JOC Article

Facile and Efficient Synthesis of *meso*-Arylamino- and Alkylamino-Substituted Porphyrins via Palladium-Catalyzed Amination

Ying Chen and X. Peter Zhang*

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600

pzhang@utk.edu

Received January 20, 2003

meso-Arylamino- and alkylamino-substituted porphyrins were efficiently synthesized by reactions of *meso*-halogenated porphyrins with amines via palladium-catalyzed amination. The combination of palladium acetate and the commercially available phosphine ligand bis(2-diphenylphosphinophenyl) ether (DPEphos) is effective for catalyzing the couplings of both [5-bromo-10,20-diphenyl porphyrino]zinc(II) and [5,15-dibromo-10,20-diphenylporphyrino]zinc(II) with amines to give the corresponding monoamino- and diamino-substituted porphyrins in high yields under mild conditions. The corresponding halogenated free-base porphyrins also underwent the cross-coupling reactions efficiently under similar catalytic conditions.

Introduction

Porphyrins and related tetrapyrrolic macrocycles play a number of essential roles in biological system such as energy migration, electron transfer, light harvesting, dioxygen transport, and substrate transformation.[1] The significance of these processes has stimulated intense efforts in the synthesis of new porphyrins and their metal complexes, with the aim of developing model systems for carrying out similar functions. As a result, synthetic porphyrins and metalloporphyrins have found many important applications in various fields, including homogeneous catalysis, controlled polymer synthesis, novel functional materials, and cancer photodynamic therapy.[2] Porphyrins are generally prepared by tetramerization of monopyrroles or condensation of dipyrrolic intermediates.[3] The standard syntheses of porphyrins often require tedious purification and typically give low yields, restraining efficient preparation of porphyrin derivatives with a variety of different substituents. Recently, new synthetic strategies have been actively pursued. Most notable are the applications of transition metal-mediated carbon−carbon bond formation reactions[4] including the Suzuki[5] and Stille[6] cross-couplings, allowing efficient synthesis of a large number of derivatives from a single β- or *meso*-halogenated porphyrin precursor.

The palladium-catalyzed amination of aryl halides and triflates has been emerging as a powerful tool for the formation of carbon−nitrogen bonds.[7] The versatility of this method has been demonstrated in many applications, including synthesis of natural products, biologically and pharmaceutically important compounds, new ligands, and interesting materials.[7] In light of the results from halogenated porphyrins in transition metal-mediated carbon−carbon bond formation reactions,[4−6] we became

* Corresponding author.

(1) Lippard, S. J.; Berg, J. M. *Principles of Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994.

(2) *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000.

(3) (a) Smith, K. M. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 1, pp 1−43. (b) Lindsey, J. S. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 1, pp 45−118.

(4) For a review, see: Sharman, W. M.; van Lier, J. E. *J. Porphyrins Phthalocyanines* **2000**, *4*, 441.

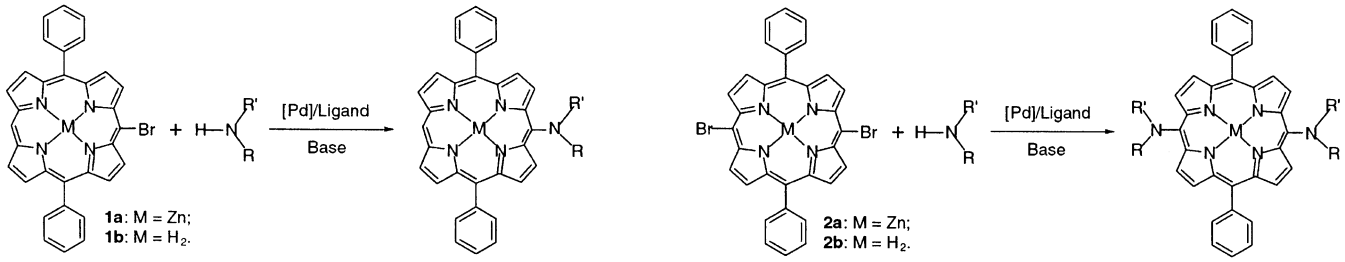
(5) (a) Chan, K. S.; Zhou, X.; Au, M. T.; Tam, C. Y. *Tetrahedron* **1995**, *51*, 3129. (b) Zhou, X.; Tse, M. K.; Wan, T. S. M.; Chan, K. S. *J. Org. Chem.* **1996**, *61*, 3590. (c) Hayashi, T.; Miyahara, T.; Koide, N.; Kato, Y.; Masuda, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1997**, *119*, 7281. (d) Liu, C.-J.; Yu, W.-Y.; Peng, S.-M.; Mak, T. C. W.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1998**, 1805. (e) Hyslop, A. G.; Kellett, M. A.; Iovine, P. M.; Therien, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 12676. (f) Zhou, X.; Chan, K. S. *J. Org. Chem.* **1998**, *63*, 99. (g) Shultz, D. A.; Gwaltney, K. P.; Lee, H. *J. Org. Chem.* **1998**, *63*, 769. (h) Muzzi, C. M.; Medforth, C. J.; Voss, L.; Cancilla, M.; Lebrilla, C.; Ma, J.-G.; Shelnutt, J. A.; Smith, K. M. *Tetrahedron Lett.* **1999**, *40*, 6159. (i) Weyermann, P.; Diederich, F. *J. Chem. Soc., Perkin Trans. 1* **2000**, 4231. (j) Tse, M. K.; Zhou, Z.-Y.; Mak, T. C. W.; Chan, K. S. *Tetrahedron* **2000**, *56*, 7779. (k) Deng, Y.; Chang, C. K.; Nocera, D. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1066. (l) Muzzi, C. M.; Medforth, C. J.; Smith, K. M.; Jia, S.-L.; Shelnutt, J. A. *Chem. Commun.* **2000**, 13. (m) Iovine, P. M.; Kellett, M. A.; Redmore, N. P.; Therien, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 8717. (n) Vaz, B.; Alvarez, R.; Nieto, M.; Paniello, A. I.; de Lera, A. R. *Tetrahedron Lett.* **2001**, *42*, 7409. (o) Mizutani, T.; Wada, K.; Kitagawa, S. *J. Am. Chem. Soc.* **2001**, *123*, 6459. (p) Yu, L.; Lindesy, J. S. *Tetrahedron* **2001**, *57*, 9285. (q) Kimura, M.; Shiba, T.; Yamazaki, M.; Hanabusa, K.; Shirai, H.; Kobayashi, N. *J. Am. Chem. Soc.* **2001**, *123*, 5636. (r) Shi, D.-F.; Wheelhouse, R. T. *Tetrahedron Lett.* **2002**, *43*, 9341. (s) Weyermann, P.; Diederich, F.; Gisselbrecht, J.-P.; Boudon, C.; Gross, M. *Helv. Chim. Acta* **2002**, *85*, 571. (t) Shi, B.; Boyle, R. W. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1397.

(6) (a) Minnetian, O. M.; Morris, I. K.; Snow, K. M.; Smith, K. M. *J. Org. Chem.* **1989**, *54*, 5567. (b) DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 2513. (c) DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. J. *J. Org. Chem.* **1993**, *58*, 5983. (d) de Rege, P. J. F.; Therien, M. J. *Inorg. Chim. Acta* **1996**, *242*, 211. (e) Wilson, G. S.; Anderson, H. L. *Chem. Commun.* **1999**, 1539. (f) Shi, X.; Amin, R.; Liebeskind, L. S. *J. Org. Chem.* **2000**, *65*, 1650. (g) Shanmugathasan, S.; Johnson, C. K.; Edwards, C.; Matthews, E. K.; Dolphin, D.; Boyle, R. W. *J. Porphyrins Phthalocyanines* **2000**, *4*, 228. (h) Odobel, F.; Suzenet, F.; Nlart, E.; Quintard, J.-P. *Org. Lett.* **2000**, *2*, 131.

(7) (a) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. (b) Yang, B. Y.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125. (c) Hartwig, J. F. *Synlett* **1997**, 329. (d) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046.

10.1021/jo034063m CCC: $25.00
Published on Web 05/02/2003

SCHEME 1. Palladium-Catalyzed Amination Reactions of *meso*-Monobromo- and *meso*-Dibromoporphyrins



interested in exploring the application of palladium-catalyzed amination in porphyrin synthesis. This would give access to substituted porphyrins with directly appended arylamino or alkylamino groups. During the course of our recent studies, a communication was published on this type of application for the synthesis of β-substituted aminoporphyrins.[8] Applying the palladium-catalyzed amination reaction to *meso*-halogenated porphyrin precursors, we report herein an efficient approach for the synthesis of a family of new porphyrins that contain *meso*-arylamino or alkylamino substituents.[9] The syntheses can be carried out under mild conditions, typically give high yields, and are suitable to a variety of amines.

Results and Discussion

Both *meso*- and β-halogenated porphyrins can be easily accessed via selective halogenation of porphyrins.[5,6] We focused our efforts on the amination of *meso*-halogenated porphyrins, which is expected to be more challenging than the case of β-halogenated porphyrins,[6b] as *meso*-substitution allows better electronic and steric tuning of the physicochemical properties of porphyrins and metalloporphyrins. The *meso*-brominated 10,20-diphenylporphyrins (**1b** and **2b**) and their respective zinc complexes (**1a** and **2a**)[6c,f,g] were adopted as representative halogenated porphyrin precursors for the establishment of the catalytic conditions (Scheme 1). We first evaluated the catalytic activities of a number of commercially available phosphine ligands (Figure 1) in combination with Pd(OAc)$_2$ or Pd$_2$(dba)$_3$ in the presence of either Cs_2CO_3 or NaO*t*-Bu for the amination reaction of **1a** with aniline in THF or toluene at various temperatures. Both the chelating ligands, DPEphos and BINAP, and the biphenyl-based electron-rich bulky monophosphine ligands, L1, L2, and L3, can catalyze the reaction. But DPEphos was selected as the ligand of choice for further investigation because of its high catalytic activity and low cost. There was no obvious difference in reactivity between the uses of Pd(OAc)$_2$ and Pd$_2$(dba)$_3$. Although both THF and toluene can be used as a reaction medium, THF gave a more homogeneous system due to better solubility of porphyrins. The weak base Cs_2CO_3 is preferred for the reaction as side products were observed in certain reactions with the use of the strong base NaO*t*-Bu.[10] An elevated temperature is normally required for high-yield synthesis because of slower reaction rates at room temperature. On the basis of these initial evaluations, subsequent reactions (Scheme 1) were typically carried out in THF at 68 °C under a nitrogen atmosphere with excess amine with use of 5 mol % of Pd(OAc)$_2$ in combination

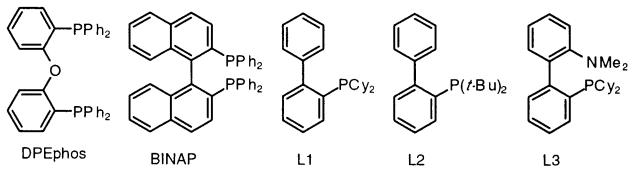


FIGURE 1. Structures of chelating ligands and biphenyl-based electron-rich bulky monophosphine ligands.

TABLE 1. Palladium-Catalyzed Amination of *meso*-Bromoporphyrins with Amines[a]

entry	reactant[b]	amine	time (h)[c]	product[d]	yield (%)[e]
1	**1a**	$PhNH_2$	13	**3a**	95
2	**1b**	$PhNH_2$	19	**3b**	98
3	**1a**	Ph(Me)NH	13	**4a**	99
4	**1b**	Ph(Me)NH	16	**4b**	94
5	**1a**	$Ph_2C{=}NH$	22	**5a**	94
6	**1b**	$Ph_2C{=}NH$	24	**5b**	84
7	**1a**	Ph_2NH	25	**6a**	61[f]
8	**1b**	Ph_2NH	40	**6b**	66
9	**1a**	*n*-$HexNH_2$	50	**7a**	80
10	**2a**	$PhNH_2$	13	**8a**	82
11	**2b**	$PhNH_2$	20	**8b**	65
12	**2a**	Ph(Me)NH	17	**9a**	82
13	**2b**	Ph(Me)NH	15	**9b**	71
14	**2a**	$Ph_2C{=}NH$	16	**10a**	84
15	**2b**	$Ph_2C{=}NH$	15	**10b**	95
16	**2a**	Ph_2NH	50	**11a**	30
17	**2a**	(4-CF_3Ph)NH_2	17	**12a**	90
18	**2a**	(4-CH_3 OPh)NH_2	16	**13a**	94
19	**2a**	(3,5-di-*t*-BuPh)NH_2	62	**14a**	95

[a] Reactions were carried out at 68 °C in THF under N_2 with 1.0 equiv of bromoporphyrin, 3.6 equiv of amine for **1b** and **2b** or 4.8 equiv of amine for **1a** and **2a**, 5 mol % of Pd(OAc)$_2$, and 7.5 mol % of DPEphos in the presence of 1.4 equiv of Cs_2CO_3 per Br. Concentration: 0.05 mmol of bromoporphyrin/5 mL of THF. [b] Structures of bromoporphyrins are shown in Scheme 1. [c] Reaction times have not been optimized. [d] Structures of aminoporphyrins are given in Figure 2. [e] Yields represent isolated yields of >95% purity as determined by ^{1}H NMR. [f] The reaction was conducted with 10 mol % of Pd(OAc)$_2$ and 15 mol % of DPEphos in the presence of 2.8 equiv of NaO*t*-Bu.

(8) Khan, M. M.; Ali, H.; van Lier, J. E. *Tetrahedron Lett.* **2001**, *42*, 1615. Note that no yields were reported in this paper.

(9) For other synthetic methods of *meso*-arylamino- and alkylamino-substituted porphyrins, see: (a) Screen, T. E. O.; Blake, I. M.; Rees, L. H.; Clegg, W.; Borwick, S. J.; Anderson, H. L. *J. Chem. Soc., Perkin Trans. 1* **2002**, 320. (b) Jayaraj, K.; Gold, A.; Ball, L. M.; White, P. S. *Inorg. Chem.* **2000**, *39*, 3652. (c) Crossley, M. J.; Hambley, T. W.; Mackay, L. G.; Try, A. C.; Walton, R. *Chem. Commun.* **1995**, 1077. (d) Smith, K. M.; Minnetian, O. M. *J. Org. Chem.* **1985**, *50*, 2073. (e) Smith, K. M.; Barnett, G. H.; Evans, B.; Martynenko, Z. *J. Am. Chem. Soc.* **1979**, *101*, 5953. (f) Connor, W. M.; Straub, D. S. *Inorg. Chem.* **1976**, *15*, 2289. (g) Ichimura, K. *Chem. Lett.* **1976**, 6411. (h) Grigg, R. *Chem. Commun.* **1967**, 1238. (i) Johnson, A. W.; Oldfield, D. *Tetrahedron Lett.* **1964**, *5*, 1615.

(10) The weak base K_2CO_3 was ineffective for the reaction. Only a very small amount of product was observed and most of the starting material remained unchanged by the end of the reaction.

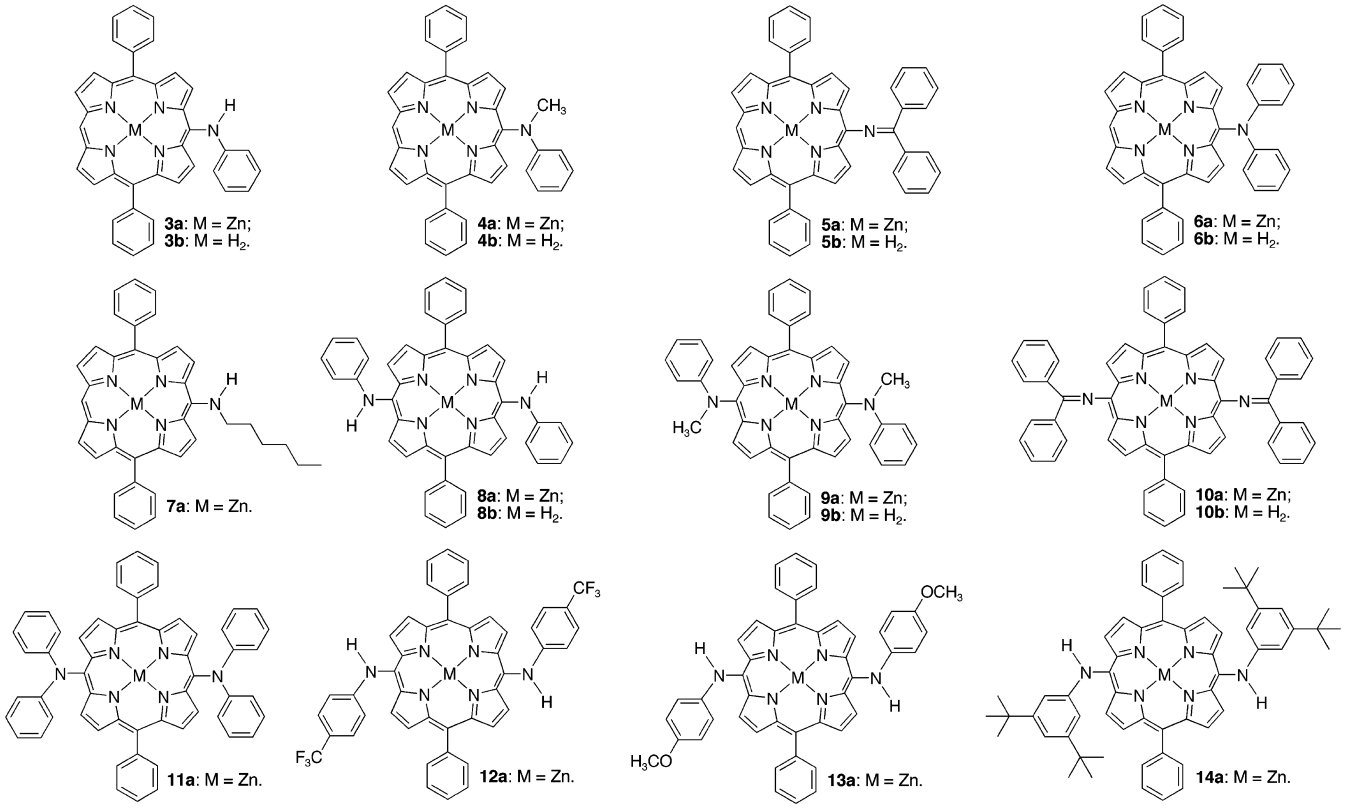


FIGURE 2. Structures of *meso*-arylamino- and alkylamino-substituted porphyrins.

with DPEphos (L/Pd = 1.5) in the presence of 1.4 equiv of Cs_2CO_3 per halide. When this procedure was used, most of the reactions proceed to completion within 24 h.

A variety of different amines can be efficiently coupled with the *meso*-brominated 10,20-dipenylporphyrins **1b** and **2b** as well as their respective zinc complexes **1a** and **2a**. The results are summarized in Table 1 with the structures of the resulting *meso*-arylamino- and alkylamino-sustituted porphyrins shown in Figure 2. For example, both the primary aniline (Table 1, entry 1) and the secondary *N*-methylaniline (Table 1, entry 3) were effectively coupled with **1a** to give monoamino-substituted porphyrins **3a** (yield 95%) and **4a** (yield 99%), respectively. When **2a** was used, the corresponding diamino-substituted porphyrins **8a** (Table 1, entry 10; yield 82%) and **9a** (Table 1, entry 12; yield 82%) were synthesized via double amination reactions. The substituted aniline derivatives such as 4-trifluoromethylaniline (Table 1, entry 17), *p*-anisidine (Table 1, entry 18), and 3,5-di-*tert*-butylaniline (Table 1, entry 19) gave similarly excellent yields (90%, 94% and 95%, respectively) of double amination products when reacted with **2a**. Primary aliphatic amines can also be well coupled as demonstrated in the case of *n*-hexylamine with **1a** (Table 1, entry 9). But the uses of secondary aliphatic and cycloaliphatic amines such as dibutylamine, piperidine, and morpholine resulted in no reactions or a mixture of products in addition to the starting material. For aromatic amines, even the sterically hindered diphenylamine was able to couple with **1a** and **2a** to afford the corresponding monoamino- and diamino-substituted porphyrins **6a** and **11a** although the yields were much lower. In addition to primary and secondary amines, imines are also suitable coupling partners under similar reaction conditions. When benzophenone imine was employed, monoimino-substituted porphyrin **5a** (Table 1, entry 5; yield 94%) and diimino-substituted porphyrin **10a** (Table 1, entry 14; yield 84%) were obtained from its reactions with **1a** and **2a**, respectively. The potential utility of this methodology is further enhanced with our later discovery that the use of a zinc ion as an "inorganic protective group" for the central −NH units is not necessary when the weak base Cs_2CO_3 is utilized. For example, similar yields were achieved when reactions were carried out for the free base porphyrins **1b** (Table 1, entries 2, 4, 6, and 8) and **2b** (Table 1, entries 11, 13, and 15). Although most of the reactions were carried out in 0.05-mmol scale (see Experimental Section), the reactions can be scaled up if needed. As an example, when the reaction of porphyrin **2b** and benzophenone imine was carried in 0.5-mmol scale, the same desired product **10b** was obtained in a 403-mg quantity and in 98% yield. The dissymmetric diamino-substituted porphyrins **8a**,**b**, **9a**,**b**, **10a**,**b**, **12a**, **13a**, and **14a** (Figure 2) are expected to exist as a mixture of α,α- and α,*β*-atropisomers with respect to the porphyrin plane. The observation of only one set of resonances in both ^1H and ^{13}C NMR spectra of these porphyrins suggests that there is a free rotation around the bond between the amino nitrogen atom and the porphyrin *meso*-carbon atom at ambient temperature.

Conclusions

In summary, a facile and efficient synthesis of amino-substituted porphyrins from the halogenated precursors via palladium-catalyzed amination has been developed.

Considering the vast availability of different amines, this methodology will allow quick access to a variety of novel porphyrins with *meso*-substituted arylamino and alkylamino groups. The physicochemical properties of the resulting porphyrins should be able to be fine-tuned or dramatically altered through the judicious use of amines with different electronic and steric properties. These new amino-substituted porphyrins could be useful for applications in many important areas such as catalysis, materials, biomimics, and medicine.

Experimental Section

General Considerations. All reactions were carried out under a nitrogen atmosphere in oven-dried glassware following standard Schlenk techniques. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. 5-Bromo-10,20-diphenylporphyrine and 5,15-dibromo-10,20-diphenylporphyrine as well as their corresponding zinc complexes [5-bromo-10,20-diphenylporphyrino]zinc(II) and [5,15-dibromo-10,20-diphenylporphyrino]zinc(II) were synthesized by literature methods.[6c,f,g] Bis(2-diphenylphosphinophenyl)ether (DPEphos) was purchased from Strem Chemical Co. Infrared spectra were obtained by using a Bomen B100 Series FT-IR spectrometer. Samples were prepared as films on a NaCl plate by evaporating THF solutions. UV−vis spectra were obtained with a Hewlett-Packard 8452A diode array spectrophotometer. Thin-layer chromatography was carried out on E. Merck Silica Gel 60 F-254 TLC plates.

General Procedures for Amination of Bromoporphyrin. The bromoporphyrin, palladium precursor, phosphine ligand, and base were placed in an oven-dried, resealable Schlenk tube. The tube was capped with a Teflon screwcap, evacuated, and backfilled with nitrogen. The screwcap was replaced with a rubber septum, and amine was added via syringe, followed by solvent. The tube was purged with nitrogen for 2 min, and then the septum was replaced with the Teflon screwcap. The tube was sealed, and its contents were heated with stirring until the starting bromoporphyrin had been completely consumed as indicated by TLC analysis. The resulting mixture was cooled to room temperature, taken up in ethyl acetate (60 mL), and transferred to a separatory funnel. The mixture was washed with water (×2), dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The crude product was then purified.

[5-(*N*-Phenylamino)-10,20-diphenylporphyrino]zinc-(II) (3a). The general procedure was used to couple [5-bromo-10,20-diphenylporphyrino]zinc(II) (30 mg, 0.050 mmol) with aniline (17 μL, 0.18 mmol), using palladium acetate (0.55 mg, 0.0025 mmol) as the palladium precursor, DPEphos (2.0 mg, 0.0038 mmol) as the phosphine ligand, and cesium carbonate (22.8 mg, 0.070 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 13 h. The title compound was isolated by flash column chromatography (silica gel, ethyl acetate:hexanes (v/v) 1:4) as purple solids (29 mg, 95%). ^{1}H NMR (300 MHz, THF-d_8): δ 10.08 (s, 1H), 9.48 (d, J = 4.8 Hz, 2H), 9.31 (s, 1H), 9.29 (d, J = 4.8 Hz, 2H), 8.92 (d, J = 4.8 Hz, 2H), 8.81 (d, J = 4.8 Hz, 2H), 8.22 (m, 4H), 7.75 (m, 6H), 7.04 (t, J = 7.2 Hz, 2H), 6.87 (d, J = 7.5 Hz, 2H), 6.65 (t, J = 7.2 Hz, 1H). ^{13}C NMR (75 MHz, THF-d_8): δ 164.8, 161.0, 160.8, 160.4, 160.2, 154.0, 145.1, 142.4, 141.7, 139.4, 139.2, 137.6, 136.8, 130.3, 130.2, 127.9, 124.6, 115.4. IR (film, cm^{-1}): 3383, 3050, 2953, 1599, 1493, 1307, 1061, 996, 793, 748. UV−vis (THF, λ_{max}, nm): 422, 554, 602. HRMS-EI ([M]$^+$): calcd for $C_{38}H_{25}N_5Zn$ 615.1401, found 615.1382, with an isotope distribution pattern that is the same as the calculated one.

5-(*N*-Phenylamino)-10,20-diphenylporphyrin (3b). The general procedure was used to couple 5-bromo-10,20-diphenylporphyrin (27 mg, 0.05 mmol) with aniline (17 μL, 0.18 mmol), using palladium acetate (0.55 mg, 0.0025 mmol) as the palledium precursor, DPEphos (2.0 mg, 0.0038 mmol) as the phosphine ligand, and cesium carbonate (22.8 mg, 0.070 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 19 h. The title compound was isolated by flash chromatography (silica gel, ethyl acetate:hexanes (v/v) 1:4) as red solids (27 mg, 98%). ^{1}H NMR (300 MHz, THF-d_8): δ 10.14 (s, 1H), 9.44 (d, J = 4.8 Hz, 2H), 9.42 (s, 1H), 9.30 (d, J = 4.8 Hz, 2H), 8.90 (d, J = 4.8 Hz, 2H), 8.77 (d, J = 4.8 Hz, 2H), 8.21 (m, 4H), 7.78 (m, 6H), 7.06 (t, J = 7.4, 2H), 6.86 (d, J = 7.4 Hz, 2H), 6.69 (J = 7.4 Hz, 1H), −2.54 (s, 2H). ^{13}C NMR (75 MHz, THF-d_8): δ 154.8, 147.7, 142.7, 135.5, 132.1, 131.9, 131.1, 129.7, 128.5, 127.7, 120.6, 120.1, 119.0, 115.5, 105.1. IR (film, cm^{-1}): 3302, 3043, 1599, 1495, 1476, 1338, 1309, 1255, 1064, 973, 958, 797, 748. UV−vis (THF, λ_{max}, nm): 412, 512, 582, 660. HRMS-EI ([M]$^+$): calcd for $C_{38}H_{27}N_5$ 553.2266, found 553.2274, with an isotope distribution pattern that is the same as the calculated one.

[5-(*N*-Methyl-*N*-phenylamino)-10,20-diphenylporphyrino]zinc(II) (4a). The general procedure was used to couple [5-bromo-10,20-diphenylporphyrino]zinc(II) (30 mg, 0.050 mmol) with *N*-methylaniline (20 μL, 0.18 mmol), using palladium acetate (0.55 mg, 0.0025 mmol) as the palladium precursor, DPEphos (2.0 mg, 0.0038 mmol) as the phosphine ligand, and cesium carbonate (22.8 mg, 0.070 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 13 h. The title compound was isolated by flash column chromatography (silica gel, THF:hexanes (v/v) 1:8) as purple solids (31 mg, 99%). ^{1}H NMR (300 MHz, THF-d_8): δ 10.20 (s, 1H), 9.36 (d, J = 4.8 Hz, 2H), 9.19 (d, J = 4.8 Hz, 2H), 8.97 (d, J = 4.8 Hz, 2H), 8.87 (d, J = 4.8 Hz, 2H), 8.23 (m, 4H), 7.77 (m, 6H), 7.05 (br, 2H), 6.69 (br, 2H), 6.61 (t, J = 7.2 Hz, 1H), 4.28 (s, 3H). ^{13}C NMR (75 MHz, THF-d_8): δ 156.0, 152.0, 151.2, 150.9, 150.7, 144.2, 135.5, 133.0, 132.8, 132.4, 130.0, 129.3, 128.1, 127.2, 125.3, 120.8, 116.7, 114.1, 106.9, 45.7. IR (film, cm^{-1}): 3054, 3023, 2978, 2876, 2807, 1596, 1498, 1341, 1120, 994, 793, 747. UV−vis (THF, λ_{max}, nm): 416, 552, 598. HRMS-EI ([M]$^+$): calcd for $C_{39}H_{27}N_5Zn$ 629.1558, found 629.1549, with an isotope distribution pattern that is the same as the calculated one.

5-(*N*-Methyl-*N*-phenylamino)-10,20-diphenylporphyrin (4b). The general procedure was used to couple 5-bromo-10,20-diphenylporphyrin (54 mg, 0.10 mmol) with *N*-methylaniline (40 μL, 0.36 mmol), using palladium acetate (1.1 mg, 0.005 mmol) as the palladium precursor, DPEphos (4.0 mg, 0.0075 mmol) as the phosphine ligand, and cesium carbonate (45.6 mg, 0.014 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 16 h. The title compound was isolated by flash column chromatography (silica gel, ethyl acetate: hexanes (v/v) 1:4) as purple solids (53 mg, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.18(s, 1H), 9.30(d, J = 4.8 Hz, 2H), 9.19 (d, J = 4.8 Hz, 2H), 9.00(d, J = 4.8 Hz, 2H), 8.90 (d, J = 4.8 Hz, 2H), 8.23 (m, 4H), 7.78 (m, 6H), 7.19 (br, 2H), 6.73 (br, 3H), 4.26 (s, 3H), −2.82 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.9, 141.6, 134.9, 131.9, 131.7, 131.6, 129.6, 129.1, 128.0, 127.2, 124.2, 119.8, 116.9, 113.9, 105.8, 45.5. IR (film, cm^{-1}): 3303, 3055, 3026, 2875, 2810, 1596, 1498, 1351, 1113, 971, 796, 731. UV−vis ($CHCl_3$, λ_{max}, nm): 410, 512, 548, 592. HRMS-EI ([M]$^+$): calcd for $C_{39}H_{29}N_5$ 567.2423, found 567.2419, with an isotope distribution pattern that is the same as the calculated one.

[5-Benzophenoneimino-10,20-diphenylporphyrino]zinc-(II) (5a). The general procedure was used to couple [5-bromo-10,20-diphenylporphyrino]zinc(II) (30 mg, 0.050 mmol) with benzophenoneimine (31 μL, 0.18 mmol), using palladium acetate (0.55 mg, 0.0025 mmol) as the palladium precursor, DPEphos (2.0 mg, 0.0038 mmol) as the phosphine ligand, and cesium carbonate (22.8 mg, 0.070 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 22 h. The title compound was isolated by flash column chromatography (silica gel, ethyl acetate:hexanes (v/v) 1:4) as purple solids (33 mg, 94%). ^{1}H NMR (300 MHz, THF-d_8): δ 9.80 (s, 1H), 9.23 (d, J = 4.8 Hz, 2H), 9.13 (d, J = 4.8 Hz, 2H), 8.79 (d, J = 4.8 Hz, 2H), 8.71 (d, J = 4.8 Hz, 2H), 8.19 (br, 6H), 7.73 (m, 6H), 7.66 (br, 3H), 7.36 (br, 2H), 6.65 (br, 3H). ^{13}C NMR (75 MHz, THF-d_8): δ 170.8, 152.0, 150.3, 149.9, 144.5, 142.5, 135, 4, 133.0, 131.6, 131.1, 130.9, 130.0, 129.4, 128.8, 127.9, 127.2,

120.6, 103.7. IR (film, cm^{-1}): 3056, 3023, 2962, 1618, 1596, 1578, 1490, 1439, 1124, 1061, 994, 794. UV−vis (THF, λ_{max}, nm): 428, 562, 610. HRMS-EI ($[M]^+$): calcd for $C_{45}H_{29}N_5Zn$ 703.1714, found 703.1699, with an isotope distribution pattern that is the same as the calculated one.

5-Benzophenoneimino-10,20-diphenylporphyrin (5b). The general procedure was used to couple 5-bromo-10,20-diphenylporphyrin (27 mg, 0.05 mmol) with benzophenoneimine (31 μL, 0.18 mmol), using palladium acetace (0.55 mg, 0.0025 mmol) as the palladium precursor, DPEphos (2.0 mg, 0.0038 mmol) as the phosphine ligand, and cesium carbonate (22.8 mg, 0.070 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 24 h. The title compound was isolated by flash column chromatography (silica gel, ethyl acetate:hexanes (v/v) 1:8) as purple solids (27 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.78 (s, 1H), 9.23 (d, J = 4.8 Hz, 2H), 9.08 (d, J = 4.8 Hz, 2H), 8.85 (d, J = 4.8 Hz, 2H), 8.75 (d, J = 4.8 Hz, 2H), 8.26 (br, 6H), 7.76 (br, 9H), 7.18 (br, 2H), 6.61 (br, 3H), −2.34 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.6, 146.0, 141.7, 134.6, 133.6, 131.6, 130.7, 129.8, 127.9, 127.5, 126.8, 119.4, 102.4. IR (film, cm^{-1}): 3306, 3057, 3026, 1808, 1616, 1595, 1576, 1476, 1442, 1405, 1316, 1241, 1097, 976, 954, 845, 797, 745. UV−vis ($CHCl_3$, λ_{max}, nm): 424, 526, 564, 604, 658. HRMS-EI ($[M]^+$): calcd for $C_{45}H_{31}N_5$ 641.2579, found 641.2591, with an isotope distribution pattern that is the same as the calculated one.

[5-(*N*-Diphenylamino)-10,20-diphenylporphyrino]zinc-(II) (6a). The general procedure was used to couple [5-bromo-10,20-diphenylporphyrino]zinc(II) (30 mg, 0.05 mmol) with diphenylamine (0.031 g, 0.18 mmol), using palladium acetate (1.1 mg, 0.005 mmol) as the palladium precursor, DPEphos (4.0 mg, 0.0075 mmol) as the phosphine ligand, and sodium *tert*-butoxide (13.5 mg, 0.14 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 25 h. The title compound was isolated by flash column chromatography (silica gel, THF:hexanes (v/v) 1:6) as purple solids (21 mg, 61%). ^{1}H NMR (300 MHz, THF-d_8): δ 10.17 (s, 1H), 9.33 (m, 4H), 8.93 (d, J = 4.8 Hz, 2H), 8.80 (d, J = 4.8 Hz, 2H), 8.20 (m, 4H), 7.75 (m, 6H), 7.33 (m, 8H), 7.12 (t, J = 7.8 Hz, 8H), 6.80 (t, J = 7.2 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.7, 153.0, 151.3, 151.0, 150.1, 144.1, 135.4, 133.3, 132.8, 132.4, 130.9, 129.8, 129.6, 128.1, 127.2, 122.9, 121.1, 120.9, 107.0. IR (film, cm^{-1}): 3055, 2961, 2361, 1598, 1587, 1490, 1293, 1273, 1062, 1003, 994, 794, 752. UV−vis (THF, λ_{max}, nm): 412, 558, 604. HRMS-EI ($[M]^+$): calcd for $C_{44}H_{29}N_5Zn$ 691.1714, found 691.1712, with an isotope distribution pattern that is the same as the calculated one.

5-(*N*-Diphenylamino)-10,20-diphenylporphyrin (6b). The general procedure was used to couple 5-bromo-10,20-diphenylporphyrin (54 mg, 0.1 mmol) with diphenylamine (0.061 g, 0.36 mmol), using palladium acetate (1.1 mg, 0.005 mmol) as the palladium precursor, DPEphos (4.0 mg, 0.0075 mmol) as the phosphine ligand, and cesium carbonate (45.6 mg, 0.014 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 40 h. The title compound was isolated by flash column chromatography (silica gel, THF:hexanes (v/v) = 1:8) as purple solids (41 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.13 (s, 1H), 9.33 (d, J = 4.8 Hz, 2H), 9.26 (d, J = 4.8 Hz, 2H), 8.96 (d, J = 4.8 Hz, 2H), 8.83 (d, J = 4.8 Hz, 2H), 8.20 (m, 4H), 7.76 (m, 6H), 7.35 (m, 4H), 7.20 (t, J = 7.2 Hz, 4H), 6.89 (t, J = 7.2 Hz, 2H), −2.69 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.5, 141.3, 134.8, 134.6, 132.0, 131.4, 130.1, 129.1, 127.8, 126.8, 122.3, 120.8, 119.6, 105.6. IR (film, cm^{-1}): 3307, 3055, 3029, 1591, 1491, 1342, 1184, 973, 796, 750, 731, 695. UV−vis ($CHCl_3$, λ_{max}, nm): 407, 523, 577, 656. HRMS-EI ($[M]^+$): calcd for $C_{44}H_{31}N_5$ 629.2579, found 629.2576, with an isotope distribution pattern that is the same as the calculated one.

[5-(*N*-Hexylamino)-10,20-diphenylporphyrino]zinc-(II) (7a). The general procedure was used to couple [5-bromo-10,20-diphenylporphyrino]zinc(II) (30 mg, 0.05 mmol) with hexylamine (0.024 mL, 0.18 mmol), using palladium acetate (0.55 mg, 0.0025 mmol) as the palladium precursor, DPEphos (2.0 mg, 0.0038 mmol) as the phosphine ligand, and cesium carbonate (22.8 mg, 0.070 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 50 h. The title compound was isolated by flash column chromatography (silica gel, THF:hexanes (v/v) 1:8) as purple solids (25 mg, 80%). ^{1}H NMR (300 MHz, THF-d_8): δ 9.63 (s, 1H), 9.43 (d, J = 4.8 Hz, 2H), 9.05 (d, J = 4.8 Hz, 2H), 8.76 (d, J = 4.8 Hz, 2H), 8.65 (d, J = 4.8 Hz, 2H), 8.18 (m, 4H), 7.75(m, 6H), 7.33 (m, 8H), 6.78(s, 1H), 4.38(m, 2H), 2.04(m, 2H), 1.58(m, 2H), 1.37 (m, 4H), 0.87 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, THF-d_8): δ 152.7, 149.9, 149.5, 147.0, 144.7, 135.3, 133.0, 131.4, 130.2, 127.8, 127.2, 126.9, 120.5, 102.4, 60.2, 32.8, 32.5, 28.0, 23.5, 14.4. IR (film, cm^{-1}): 3330, 3053, 2954, 2925, 2854, 1584, 1542, 1489, 1440, 1213, 1062, 1010, 1002, 992, 836, 789, 780, 750. UV−vis (THF, λ_{max}, nm): 428, 606. HRMS-EI ($[M]^+$): calcd for $C_{38}H_{33}N_5Zn$ 623.2027, found 623.2009, with an isotope distribution pattern that is the same as the calculated one.

[5,15-Bis(*N*-phenylamino)-10,20-diphenylporphyrino]-zinc(II) (8a). The general procedure was used to couple [5,-15-dibromo-10,20-diphenylporphyrino]zinc(II) (34 mg, 0.050 mmol) with aniline (22 μL, 0.24 mmol), using palladium acetate (1.1 mg, 0.0050 mmol) as the palladium precursor, DPEphos (4.0 mg, 0.0075 mmol) as the phosphine ligand, and cesium carbonate (45.6 mg, 0.14 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 13 h. The title compound was isolated by flash column chromatography (silica gel, THF:hexanes (v/v) 1:4) as purple solids (29 mg, 82%). ^{1}H NMR (300 MHz, THF-d_8): δ 9.36 (d, J = 4.8 Hz, 4H), 9.17 (s, 2H), 8.69 (d, J = 4.8 Hz, 4H), 8.16 (m, 4H), 7.72 (m, 6H), 7.03 (t, J = 6.9, 7.2 Hz, 4H), 6.84 (d, J = 8.4 Hz, 4H), 6.64 (t, J = 7.2 Hz, 2H). ^{13}C NMR (75 MHz, THF-d_8): δ 155.1, 152.0, 150.5, 144.4, 135.3, 132.2, 129.7, 129.6, 128.0, 127.2, 121.0, 119.9, 118.2, 115.0. IR (film, cm^{-1}): 3380, 3047, 3020, 2953, 1599, 1492, 1339, 1308, 1063, 1003, 795, 747. UV−vis (THF, λ_{max}, nm): 440, 564, 620. HRMS-EI ($[M]^+$): calcd for $C_{44}H_{30}N_6Zn$ 706.1823, found 706.1840, with an isotope distribution pattern that is the same as the calculated one.

5,15-Bis(*N*-phenylamino)-10,20-diphenylporphyrin (8b). The general procedure was used to couple 5,15-dibromo-10,-20-diphenylporphyrin (31 mg, 0.05 mmol) with aniline (22 μL, 0.24 mmol), using palladium acetate (1.1 mg, 0.0050 mmol) as the palladium precursor, DPEphos (4.0 mg, 0.0075 mmol) as the phosphine ligand, and cesium carbonate (45.6 mg, 0.14 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 20 h. The title compound was isolated by flash column chromatography (silica gel, ethyl acetate:hexanes (v/v) 1:4) as purple solids (21 mg, 65%). ^{1}H NMR (300 MHz, THF-d_8): δ 9.32 (d, J = 4.8 Hz, 4H), 9.29 (s, 2H), 8.65 (d, J = 4.8 Hz, 4H), 8.17 (m, 4H), 7.75 (m, 6H), 7.07 (t, J = 8.1 Hz, 4H), 6.86 (d, J = 8.1 Hz, 4H), 6.69 (t, J = 7.4 Hz, 2H), −2.03 (s, 2H). ^{13}C NMR (75 MHz, THF-d_8): δ 154.5, 142.9, 137.1, 135.3, 129.7, 128.5, 127.6, 120.5, 119.7, 118.9, 115.4. IR (film, cm^{-1}): 3307, 1599, 1496, 1474, 1340, 1306, 1258, 1071, 974, 797, 732. UV−vis (THF, λ_{max}, nm): 438, 526, 592, 680. HRMS-EI ($[M]^+$): calcd for $C_{44}H_{32}N_6$ 644.2688, found 644.2704, with an isotope distribution pattern that is the same as the calculated one.

[5,15-Bis(*N*-methyl-*N*-phenylamino)-10,20-diphenylporphyrino]zinc(II) (9a). The general procedure was used to couple [5,15-dibromo-10,20-diphenylporphyrino]zinc(II) (34 mg, 0.050 mmol) with *N*-methylaniline (26 μL, 0.24 mmol), using palladium acetate (1.1 mg, 0.0050 mmol) as the palladium precursor, DPEphos (4.0 mg, 0.0075 mmol) as the phosphine ligand, and cesium carbonate (45.6 mg, 0.14 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 17 h. The title compound was isolated by flash column chromatography (silica gel, THF:hexanes (v/v) 1:8) as purple solids (30 mg, 82%). ^{1}H NMR (300 MHz, THF-d_8): δ 9.10 (d, J = 4.8 Hz, 4H), 8.75 (d, J = 4.8 Hz, 4H), 8.15 (m, 4H), 7.73 (m, 6H), 7.04 (br, 4H), 6.69 (br, 4H), 6.59 (t, J = 7.2 Hz, 2H), 4.25 (s, 6H). ^{13}C NMR (75 MHz, THF-d_8): δ 155.8, 152.4, 150.9, 144.0, 135.2, 133.1, 130.1, 129.3, 128.2, 127.2, 125.7, 121.2, 116.8, 114.2, 45.6. IR (film, cm^{-1}): 3054, 2985, 2883, 2807,

1597, 1496, 1346, 1118, 1000, 796, 747. UV−vis (THF, λ_{max}, nm): 422, 562, 608. HRMS-EI ([M]$^+$): calcd for $C_{46}H_{34}N_6Zn$ 734.2136, found 734.2128, with an isotope distribution pattern that is the same as the calculated one.

5,15-Bis(*N*-methyl-*N*-phenylamino)-10,20-diphenylporphyrin (9b). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31 mg, 0.05 mmol) with *N*-methylaniline (26 μL, 0.24 mmol), using palladium acetate (1.1 mg, 0.0050 mmol) as the palladium precursor, DPEphos (4.0 mg, 0.0075 mmol) as the phosphine ligand, and the cesium carbonate (45.6 mg, 0.14 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 15 h. The title compound was isolated by flash column chromatography (silica gel, ethyl acetate:hexanes (v/v) 1:4) as red solids (24 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.08 (d, J = 4.8 Hz, 4H), 8.77 (d, J = 4.8 Hz, 4H), 8.16 (m, 4H), 7.72 (m, 6H), 7.14 (m, 4H), 6.72 (m, 6H), 4.23 (s, 6H), −2.54 (s, 2H). ^{13}C NMR (75 MHz, CDCl3): δ 154.4, 141.3, 134.5, 131.9, 128.9, 128, 127.8, 126.8, 124.3, 119.9, 116.7, 113.8, 45.1. IR (film, cm^{-1}): 3315, 3026, 2359, 1596, 1498, 1475, 1354, 1114, 972, 798. UV−vis ($CHCl_3$, λ_{max}, nm): 412, 522, 562, 596, 608. HRMS-EI ([M]$^+$): calcd for $C_{46}H_{36}N_6$ 672.3001, found 672.3003, with an isotope distribution pattern that is the same as the calculated one.

[5,15-Bis(benzophenoneimino)-10,20-diphenylporphyrino]zinc(II) (10a). The general procedure was used to couple [5,15-dibromo-10,20-diphenylporphyrino]zinc(II) (34 mg, 0.050 mmol) with benzophenoneimine (41 μL, 0.24 mmol), using palladium acetate (1.1 mg, 0.0050 mmol) as the palladium precursor, DPEphos (4.0 mg, 0.0075 mmol) as the phosphine ligand, and cesium carbonate (45.6 mg, 0.14 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 16 h. The title compound was isolated by flash column chromatography (silica gel, ethyl acetate:hexanes (v/v) 1:4) as purple solids (37 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.06 (d, J = 4.8 Hz, 4H), 8.57 (d, J = 4.8 Hz, 4H), 8.19 (m, 4H), 8.07 (m, 4H), 7.68 (m, 6H), 7.61 (m, 6H), 7.33 (m, 4H), 6.62 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8, 149.4, 144.7, 143.8, 135.4, 135.2, 132.7, 131.9, 131.5, 130.8, 129.9, 129.3, 128.4, 128.0, 127.7, 127.2, 127.1, 126.9, 120.9. IR (film, cm^{-1}): 3054, 3027, 2976, 1618, 1597, 1485, 1442, 1338, 1212, 1118, 1004, 793, 753. UV−vis (THF, λ_{max}, nm): 438, 652. HRMS-EI ([M]$^+$): calcd for $C_{58}H_{38}N_6Zn$, 882.2449, found, 882.2464, with an isotope distribution pattern that is the same as the calculated one.

5,15-Bis(benzophenoneimino)-10,20-diphenylporphyrin (10b). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31 mg, 0.05 mmol) with benzophenoneimine (41 μL, 0.24 mmol), using palladium acetate (1.1 mg, 0.0050 mmol) as the palladium precursor, DPEphos (4.0 mg, 0.0075 mmol) as the phosphine ligand, and cesium carbonate (45.6 mg, 0.14 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 15 h. The title compound was isolated by flash column chromatography (silica gel, ethyl acetate:hexanes (v/v) 1:4) as purple solids (39 mg, 95%). ^{1}H NMR(300 MHz, THF-d_8): δ 9.09 (d, J = 4.8 Hz, 4H), 8.57 (d, J = 4.8 Hz, 4H), 8.10 (m, 8H), 7.64 (m, 12H), 7.23 (br, 4H), 6.62 (br, 6H), −1.87(s, 2H). ^{13}C NMR (75 MHz, THF-d_8): δ 172.3, 143.2, 140.8, 137.9, 135.4, 135.1, 132.1, 131.0, 129.3, 128.9, 128.3, 128.2, 127.5, 120.3, 108.4. IR (film, cm^{-1}) 3316, 3056, 3022, 1614, 1596, 1575, 1465, 1443, 1351, 1316, 1278, 1244, 1105, 1066, 976, 950, 798, 725. UV−vis (THF, λ_{max}, nm): 434, 592, 700. HRMS-EI ([M]$^+$): calcd for $C_{58}H_{40}N_6$ 820.3314, found 820.3308, with an isotope distribution pattern that is the same as the calculated one.

[5,15-Bis(*N*-diphenylamino)-10,20-diphenylporphyrino]-zinc(II) (11a). The general procedure was used to couple [5,-15-dibromo-10,20-diphenylporphyrino]zinc(II) (34 mg, 0.05 mmol) with diphenylamine (0.041 g, 0.24 mmol), using palladium acetate (1.1 mg, 0.0050 mmol) as the palladium precursor, DPEphos (4.0 mg, 0.0075 mmol) as the phosphine ligand, and sodium *tert*-butoxide (13.5 mg, 0.14 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 50 h. The title compound was isolated by flash column chromatography (silica gel, THF:hexanes (v/v) 1:6) as purple solids (13 mg, 30%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (d, J = 4.8 Hz, 4H), 8.75 (d, J = 4.8 Hz, 4H), 8.09 (m, 4H), 7.66 (m, 6H), 7.29 (m, 8H), 7.15 (t, J = 7.8 Hz, 8H), 6.85 (t, J = 7.4 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.6, 152.3, 149.7, 142.1, 134.3, 133.3, 130.5, 129.1, 127.6, 126.5, 122.8, 122.1, 121.0, 120.7. IR (film, cm^{-1}): 3056, 2360, 1595, 1590, 1490, 1341, 1294, 1249, 1002, 794, 750. UV−vis ($CHCl_3$, λ_{max}, nm): 406, 460, 572, 628. HRMS-EI ([M]$^+$): calcd for $C_{56}H_{38}N_6Zn$ 858.2449, found 858.2436, with an isotope distribution pattern that is the same as the calculated one.

[5,15-Bis(*N*-4-trifluoromethylphenylamino)-10,20-diphenylporphyrino]zinc(II) (12a). The general procedure was used to couple [5,15-dibromo-10,20-diphenylporphyrino]-zinc(II) (34 mg, 0.05 mmol) with 4-trifluoromethylaniline (0.030 mL, 0.24 mmol), using palladium acetate (1.1 mg, 0.0050 mmol) as the palladium precursor, DPEphos (4.0 mg, 0.0075 mmol) as the phosphine ligand, and cesium carbonate (45.6 mg, 0.14 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 17 h. The title compound was isolated by flash column chromatography (silica gel, ethyl acetate: hexanes (v/v) 1:2) as purple solids (38 mg, 90%). ^{1}H NMR (300 MHz, THF-d_8): δ 9.84 (s, 2H), 9.43 (d, J = 4.8 Hz, 4H), 8.84 (d, J = 4.8 Hz, 4H), 8.22 (m, 4H), 7.78 (m, 6H), 7.41 (d, J = 8.2 Hz, 4H), 6.93 (d, J = 8.2 Hz, 4H). ^{13}C NMR (75 MHz, THF-d_8): δ 157.5, 151.7, 151.0, 144.1, 135.4, 132.9, 129.7, 128.2, 127.3, 127.2, 127.1, 121.6, 119.3, 118.1, 114.1. IR (film, cm^{-1}): 3376, 1614, 1522, 1322, 1110, 1065, 1003, 828, 797. UV−vis (THF, λ_{max}, nm): 435, 562, 612. HRMS-EI ([M]$^+$):calcd for $C_{46}H_{28}N_6F_6Zn$ 842.1571, found 842.1590, with an isotope distribution pattern that is the same as the calculated one.

[5,15-Bis(*N*-4-methoxyphenylamino)-10,20-diphenylporphyrino]zinc(II) (13a). The general procedure was used to couple [5,15-dibromo-10,20-diphenylporphyrino]zinc(II) (34 mg, 0.05 mmol) with *p*-anisidine (30 mg, 0.24 mmol), using palladium acetate (1.1 mg, 0.0050 mmol) as the palladium precursor, DPEphos (4.0 mg, 0.0075 mmol) as the phosphine ligand, and cesium carbonate (45.6 mg, 0.14 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 16 h. The title compound was isolated by flash column chromatography (silica gel, ethyl acetate:hexanes (v/v) 1:3) as purple solids (36 g, 94%). ^{1}H NMR (300 MHz, THF-d_8): δ 9.34 (d, J = 4.8 Hz, 4H), 8.88 (s, 2H), 8.66 (d, J = 4.8 Hz, 4H), 8.17 (m, 4H), 7.73 (m, 6H), 6.87 (d, J = 9.0 Hz, 4H), 6.69 (d, J = 9.0 Hz, 4H), 3.65 (s, 6H). ^{13}C NMR (75 MHz, THF-d_8): δ 153.5, 151.9, 150.2, 149.6, 144.6, 135.3, 131.9, 129.3, 127.8, 127.1, 121.2, 120.7, 116.6, 115.0, 55.6. IR (film, cm^{-1}): 3372, 1597, 1507, 1489, 1339, 1234, 1036, 1002, 797. UV−vis (THF, λ_{max}, nm): 447, 571, 629. HRMS-EI ([M]$^+$): calcd for $C_{46}H_{34}N_6O_2Zn$ 766.2035, found 766.2040.

[5,15-Bis(*N*-3,5-di-*tert*-butylphenylamino)-10,20-diphenylporphyrino]zinc(II) (14a). The general procedure was used to couple [5,15-dibromo-10,20-diphenylporphyrino]zinc-(II) (34 mg, 0.05 mmol) with 3,5-di-*tert*-butylaniline (0.050 g, 0.24 mmol), using palladium acetate (1.1 mg, 0.0050 mmol) as the palladium precursor, DPEphos (4.0 mg, 0.0075 mmol) as the phosphine ligand, and cesium carbonate (45.6 mg, 0.14 mmol) as the base. The reaction was conducted in THF (5 mL) at 68 °C for 62 h. The title compound was isolated by flash column chromatography (silica gel, ethyl acetate:hexanes (v/v) 1:4) as purple solids (44 mg, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.28 (d, J = 4.8 Hz, 4H), 8.68 (d, J = 4.8 Hz, 4H), 8.14 (m, 4H), 7.71 (m, 8H), 6.87 (m, 6H), 1.21 (s, 36H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.1, 151.5, 150.6, 149.4, 143.0, 134.8, 131.7, 128.5, 127.1, 126.4, 120.4, 118.8, 113.4, 109.6, 34.7, 31.3. IR (film, cm^{-1}): 3383, 3055, 2961, 2902, 2867, 1595, 1488, 1436, 1340, 1064, 1004, 796. UV−vis (THF, λ_{max}, nm): 448, 576, 634. HRMS-EI ([M]$^+$): calcd for $C_{60}H_{62}N_6Zn$ 930.4327, found 930.4354, with an isotope distribution pattern that is the same as the calculated one.

Acknowledgment. We are grateful for financial support of this work from the Department of Chemistry and the Center for Excellence for Structural Biology (CESB) of the University of Tennessee. We wish to acknowledge Dr. Al Tuinman of UT Mass Spectroscopy Center for assistance with high-resolution mass spectroscopy. Cesium carbonate was obtained as a gift from Chemetall Chemical Products, Inc.

JO034063M