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Synthesis of *meso*-Arylsulfanyl- and Alkylsulfanyl-Substituted Porphyrins via Palladium-Mediated C−S Bond Formation

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A family of new *meso*-arylsulfanyl- and alkylsulfanyl-substituted porphyrins were efficiently synthesized from direct reactions of *meso*-brominated porphyrins with thiols via palladium-mediated C−S bond formation. The catalytic method can be performed under mild conditions with both mono- and bis-substituted *meso*-bromoporphyrins as well as their zinc complexes and is suitable for different types of thiols. With the use of selenols, *meso*-seleno-substituted porphyrins can also be prepared similarly.

Introduction

Biologically relevant porphyrins are a unique class of heteroaromatic macrocycles that have found wide applications in many fields, including catalysis, medicine, and materials.[1] In addition to diverse characteristics resulting from versatile metal coordination ability of the central nitrogen core, the physical, chemical, and biological properties of porphyrins can be systematically regulated through introduction of peripheral substituents having varied electronic, steric, and conformational environments.[1] Standard synthesis of porphyrins, which involves multiple condensations of pyrroles with aldehydes under acidic and oxidative conditions, however, produces low yields, meets difficulty in separation, and limits elaboration of derivatives with functional and sensitive groups.[2] The new condition introduced by Lindsey and co-workers[3] has significantly improved the synthesis and can be extended to a wider range of aldehydes.

A recent strategy involving the applications of transition-metal-mediated cross-coupling reactions to preformed halogenated porphyrins has proved effective and advantageous,[4] permitting synthesis of a large number of porphyrin derivatives from a single halogenated precursor. Examples of this post-derivatization strategy include successful applications of Suzuki and Stille cross-coupling reactions for the fabrication of various alkyl- and aryl-substituted porphyrins.[5] In addition to the applications of carbon−carbon bond couplings,[4,5] we[6] and others[7] have more recently applied metal-catalyzed carbon−heteroatom bond formation reactions[8] for porphyrin synthesis. For example, we have developed several general and efficient methods for the syntheses of a variety of heteroatom-substituted porphyrins, including amino, amido, and oxy functionalities, from the reactions of brominated porphyrins with amines, amides, and alcohols, respectively.[6]

Extending the synthetic strategy to recent palladium-mediated C−S bond formation reaction,[9,10] we report

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(1) Kadish, K. M.; Smith, K. M.; Guilard, R.; Eds. *The Porphyrin Handbook*; Academic Press: San Diego, 2000−2003; Vol. 1−20.

(2) (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.

(3) (a) Lindsey, J. S.; Hsu, H. C.; Schreiman, I. C. *Tetrahedron Lett.* **1986**, *27*, 4969−4970. (b) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827−836.

(4) For a review on this topic, see: Sharman, W. M.; Van Lier, J. E. *J. Porphyr. Phthalocyanines* **2000**, *4*, 441−453.

(5) For selective examples that applied Suzuki and Stille cross-coupling reactions for porphyrin synthesis, see: (a) DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 2513. (b) DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. J. *J. Org. Chem.* **1993**, *58*, 5983. (c) Hyslop, A. G.; Kellett, M. A.; Iovine, P. M.; Therien, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 12676. (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) Shi, X.; Amin, R.; Liebeskind, L. S. *J. Org. Chem.* **2000**, *65*, 1650. (f) Shanmugathasan, S.; Johnson, C. K.; Edwards, C.; Matthews, E. K.; Dolphin, D.; Boyle, R. W. *J. Porphyrins Phthalocyanines* **2000**, *4*, 228. (g) Iovine, P. M.; Kellett, M. A.; Redmore, N. P.; Therien, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 8717. (h) Deng, Y.; Chang, C. K.; Nocera, D. G. *Angew. Chem., Int. Ed*. **2000**, *39*, 1066. (i) Chng, L. L.; Chang, C. J.; Nocera, D. G. *J. Org. Chem.* **2003**, *68*, 4075.

(6) (a) Chen, Y.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 4432. (b) Gao, G. Y.; Chen, Y.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 6215. (c) Gao, G. Y.; Colvin, A. J.; Chen, Y.; Zhang, X. P. *Org. Lett.* **2003**, *5*, 3261. (d) Gao, G. Y.; Chen, Y.; Zhang, X. P. *Org. Lett.* **2004**, *6*, 1837.

(7) (a) Khan, M. M.; Ali, H.; van Lier, J. E. *Tetrahedron Lett.* **2001**, *42*, 1615. Note: no yields were reported in this paper. (b) Takanami, T.; Hayashi, M.; Hino, F.; Suda, K. *Tetrahedron Lett.* **2003**, *44*, 7353. Note: this paper reported the utilization of a *meso*-brominated Ni(II) porphyrin precursor for the preparation of *meso*-amino- and *meso*-amidoporphyrins.

(8) (a) Ley, S. V.; Thomas, A. W. *Angew. Chem., Int. Ed*. **2003**, *42*, 5400. (b) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131. (c) Hartwig, J. F. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley-Interscience: New York, 2002; p 1051. (d) Prim, D.; Campagne, J.-M.; Joseph, D.; Andrioletti, B. *Tetrahedron* **2002**, *58*, 2041. (e) Yang, B. Y.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125. (f) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. (g) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046. (h) Hartwig, J. F. *Synlett* **1997**, 329.

(9) For a recent review on metal-catalyzed carbon−sulfur bond formation, see: Kondo, T.; Mitsudo, T. *Chem. Rev*. **2000**, *100*, 3205.

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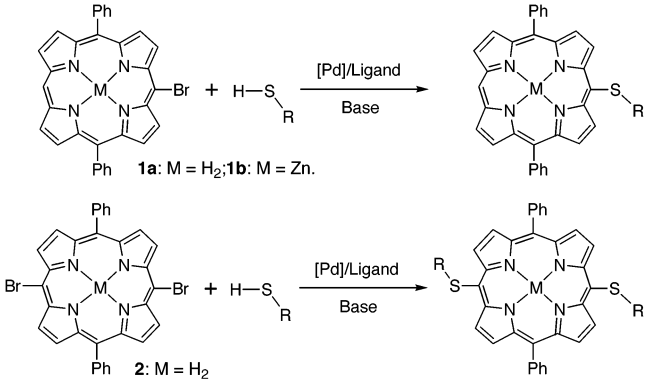
SCHEME 1. Palladium-Catalyzed C−S Bond Formation of *meso*-Monobromo- and *meso*-Dibromoporphyrins



herein a general method for the synthesis of *meso*-arylsulfanyl- and alkylsulfanyl-substituted porphyrins from the corresponding bromoporphyrin precursors (Scheme 1). The synthesis can be conducted under mild conditions in high yields with different types of thiols, producing a family of new porphyrins with a mercapto functionality directly attached at the *meso*-position with its sulfur atom.[11] Similarly, *meso*-seleno-substituted porphyrins can also be prepared from reactions with selenols via palladium-mediated C−Se bond formation.

Results and Discussion

The *meso*-brominated porphyrins 5-bromo-10,20-diphenylporphyrin (**1a**), its zinc complex (**1b**), and 5,15-dibromo-10,20-diphenylporphyrin (**2**) (Scheme 1), which were synthesized by selective bromination,[5b,e,f] were employed as representative halogenated porphyrin precursors for palladium-catalyzed C−S bond formation reactions. In combination with $Pd_2(dba)_3$, we first evaluated the catalytic activities of different ligands (Figure 1) for the model reaction between **1a** and 4-methoxythiophenol under similar conditions (Table 1). The common chelating diphosphines **A**−**D** (Table 1, entries 1−4) as well as the biaryl-based electron-rich bulky monophosphines **E**−**I** (Table 1, entries 5−9) were active ligands for supporting the palladium-catalyzed C−S bond formation reaction, affording the desired *meso*-arylsulfanyl-substituted porphyrins in high yields.[12] Although a relatively lower yield was obtained, triphenylphosphine **J** could also catalyze the reaction (Table 1, entry 10). In addition, *N*-heterocyclic carbene ligand **K** was active in mediating the C−S coupling reaction (Table 1, entry 11).

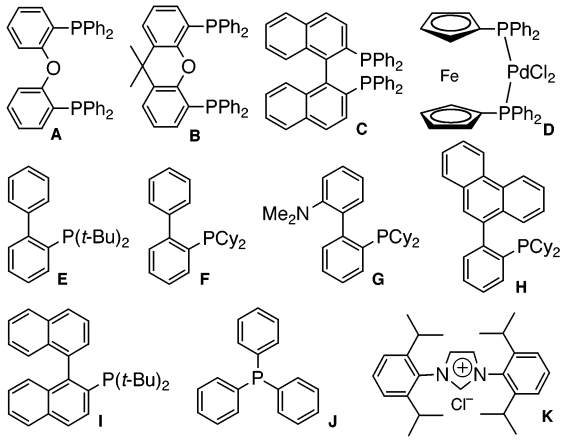


FIGURE 1. Structures of various supporting ligands.

TABLE 1. Palladium-Catalyzed C−S Bond Formation of Bromoporphyrin 1a with 4-Methoxythiophenol[a]

entry	ligand[b]	yield[c] (%)	entry	ligand[b]	yield[c] (%)
1	**A**	75	7	**G**	73
2[d]	**B**	83	8	**H**	83
3	**C**	95	9[d]	**I**	77
4[d]	**D**	73	10[d]	**J**	73
5	**E**	94	11	**K**	93
6	**F**	76			

[a] Reactions were carried out in toluene at 100 °C under N_2 for 20 h with 1.0 equiv of **1a**, 3.0 equiv of 4-methoxythiophenol, 5 mol % $Pd_2(dba)_3$, and 20 mol % ligand in the presence of 4.0 equiv of Cs_2CO_3. Concentration: 0.01 mmol of **1a**/mL of toluene. [b] See Figure 1 for structures of ligands. [c] Yields represent isolated yields. [d] 4.0 equiv of 4-methoxythiophenol and 2.0 equiv of Cs_2CO_3 were used.

Under similar palladium-based catalytic conditions, a variety of thiols could be coupled with **1a** to form the corresponding *meso*-monosulfanyl-substituted porphyrins (Table 2).[13] In addition to 4-methoxythiophenol, other aromatic thiols such as thiophenols containing 4-chloro and 2-methyl groups as well as 2-naphthelenethiol were suitable coupling partners (Table 2, entries 1−4). Although a low yield was obtained with a benzyl-type thiol (Table 2, entry 5), both open-chain primary and cyclic secondary aliphatic thiols could be successfully coupled in good yields (Table 2, entries 6 and 7). As demonstrated with *N*-(4-mercaptophenyl)acetamide, the catalytic reaction could selectively proceed without affecting the amide functionality (Table 2, entry 8), indicating C−S bond formation is more facile than amidation under the conditions. Considering our recent results on the synthesis of *meso*-amidoporphyrins,[6d] the resulting functional porphyrin might be useful for construction of unsymmetric bisporphyrins upon reacting with another equivalent of brominated porphyrins.[14] Heterocyclic thiols such as benzothiazole-2-thiol could also be converted to the desired *meso*-monosulfanyl-substituted porphyrin in high yield (Table 2, entry 9). When an excess amount of propane-1,3-dithiol was used, the coupling reaction could

(10) For recent examples of palladium-catalyzed carbon−sulfur bond formation, see: (a) Moreau, X.; Campagne, J.-M. *J. Organomet. Chem.* **2003**, *687*, 322. (b) Schopfer, U.; Schlapbach, A. *Tetrahedron* **2001**, *57*, 3069. (c) Li, G. Y.; Zheng, G.; Noonan, A. F. *J. Org. Chem.* **2001**, *66*, 8677. (d) Harr, M. S.; Presley, A. L.; Thorarensen, A. *Synlett* **1999**, 1579. (e) Zheng, N.; McWilliams, J. C.; Fleitz, F. J.; Armstrong, J. D.; Volante, R. P. *J. Org. Chem.* **1998**, *63*, 9606.

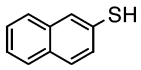
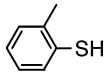
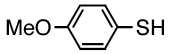
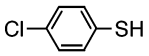
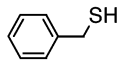
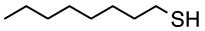
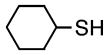
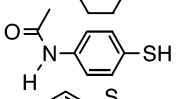
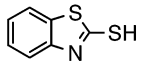
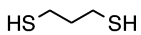
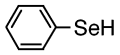
(11) For limited examples of *meso*-arylsulfanyl- and alkylsulfanyl-substituted porphyrins, see: (a) Crossley, M. J.; King, L. G.; Pyke, S. M.; Tansey, C. W. *J. Porphyrins Phthalocyanines* **2002**, *6*, 685. (b) Clezy, P. S.; Fookes, C. J. R.; Smythe, G. A. *Aust. J. Chem.* **1981**, *34*, 2595.

(12) 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 **1a** and 4-methoxylthiophenol was carried in 0.5 mmol scale under the same conditions as described in Table 1, entry 3, the desired product was obtained in 290 mg quantity and in 96.5% yield.

(13) Although the highest yield was obtained for the coupling reaction of **1a** with 4-methoxylthiophenol using BINAP **C** (see Table 1), different supporting ligands were needed to be used for different thiol substrates in order to achieve the highest yields (Tables 2−4).

(14) For a review on applications of diporphyrins, see: Harvey, P. D. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2003; Vol. 18, pp 63−250.

TABLE 2. Palladium-Catalyzed C−S Bond Formation of Monobromoporphyrin 1a with Different Thiols[a]

entry	thiols	ligand[b]	temp (°C)	time (h)	yield (%)[c]
1		**A**	100	20	64
2		**A**	100	20	68
3		**E**	100	21	94
4		**A**	100	20	71
5		**A**	80	24	38
6		**A**	80	48	52
7[d]		**C**	100	23	66
8[d,e]		**B**	100	24	61
9		**A**	100	20	77
10[f]		**E**	100	25	70
11		**A**	60	24	49

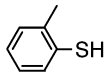
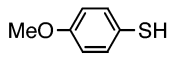
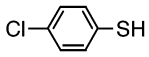
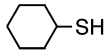
[a] Reactions were carried out in toluene under N_2 with 1.0 equiv of **1a**, 3.0 equiv of thiol, 5 mol % $Pd_2(dba)_3$, and 20 mol % ligand in the presence of 4.0 equiv of Cs_2CO_3. Concentration: 0.01 mmol **1a**/mL toluene. [b] See Figure 1 for structures of ligands. [c] Yields represent isolated yields. [d] 4.0 equiv of thiol and 2.0 equiv of Cs_2CO_3 were used. [e] 5 mol % $Pd(OAc)_2$ was used. [f] 8.0 equiv of thiol and 2.5 mol % $Pd_2(dba)_3$ were used.

be controlled to take place with only one of the thiol groups, affording a porphyrin with an appended free thiol functionality in good yield (Table 2, entry 10). In view of the ready availability of dithiols with various chain lengths, this provides a convenient method for the synthesis of thiol-derivatized porphyrins, which have found interesting applications.[15]

With the use of selenols, *meso*-seleno-substituted porphyrins can also be prepared similarly. For example, the reaction of **1a** with benzeneselenol produced 10-phenylselanyl-5,15-diphenylporphyrin in 49% yield (Table 2, entry 11). To the best of our knowledge, this represents the first example of porphyrin with directly attached seleno functionality.

The catalytic reaction can also be applied for the synthesis of *meso*-disulfanyl-substituted porphyrins from *meso*-dibromoporphyrin precursors via one-pot, double C−S bond formation reactions. For example, when dibromoporphyrin **2** was used, different thiols were successfully coupled to form the corresponding *meso*-diarylsulfanyl- and dialkylsulfanyl-substituted porphyrins in good yields (Table 3). Representative examples that were evaluated include aromatic thiols having sterically hindered, electron-donating, and electron-withdrawing groups (Table 3, entries 1−3) as well as open-chain primary and cyclic secondary aliphatic thiols (Table 3, entries 4 and 5).

TABLE 3. Palladium-Catalyzed Double C−S Bond Formation of Dibromoporphyrin 2 with Different Thiols[a]

entry	thiols	ligand[b]	temp (°C)	time (h)	yield (%)[c]
1[d]		**A**	100	27	71
2[d]		**A**	100	27	87
3		**C**	100	25	72
4		**C**	100	24	75
5		**C**	100	24	74

[a] Reactions were carried out in toluene under N_2 with 1.0 equiv of **2**, 8.0 equiv of thiol, 10 mol % $Pd_2(dba)_3$ and 20 mol % ligand in the presence of 4.0 equiv of Cs_2CO_3. Concentration: 0.01 mmol **2**/mL toluene. [b] See Figure 1 for structures of ligands. [c] Yields represent isolated yields. [d] 40 mol % ligand was used.

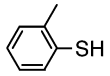
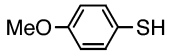
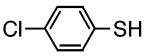
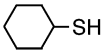
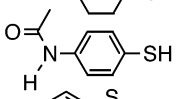
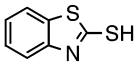
As we showed previously for palladium-catalyzed amination, etheration, and amidation reactions,[6] the above results (Tables 1−3) demonstrate again that free base porphyrins can be directly employed for palladium-catalyzed cross-coupling reactions without the need of a zinc or other metal ions as an "inorganic protective group" for the central NH units,[16] eliminating extra metalation and demetaltion steps. If desirable, however, metalloporphyrins can also be effectively coupled with thiols to give their corresponding *meso*-sulfanyl-substituted metalloporphyrins. For example, the C−S bond formation reactions of the zinc complex **1b** with different thiols could proceed in similar scope, selectivity, and yields (Table 4).

While the precise mechanistic details of the C−S cross-coupling reaction remain to be established,[10] it is assumed that the overall catalytic cycle of the synthesis is similar to that proposed for the synthesis of *meso*-aryloxy- and alkoxy-substituted porphyrins via palladium-mediated etheration.[6c] As shown in Scheme 2, oxidative addition of bromoporphyrin to Pd(0) center **A** offers porphyrin Pd(II) bromide **B**, which proceeds transmetalation with cesium thiolate to form porphyrin Pd(II) thiolate **C**. Reductive elimination of intermediate **C** gives the desired product and regenerates the active species **A** for another catalytic cycle. Due to the fact that the catalytic reactions proceeded well even for secondary thiols using simple non-electron-rich and nonbulky bidentate DPEphos **A** and BINAP **C**, the porphyrin units might contribute to the success of the catalytic process including prevention of intermediate **C** from β-hydride-elimination side reaction.

(15) For selected applications of thiol-derivatized porphyrins, see: (a) Lu, X.; Lv, B.; Xue, Z.; Zhang, M.; Wang, Y.; Kang, J. *Anal. Lett.* **2002**, *35*, 1811. (b) Imahori, H.; Hasobe, T.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Fukuzumi, S. *Langmuir* **2001**, *17*, 4925. (c) Redman, J. E.; Sanders, J. K. M. *Org. Lett.* **2000**, *2*, 4141. (d) Gryko, D. T.; Clausen, C.; Roth, K. M.; Dontha, N.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7345. (e) Gryko, D. T.; Clausen, C.; Lindsey, J. S. *J. Org. Chem.* **2000**, *64*, 8635. (f) Postlethwaite, T. A.; Hutchison, J. E.; Hathcock, K. W.; Murray, R. W. *Langmuir* **1995**, *11*, 4109. (g) Hutchison, J. E.; Postlethwaite, T. A.; Murray, R. W. *Langmuir* **1993**, *9*, 3277. (h) Zak, J.; Yuan, H.; Ho, M.; Woo, L. K.; Porter, M. D. *Langmuir* **1993**, *9*, 2772.

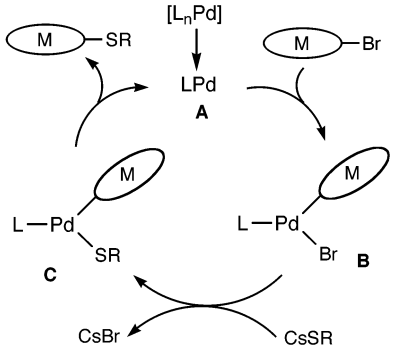
(16) Most of reported examples that applied metal-mediated cross-coupling reactions for porphyrin synthesis employed zinc porphyrins or other metalloporphyrins as the precursors. See refs 4, 5, and 7.

TABLE 4. Palladium-Catalyzed C−S Bond Formation of Zinc Complex of Monobromoporphyrin 1b with Different Thiols[a]

entry	thiols	ligand[b]	temp (°C)	time (h)	yield (%)[c]
1		**A**	100	24	79
2		**A**	100	24	75
3		**A**	100	24	75
4		**A**	100	24	77
5		**A**	100	24	81
6[d]		**C**	100	32	64
7		**A**	100	32	54

[a] Reactions were carried out in toluene under N_2 with 1.0 equiv of **1b**, 4.0 equiv of thiol, 5 mol % $Pd_2(dba)_3$, and 20 mol % ligand in the presence of 2.0 equiv of Cs_2CO_3. Concentration: 0.01 mmol of **1b**/mL of toluene. [b] See Figure 1 for structures of ligands. [c] Yields represent isolated yields. [d] 10 mol % ligand was used.

SCHEME 2. Proposed Catalytic Cycle



Conclusions

In summary, a general and efficient methodology has been developed for the synthesis of *meso*-arylsulfanyl- and alkylsulfanyl-substituted porphyrins from the brominated precursors via palladium-mediated C−S bond formation. Due to ready availability of a variety of thiols and dithiols, this new method will grant access to a family of sulfur-containing porphyrins that could find interesting applications. The similar approach can also be applied for the synthesis of previously unknown *meso*-seleno-substituted porphyrins.

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 thiols 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, **A**) and 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (Xantphos, **B**), (±) BINAP (**C**), dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) ([(dppf)Fe]$PdCl_2$, **D**), 2-(di-*tert*-butylphosphino)biphenyl (**E**), 2-(dicyclohexylphosphino)biphenyl (**F**), 2-dicyclohexylphosphino-2′-(*N,N*-di-methylamino)biphenyl (**G**), *racemic*-2-(di-*tert*-butylphosphino)-1,1′-binaphthyl (**I**), triphenylphosphine (**J**), and 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (**K**) were purchased from Strem Chemical Co.; 2-(9-phenanthryl)phenyldicyclohexylphosphine (**H**) was synthesized by literature methods.[17] 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 the literature.[3,5b,e,f]

General Procedures for Synthesis of *meso*-Sulfanyl-Substituted Porphyrin and Zinc(II) Complex. 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 (10−20 mol %), bromoporphyrin (0.05 mmol), and base (2.0−4.0 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 thiol (3.0−4.0 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 being cooled to room temperature, the reaction mixture was diluted with ethyl acetate, washed with water (×3), and concentrated to dryness. The solid residue was purified by flash chromatography.

10-(Naphthalen-1-ylsulfanyl)-5,15-diphenylporphyrin (Table 2, Entry 1). The general procedure was used to couple 5-bromo-10,20-diphenylporphyrin (27.0 mg, 0.05 mmol) with 2-naphthalenethiol (24 mg, 0.15 mmol), using $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) and DPEphos (5.3 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 20 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 1:2) as a purple solid (22.1 mg, 64% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.23 (s, 1H), 10.00 (d, J = 4.8 Hz, 2H), 9.31 (d, J = 4.2 Hz, 2H), 8.99 (d, J = 4.8 Hz, 2H), 8.96 (d, J = 4.8 Hz, 2H), 8.24 (dd, J = 7.5, 1.8 Hz, 4H), 7.79 (m, 6H), 7.61 (d, J = 8.1 Hz, 1H), 7.52 (d, J = 8.7 Hz, 1H) 7.31−7.18 (m, 5H), −2.86 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.4, 141.3, 134.6, 133.7, 132.4, 132.0, 131.6, 131.1, 128.2, 127.9, 127.5, 126.9, 126.3, 125.2, 125.1, 124.5, 120.3, 107.0, 106.8. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 417 (5.29), 513 (4.17), 549 (3.67), 587 (3.73), 642 (3.34). HRMS-EI ($[M]^+$): calcd for $C_{42}H_{28}N_4S$ 620.2035, found 620.2049, with an isotope distribution pattern that is the same as the calculated one.

10-(*o*-Tolylsulfanyl)-5,15-diphenylporphyrin (Table 2, Entry 2). The general procedure was used to couple 5-bromo-10,20-diphenylporphyrin (27.5 mg, 0.05 mmol) with 2-methylbenzenethiol (18.6 mg, 0.15 mmol), using $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) and DPEphos (5.3 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 20 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 1:2) as a purple solid (21.9 mg, 68% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.20 (s, 1H), 9.86 (d, J = 4.8 Hz, 2H), 9.29 (d, J = 4.5 Hz, 2H), 8.96 (d J = 4.8 Hz, 2H), 8.92 (d, J = 4.8 Hz, 2H), 8.21 (d, J = 7.2, 1.8 Hz, 4H), 7.78 (m, 6H), 7.26 (d, J = 7.5 Hz, 1H), 6.84 (t, J = 7.5 Hz, 1H), 6.41 (t, J = 7.65 Hz, 1H), 5.93 (d, J = 8.1 Hz, 1H), 2.91 (s, 3H). −2.89 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.3, 141.4, 134.6, 132.7, 132.3, 131.9, 131.5, 131.3, 129.6, 127.8,

(17) (a) Tomori, H.; Fox, J. M.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 5334−5341. (b) Kaye, S.; Fox, J. M.; Hicks, F. A.; Buchwald, S. L. *Adv. Synth. Catal.* **2001**, *343*, 789−794. (c) Yin, J. J.; Rainka, M. P.; Zhang, X. X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1162−1163.

127.7, 126.8, 126.4, 124.2, 120.2, 106.9, 106.5, 20.4. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 416 (5.25), 514 (4.18), 547 (3.77), 589 (3.85), 641 (3.61). HRMS-MALDI ([M + H]$^+$): calcd for $C_{39}H_{29}N_4S$ 585.2107, found 585.2123, with an isotope distribution pattern that is the same as the calculated one.

10-(4′-Methoxyphenylsulfanyl)-5,15-diphenylporphyrin (Table 2, Entry 3). The general procedure was used to couple 5-bromo-10,20-diphenylporphyrin (27.7 mg, 0.05 mmol) with 4-methoxylbenzenethiol (25 μL, 0.2 mmol), using $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) and 2-(di-*tert*-butylphosphino)-biphenyl (2.9 mg, 0.01 mmol) in the presence of Cs_2CO_3 (37.6 mg, 0.1 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 21 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 4:1) as a purple solid (28.2 mg, 94% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.17 (s, 1H), 10.01 (d, J = 4.8 Hz, 2H), 9.26 (d, J = 4.5 Hz, 2H), 8.96 (d, J = 4.2 Hz, 4H), 8.22 (dd, J = 7.5, 1.8 Hz, 4H), 7.79 (m, 6H), 7.11 (d, J = 8.7 Hz, 2H), 6.56 (d, J = 9.0 Hz, 2H), 3.56 (s, 3H), −2.94 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.5, 141.4, 134.6, 134.2, 132.1, 131.5, 129.0, 127.8, 126.8, 120.2, 114.4, 109.0, 106.7, 55.1. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 415 (5.55), 514 (4.41), 549 (3.82), 588 (3.90), 642 (3.38). HRMS-MALDI ([M + H]$^+$): calcd for $C_{39}H_{29}N_4$ OS 601.2057, found 601.2067, with an isotope distribution pattern that is the same as the calculated one.

10-(4′-Chlorophenylsulfanyl)-5,15-diphenylporphyrin (Table 2, Entry 4). The general procedure was used to couple 5-bromo-10,20-diphenylporphyrin (27.6 mg, 0.05 mmol) with 4-chlorobenzenethiol (22 mg, 0.15 mmol), using $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) and DPEphos (5.3 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 20 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 2:1) as a red solid (23.8 mg, 71% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.22 (s, 1H), 9.89 (d, J = 4.8 Hz, 2H), 9.29 (d, J = 4.5 Hz, 2H), 8.95 (t, J = 4.95 Hz, 4H), 8.21 (dd, J = 7.5, 2.1 Hz, 4H), 7.79 (m, 6H), 6.92 (q, J = 8.1 Hz, 4H), −2.95 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.0, 141.3, 134.6, 132.4, 131.7, 130.6, 128.8, 127.9, 127.6, 126.8, 120.4, 107.1, 106.2. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 416 (5.30), 514 (4.11), 547 (3.60), 587 (3.66), 641 (3.33). HRMS-MALDI ([M + H]$^+$): calcd for $C_{38}H_{26}ClN_4S$ 605.1561, found 605.1546, with an isotope distribution pattern that is the same as the calculated one.

10-Benzylsulfanyl-5,15-diphenylporphyrin (Table 2, Entry 5). The general procedure was used to couple 5-bromo-10,20-diphenylporphyrin (27.0 mg, 0.05 mmol) with phenylmethanethiol (18.6 mg, 0.15 mmol), using $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) and DPEphos (5.3 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene (5 mL) at 80 °C for 24 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 2:1) as a red solid (12.3 mg, 38% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.20 (s, 1H), 9.88 (d, J = 4.8 Hz, 2H), 9.29 (d, J = 4.5 Hz, 2H), 8.96 (d, J = 4.5 Hz, 2H), 8.90 (d, J = 4.2 Hz, 2H), 8.22 (m, 4H), 7.78 (m, 6H), 7.03 (m, 2H), 6.89 (m, 3H), 4.61 (s, 2H), −3.06 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.2, 141.6, 138.0, 134.8, 134.7, 131.6, 131.0, 128.8, 128.2, 127.8, 126.9, 126.8, 120.0, 106.3, 105.2, 48.0. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 406 (5.40), 504 (4.08), 535 (3.58), 577 (3.64), 657 (2.95). HRMS-EI ([M]$^+$): calcd for $C_{39}H_{28}N_4S$ 584.2035, found 584.2033, with an isotope distribution pattern that is the same as the calculated one.

10-Octylsulfanyl-5,15-diphenylporphyrin (Table 2, Entry 6). The general procedure was used to couple 5-bromo-10,20-diphenylporphyrin (27.4 mg, 0.05 mmol) with octane-1-thiol (22 mg, 0.15 mmol), using $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) and DPEphos (5.3 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene (5 mL) at 80 °C for 48 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 2:1) as a red solid (17.5 mg, 52% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.18 (S, 1H), 10.07 (d, J = 4.8 Hz, 2H), 9.28 (d, J = 4.8 Hz, 2H), 8.98 (d, J = 4.8 Hz, 2H), 8.96 (d, J = 4.2 Hz, 2H), 8.24 (m, 4H), 7.79 (m, 6H), 3.44 (t, J = 7.4 Hz, 2H), 1.63−1.10 (m, 12H), 0.76 (t, J = 6.9 Hz, 3H), −3.06 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.6, 134.7, 132.0, 131.4, 127.8, 126.8, 119.9, 112.5, 106.0, 43.6, 31.6, 29.9, 29.1, 28.8, 22.5, 14.0. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 414 (6.11), 511 (4.88), 544 (4.50), 587 (4.47), 642 (4.29). HRMS-EI ([M]$^+$): calcd for $C_{40}H_{38}N_4S$ 606.2817, found 606.2810, with an isotope distribution pattern that is the same as the calculated one.

10-Cyclohexylsulfanyl-5,15-diphenylporphyrin (Table 2, Entry 7). The general procedure was used to couple 5-bromo-10,20-diphenylporphyrin (27.2 mg, 0.05 mmol) with cyclohexanethiol (25 μL, 0.2 mmol), using $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) and (±)-BINAP (6.2 mg, 0.01 mmol) in the presence of Cs_2CO_3 (37.6 mg, 0.1 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 22.5 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 2:3) as a brown solid (19 mg, 66% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.19 (s, 1H), 10.06 (d, J = 4.8 Hz, 2H), 9.29 (d, J = 4.2 Hz, 2H), 8.96 (t, J = 4.35 Hz, 4H), 8.22 (dd, J = 7.5, 2.4 Hz, 4H), 7.79 (m, 6H), 3.53 (m, 1H), 1.91 (d, J = 9.3 Hz, 2H), 1.63 (m, 4H), 1.14 (m, 4H) −3.06 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.6, 134.6, 131.3, 127.7, 126.8, 119.9, 106.0, 54.8, 33.8, 26.1, 25.7. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 416 (5.28), 512 (4.04), 546 (3.53), 586 (3.58), 642 (3.22). HRMS-MALDI ([M + H]$^+$): calcd for $C_{38}H_{33}N_4S$ 577.2420, found 577.2439, with an isotope distribution pattern that is the same as the calculated one.

10-(4′-Acetamidobenezensulfanyl)-5,15-diphenylporphyrin (Table 2, Entry 8). The general procedure was used to couple 5-bromo-10,20-diphenylporphyrin (27.3 mg, 0.05 mmol) with *N*-(4-mercaptophenyl)acetamide (33.4 mg, 0.2 mmol), using $Pd(OAc)_2$ (1.1 mg 0.005 mmol) and Xantphos (5.8 mg, 0.01 mmol) in the presence of Cs_2CO_3 (37.6 mg, 0.1 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 24 h. The title compound was isolated via flash chromatography (silica gel, methylene chloride/ethyl acetate = 9.5:0.5) as red solid (19 mg, 61% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.17 (s, 1H), 9.89 (d, J = 4.8 Hz, 2H), 9.25 (d, J = 4.2 Hz, 2H), 8.93 (d, J = 4.8 Hz, 2H), 8.91 (d, J = 4.8 Hz, 2H), 8.18 (d, J = 7.5 Hz, 4H), 7.76 (m, 6H), 7.02 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 6.81 (s, 1H), 1.93 (s, 3H), −2.96 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 141.3, 138.9, 135.0, 134.6, 132.3, 132.0, 127.9, 127.5, 126.9, 120.4, 120.3, 117.3, 106.9, 24.4. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 416 (5.47), 514 (4.31), 550 (3.72), 588 (3.79), 642 (3.22). HRMS-MALDI ([M + H]$^+$): calcd for $C_{40}H_{30}N_5OS$ 628.2166, found: 628.2148, with an isotope distribution pattern that is the same as the calculated one.

10-(Benzothiazol-2-ylsulfanyl)-5,15-diphenylporphyrin (Table 2, Entry 9). The general procedure was used to couple 5-bromo-10,20-diphenylporphyrin (27.4 mg, 0.05 mmol) with benzothiazole-2-thiol (25 mg, 0.15 mmol), using $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) and DPEphos (5.3 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 20 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 3:1) as a purple solid (26.7 mg, 77% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.17 (s, 1H), 9.94 (d, J = 4.8 Hz, 2H), 9.23 (d, J = 4.8 Hz, 2H), 8.97 (d, J = 4.8 Hz, 2H), 8.94 (d, J = 4.8 Hz, 2H), 8.18 (m, 4H), 7.96 (d, J = 8.4 Hz, 1H), 7.78 (m, 6H), 7.32 (t, J = 6.9 Hz, 1H), 7.06−6.97 (m, 2H), −2.93 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.3, 153.5, 141.1, 135.9, 134.6, 132.9, 131.9, 131.2, 128.0, 126.9, 126.0, 123.8, 121.8, 120.9, 120.6, 108.0, 103.0. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 418 (5.36), 514 (4.28), 547 (3.70), 585 (3.75), 640 (3.10). HRMS-EI ([M]$^+$): calcd for $C_{39}H_{25}N_5S_2$ 627.1551, found 627.1542, with an isotope distribution pattern that is the same as the calculated one.

10-(Propane-3-thiol)sulfanyl-5,15-diphenylporphyrin (Table 2, Entry 10). The general procedure was used to couple 5-bromo-10,20-diphenylporphyrin (27.5 mg, 0.05 mmol)

with propane-1,3-dithiol (40.2 μL, 0.40 mmol), using $Pd_2(dba)_3$ (1.2 mg 0.00125 mmol) and 2-(di-*tert*-butylphosphino)biphenyl (2.98 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 24.5 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 1:1) as a purple solid (19.8 mg, 70% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.18 (s, 1H), 10.03 (d, J = 4.8 Hz, 2H), 9.28 (d, J = 4.5 Hz, 2H), 8.99 (d, J = 4.8 Hz, 2H), 8.96 (d, J = 4.8 Hz, 2H), 8.22 (m, 4H), 7.80 (m, 6H), 3.53 (t, J = 7.4 Hz, 2H), 2.58 (q, J = 7.3 Hz, 2H), 1.78 (t, J = 7.0 Hz, 2H), −3.05 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.5, 134.8, 134.6, 131.7, 131.4, 127.8, 126.8, 120.0, 106.3, 41.4, 33.7, 23.4. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 415 (5.24), 512 (4.00), 545 (3.41), 587 (3.46), 646 (3.33). HRMS-EI ([M]$^+$): calcd for $C_{35}H_{28}N_4S_2$ 568.1755, found 568.1756, with an isotope distribution pattern that is the same as the calculated one.

10-Phenylselanyl-5,15-diphenylporphyrin (Table 2, Entry 11). The general procedure was used to couple 5-bromo-10,20-diphenylporphyrin (27.2 mg, 0.05 mmol) with benzeneselenol (24 mg, 0.15 mmol), using $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) and DPEphos (5.3 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene (5 mL) at 60 °C for 24 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 2:1) as a red solid (16.8 mg, 49% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.20 (s, 1H), 10.05 (d, J = 4.8 Hz, 2H), 9.29 (d, J = 4.5 Hz, 2H), 8.98 (d, J = 4.5 Hz, 2H), 8.94 (d J = 4.8 Hz, 2H), 8.22 (m, 4H), 7.78 (m, 6H), 7.17 (m, 2H), 6.95 (m, 3H), −3.06 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.5, 141.3, 137.4, 134.6, 134.2, 132.1, 131.5, 129.3, 129.0, 127.8, 126.9, 126.8, 125.6, 120.2, 106.6, 105.5. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 415 (6.02), 512 (4.88), 545 (4.32), 586 (3.43), 640 (4.05). HRMS-EI ([M]$^+$): calcd for $C_{38}H_{26}N_4Se$ 618.1326, found 618.1314, with an isotope distribution pattern that is the same as the calculated one.

5,15-Bis(2′-methylphenylsulfanyl)-10,20-diphenylporphyrin (Table 3, Entry 1). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31 mg, 0.05 mmol) with 2-methylbenzenethiol (47 μL, 0.4 mmol), using $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) and DPEphos (10.6 mg, 0.02 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 27 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 3:2) as a purple solid (25 mg, 71% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.74 (d, J = 4.8 Hz, 4H), 8.80 (d, J = 4.8 Hz, 4H), 8.15 (dd, J = 7.5, 1.5 Hz, 4H), 7.74 (m, 6H), 7.24 (d, J = 7.2 Hz, 2H), 6.86 (t, J = 7.5 Hz, 2H), 6.43 (t, J = 7.8 Hz, 2H), 5.96 (d, J = 8.1 Hz, 2H), 2.89 (s, 6H), −2.57 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.9, 141.4, 134.6, 134.5, 133.0, 131.6, 130.0, 128.0, 127.8, 126.8, 126.7, 126.4, 124.4, 121.2, 108.8, 20.4. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ) 421 (5.36), 523 (4.38), 563 (4.28), 599 (4.14), 657 (4.12). HRMS-MALDI ([M + H]$^+$): calcd for $C_{46}H_{35}N_4S_2$ 707.2298, found 707.2327, with an isotope distribution pattern that is the same as the calculated one.

5,15-Bis(4′-methoxyphenylsulfanyl)-10,20-diphenylporphyrin (Table 3, Entry 2). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31 mg, 0.05 mmol) with 4-methoxybenzenethiol (50 μL, 0.4 mmol), using $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) and DPEphos (10.6 mg, 0.02 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 27 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 4:1) as a purple solid (32 mg, 87% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.87 (d, J = 4.5 Hz, 4H), 8.81 (d, J = 4.8 Hz, 4H), 8.14 (dd, J = 7.5, 1.5 Hz, 4H), 7.75 (m, 6H), 7.11 (d, J = 8.4 Hz, 4H), 6.56 (d, J = 9.0 Hz, 4H), 3.58 (s, 6H), −2.67 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.5, 134.6, 134.4, 132.8, 129.3, 127.9, 126.7, 121.1, 114.5, 55.1. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 426 (5.31), 525 (4.20), 565 (4.09), 601 (3.84), 658 (3.84). HRMS-MALDI ([M + H]$^+$): calcd for $C_{46}H_{35}N_4O_2S_2$ 739.2196, found 739.2164, with an isotope distribution pattern that is the same as the calculated one.

5,15-Bis(4′-chlorophenylsulfanyl)-10,20-diphenylporphyrin (Table 3, Entry 3). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31 mg, 0.05 mmol) with 4-chlorobenzenethiol (57.8 mg, 0.4 mmol), using $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) and (±)−BINAP (6.2 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 24.5 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 2:3) as a purple solid (27 mg, 72% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.79 (d, J = 4.8 Hz, 4H), 8.83 (d, J = 4.8 Hz, 4H), 8.15 (d, J = 6.3 Hz, 4H), 7.76 (m, 6H), 6.89−6.98 (m, 8H), −2.69 (s, 2H). UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 421 (6.09), 522 (4.97), 558 (4.80), 600 (4.63), 656 (4.63). HRMS-MALDI ([M + H]$^+$): calcd for $C_{44}H_{29}Cl_2N_4S_2$ 747.1205, found 747.1201, with an isotope distribution pattern that is the same as the calculated one.

5,15-Bis(propylsulfanyl)-10,20-diphenylporphyrin (Table 3, Entry 4). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31 mg, 0.05 mmol) with 1-propanethiol (35.8 μL, 0.4 mmol), using $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) and (±)−BINAP (6.2 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 24 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 2:3) as a purple solid (23 mg, 75% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.93 (d, J = 4.8 Hz, 4H), 8.86 (d, J = 4.8 Hz, 4H), 8.19 (dd, J = 8.1, 1.8 Hz, 4H), 7.78 (m, 6H), 3.38 (t, J = 7.2 Hz, 4H), 1.54 (m, 4H), 0.92 (t, J = 7.2 Hz, 6H), −2.79 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.6, 134.5, 127.9, 126.8, 126.7, 45.3, 23.3, 13.4. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 421 (5.75), 521 (4.48), 559 (4.27), 599 (4.02), 655 (3.99). HRMS-MALDI ([M + H]$^+$): calcd for $C_{38}H_{35}N_4S_2$ 611.2298, found 611.2289, with an isotope distribution pattern that is the same as the calculated one.

5,15-Bis(cyclohexylsulfanyl)-10,20-diphenylporphyrin (Table 3, Entry 5). The general procedure was used to couple 5,15-dibromo-10,20-diphenylporphyrin (31 mg, 0.05 mmol) with cyclohexylmercaptan (49 μL, 0.4 mmol), using $Pd_2(dba)_3$ (4.6 mg 0.005 mmol) and (±)−BINAP (6.2 mg, 0.01 mmol) in the presence of Cs_2CO_3 (65.2 mg, 0.2 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 24 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 2:3) as a purple solid (25.5 mg, 74% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.94 (d, J = 4.5 Hz, 4H), 8.86 (d, J = 4.8 Hz, 4H), 8.20 (dd, J = 7.5, 1.5 Hz, 4H), 7.78 (m, 6H), 3.50 (m, 2H), 1.90 (d, J = 11.7 Hz, 4H), 1.45−1.68 (m, 8H), 1.07 (m, 8H) −2.79 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.9, 134.6, 134.5, 127.9, 126.8, 126.7, 120.6, 112.3, 54.8, 33.8, 26.1, 25.7. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 421 (6.17), 522 (4.91), 560 (4.72), 599 (4.49), 655 (4.44). HRMS-MALDI ([M + H]$^+$): calcd for $C_{44}H_{43}N_4S_2$ 691.2924, found 691.2947, with an isotope distribution pattern that is the same as the calculated one.

[10-(2′-Methylphenylsulfanyl)-5,15-diphenylporphinato]zinc(II) (Table 4, Entry 1). The general procedure was used to couple [5-bromo-10,20-diphenylporphinato]zinc(II) (30.2 mg, 0.05 mmol) with 2-methylbenzenethiol (24 μL, 0.2 mmol), using $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) and DPEphos (5.3 mg, 0.01 mmol) in the presence of Cs_2CO_3 (37.6 mg, 0.1 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 24 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 3:2) as a red solid (25.5 mg, 79% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.14 (s, 1H), 9.81 (d, J = 4.8 Hz, 2H), 9.29 (d, J = 4.2 Hz, 2H), 8.98 (d, J = 4.8 Hz, 2H), 8.94 (d, J = 4.8 Hz, 2H), 8.18 (m, 4H), 7.76 (m, 6H), 7.22 (d, J = 7.5 Hz, 1H), 6.79 (t, J = 7.5 Hz, 1H), 6.35 (t, J = 7.8 Hz, 1H) 5.85 (d, J = 8.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.7, 150.6, 149.3, 142.3, 134.6, 134.5, 132.4, 132.3, 132.1, 131.7, 129.5, 127.6, 127.5, 126.6, 126.2, 124.0, 121.0,

107.8, 20.4. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 417 (4.97), 545 (4.13). HRMS-MALDI ($[M]^+$): calcd for $C_{39}H_{26}N_4SZn$ 648.1146, found 648.1082, with an isotope distribution pattern that is the same as the calculated one.

[10-(4′-Methoxyphenylsulfanyl)-5,15-diphenylporphinato]zinc(II) (Table 4, Entry 2). The general procedure was used to couple [5-bromo-10,20-diphenylporphinato]zinc(II) (30.2 mg, 0.05 mmol) with 4-methoxybenzenethiol (25 μL, 0.2 mmol), using $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) and DPEphos (5.3 mg, 0.01 mmol) in the presence of Cs_2CO_3 (37.6 mg, 0.1 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 24 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 4:1) as a red solid (25 mg, 75% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.1 (s, 1H), 9.99 (d, J = 4.5 Hz, 2H), 9.26 (d, J = 4.8 Hz, 2H), 8.97 (d, J = 4.8 Hz, 2H), 8.96 (d, J = 4.8 Hz, 2H), 8.16 (dd, J = 8.1, 1.8 Hz, 4H), 7.78 (m, 6H), 7.04 (d, J = 9.0 Hz, 2H), 6.45 (d, J = 8.7 Hz, 2H), 3.46 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.6, 150.6, 149.3, 142.3, 134.5, 133.2, 132.6, 132.4, 132.0, 129.0, 127.6, 126.6, 114.4, 107.6, 55.1. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 419 (5.55), 548 (4.36). HRMS-MALDI ($[M]^+$): Calcd for $C_{39}H_{26}N_4OSZn$ 664.1095, found 664.1030, with an isotope distribution pattern that is the same as the calculated one.

[10-(4′-Chlorophenylsulfanyl)-5,15-diphenylporphinato]zinc(II) (Table 4, Entry 3). The general procedure was used to couple [5-bromo-10,20-diphenylporphinato]zinc(II) (30.2 mg, 0.05 mmol) with 4-chlorobenzenethiol (28.4 mg, 0.2 mmol), using $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) and DPEphos (5.3 mg, 0.01 mmol) in the presence of Cs_2CO_3 (37.6 mg, 0.1 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 24 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 4:1) as a red solid (25 mg, 75% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.0 (s, 1H), 9.83 (d, J = 4.8 Hz, 2H), 9.19 (d, J = 4.8 Hz, 2H), 8.94 (t, J = 4.8 Hz, 4H), 8.12 (dd, J = 6.9, 1.2 Hz, 4H), 7.76 (m, 6H), 6.90 (d, J = 9.0 Hz, 2H), 6.83 (d, J = 9.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.3, 150.6, 150.5, 149.2, 142.3, 142.1, 134.5, 133.4, 132.4, 132.1, 130.4, 128.7, 127.6, 126.6, 121.1, 107.8. UV-*vis*, CH_2Cl_2, λ_{max}, nm (Log ϵ): 419 (6.07), 547 (4.92). HRMS-MALDI ($[M + H]^+$): calcd for $C_{38}H_{23}ClN_4SZn$ 668.0596, found 668.0550, with an isotope distribution pattern that is the same as the calculated one.

[10-Propylsulfanyl-5,15-diphenylporphinato]zinc(II) (Table 4, Entry 4). The general procedure was used to couple [5-bromo-10,20-diphenylporphinato]zinc(II) (30.2 mg, 0.05 mmol) with 1-propanethiol (18 μL, 0.2 mmol), using $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) and DPEphos (5.4 mg, 0.01 mmol) in the presence of Cs_2CO_3 (37.6 mg, 0.1 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 24 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 4:1) as a red solid (23 mg, 77% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.07 (d, J = 4.8 Hz, 2H), 10.02 (s, 1H), 9.21 (d, J = 4.2 Hz, 2H), 9.01 (d, J = 4.8 Hz, 2H), 8.94 (d, J = 4.5 Hz, 2H), 8.17 (dd, J = 6.9, 1.2 Hz, 4H), 7.78 (m, 6H), 3.39 (t, J = 7.2 Hz, 2H), 1.56 (dd, J = 7.2 Hz, 2H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.3, 150.5, 150.2, 149.3, 142.5, 134.5, 132.7, 132.5, 132.3, 131.8, 127.5, 126.5, 120.7, 106.9, 45.3, 23.3, 13.4. UV-*vis*, CH_2Cl_2, λ_{max}, nm (Log ϵ): 418 (5.61), 547 (4.36). HRMS-MALDI ($[M]^+$): calcd for $C_{35}H_{26}N_4SZn$ 598.1164, found 598.1159, with an isotope distribution pattern that is the same as the calculated one.

[10-Cyclohexylsulfanyl-5,15-diphenylporphinato]zinc(II) (Table 4, Entry 5). The general procedure was used to couple [5-bromo-10,20-diphenylporphinato]zinc(II) (30.2 mg, 0.05 mmol) with cyclohexanethiol (25 μL, 0.2 mmol), using $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) and DPEphos (5.4 mg, 0.01 mmol) in the presence of Cs_2CO_3 (37.6 mg, 0.1 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 24 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 4:1) as a brown solid (26 mg, 81% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.12 (s, 1H), 10.08 (d, J = 4.8 Hz, 2H), 9.28 (d, J = 4.2 Hz, 2H), 9.02 (d, J = 4.8 Hz, 2H), 8.98 (d, J = 4.8 Hz, 2H), 8.19 (dd, J = 7.5, 1.5 Hz, 4H), 7.76 (m, 6H), 3.53 (m, 1H), 1.90 (d, J = 9.6 Hz, 2H), 1.67 (m, 4H), 1.23−1.48 (m, 2H), 1.08 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.9, 150.5, 149.3, 142.5, 134.6, 134.5, 132.9, 132.5, 132.4, 131.9, 127.5, 126.6, 120.7, 107.0, 54.7, 33.9, 26.1, 25.8. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 417 (6.22), 547 (4.93), 588 (4.11). HRMS-MALDI ($[M]^+$): calcd for $C_{38}H_{30}N_4SZn$ 638.1477, found 638.1466, with an isotope distribution pattern that is the same as the calculated one.

[10-(4′-Acetamidobenezensulfanyl)-5,15-diphenylporphinato]zinc(II) (Table 4, Entry 6). The general procedure was used to couple [5-bromo-10,20-diphenylporphyrinato]zinc-(II) (30.2 mg, 0.05 mmol) with *N*-(4-mercaptophenyl)acetamide (33.4 mg, 0.2 mmol), using $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) and (±)-BINAP((3.12 mg, 0.005 mmol) in the presence of Cs_2CO_3 (37.6 mg, 0.1 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 32 h. The title compound was isolated via flash chromatography (silica gel, methylene chloride/ethyl acetate = 9.5:0.5) as red solid (22 mg, 64% yield). ^{1}H NMR (300 MHz, DMSO): δ 10.40 (s, 1H), 9.90 (d, J = 4.8 Hz, 2H), 9.78 (s, 1H), 9.48 (d, J = 4.2 Hz, 2H), 8.86 (d J = 4.8 Hz, 2H), 8.84 (d, J = 4.8 Hz, 2H), 8.20 (dd, J = 7.5, 1.8 Hz, 4H), 7.82 (m, 6H), 7.26 (d, J = 9.0 Hz, 2H), 7.01 (d, J = 8.7 Hz, 2H), 1.87 (s, 3H). ^{13}C NMR (75 MHz, DMSO): δ 168.1, 153.8, 150.0, 149.9, 149.7, 149.1, 142.3, 140.0, 136.9, 136.7, 134.4, 134.3, 132.8, 132.1, 131.8, 127.6, 126.8, 120.4, 119.7, 23.8. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 421 (5.47), 549 (4.30). HRMS-MALDI ($[M]^+$): calcd for $C_{40}H_{27}N_5OSZn$ 689.1222, found 689.1204, with an isotope distribution pattern that is the same as the calculated one.

[10-(Benzothiazol-2-ylsulfanyl)-5,15-diphenylporphinato]zinc(II) (Table 4, Entry 7). The general procedure was used to couple [5-bromo-10,20-diphenylporphinato]zinc(II) (30.2 mg, 0.05 mmol) with benzothiazole-2-thiol (38.5 mg, 0.2 mmol), using $Pd_2(dba)_3$ (2.3 mg 0.0025 mmol) and DPEphos (5.3 mg, 0.01 mmol) in the presence of Cs_2CO_3 (37.6 mg, 0.1 mmol). The reaction was conducted in toluene (5 mL) at 100 °C for 32 h. The title compound was isolated by flash chromatography (silica gel, CH_2Cl_2/hexanes (v/v) = 4:1) as a brown solid (18.5 mg, 54% yield). ^{1}H NMR (300 MHz, DMSO): δ 10.48 (s, 1H), 9.88 (d, J = 4.8 Hz, 2H), 9.52 (d, J = 4.5 Hz, 2H), 8.90 (d, J = 4.2 Hz, 2H), 8.86 (d, J = 4.8 Hz, 2H), 8.19 (dd, J = 7.8, 1.8 Hz, 4H), 7.83 (m, 6H), 7.38 (t, J = 7.8 Hz, 2H), 7.11 (t, J = 7.2 Hz 2H). ^{13}C NMR (75 MHz, DMSO): δ 153.5, 150.4, 150.0, 149.0, 142.0, 135.2, 134.3, 133.5, 133.2, 131.9, 131.3, 127.8, 126.8, 121.5, 121.1, 109.8, 101.7. UV−vis, CH_2Cl_2, λ_{max}, nm (log ϵ): 418 (5.67), 546 (4.32), 579 (3.84). HRMS-MALDI ($[M]^+$): calcd for $C_{39}H_{23}N_5S_2Zn$ 689.0681, found 689.0643, with an isotope distribution pattern that is the same as the calculated one.

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Supporting Information Available: ^{1}H NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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