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PALLADIUM-CATALYZED CROSS-COUPLING REACTIONS OF BROMINATED PORPHYRINS WITH FUNCTIONALIZED ORGANOMAGNESIUM REAGENTS: DIRECT PREPARATION OF FUNCTIONAL-GROUP-BEARING FREE BASE PORPHYRINS

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Abstract – The direct preparation of free-base porphyrins possessing reactive functional groups such as esters, halides, amide, nitriles, and acetals is described. This method relies on a simple one-pot procedure that involves sequential palladium-catalyzed cross-coupling of brominated free-base porphyrins with functionalized aryl and alkenylmagnesium reagents, which are readily prepared by iodine–magnesium exchange of the corresponding organic iodides with the turbo Grignard reagent *i*-PrMgCl·LiCl, followed by demetallation of the resulting magnesium porphyrins under very mild conditions involving either a 1.2 M aqueous methanol solution of HCl or a 0.1 M methanol solution of citric acid at ambient temperature.

INTRODUCTION

Porphyrins are becoming increasingly important target structures since compounds of this class have found widespread use in many fields[1] including catalysis,[2] medicine,[3] materials,[4] and molecular recognition/sensing.[5] The physical, chemical, and biological properties of porphyrins can be fine-tuned or dramatically changed by the selection of the peripheral substituents having different electronic and steric properties and by the central metal ions coordinated to the nitrogen core.[1] Accordingly, significant interest has arisen in developing new synthetic intermediates and strategies for preparing porphyrin derivatives that possess various peripheral substituents.[6,7] In a related contribution, we previously reported an approach to prepare functionalized porphyrins via palladium-catalyzed Negishi cross-coupling of bromoporphyrins **H_2-1** with functional-group-bearing organozinc reagents **2** (Scheme 1).[8] The functionalized zinc porphyrin products **Zn-3** of the reaction, where the peripheral substituents of

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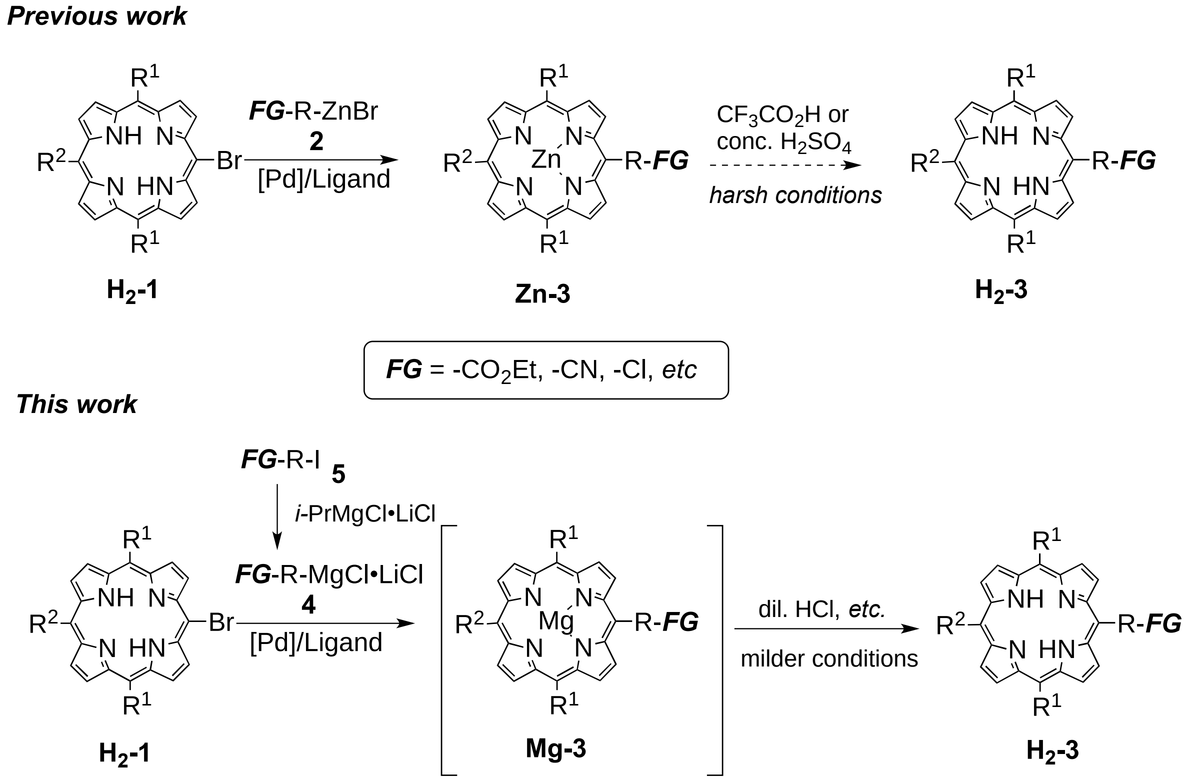
This work is dedicated to Professor Dr. Lutz F. Tietze on the occasion of his 75th birthday.



Scheme 1. Preparation of functional-group-bearing free-base porphyrins

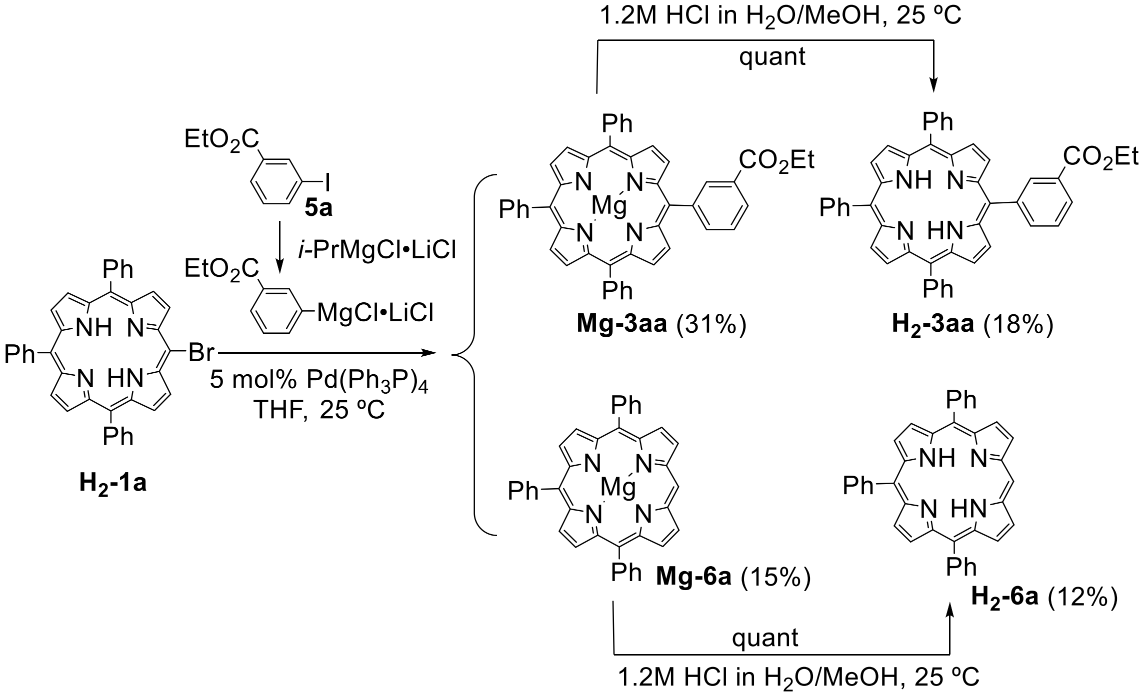
Zn-3 bear chemically reactive function- alities such as ester, amide, halogen, and nitrile groups, could serve as synthetic intermediates for more complicated porphyrin derivatives because these reactive functional groups can provide a convenient handle for further functionalization. However, when the desired product is not zinc porphyrin complexes but other metalloporphyrins, multiple chemical transformations are necessary to remove the central zinc metal from **Zn-3** or its zincated derivatives and install other metals into the resulting free base. In addition, the demetallation of zinc porphyrins typically requires the use of strong acidic conditions such as those afforded by CF_3CO_2H and conc. H_2SO_4, which might lead to undesired decomposition of the substrates. Therefore, from the perspective of synthetic divergence and step economy, functional-group-bearing free-base porphyrins **H_2-3**, a demetallated analog of zinc porphyrins **Zn-3**, would be more attractive as an efficient and versatile synthetic intermediate in the construction of complicated porphyrin derivatives. The use of these free-base porphyrins **H_2-3** as a synthetic building block for the construction of complex porphyrin derivatives should enable the insertion of desired metal ions even in the case of the late-stage functionalization of porphyrins in a multistep synthetic sequence in order to avoid involving a dezincation process under harsh conditions. Despite recent significant advances in the transition-metal-catalyzed porphyrin functionalization with organometallic reagents, a majority of the reported methods afford metallated porphyrins, such as zinc(II), nickel(II), and copper(II) porphyrins, as the products even when free-base porphyrins are used as starting substrates.[6-9] Thus, a novel, mild, and direct method that can provide functional-group-bearing free-base porphyrins including **H_2-3** remains in demand.

Recently, Knochel's aryl and alkenylmagnesium reagents **4**, which are readily prepared in situ from the corresponding aryl and alkenyl iodides with the turbo Grignard reagent *i*-PrMgCl·LiCl, have garnered considerable interest in synthetic chemistry because of their high synthetic potential on the basis of their facile availability and significant functional tolerability.[10] However, despite their numerous elegant applications in laboratory synthesis and up-scaled industrial processes, to the best of our knowledge, the literature contains no account of the functionalization of porphyrins utilizing these organomagnesium reagents **4**.[7] We expected that the transition-metal-catalyzed cross-coupling reaction of halogenated free-base porphyrin **H_2-1** with a functionalized organomagnesium reagent **4** would initially provide the corresponding functionalized magnesium porphyrin **Mg-3** (Scheme 1). Unlike zinc, nickel, and copper porphyrins,[11] magnesium porphyrins are highly sensitive toward acidic conditions.[9,12,13] Therefore, the resulting magnesium complex **Mg-3** would be easily transformed into the corresponding free-base porphyrins **H_2-3** under very mild conditions without destruction of the acid-sensitive peripheral functional groups.

Here, we present an efficient, direct method for preparing functional-group-bearing free-base porphyrins **H_2-3** via a simple one-pot procedure involving palladium-catalyzed cross-coupling reaction of brominated free-base porphyrins **H_2-1** with functionalized aryl and alkenylmagnesium reagents **4**, followed by demetallation of the resulting magnesium porphyrins **Mg-3** under very mild acidic conditions using either a 1.2 M aqueous methanol solution of HCl or a 0.1 M methanol solution of citric acid at ambient temperature. The exceptional mildness of these reaction conditions offers high functional tolerability to the present method, thereby providing the desired free-base porphyrins **H_2-3** bearing reactive functional groups such as esters, nitriles, amides, silyls, and acetals in good to high yields.

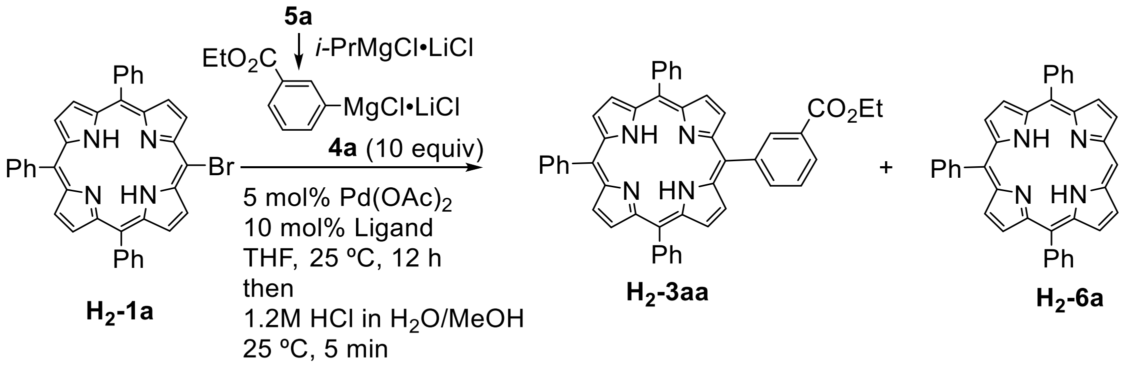
RESULTS AND DISCUSSION

In a preliminary experiment, we examined the cross-coupling of 5-bromo-10,15,20-triphenylporphyrin **H_2-1a** with 3-(ethoxycarbonyl)phenylmagnesium chloride lithium chloride **4a**, which was generated by a metallation of ethyl 3-iodobenzoate **5a** using the turbo Grignard reagent *i*-PrMgCl·LiCl, in the presence of $Pd(Ph_3P)_4$ as a catalyst in THF at 25 °C (Scheme 2). Upon completion of the reaction, the mixture was concentrated in vacuo and chromatographed on silica gel to give the desired *meso*-functionalized free-base porphyrin **H_2-3aa** along with the debrominated free base **H_2-6a** and their magnesium complexes **Mg-3aa** and **Mg-6a**. These magnesium complexes **Mg-3aa** and **Mg-6a** were quantitatively transformed to the corresponding free bases **H_2-3aa** and **H_2-6a** by hydrolysis upon treatment with a 1.2 M aqueous



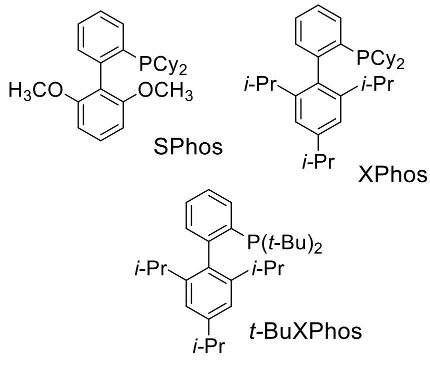
Scheme 2. Palladium-catalyzed coupling of free-base bromoporphyrins **H$_2$-1** with functionalized arylmagnesium reagents **4a** and demagnesiation of **Mg-3aa** and **Mg-6a** with a 1.2 M aqueous methanol solution of HCl

Table 1. Ligand screening for the Pd(OAc)$_2$-catalyzed coupling of *meso*-bromoporphyrin **H$_2$-1a** with functionalized arylmagnesium reagent **4a**



entry	ligand	yield[a] (%) of **H$_2$-3aa**	yield[a] (%) of **H$_2$-6a**
1	*rac*-BINAP	27	61
2	Cy$_3$P	38	58
3	(*t*-Bu)$_3$P	51	38
4	Ph$_3$P	45	49
5	SPhos	75	21
6	XPhos	62	24
7	*t*-BuXPhos	83	12

[a] Isolated yield.



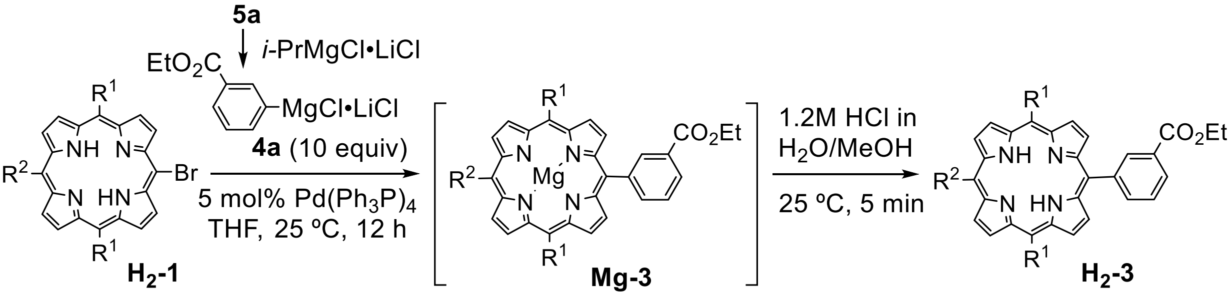
methanol solution of HCl. As expected, these cross-coupling and demetallation processes could be conducted in a one-pot manner. Thus, the sequential one-pot treatment of *meso*-bromoporphyrin **H_2-1a** with 10 equiv of arylmagnesium reagent **4a** in the presence of $Pd(Ph_3P)_4$ (5 mol%) in THF followed by the addition of a 1.2 M aqueous methanol solution of HCl at 25 °C afforded the desired functionalized base porphyrin **H_2-3aa** and debrominated free base **H_2-6a** in 55% and 38% yields, respectively, without their magnesium complexes **Mg-3aa** and **Mg-6a**.

Having established demetallation conditions, we explored the catalyst systems on the basis of the combination of $Pd(OAc)_2$ and different phosphine ligands for optimizing the formation of the functionalized base porphyrin **H_2-3aa**. As shown in Table 1, ligand screening indicated that bidentate phosphine ligand was less effective (entry 1) and the steric hindrance of monodentate phosphine ligands greatly influenced the catalytic reactivity (entries 2–6). Ultimately, *t*-BuXPhos was the most effective ligand among those screened as it afforded the desired free-base porphyrin **H_2-3aa** in 83% isolated yield without erosion of the ester functionality and significantly reduced the formation of the debrominated free-base byproduct **H_2-6a** to 12% yield.

Having developed an optimum catalyst system, we examined the substrate scope of the method for the preparation of functional-group-bearing free-base porphyrins. The examples described in Table 2 indicate that the sequential method involving the palladium-catalyzed cross-coupling followed by demetallation with a 1.2 M aqueous methanol solution of HCl can be readily applied to the cross-coupling reactions of the functionalized arylmagnesium reagent **4a** with a variety of di- and tri-substituted *meso*-bromoporphyrins **H_2-1**. The reaction tolerated well a range of substituents on the phenyl ring, including alkyl, vinyl, silylethynyl, and alkoxy groups, to give the corresponding functionalized free bases **H_2-3** in good to high yields (entries 5–10). Alkyl-substituted substrates **H_2-1b** and **H_2-1m** could also undergo the reaction to afford the corresponding functionalized free bases in good yields (entries 2 and 13). The present catalytic conditions were suitable for C_6F_5 and thienyl substituents on the *meso*-brominated porphyrins, and the desired products were obtained in good yields (entries 11 and 12). As shown in Scheme 3, performing the reaction with β-bromoporphyrin **H_2-1n** gave the desired β-functionalized product **H_2-3na** in 86% yield. Under similar conditions, double functionalization at the *meso* positions could also proceed smoothly using 5,15-dibromoporphyrin **H_2-1o** as the substrate (Scheme 4).

The scope of functionalized arylmagnesium reagents prepared in situ from the corresponding aryl iodides and *i*-PrMgCl·LiCl was then examined. As shown in Table 3, the mild conditions employed with the $Pd(OAc)_2$/*t*-BuXPhos catalyst system and a 1.2 M aqueous methanol solution of HCl afforded a range of functional groups including ester, nitrile, halogenic, amino, and silyl groups on the phenyl ring of arylmagnesium reagents **4a**—**4l** to be tolerated in the reaction with *meso*-bromoporphyrin **H_2-1a**. The *ortho*-substitution was not consequential with respect to reaction yield (products **H_2-3ab** and **H_2-3ah**,

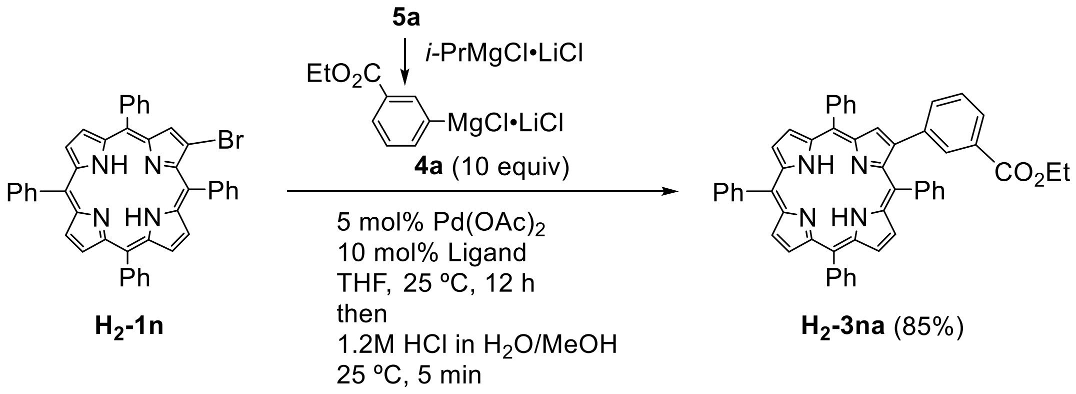
Table 2. Palladium-catalyzed coupling of **4a** with various *meso*-bromoporphyrins **H2-1**



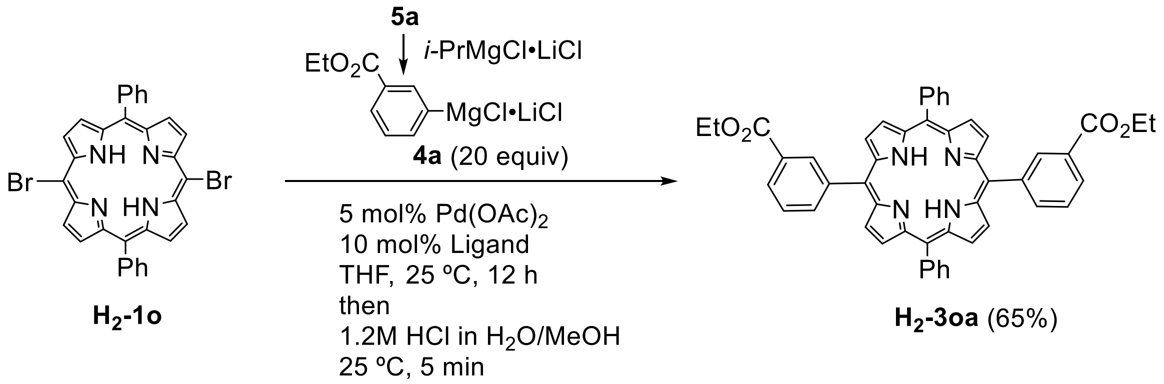
entry	R^1	R^2	substrate	product	yield[a] (%)
1	Ph	Ph	**1a**	**H_2-3aa**	83
2	Ph	*n*-Bu	**1b**	**H_2-3ba**	66
3	Ph	C_6F_5	**1c**	**H_2-3ca**	69
4	Ph	H	**1d**	**H_2-3da**	75
5	*p*-tolyl	H	**1e**	**H_2-3ea**	70
6	3-(CH_2=CH)C_6H_4	H	**1f**	**H_2-3fa**	81
7	4-(*i*-Pr_3SiC≡C)C_6H_4	H	**1g**	**H_2-3ga**	62
8	3-(MeO)C_6H_4	H	**1h**	**H_2-3ha**	72
9	3,5-(*t*-Bu)$_2C_6H_3$	H	**1i**	**H_2-3ia**	64
10	2,4,6-$Me_3C_6H_2$	H	**1j**	**H_2-3ja**	70
11	C_6F_5	Ph	**1k**	**H_2-3ka**	73
12	2-thienyl	H	**1l**	**H_2-3la**	77
13	*i*-Bu	H	**1m**	**H_2-3ma**	69

[a] Isolated yield.

62% and 64% yields). As expected, heteroarylmagnesium reagents **4k** and **4l** could also be used to access free-base porphyrins **H_2-3ak** and **H_2-3al** bearing pyridyl and thienyl groups, respectively, in good yields. To further demonstrate the generality of this novel preparation of functional-group-bearing free-base porphyrins, we sought to employ functional-group-bearing alkenylmagnesium reagents, which are readily prepared from alkenyl iodides and *i*-PrMgCl·LiCl in a similar manner for the preparation of arylmagnesium reagents (Table 4). With acyclic alkenylmagnesium reagents **4m**–**4r**, the present cross-coupling/demetallation method was again very effective in producing good yields of the desired free-base alkenylporphyrins **H_2-3am**–**H_2-3ar** containing various functional groups such as nitrile, ester, amide, and silyl functionalities, although a longer reaction time and an increased amount of the magnesium



Scheme 3. Preparation of *β*-(3-ethoxycarbonylphenyl)-substituted porphyrin **H_2-3na**

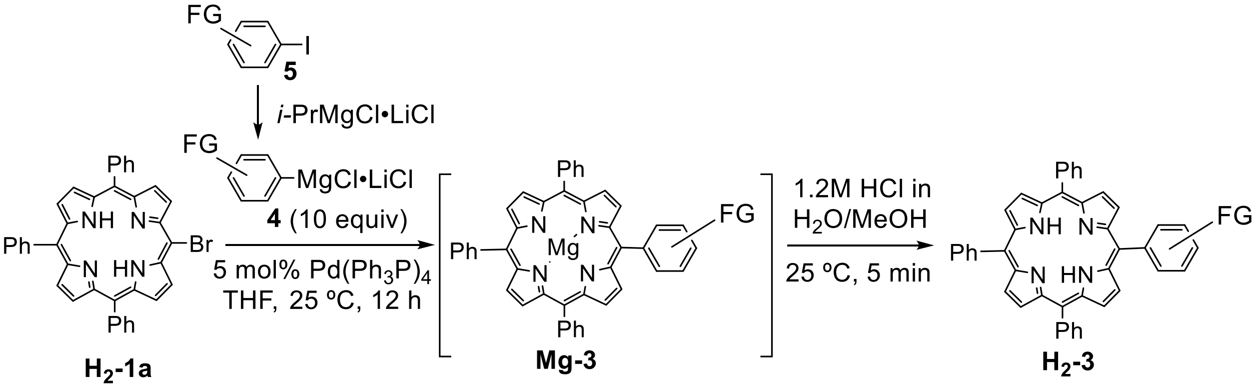


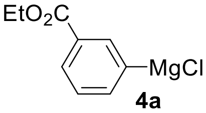
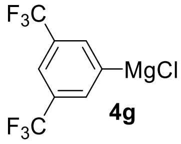
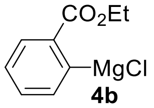
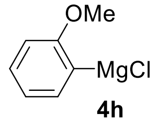
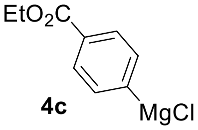
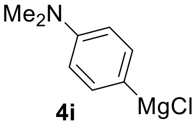
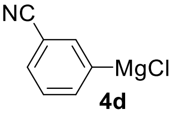
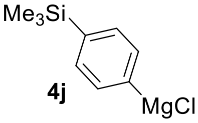
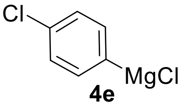
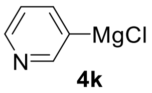
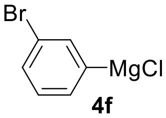
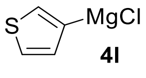
Scheme 4. Preparation of bis(3-ethoxycarbonylphenyl)porphyrin **H_2-3oa**

reagents were required to complete the reaction. Notably, the stereochemistry of the parent alkenyl iodides were completely preserved during the cross-coupling/demetallation (entries 1–5); in contrast, a previous method for preparing these alkenylporphyrins via the palladium-catalyzed Heck reaction of *meso*-bromoporphyrins with vinyl derivatives such as acrylonitrile has resulted in the formation of an inseparable mixture of *trans* and *cis* isomers.[14] As expected, bromo-substituted cyclic alkenylmagnesium reagent **4s** was also suitable for the reaction, affording the desired free base **H_2-3as** in 65% yield; the bromo functionality on the olefinic moiety was well tolerated (entry 7).

Finally, we examined the coupling reactions of *meso*-bromoporphyrin **H_2-1a** with arylmagnesium reagents **4t** and **4u**, which possess acetal units; these units are more challenging functionalities because of their highly sensitive nature toward acidic conditions. As illustrated in Schemes 5 and 6, arylmagnesium reagents of the protected phenol and aldehyde **4t** and **4u**, respectively, underwent the sequential cross-coupling/demetallation under optimal conditions using the $Pd(OAc)_2$/*t*-BuXPhos catalyst system and a 1.2 M aqueous methanol solution of HCl. However, the free-base products obtained were not the desired acetal derivatives **H_2-3at** and **H_2-3au** but deprotected phenol and aldehyde derivatives **H_2-7** and **H_2-8**. We subsequently reinvestigated the demetallation conditions and observed that a 0.1 M methanol solution of citric acid could be sufficient for the demetallation of the initially produced magnesium complexes yet compatible with the acetal functional groups. Thus, exposure of *meso*-bromoporphyrin

Table 3. Palladium-catalyzed coupling of **H_2-1a** with various arylmagnesium reagents

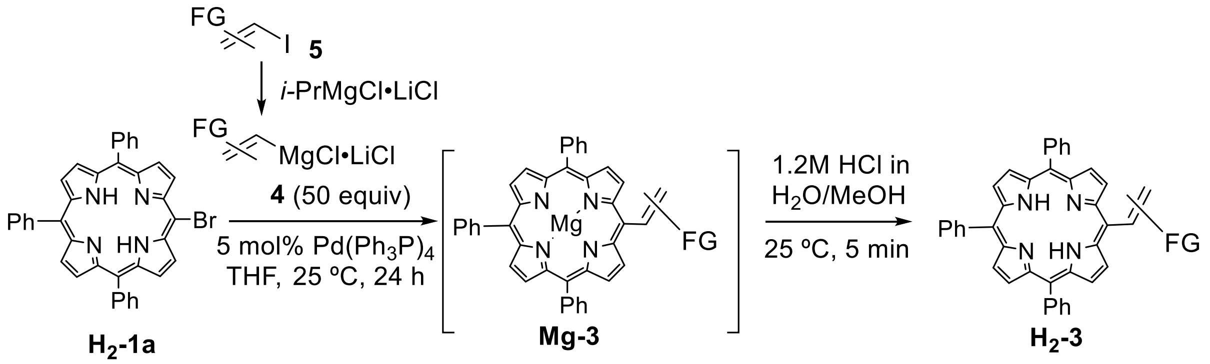


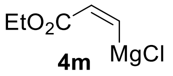
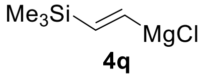
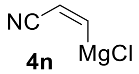
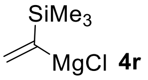
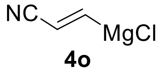
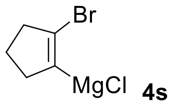
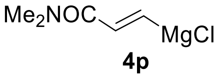
entry	FG-ArMgCl	product	yield[a] (%)	entry	FG-ArMgCl	product	yield[a] (%)
1	 **4a**	**H_2-3aa**	83	7	 **4g**	**H_2-3ag**	72
2	 **4b**	**H_2-3ab**	62	8	 **4h**	**H_2-3ah**	64
3	 **4c**	**H_2-3ac**	81	9	 **4i**	**H_2-3ai**	79
4	 **4d**	**H_2-3ad**	73	10	 **4j**	**H_2-3aj**	81
5	 **4e**	**H_2-3ae**	80	11	 **4k**	**H_2-3ak**	51
6	 **4f**	**H_2-3af**	68	12	 **4l**	**H_2-3al**	55

[a] Isolated yield.

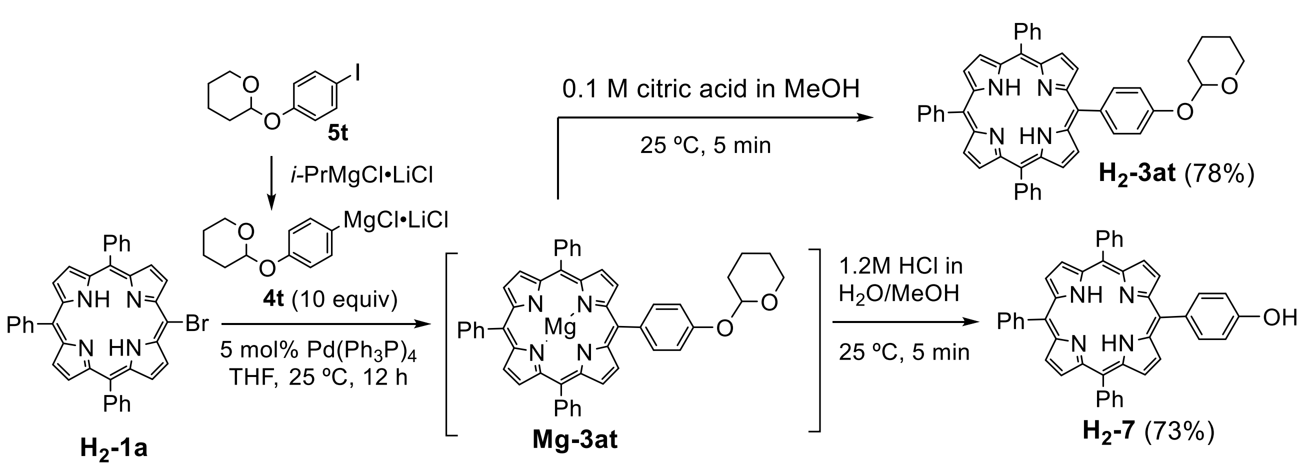
H_2-3a to arylmagnesium reagents **4t** and **4u** in the presence of $Pd(OAc)_2$ and *t*-BuXPhos followed by treatment with a 0.1 M methanol solution of citric acid afforded the corresponding adducts **H_2-3at** and **H_2-3au** in 78% and 76% isolated yields, respectively, leaving the highly acid-sensitive acetal groups untouched.

Table 4. Palladium-catalyzed coupling of **H_2-1a** with various alkenylmagnesium reagents

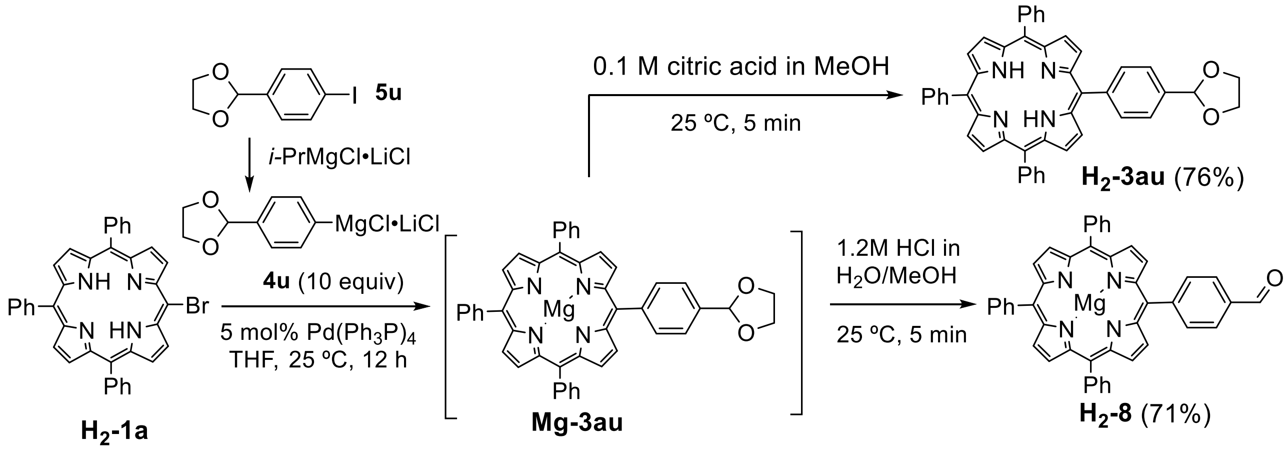


entry	FG-alkenyl-MgCl	product	yield[a] (%)	entry	FG-alkenyl-MgCl	product	yield[a] (%)
1	 **4m**	**H_2-3am**	55	5	 **4q**	**H_2-3aq**	74
2	 **4n**	**H_2-3an**	52	6	 **4r**	**H_2-3ar**	85
3	 **4o**	**H_2-3ao**	61	7	 **4s**	**H_2-3as**	65
4	 **4p**	**H_2-3ap**	56				

[a] Isolated yield.



Scheme 5. Preparation of free-base porphyrin **H_2-3at** bearing a protected phenol functional group



Scheme 6. Preparation of free-base porphyrin **H_2-3au** bearing a protected aldehyde functional group

In summary, we developed a facile, direct method for the preparation of free-base porphyrins that include reactive functionalities such as esters, nitriles, amides, halides, silyls, and acetals. The procedure involves a sequential palladium-catalyzed cross-coupling of free-base bromoporphyrins with functionalized aryl and alkenylmagnesium reagents, which are readily available from their iodide precursor and the turbo Grignard reagent *i*-PrMgCl·LiCl, followed by demagnesiation of the initially formed magnesium porphyrins with either a 1.2 M aqueous methanol solution of HCl or a 0.1 M methanol solution of citric acid at room temperature to give the corresponding functional-group-bearing free-base porphyrins in good to high yields. We expect these functional-group-bearing free-base porphyrins will be a valuable addition to the building blocks available in the total synthesis of more complicated porphyrin systems, thereby allowing the insertion of desired metal ions for later transformation in a multistep synthetic sequence while preventing the demetallation process under harsh conditions. We are currently conducting further synthetic studies using these functional-group-bearing free-base porphyrins, and the results will be reported in due course.

EXPERIMENTAL

General ^{1}H and ^{13}C NMR spectra were recorded at rt on 300, 400, and 500 MHz spectrometers using perdeuterated solvents as internal standards. Chemical shifts of ^{1}H and ^{13}C spectra are given in ppm relative to residual protiated solvent and relative to the solvent respectively. ^{19}F NMR spectra were recorded at rt on a 500 MHz spectrometer using benzotrifluoride as an external standard. The chemical shift values are expressed as δ values (ppm) and the couple constants values (J) are in Hertz (Hz). The following abbreviations were used for signal multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad. UV–visible spectra were recorded using a dual-beam grating spectrophotometer with a 1 cm quartz cell. The melting point data were not available for the porphyrin derivatives obtained because these compounds are infusible below 300 °C.

Reactions involving moisture sensitive reagents were carried out under an argon atmosphere using standard vacuum line techniques and glassware that was flame-dried and cooled under argon before use. Dry THF was purchased for the reactions and used without further desiccation. Bromoporphyrin derivatives, **H_2-1a–H_2-1b**,[8] **H_2-1d–H_2-1h**,[9] **H_2-1i**,[8] **H_2-1j**,[9] **H_2-1m**,[8] **H_2-1n**,[9] and **H_2-1o**,[8] were prepared according to the method described in literature. Other chemicals were purchased from commercial sources and used as received unless stated otherwise.

Preparation of 5,15-diphenyl-10-pentafluorophenylporphyrin. [5,15-Diphenyl-10-pentafluorophenylporphyrinato]zinc(II)[15] (830 mg, 1.200 mmol) was dissolved in a mixture of CH_2Cl_2 (60 mL) and MeOH (9 mL) and the solution was treated with trifluoroacetic acid (15 mL) at rt for 30 min. The solution was diluted with CH_2Cl_2 (300 mL) and washed with saturated $NaHCO_3$ (150 mL × 2) and H_2O (150 mL). The organic solution was dried over $MgSO_4$ and removal of the solvent offered 5,15-diphenyl-10-pentafluorophenylporphyrin (754 mg, quant.) as a purple solid. R_f = 0.55 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.21 (1H, s), 9.29 (2H, d, J = 4.8 Hz), 9.02 (2H, d, J = 4.8 Hz), 9.01 (2H, d, J = 4.8 Hz), 8.84 (2H, d, J = 4.8 Hz), 8.29–8.20 (4H, m), 7.85–7.73 (6H, m), –2.90 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.8, 147.3, 146.8 (2C, d, J_{CF} = 246.0 Hz), 145.9, 145.5, 142.0 (1C, d, J_{CF} = 255.9 Hz), 141.5, 137.6 (2C, d, J_{CF} = 254.7 Hz), 134.7, 132.3, 131.8, 131.5, 129.2, 128.0, 126.9, 120.5, 117.4, 106.6, 100.7; ^{19}F NMR ($CDCl_3$, 466 MHz) δ –138.3 (2F, ddd, J_{FF} = 23.1, 8.0, 5.9), –154.5 (1F, tt, J_{FF} = 20.5, 8.1 Hz), –163.8 (2F, ddd, J_{FF} = 23.1, 20.5, 8.5 Hz); IR (KBr) 3298, 3116, 3062, 1496, 1068, 984, 922, 856, 791, 725 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 417.0 (5.7), 546.5 (4.3) nm ; HRMS (EI) calcd for $C_{38}H_{22}F_5N_4$ 629.1765, found 629.1769.

Preparation of 5-bromo-10,20-diphenyl-15-pentafluolophenylporphyrin (H_2-1c). To a solution of 5,15-diphenyl-10-pentafluorophenylporphyrin (629 mg, 1.000 mmol) in $CHCl_3$ (200 mL) was added NBS (196 mg, 1.100 mmol, 1.1 equiv) at rt. After stirring for 15 min, the solution was concentrated in vacuo. Column chromatography on silica gel (5:1 hexane/toluene) followed by recrystallization from hexane/CH_2Cl_2 gave the product **H_2-1c** (672 mg, 95%) as a purple solid. R_f = 0.65 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.65 (2H, d, J = 4.9 Hz), 8.89 (2H, d, J = 4.9 Hz), 8.87 (2H, d, J = 4.9 Hz), 8.75 (2H, d, J = 4.9 Hz), 8.21–8.14 (4H, m), 7.81–7.73 (6H, m), –2.63 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.2 (8C, br), 146.7 (2C, d, J_{CF} = 243.3 Hz), 142.1 (1C, d, J_{CF} = 256.6 Hz), 141.5, 137.7 (2C, d, J_{CF} = 254.9 Hz), 134.6, 133.0, 132.6, 132.4, 129.2, 128.1, 126.9, 121.6, 116.7, 105.2, 101.1; ^{19}F NMR ($CDCl_3$, 466 MHz) δ –136.6 (2F, ddd, J_{FF} = 24.0, 8.9, 6.8), –152.3 (1F, tt, J_{FF} = 21.4, 6.8 Hz), –161.8 (2F, ddd, J_{FF} = 24.0, 21.4, 8.0 Hz); IR (KBr) 3321, 3059, 3028, 1489, 1346, 980, 926, 791, 717 cm^{-1}; UV/vis

($CHCl_3$) λ_{max} (log ε) 419.0 (5.6), 516.5 (4.2), 549.5 (3.6), 595.0 (3.4), 649.5 (2.9) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{38}H_{21}BrF_5N_4$ 707.0870, found 707.0875.

Preparation of [5,15-bis(pentafluorophenyl)-10-bromoporphyrinato]zinc(II). To a solution of [5,15-bis(pentafluorophenyl)porphyrinato]zinc(II)[16] (690 mg, 0.978 mmol) in $CHCl_3$ (210 mL) and pyridine (0.8 mL) was added NBS (192 mg, 1.076 mmol, 1.1 equiv) at room temperature. After stirring for 15 min, the solution was concentrated in vacuo. Column chromatography on silica gel (5:1 hexane/toluene) followed by recrystallization from hexane/CH_2Cl_2 gave the [5,15-bis(pentafluorophenyl)-10-bromoporphyrinato]zinc(II) (430 mg, 56%) as a red-purple solid. R_f = 0.57 (2:1 hexane/THF); ^{1}H NMR (THF-d_8, 300 MHz) δ 10.31 (1H, s), 9.84 (2H, d, J = 4.8 Hz), 9.47 (2H, d, J = 4.8 Hz), 9.09 (2H, d, J = 4.8 Hz), 9.08 (2H, d, J = 4.8 Hz); ^{13}C NMR (THF-d_8, 100 MHz) δ 152.4, 150.91, 150.86, 150.8, 147.7 (4C, d, J_{CF} = 248.5 Hz), 143.0 (2C, d, J_{CF} = 252.8 Hz), 138.7 (4C, d, J_{CF} = 252.2 Hz), 134.7, 134.4, 131.92, 131.87, 118.4, 107.9, 105.9, 103.2; ^{19}F NMR (THF-d_8, 466 MHz) δ –142.9 (4F, ddd, J_{FF} = 24.3, 8.0, 6.1 Hz), –160.1 (2F, tt, J_{FF} = 20.7, 6.1 Hz), –168.7 (4F, ddd, J_{FF} = 24.3, 20.7, 8.2 Hz); IR (KBr) 3097, 3028, 2966, 2924, 2862, 2800, 2750, 1493, 1288, 1061, 987, 856, 775 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 419.5 (5.8), 550.0 (4.4), 584.0 (3.7) nm; HRMS-FAB$^+$ (M^+) calcd for $C_{32}H_9BrF_{10}N_4Zn$ 781.9142, found 781.9146.

Preparation of 5,15-bis(pentafluorophenyl)-10-bromoporphyrin (H_2-1k). [5,15-Bis(pentafluorophenyl)-10-bromoporphyrinato]zinc(II) (300 mg, 0.382 mmol) was dissolved in a mixture of CH_2Cl_2 (20 mL) and MeOH (3 mL) and the solution was treated with trifluoroacetic acid (5 mL) at rt for 1.5 h. The solution was diluted with CH_2Cl_2 (100 mL) and washed with saturated $NaHCO_3$ (50 mL × 2) and H_2O (50 mL). The organic solution was dried over $MgSO_4$ and removal of the solvent offered pure compound **H_2-1k** (276 mg, quant.) as a purple solid. R_f = 0.65 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.21 (1H, s), 9.80 (2H, d, J = 4.9 Hz), 9.35 (2H, d, J = 4.9 Hz), 8.88 (2H, d, J = 4.9 Hz), 8.86 (2H, d, J = 4.9 Hz), –3.00 (2H, br s); ^{13}C NMR data was not available due to their poor solubility; ^{19}F NMR ($CDCl_3$, 466 MHz) δ –138.4 (4F, ddd, J_{FF} = 23.2, 8.9, 6.8 Hz), –153.4 (2F, tt, J_{FF} = 19.6, 6.8 Hz), –163.3 (4F, ddd, J_{FF} = 23.2, 19.6, 8.7 Hz); IR (KBr) 3313, 3101, 3039, 2927, 1500, 1323, 1142, 1045, 980, 918, 771 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 412.5 (5.6), 507.5 (4.4), 540.5 (3.8) 585.0 (3.9), 640.5 (3.4) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{32}H_{12}BrF_{10}N_4$ 721.0086, found 721.0089; Anal. calcd for $C_{32}H_{11}BrF_{10}N_4$: C, 53.28; H, 1.54; N, 7.77, found: C, 53.32; H, 1.72; N, 7.52.

Preparation of 10-bromo-5,15-di(2-thienyl)porphyrin (H_2-1l). To a solution of 5,15-di-2-thienylporphyrin[17] (382 mg, 0.805 mmol) in $CHCl_3$ (160 mL) was added NBS (158 mg, 0.886 mmol, 1.1 equiv) at rt. After stirring for 15 min, the solution was concentrated in vacuo. Column chromatography on silica gel (3:1 hexane/toluene) followed by recrystallization from hexane/CH_2Cl_2 gave the product **H_2-1l** (275 mg, 62%) as a purple solid. R_f = 0.55 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.08 (1H, s), 9.70 (2H, d, $J = 4.9$ Hz), 9.22 (2H, d, $J = 4.9$ Hz), 9.13 (2H, d, $J = 4.9$ Hz), 9.12 (2H, d, $J = 4.9$ Hz), 7.90 (2H, dd, $J = 3.4$, 1.3 Hz), 7.87 (2H, dd, $J = 5.4$, 1.3 Hz), 7.51 (2H, dd, $J = 5.4$, 3.4 Hz), –2.89 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.3 (4C, br), 146.8 (br), 145.8 (br), 142.2, 134.0, 132.7, 131.9, 131.8 (4C), 128.1, 126.3, 112.0, 106.1, 104.5; IR (KBr) 3309, 3105, 1400, 1323, 1242, 1049, 972, 791, 714 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 419.5 (5.6), 515.5 (4.3), 552.5 (4.0), 591.0 (3.8), 650.5 (3.6) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{28}H_{18}BrN_4S_2$ 553.0156, found 553.0157.

Preparation of Functionalized Organomagnesium Reagents (4). All the organomagnesium reagents used were prepared according to the method described in literature[18] as follows. To a well-stirred mixture of aryl or alkenyl iodide **5** (1.620 mmol) in 6.5 mL of THF was slowly added a solution of *i*PrMgCl·LiCl (1.250 mL, 1.620 mmol, 1.3 M in THF) at -20 °C. The mixture was stirred for 30 min at this temperature and was used immediately.

General Procedure for the Palladium-Catalyzed Reaction of Bromoporphyrins with Functionalized Organomagnesium Reagents. An oven-dried 100 mL two-necked flask equipped with a magnetic stirring bar and rubber septum was charged with a free base bromoporphyrin **H$_2$-1** (0.162 mmol), $Pd(OAc)_2$ (1.8 mg, 8.1 μmol, 5 mol%), and *t*-BuXPhos (6.9 mg, 16.2 μmol, 10 mol%). The reaction vessel was evacuated and flushed with argon (three times), and then dry THF (30 mL) was added. To the solution was slowly added 0.2 M THF solution of an organomagnesium reagent **4** (8.0 mL, 1.620 mmol, 10 equiv) via cannula at rt. The mixture was stirred at rt (or 40 °C) for several hours (1–24 h), having been monitored by TLC (2:1 hexane/THF). To the solution of was added 5 mL of a 1.2 M aqueous methanol solution of HCl (a 1:9 mixture of conc. HCl and MeOH), and the solution was stirred for 5 min. The solvent was evaporated and the resulting solid was dissolved in CH_2Cl_2 (50 mL) and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (1:1 toluene/hexane) followed by recrystallization from MeOH/CH_2Cl_2 gave the pure product **H$_2$-3**.

5-(3-Ethoxycarbonylphenyl)-10,15,20-triphenylporphyrin (H$_2$-3aa): Prepared from bromoporphyrin **H$_2$-1a** (100.0 mg, 0.162 mmol) and arylmagnesium reagent **4a** following the general procedure; Purple solid; 92.8 mg, 83% yield; $R_f = 0.31$ (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.90 (1H, s), 8.85 (6H, d, $J = 4.9$ Hz), 8.77 (2H, d, $J = 4.9$ Hz), 8.48 (1H, d, $J = 7.9$ Hz), 8.39 (1H, d, $J = 7.5$ Hz), 8.27–8.15 (6H, m), 7.82 (1H, dd, $J = 7.9$, 7.5 Hz), 7.80–7.68 (9H, m), 4.46 (2H, q, $J = 7.1$ Hz), 1.39 (3H, t, $J = 7.1$ Hz), –2.71 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.8, 146.9 (8C, br), 142.6, 142.24, 142.21, 138.3, 134.8, 134.6 (6C), 131.2 (6C), 130.8, 129.4, 129.0, 127.8 (3C), 126.8, 126.7 (6C), 120.5, 120.4, 118.7, 61.2, 14.4; IR (KBr) 3317, 3055, 3028, 2981, 1724, 1473, 1281, 1223, 972, 798, 737, 702 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 418.5 (5.7), 515.5 (4.3), 550.0 (3.9), 645.5 (3.6) nm; HRMS-FAB$^+$ ([M+H]$^+$)

calcd for $C_{47}H_{35}N_4O_2$ 687.2760, found 687.2756; Anal. Calcd for $C_{47}H_{34}N_4O_2$: C, 82.19; H, 4.99; N, 8.16. Found: C, 82.17; H, 5.32; N, 7.90.

5-(*n*-Butyl)-10,20-diphenyl-15-(3-ethoxycarbonylphenyl)porphyrin (H$_2$-3ba): Prepared from bromoporphyrin **H$_2$-1b** (96.8 mg, 0.162 mmol) and arylmagnesium reagent **4a** following the general procedure; Purple solid; 71.4 mg, 66% yield; R_f = 0.35 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.47 (2H, d, J = 4.9 Hz), 8.94 (2H, d, J = 4.9 Hz), 8.93 (1H, s), 8.84 (2H, d, J = 4.9 Hz), 8.76 (2H, d, J = 4.9 Hz), 8.49 (1H, d, J = 8.3 Hz), 8.38 (1H, d, J = 7.4 Hz), 8.27–8.19 (4H, m), 7.82 (1H, dd, J = 8.3, 7.4 Hz), 7.81–7.69 (6H, m), 4.98 (2H, t, J = 7.8 Hz), 4.49 (2H, q, J = 7.0 Hz), 2.56 (2H, tt, J = 7.8, 7.5 Hz), 1.82 (2H, tq, J = 7.5, 7.3 Hz), 1.42 (3H, t, J = 7.0 Hz), 1.15 (3H, t, J = 7.3 Hz), –2.58 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 146.6 (8C, br), 142.6, 142.5, 138.3, 134.9, 134.5, 131.6, 131.5, 130.4, 129.5, 129.0, 128.1, 127.7, 126.8, 126.6, 121.0, 119.8, 117.9, 61.2, 40.9, 35.3, 23.6, 14.3, 14.1; IR (KBr) 3317, 3101, 3055, 2958, 2924, 2862, 1720, 1473, 1281, 976, 795, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 419.0 (5.9), 516.5 (4.5), 551.0 (4.1), 592.5 (3.9), 648.5 (3.9) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{45}H_{39}N_4O_2$ 667.3073, found 667.3067; Anal. Calcd for $C_{45}H_{38}N_4O_2$: C, 81.05; H, 5.74; N, 8.40. Found: C, 81.09; H, 5.72; N, 8.44.

5,15-Diphenyl-10-(3-ethoxycarbonylphenyl)-20-pentafluorophenylporphyrin (H$_2$-3ca): Prepared from bromoporphyrin **H$_2$-1c** (114.6 mg, 0.162 mmol) and arylmagnesium reagent **4a** following the general procedure; Purple solid; 85.8 mg, 69% yield; R_f = 0.42 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.93 (2H, d, J = 4.9 Hz), 8.88 (1H, s), 8.84 (2H, d, J = 4.9 Hz), 8.77 (2H, d, J = 4.9 Hz), 8.76 (2H, d, J = 4.9 Hz), 8.48 (1H, d, J = 8.1 Hz), 8.36 (1H, d, J = 7.8 Hz), 8.23–8.17 (4H, m), 7.82 (1H, dd, J = 8.1, 7.8 Hz), 7.80–7.71 (6H, m), 4.45 (2H, q, J = 7.0 Hz), 1.39 (3H, t, J = 7.0 Hz), –2.73 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.7, 146.69 (2C, d, J_{CF} = 247.5 Hz), 146.66 (8C, br), 142.3, 141.9 (1C, d, J_{CF} = 247.5 Hz), 141.7, 138.2, 137.6 (2C, d, J_{CF} = 249.1 Hz), 134.7, 134.6, 132.7, 131.5 (4C), 129.4, 129.2, 129.0, 128.0, 126.8 (5C), 121.1, 120.6, 116.8 (1C, t, J_{CF} = 20.3 Hz), 100.5, 61.3, 14.3; ^{19}F NMR ($CDCl_3$, 466 MHz) δ –138.3 (2F, ddd, J_{FF} = 24.9, 8.5, 6.4 Hz), –154.3 (1F, tt, J_{FF} = 20.6, 6.4 Hz), –163.8 (2F, ddd, J_{FF} = 24.9, 20.6, 8.6 Hz); IR (KBr) 3321, 3101, 3059, 2985, 2924, 1716, 1508, 1281, 984, 922, 798, 748 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 417.5 (5.6), 513.5 (4.2), 547.0 (3.5), 588.5 (3.6), 642.0 (3.2) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{47}H_{30}F_5N_4O_2$ 777.2289, found 777.2296.

5,15-Diphenyl-10-(3-ethoxycarbonylphenyl)porphyrin (H$_2$-3da): Prepared from bromoporphyrin **H$_2$-1d** (87.7 mg, 0.162 mmol) and arylmagnesium reagent **4a** following the general procedure; Purple solid; 74.2 mg, 75% yield; R_f = 0.32 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.23 (1H, s), 9.34 (2H, d, J = 4.8 Hz), 9.02 (2H, d, J = 4.8 Hz), 8.90 (2H, d, J = 4.8 Hz), 8.84 (1H, s), 8.78 (2H, d, J = 4.8 Hz), 8.45 (1H, d, J = 7.9 Hz), 8.37 (1H, d, J = 7.5 Hz), 8.28–8.19 (4H, m), 7.85–7.72 (7H, m), 4.40 (2H, q, J = 7.1 Hz), 1.35 (3H, t, J = 7.1 Hz), –3.02 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.8, 146.9

(4C, br), 146.0 (4C, br), 142.8, 141.6, 138.2, 134.7, 131.5 (4C), 131.2, 131.0, 129.0 (2C), 127.8 (3C), 126.8, 126.6, 119.8, 119.0, 105.1, 61.2, 14.3; IR (KBr) 3055, 2924, 1720, 1593, 1477, 1404, 1288, 1080, 968, 849, 795, 733 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 413.0 (5.6), 509.5 (4.2), 543.0 (3.7), 583.0 (3.7), 638.5 (3.2) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{41}H_{31}N_4O_2$ 611.2447, found 611.2446.

5,15-Di(*p*-tolyl)-10-(3-ethoxycarbonylphenyl)porphyrin (H$_2$-3ea): Prepared from bromoporphyrin **H$_2$-1e** (92.3 mg, 0.162 mmol) and arylmagnesium reagent **4a** following the general procedure; Purple solid; 72.4 mg, 70% yield; R_f = 0.35 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.18 (1H, s), 9.30 (2H, d, J = 4.8 Hz), 9.03 (2H, d, J = 4.8 Hz), 8.92 (2H, d, J = 4.8 Hz), 8.88 (1H, s), 8.77 (2H, d, J = 4.8 Hz), 8.48 (1H, d, J = 8.0 Hz), 8.37 (1H, d, J = 7.6 Hz), 8.11 (4H, d, J = 7.8 Hz), 7.80 (1H, dd, J = 8.0, 7.6 Hz), 7.57 (4H, d, J = 7.8 Hz), 4.45 (2H, q, J = 7.1 Hz), 2.71 (6H, s), 1.38 (3H, t, J = 7.1 Hz), –2.91 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.9, 147.4 (4C, br), 146.1 (br), 145.9 (br), 143.1, 138.9, 138.2, 137.5, 134.7, 134.5, 131.5, 131.3, 131.0 (4C), 129.0, 127.6, 127.3, 126.6, 120.0, 119.8, 104.9, 61.2, 21.5, 14.3; IR (KBr) 3309, 3116, 3024, 2978, 2924, 2870, 1720, 1469, 1404, 1284, 1215, 1103, 968, 795, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 415.0 (5.7), 511.5 (4.3), 546.5 (3.8), 587.0 (3.8), 641.0 (3.4) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{43}H_{35}N_4O_2$ 639.2760, found 639.2769.

5,15-Bis(3-vinylphenyl)-10-(3-ethoxycarbonylphenyl)porphyrin (H$_2$-3fa): Prepared from bromoporphyrin **H$_2$-1f** (96.1 mg, 0.162 mmol) and arylmagnesium reagent **4a** following the general procedure; Brown-purple solid; 87.1 mg, 81% yield; R_f = 0.35 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.16 (1H, s), 9.29 (2H, d, J = 4.8 Hz), 9.06 (2H, d, J = 4.8 Hz), 9.00 (2H, d, J = 4.8 Hz), 8.99 (1H, s), 8.87 (2H, d, J = 4.8 Hz), 8.54 (1H, d, J = 7.8 Hz), 8.43 (1H, d, J = 7.3 Hz), 8.34 (2H, s), 8.17 (2H, d, J = 6.8 Hz), 7.86 (2H, d, J = 7.5 Hz), 7.84 (1H, dd, J = 7.8, 7.3 Hz), 7.74 (2H, dd, J = 7.5, 6.8 Hz), 7.03 (2H, dd, J = 17.6, 10.7 Hz), 6.00 (2H, d, J = 17.6 Hz), 5.43 (2H, d, J = 10.7 Hz), 4.51 (2H, q, J = 7.0 Hz), 1.43 (3H, t, J = 7.0 Hz), –2.83 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 147.2 (4C, br), 146.2 (br), 146.1 (br), 143.0, 142.1, 138.2, 136.9, 136.3, 134.8, 134.2, 132.7, 131.4 (4C), 131.2, 131.0, 129.3, 129.1, 127.0, 126.7, 125.7, 119.63, 119.2, 114.8, 105.1, 61.2, 14.3; IR (KBr) 3309, 3097, 3051, 2981, 2927, 1716, 1589, 1473, 1400, 1281, 1099, 976, 910, 791, 733 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 414.0 (5.8), 509.5 (4.4), 543.0 (3.9), 582.5 (3.9), 636.5 (3.4) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{45}H_{35}N_4O_2$ 663.2760, found 663.2769; Anal. Calcd for $C_{45}H_{34}N_4O_2$: C, 81.55; H, 5.17; N, 8.45. Found: C, 81.73; H, 5.28; N, 8.39.

5,15-Bis[4-{2-(triisopropylsilyl)ethynyl}phenyl]-10-(3-ethoxycarbonylphenyl)porphyrin (H$_2$-3ga): Prepared from bromoporphyrin **H$_2$-1g** (146.2 mg, 0.162 mmol) and arylmagnesium reagent **4a** following the general procedure; Brown-purple solid; 97.7 mg, 62% yield; R_f = 0.43 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.19 (1H, s), 9.31 (2H, d, J = 4.4 Hz), 9.00 (2H, d, J = 4.4 Hz), 8.90 (2H, d, J = 4.9 Hz), 8.88 (1H, s), 8.80 (2H, d, J = 4.4 Hz), 8.49 (1H, d, J = 8.3 Hz), 8.37 (1H, d, J = 7.3 Hz), 8.18 (4H, d, *J* = 7.8 Hz), 7.90 (4H, d, *J* = 7.8 Hz), 7.82 (1H, dd, *J* = 8.3, 7.3 Hz), 4.46 (2H, q, *J* = 7.1 Hz), 1.39 (3H, t, *J* = 7.1 Hz), 1.35–1.18 (42H, m), –2.94 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 147.0 (4C, br), 146.2 (4C, br), 142.9, 141.9, 138.2, 134.6, 134.4, 131.6, 131.4, 131.3, 130.8, 130.6, 130.3, 129.1, 126.7, 123.3, 119.4, 119.2, 107.3, 105.3, 92.2, 61.2, 18.8, 14.3, 11.6; IR (KBr) 3309, 3109, 3066, 3032, 2943, 2866, 1724, 1466, 1396, 1281, 1242, 1107, 972, 798, 737, 671 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 417.0 (5.7), 512.0 (4.4), 547.0 (4.0), 586.0 (3.9), 640.5 (3.6) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{63}H_{71}N_4O_2Si_2$ 971.5116, found 971.5114; Anal. Calcd for $C_{63}H_{70}N_4O_2$ Si_2: C, 77.89; H, 7.26; N, 5.77. Found: C, 77.54; H, 7.24; N, 5.43.

5,15-Bis(3-methoxyphenyl)-10-(3-ethoxycarbonylphenyl)porphyrin (H$_2$-3ha): Prepared from bromoporphyrin **H$_2$-1h** (97.4 mg, 0.162 mmol) and arylmagnesium reagent **4a** following the general procedure; Purple solid; 78.1 mg, 72% yield; R_f = 0.27 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.18 (1H, s), 9.30 (2H, d, *J* = 4.8 Hz), 9.06 (2H, d, *J* = 4.8 Hz), 8.97 (2H, d, *J* = 4.8 Hz), 8.91 (1H, s), 8.80 (2H, d, *J* = 4.8 Hz), 8.50 (1H, d, *J* = 7.9 Hz), 8.39 (1H, d, *J* = 7.7 Hz), 7.90–7.75 (5H, m), 7.66 (2H, dd, *J* = 8.0, 7.6 Hz), 7.35 (2H, d, *J* = 8.0 Hz), 4.47 (2H, q, *J* = 7.1 Hz), 4.00 (6H, s), 1.40 (3H, t, *J* = 7.1 Hz), –2.91 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.8, 158.3, 147.1 (br), 147.1 (br), 146.2 (br), 146.0 (br), 143.2, 143.0, 138.2, 134.8, 131.5, 131.4, 131.1, 131.0, 129.3, 129.1, 127.8, 127.7, 126.7, 120.9, 119.6, 119.1, 113.8, 105.0, 61.2, 55.6, 14.3; IR (KBr) 3309, 3101, 3059, 2947, 2835, 1716, 1589, 1466, 1277, 1038, 791 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 414.0 (5.8), 509.5 (4.4), 543.0 (3.8), 582.0 (3.9), 636.0 (3.3) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{43}H_{35}N_4O_4$ 671.2658, found 671.2659; Anal. Calcd for $C_{43}H_{35}N_4O_4$: C, 77.00; H, 5.11; N, 8.35. Found: C, 76.91; H, 5.23; N, 8.16.

5,15-Bis[3,5-di(*t*-butyl)phenyl]-10-(3-ethoxycarbonylphenyl)porphyrin (H$_2$-3ia): Prepared from bromoporphyrin **H$_2$-1i** (124.1 mg, 0.162 mmol) and arylmagnesium reagent **4a** following the general procedure; Brown-purple solid; 86.6 mg, 64% yield; R_f = 0.38 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.21 (1H, s), 9.33 (2H, d, *J* = 4.8 Hz), 9.06 (2H, d, *J* = 4.8 Hz), 8.95 (2H, d, *J* = 4.8 Hz), 8.91 (1H, s), 8.80 (2H, d, *J* = 4.8 Hz), 8.48 (1H, d, *J* = 8.1 Hz), 8.40 (1H, d, *J* = 7.7 Hz), 8.13 (4H, d, *J* = 1.5 Hz), 7.85 (2H, d, *J* = 1.5 Hz), 7.82 (1H, dd, *J* = 8.1, 7.7 Hz), 4.46 (2H, q, *J* = 7.1 Hz), 1.57 (36H, s), 1.39 (3H, t, *J* = 7.1 Hz), –2.83 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.9, 149.1, 147.6 (br), 147.5 (br), 146.0 (br), 145.8 (br), 143.3, 140.9, 138.2, 134.7, 131.7, 131.2 (4C), 131.0, 130.0, 129.7, 129.0, 126.6, 121.3, 121.2, 118.8, 104.8, 61.2, 35.1, 31.8, 14.3; IR (KBr) 3313, 3066, 2962, 2870, 1720, 1589, 1481, 1365, 1246, 1103, 972, 914, 795, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 416.0 (5.7), 511.5 (4.3), 547.0 (3.9), 586.0 (3.8), 641.5 (3.5) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{57}H_{63}N_4O_2$ 835.4951, found 835.4952; Anal. Calcd for $C_{57}H_{62}N_4O_2$: C, 81.98; H, 7.48; N, 6.71. Found: C, 81.77; H, 7.51; N, 6.57.

5,15-Bis(2,4,6-trimethylphenyl)-10-(3-ethoxycarbonylphenyl)porphyrin (H$_2$-3ja): Prepared from bromoporphyrin **H$_2$-1j** (101.3 mg, 0.162 mmol) and arylmagnesium reagent **4a** following the general procedure; Purple solid; 78.9 mg, 70% yield; $R_f = 0.38$ (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.13 (1H, s), 9.27 (2H, d, $J = 4.8$ Hz), 8.93 (1H, s), 8.85 (2H, d, $J = 4.8$ Hz), 8.77 (4H, d, $J = 4.8$ Hz), 8.49 (1H, d, $J = 7.9$ Hz), 8.41 (1H, d, $J = 7.5$ Hz), 7.82 (1H, dd, $J = 7.9, 7.5$ Hz), 7.33 (4H, s), 4.48 (2H, q, $J = 7.0$ Hz), 2.66 (6H, s), 1.88 (12H, s), 1.42 (3H, t, $J = 7.0$ Hz), –2.76 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.9, 146.9 (4C, br), 146.3 (4C, br), 142.9, 139.5, 138.2, 138.1, 137.9, 134.7, 131.6, 131.4, 130.4, 130.0, 129.3, 129.0, 127.9, 126.6, 118.4, 118.1, 104.4, 61.2, 21.6, 21.4, 14.3; IR (KBr) 3309, 3097, 2970, 2920, 2866, 1724, 1570, 1466, 1277, 1111, 972, 798, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 416.0 (5.6), 512.5 (4.3), 547.5 (3.7), 589.0 (3.7), 647.5 (3.3) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{47}H_{43}N_4O_2$ 695.3386, found 695.3386.

5,15-Bis(pentafluorophenyl)-10-(3-ethoxycarbonylphenyl)porphyrin (H_2-3ka): Prepared from bromoporphyrin **H_2-1k** (116.9 mg, 0.162 mmol) and arylmagnesium reagent **4a** following the general procedure; Purple solid; 93.6 mg, 73% yield; $R_f = 0.43$ (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.22 (1H, s), 9.37 (2H, d, $J = 4.8$ Hz), 8.95 (2H, d, $J = 4.6$ Hz), 8.91 (2H, d, $J = 4.8$ Hz), 8.90 (1H, s), 8.86 (2H, d, $J = 4.8$ Hz), 8.53 (1H, d, $J = 7.9$ Hz), 8.36 (1H, d, $J = 7.5$ Hz), 7.84 (1H, dd, $J = 7.9, 7.5$ Hz), 4.48 (2H, q, $J = 7.1$ Hz), 1.40 (3H, t, $J = 7.1$ Hz), –2.99 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.6, 147.0 (4C, br), 146.7 (4C, d, $J_{CF} = 252.2$ Hz), 146.4 (4C, br), 142.2 (2C, d, $J_{CF} = 259.0$ Hz), 142.0, 138.2, 137.7 (4C, d, $J_{CF} = 253.5$ Hz), 134.7 , 132.9, 132.8, 130.0, 129.6, 129.5 (3C), 126.9, 120.6, 116.2 (2C, t, $J_{CF} = 19.6$ Hz), 106.1, 102.0, 61.3, 14.3; ^{19}F NMR ($CDCl_3$, 466 MHz) δ –138.3 (4F, ddd, $J_{FF} = 24.1, 8.1, 6.2$ Hz), –153.8 (2F, tt, $J_{FF} = 21.4, 6.2$ Hz), –163.4 (4F, ddd, $J_{FF} = 24.1, 21.4, 8.0$ Hz); IR (KBr) 3317, 3105, 3043, 2981, 2935, 1720, 1512, 1281, 987, 914, 733 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 409.5 (5.7), 504.5 (4.4), 536.0 (3.9), 579.0 (3.9), 634.0 (3.6) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{41}H_{21}F_{10}N_4O_2$ 791.1505, found 791.1501. Anal. Calcd for $C_{41}H_{20}F_{10}N_4O_2$: C, 62.29; H, 2.55; N, 7.09. Found: C, 62.38; H, 2.84; N, 6.82.

5,15-Di(2-thienyl)-10-(3-ethoxycarbonylphenyl)porphyrin (H_2-3la): Prepared from bromoporphyrin **H_2-1l** (89.7 mg, 0.162 mmol) and arylmagnesium reagent **4a** following the general procedure; Purple solid; 77.8 mg, 77% yield; $R_f = 0.30$ (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.15 (1H, s), 9.29 (2H, d, $J = 4.8$ Hz), 9.21 (2H, d, $J = 4.8$ Hz), 9.11 (2H, d, $J = 4.8$ Hz), 8.88 (1H, s), 8.78 (2H, d, $J = 4.8$ Hz), 8.49 (1H, d, $J = 7.9$ Hz), 8.36 (1H, d, $J = 7.5$ Hz), 7.93 (2H, dd, $J = 3.5, 1.3$ Hz), 7.86 (2H, dd, $J = 5.1, 1.3$ Hz), 7.82 (1H, dd, $J = 7.9, 7.5$ Hz), 7.51 (2H, dd, $J = 5.1, 3.5$ Hz), 4.46 (2H, q, $J = 7.1$ Hz), 1.39 (3H, t, $J = 7.1$ Hz), –2.83 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.8, 148.1 (br), 148.0 (br), 146.4 (br), 146.2 (br), 142.8, 142.5, 138.2, 134.8, 133.9, 131.6, 131.43, 131.38, 130.9, 129.4, 129.1, 128.0, 126.7, 126.2, 119.9, 111.5, 105.7, 61.2, 14.3; IR (KBr) 3305, 3105, 3074, 2962, 2927, 2866, 1712, 1589, 1365, 1288, 1103, 949, 795, 702 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 417.5 (5.7), 512.5 (4.3), 550.5 (4.0), 587.5 (3.9), 643.0 (3.6) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{37}H_{27}N_4O_2S_2$ 623.1575, found 623.1579.

5,15-Di(*i*-butyl)-10-(3-ethoxycarbonylphenyl)porphyrin (H_2-3ma): Prepared from bromoporphyrin **H_2-1m** (81.2 mg, 0.162 mmol) and arylmagnesium reagent **4a** following the general procedure; Brown-purple solid; 63.8 mg, 69% yield; R_f = 0.33 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.05 (1H, s), 9.51 (2H, d, J = 4.8 Hz), 9.41 (2H, d, J = 4.8 Hz), 9.32 (2H, d, J = 4.8 Hz), 8.90 (1H, s), 8.80 (2H, d, J = 4.8 Hz), 8.52 (1H, d, J = 7.9 Hz), 8.36 (1H, d, J = 7.5 Hz), 7.82 (1H, dd, J = 7.9, 7.5 Hz), 4.83 (4H, d, J = 7.2 Hz), 4.49 (2H, q, J = 7.0 Hz), 2.92–2.69 (2H, m), 1.41 (3H, t, J = 7.0 Hz), 1.22 (12H, d, J = 6.4 Hz), –2.74 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.9, 148.1, 147.9, 145.0, 144.9, 143.6, 138.1, 134.6, 131.6, 131.5, 129.1, 128.9, 128.7, 128.1, 126.5, 118.4, 118.0, 104.2, 61.2, 43.4, 36.7, 23.3, 14.3; IR (KBr) 3290, 3116, 2954, 2870, 1716, 1581, 1466, 1281, 1107, 787 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 412.5 (5.6), 511.5 (4.3), 544.5 (3.8), 586.0 (3.8), 642.0 (3.6) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{37}H_{39}N_4O_2$ 571.3073, found 571.3073.

2-(3-Ethoxycarbonylphenyl)-5,10,15,20-tetraphenylporphyrin (H_2-3na): Prepared from bromoporphyrin **H_2-1n** (112.4 mg, 0.162 mmol) and arylmagnesium reagent **4a** following the general procedure; Purple solid; 106.3 mg, 86% yield; R_f = 0.32 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.95 (1H, d, J = 4.9 Hz), 8.94 (2H, d, J = 4.9 Hz), 8.92 (1H, d, J = 4.9 Hz), 8.88 (1H, s), 8.86 (1H, d, J = 4.9 Hz), 8.81 (1H, d, J = 4.9 Hz), 8.36–8.27 (6H, m), 8.07 (1H, s), 8.03–7.95 (2H, m), 7.90 (1H, d, J = 8.3 Hz), 7.86–7.76 (9H, m), 7.67 (1H, d, J = 7.8 Hz), 7.36–7.22 (4H, m), 4.47 (2H, q, J = 7.2 Hz), 1.48 (3H, t, J = 7.2 Hz), –2.49 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.6, 148.1 (br), 147.3 (2C, br), 146.9 (3C, br), 144.8, 144.1 (br), 143.4 (br), 142.6, 142.4, 142.0, 140.6, 139.1, 135.7 (2C), 134.6 (2C), 134.6 (2C), 134.6 (2C), 134.6 (2C), 134.3, 134.3, 131.8, 131.6 (2C), 131.4, 131.0 (2C), 130.8, 129.7, 127.8 (3C), 127.5, 127.4, 127.1, 126.8 (2C), 126.7 (4C), 126.1 (2C), 121.2, 120.5, 120.2, 120.0, 60.8, 14.4; IR (KBr) 3321, 3055, 3028, 2981, 2931, 2908, 1716, 1597, 1473, 1281, 1107, 987, 798, 725 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 422.0 (5.8), 518.5 (4.4), 553.5 (3.9), 593.0 (3.7), 650.5 (3.4) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{53}H_{39}N_4O_2$ 763.3073, found 763.3067.

5,15-Diphenyl-10,20-di(3-ethoxycarbonylphenyl)porphyrin (H_2-3oa): The general procedure with dibromoporphyrin **H_2-1o** (100.5 mg, 0.162 mmol) and 20 equiv instead of 10 equiv of arylmagnesium reagent **4a** (16 mL of its ca. 0.2 M solution in THF, ca. 3.2 mmol) gave the title compound as a purple solid (80.0 mg, 65% yield); R_f = 0.22 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.96 (2H, s), 8.91 (4H, d, J = 4.9 Hz), 8.83 (4H, d, J = 4.9 Hz), 8.52 (2H, d, J = 7.8 Hz), 8.43 (2H, d, J = 7.3 Hz), 8.30–8.21 (4H, m), 7.84 (2H, dd, J = 7.8, 7.3 Hz), 7.81–7.71 (6H, m), 4.50 (4H, q, J = 7.2 Hz), 1.43 (6H, t, J = 7.2 Hz), –2.61 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 146.8 (8C, br), 142.6, 142.2, 138.3, 134.9, 134.6, 131.5, 130.9, 129.5, 129.1, 127.8, 126.8, 126.7, 120.6, 119.0, 61.2, 14.3; IR (KBr) 3317, 3097, 3059, 3032, 2985, 2931, 2908, 1712, 1435, 1358, 1281, 1107, 972, 802, 744 cm^{-1}; UV/vis ($CHCl_3$)

λ_{max} (log ε) 419.0 (5.7), 505.0 (4.2), 549.0 (3.6), 588.5 (3.4), 644.5 (2.9) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{50}H_{39}N_4O_4$ 759.2971, found 759.2968.

5-(2-Ethoxycarbonylphenyl)-10,15,20-triphenylporphyrin (H$_2$-3ab): Prepared from bromoporphyrin **H$_2$-1a** (100.0 mg, 0.162 mmol) and arylmagnesium reagent **4b** following the general procedure; Purple solid; 69.1 mg, 62% yield; R_f = 0.32 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.86 (2H, d, J = 4.9 Hz), 8.85 (2H, d, J = 4.9 Hz), 8.83 (2H, d, J = 4.9 Hz), 8.70 (2H, d, J = 4.9 Hz), 8.41 (1H, d, J = 7.8 Hz), 8.28–8.20 (6H, m), 8.18 (1H, d, J = 7.3 Hz), 7.87 (1H, dd, J = 7.8, 7.6 Hz), 7.81 (1H, dd, J = 7.6, 7.3 Hz), 7.78–7.71 (9H, m), 3.21 (2H, q, J = 7.0 Hz), –0.42 (3H, t, J = 7.0 Hz), –2.56 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.5, 146.8 (8C, br), 142.5, 142.44, 142.35, 135.8, 135.1, 134.60, 134.57, 131.2, 131.0 (4C), 130.4, 129.6, 129.5, 128.3, 127.7 (3C), 126.7 (6C), 120.20, 120.16, 119.3, 60.0, 12.4; IR (KBr) 3317, 3059, 3028, 2981, 2924, 1720, 1469, 1254, 1080, 968, 798, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 419.0 (5.7), 516.0 (4.3), 550.5 (3.7), 591.0 (3.6), 646.5 (3.2) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{47}H_{35}N_4O_2$ 687.2760, found 687.2757; Anal. Calcd for $C_{47}H_{34}N_4O_2$: C, 82.19; H, 4.99; N, 8.16. Found: C, 82.38; H, 5.07; N, 8.03.

5-(4-Ethoxycarbonylphenyl)-10,15,20-triphenylporphyrin (H$_2$-3ac): Prepared from bromoporphyrin **H$_2$-1a** (100.0 mg, 0.162 mmol) and arylmagnesium reagent **4c** following the general procedure; Purple solid; 90.2 mg, 81% yield; R_f = 0.32 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.86 (6H, d, J = 4.9 Hz), 8.80 (2H, d, J = 4.9 Hz), 8.45 (2H, d, J = 8.2 Hz), 8.31 (2H, d, J = 8.2 Hz), 8.25–8.17 (6H, m), 7.83–7.66 (9H, m), 4.59 (2H, q, J = 7.1 Hz), 1.56 (3H, t, J = 7.1 Hz), –2.67 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.8, 147.1, 146.9 (8C, br), 142.2 (3C), 134.6 (8C), 131.4, 131.2 (4C), 130.7, 130.2, 127.9, 127.8 (3C), 126.7 (6C), 120.6, 120.4, 118.7, 61.3, 14.5; IR (KBr) 3317, 3105, 3055, 3028, 2978, 2927, 2858, 1720, 1604, 1481, 1358, 1273, 1180, 1107, 964, 802, 706 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 419.0 (5.7), 515.5 (4.3), 551.5 (4.0), 590.5 (3.8), 645.0 (3.6) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{47}H_{35}N_4O_2$ 687.2760, found 687.2756; Anal. Calcd for $C_{47}H_{34}N_4O_2$: C, 82.19; H, 4.99; N, 8.16. Found: C, 82.01; H, 5.25; N, 7.91.

5-(3-Cyanophenyl)-10,15,20-triphenylporphyrin (H$_2$-3ad): Prepared from bromoporphyrin **H$_2$-1a** (100.0 mg, 0.162 mmol) and arylmagnesium reagent **4d** following the general procedure; Purple solid; 75.6 mg, 73% yield; R_f = 0.35 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.90 (2H, d, J = 4.8 Hz), 8.86 (4H, d, J = 4.8 Hz), 8.71 (2H, d, J = 4.8 Hz), 8.54 (1H, s), 8.45 (1H, d, J = 7.9 Hz), 8.27–8.16 (6H, m), 8.07 (1H, d, J = 7.7 Hz), 7.84 (1H, dd, J = 7.9, 7.7 Hz), 7.80–7.70 (9H, m), –2.68 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.0 (8C, br), 143.9, 142.2, 142.1, 138.2, 137.1, 134.6 (6C), 131.7, 131.5, 131.3 (4C), 130.2, 127.9 (3C), 127.6, 126.8, 126.7, 121.0, 120.7, 118.8, 116.6, 111.5; IR (KBr) 3317, 3101, 3059, 3028, 2233, 1562, 1473, 1349, 1184, 972, 798, 729, 702 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε)

419.0 (5.7), 515.0 (4.3), 550.0 (3.9), 591.0 (3.8), 647.5 (3.6) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{45}H_{30}N_5$ 640.2501, found 640.2504.

5-(4-Chlorophenyl)-10,15,20-triphenylporphyrin (H$_2$-3ae): Prepared from bromoporphyrin **H$_2$-1a** (100.0 mg, 0.162 mmol) and arylmagnesium reagent **4e** following the general procedure; Purple solid; 84.0 mg, 80% yield; R_f = 0.65 (1:1 hexane/toluene); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.88 (4H, d, J = 4.8 Hz), 8.86 (2H, d, J = 4.8 Hz), 8.83 (2H, d, J = 4.8 Hz), 8.28–8.19 (6H, m), 8.15 (2H, d, J = 8.2 Hz), 7.82–7.67 (11H, m), –2.66 (2H, br s); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 146.9 (8C, br), 142.3 (3C), 140.9, 135.6 (6C), 134.6, 134.3, 131.2 (6C), 130.7, 127.8 (3C), 127.0, 126.7 (6C), 120.5, 120.4, 118.4; IR (KBr) 3317, 3055, 1558, 1473, 1350, 1180, 1088, 968, 798, 729 cm^{-1}; UV/vis (CHCl$_3$) λ_{max} (log ε) 418.5 (5.7), 515.0 (4.4), 550.0 (4.1), 591.0 (4.0), 645.5 (3.9) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{44}H_{30}ClN_4$ 649.2159, found 649.2159; Anal. Calcd for $C_{44}H_{29}ClN_4$: C, 81.41; H, 4.50; N, 8.63. Found: C, 81.78; H, 4.70; N, 8.70.

5-(3-Bromophenyl)-10,15,20-triphenylporphyrin (H$_2$-3af): Prepared from bromoporphyrin **H$_2$-1a** (100.0 mg, 0.162 mmol) and arylmagnesium reagent **4f** following the general procedure; Purple solid; 76.7 mg, 68% yield; R_f = 0.62 (1:1 hexane/toluene); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.89 (2H, d, J = 4.9 Hz), 8.86 (4H, d, J = 4.9 Hz), 8.85 (2H, d, J = 4.9 Hz), 8.41 (1H, s), 8.28–8.19 (6H, m), 8.17 (1H, d, J = 7.5 Hz), 7.92 (1H, d, J = 8.2 Hz), 7.82–7.70 (9H, m), 7.61 (1H, dd, J = 8.2, 7.5 Hz), –2.77 (2H, br s); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 146.9 (8C, br), 144.5, 142.3, 142.2 , 137.3 , 134.6 (6C), 133.2, 131.4, 131.2 (4C), 131.0, 130.7, 128.1, 127.8 (3C), 126.7 (6C), 121.2, 120.6, 120.4, 118.0; IR (KBr) 3317, 3101, 3055, 3028, 1585, 1558, 1469, 1350, 972, 798, 702 cm^{-1}; UV/vis (CHCl$_3$) λ_{max} (log ε) 418.5 (5.8), 515.5 (4.4), 550.5 (4.0), 590.0 (3.9), 645.5 (3.8) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{44}H_{30}BrN_4$ 693.1654, found 693.1645.

5-[3,5-Bis(trifluoromethyl)phenyl]-10,15,20-triphenylporphyrin (H$_2$-3ag): Prepared from bromoporphyrin **H$_2$-1a** (100.0 mg, 0.162 mmol) and arylmagnesium reagent **4g** following the general procedure; Purple solid; 87.6 mg, 72% yield; R_f = 0.70 (1:1 hexane/toluene); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.98 (2H, d, J = 4.9 Hz), 8.92 (2H, d, J = 4.9 Hz), 8.91 (2H, d, J = 4.9 Hz), 8.78 (2H, s), 8.75 (2H, d, J = 4.9 Hz), 8.41 (1H, s), 8.30–8.22 (6H, m), 7.84–7.74 (9H, m), –2.62 (2H, br s); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 147.1 (8C, br), 144.8, 142.11, 142.05, 134.6 (6C), 133.9, 132.1, 131.6, 131.5, 130.5 (2C, q, J_{CF} = 33.7 Hz), 129.9, 128.0, 127.9, 126.81, 126.78, 123.8 (2C, q, J_{CF} = 273.1 Hz), 121.9–121.6 (1C, m), 121.3, 120.9, 115.5; ^{19}F NMR (CDCl$_3$, 466 MHz) δ –63.9 (6F, s); IR (KBr) 3317, 3051, 1381, 1346, 1273, 1176, 1138, 968, 910, 798, 717 cm^{-1}; UV/vis (CHCl$_3$) λ_{max} (log ε) 419.0 (5.7), 515.0 (4.4), 551.0 (4.0), 590.5 (3.9), 645.5 (3.6) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{46}H_{29}F_6N_4$ 751.2296, found 751.2302.

5-(2-Methoxyphenyl)-10,15,20-triphenylporphyrin (H$_2$-3ah): Prepared from bromoporphyrin **H$_2$-1a** (100.0 mg, 0.162 mmol) and arylmagnesium reagent **4h** following the general procedure; Purple solid;

66.8 mg, 64% yield; R_f = 0.48 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.81 (6H, d, *J* = 4.9 Hz), 8.78 (2H, d, *J* = 4.9 Hz), 8.28–8.13 (6H, m), 8.01 (1H, d, *J* = 7.3 Hz), 7.81–7.62 (10H, m), 7.39–7.29 (2H, m), 3.58 (3H, s), –2.64 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.7, 146.8 (8C, br), 142.5, 142.4, 135.7, 134.6, 131.4, 131.1, 130.9 (6C), 129.9, 127.7 (3C), 126.6 (6C), 120.2, 119.9, 119.6, 116.2, 111.3, 56.0;IR (KBr) 3321, 3132, 3055, 3024, 2939, 1593, 1473, 1250, 972, 798, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 418.5 (5.7), 515.0 (4.3), 549.5 (3.7), 589.0 (3.6), 644.5 (3.1) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{45}H_{33}N_4O$ 645.2654, found 645.2656.

5-(4-*N,N*-Dimethylaminophenyl)-10,15,20-triphenylporphyrin (H_2-3ai): Prepared from bromoporphyrin **H_2-1a** (100.0 mg, 0.162 mmol) and arylmagnesium reagent **4i** following the general procedure; Purple solid; 84.2 mg, 79% yield; R_f = 0.24 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.98 (2H, d, *J* = 4.8 Hz), 8.86 (4H, d, *J* = 4.6 Hz), 8.85 (2H, d, *J* = 4.8 Hz), 8.29–8.19 (6H, m), 8.10 (2H, d, *J* = 8.6 Hz), 7.81–7.70 (9H, m), 7.10 (2H, d, *J* = 8.6 Hz), 3.22 (6H, s), –2.58 (2H, br s); ^{13}C NMR (CDCl3, 00 MHz) δ 150.2, 146.8 (8C, br), 142.54, 142.46, 135.7, 134.6 (6C), 131.5, 131.0, 130.8 (4C), 130.4, 127.6 (3C), 126.6 (6), 121.5, 120.0, 119.6, 110.8, 40.7; IR (KBr) 3317, 3028, 2897, 2854, 2800, 1604, 1516, 1473, 1354, 1188, 968, 802, 741 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 420.0 (5.5), 519.5 (4.3), 558.5 (4.1), 596.0 (3.9), 651.0 (3.9) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{46}H_{36}N_5$ 658.2971, found 658.2971; Anal. Calcd for $C_{46}H_{35}N_5$: C, 83.99; H, 5.36; N, 10.65. Found: C, 83.98; H, 5.35; N, 10.56.

5-(4-Trimethylsilylphenyl)-10,15,20-triphenylporphyrin (H_2-3aj): Prepared from bromoporphyrin **H_2-1a** (100.0 mg, 0.162 mmol) and arylmagnesium reagent **4j** following the general procedure; Purple solid; 90.2 mg, 81% yield; R_f = 0.75 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.91 (2H, d, *J* = 4.9 Hz), 8.87 (4H, d, *J* = 4.9 Hz), 8.87 (2H, d, *J* = 4.9 Hz), 8.29–8.20 (8H, m), 7.92 (2H, d, *J* = 7.8 Hz), 7.82–7.69 (9H, m), 0.55 (9H, s), –2.62 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.9 (8C, br), 142.7, 142.41 (3C), 139.7, 134.61 (6C), 134.1, 131.7, 131.1 (8C), 127.7 (3C), 126.7 (6C), 120.4, 120.2 (3C), –0.81; IR (KBr) 3321, 3059, 3024, 2954, 1597, 1473, 1350, 1250, 972, 841, 798, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 419.0 (5.8), 516.0 (4.4), 551.0 (4.0), 590.5 (3.8), 646.0 (3.7) nm; HRMS-FAB$^+$ ($[M+H]^+$) calcd for $C_{47}H_{39}N_4Si$ 687.2944, found 687.2946; Anal. Calcd for $C_{47}H_{38}N_4Si$: C, 82.18; H, 5.58; N, 8.16. Found: C, 82.47; H, 5.81; N, 7.86.

5-(3-Pyridyl)-10,15,20-triphenylporphyrin (H_2-3ak): Prepared from bromoporphyrin **H_2-1a** (100.0 mg, 0.162 mmol) and heteroarylmagnesium reagent **4k** following the general procedure; Purple solid; 50.9 mg, 51% yield; R_f = 0.28 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.50 (1H, s), 9.04 (1H, d, *J* = 3.8 Hz), 8.91 (2H, d, *J* = 4.8 Hz), 8.88 (2H, d, *J* = 4.8 Hz), 8.87 (2H, d, *J* = 4.8 Hz), 8.80 (2H, d, *J* = 4.8 Hz), 8.51 (1H, d, *J* = 7.7 Hz), 8.28–8.18 (6H, m), 7.83–7.66 (10H, m), –2.65 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.8, 149.1, 147.0 (8C, br), 142.18, 142.16, 140.8, 138.3, 134.6 (6C), 131.7, 131.3 (4C), 130.4, 127.8 (3C), 126.7 (6C), 121.9, 120.8, 120.6, 115.5; IR (KBr), 3317, 3055, 3028, 1558, 1473, 1404, 1350, 1184, 972, 798, 729, 706 cm^{-1}; UV/vis (CHCl$_3$) λ_{max} (log ε) 418.5 (5.8), 515.5 (4.4), 550.0 (4.0), 590.5 (3.9), 645.5 (3.7) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{43}H_{30}N_5$ 616.2501, found 616.2501.

5-(3-Thienyl)-10,15,20-triphenylporphyrin (H$_2$-3al): Prepared from bromoporphyrin **H$_2$-1a** (100.0 mg, 0.162 mmol) and heteroarylmagnesium reagent **4l** following the general procedure; Purple solid; 55.4 mg, 55% yield; R_f = 0.40 (1:1 hexane/toluene); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.98 (2H, d, J = 4.9 Hz), 8.86 (2H, d, J = 4.9 Hz), 8.85 (4H, d, J = 4.9 Hz), 8.25–8.20 (6H, m), 8.02 (1H, dd, J = 2.9, 1.0 Hz), 8.00 (1H, ddd, J = 4.9, 2.9, 1.0 Hz), 7.81–7.72 (9H, m), 7.70 (1H, ddd, J = 4.9, 2.9, 1.0 Hz), –2.65 (2H, br s); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 146.9 (8C, br), 142.5, 142.4 (3C), 134.6 (6C), 131.1 (6C), 130.8, 128.3, 127.8 (3C), 126.7 (6C), 123.4 (2C), 120.4, 120.3, 114.5; IR (KBr) 3321, 3101, 3055, 3028, 1473, 1346, 1176, 972, 798, 741, 702 cm^{-1}; UV/vis (CHCl$_3$) λ_{max} (log ε) 419.0 (5.4), 516.0 (4.3), 552.5 (4.0), 590.5 (3.8), 647.5 (3.6) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{42}H_{29}N_4S$ 621.2113, found 621.2114.

(*Z*)-5-(2-Ethoxycarbonyl)vinyl-10,15,20-triphenylporphyrin (H$_2$-3am): The general procedure with bromoporphyrin **H$_2$-1a** (100.0 mg, 0.162 mmol) and 40 equiv instead of 10 equiv of alkenykmagnesium reagent **4m** (32 mL of its ca. 0.2 M solution in THF, ca. 6.4 mmol) gave the title compound as a purple solid (56.7 mg, 55%); R_f = 0.34 (1:1 hexane/toluene); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 10.33 (1H, d, J = 15.6 Hz), 9.55 (2H, d, J = 4.9 Hz), 8.99 (2H, d, J = 4.9 Hz), 8.87 (2H, d, J = 4.9 Hz), 8.85 (2H, d, J = 4.9 Hz), 8.31–8.21 (6H, m), 7.86–7.72 (9H, m), 6.92 (1H, d, J = 15.6 Hz), 4.60 (2H, q, J = 7.0 Hz), 1.59 (3H, t, J = 7.0 Hz), –2.36 (2H, br s); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 166.3, 146.8 (8C, br), 145.7, 142.1, 141.9, 134.54, 134.49, 132.1, 131.4, 131.3 (4C), 128.8, 127.9 (3C), 126.8 (6C), 121.8, 121.1, 112.3, 60.9, 14.5; IR (KBr) 3317, 3055, 2981, 2904, 1712, 1620, 1469, 1362, 1273, 1165, 972, 725 cm^{-1}; UV/vis (CHCl$_3$) λ_{max} (log ε) 425.0 (5.6), 522.0 (4.1), 565.5 (4.1), 657.5 (3.6) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{43}H_{33}N_4O_2$ 637.2604, found 637.2599; Anal. Calcd for $C_{43}H_{32}N_4O_2$: C, 81.11; H, 5.07; N, 8.80. Found: C, 81.17; H, 5.19; N, 8.58.

(*Z*)-5-(2-Cyano)vinyl-10,15,20-triphenylporphyrin (H$_2$-3an): The general procedure with bromoporphyrin **H$_2$-1a** (100.0 mg, 0.162 mmol) and 40 equiv instead of 10 equiv of alkenykmagnesium reagent **4n** (32 mL of its ca. 0.2 M solution in THF, ca. 6.4 mmol) gave the title compound as a purple solid (49.7 mg, 52%); R_f = 0.37 (1:1 hexane/toluene); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 9.64 (1H, d, J = 11.2 Hz), 9.24 (2H, d, J = 4.9 Hz), 8.93 (2H, d, J = 4.9 Hz), 8.80 (2H, d, J = 4.9 Hz), 8.78 (2H, d, J = 4.9 Hz), 8.28–8.12 (6H, m), 7.84–7.67 (9H, m), 6.59 (1H, d, J = 11.2 Hz), –2.55 (2H, br s); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 151.2, 146.9 (8C, br), 142.0 (3C), 134.6, 134.5, 132.4, 131.5, 131.2, 128.6, 127.9 (3C), 126.8, 126.7, 122.1, 121.1, 116.5, 109.6, 106.5; IR (KBr) 3321, 3055, 3032, 2954, 2920, 2222, 1601, 1558, 1469, 1354, 1157, 1072, 972, 798, 706 cm^{-1}; UV/vis (CHCl$_3$) λ_{max} (log ε) 423.0 (5.7), 519.5 (4.4), 558.5 (4.2), 594.5 (4.0), 652.5 (3.5) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{41}H_{28}N_5$ 590.2345, found 590.2350.

(*E*)-5-(2-Cyano)vinyl-10,15,20-triphenylporphyrin (H_2-3ao): The general procedure with bromoporphyrin **H_2-1a** (100.0 mg, 0.162 mmol) and 40 equiv, instead of 10 equiv, of alkenykmagnesium reagent **4o** (32 mL of its ca. 0.2 M solution in THF, ca. 6.4 mmol) gave the title compound as a purple solid (58.3 mg, 61%); R_f = 0.37 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.92 (1H, d, J = 16.1 Hz), 9.32 (2H, d, J = 4.9 Hz), 8.92 (2H, d, J = 4.9 Hz), 8.79 (2H, d, J = 4.9 Hz), 8.76 (2H, d, J = 4.9 Hz), 8.22–8.12 (6H, m), 7.84–7.68 (9H, m), 6.20 (1H, d, J = 16.1 Hz), –2.46 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.8, 146.8 (8C, br), 141.9, 141.7, 134.51, 134.47, 132.6, 131.6, 131.4, 128.1, 128.03, 127.95, 126.9, 126.8, 122.6, 121.6, 118.2, 110.4, 107.8; IR (KBr) 3317, 3105, 3059, 3028, 2214, 1604, 1477, 1354, 1165, 968, 798, 733 cm^{-1}; UV/vis ($CHCl_3$) λ_max (log ε) 427.5 (5.5), 525.5 (4.1), 566.5 (4.1), 659.0 (3.8) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{41}H_{28}N_5$ 590.2345, found 590.2350; Anal. Calcd for $C_{41}H_{27}N_5$: C, 83.51; H, 4.61; N, 11.88. Found: C, 83.73; H, 4.72; N, 12.02.

(*E*)-5-(2-*N,N*-Dimethylaminocarbonyl)vinyl-10,15,20-triphenylporphyrin (H_2-3ap): The general procedure with bromoporphyrin **H_2-1a** (100.0 mg, 0.162 mmol) and 40 equiv instead of 10 equiv of alkenykmagnesium reagent **4p** (32 mL of its ca. 0.2 M solution in THF, ca. 6.4 mmol) gave the title compound as a purple solid (57.8 mg, 56%); R_f = 0.24 (1:1 hexane/toluene); ^{1}H NMR (THF-d_8, 400 MHz) δ 10.08 (1H, d, J = 15.1 Hz), 9.48 (2H, d, J = 4.9 Hz), 8.85 (2H, d, J = 4.9 Hz), 8.76 (2H, d, J = 4.9 Hz), 8.75 (2H, d, J = 4.9 Hz), 8.23–8.08 (6H, m), 7.79–7.63 (9H, m), 7.26 (1H, d, J = 15.1 Hz), 3.18 (6H, br s), –2.45 (2H, br s); ^{13}C NMR (THF-d_8, 100 MHz) δ 165.0, 146.7 (8C, br), 142.4, 142.2, 141.8, 134.37, 134.35, 132.9, 131.4, 130.8 (4C), 128.9, 127.7 (3C), 126.6 (6C), 120.8, 120.5, 114.7, 36.3 (br), 34.9 (br); IR (KBr) 3317, 3105, 3055, 2920, 2858, 1647, 1608, 1473, 1396, 1350, 1142, 972, 802, 741 cm^{-1}; UV/vis ($CHCl_3$) λ_max (log ε) 425.5 (5.6), 524.5 (4.2), 563.0 (4.2), 657.0 (3.8) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{43}H_{34}N_5O$ 636.2763, found 636.2766.

(*E*)-5-(2-Trimethylsilyl)vinyl-10,15,20-triphenylporphyrin (H_2-3aq): The general procedure with bromoporphyrin **H_2-1a** (100.0 mg, 0.162 mmol) and 40 equiv instead of 10 equiv of alkenykmagnesium reagent **4q** (32 mL of its ca. 0.2 M solution in THF, ca. 6.4 mmol) gave the title compound as a purple solid (76.2 mg, 74%); R_f = 0.68 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.49 (1H, d, J = 18.9 Hz), 9.47 (2H, d, J = 4.8 Hz), 8.94 (2H, d, J = 4.8 Hz), 8.84 (4H, d, J = 4.8 Hz), 8.30–8.20 (6H, m), 7.84–7.71 (9H, m), 6.97 (1H, d, J = 18.9 Hz), 0.60 (9H, s), –2.48 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.3, 146.7 (8C, br), 144.2, 142.5, 142.3, 134.6, 134.5, 131.2, 131.1, 131.0, 129.4, 127.7 (3C), 126.7 (6C), 120.24, 120.17, 119.6, –0.9; IR (KBr) 3317, 3055, 2951, 2924, 2854, 1593, 1469, 1250, 976, 864, 795, 729 cm^{-1}; UV/vis ($CHCl_3$) λ_max (log ε) 421.5 (5.6), 520.5 (4.2), 558.5 (4.0), 598.0 (3.8), 654.0 (3.7) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{43}H_{37}N_4Si$ 637.2787, found 637.2797; Anal. Calcd for $C_{43}H_{36}N_4Si$: C, 81.09; H, 5.70; N, 8.80. Found: C, 80.76; H, 5.66; N, 8.62.

5-(1-Trimethylsilyl)vinyl-10,15,20-triphenylporphyrin (H_2-3ar): The general procedure with bromoporphyrin **H_2-1a** (100.0 mg, 0.162 mmol) and 40 equiv, instead of 10 equiv, of alkenykmagnesium reagent **4r** (32 mL of its ca. 0.2 M solution in THF, ca. 6.4 mmol) gave the title compound as a purple solid (87.8 mg, 85%); R_f = 0.70 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.22 (2H, d, J = 4.8 Hz), 8.87 (2H, d, J = 4.8 Hz), 8.83 (2H, d, J = 4.8 Hz), 8.81 (2H, d, J = 4.8 Hz), 8.37–8.06 (6H, m), 7.84–7.64 (9H, m), 6.84 (1H, d, J = 3.3 Hz), 6.69 (1H, d, J = 3.3 Hz), 0.18 (9H, s), –2.70 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.8, 146.7 (6C), 145.0, 142.49, 142.45, 134.6 (6C), 132.4, 131.2, 130.9, 130.7, 130.6, 127.7 (3C), 126.7 (6C), 124.1, 119.9, 119.3, -0.7; IR (KBr) 3317, 3055, 2954, 2897, 1469, 1346, 1250, 972, 845, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 419.0 (5.7), 517.5 (4.3), 553.0 (4.0), 593.5 (3.7), 648.5 (3.7) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{43}H_{37}N_4Si$ 637.2787, found 637.2789; Anal. Calcd for $C_{43}H_{36}N_4Si$: C, 81.09; H, 5.70; N, 8.80. Found: C, 81.01; H, 5.66; N, 8.80.

5-(2-Bromocyclopent-1-enyl)-10,15,20-triphenylporphyrin (H_2-3as): The general procedure with bromoporphyrin **H_2-1a** (100.0 mg, 0.162 mmol) and 40 equiv instead of 10 equiv of alkenylmagnesium reagent **4s** (32 mL of its ca. 0.2 M solution in THF, ca. 6.4 mmol) gave the title compound as a purple solid (72.0 mg, 65%); R_f = 0. 68 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.21 (2H, d, J = 4.9 Hz), 8.96 (2H, d, J = 4.9 Hz), 8.86 (2H, d, J = 4.9 Hz), 8.85 (2H, d, J = 4.9 Hz), 8.32–8.19 (6H, m), 7.83–7.70 (9H, m), 3.62 (2H, t, J = 7.3 Hz), 3.48 (2H, t, J = 7.6 Hz), 2.68 (2H, tt, J = 7.6, 7.3 Hz), –2.66 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.9 (8C, br), 143.2, 142.4, 142.2, 134.6, 134.5, 131.8, 131.2, 131.0, 129.4, 127.7 (3C), 126.7, 126.6, 125.5, 120.6, 112.0, 114.6, 45.1, 41.8, 23.9; IR (KBr) 3321, 3093, 3055, 3024, 2943, 2850, 1558, 1473, 1350, 1184, 972, 798, 733 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 418.5 (5.7), 514.5 (4.3), 549.5 (3.9), 590.5 (3.8), 645.5 (3.6) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{43}H_{32}BrN_4$ 683.1810, found 683.1813; Anal. Calcd for $C_{43}H_{31}BrN_4$: C, 75.55; H, 4.57; N, 8.20. Found: C, 75.44; H, 4.56; N, 8.03.

5-[4-{(Tetrahydro-2H-pyran-2-yl)oxy}phenyl]-10,15,20-triphenylporphyrin (H_2-3at): The general procedure with bromoporphyrin **H_2-1a** (100.0 mg, 0.162 mmol) and arylmagnesium reagent **4t**, followed by demetalation with 5 mL of a 0.1 M methanol solution of citric acid, instead of a 1.2 M aqueous MeOH solution of HCl (a 1:9 mixture of conc. HCl and MeOH), gave the title compound as a purple solid (90.2 mg, 78%); R_f = 0.42 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.93 (2H, d, J = 4.9 Hz), 8.86 (6H, d, J = 4.9 Hz), 8.28–8.20 (6H, m), 8.14 (2H, d, J = 8.3 Hz), 7.81–7.70 (9H, m), 7.45 (2H, d, J = 8.3 Hz), 5.73 (1H, t, J = 3.4 Hz), 4.20 (1H, td, J = 10.4, 3.8 Hz), 3.85–3.77 (1H, m), 2.26–2.12 (1H, m), 2.11–2.02 (2H, m), 1.88–1.69 (3H, m), –2.67 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.2, 146.9 (8C, br), 142.4, 135.6 (3C), 135.5, 134.6 (6C), 131.0 (8C, br), 127.7 (3C), 126.7 (6C), 120.2, 120.1, 120.0, 114.8, 97.0, 62.5, 30.7, 25.4, 19.1; IR (KBr) 3321, 3101, 3055, 3028, 2943, 2873, 1601, 1470, 1350, 1230, 964, 798, 741 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 419.5 (5.8), 516.0 (4.3), 552.0 (3.9), 591.5 (3.6), 647.0 (3.5) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{49}H_{39}N_4O_2$ 715.3073, found 715.3080; Anal. Calcd for $C_{49}H_{38}N_4O_2$: C, 82.33; H, 5.36; N, 7.84. Found: C, 82.28; H, 5.42; N, 7.74.

5-(4-Hydroxyphenyl)-10,15,20-triphenylporphyrin (H$_2$-7): Prepared from bromoporphyrin **H$_2$-1a** (100.0 mg, 0.162 mmol) and arylmagnesium reagent **4t** following the general procedure; Purple solid; 74.6 mg, 73% yield; R_f = 0.22 (1:1 hexane/toluene); ^{1}H NMR (THF-d_8, 400 MHz) δ 8.92 (2H, d, J = 4.9 Hz), 8.81 (6H, d, J = 4.9 Hz), 8.58 (1H, br s), 8.24-8.15 (6H, m), 8.03 (2H, d, J = 8.3 Hz), 7.75-7.65 (9H, m), 7.17 (2H, d, J = 8.3 Hz), -2.58 (2H, br s); ^{13}C NMR (THF-d_8, 100 MHz) δ 158.8, 147.7 (8C, br), 143.5, 143.4, 136.4, 135.3 (6C), 134.1, 131.9, 131.5 (6C, br), 128.5 (3C), 127.5 (6C), 121.6, 120.9, 120.7, 114.6; IR (KBr) 3317, 3051, 1701, 1601, 1562, 1473, 1350, 1211, 968, 798, 702 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 420.0 (5.6), 516.5 (4.4), 552.5 (3.9), 592.0 (3.6), 647.5 (3.5) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{44}H_{31}N_4O$ 631.2498, found 631.2496; Anal. Calcd for $C_{44}H_{30}N_4O$: C, 83.79; H, 4.79; N, 8.88. Found: C, 83.62; H, 5.00; N, 8.71.

5-[4-(1,3-Dioxolan-2-yl)phenyl]-10,15,20-triphenylporphyrin (H$_2$-3au): The general procedure with bromoporphyrin **H$_2$-1a** (100.0 mg, 0.162 mmol) and arylmagnesium reagent **2u**, followed by demetalation with 5 mL of a 0.1 M MeOH solution of citric acid, instead of a 1.2 M aqueous MeOH solution of HCl (a 1:9 mixture of conc. HCl and MeOH), gave the title compound as a purple solid (84.8 mg, 76%); R_f = 0.43 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.87 (8H, d, J = 4.8 Hz), 8.26 (2H, d, J = 8.2 Hz), 8.24–8.19 (6H, m), 7.88 (2H, d, J = 8.2 Hz), 7.82–7.67 (9H, m), 6.15 (1H, s), 4.35 (2H, t, J = 7.0 Hz), 4.21 (2H, t, J = 7.0 Hz), –2.69 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.8 (8C, br), 143.3, 142.3 (3C), 137.4, 134.6 (8C), 131.1 (8C, br), 127.7 (3C), 126.7 (6C), 124.9, 120.3, 120.2, 119.6, 104.1, 65.6; IR (KBr) 3317, 3055, 3028, 2954, 2924, 2877, 1601, 1473, 1350, 1219, 1076, 972, 802, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 418.5 (5.8), 515.5 (4.3), 550.0 (3.8), 589.5 (3.6), 645.5 (3.3) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{47}H_{35}N_4O_2$ 687.2760, found 687.2756; Anal. Calcd for $C_{47}H_{34}N_4O_2$: C, 82.19; H, 4.99; N, 8.16. Found: C, 82.10; H, 5.05; N, 7.86.

5-(4-Formylphenyl)-10,15,20-triphenylporphyrin (H$_2$-8): Prepared from bromoporphyrin **H$_2$-1a** (100.0 mg, 0.162 mmol) and arylmagnesium reagent **4u** following the general procedure; Purple solid; 73.9 mg, 71% yield; R_f = 0.41 (1:1 hexane/toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.34 (1H, s), 8.89 (4H, d, J = 4.8 Hz), 8.88 (2H, d, J = 4.8 Hz), 8.78 (2H, d, J = 4.8 Hz), 8.39 (2H, d, J = 7.9 Hz), 8.27-8.19 (8H, m), 7.80-7.71 (9H, m), -2.68 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 192.2, 148.7, 146.7 (8C, br), 142.09, 142.07, 135.7, 135.2, 134.5 (6C), 131.6, 131.3 (4C, br), 130.5, 127.9, 127.8 (3C), 126.7 (6C), 120.8, 120.5, 118.1; IR (KBr) 3579, 3518, 3425, 3317, 3055, 3028, 1601, 1473, 1350, 1265, 1176, 972, 802, 706 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 419.5 (5.8), 516.5 (4.3), 551.5 (3.8), 590.5 (3.6), 647.0 (3.3) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{45}H_{31}N_4O$ 643.2498, found 643.2495; Anal. Calcd for $C_{45}H_{30}N_4O$: C, 84.09; H, 4.70; N, 8.72. Found: C, 84.39; H, 4.80; N, 8.48.

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