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Metal-Free Synthesis of *meso*-Aminoporphyrins through Reduction of *meso*-Azidoporphyrins Generated *in Situ* by Nucleophilic Substitution Reactions of *meso*-Bromoporphyrins

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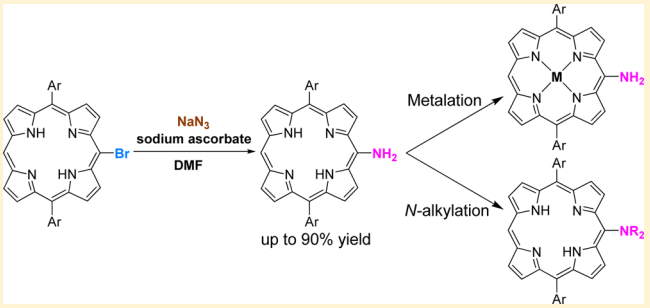
Supporting Information

ABSTRACT: A facile and metal-free method for the preparation of free base *meso*-aminodiarylporphyrins from readily available *meso*-bromodiarylporphyrins is described. Simple treatment of *meso*-bromoporphyrins with sodium azide and sodium ascorbate in DMF affords the corresponding *meso*-aminoporphyrins in very good yields. This method involves the aromatic nucleophilic substitution (S_NAr) of a bromo group with an azido group and the subsequent *in situ* reduction of the introduced azido group by sodium ascorbate. This amination reaction can be scaled up to gram scale without any decrease of the product yield. The amination reaction of free base *meso*-dibromoporphyrin affords a monoaminated product selectively, whereas that of the Ni(II) complex furnishes a diaminated product that is oxidized by air under ambient conditions but isolable as a trifluoroacetyl ester. Metal-insertion reactions of the obtained free base aminoporphyrins afford the corresponding metal complexes (Ni(II), Cu(II), Zn(II), and Pd(II)) all in good yields except the Pd(II) complex. Synthetic methods for the preparation of *N*-mono- or dialkylaminoporphyrins from the free base *meso*-aminoporphyrins have been also established.

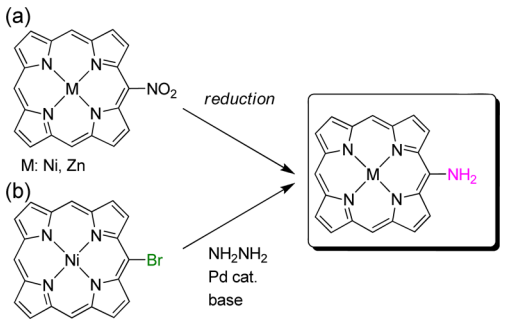


INTRODUCTION

Porphyrins and their metal complexes have been attracting significant attention because they possess characteristic chemical or physicochemical properties, e.g., electronic absorption or redox potential that are derived from their 18π aromaticity. Substituents at the *meso* positions of porphyrins affect the π-electron system of the aromatic ring, thereby changing the properties of porphyrins.[1] Nitrogen substituents (e.g., amino, amido, imido, imino, and azo groups) have been introduced to the porphyrin periphery because of their strong influence on the π-electron system of the porphyrin ring. *meso*-Aminoporphyrins are the simplest nitrogen-substituted porphyrins. In the same manner as anilines, *meso*-aminoporphyrins are useful precursors for the synthesis of nitrogen-substituted porphyrins by various methods (e.g., *N*-alkylation,[2] amide or imide formation,[2,3] imine formation,[4] Sandmeyer-type reaction,[5] and oxidative dimerization[6]). The oxidative degradation of *meso*-aminooctaethylporphyrins by oxygen has been also investigated by Balch and co-workers.[7]

Despite the synthetic usefulness of *meso*-aminoporphyrins, only a few practical methods are available for their preparation. A typical synthetic method involves the *meso*-nitration of *meso*-unsubstituted porphyrins followed by the reduction of the introduced nitro group with $NaBH_4$–Pd/C or Sn metal (Scheme 1a).[8] However, this method is applicable to only

Scheme 1. Reported Procedures for the Synthesis of *meso*-Aminoporphyrins[a]



[a](a) Reduction of nitro group.[8] (b) Palladium-catalyzed amination of *meso*-bromoporphyrin with hydrazine.[9].

octaethylporphyrin or metalated *meso*-di- or triarylporphyrins (e.g., Ni(II) and Zn(II) complexes). The reduction of free base *meso*-nitrodiarylporphyrins results in decomposition under the reaction conditions. Arnold and co-workers reported an alternative method that involved a palladium-catalyzed C–N bond formation reaction (Buchwald–Hartwig reaction) of

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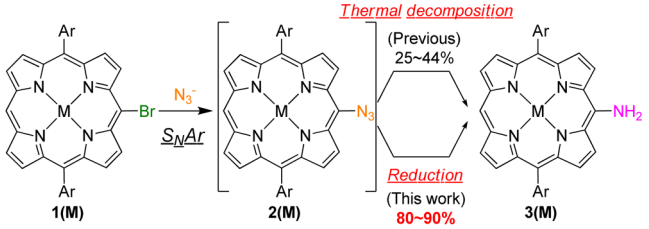
Ni(II) *meso*-bromoporphyrin with hydrazine as the nitrogen source (Scheme 1b).[9] However, the yield of the aminoporphyrin is not sufficiently high (51%) because of undesired side reactions.

We have reported a catalyst-free aromatic nucleophilic substitution (S_NAr) reaction of *meso*-bromodiarylporphyrins **1(M)** with azide anions (Scheme 2).[10,11] The reaction of Ni(II)

Scheme 2. Aromatic Nucleophilic Substitution Reaction of *meso*-Bromodiarylporphyrins 1(M) with Azide Anions, and Their Transformation into *meso*-Aminoporphyrins 3(M).[10]



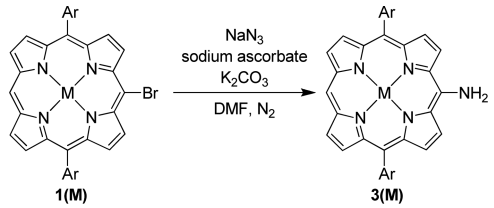
complexes **1(Ni)** with sodium azide in *N*,*N*-dimethylformamide (DMF) affords the corresponding azidoporphyrins **2(Ni)** in high yields, and the structures of **2(Ni)** have been unambiguously elucidated by X-ray crystallography. On the other hand, the reaction of free base porphyrins **1(2H)** results in the rapid thermal decomposition of azides **2(2H)** under the reaction conditions to afford *meso*-aminoporphyrins **3(2H)** and a few uncharacterized products. In this reaction, the yield of **3(2H)** is lower than 50%. We anticipated that **3(2H)** might be obtained without any byproducts by reducing the introduced azide groups *in situ* quickly before the thermal decomposition takes place. Based on this idea, we modified the reaction conditions to establish a novel synthetic method for the preparation of *meso*-aminoporphyrins **3(M)** including free base porphyrins.

RESULTS AND DISCUSSION

Amination Reactions of *meso*-Bromodiarylporphyrins 1(M). Initially, the reaction conditions for the amination of *meso*-bromodiarylporphyrin **1a(2H)** were optimized to improve the yield of *meso*-aminoporphyrin **3a(2H)** (Table 1). In our previous attempt,[10] **1a(2H)** was treated with 10 equiv of sodium azide in DMF at 60 °C under N_2 (entry 1). Those conditions afforded **3a(2H)** in 44% yield as well as a few uncharacterized byproducts in considerable yields. ^{1}H NMR measurement of the byproducts indicated loss of the characteristic 18π aromaticity. We speculated that the byproducts might be formed as oxidized products of **2a(2H)** together with the reduced product (i.e., **3a(2H)**) by thermal decomposition of **2a(2H)**. This result prompted us to examine the reaction in the presence of a reducing agent to form **3a(2H)** selectively.

We found that sodium ascorbate was an effective reducing agent for the *in situ* reduction of **2a(2H)**.[12] In fact, the reactions in the presence of sodium ascorbate improved the yield of **3a(2H)** (entries 2−5). The addition of 10 equiv of sodium ascorbate led to the almost complete disappearance of the byproducts, indicated by TLC and ^{1}H NMR analyses of the crude product (entry 5). In this condition, **3a(2H)** was obtained in the highest yield (89%). Moreover, we found that the combination of sodium L-ascorbate and K_2CO_3 was more

Table 1. Amination Reactions of *meso*-Bromodiarylporphyrins 1(M) Mediated by Azide Anion under Various Conditions[a]



entry	1(M)	equiv of sodium ascorbate	equiv of K_2CO_3	temp (°C)	time (h)	yield[b] (%)
1[c]	**1a(2H)**			60	2.5	44[d]
2	**1a(2H)**	1		60	2.5	66[d]
3	**1a(2H)**	2		60	2.5	68[d]
4	**1a(2H)**	5		60	2.5	82[d]
5	**1a(2H)**	10		60	2.5	89
6	**1a(2H)**	2	5	60	2.5	89
7	**1a(2H)**		10	60	2.5	43[d]
8	**1b(2H)**	2	5	60	3	86
9[c]	**1a(Ni)**			90	3	33[d]
10	**1a(Ni)**	10		90	2.5	84
11	**1a(Ni)**	2	5	90	2.5	83
12	**1a(Cu)**	2	5	90	3	90
13	**1a(Pd)**	2	5	90	3	96

[a]Reaction conditions: **1(M)** 10 mM, NaN_3 (10 equiv) in DMF under N_2 atmosphere with protection from light. Reaction was monitored by TLC. [b]Isolated yields. [c]Ref 10. [d]Green byproducts were also obtained.

effective than sodium ascorbate alone presumably because its reducing ability was increased in basic media.[13] Use of only 2 equiv of sodium ascorbate in the presence of 5 equiv of K_2CO_3 gave a comparable yield of **3a(2H)** (entry 6). By contrast, K_2CO_3 alone did not seem to affect the reaction (entry 7). Likewise, the reaction of *meso*-bromodiphenylporphyrin **1b(2H)** also gave **3b(2H)** in 86% yield (entry 8).

Because we had previously reported the central metal dependence of the azidation reaction,[10] we examined the amination reactions of metalated bromoporphyrins **1a(M)**. As has been previously described, the azidation reaction of **1a(Ni)** is significantly faster than that of free base analogue **1a(2H)**. However, the complete conversion of intermediate Ni(II)-azidoporphyrin **2a(Ni)** requires a high reaction temperature (90 °C) (entry 9).[10] Similar to the reaction of the free base analogues, the addition of sodium ascorbate led to a significant improvement of the yield of **3a(Ni)** (entries 10 and 11). The reaction of Cu(II)- and Pd(II)-bromoporphyrins **3a(Cu)** and **3a(Pd)** also afforded the corresponding products in very good yields (entries 12 and 13). We did not perform the reaction of **1a(Zn)** because **1a(Zn)** was less reactive toward the nucleophilic substitution, as described previously.[10]

It is worth noting that all additives and DMF are easily removed by washing the reaction mixture with water after the completion of the reaction. Furthermore, the amination reaction could be scaled up without any decrease of the yield. For example, the use of 2.20 g (2.48 mmol) of **1a(2H)** provided **3a(2H)** in 86% isolated yield.

Amination Reactions of *meso*-Dibromodiarylporphyrins 4(M). With the optimized conditions in hand, the amination reaction of 5,15-dibromodiarylporphyrin **4(2H)**

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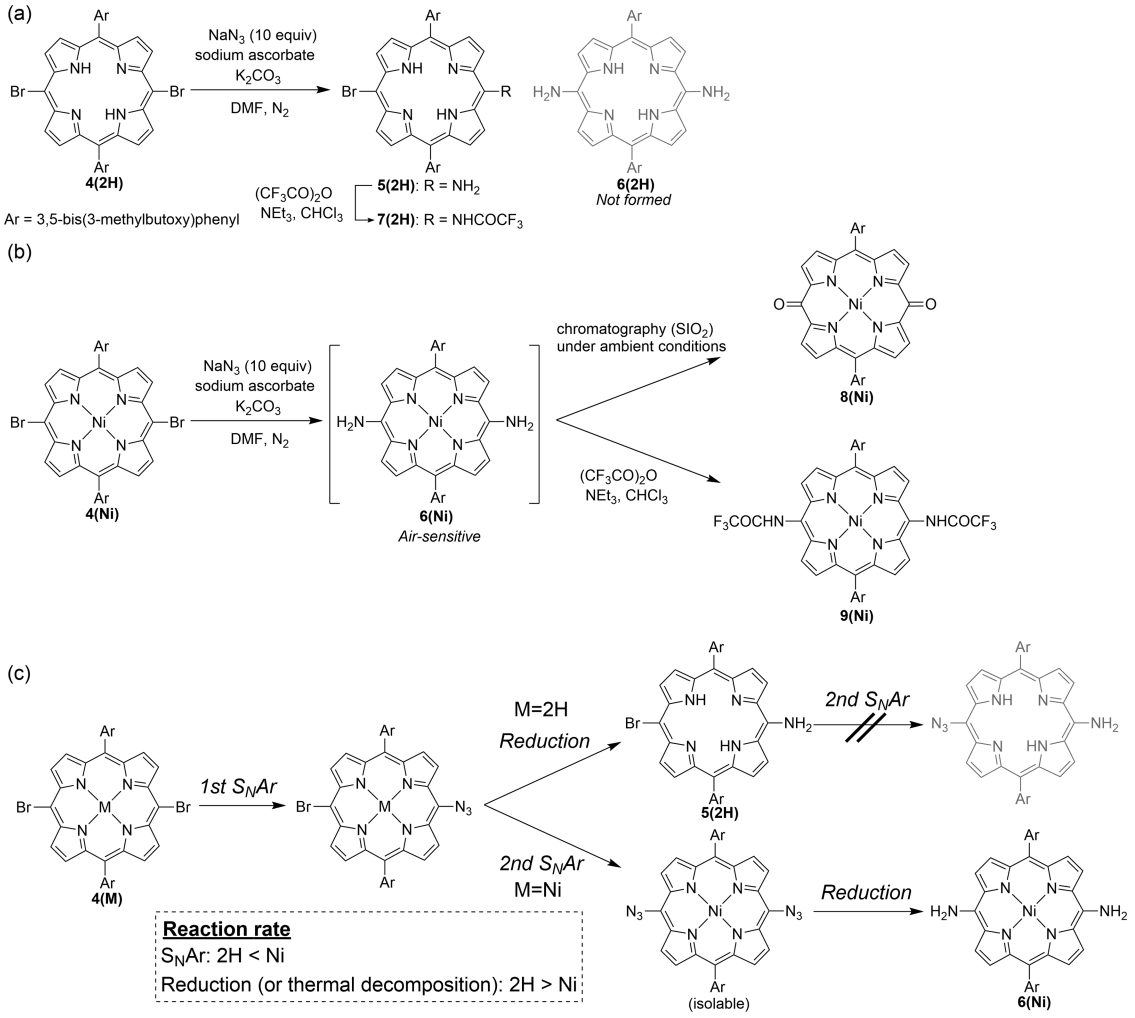
Scheme 3. Amination Reactions of *meso*-Dibromodiarylporphyrin 4(M) Mediated by Azide Anion[a]



[a](a) M = 2H. (b) M = Ni. (c) Plausible reaction mechanism.

was examined (Scheme 3a). Interestingly, monoaminated porphyrin **5(2H)** was preferentially obtained in 80% yield, whereas diaminated product **6(2H)** was not obtained at all in those conditions. Because **5(2H)** was slowly degraded even under ambient conditions, crude **5(2H)** was treated with trifluoroacetic anhydride to afford more stable trifluoroacetamide **7(2H)** in 72% yield (two steps).

The amination reaction of Ni(II) complex **4(Ni)** afforded a different product from that of **4(2H)** (Scheme 3b). The sole product was not **5(Ni)** but green diaminated porphyrin **6(Ni)**, which was moderately stable in solution or the solid state but was readily oxidized by air during purification by silica gel column chromatography to afford quinone compound **8(Ni)**.[14] We were not able to obtain sufficient identification data for **6(Ni)** because its ^{1}H NMR spectrum displayed severely broadened signals. Thus, crude **6(Ni)** was successfully converted into stable brown bis(trifluoroacetamide) **9(Ni)** in 81% yield (two steps from **4(Ni)**).

A plausible reaction mechanism for the amination reaction of **4(M)** is shown in Scheme 3c. As described above, the order of the reactivity for the S_NAr reaction is Ni > 2H (free base) whereas that for the reduction (or thermal decomposition) of the azide groups is the opposite. Thus, free base monoazide undergoes reduction of the azide groups faster than the second S_NAr reaction. Furthermore, the introduced amino group on product **5(2H)** strongly decreases the reactivity toward further S_NAr reaction because of the strong electron-donating nature of the introduced amino group. On the other hand, Ni monoazide undergoes the second S_NAr reaction to afford diazidoporphyrin faster than the reduction of the azide group. We previously isolated and unambiguously characterized the diazidoporphyrin.[10] Then, the diazidoporphyrin undergoes the reduction to afford diaminoporphyrin **6(Ni)**.

Metal-Insertion Reactions of Free Base *meso*-Aminoporphyrin 3a(2H). To establish the usefulness of free base aminoporphyrins as a precursor for the synthesis of several nitrogen-substituted porphyrins and their complexes, we first performed the metal-insertion reactions of **3a(2H)**. Complexation of free base aminoporphyrin **3a(2H)** with Ni(II), Cu(II) or Zn(II) ion through typical metal-insertion procedures afforded corresponding metal complexes **3a(Ni)**, **3a(Cu)**, or **3a(Zn)** in acceptable yields (Scheme 4). By contrast, treatment of **3a(2H)** with Pd(II) ion in $CHCl_3$ afforded **3a(Pd)** in only 7% yield and considerable amounts of insoluble black byproducts presumably because of the strong association of the Pd(II) ion with the amino groups and/or the porphyrin macrocycles.

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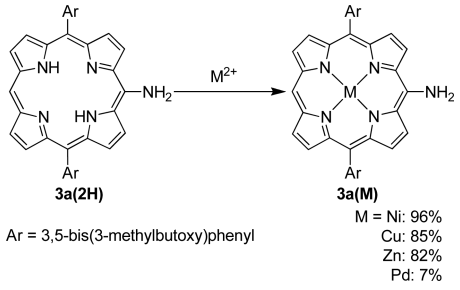
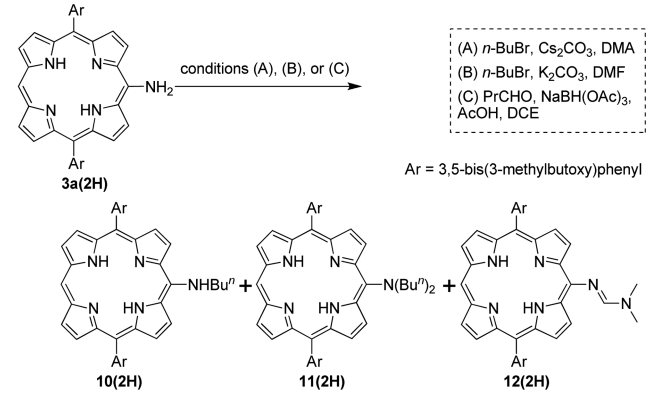
Scheme 4. Complexation of *meso*-Aminoporphyrin 3a(2H) with Ni(II), Cu(II), Zn(II), and Pd(II) ions[a]



[a]Reaction conditions: $Ni(acac)_2$ (10 equiv), toluene, reflux, 6.5 h for **3a(Ni)**; $Cu(OAc)_2·H_2O$ (10 equiv), $CHCl_3$/MeOH (10:1), rt, 0.5 h for **3a(Cu)**; $Zn(OAc)_2·2H_2O$ (10 equiv), $CHCl_3$/MeOH (10:1), rt, 1 h for **3a(Zn)**; $Pd(OAc)_2$ (3 equiv), $CHCl_3$, rt, 0.75 h for **3a(Pd)**.

Alkylation Reactions of Amino Group on Free Base *meso*-Aminoporphyrin 3a(2H). Surprisingly, there have been only a few reports on the alkylation reactions of *meso*-aminoporphyrins[2] whereas the reactions of *meso*-haloporphyrins with alkylamine, which afford *meso*-(*N*-alkylamino)-porphyrins, have been considerably investigated.[11,15] Therefore, we next examined the alkylation of the amino group on **3a(2H)**. When **3a(2H)** was treated with 4 equiv of 1-bromobutane in the presence of Cs_2CO_3 in *N*,*N*-dimethylacetamide (DMA) at 60 °C, *N*-monobutylated product **10(2H)** and *N*,*N*-dibutylated product **11(2H)** were obtained in 66% and 5% yields, respectively (Scheme 5, condition (A)). The use

Scheme 5. Alkylation Reaction of Aminoporphyrin 3a(2H)



of 1-iodobutane significantly decreased the yields of **10(2H)** and **11(2H)** because of the progress of undesired alkylation reactions of the inner NH on the porphyrin ring. Interestingly, the use of DMF as solvent resulted in an unexpected condensation reaction between **3a(2H)** and DMF to afford *N*,*N*-dimethylformamidine **12(2H)** in 36% yield along with **10(2H)** and **11(2H)** (Scheme 5, condition (B)). The structure of **12(2H)** was unambiguously elucidated by NMR, HR-MS, and X-ray crystallography (Figure 1). As far as we know, this type of condensation reactions between amines and DMF has been rarely reported.[16,17] To understand this condensation reaction, **3a(2H)** was treated with only K_2CO_3 in DMF. In this condition, no products were obtained, indicating that the presence of alkyl halide is essential to form **12(2H)**. The

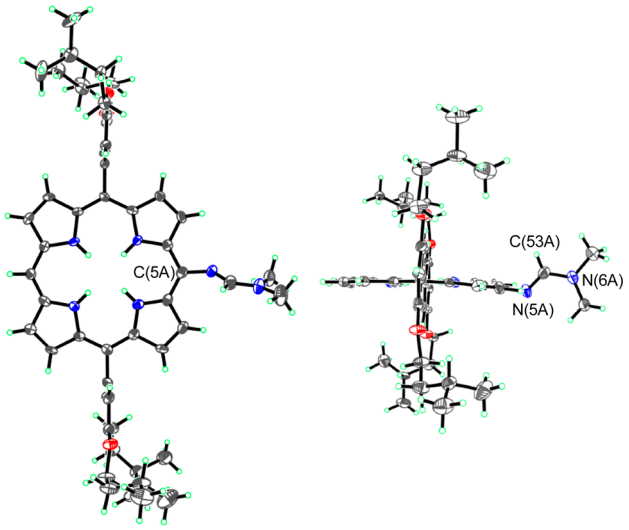


Figure 1. Crystal structure of **12(2H)** (C = black, H = green, N = blue, and O = red). Thermal ellipsoids are drawn at 50% probability level. Two crystallographically independent molecules with similar structural parameters are found in the asymmetric unit, and only one molecule is represented. Two inner NH protons are statistically disordered. Selected bond lengths (Å) and angles (deg): C(5A)–N(5A) 1.398(7), N(5A)–C(53A) 1.256(7), C(53A)–N(6A) 1.341(8), C(5A)–N(5A)–C(53A) 119.1(5), N(5A)–C(53A)–N(6A) 119.9(5).

reaction of DMF and alkyl halide might afford an iminium salt (Vilsmeier–Haack reagent),[17,18] which might be subsequently reacted with the amino group on **3a(2H)** to form *N*,*N*-dimethylformamidine.[17,19] The selective formation of **11(2H)** was achieved by the reductive *N*-alkylation reaction. Treatment of **3a(2H)** with 10 equiv of butanal in the presence of $NaBH(OAc)_3$ and acetic acid in 1,2-dichloroethane (DCE) afforded **11(2H)** in 92% yield (Scheme 5, condition (C)).

Structure Elucidation of *meso*-Aminoporphyrin 3a(M). The crystal and molecular structures of **3a(M)** (M = 2H, Ni, Cu, and Pd) were elucidated by X-ray crystallographic analysis. Purple crystals of **3a(2H)**, **3a(Ni)**, **3a(Cu)**, and **3a(Pd)** were grown by slowly diffusing methanol vapor into chloroform solutions of **3a(2H)**, **3a(Ni)**, **3a(Cu)**, and **3a(Pd)** in the dark. Crystallographic data for **3a(M)** are summarized in Table 2. All compounds crystallize in monoclinic space group $P2_1/n$ with almost identical unit cell parameters. Thus, only the molecular structure of **3a(2H)** is illustrated in Figure 2, and those of the other crystals are illustrated in Supporting Information. An NH_2 group is statistically disordered at the two *meso* positions of the porphyrin core, and there is no hydrogen bonding with the neighboring molecules. The characteristic structural differences among **3a(M)** are the $N_{amine}–C_{meso}$ bond distance and the out-of-plane displacement of the N_{amine} atom from the least-squares plane defined by 24 porphyrin core atoms (Δ_{24}). The data are shown in Table 3. Both $N_{amine}–C_{meso}$ bond distance and $N_{amine}\cdots\Delta_{24}$ distance tend to increase in the order Cu > 2H > Ni > Pd, and this order is consistent with the electronegativities of the central metals. Similar trends have emerged for the reported structure of aminoporphyrins.[7b,c,9] Although DFT calculations were performed to clarify the central metal dependence, the optimized structures were not consistent with the experimental ones; e.g., the calculated $N_{amine}–C_{meso}$ distances are 1.384–1.395 Å regardless of the central metal (Table S2). The results would suggest that the

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Table 2. Selected Crystallographic Data for 3a(2H), 3a(Ni), 3a(Cu), and 3a(Pd)[a]

	3a(2H)	3a(Ni)	3a(Cu)	3a(Pd)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	6.3848(16)	6.3593(10)	6.3352(4)	6.4215(14)
b/Å	20.457(5)	20.462(3)	20.2924(12)	20.520(4)
c/Å	16.933(4)	16.964(3)	17.0320(10)	16.966(4)
β/deg	92.499(5)	92.531(3)	92.3450(10)	92.560(4)
V/Å^3	2209.6(10)	2205.3(6)	2187.7(2)	2233.4(8)
Z	2	2	2	2
D (calcd)/g cm^{-3}	1.236	1.323	1.341	1.378
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0912	R_1 = 0.0776	R_1 = 0.0519	R_1 = 0.0926
	wR_2 = 0.2728	wR_2 = 0.2029	wR_2 = 0.1258	wR_2 = 0.2567
R indices (all data)	R_1 = 0.1633	R_1 = 0.1248	R_1 = 0.0643	R_1 = 0.1271
	wR_2 = 0.3211	wR_2 = 0.2556	wR_2 = 0.1320	wR_2 = 0.2709

[a] $R_1 = \sum||F_0|-|F_c||/\sum|F_0|$, $wR_2 = [\sum[w(F_0^2-F_c^2)^2]/\sum w(F_0^2)^2]^{1/2}$

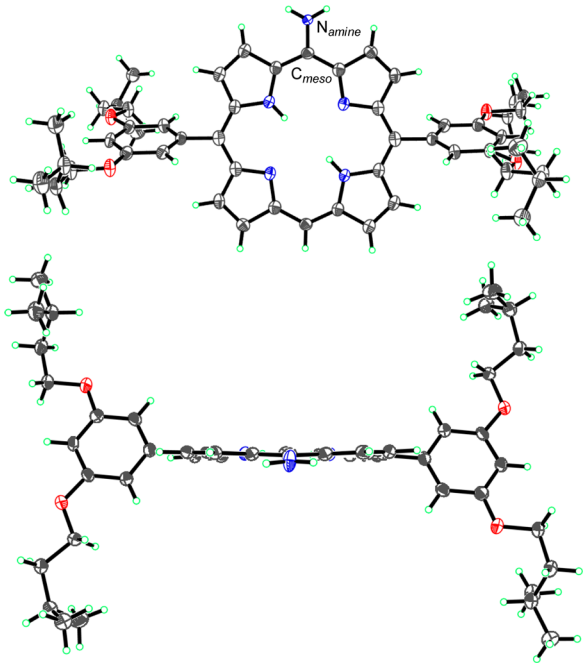

Figure 2. Crystal structure of 3a(2H) (C = black, H = green, N = blue, and O = red). Thermal ellipsoids are drawn at 50% probability level. An NH_2 group is statistically disordered at the two *meso* positions of the porphyrin core, and only one site is represented.

Table 3. Selected Distances (Å) in 3a(2H), 3a(Ni), 3a(Cu), and 3a(Pd)

	3a(2H)	3a(Ni)	3a(Cu)	3a(Pd)
$N_{amine}-C_{meso}$	1.357(8)	1.332(9)	1.427(5)	1.305(15)
$N_{amine}\cdots\Delta_{24}$	0.279	0.149	0.306	0.079

central metal dependence is not a nature of a single molecule but is derived from the electronic interaction between neighboring molecules in the crystal.

Stability of *meso*-Aminoporphyrin 3a(M). Finally, we evaluated the stability of 3a(M) by UV−vis absorption measurement because degradation of *meso*-aminoporphyrins have been reported.[7,20] No UV−vis spectral change was observed when the toluene solution of 1a(M) (M = 2H, Ni, and Cu) was left to stand under ambient room light and air for 50 h (Figures S8−S10). On the other hand, 1a(Zn) is more sensitive to room light under the atmospheric condition (Figure S11). Intense Soret band for 1a(Zn) observed at 429 nm was disappeared within 24 h when a solution of 1a(Zn) was left to stand under room light. No spectral change was observed when the solution of 1a(Zn) was left to stand in the dark under the atmospheric condition. Therefore, we suppose that this degradation involves the oxidation by oxygen.

CONCLUSION

We have established a practical and efficient method for the synthesis of *meso*-aminoporphyrins, which includes the catalyst-free nucleophilic substitution reactions of *meso*-bromodiarylporphyrins with sodium azide in the presence of sodium ascorbate. This method requires no expensive or unstable reagents, and the starting materials, *meso*-bromoporphyrins, are easily available. The reaction of *meso*-bromodiarylporphyrins 1(M) (M = 2H, Ni, Cu, and Pd) afforded corresponding *meso*-aminoporphyrins 3(M) in good yields. On the other hand, the reaction of *meso*-dibromoporphyrins 4(M) (M = 2H and Ni) furnished different products depending on the central metal. Metalation reactions of 3a(2H) afforded corresponding metal complexes 3a(M) in quantitative yields except for palladium. We also established a selective *N*-mono- or dialkylation reaction of the amino group on 3a(2H). The molecular structures of 3a(M) (M = 2H, Ni, Cu, and Pd) were elucidated by X-ray crystallography. We anticipate that this method would contribute the further development of the chemistry of *meso*-aminoporphyrins. We are currently developing the new chemistry of *meso*-aminoporphyrins, and the results will be reported elsewhere.

EXPERIMENTAL SECTION

General Experimental Methods. *N*,*N*-Dimethylformamide (DMF) was distilled over CaH_2. All other chemicals were of reagent grades and used without any further purification. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F_{254} plates. Flash column chromatography was performed using silica gel 60N (spherical, neutral, 40−50 μm). All NMR spectral data were recorded on 500 MHz spectrometers. These data were collected at ambient temperature (25 °C) unless otherwise noted. ^{1}H NMR spectra were referenced internally to tetramethylsilane as a standard. ^{13}C NMR spectra were referenced internally to solvent signals (δ = 77.0 ppm for $CDCl_3$, and δ = 29.8 ppm for acetone-d_6). ^{19}F NMR spectra were referenced internally to $CF_3C_6H_5$ (δ = −63.7 ppm) as a standard. *Caution: Sodium azide and azidoporphyrins are potentially explosive and should be handled with care.*

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*Synthesis of [5-Bromo-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)-porphyrinato]copper(II) (**1a(Cu)**).* A mixture of 5-bromo-10,20-bis[3,5-bis(3-methylbutoxy)phenyl]porphyrin (**1a(2H)**) (88.6 mg, 0.10 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (99.8 mg, 0.50 mmol) in $CHCl_3$ (5 mL) and MeOH (0.5 mL) was stirred at 60 °C for 1 h. The reaction mixture was directly poured on top of a basic alumina column packed with $CHCl_3$, then eluted with $CHCl_3$. The solvent was removed under reduced pressure. The crude product was recrystallized from toluene−hexane to give [5-bromo-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)porphyrinato]copper(II) (**1a(Cu)**) as violet needle crystals (67.6 mg, 0.071 mmol, 71%). MS (MALDI-TOF) *m*/*z*: 945.6. UV−vis (toluene): λ_{max} (Log(ε)) = 416 (5.59), 500 (3.50), 538 (4.29), 570 nm (sh, 3.37). IR (ATR): 2954, 2926, 2869, 1585, 1534, 1463, 1433, 1381, 1347, 1321, 1299, 1289, 1190, 1165, 1150, 1068, 1056, 1027, 996, 982, 939, 834, 806, 786, 730, 694 cm^{-1}. m.p.: 296−297 °C. Anal. Calcd for $C_{52}H_{59}N_4O_4CuBr$: C, 65.92; H, 6.28; N, 5.91. Found: C, 65.81; H, 6.21; N, 5.70.

*Synthesis of [5-Bromo-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)-porphyrinato]palladium(II) (**1a(Pd)**).* A mixture of 5-bromo-10,20-bis[3,5-bis(3-methylbutoxy)phenyl]porphyrin (**1a(2H)**) (44.3 mg, 0.050 mmol) and $Pd(OAc)_2$ (56.1 mg, 0.25 mmol) in $CHCl_3$ (5 mL) and MeOH (0.5 mL) was stirred at 30 °C for 1 h. The reaction mixture was directly poured on top of a silica gel column packed with $CHCl_3$, then eluted with $CHCl_3$. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane: toluene = 1:1, then 1:2), and then recrystallized from CH_2Cl_2−hexane to give [5-bromo-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)porphyrinato]palladium(II) (**1a(Pd)**) as orange needle crystals (33.7 mg, 0.034 mmol, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 10.08 (s, 1H), 9.66 (d, *J* = 4.9 Hz, 2H), 9.15 (d, *J* = 4.8 Hz, 2H), 9.12−9.10 (m, 4H), 7.31 (d, *J* = 2.3 Hz, 4H), 6.90 (t, *J* = 2.3 Hz, 2H), 4.15 (t, *J* = 6.7 Hz, 8H), 1.88 (m, 4H), 1.77 (q, *J* = 6.8 Hz, 8H), 0.98 (d, *J* = 6.6 Hz, 24H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 158.4 (Cq), 142.9 (Cq), 141.85 (Cq), 141.83 (Cq), 141.4 (Cq), 141.1 (Cq), 132.2 (CH), 132.00 (CH), 131.97 (CH), 131.2 (CH), 121.7 (Cq), 114.0 (CH), 107.2 (CH), 105.3 (Cq), 101.2 (CH), 66.8 (CH_2), 38.1 (CH_2), 25.1 (CH), 22.7 (CH_3). MS (MALDI-TOF) *m*/*z*: 988.5. UV−vis (toluene): λ_{max} (Log(ε)) = 415 (5.41), 483 (3.45), 522 (4.40), 553 nm (3.69). IR (ATR): 2954, 2927, 2869, 1587, 1537, 1462, 1434, 1386, 1348, 1302, 1299, 1198, 1163, 1057, 1011, 984, 834, 802, 785, 727, 693 cm^{-1}. m.p.: 280−282 °C. Anal. Calcd for $C_{52}H_{59}N_4O_4PdBr$: C, 63.06; H, 6.00; N, 5.66. Found: C, 63.03; H, 5.93; N, 5.46.

*Synthesis of 5-Amino-10,20-bis[3,5-bis(3-methylbutoxy)phenyl]-porphyrin (**3a(2H)**).* 5-Bromo-10,20-bis[3,5-bis(3-methylbutoxy)-phenyl]porphyrin (**1a(2H)**) (2.199 g, 2.48 mmol), NaN_3 (1.614 g, 24.8 mmol), sodium ascorbate (985 mg, 4.96 mmol), and K_2CO_3 (1.714 g, 12.4 mmol) were mixed in dry DMF (250 mL). The mixture was purged with N_2, and stirred at 60 °C for 3 h with protection from light. The reaction mixture was diluted with $CHCl_3$, washed with water (8 × 400 mL), dried over $MgSO_4$, and concentrated under the reduced pressure. The crude product was purified by flash column chromatography (silica gel, toluene) to give **3a(2H)** as a purple solid (1.753 g, 2.13 mmol, 86%). Analytically pure sample was obtained by recrystallization from ethyl acetate as purple needle crystals (1.644 g, 2.00 mmol, 80%). Spectral data were consistent with the previously reported ones.[10]

*Synthesis of 5-Amino-10,20-diphenylporphyrin (**3b(2H)**).* 5-Bromo-10,20-diphenylporphyrin (**1b(2H)**) (21.65 mg, 0.0400 mmol), NaN_3 (26.0 mg, 0.40 mmol), sodium ascorbate (15.9 mg, 0.080 mmol), and K_2CO_3 (27.6 mg, 0.20 mmol) were mixed in dry DMF (4 mL). The mixture was purged with N_2, and stirred at 60 °C for 3 h with protection from light. The reaction mixture was diluted with $CHCl_3$, washed with water (4 × 10 mL), dried over $MgSO_4$, and concentrated under the reduced pressure. The crude product was purified by flash column chromatography (silica gel, $CHCl_3$) to give **3b(2H)** as a purple solid (16.46 mg, 0.0345 mmol, 86%). Analytically pure sample was obtained by recrystallization from 1,2-dichloroethane as a purple powder. ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ (ppm) = 9.38 (s, 1H), 9.03 (d, *J* = 4.7 Hz, 2H), 8.83 (d, *J* = 4.7 Hz, 2H), 8.63 (d, *J* = 4.7 Hz, 2H), 8.52 (d, *J* = 4.7 Hz, 2H), 8.12 (m, 4H), 7.73−7.70 (m, 6H), 6.38 (s, 2H), − 0.85 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) δ (ppm) = 142.0 (Cq), 134.3 (CH), 132.3 (CH), 132.0 (Cq), 130.4 (CH), 128.4 (CH), 127.6 (CH), 126.9 (CH), 122.2 (CH), 119.6 (Cq), 99.8 (CH). Four signals for pyrrole α carbons were not observed because of the severe exchange broadening due to NH tautomerism. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_{32}H_{24}N_5$ 478.2026; Found 478.2017. UV−vis (toluene): λ_{max} (Log(ε)) = 421 (5.42), 499 (3.57), 532 (3.86), 571 (4.23), 618 (3.56), 676 nm (4.24). IR (KBr): 3308, 3315, 1623, 1593, 1479, 1441, 1401, 1352, 1248, 1174, 1063, 1002, 993, 972, 953, 792, 747, 723, 701, 653 cm^{-1}. m.p.: > 300 °C. Anal. Calcd for $C_{32}H_{23}N_5$: C, 80.48; H, 4.85; N, 14.66. Found: C, 80.74; H, 4.62; N, 14.66.

*Synthesis of [5-Amino-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)-porphyrinato]nickel(II) (**3a(Ni)**).* [5-Bromo-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)porphyrinato]nickel(II) (**1a(Ni)**) (18.89 mg, 0.020 mmol), NaN_3 (13.0 mg, 0.20 mmol), sodium ascorbate (7.9 mg, 0.04 mmol), and K_2CO_3 (13.8 mg, 0.10 mmol) were mixed in dry DMF (2 mL). The mixture was purged with N_2, and stirred at 90 °C for 2.5 h with protection from light. The reaction mixture was diluted with $CHCl_3$, washed with water (5 × 3 mL), dried over $MgSO_4$, and concentrated under the reduced pressure. The crude product was purified by flash column chromatography (silica gel, toluene) to give **3a(Ni)** as a purple solid (14.57 mg, 0.0166 mmol, 83%). Spectral data were consistent with the previously reported ones.[10]

*Synthesis of [5-Amino-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)-porphyrinato]copper(II) (**3a(Cu)**).* [5-Bromo-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)porphyrinato]copper(II) (**1a(Cu)**) (9.53 mg, 0.0101 mmol), NaN_3 (6.5 mg, 0.10 mmol), sodium ascorbate (4.0 mg, 0.020 mmol), and K_2CO_3 (7.2 mg, 0.52 mmol) were mixed in dry DMF (1 mL). The mixture was purged with N_2, and stirred at 90 °C for 3 h with protection from light. The reaction mixture was diluted with $CHCl_3$, washed with water (5 × 3 mL), dried over $MgSO_4$, and concentrated under the reduced pressure. The crude product was purified by flash column chromatography (silica gel, toluene) to give **3a(Cu)** as a violet solid (8.00 mg, 0.0091 mmol, 90%). HRMS (APCI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_{52}H_{62}N_5O_4Cu$ 883.4092; Found 883.4074. UV−vis (toluene): λ_{max} (Log(ε)) = 426 (5.51), 544 (3.90), 556 (3.87), 607 nm (4.21). IR (KBr): 3398, 2957, 2928, 2871, 1599, 1587, 1464, 1432, 1385, 1340, 1290, 1168, 1060, 996, 833, 780, 733, 707, 698 cm^{-1}. m.p.: 252−255 °C. Anal. Calcd for $C_{52}H_{61}N_5O_4Cu$: C, 70.68; H, 6.96; N, 7.93. Found: C, 70.79; H, 7.11; N, 7.86.

*Synthesis of [5-Amino-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)-porphyrinato]palladium(II) (**3a(Pd)**).* [5-Bromo-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)porphyrinato]palladium(II) (**1a(Pd)**) (9.01 mg, 0.0091 mmol), NaN_3 (6.6 mg, 0.10 mmol), sodium ascorbate (4.1 mg, 0.020 mmol), and K_2CO_3 (7.3 mg, 0.053 mmol) were mixed in dry DMF (1 mL). The mixture was purged with N_2, and stirred at 90 °C for 3 h with protection from light. The reaction mixture was diluted with $CHCl_3$, washed with water (5 × 3 mL), dried over $MgSO_4$, and concentrated under the reduced pressure. The crude product was purified by flash column chromatography (silica gel, toluene) to give **3a(Pd)** as a purple solid (8.13 mg, 0.0088 mmol, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 9.58 (s, 1H), 9.09 (d, *J* = 4.8 Hz, 2H), 8.89 (d, *J* = 4.8 Hz, 2H), 8.78 (d, *J* = 4.8 Hz, 2H), 8.73 (d, *J* = 4.8 Hz, 2H), 7.27 (d, *J* = 2.3 Hz, 4H), 6.85 (t, *J* = 2.3 Hz, 2H), 6.21 (brs, 2H), 4.14 (t, *J* = 6.8 Hz, 8H), 1.88 (m, 4H), 1.76 (q, *J* = 6.8 Hz, 8H), 0.98 (d, *J* = 6.6 Hz, 24H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 158.5 (Cq), 143.8 (Cq), 143.4 (Cq), 140.0 (Cq), 139.9 (Cq), 132.7 (Cq), 132.3 (CH), 132.1 (Cq), 130.1 (CH), 128.7 (CH), 122.2 (CH), 121.1 (Cq), 113.5 (CH), 102.4 (CH), 101.0 (CH), 66.7 (CH_2), 38.1 (CH_2), 25.1 (CH), 22.7 (CH_3). HRMS (APCI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{52}H_{62}N_5O_4Pd$ 926.3849; Found 926.3841. UV−vis (toluene): λ_{max} (Log(ε)) = 349 (4.02), 424 (5.39), 531 (3.94), 588 nm (4.15). IR (ATR): 3385, 2956, 2928, 2871, 1587, 1489, 1463, 1433, 1386, 1351, 1292, 1166, 1059, 1011, 1000, 833, 778, 754, 694 cm^{-1}. m.p.: 277−279 °C. Anal. Calcd for $C_{52}H_{61}N_5O_4Pd$: C, 67.41; H, 6.64; N, 7.56. Found: C, 67.38; H, 6.63; N, 7.55.

*Complexation of **3a(2H)** with Ni(II) Ion.* A mixture of 5-amino-10,20-bis[3,5-bis(3-methylbutoxy)phenyl]porphyrin (**3a(2H)**) (117

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mg, 0.142 mmol) and $Ni(acac)_2$ (365 mg, 1.42 mmol) in toluene (5 mL) was heated under reflux for 6.5 h. The reaction mixture was directly poured on top of silica gel column packed with toluene, then eluted with toluene. The solvent was removed under reduced pressure to give **3a(Ni)** as a purple solid (120 mg, 0.136 mmol, 96%). Spectral data were consistent with those for the product obtained by the S_NAr reaction described above.

*Complexation of **3a(2H)** with Cu(II) Ion.* A mixture of 5-amino-10,20-bis[3,5-bis(3-methylbutoxy)phenyl]porphyrin (**3a(2H)**) (41.11 mg, 0.050 mmol) and $Cu(OAc)_2·H_2O$ (99.8 mg, 0.50 mmol) in $CHCl_3$ (1 mL) and MeOH (0.1 mL) was stirred at room temperature for 0.5 h with protection from light. The reaction mixture was directly poured on top of a basic alumina column packed with $CHCl_3$, then eluted with $CHCl_3$. The solvent was removed under reduced pressure. The crude product was recrystallized from toluene-hexane to give [5-amino-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)porphyrinato]-copper(II) (**3a(Cu)**) as violet needle crystals (37.49 mg, 0.042 mmol, 85%). Spectral data were consistent with those for the product obtained by the S_NAr reaction described above.

*Complexation of **3a(2H)** with a Zn(II) Ion.* A mixture of 5-amino-10,20-bis[3,5-bis(3-methylbutoxy)phenyl]porphyrin (**3a(2H)**) (41.11 mg, 0.050 mmol) and $Zn(OAc)_2·2H_2O$ (110 mg, 0.50 mmol) in $CHCl_3$ (1 mL) and MeOH (0.1 mL) was stirred at room temperature for 1 h with protection from light. The reaction mixture was directly poured on top of a basic alumina column packed with $CHCl_3$, then eluted with $CHCl_3$. The solvent was removed under reduced pressure. The crude product was recrystallized from toluene-hexane to give [5-amino-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)porphyrinato]zinc-(II) (**3a(Zn)**) as violet needle crystals (36.25 mg, 0.041 mmol, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 9.50 (s, 1H), 9.00 (d, J = 4.6 Hz, 2H), 8.96 (d, J = 4.6 Hz, 2H), 8.88 (d, J = 4.6 Hz, 2H), 8.75 (d, J = 4.5 Hz, 2H), 7.31 (d, J = 2.3 Hz, 4H), 6.85 (t, J = 2.3 Hz, 2H), 6.17 (brs, 2H), 4.15 (t, J = 6.8 Hz, 8H), 1.88 (m, 4H), 1.77 (q, J = 6.8 Hz, 8H), 0.98 (d, J = 6.6 Hz, 24H). ^{13}C NMR (125 MHz, acetone-d_6) δ (ppm) = 159.4 (*C*q), 154.3 (*C*q), 148.9 (*C*q), 148.2 (*C*q), 146.0 (*C*q), 140.52 (*C*q), 140.49 (*C*q), 133.4 (*C*H), 131.0 (*C*H), 128.7 (*C*H), 123.9 (*C*H), 120.7 (*C*q), 114.4 (*C*H), 101.1 (*C*H), 100.0 (*C*H), 67.3 (CH_2), 38.9 (CH_2), 25.9 (*C*H), 22.9 (CH_3). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{52}H_{62}N_5O_4Zn$ 884.4088; Found 884.4079. UV−vis (toluene): λ_{max} (Log(ε)) = 349 (4.05), 429 (5.62), 517 (sh, 3.48), 555 (3.84), 576 (3.84), 622 nm (4.31). IR (KBr): 3312, 2956, 2929, 2871, 1588, 1463, 1432, 1385, 1347, 1289, 1164, 1064, 995, 847, 782, 703 cm^{-1}. m.p.: 244−246 °C. Anal. Calcd for $C_{52}H_{61}N_5O_4Zn$: C, 70.54; H, 6.94; N, 7.91. Found: C, 70.53; H, 6.97; N, 7.83.

*Complexation of **3a(2H)** with a Pd(II) Ion.* A mixture of 5-amino-10,20-bis[3,5-bis(3-methylbutoxy)phenyl]porphyrin (**3a(2H)**) (8.23 mg, 0.010 mmol) in $CHCl_3$ (1 mL) was added $Pd(OAc)_2$ (6.75 mg, 0.030 mmol). The mixture was purged with N_2, and stirred at room temperature for 45 min with protection from light. The reaction mixture was directly poured on top of a basic alumina column packed with $CHCl_3$, then eluted with $CHCl_3$. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica gel, toluene) to give [5-amino-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)porphyrinato]palladium(II) (**3a(Pd)**) as a purple solid (0.67 mg, 0.00072 mmol, 7%). Spectral data were consistent with those for the product obtained by the S_NAr reaction described above.

*Synthesis of 5-Amino-15-bromo-10,20-bis[3,5-bis(3-methylbutoxy)phenyl]porphyrin (**5(2H)**).* 5,15-Dibromo-10,20-bis-[3,5-bis(3-methylbutoxy)phenyl]porphyrin (**4(2H)**) (19.29 mg, 0.0200 mmol), NaN_3 (13.0 mg, 0.20 mmol), sodium ascorbate (7.9 mg, 0.040 mmol), K_2CO_3 (13.8 mg, 0.10 mmol) were mixed in dry DMF (1 mL). The mixture was purged with N_2, and stirred at 60 °C for 2.5 h with protection from light. The reaction mixture was diluted with $CHCl_3$, washed with water (5 × 4 mL), dried over $MgSO_4$, and concentrated under the reduced pressure. The crude product was purified by flash column chromatography (silica gel, toluene) to give **5(2H)** as a purple solid (14.3 mg, 0.0159 mmol, 79%). This compound was gradually degraded in solution even at room temperature. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 9.20 (d, J = 4.9 Hz, 2H), 8.94 (d, J = 4.7 Hz, 2H), 8.67 (d, J = 4.9 Hz, 2H), 8.56 (d, J = 4.7 Hz, 2H), 7.24 (d, J = 2.2 Hz, 4H), 6.84 (t, J = 2.2 Hz, 2H), 6.36 (s, 2H), 4.13 (t, J = 6.7 Hz, 8H), 1.88 (m, 4H), 1.76 (q, J = 6.8 Hz, 8H), 0.98 (d, J = 6.6 Hz, 24H), − 0.73 (brs, 2H). A clear ^{13}C NMR spectrum was not obtained because of the degradation during the measurement. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{52}H_{62}BrN_5O_4$ 900.4058 and 902.4041; Found 900.4049 and 902.4023.

*Synthesis of 5-Bromo-15-(trifluoroacetamido)-10,20-bis[3,5-bis-(3-methylbutoxy)phenyl]porphyrin (**7(2H)**).* 5,15-Dibromo-10,20-bis-[3,5-bis(3-methylbutoxy)phenyl]porphyrin (**4(2H)**) (19.29 mg, 0.0200 mmol), NaN_3 (13.0 mg, 0.20 mmol), sodium ascorbate (7.9 mg, 0.040 mmol), K_2CO_3 (13.8 mg, 0.10 mmol) were mixed in dry DMF (1 mL). The mixture was purged with N_2, and stirred at 60 °C for 2.5 h with protection from light. The reaction mixture was diluted with $CHCl_3$, washed with water (5 × 4 mL), dried over $MgSO_4$, and concentrated under the reduced pressure. The crude product was dissolved in dry CH_2Cl_2 (2 mL) and triethylamine (85 μL, 0.61 mmol). The solution was cooled to 0 °C, and then trifluoroacetic anhydride (56 μL, 0.40 mmol) was added to the solution. The resultant solution was stirred at 0 °C for 30 min. The resultant solution was washed with water (3 × 4 mL), dried over $MgSO_4$, and concentrated under the reduced pressure. The crude product was purified by flash column chromatography (silica gel, toluene) to give **7(2H)** as a purple solid (14.42 mg, 0.014 mmol, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 9.85 (s, 1H), 9.65 (d, J = 4.7 Hz, 2H), 9.15 (d, J = 4.8 Hz, 2H), 9.02−8.99 (m, 4H), 7.32 (d, J = 2.2 Hz, 4H), 6.91 (t, J = 2.2 Hz, 2H), 4.16 (t, J = 6.7 Hz, 8H), 1.90 (m, 4H), 1.78 (q, J = 6.7 Hz, 8H), 0.99 (d, J = 6.6 Hz, 24H), − 2.84 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) δ (ppm) = 158.4 (q, J = 37 Hz, CF_3CO), 158.7 (*C*q), 142.8 (*C*q), 132.6 (br, 3 × *C*H), 126.9 (br, *C*H), 121.6 (*C*q), 116.9 (q, J = 289 Hz, CF_3), 114.7 (*C*H), 107.3 (*C*q), 105.1 (*C*q), 101.7 (*C*H), 67.0 (CH_2), 38.3 (CH_2), 25.3 (*C*H), 22.7 (CH_3). Four signals for pyrrole α carbons were not observed because of the severe exchange broadening due to NH tautomerism. ^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) = −75.6. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{54}H_{62}BrF_3N_5O_5$ 996.3881 and 998.3865; Found 996.3869 and 998.3868. UV−vis (toluene): λ_{max} (Log(ε)) = 424 (5.52), 486 (3.56), 517 (4.28), 551 (3.78), 596 (3.73), 653 nm (3.41). IR (ATR): 3369, 3326, 2955, 2928, 2870, 1743, 1587, 1506, 1467, 1429, 1384, 1362, 1228, 1162, 973, 924, 903, 830, 800, 791, 779, 733, 716, 692 cm^{-1}. m.p.: 295−296 °C. Anal. Calcd for $C_{54}H_{61}N_5O_5BrF_3$: C, 65.05; H, 6.17; N, 7.02; found: C, 65.21; H, 6.11; N, 6.83.

*Synthesis of [5,15-Dioxo-10,20-bis(3,5-bis(3-methylbutoxy)-phenyl)porphodimethene]nickel(II) (**8(Ni)**).* [5,15-Bibromo-10,20-bis-(3,5-bis(3-methylbutoxy)phenyl)porphyrinato]nickel (**4(Ni)**) (20.43 mg, 0.020 mmol), NaN_3 (13.00 mg, 0.20 mmol), sodium ascorbate (15.85 mg, 0.080 mmol), and K_2CO_3 (27.6 mg, 0.20 mmol) were mixed in dry DMF (2 mL). The mixture was purged with N_2, and stirred at 40 °C for 30 min with protection from light. Then, reaction temperature was raised to 90 °C and stirred for 3 h. The green reaction mixture was diluted with $CHCl_3$, washed with water (5 × 3 mL), dried over $MgSO_4$, and concentrated under the reduced pressure. The green crude product was purified by flash column chromatography (silica gel, toluene). Color of the product was immediately changed from green to brown after loading the crude sample onto the top of the column. The brown fraction was collected, and the solvent was removed under the reduced pressure to give **8(Ni)** as a dark brown solid (16.84 mg, 0.0188 mmol, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 6.54 (d, J = 4.6 Hz, 4H), 6.52 (d, J = 2.2 Hz, 2H), 6.47 (d, J = 2.0 Hz, 4H), 6.31 (d, J = 4.6 Hz, 4H), 3.97 (t, J = 6.7 Hz, 8H), 1.82 (m, 4H), 1.68 (q, J = 6.8 Hz, 8H), 0.96 (d, J = 6.7 Hz, 24H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 178.9 (*C*q), 159.7 (*C*q), 153.6 (*C*q), 152.5 (*C*q), 142.1 (*C*q), 137.1 (*C*q), 133.6 (*C*H), 121.0 (*C*H), 108.1 (*C*H), 102.4 (*C*H), 66.7 (CH_2), 37.9 (CH_2), 25.1 (*C*H), 22.6 (CH_3). APCI HRMS: m/z calcd for $C_{52}H_{59}N_4NiO_6$ ($[M + H]^+$) 893.3783, found 893.3781. UV−vis (toluene): λ_{max} (Log(ε)) = 326 (4.51), 367 (sh, 4.27), 533 (4.25), 670 nm (br, 3.67). IR (ATR): 2954, 2869, 1622, 1589, 1551, 1492, 1463, 1434, 1384, 1345, 1329, 1295,

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1266, 1159, 1052, 1016, 977, 849, 834, 812, 761, 726, 700, 558, 444 cm^{-1}.

*Synthesis of [5,15-Bis(trifluoroacetamido)-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)porphyrinato]nickel(II) (**9(Ni)**).* [5,15-Bibromo-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)porphyrinato]nickel (**4(Ni)**) (20.43 mg, 0.0200 mmol), NaN_3 (13.1 mg, 0.20 mmol), sodium ascorbate (15.8 mg, 0.08 mmol), K_2CO_3 (27.7 mg, 0.20 mmol) were mixed in dry DMF (2 mL). The mixture was purged with N_2, and stirred at 40 °C for 30 min with protection from light. Then, reaction temperature was raised to 90 °C and stirred for 3 h. The green reaction mixture was diluted with $CHCl_3$, washed with water (6 × 3 mL), dried over $MgSO_4$, and concentrated under the reduced pressure. The green crude product was dissolved in CH_2Cl_2 (1.5 mL). Triethylamine (170 μL) was added to the solution, and then the resulting solution was cooled to 0 °C. Trifluoroacetic anhydride (42 μL, 0.30 mmol) was added to the solution. The resultant solution was stirred at 0 °C for 1.5 h. The resultant purple solution was diluted with $CHCl_3$, washed with water (4 × 3 mL), dried over $MgSO_4$, and concentrated under the reduced pressure. The crude product was purified by flash column chromatography (silica gel, toluene) to give **9(Ni)** as a reddish purple solid (17.61 mg, 0.0162 mmol, 81%). Analytically pure **9(Ni)** was obtained by recrystallization from cyclohexane as red needle crystals. ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ (ppm) = 9.29 (brs, 2H), 8.85 (d, J = 5.0 Hz, 4H), 8.75 (d, J = 5.0 Hz, 4H), 7.01 (d, J = 2.2 Hz, 4H), 6.82 (t, J = 2.2 Hz, 2H), 4.10 (t, J = 6.7 Hz, 8H), 1.87 (m, 4H), 1.75 (q, J = 6.7 Hz, 8H), 0.98 (d, J = 6.7 Hz, 24H). ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) δ (ppm) = 158.8 (Cq), 158.4 (q, J = 37 Hz, CF_3CO), 143.5 (Cq), 141.5 (Cq), 141.4 (Cq), 133.9 (CH), 127.9 (CH), 120.5 (Cq), 116.7 (q, J = 289 Hz, CF_3), 113.9 (CH), 108.4 (Cq), 101.8 (CH), 67.1 (CH_2), 38.2 (CH_2), 25.3 (CH), 22.6 (CH_3). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{56}H_{61}F_6N_6NiO_6$ 1085.3905; Found 1085.3897. UV−vis (toluene): λ_{max} (Log(ε)) = 414 (5.34), 529 (4.19), 562 nm (4.07). IR (ATR): 3285, 2957, 2872, 1733, 1589, 1520, 1464, 1429, 1386, 1362, 1313, 1294, 1229, 1212, 1186, 1133, 1057, 1009, 950, 909, 950, 909, 830, 789, 731, 700, 680, 649, 567, 511 cm^{-1}. m.p.: > 300 °C. Anal. Calcd for $C_{56}H_{60}F_6N_6NiO_6$: C, 61.95; H, 5.57; N, 7.74. Found: C, 62.21; H, 5.55; N, 7.82.

*N-Alkylation of **3a(2H)** by the Nucleophilic Substitution Reaction (Condition A).* To a solution of 5-amino-10,20-bis[3,5-bis(3-methylbutoxy)phenyl]porphyrin (**3a(2H)**) (32.85 mg, 0.040 mmol) and Cs_2CO_3 (39.0 mg, 0.12 mmol) in *N*,*N*-dimethylacetamide (2 mL) was added 1-bromobutane (17 μL, 0.16 mmol). The mixture was purged with N_2, and stirred at 60 °C for 6 h with protection from light. The reaction mixture was diluted with $CHCl_3$, washed with water (5 × 5 mL), dried over $MgSO_4$, and concentrated under the reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane/toluene = 1:10). The second purple fraction was collected to give *N*-monobutylated porphyrin **10(2H)** as a purple solid (23.16 mg, 0.026 mmol, 66%). The first faction contained *N*,*N*-dibutylated porphyrin **11(2H)** (2.04 mg, 0.0021 mmol, 5%).

*N-Alkylation of **3a(2H)** by the Nucleophilic Substitution Reaction (Condition B).* To a solution of 5-amino-10,20-bis[3,5-bis(3-methylbutoxy)phenyl]porphyrin (**3a(2H)**) (16.48 mg, 0.020 mmol) and K_2CO_3 (8.30 mg, 0.06 mmol) in *N*,*N*-dimethylformamide (1 mL) was added 1-bromobutane (8.6 μL, 0.080 mmol). The mixture was purged with N_2, and stirred at 60 °C for 48 h with protection from light. The reaction mixture was diluted with $CHCl_3$, washed with water (5 × 4 mL), dried over $MgSO_4$, and concentrated under the reduced pressure. The crude product was purified by flash column chromatography (silica gel, toluene). The first, second, third, and fourth fractions contained *N*,*N*-disubstituted porphyrin **11(2H)** (0.48 mg, 0.00051 mmol, 3%), *N*-monobutylated porphyrin **10(2H)** (6.31 mg, 0.0072 mmol, 33%), **3a(2H)** (1.96 mg, 0.0024 mmol, 12%), and formamidine **12(2H)** (5.77 mg, 0.0066 mmol, 36%), respectively.

*N,N-Dialkylation of **3a(2H)** by the Reductive Alkylation Reaction (Condition C).* To a solution of 5-amino-10,20-bis[3,5-bis(3-methylbutoxy)phenyl]porphyrin (**3a(2H)**) (16.48 mg, 0.020 mmol) in 1,2-dichloroehtane (2 mL) was added 1-butanal (18 μL, 0.20 mmol) and AcOH (0.1 mL). The resulting mixture was stirred at room temperature for 30 min with protection from light. $NaBH(OAc)_3$ (42.4 mg, 0.20 mmol) was added, and the resulting mixture was stirred at room temperature for 3 h. The reaction mixture was washed with saturated $NaHCO_3$ aq. and water. The organic layer was dried over $MgSO_4$, and concentrated under the reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane/toluene = 1:1) to give **11(2H)** as a purple solid (17.19 mg, 0.018 mmol, 92%).

*Physical Properties of 5-(N-Butylamino)-10,20-bis[3,5-bis(3-methylbutoxy)phenyl]porphyrin (**10(2H)**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 9.59 (s, 1H), 9.20 (d, J = 4.7 Hz, 2H), 8.99 (d, J = 4.7 Hz, 2H), 8.88 (d, J = 4.7 Hz, 2H), 8.78 (d, J = 4.7 Hz, 2H), 7.33 (d, J = 2.2 Hz, 4H), 6.87 (t, J = 2.3 Hz, 2H), 6.11 (brs, 1H), 4.37 (t, J = 7.3 Hz, 2H), 4.16 (t, J = 6.8 Hz, 8H), 2.03 (m, 2H), 1.89 (m, 4H), 1.77 (q, J = 6.8 Hz, 8H), 1.63 (m, 2H), 1.02−0.99 (m, 27H), − 1.72 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) δ (ppm) = 158.6 (Cq), 148.2 (Cq), 145.8 (Cq), 145.4 (Cq), 143.7 (Cq), 142.2 (Cq), 133.0 (Cq), 132.0 (CH), 130.3 (CH), 129.0 (CH), 125.1 (CH), 119.4 (Cq), 114.4 (CH), 101.3 (CH), 101.0 (CH), 66.9 (CH_2), 58.3 (CH_2), 38.3 (CH_2), 34.0 (CH_2), 25.2 (CH), 22.6 (CH_3), 20.5 (CH_2), 14.0 (CH_3). HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{56}H_{72}N_5O_4$ 878.5579; Found 878.5574. UV−vis (toluene): λ_{max} (Log(ε)) = 424 (5.45), 522 (3.94), 571 (4.01), 671 nm (3.88). IR (ATR): 3309, 2954, 2929, 2869, 1739, 1586, 1465, 1428, 1384, 1346, 1154, 1060, 924, 827, 775, 733, 690 cm^{-1}. m.p.: 149−151 °C. Anal. Calcd for $C_{56}H_{71}N_5O_4$: C, 76.59; H, 8.15; N, 7.97. Found: C, 76.41; H, 8.14; N, 7.92.

*Physical Properties of 5-(N,N-Dibutylamino)-10,20-bis[3,5-bis(3-methylbutoxy)phenyl]porphyrin (**11(2H)**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 10.01 (s, 1H), 9.53 (d, J = 4.7 Hz, 2H), 9.21 (d, J = 4.7 Hz, 2H), 9.03 (d, J = 4.7 Hz, 2H), 8.96 (d, J = 4.7 Hz, 2H), 7.39 (d, J = 2.2 Hz, 4H), 6.90 (t, J = 2.3 Hz, 2H), 4.30 (t, J = 7.8 Hz, 4H), 4.18 (t, J = 6.8 Hz, 8H), 1.90 (m, 4H), 1.83−1.76 (m, 12H), 1.36 (m, 4H), 0.99 (d, J = 6.6 Hz, 24H), 0.80 (t, J = 7.4 Hz, 6H), − 2.87 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) δ (ppm) = 158.6 (Cq), 143.8 (Cq), 131.4 (Cq and CH), 130.7 (CH), 130.2 (CH), 129.5 (CH), 119.1 (Cq), 114.7 (CH), 103.7 (CH), 101.3 (CH), 67.0 (CH_2), 62.0 (CH_2), 38.3 (CH_2), 32.5 (CH_2), 25.3 (CH), 22.7 (CH_3), 20.7 (CH_2), 14.0 (CH_3). Four signals for pyrrole α carbons were not observed because of the severe exchange broadening due to NH tautomerism. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{60}H_{80}N_5O_4$ 934.6205; Found 934.6202. UV−vis (toluene): λ_{max} (Log(ε)) = 416 (5.34), 510 (4.14), 584 (3.74), 643 nm (3.20). IR (ATR): 3316, 2950, 2921, 2867, 1638, 1586, 1464, 1433, 1362, 1348, 1239, 1166, 1087, 1059, 994, 963, 925, 836, 795, 779, 739, 695 cm^{-1}. m.p.: 136−139 °C. Anal. Calcd for $C_{60}H_{79}N_5O_4$: C, 77.13; H, 8.52; N, 7.50. Found: C, 77.03; H, 8.53; N, 7.45.

*Physical Properties of 5-[(N,N-dimethylamino)methyleneamino]-10,20-bis[3,5-bis(3-methylbutoxy)phenyl]porphyrin (**12(2H)**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 9.76 (s, 1H), 9.26 (d, J = 4.6 Hz, 2H), 9.09 (d, J = 4.6 Hz, 2H), 8.96 (d, J = 4.6 Hz, 2H), 8.86 (d, J = 4.6 Hz, 2H), 7.94 (s, 1H), 7.36 (d, J = 2.3 Hz, 4H), 6.88 (t, J = 2.3 Hz, 2H), 4.16 (t, J = 6.7 Hz, 8H), 3.62 (brs, 3H), 3.35 (brs, 3H), 1.89 (m, 4H), 1.78 (q, J = 6.8 Hz, 8H), 0.98 (d, J = 6.6 Hz, 24H), − 2.14 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 159.3 (CH), 158.5 (Cq), 143.8 (Cq), 136.2 (Cq), 131.7 (CH), 130.4 (CH), 129.0 (CH), 127.9 (CH), 119.1 (Cq), 114.2 (CH), 101.4 (CH), 101.0 (CH), 66.7 (CH_2), 40.6 (CH_3), 38.1 (CH_2), 35.3 (CH_3), 25.1 (CH), 22.7 (CH_3). Four signals for pyrrole α carbons were not observed because of the severe exchange broadening due to NH tautomerism. HRMS (APCI-TOF) m/z: $[M+H]^+$ Calcd for $C_{55}H_{69}N_6O_4$ 877.5375; Found 877.5371. UV−vis (toluene): λ_{max} (Log(ε)) = 424 (5.53), 526 (3.97), 566 (4.17), 601 (3.57), 658 nm (3.98). IR (ATR): 3318, 2957, 2929, 2868, 1739, 1587, 1460, 1433, 1379, 1347, 1292, 1237, 1167, 1060, 994, 963, 925, 845, 833, 803, 781, 738, 694 cm^{-1}. m.p.: 166−168 °C. Anal. Calcd for $C_{55}H_{68}N_6O_4$: C, 75.31; H, 7.81; N, 9.58; Found. C, 75.03; H, 7.78; N, 9.31.

X-ray Crystal Structure Determinations. Single-crystal X-ray diffraction data for **3a(M)** (M = 2H, Ni, Cu, and Pd) and **12(2H)** were collected on a Bruker Smart APEX CCD diffractometer with a

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cryostat system equipped with a N_2 generator (Japan Thermal Eng. Co. Ltd.) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) by the ω scan mode. Diffraction data were collected at −180 °C. The program SAINT was used for integration of the diffraction profiles. Empirical absorption corrections were applied by using the SADABS program. The structures were solved by direct methods (SHELXS97) and refined by full-matrix least-squares calculations on F^2 (SHELXL97)[21] using the SHELXTL program package (Version 6.10). All non-hydrogen atoms were modeled anisotropically. Hydrogen atoms were fixed at calculated positions and refined with a riding model.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02159.

UV−vis absorption spectra, summary of DFT calculation, and copies of ^{1}H and ^{13}C NMR of new compounds (PDF)

X-Ray crystallographic data for **3a(2H)**, **3a(Ni)**, **3a(Cu)**, **3a(Pd)**, and **12(2H)** (CIF)

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Notes

The authors declare no competing financial interest.

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