40 mg, 0.05 mmol) with 1-hexanol (50.2 μL , 0.4 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and DPEphos (13.5 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 $^\circ\text{C}$ for 40 h. The title compound was isolated by flash chromatography as a purple solid (34.3 mg, 81.4%). ^1H NMR (300 MHz, CDCl_3): δ 9.46 (d, $J = 4.8$ Hz, 4H), 8.94 (d, $J = 4.8$ Hz, 4H), 7.45 (s, 4H), 5.00 (t, $J = 6.6$ Hz, 4H), 4.18 (s, 6H), 3.99 (s, 12H), 2.38 (m, 4H), 1.91 (m, 4H), 1.51 (m, 8H), 1.00 (m, 4H),

-2.65 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 151.5, 137.8, 137.7, 137.1, 130.7, 127.0, 119.4, 112.7, 84.9, 61.3, 56.4, 31.9, 31.1, 26.2, 22.8, 14.2. UV-vis (CHCl_3 , λ_{max} , nm): 402 (sh), 419, 519, 556. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{50}\text{H}_{59}\text{N}_4\text{O}_8$, 843.4327, found 843.4300.

5,15-Bis(*n*-butoxy)-10,20-bis(3',4',5'-trimethoxy-phenyl)porphyrin (Table 3, entry 13). The general procedure was used to couple 5,15-dibromo-10,20-bis(3',4',5'-trimethoxyphenyl)porphyrin (40 mg, 0.05 mmol) with *n*-butanol (36.6 μL , 0.2 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and Xantphos (14.5 mg, 0.025 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 $^\circ\text{C}$ for 38.5 h. The title compound was isolated by flash chromatography as a purple solid (31.6 mg, 80.3%). ^1H NMR (300 MHz, CDCl_3): δ 9.46 (d, J = 4.8 Hz, 4H), 8.93 (d, J = 4.8 Hz, 4H), 7.45 (s, 4H), 5.01 (t, J = 6.7 Hz, 4H), 4.18 (s, 6H), 3.99 (s, 12H), 2.35 (m, 4H), 1.96 (m, 4H), 1.20 (m, 4H), -2.65 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 151.5, 137.8, 137.1, 130.7, 127.0, 119.6, 112.7, 84.7, 61.3, 56.4, 33.1, 19.7, 14.2. UV-vis (CHCl_3 , λ_{max} , nm): 401 (sh), 419, 519, 556. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{46}\text{H}_{51}\text{N}_4\text{O}_8$, 787.3701, found 787.3678.

5,15-Bis(α,α,α -trifluoroethoxy)-10,20-bis(3',4',5'-trimethoxyphenyl)porphyrin (Table 3, entry 14). The general procedure was used to couple 5,15-dibromo-10,20-bis(3',4',5'-trimethoxyphenyl)porphyrin (40 mg, 0.05 mmol) with α,α,α -trifluoroethanol (29.2 μL , 0.4 mmol), using $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and DPEphos (13.5 mg, 0.025 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene at 100 $^\circ\text{C}$ for 24 h. The title compound was isolated by flash chromatography as a purple solid (22.6 mg, 53.9%). ^1H NMR (300 MHz, CDCl_3): δ 9.48 (d, J = 4.8 Hz, 4H), 8.90 (d, J = 4.8 Hz, 4H), 7.43 (s, 4H), 5.34 (m, 2H), 4.18 (s, 6H), 3.99 (s, 12H), -2.79 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 151.7, 138.8, 136.5, 135.5, 131.7, 126.7, 120.5, 112.8, 61.3, 56.4. UV-vis (CHCl_3 , λ_{max} , nm): 400 (sh), 418, 515, 552. HRMS-MALDI ($[\text{M}+\text{H}]^+$): calcd for $\text{C}_{42}\text{H}_{37}\text{F}_6\text{N}_4\text{O}_8$, 839.2510, found 839.2540.

Reference

1. (a) Lindsey, J. S.; Schreiman, I.C.; Hsu, H.C. Kearney, P.C. and Marguerettaz, A.M. *J. Org. Chem.* **1987**, *52*, 827. (b) DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. J. *J. Org. Chem.* **1993**, *58*, 5983. (c) Shi, X.; Amin, R.; Liebeskind, L. S. *J. Org. Chem.* **2000**, *65*, 1650. (d) Shanmugathasan, S.; Johnson, C. K.; Edwards, C.; Matthews, E. K.; Dolphin, D.; Boyle, R. *W. J. Porphyrins Phthalocyanines* **2000**, *4*, 228.