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Palladium-catalyzed Kumada Coupling Reaction of Bromoporphyrins with Silylmethyl Grignard Reagents: Preparation of Silylmethyl-substituted Porphyrins as a Multipurpose Synthon for Fabrication of Porphyrin Systems

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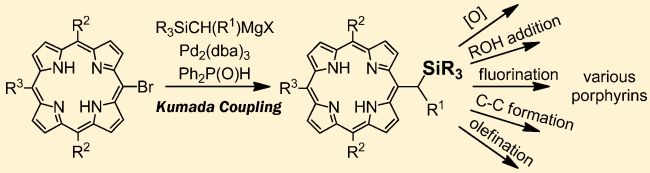
Supporting Information

ABSTRACT: We have developed an efficient method for preparing silylmethyl-substituted porphyrins via the palladium-catalyzed Kumada cross-coupling reaction of bromoporphyrins with silylmethyl Grignard reagents. We demonstrated the synthetic utility of these silylmethylporphyrins as a multipurpose synthon for fabricating porphyrin derivatives through a variety of transformations of the silylmethyl groups, including the DDQ-promoted oxidative conversion to CHO, CH_2OH, CH_2OMe, and CH_2F functionalities and the fluoride ion-mediated desilylative introduction of carbon−carbon single and double bonds.



INTRODUCTION

Porphyrins are a class of chemically and biologically important aromatic compounds that are used in catalysis, molecular recognition, pharmaceuticals, and materials.[1−5] The physical, chemical, and biological properties of porphyrins are strongly dependent on the electronic and steric environments of their peripheral substituents.[1] Therefore, the discovery of new synthetic intermediates and strategies for preparing porphyrin derivatives possessing a variety of peripheral substituents has been actively pursued.[6−9]

Recently, our interest in constructing porphyrin-based molecular devices has required efficient and versatile multipurpose synthons bearing reactive functional groups on the porphyrin core which can be converted to many other functional groups with different chemical and structural properties. Silylmethyl groups (R_3SiCH_2-), particularly as a substituent on an aromatic ring, often play an important role in synthetic chemistry, because of their versatility and diverse transformations to a wide variety of functional groups.[10−15] For instance, silylmethyl-substituted arenes can be deprotonated at the benzylic position with a base or desilylated with fluoride ions to generate the benzylic anion. This anion can readily react with a variety of electrophiles to create new carbon−carbon[11] or carbon-heteroatom bonds[12] at the benzylic position. In addition, silyl groups at the benzylic position of arenes function as an electro-auxiliary that reduces the oxidation potential compared with that of the parent arenes without the silyl substituents. This can effectively promote the oxidative substitution of the silyl groups with oxygen functional groups to afford the corresponding products, such as formyl- and hydroxylmethyl-substituted derivatives.[11b,13,14] Therefore, silylmethyl-substituted porphyrins are a potential multipurpose synthon for constructing diverse porphyrin derivatives of higher complexity. To our knowledge, the direct introduction of silylmethyl groups onto the porphyrin core has not been reported. We have focused on functionalizing porphyrins by transition-metal catalysis[8] and S_NAr reactions with organolithium reagents.[9] In this paper, we describe an efficient palladium-catalyzed Kumada coupling reaction between bromoporphyrin derivatives **1** and silylmethyl Grignard reagents **2**. This reaction provides a facile route to a variety of silylmethyl-substituted porphyrins **3**, including *meso*-mono-, *meso*-bis-, and *β*-monosilylmethylporphyrins. We also report the convenient transformation of the silylmethyl groups to other functionalities, including hydroxymethyl, formyl, alkoxymethyl, fluoromethyl, and alkenyl groups, and to elongated alkyl chains.

RESULTS AND DISCUSSION

We have recently reported a one-pot procedure for the direct conversion of 5,15-disubstituted porphyrins into *meso*-formylporphyrins **A** via a sequential S_NAr reaction with (2-pyridyldimethylsilyl)methyllithium ($PyMe_2SiCH_2Li$) followed by oxidation with DDQ (Scheme 1).[9a] We tentatively assumed that this transformation involves the sequential generation of silylmethyl-substituted dihydroporphyrin **B** and silylmethyl-substituted porphyrin **C** (Scheme 1). Thus, we predicted that silylmethylporphyrins could be prepared via this transformation if the intermediate **C** could be isolated. However, our attempts at isolating the intermediate silylmethylporphyrins **C** were unsuccessful, probably because of their instability under the oxidation conditions; even the use of molecular oxygen instead of DDQ did not suppress the overoxidation of the desired

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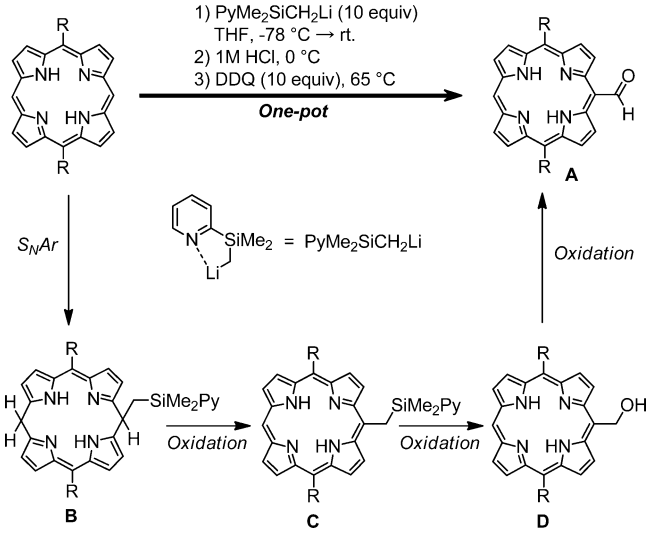
Scheme 1. Our Previous Protocol for Direct *meso*-Formylation of 5,15-Disubstituted Porphyrins



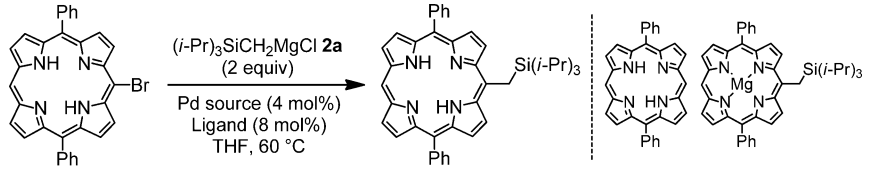
silylmethylporphyrins **C**, and hydroxymethyl-substituted porphyrins **D** were obtained as the sole isolable products.[9c] Therefore, we turned our attention to a Pd-based cross-coupling method using bromoporphyrins **1** as the precursor for silylmethyl-substituted porphyrins **3**. Silylmethyl Grignard reagents **2** were selected as the coupling partner because of their easy accessibility; a number of different silylmethyl Grignard reagents **2** can be prepared in situ from readily available (halomethyl)silane derivatives, some of which are commercially available, according to conventional procedures for making Grignard reagents.[16−19]

We initially examined the catalytic activity of different palladium complexes and phosphine ligands for the model reaction between free base 5-bromo-10,20-diphenylporphyrin **1a** and (tri-*iso*-propylsilyl)methylmagnesium chloride **2a** in THF at 60 °C (Table 1). The use of well-defined palladium tertiary phosphine complexes, either generated in situ or preformed, was ineffective in the coupling reaction, and afforded only low yields of the desired silylmethyl-substituted porphyrin **3aa** and the dehalogenated product **4a**.[20] The palladium *N*-heterocyclic carbene complex, PEPPSI, which is often an effective catalyst in the Kumada reaction,[21] was less effective (entry 3). In contrast, the complex with a secondary phosphine oxide ligand, $Ph_2P(O)H$, and $Pd(OAc)_2$ was promising (entry 7).[22] Finally, the combination of the phosphine oxide ligand and $Pd_2(dba)_3$ as the palladium source produced optimal yields (entry 11). Notably, under these conditions, no formation of the corresponding metalated complex **Mg-3aa** was observed, and the free base silylmethylporphyrin **3aa** was obtained as the sole isolable product.

Next, we examined the Pd(0) catalyzed cross-coupling reactions of bromoporphyrin **1a** with a series of silylmethyl magnesium reagents **2**, which contained different substituents on the silicon atom or the carbon α to the silyl group (Table 2). A facile, efficient *meso*-silylmethylation of **1a** with yields above 70% was observed for all the silylmethyl magnesium reagents examined. The (trialkylsilyl)methyl magnesium reagents, **2a**−**2c**, and the Grignard reagents, **2d** and **2e**, bearing phenyl substituents on the silicon atom readily participated in the silylmethylation of diphenylporphyrin **1a** to afford the corresponding *meso*-silylmethylated products in good yields (entries 1−5). The *i*-PrO and benzyl substituents on the silicon atom were also tolerated well under these reaction conditions (entries 6 and 7). Moreover, the sterically demanding bis(trimethylsily)methyl magnesium reagent **2h**[23] provided **3ah** in 71% yield, though an increase in the amount of the Grignard reagent was necessary to complete the reaction (entry 8). Notably, in these reactions examined, desilylation of the products could not be observed; none of desilylative products, such as *meso*-methylporphyrin **5a**, could be detected in the ^{1}H NMR spectrum of the crude products.

A variety of mono- and dibromoporphyrins **1** were also examined using readily available (trimethylsilyl)-

Table 1. Palladium Catalyst Screening for Kumada Cross-Coupling



1a **3aa** **4a** **Mg-3aa**

entry	Pd source	ligand	*t* (h)	yield[a] (%) of **3aa**	yield[a] (%) of **4a**
1	$Pd(PCy_3)_2Cl_2$		8	26	70
2	$Pd(P(t\text{-}Bu)_3)_2$		8	18	73
3	PEPPSI[b]		4	22	76
4	$Pd(OAc)_2$	*rac*-BINAP[c]	12	0	>99
5		SPhos[d]	12	0	98
6		$BPPCy_2$[e]	12	trace	94
7		$Ph_2P(O)H$	10	43	53
8	$Pd_2(dba)_3$[f]	*rac*-BINAP	12	0	>99
9		SPhos	12	0	>99
10		$BPPCy_2$	10	16	79
11		$Ph_2P(O)H$	6	87	8

[a]Isolated yield. [b]PEPPSI: [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride. [c]BINAP: 2,2′-bis-(diphenylphosphino)-1,1′-binaptharene. [d]SPhos: 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl. [e]$BPPCy_2$: 2-(dicyclohexylphosphino)biphenyl. [f]2 mol % $Pd_2(dba)_3$ was used.

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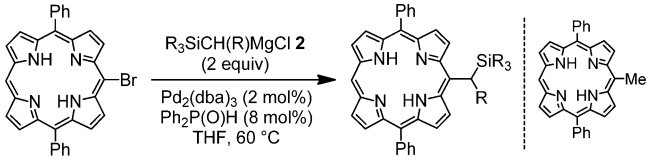
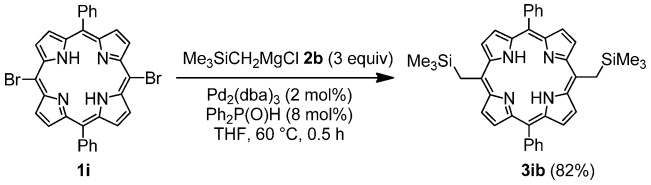
Table 2. Palladium-catalyzed Cross-Coupling of 1a with Various Grignard Reagents



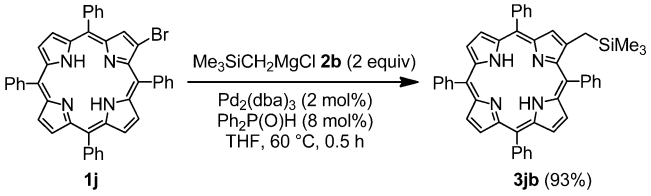
entry	silylmethyl Grignard reagent	product	t (h)	yield[a] (%)
1	i-Pr_3SiCH_2MgCl (**2a**)	**3aa**	6	87
2	Me_3SiCH_2MgCl (**2b**)	**3ab**	1	86
3	Et_3SiCH_2MgCl (**2c**)	**3ac**	2	83
4	Ph_3SiCH_2MgCl (**2d**)	**3ad**	6	75
5	$PhMe_2SiCH_2MgCl$ (**2e**)	**3ae**	1	87
6	$PhCH_2Me_2SiCH_2MgCl$ (**2f**)	**3af**	1	88
7	i-$PrOMe_2SiCH_2MgCl$ (**2g**)	**3ag**	0.5	81
8	$(Me_3Si)_2CHMgCl$ (**2h**)[b]	**3ah**	4	71

[a]Isolated yield. [b]5 equiv of **2h** was used.

Scheme 2. Preparation of Bis(trimethylsilylmethyl)porphyrin 3ib



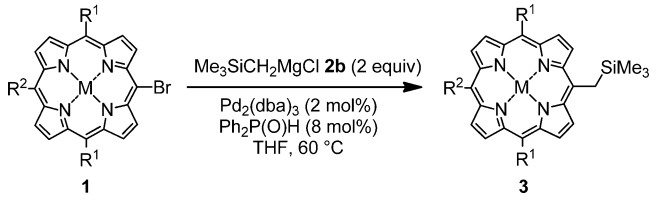
Scheme 3. Preparation of β-Silylmethyl-substituted Porphyrin 3jb



methylmagnesium chloride **2b** as the coupling partner with the optimized conditions (Table 3). These conditions were suitable for various phenyl substituents on the *meso*-brominated free base diarylporphyrins, and the desired products were obtained in good to high yields (entries 1−6). Likewise, other free bases, including 10,20-dialkyl- and 10,15,20-trisubstituted bromoporphyrins, readily participated in the catalytic silylmethylation (entries 7 and 8). In addition, the silylmethylation reaction also proceeded with a series of metalloporphyrin complexes, such as Zn(II), Mg(II), and Ni(II) complexes of **1a**, affording the corresponding metal-containing, silylmethyl-substituted porphyrins in high yields (entries 9−11). Moreover, the direct conversion of dibromoporphyrin **1i** to porphyrin **3ib**, which contained two silylmethyl substituents at the *meso* positions, was achieved under similar reaction conditions (Scheme 2). Silylmethylation at the β-position of the porphyrin core was also achieved under the same reaction conditions; β-silylmethylated porphyrin **3jb** was obtained in 93% isolated yield from the corresponding base porphyrin **1j** (Scheme 3).

To evaluate the synthetic utility of silylmethylporphyrins **3** as a multipurpose synthon for constructing porphyrin derivatives, we investigated several transformations of the silylmethyl group to other functionalities (Schemes 4−8). The oxidation of silylmethylporphyrin **3ab** with 10 equiv of DDQ in the presence of water in a mixed solvent system (THF/CH_3CN = 1:1) at 60 °C gave the corresponding *meso*-formylporphyrin **5** in 92% yield (Scheme 4a). Under the same reaction conditions, the *meso*-di- and β-formyl-substituted derivatives, **13** and **14**, were obtained from the *meso*-bis- and β-silylmethyl-substituted porphyrins, respectively, in good yields (Schemes 5 and 6). To our knowledge, these results are the first examples of direct, regioselective *meso*-di- and β-formylation of free base porphyrins under mild conditions. The traditional Vilsmeier formylation and related protocols for the formylation of porphyrins are usually conducted under highly acidic conditions, only work well with Ni(II) and Cu(II) complexes, and allow limited control over the site of formylation.[9a,24] Additional investigation of the oxidation reaction conditions

Table 3. Palladium-catalyzed Cross-Coupling of 2b with Various Bromoporphyrins



entry	R^1	R^2	M	porphyrin (**1**)	product (**2**)	t (h)	yield[a] (%)
1	Ph	H	2H	**1a**	**3ab**	1	86
2	*p*-tolyl	H	2H	**1b**	**3bb**	1	83
3	3-$(CH_2{=}CH)C_6H_4$	H	2H	**1c**	**3cb**	1.5	77
4	4-(i-$Pr_3SiC{\equiv}C)C_6H_4$	H	2H	**1d**	**3db**	0.5	95
5	2,4,6-$Me_3C_6H_2$	H	2H	**1e**	**3eb**	1.5	87
6	3-$(MeO)C_6H_4$	H	2H	**1f**	**3fb**	1.5	84
7	*n*-Bu	H	2H	**1g**	**3gb**	1	86
8	Ph	Ph	2H	**1h**	**3hb**	1	82
9[b]	Ph	H	Zn	**Zn-1a**	**Zn-3ab**	0.5	94
10	Ph	H	Mg	**Mg-1a**	**Mg-3ab**	0.5	91
11	Ph	H	Ni	**Ni-1a**	**Ni-3ab**	0.5	85

[a]Isolated yield.

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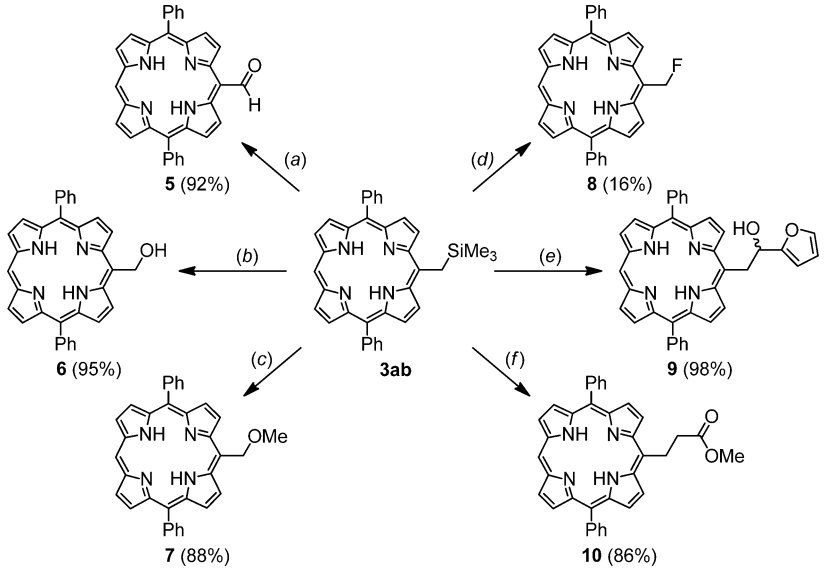
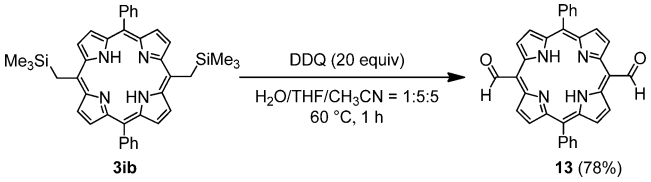
Scheme 4. Transformation of the Silylmethyl Group of Porphyrin 3ab[a]



[a]Reagents and conditions: (a) DDQ (10 equiv), H_2O/THF/CH_3CN = 1:5:5, 60 °C, 1 h; (b) DDQ (3 equiv), H_2O/THF = 1:10, 25 °C, 0.5 h; (c) DDQ (3 equiv), MeOH/dioxane = 1:10, 25 °C, 12 h; (d) DDQ (5 equiv), DAST (1.5 equiv), CH_2Cl_2, 25 °C, 3 h; (e) TBAF (1 equiv), furfural **11** (10 equiv), THF, 4 ÅMS, 25 °C, 5 min; (f) TBAF (1 equiv), $BrCH_2CO_2Me$ **12** (10 equiv), THF, 4 ÅMS, 25 °C, 5 min.

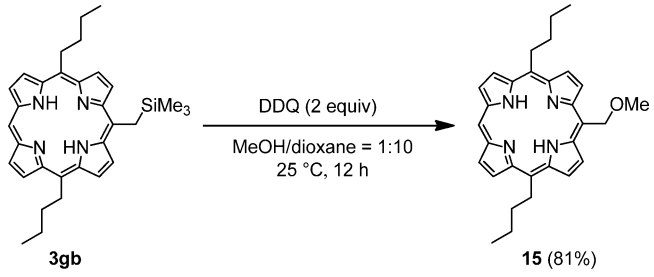
Scheme 5. Preparation of *meso*-Diformylporphyrin 13



Scheme 6. Preparation of *β*-Formylporphyrin 14

using **3ab** as the substrate revealed that reducing the amount of DDQ to 3 equiv in THF at a lower temperature (25 °C) produced *meso*-hydroxymethylporphyrin **6** in 95% yield, without further oxidation of the hydroxymethyl functionality to the CHO group (Scheme 4b). When the DDQ-mediated oxidation of **3ab** was performed in the presence of methanol, only the corresponding methoxymethyl-substituted product **7** was obtained (Scheme 4c). Peng, Osuka, and co-workers have reported a similar benzylic alkoxylation of alkyl-substituted porphyrins via oxidation with DDQ.[7a] However, limited control over the site of the alkoxylation, which resulted in a complex mixture of mono- and multiple-alkoxylated products at the benzylic positions, appears to be a major complication of that reaction. In contrast, we achieved the highly selective conversion of the silyl group to the methoxy functionality by oxidizing silylmethyl-substituted dialkylporphyrin **3gb** with DDQ in the presence of methanol, which exclusively afforded the corresponding methoxymethyl-substituted dialkylporphyrin **15** in 81% isolated yield, without the formation of further methoxylated products at the benzylic positions of the alkyl side chain (Scheme 7). The present DDQ-mediated oxidation of the silylmethyl-substituted porphyrins is not limited to the

Scheme 7. Regioselective Benzylic Alkoxylation of Silylmethyl-substituted Dialkylporphyrin 3gb



introduction of oxygen functionalities; fluoromethyl-substituted porphyrin **8** was cleanly obtained by the oxidation of **3ab** in the presence of DAST [*N*,*N*-diethylaminosulfur trifluoride] as a fluoride ion source, although further optimization is necessary (Scheme 4d).

The silylmethyl group on the porphyrin core is also valuable for the installation of carbon functionalities. Accordingly, the silylmethylporphyrin **3ab** reacts with carbon electrophiles, such as aldehyde **11** and alkylhalide **12**, in the presence of TBAF as a fluoride ion source to afford **9** and **10**, respectively, in high yields (Scheme 4e and f). Finally, we explored the installation of a carbon−carbon double bond at the carbon *α* to the porphyrin core via the Peterson olefination, which one of the most valuable transformations in organosilicon chemistry. The Peterson olefination reactions of **3ab** with aldehyde **11** in the presence of several bases, such as *n*-BuLi, *t*-BuLi and LDA,[11c,25] produced an inseparable complex mixture. However, when bis(trimethylsilyl)methyl-substituted porphyrin **3ah** was used as the substrate, the desilylative Peterson olefination was successful.[25,26] Thus, the reaction of porphyrin **3ah** and aldehyde **11** proceeded smoothly in the presence of TBAF,

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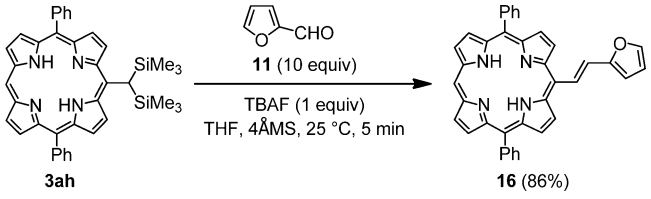
reaching completion within 5 min. The desired Peterson olefination product **16** was obtained in 86% yield (Scheme 8).

Scheme 8. Desilylative Peterson Olefination of Bis(trimethylsilyl)-substituted Porphyrin 3ah



CONCLUSION

In summary, we have developed a facile protocol for preparing silylmethyl-substituted porphyrins via the Pd(0)-catalyzed Kumada cross-coupling of bromoporphyrins with silylmethyl magnesium reagents. These cross-coupling reactions were accomplished by a novel catalytic system consisting of a $Pd_2(dba)_3$ palladium source and a $Ph_2P(O)H$ ligand. The conditions were compatible with an array of *meso*-mono-, *meso*-di-, and *β*-bromo-substituted porphyrins as well as a variety of silylmethyl magnesium reagents, and achieved good yields. The synthetic utility of these silylmethylporphyrins as a multipurpose synthon for accessing more complex porphyrin derivatives was demonstrated by a variety of transformations of the silylmethyl substituents, including the DDQ-promoted oxidative conversion into CHO, CH_2OH, CH_2OMe, and CH_2F functionalities as well as the fluoride ion-mediated desilylative introduction of carbon−carbon single and double bonds. We expect these silylmethylporphyrins to be useful as building blocks in the total synthesis of more complex porphyrin systems by optimizing the step-economy. We are currently conducting further synthetic studies using silylmethylporphyrins, and the results will be reported in due course.

EXPERIMENTAL SECTION

General. ^1H 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 ^1H 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, **1a**−**1c**,[8c] **1e**−**1i**,[8c] **1j**,[8b] **Zn-1a**,[8c] and **Ni-1a**,[8c] were prepared according to the method described in literature. (Chloromethyl)triisopropylsilane and (chloromethyl)-triphenylsilane were prepared by the literature method.[18] Other chemicals were purchased from commercial sources and used as received unless stated otherwise.

Preparation of 5,15-Bis[4-{2-(triisopropylsilyl)ethynyl}-phenyl]-10-bromoporphyrin (1d). To a solution of 5,15-bis[4-{2-(triisopropylsilyl)ethynyl}phenyl]porphyrin[9a] (610 mg, 740 μmol) in $CHCl_3$ (300 mL) was added NBS (145 mg, 815 μmol, 1.1 equiv) at rt. After stirring for 15 min, the solution was concentrated in vacuo. Column chromatography on silica gel (*n*-hexane/toluene = 5:1) followed by recrystallization from CH_2Cl_2/*n*-hexane gave the product **1d** (343 mg, 51%) as a brown-purple solid. R_f = 0.68 (1:2 THF/hexane); ^1H NMR (benzene-d_6, 400 MHz) δ 9.73 (1H, s), 9.66 (2H, d, J = 4.9 Hz), 8.86 (2H, d, J = 4.9 Hz), 8.71 (2H, d, J = 4.9 Hz), 8.70 (2H, d, J = 4.9 Hz), 7.79−7.71 (8H, m), 1.39−1.26 (42, m), −2.71 (2H, br s); ^{13}C NMR (benzene-d_6, 100 MHz) δ 147.42, 147.35, 146.8, 146.1, 142.0, 134.7, 132.9, 131.9, 131.8, 131.5, 130.8, 123.5, 119.9, 108.2, 105.9, 104.3, 92.2, 19.1, 12.0; IR (KBr) 3313, 3113, 3032, 2947, 2866, 2156, 1466, 964, 795, 671 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 418.5 (5.6), 513.5 (4.3), 548.0 (4.1), 589.0 (3.9), 646 (3.8) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{54}H_{62}BrN_4Si_2$ 901.3696, found 901.3703; Anal. calcd for $C_{54}H_{61}BrN_4Si_2$: C, 71.89; H, 6.82: N, 6.21, found: C, 71.97; H, 6.90: N, 6.15.

Preparation of [10-Bromo-5,15-diphenylporphyrinato]-magnesium(II) (Mg-1a). To a solution of 10-bromo-5,15-diphenylporphyrin **1a** (100 mg, 185 μmol) in $CHCl_3$ (15 mL) was added $MgBr_2{\cdot}OEt_2$ (478 mg, 1850 μmol, 10 equiv) and triethylamine (1 mL) at rt. After stirring for 2 h, the solution was poured into water (50 mL). The resulting precipitate was collected and washed with water to give the magnesium complex (**Mg-1a**) as a red-purple solid in a nearly quantitative yield (103 mg, 98%). R_f = 0.63 (1:2 THF/hexane); ^1H NMR (THF-d_8, 400 MHz) δ 10.13 (1H, s), 9.68 (2H, d, J = 4.4 Hz), 9.26 (2H, d, J = 4.4 Hz), 8.89 (4H, d, J = 4.4 Hz), 8.26−8.20 (4H, m), 7.82−7.74 (6H, m); ^{13}C NMR (THF-d_8, 100 MHz) δ 150.74, 150.73, 150.65, 149.5, 144.8, 135.8, 133.3, 133.0, 132.9, 132.6, 127.9, 127.1, 122.5, 107.7, 105.3; IR (KBr) 3101, 3059, 3024, 1485, 1315, 1068, 1003, 787, 741, 702 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 405.5sh (4.8), 426.5 (5.8), 569.0 (4.3), 608.5 (4.1) nm; HRMS-FAB$^+$ (M$^+$) calcd for $C_{32}H_{19}BrMgN_4$ 562.0644, found 562.0641.

Silylmethyl Grignard Reagents (2). All the silylmethyl Grignard reagents used were prepared according to the method described in literature[19] as follows. To a well-stirred mixture of Mg turnings (95 mg, 3.9 mmol) in 0.3 mL of THF was added a solution of a (chloromethyl)silane (3.7 mmol) in 4.7 mL of THF. The mixture was stirred for 3 h at rt and was used immediately.

General Procedure for the Palladium-Catalyzed Coupling Reactions of Bromoporphyrins with Silylmethyl Grignard 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 **1** (0.185 mmol), $Pd_2(dba)_3$ (3.4 mg, 3.7 μmol, 2 mol %), and $Ph_2P(O)H$ (3.0 mg, 14.8 μmol, 8 mol %). The reaction vessel was evacuated and flushed with argon (three times), and then dry THF (30 mL) was added. To the solution was added a 0.6 M THF solution of a silylmethyl Grignard reagent (0.62 mL, 0.37 mmol, 2 equiv) at rt. The mixture was stirred at 60 °C for several hours (0.5−6 h), having been monitored by TLC (THF/hexane = 1:2). Upon completion of the reaction, the mixture was allowed to reach room temperature. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was charged on the top of a silica gel column packed with *n*-hexane/CH_2Cl_2/Et_3N (10:1:0.5), and the column was eluted with *n*-hexane/CH_2Cl_2 (10:1). The fractions containing product were collected and concentrated under a reduced pressure. The resulting crude product was recrystallized from CH_2Cl_2/MeOH to give the pure silylmethyl-substituted porphyrin **3**.

*5,15-Diphenyl-10-(triisopropylsilyl)methylporphyrin (**3aa**).* Brown-purple solid; 101.9 mg, 87% yield; R_f = 0.68 (1:2 THF/hexane); ^1H NMR ($CDCl_3$, 500 MHz) δ 9.93 (1H, s), 9.45 (2H, d, J = 4.6 Hz), 9.17 (2H, d, J = 4.6 Hz), 8.90 (2H, d, J = 4.6 Hz), 8.86 (2H, d, J = 4.6 Hz), 8.25−8.20 (4H, m), 7.81−7.74 (6H, m), 4.64 (2H, s), 1.39−1.30 (3H, m), 0.84 (18H, d, J = 7.3 Hz), −2.57 (2H, br s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.1 (8C, br), 142.3, 134.6, 131.7, 130.5 (4C), 128.3, 127.6, 126.7, 122.6, 119.1, 102.8, 20.8, 18.6, 11.9; IR (KBr) 3313, 3055, 2924, 2858, 1597, 1477, 1065, 976, 791, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 413.0 (5.7), 510.0 (4.4), 544.5 (3.9), 585.0 (3.8), 641.5 (3.6) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{42}H_{45}N_4Si$ 633.3413, found 633.3412.

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*5,15-Diphenyl-10-(trimethylsilyl)methylporphyrin (**3ab**).* Brown-purple solid; 87.5 mg, 86% yield; R_f = 0.69 (1:2 THF/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.94 (1H, s), 9.39 (2H, d, J = 4.9 Hz), 9.18 (2H, d, J = 4.9 Hz), 8.92 (2H, d, J = 4.9 Hz), 8.90 (2H, d, J = 4.9 Hz), 8.27−8.23 (4H, m), 7.83−7.75 (6H, m), 4.64 (2H, s), 0.08 (9H, s), −2.55 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.2 (8C, br), 142.3, 134.6, 131.7, 130.7, 130.4, 128.6, 127.6, 126.7, 121.6, 119.1, 103.0, 27.3, −0.8; IR (KBr) 3309, 3104, 3024, 2947, 1593, 1477, 1246, 1134, 968, 849, 791, 733 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 416.5 (5.6), 516.0 (4.2), 551.0 (4.0), 591.5 (3.7), 648.0 (3.8) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{36}H_{33}N_4Si$ 549.2474, found 549.2479; Anal. calcd for $C_{36}H_{32}N_4Si$: C, 78.79; H, 5.88; N, 10.21, found: C, 78.57; H, 5.79; N, 10.00.

*5,15-Diphenyl-10-(triethylsilyl)methylporphyrin (**3ac**).* Brown-purple solid; 90.6 mg, 83% yield; R_f = 0.68 (1:2 THF/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.94 (1H, s), 9.40 (2H, d, J = 4.9 Hz), 9.17 (2H, d, J = 4.9 Hz), 8.89 (2H, d, J = 4.9 Hz), 8.86 (2H, d, J = 4.9 Hz), 8.25−8.18 (4H, m), 7.82−7.72 (6H, m), 4.63 (2H, s), 0.75 (9H, t, J = 7.8 Hz), 0.57 (6H, q, J = 7.8 Hz), −2.64 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.5 (8C, br), 142.2, 134.6, 131.7, 130.7 (4C), 128.5, 127.6, 126.7, 122.1, 119.1, 102.9, 23.0, 7.3, 3.9; IR (KBr) 3313, 3055, 2951, 2924, 2873, 1477, 1404, 968, 791, 729 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 415.0 (5.6), 512.5 (4.2), 551.0 (3.8), 589.5 (3.6), 646.5 (3.5) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{39}H_{39}N_4Si$ 591.2944, found 591.2938.

*5,15-Diphenyl-10-(triphenylsilyl)methylporphyrin (**3ad**).* Brown-purple solid; 102.3 mg, 75% yield; R_f = 0.70 (1:2 THF/hexane); ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 10.00 (1H, s), 9.23 (2H, d, J = 4.8 Hz), 8.96 (2H, d, J = 4.8 Hz), 8.90 (2H, d, J = 4.8 Hz), 8.46 (2H, d, J = 4.8 Hz), 8.19−8.11 (4H, m), 7.84−7.72 (6H, m), 7.26 (3H, t, J = 7.4 Hz), 7.18 (6H, d, J = 7.3 Hz), 7.02 (6H, dd, J = 7.4, 7.3 Hz), 5.24 (2H, s), −2.83 (2H, br s); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 146.7 (8C, br), 142.5, 136.4, 135.0, 134.1, 131.9, 131.1, 130.3, 129.9, 129.1, 128.1, 128.0, 127.1, 119.5, 119.1, 103.6, 25.4; IR (KBr) 3294, 3062, 2924, 2854, 1431, 1103, 791, 710 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 419.0 (5.6), 517.5 (4.2), 551.5 (3.9), 591.5 (3.7), 648.5 (3.6) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{51}H_{39}N_4Si$ 735.2944, found 735.2952.

*10-(Dimethylphenylsilyl)methyl-5,15-diphenylporphyrin (**3ae**).* Brown-purple solid; 98.5 mg, 87% yield; R_f = 0.69 (1:2 THF/hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.95 (1H, s), 9.25 (2H, d, J = 4.8 Hz), 9.19 (2H, d, J = 4.8 Hz), 8.92 (2H, d, J = 4.8 Hz), 8.81 (2H, d, J = 4.8 Hz), 8.28−8.20 (4H, m), 7.84−7.74 (0H, m), 7.52 (2H, d, J = 7.3 Hz), 7.43 (1H, t, J = 7.4 Hz), 7.32 (2H, dd, J = 7.4, 7.3 Hz), 4.81 (2H, s), 0.21 (6H, s), −2.58 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.3 (8C, br), 142.3, 138.6, 134.6, 133.8, 131.7, 130.7, 130.3, 129.3, 128.6, 128.0, 127.6, 126.7, 120.5, 119.1, 103.1, 26.9, −2.6; IR (KBr) 3313, 3059, 2954, 1477, 1246, 980, 840, 787, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 417.0 (5.7), 515.0 (4.3), 551.5 (4.0), 591.5 (3.7), 646.5 (3.7) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{41}H_{35}N_4Si$ 611.2631, found 611.2640; Anal. calcd for $C_{41}H_{34}N_4Si$: C, 80.73; H, 5.81; N, 8.97, found: C, 80.77; H, 5.62; N, 9.09.

*10-(Benzyldimethylsilyl)methyl-5,15-diphenylporphyrin (**3af**).* Brown-purple solid; 101.8 mg, 88%yield; R_f = 0.67 (1:2 THF/hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.97 (1H, s), 9.21 (2H, d, J = 4.6 Hz), 9.20 (2H, d, J = 4.6 Hz), 8.93 (2H, d, J = 4.6 Hz), 8.87 (2H, d, J = 4.6 Hz), 8.26−8.22 (4H, m), 7.85−7.75 (6H, m), 7.29 (2H, dd, J = 7.9, 7.3 Hz), 7.17 (1H, t, J = 7.3 Hz), 7.08 (2H, d, J = 7.9 Hz), 4.64 (2H, s), 2.34 (2H, s), −0.08 (6H, s), −2.63 (2H, br s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.1 (8C, br), 142.1, 139.6, 134.6, 131.7, 130.7 (6C), 128.4, 128.3, 127.6, 126.7, 124.4, 120.7, 119.1, 103.1, 26.2, 25.1, −2.9; IR (KBr) 3317, 3055, 3028, 2951, 1593, 1481, 1404, 1246, 1153, 968, 837, 791, 737, 698 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 417.0 (5.7), 516.5 (4.3), 552.5 (4.1), 592.5 (3.8), 647.5 (3.8) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{42}H_{37}N_4Si$ 625.2787, found 625.2790; Anal. calcd for $C_{42}H_{36}N_4Si$: C, 80.73; H, 5.81; N, 8.97, found: C, 80.73; H, 5.91; N, 8.69.

*5,15-Diphenyl-10-(iso-propoxyldimethylsilyl)methylporphyrin (**3ag**).* Brown-purple solid; 89.1 mg, 81%yield; R_f = 0.61 (1:2 THF/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.94 (1H, s), 9.47 (2H, d, J = 4.9 Hz), 9.17 (2H, d, J = 4.9 Hz), 8.89 (2H, d, J = 4.9 Hz), 8.87 (2H, d, J = 4.9 Hz), 8.26−8.18 (4H, m), 7.82−7.72 (6H, m), 4.71 (2H, s), 4.10−4.01 (1H, m), 1.15 (6H, d, J = 5.9 Hz), 0.05 (6H, s), −2.62 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.2 (8C, br), 142.3, 134.6, 131.7, 130.7, 130.4, 128.9, 127.6, 126.7, 120.3, 119.1, 103.0, 65.7, 28.2, 25.9, −0.8; IR (KBr) 3313, 3113, 3028, 2962, 1593, 1477, 1246, 1115, 1026, 802,740 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 416.5 (5.7), 516.5 (4.3), 551.5 (4.0), 591.5 (3.7), 646.5 (3.8) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{38}H_{37}N_4OSi$ 593.2737, found 593.2742.

*10-Bis(trimethylsilyl)methyl-5,15-diphenylporphyrin (**3ah**).* The general procedure with 5 equiv, instead of 2 equiv, of the Grignard reagent **2h** gave the title compound as a brown-purple solid (84.1 mg, 71%); R_f = 0.68 (1:2 THF/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.89 (1H, s), 9.42 (1H, d, J = 4.9 Hz), 9.40 (1H, d, J = 4.9 Hz), 9.16 (1H, d, J = 4.9 Hz), 9.15 (1H, d, J = 4.9 Hz), 8.89 (1H, d, J = 4.9 Hz), 8.88 (1H, d, J = 4.9 Hz), 8.87 (1H, d, J = 4.9 Hz), 8.85 (1H, d, J = 4.9 Hz), 8.27−8.21 (4H, m), 7.82−7.74 (6H, m), 4.52 (1H, s), 0.23 (18H, s), −2.42 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.5 (8C, br), 142.5, 142.5, 134.6, 132.0, 131.7, 130.9, 130.7 (2C), 130.5 (2C), 129.6, 127.6, 127.6, 127.5, 127.0, 126.68, 126.65, 119.2, 119.0, 102.6, 31.0, 1.6; IR (KBr) 3317, 3093, 3051, 2954, 2900, 1593, 1469, 1246, 1065, 978, 852, 791, 741, 694 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 419.0 (5.6), 519.5 (4.2), 555.5 (4.1), 595.5 (3.6), 651.0 (3.8) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{39}H_{41}N_4Si_2$ 621.2870, found 621.2866; Anal. calcd for $C_{39}H_{40}N_4Si_2$: C, 75.44; H, 6.49: N, 9.02, found: C, 75.62; H, 6.51; N, 9.16.

*5,15-Di(p-tolyl)-10-(trimethylsilyl)methylporphyrin (**3bb**).* Brown-purple solid; 88.5 mg, 83% yield; R_f = 0.68 (1:2 THF/hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.95 (1H, s), 9.40 (2H, d, J = 4.9 Hz), 9.19 (2H, d, J = 4.9 Hz), 8.96 (2H, d, J = 4.9 Hz), 8.94 (2H, d, J = 4.9 Hz), 8.14 (4H, d, J = 7.6 Hz), 7.59 (4H, d, J = 7.6 Hz), 4.65 (2H, s), 2.74 (6H, s), 0.07 (9H, s), −2.60 (2H, br s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.1 (8C, br), 139.2, 137.2, 134.5, 131.7, 130.5 (4C), 128.5, 127.4, 121.4, 119.1, 102.8, 27.2, 21.5, −0.8; IR (KBr) 3313, 3020, 2951, 1477, 1404, 1246, 1153, 968, 845, 791, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 417.5 (5.7), 516.5 (4.2), 552.5 (4.1), 591.5 (3.7), 649.0 (3.8) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{38}H_{37}N_4Si$ 577.2787, found 577.2783; Anal. calcd for $C_{38}H_{36}N_4Si$: C, 79.13; H, 6.29; N, 9.71, found: C, 78.73; H, 6.28; N, 9.44.

*5,15-Bis(3-vinylphenyl)-10-(trimethylsilyl)methylporphyrin (**3cb**).* Brown-purple solid; 85.3 mg, 77% yield; R_f = 0.67 (1:2 THF/hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.95 (1H, s), 9.40 (2H, d, J = 4.6 Hz), 9.19 (2H, d, J = 4.6 Hz), 8.97 (2H, d, J = 4.6 Hz), 8.95 (2H, d, J = 4.6 Hz), 8.32 (2H, s), 8.15 (2H, d, J = 7.3 Hz), 7.88 (2H, d, J = 7.9 Hz), 7.74 (2H, dd, J = 7.9, 7.3 Hz), 7.04 (2H, dd, J = 17.7, 11.0 Hz), 6.02 (2H, d, J = 17.7 Hz), 5.45 (2H, d, J = 11.0 Hz), 4.64 (2H, s), 0.09 (9H, s), −2.56 (2H, br s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.0 (8C, br), 142.4, 136.9, 135.9, 134.1, 132.4, 131.6, 130.5 (4C), 128.6, 126.8, 125.4, 121.7, 118.8, 114.7, 103.0, 27.2, −0.8; IR (KBr) 3313, 3093, 3051, 2954, 1589, 1473, 1396, 1335, 1250, 1157, 1065, 984, 906, 849, 787, 733 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 418.0 (5.6), 516.5 (4.2), 552.5 (4.0), 592.5 (3.7), 648.5 (3.8) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{40}H_{37}N_4Si$: 601.2787, found 601.2792.

*5,15-Bis[4-{2-(triisopropylsilyl)ethynyl}phenyl]-10-(trimethylsilyl)-methylporphyrin (**3db**).* Brown-purple solid; 160.2 mg, 95% yield; R_f = 0.65 (1:2 THF/hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.92 (1H, s), 9.36 (2H, d, J = 4.8 Hz), 9.16 (2H, d, J = 4.8 Hz), 8.89 (2H, d, J = 4.8 Hz), 8.87 (2H, d, J = 4.8 Hz), 8.17 (4H, d, J = 7.9 Hz), 7.92 (4H, d, J = 7.9 Hz), 4.60 (2H, s), 1.57−1.10 (42H, m), 0.07 (9H, s), −2.59 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.1 (br), 145.8 (6C, br), 142.4, 134.5, 131.5, 130.9, 130.5, 130.2, 128.7, 123.1, 122.0, 118.4, 107.4, 103.2, 91.9, 27.3, 18.9, 11.6, −0.8; IR (KBr) 3313, 3116, 3035, 2947, 2866, 1466, 1400, 1246, 987, 845, 795, 671 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε): 420.0 (5.6), 517.0 (4.2), 554.0 (4.1), 592.0 (3.7), 649.5 (3.9) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{58}H_{73}N_4Si_3$: 909.5143, found 909.5158; Anal. calcd for $C_{58}H_{72}N_4Si_3$: C, 76.60; H, 7.98; N, 6.16, found: C, 76.81; H, 7.97; N, 5.78.

*5,15-Bis(2,4,6-trimethylphenyl)-10-(trimethylsilyl)-methylporphyrin (**3eb**).* Brown-purple solid; 101.8 mg, 87% yield; R_f = 0.69 (1:2 THF/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.94 (1H,

s), 9.42 (2H, d, J = 4.9 Hz), 9.21 (2H, d, J = 4.9 Hz), 8.86 (2H, d, J = 4.9 Hz), 8.83 (2H, d, J = 4.9 Hz), 7.42 (4H, s), 4.70 (2H, s), 2.76 (6H, s), 2.00 (12H, s), 0.16 (9H, s), −2.27 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.1 (8C, br), 139.6, 138.7, 137.7, 131.0, 130.7, 129.2, 128.9, 127.9, 120.9, 117.4, 102.3, 27.1, 21.6, 21.5, −0.8; IR (KBr) 3317, 3113, 2951, 2920, 1473, 1246, 980, 849, 791 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 417.0 (5.6), 515.5 (4.2), 550.5 (3.9), 592.0 (3.6), 647.5 (3.6) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{42}H_{45}N_4Si$ 633.3413, found 633.3406; Anal. calcd for $C_{42}H_{44}N_4Si$: C, 79.70; H, 7.01; N, 8.85, found: C, 79.42; H, 6.92; N, 8.69.

*5,15-Bis(3-methoxyphenyl)-10-(trimethylsilyl)methylporphyrin (**3fb**).* Brown-purple solid; 94.5 mg, 84% yield; R_f = 0.58 (1:2 THF/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.94 (1H, s), 9.37 (2H, d, J = 4.9 Hz), 9.18 (2H, d, J = 4.9 Hz), 8.94 (2H, d, J = 4.9 Hz), 8.91 (2H, d, J = 4.9 Hz), 7.81 (2H, d, J = 7.8 Hz), 7.78 (2H, s), 7.65 (2H, dd, J = 8.3, 7.8 Hz), 7.33 (2H, d, J = 8.3 Hz), 4.64 (2H, s), 4.00 (6H, s), 0.04 (9H, s), −2.69 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.2, 146.2 (8C, br), 143.6, 131.7, 130.6, 130.4, 128.5, 127.8, 127.5, 121.6, 120.8, 118.9, 113.5, 103.0, 55.6, 27.3, −0.7; IR (KBr) 3321, 3070, 2927, 2854, 1601, 1473, 1281, 1250, 1149, 1049, 849, 791, 741 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 417.5 (5.6), 515.5 (4.2), 551.5 (3.9), 591.5 (3.6), 648.5 (3.7) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{38}H_{37}N_4O_2Si$ 609.2686, found 609.2689.

*5,15-Di(n-butyl)-10-(trimethylsilyl)methylporphyrin (**3gb**).* Dark-brown solid; 80.9 mg, 86% yield; R_f = 0.62 (1:2 THF/hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.80 (1H, s), 9.46 (2H, d, J = 4.6 Hz), 9.44 (4H, d, J = 4.6 Hz), 9.21 (2H, d, J = 4.6 Hz), 4.93 (4H, t, J = 8.1 Hz), 4.64 (2H, s), 2.54 (4H, tt, J = 8.1, 7.8 Hz), 1.85 (4H, tq, J = 7.8, 7.5 Hz), 1.18 (6H, t, J = 7.5 Hz), 0.09 (9H, s), −2.50 (2H, br s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.1 (6C, br), 144.5 (br), 131.1, 129.0, 128.4, 126.9, 120.2, 118.6, 101.9, 40.6, 34.8, 27.3, 23.7, 14.2, −0.7; IR (KBr) 3309, 3124, 2954, 2870, 1485, 1246, 1157, 849, 791, 741 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 416.5 (5.6), 518.0 (4.1), 554.5 (4.0), 597.0 (3.5), 654.0 (3.8) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{32}H_{41}N_4Si$ 509.3100, found 509.3094.

*5-(Trimethylsilyl)methyl-10,15,20-triphenylporphyrin (**3hb**).* Brown-purple solid; 94.8 mg, 82% yield; R_f = 0.67 (1:2 THF/hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.33 (2H, d, J = 4.8 Hz), 8.84 (2H, d, J = 4.8 Hz), 8.77 (2H, d, J = 4.8 Hz), 8.75 (2H, d, J = 4.8 Hz), 8.26−8.15 (6H, m), 7.82−7.69 (9H, m), 4.59 (2H, s), 0.07 (9H, s), −2.31 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.6 (br), 146.1 (6C, br), 142.7, 142.3, 134.5 (6C), 131.4, 130.7, 130.5, 128.3, 127.61, 127.57, 126.7, 126.6, 121.1, 119.6, 118.3, 26.9, −0.8; IR (KBr) 3317, 3028, 2954, 1473, 1354, 1250, 1153, 972, 849, 795, 737, 702 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 421.5 (5.7), 522.0 (4.2), 559.0 (4.2), 599.0 (3.7), 656.0 (3.9) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{42}H_{37}N_4Si$ 625.2787, found 625.2786.

*10,20-Bis(trimethylsilyl)methyl-5,15-diphenylporphyrin (**3ib**).* The general procedure with 3 equiv, instead of 2 equiv, of the Grignard reagent **2b** gave the title compound as a brown-purple solid (96.5 mg, 82%); R_f = 0.66 (1:2 THF/hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.28 (4H, d, J = 4.6 Hz), 8.82 (4H, d, J = 4.6 Hz), 8.29−8.22 (4H, m), 7.86−7.73 (6H, m), 4.51 (4H, s), 0.10 (18H, s), −2.09 (2H, br s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.8 (4C, br), 145.0 (4C, br), 143.0, 134.4, 131.0, 127.9, 127.5, 126.5, 118.8, 118.6, 26.2, −0.8; IR (KBr) 3317, 3055, 2954, 1469, 1350, 1250, 1157, 976, 849, 791, 737, 702 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 424.5 (5.6), 529.0 (4.1), 568.0 (4.3), 609.0 (3.6), 669.0 (4.1) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{40}H_{43}N_4Si_2$ 635.3026, found 635.3022.

*5,10,15,20-Tetraphenyl-2-(trimethylsilyl)methylporphyrin (**3jb**).* Brown-purple solid; 120.7 mg, 93% yield; R_f = 0.69 (1:2 THF/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.95 (2H, d, J = 4.9 Hz), 8.87 (1H, d, J = 4.9 Hz), 8.84 (1H, d, J = 4.9 Hz), 8.81 (1H, d, J = 4.9 Hz), 8.72 (1H, d, J = 4.9 Hz), 8.58 (1H, s), 8.29 (6H, d, J = 6.8 Hz), 8.20 (2H, d, J = 6.8 Hz), 7.86−7.72 (12H, m), 2.51 (2H, s), −0.10 (9H, s), −2.56 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.6 (br), 151.8 (2C, br), 150.9 (br), 143.2, 142.7, 142.4, 142.2, 142.1, 141.2 (br), 140.8 (br), 139.9 (br), 134.7, 134.6, 134.4, 134.2, 133.1, 132.8 (2C), 132.5, 129.3 (2C), 129.2, 128.5, 128.0, 127.67, 127.66, 127.6, 126.8, 126.7, 126.6, 126.5, 120.6, 120.1, 119.7, 118.3, 20.4, −1.4; IR (KBr) 3305, 3055, 2954, 2893, 1350, 1250, 1165, 968, 849, 795, 733, 702 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 421.0 (5.7), 518.5 (4.3), 552.5 (3.8), 590.5 (3.8), 644.0 (3.6) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{48}H_{41}N_4Si$ 701.3100, found 701.3105; Anal. calcd for $C_{48}H_{40}N_4Si$: C, 82.25; H, 5.75: N, 7.99, found: C, 82.49; H, 5.75; N, 7.59.

*[5,15-Diphenyl-10-(trimethylsilyl)methylporphyrinato]zinc(II) (**Zn-3ab**).* The general procedure with the zinc(II) complex **Zn-3a** in place of a free base porphyrin and column chromatography (n-hexane/THF/Et_3N = 20:1:1) followed by recrystallization (n-hexane/CH_2Cl_2) gave the title compound as a red-purple solid (106.8 mg, 94%); R_f = 0.63 (1:2 THF/hexane); ^{1}H NMR (THF-d_8, 400 MHz) δ 9.94 (1H, s), 9.52 (2H, d, J = 4.9 Hz), 9.21 (2H, d, J = 4.9 Hz), 8.89 (2H, d, J = 4.9 Hz), 8.88 (2H, d, J = 4.9 Hz), 8.24−8.20 (4H, m), 7.82−7.70 (6H, m), 4.77 (2H, s), 0.06 (9H, s); ^{13}C NMR (THF-d_8, 100 MHz) δ 151.7, 150.5, 150.2, 150.1, 144.8, 135.5, 132.8, 131.8, 131.5, 129.9, 127.9, 127.1, 122.3, 120.4, 104.4, 27.4, −0.6; IR (KBr) 3062, 3024, 2951,1589, 1489, 1323, 1250, 1142, 1068, 999, 849, 702 cm^{-1}; UV/vis (THF) λ_{max} (log ε) 402.5sh (4.8), 422.0 (5.8), 555.5 (4.3), 599.5 (4.1) nm; HRMS-FAB$^+$ (M$^+$) calcd for $C_{36}H_{30}N_4SiZn$ 610.1531, found 610.1538.

*[5,15-Diphenyl-10-(trimethylsilyl)methylporphyrinato]-magnesium(II) (**Mg-3ab**).* The general procedure with the magnesium(II) complex **Mg-3a** in place of a free base porphyrin and column chromatography (n-hexane/THF/Et_3N = 20:1:1) followed by recrystallization (n-hexane/CH_2Cl_2) gave the title compound as a blue-purple solid (96.1 mg, 91%); R_f = 0.61 (1:2 THF/hexane); ^{1}H NMR (THF-d_8, 400 MHz) δ 9.90 (1H, s), 9.50 (2H, d, J = 4.4 Hz), 9.18 (2H, d, J = 4.4 Hz), 8.85 (2H, d, J = 4.4 Hz), 8.84 (2H, d, J = 4.4 Hz), 8.27−8.23 (4H, m), 7.80−7.75 (6H, m), 4.86 (2H, s), 0.07 (9H, s).; ^{13}C NMR (THF-d_8, 100 MHz) δ 151.2, 150.0, 149.7, 149.5, 145.6, 135.7, 132.7, 131.7, 131.4, 129.8, 127.6, 126.9, 123.0, 121.2, 104.8, 27.6, −0.5; IR (KBr) 3051, 2954, 2889, 1142, 999, 849, 787, 702 cm^{-1}; UV/vis (THF) λ_{max} (log ε) 407sh (4.8), 428 (5.8), 571 (4.1), 620 (4.1) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{36}H_{31}MgN_4Si$: 571.2168, found 571.2171.

*[5,15-Diphenyl-10-(trimethylsilyl)methylporphyrinato]nickel(II) (**Ni-3ab**).* The general procedure with the nickel(II) complex **Ni-3a** in place of a free base porphyrin and column chromatography (n-hexane/THF/Et_3N = 20:1:1) followed by recrystallization (n-hexane/CH_2Cl_2) gave the title compound as a red-purple solid (95.6 mg, 85%); R_f = 0.63 (1:2 THF/hexane); ^{1}H NMR (dioxane-d_8, 400 MHz) δ 9.60 (1H, s), 9.26 (2H, d, J = 4.9 Hz), 8.98 (2H, d, J = 4.9 Hz), 8.70 (2H, d, J = 4.9 Hz), 8.69 (2H, d, J = 4.9 Hz), 8.02−7.98 (4H, m), 7.68−7.61 (6H, m), 4.28 (2H, s), −0.17 (9H, s); ^{13}C NMR (dioxane-d_8, 100 MHz) δ 144.3, 143.0, 142.8, 142.6, 142.2, 134.4, 132.9, 132.3, 131.7, 130.3, 128.0, 127.3, 119.6, 118.6, 103.5, 25.3, −1.2; IR (KBr) 3055, 3024, 2954, 2893, 1338, 1165, 1072, 1007, 846, 787, 748, 702 cm^{-1}; UV/vis (THF) λ_{max} (log ε) 412.5 (5.4), 527.0 (4.3) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{36}H_{31}N_4NiSi$: 605.1671, found 605.1670; Anal. calcd for $C_{36}H_{30}N_4NiSi$: C, 71.42; H, 4.99: N, 9.25, found: C, 71.41; H, 4.79: N, 9.21.

5-Formyl-10,20-diphenylporphyrin (5). To a solution of 5,15-diphenyl-10-(trimethylsilyl)methylporphyrin **3ab** (48 mg, 88 μmol) in a 55 mL mixed solvent of H_2O/THF/CH_3CN (1:5:5) was added DDQ (200 mg, 880 μmol, 10 equiv) at rt. After being stirred at 60 °C for 1 h, the reaction was quenched with Et_3N (1 mL). The mixture was diluted with CH_2Cl_2 (100 mL) and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (n-hexane/CH_2Cl_2 = 5:1) followed by recrystallization from CH_2Cl_2/n-hexane gave **5** (39.8 mg, 92%) as a dark purple solid. R_f = 0.52 (1:1 n-hexane/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.50 (1H, s), 10.10 (1H, s), 9.98 (2H, d, J = 4.9 Hz), 9.16 (2H, d, J = 4.9 Hz), 8.98 (2H, d, J = 4.9 Hz), 8.81 (2H, d, J = 4.9 Hz), 8.17−8.12 (4H, m), 7.83−7.74 (6H, m), −2.52 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 195.0, 148.5 (4C, br), 145.6 (4C, br), 141.2, 134.4, 133.8, 131.8, 131.1, 128.7, 128.1, 126.9, 122.1, 109.8, 108.2; IR (KBr) 3317, 1670, 1550, 1173, 1107, 1057, 964, 922, 856, 787, 737, 702, 633 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 422.0 (5.5), 523.0 (4.3), 561.0 (4.2), 594.0 (4.0), 649.5 (4.0), 707.0 (3.5) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{33}H_{23}N_4O$ 491.1872, found

491.1874; Anal. calcd for $C_{33}H_{22}N_4O$: C, 80.80; H, 4.52: N, 11.42, found: C, 80.80; H, 4.61: N, 11.31.

10,20-Diphenyl-5-hydroxymethylporphyrin (6). To a solution of 5,15-diphenyl-10-(trimethylsilyl)methylporphyrin **3ab** (48 mg, 88 μmol) in a mixed solution of H_2O/THF (1:10, 55 mL) was added DDQ (60 mg, 264 μmol, 3 equiv) at rt. After being stirred at rt for 0.5 h, the reaction was quenched with Et_3N (1 mL). Then, the mixture was diluted with CH_2Cl_2 (100 mL) and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 3:1) followed by recrystallization from CH_2Cl_2/*n*-hexane gave **6** (41.3 mg, 95%) as a brown-purple solid. R_f = 0.28 (1:1 *n*-hexane/CH_2Cl_2); ^{1}H NMR (THF-d_8, 500 MHz) δ 10.22 (1H, s), 9.80 (2H, d, *J* = 4.6 Hz), 9.33 (2H, d, *J* = 4.6 Hz), 8.96 (2H, d, *J* = 4.6 Hz), 8.92 (2H, d, *J* = 4.6 Hz), 8.27−8.18 (4H, m), 7.83−7.73 (6H, m), 6.92 (2H, s), 5.35 (1H, br s), −3.04 (2H, br s); ^{13}C NMR (THF-d_8, 125 MHz) δ 157.2 (8C, br), 152.7, 145.1, 141.4 (6C), 139.5, 138.1, 137.2, 129.6, 128.4, 115.5, 73.9; IR (KBr) 3359, 3302, 3097, 3047, 2912, 1485, 1404, 1335, 1065, 991, 791, 725 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 412.0 (5.6), 508.5 (4.3), 582.5 (3.8) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{33}H_{25}N_4O$ 493.2028, found 493.2031.

10,20-Diphenyl-5-methoxymethylporphyrin (7). An oven-dried 100 mL two-necked flask equipped with a magnetic stirring bar and rubber septum was charged with 5,15-diphenyl-10-(trimethylsilyl)methylporphyrin **3ab** (48 mg, 88 μmol). The reaction vessel was evacuated and flushed with argon (three times), and then absolute MeOH (5 mL) and absolute dioxane (50 mL) was added. The reaction mixture was stirred for 5 min at rt, and then DDQ (60 mg, 264 μmol, 3 equiv) was added. After being stirred at room temperature for 12 h, the reaction was quenched with Et_3N (1 mL). The mixture was diluted with CH_2Cl_2 (100 mL) and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 7:1) followed by recrystallization from CH_2Cl_2/MeOH gave **7** (39.2 mg, 88%) as a brown-purple solid. R_f = 0.56 (1:1 *n*-hexane/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.14 (1H, s), 9.62 (2H, d, *J* = 4.8 Hz), 9.26 (2H, d, *J* = 4.8 Hz), 9.02 (2H, d, *J* = 4.8 Hz), 8.97 (2H, d, *J* = 4.8 Hz), 8.27−8.20 (4H, m), 7.85−7.74 (6H, m), 6.73 (2H, s), 3.73 (3H, s), −3.03 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.1 (6C, br), 145.8 (br), 142.0, 134.7, 131.7, 131.3, 131.2, 128.6, 127.8, 126.8, 119.6, 112.8, 105.5, 73.3, 58.2; IR (KBr) 3317, 3097, 3051, 2974, 2927, 1593, 1481, 1400, 1338, 1176, 1080, 957, 791, 741 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 412.0 (5.6), 508.0 (4.3), 581.0 (3.8) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{34}H_{27}N_4O$ 507.2185, found 507.2185.

5,15-Diphenyl-10-fluoromethylporphyrin (8). An oven-dried 100 mL two-necked flask equipped with a magnetic stirring bar and rubber septum was charged with 5,15-diphenyl-10-(trimethylsilyl)-methylporphyrin **3ab** (48 mg, 88 μmol). The reaction vessel was evacuated and flushed with argon (three times), and then absolute CH_2Cl_2 (50 mL) and DDQ (100 mg, 440 μmol, 5 equiv) were added at room temperature. The reaction mixture was stirred for 5 min, and then DAST (17.4 μL, 132 μmol, 1.5 equiv) was added. After being stirred at room temperature for 3 h, the reaction was quenched with Et_3N (1 mL). The mixture was diluted with CH_2Cl_2 (100 mL) and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10:1) followed by recrystallization from CH_2Cl_2/MeOH gave **8** (7.1 mg, 16%) as a brown-purple solid. R_f = 0.60 (1:1 *n*-hexane/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.08 (1H, s), 9.59 (2H, d, *J* = 4.9 Hz), 9.24 (2H, d, *J* = 4.9 Hz), 8.96 (2H, d, *J* = 4.9 Hz), 8.94 (2H, d, *J* = 4.9 Hz), 8.28−8.18 (4H, m), 7.82−7.72 (6H, m), 5.17 (1H, dd, *J* = 394.6, 12.7 Hz), 5.15 (1H, dd, *J* = 405.8, 12.7 Hz), −2.96 (2H, br s).; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.7 (8C, br), 142.2, 134.7, 131.6 (4C), 131.3, 131.0, 127.7, 127.2 (1C, d, J_{CF} = 337.7 Hz), 126.7, 119.2, 118.9, 104.2; ^{19}F-NMR ($CDCl_3$, 466 MHz) δ −138.1 (1F, tdd, J_{FH} = 32.7, 21.6, 11.0 Hz); IR (KBr) 3313, 3055, 2924, 2854, 1597, 1469, 1377, 1241, 1149, 1061, 972, 845, 791, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 413.0 (5.6), 509.5 (4.4), 544.5 (4.1), 586.0 (4.0), 639.5 (3.8) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{33}H_{24}FN_4$ 495.1985, found 495.1983.

5-[(2-Furan-2-yl)-2-hydryoxyethyl]-10,20-diphenylporphyrin (9). An oven-dried 50 mL two-necked flask equipped with a magnetic stirring bar and rubber septum was charged with 5,15-diphenyl-10-(trimethylsilyl)methylporphyrin **3ab** (48 mg, 88 μmol) and 4 Å powdered molecular sieves (100 mg). The reaction vessel was evacuated and flushed with argon (three times), and then furfural **11** (73 μL, 880 μmol, 10 equiv) and dry THF (15 mL) were added at rt. The reaction mixture was stirred for 10 min, and then 1 M THF solution of TBAF (88 μL, 88 μmol, 1 equiv) was added. After being stirred at room temperature for 5 min, 1 mL of water was added to the mixture. The resulting mixture was diluted with CH_2Cl_2 (100 mL) and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 5:1) followed by recrystallization from CH_2Cl_2/MeOH gave **9** (49.4 mg, 98%) as a brown-purple solid. R_f = 0.35 (1:1 *n*-hexane/CH_2Cl_2); ^{1}H NMR (THF-d_8, 300 MHz) δ 10.10 (1H, s), 9.62 (2H, d, *J* = 4.9 Hz), 9.25 (2H, d, *J* = 4.9 Hz), 8.89 (2H, d, *J* = 4.9 Hz), 8.88 (2H, d, *J* = 4.9 Hz), 8.23−8.17 (4H, m), 7.81−7.71 (6H, m), 7.48 (1H, d, *J* = 1.8 Hz), 6.27 (1H, dd, *J* = 3.1, 1.8 Hz), 6.22 (1H, d, *J* = 3.1 Hz), 5.72 (1H, dd, *J* = 8.0, 4.8 Hz), 5.57 (1H, dd, *J* = 14.4, 4.8 Hz), 5.39 (1H, dd, *J* = 14.4, 8.0 Hz), 4.60 (1H, br s), −2.94 (2H, br s); ^{13}C NMR (THF-d_8, 75 MHz) δ 159.0, 148.1 (br), 147.4 (6C, br), 143.3, 142.4, 135.5, 131.8, 131.7, 131.6, 130.0, 128.4, 127.5, 119.8, 117.2, 110.9, 106.4, 105.0, 74.4, 43.4; IR (KBr) 3560, 3440, 3313, 3113, 3055, 2924, 1593, 1481, 1404, 1065, 964, 791, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 413.0 (5.4), 509.5 (4.2), 585.5 (3.7), 643.5 (3.5) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{38}H_{29}N_4O_2$ 573.2291, found 573.2295.

5,15-Diphenyl-5-(3-methoxycarbonylpropyl)porphyrin (10). An oven-dried 50 mL two-necked flask equipped with a magnetic stirring bar and rubber septum was charged with 5,15-diphenyl-10-(trimethylsilyl)methylporphyrin **3ab** (48 mg, 88 μmol) and 4 Å powdered molecular sieves (100 mg). The reaction vessel was evacuated and flushed with argon (three times), and then methyl bromoacetate **12** (81 μL, 880 μmol, 10 equiv) and dry THF (15 mL) were added at room temperature. The reaction mixture was stirred for 10 min, and then 1 M THF solution of TBAF (88 μL, 88 μmol, 1 equiv) was added. After being stirred at room temperature for 5 min, 1 mL of water was added to the mixture. The resulting mixture was diluted with CH_2Cl_2 (100 mL) and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 5:1) followed by recrystallization from CH_2Cl_2/MeOH gave **10** (41.6 mg, 86%) as a brown-purple solid. R_f = 0.47 (1:1 *n*-hexane/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.07 (1H, s), 9.56 (2H, d, *J* = 4.9 Hz), 9.23 (2H, d, *J* = 4.9 Hz), 8.99 (2H, d, *J* = 4.9 Hz), 8.95 (2H, d, *J* = 4.9 Hz), 8.25−8.21 (4H, m), 7.84−7.74 (6H, m), 5.44 (2H, t, *J* = 8.3 Hz), 3.77 (3H, s), 3.56 (2H, t, *J* = 8.3 Hz), −2.96 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.1, 146.5 (8C, br), 142.0, 134.7, 131.7, 131.6 (4C), 131.1, 127.9, 126.8, 119.4, 117.7, 104.5, 51.8, 42.0, 31.1; IR (KBr) 3313, 3101, 3051, 2947, 1739, 1481, 1338, 1230, 1146, 968, 791, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 413.0 (5.6), 509.0 (4.3), 544.5 (3.7), 585.0 (3.7), 639.0 (3.3) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{36}H_{29}N_4O_2$ 549.2291, found 549.2299; Anal. calcd for $C_{36}H_{28}N_4O_2$: C, 78.81; H, 5.14; N, 10.21, found: C, 78.62; H, 5.20; N, 9.94.

5,15-Diformyl-10,20-diphenylporphyrin (13). To a solution of 10,20-bis(trimethylsilyl)methyl-5,15-diphenylporphyrin (**3ib**) (56 mg, 88 μmol) in a 55 mL mixed solvent H_2O/THF/CH_3CN (1:5:5) was added DDQ (400 mg, 1760 μmol, 20 equiv) at rt. After being stirred at 60 °C for 1 h, the reaction was quenched with Et_3N (1 mL). The mixture was diluted with CH_2Cl_2 (100 mL) and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 4:1) followed by recrystallization from CH_2Cl_2/*n*-hexane gave **13** (35.6 mg, 78%) as a brown-purple solid. R_f = 0.33 (1:1 *n*-hexane/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 12.47 (2H, s), 9.81 (4H, d, *J* = 4.9 Hz), 8.89 (4H, d, *J* = 4.9 Hz), 8.23−8.16 (4H, m), 7.83−7.74

(6H, m), −2.86 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.4, 146.3 (8C, br), 142.8, 134.3, 131.9, 129.1, 128.2, 126.8, 122.5, 108.7; IR (KBr) 3325, 3159, 3116, 3032, 2904, 2792, 1678, 1550, 1346, 1122, 960, 922, 814, 741 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 426.5 (5.2), 535.0 (3.7), 585.5 (4.1), 685.0 (4.0) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{34}H_{23}N_4O_2$ 519.1821, found 519.1822.

2-Formyl-5,10,15,20-tetraphenylporphyrin (14). To a solution of 5,10,15,20-tetraphenyl-2-(trimethylsilyl)methylporphyrin **3jb** (62 mg, 88 μmol) in a 55 mL mixed solvent of $H_2O/CH_2Cl_2/CH_3CN$ (1:5:5) was added DDQ (200 mg, 880 μmol, 10 equiv) at rt. After being stirred at 60 °C for 1 h, the reaction was quenched with Et_3N (1 mL). The mixture was diluted with CH_2Cl_2 (100 mL) and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 5:1) followed by recrystallization from CH_2Cl_2/*n*-hexane gave **14** (32.7 mg, 58%) as a dark purple solid. R_f = 0.40 (1:1 *n*-hexane/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.42 (1H, s), 9.29 (1H, s), 8.90 (1H, d, J = 4.9 Hz), 8.89 (1H, d, J = 4.9 Hz), 8.85 (2H, d, J = 4.9 Hz), 8.79 (1H, d, J = 4.9 Hz), 8.77 (1H, d, J = 4.9 Hz), 8.28−8.16 (8H, m), 7.86−7.70 (12H, m), −2.45 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.1, 151.6 (2C, br), 147.2 (br), 146.3 (br), 144.7 (2C, br), 143.8 (br), 142.6, 142.4 (br), 142.3, 141.9, 141.7 (2C), 137.1, 135.0, 134.7, 134.6, 134.6, 133.2 (2C), 130.9 (2C), 130.2, 129.9, 129.0, 128.2, 127.9 (2C), 127.4, 126.9 (4C), 126.8, 122.6, 120.6, 120.3, 120.1; IR (KBr) 3321, 3055, 2881, 1670, 1554, 1477, 1350, 1169, 968, 798, 710 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 432.5 (5.5), 526.0 (4.2), 567.0 (3.8), 604.0 (3.7), 662.5 (3.8) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{45}H_{31}N_4O$ 643.2498, found 643.2495.

5,15-Di(*n*-bulyl)-10-methoxymethylporphyrin (15). An oven-dried 100 mL two-necked flask equipped with a magnetic stirring bar and rubber septum was charged with 5,15-di(*n*-bulyl)-10-(trimethylsilyl)methylporphyrin (**3gb**) (45 mg, 88 μmol). The reaction vessel was evacuated and flushed with argon (three times), and then absolute MeOH (5 mL) and absolute dioxane (50 mL) were added. The reaction mixture was stirred for 5 min at rt, and then 2 equiv of DDQ (40 mg, 176 μmol) was added. After being stirred at room temperature for 12 h, the reaction was quenched with Et_3N (1 mL). The mixture was diluted with CH_2Cl_2 (100 mL) and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 7:1) followed by recrystallization from CH_2Cl_2/MeOH gave **15** (33.2 mg, 81%) as a brown-purple solid. R_f = 0.52 (1:1 *n*-hexane/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.96 (1H, s), 9.62 (2H, d, J = 4.8 Hz), 9.49 (2H, d, J = 4.8 Hz), 9.45 (2H, d, J = 4.8 Hz), 9.25 (2H, d, J = 4.8 Hz), 6.70 (2H, s), 4.92 (4H, t, J = 8.0 Hz), 3.75 (3H, s), 2.51 (4H, tt, J = 8.0, 7.7 Hz), 1.81 (4H, tq, J = 7.7, 7.4 Hz), 1.15 (6H, t, J = 7.4 Hz), −3.02 (2H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.3, 146.9, 146.3, 144.6, 131.6, 128.9, 128.3, 127.9, 119.1, 111.4, 104.6, 73.6, 58.2, 40.7, 34.7, 23.6, 14.1; IR (KBr) 3302, 3109, 2954, 2924, 2866, 2808, 1466, 1369, 1146, 1088, 933, 849, 779, 721 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 411.5 (5.6), 510.5 (4.2), 544.0 (3.5), 586.5 (3.7), 643.0 (3.3) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{30}H_{35}N_4O$ 467.2811, found 467.2808.

***(E)*-5-(2-Furan-2-yl)vinyl-10,20-diphenylporphyrin (16).** An oven-dried 50 mL two-necked flask equipped with a magnetic stirring bar and rubber septum was charged with 10-bis(trimethylsilyl)methyl-5,15-diphenylporphyrin **3ah** (55 mg, 88 μmol) and 4 Å powdered molecular sieves (100 mg). The reaction vessel was evacuated and flushed with argon (three times), and then furfural **11** (73 μL, 880 μmol, 10 equiv) and dry THF (15 mL) were added at rt. The reaction mixture was stirred for 10 min, and then a 1 M THF solution of TBAF (88 μL, 88 μmol) was added. After being stirred at room temperature for 5 min, 1 mL of water was added to the mixture (1 mL). The resulting mixture was diluted with CH_2Cl_2 (100 mL) and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 7:1) followed by recrystallization from CH_2Cl_2/MeOH gave **16** (42.0 mg, 86%) as a brown-purple solid. R_f = 0.56 (1:1 *n*-hexane/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.63 (1H, d, J = 15.6 Hz), 9.54 (2H, d, J = 4.9 Hz), 9.22 (2H, d, J = 4.9 Hz), 8.93 (2H, d, J = 4.9 Hz), 8.92 (2H, d, J = 4.9 Hz), 8.28−8.18 (4H, m), 7.83−7.74 (6H, m), 7.66 (1H, d, J = 2.0 Hz), 7.16 (1H, d, J = 15.6 Hz), 6.65 (1H, d, J = 3.4 Hz), 6.61 (1H, dd, J = 3.4, 2.0 Hz), −2.69 (2H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.0, 146.7 (6C, br), 145.5 (br), 142.6, 142.0, 134.7, 131.5, 131.1, 130.9, 130.9, 129.4, 128.0, 127.8, 126.8, 119.9, 117.2, 112.0, 109.8, 104.7; IR (KBr) 3313, 3113, 3051, 1477, 968, 791, 737 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 425.5 (5.3), 519.5 (4.1), 567.0 (4.1), 656.5 (3.7) nm; HRMS-FAB$^+$ ([M + H]$^+$) calcd for $C_{38}H_{27}N_4O$ 555.2185, found 555.2180.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This work is dedicated to Dr. Masanori Sakamoto, Professor Emeritus of Meiji Pharmaceutical University, on the occasion of his 77th birthday (KIJU).

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