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PREPARATION OF *meso*-SILYLPORPHYRINS VIA NICKEL-CATALYZED COUPLING OF *meso*-BROMINATED Ni(II) PORPHYRINS WITH SILYLZINC REAGENTS

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Abstract – In this paper, we developed a technique for the nickel-catalyzed coupling of *meso*-brominated Ni(II) porphyrins with silylzinc reagents in order to prepare *meso*-silyl-substituted Ni(II) porphyrins. Porphyrin silylation occurs under mild conditions and exhibits both excellent substrate generality and functional group compatibility.

INTRODUCTION

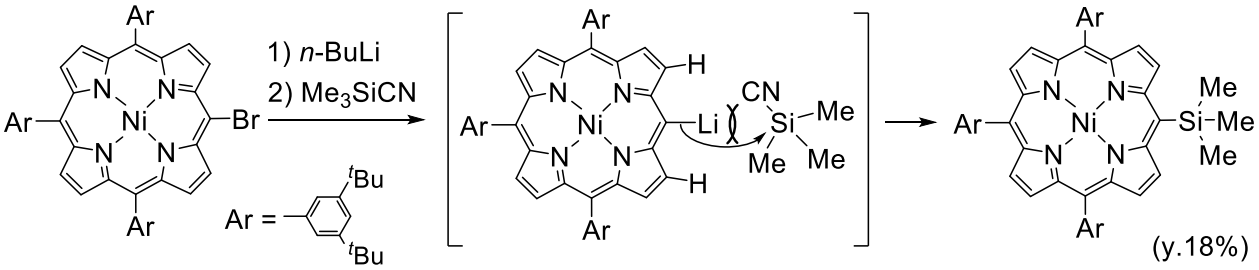
Porphyrins and metalloporphyrins are compounds that are widely investigated in fields ranging from organic/inorganic chemistry to materials science.[1] Peripheral porphyrin functionalization has attracted attention because the physical, chemical, and biological properties of porphyrins can be precisely modified, using steric and electronic substituent characteristics, on the porphyrin ring.[2] To date, numerous methods exist in order to introduce various functional groups (e.g., amino, alkoxy, ester, boryl, CN, NO_2, and CF_3) into porphyrins.[3] Silyl groups, particularly as an aromatic ring substituent, often play an important role in synthetic chemistry because of their versatile transformation to various functional groups.[4,5] Therefore, silyl-substituted porphyrins could be a pivotal intermediary in the construction of porphyrin derivatives. Recently, we reported the properties of a highly regioselective β-silylation porphyrin via Ir-catalyzed C–H activation with a silylating agent ($HSiMe(OSiMe_3)_2$).[5] However, there is currently no method available for porphyrin *meso*-silylation. This is most likely due to the stereochemical environment surrounding the *meso*-carbon on the porphyrin ring, which is too crowded for silyl groups (e.g., they have one of the bulkiest functionalities in organic synthesis). The only known method of C–Si bond formation, which uses the reaction of *meso*-lithiated porphyrin with Me_3SiCN at the *meso*-position on the porphyrin core, yielded only 18% of the desired silylated product (Scheme 1a).[6] Therefore, the introduction of efficient, regioselective silyl groups into the *meso*-position of the porphyrin remains a

This work is dedicated to Professor Dr. Kiyoshi Tomioka on the occasion of his 70th birthday.

challenging and highly demanding task.

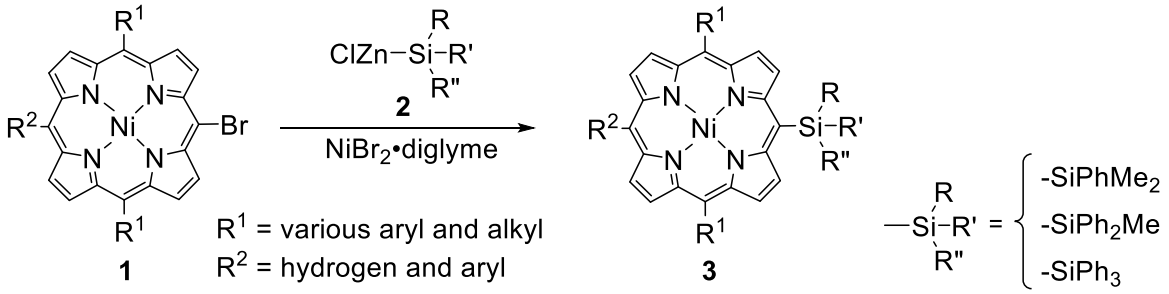
Here, we report an efficient method to synthesize *meso*-silylated Ni(II) porphyrins via a Ni-catalyzed cross-coupling reaction between *meso*-brominated Ni(II) porphyrin (**1**) and silylzinc halides (**2**). Silylation can be carried out under mild conditions and is suitable for a variety of *meso*-bromoporphyrins (**1**). Furthermore, *meso*-silylporphyrins (**3**) are capable of transformations that convert C–Si bonds to C–C, C–O, and C–halogen bonds.

a. *meso*-Silylation of porphyrins via *meso*-lithiation



Steric hindrance between the *meso*-carbon of the porphyrin and a bulky electrophile may contribute to lowering the yield.

b. This work:
meso-silylation of porphyrins via coupling of _meso_-bromoporphyrins with silylzinc reagents



Scheme 1. The preparation of *meso*-silylated porphyrins

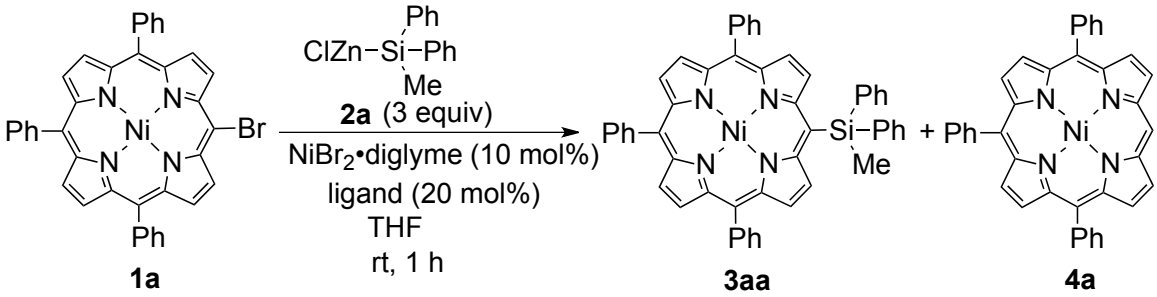
RESULTS AND DISCUSSION

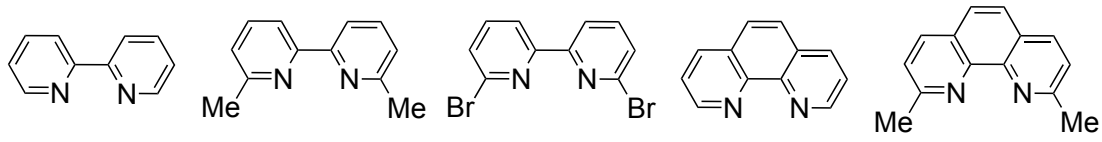
Recently, Fu and coworkers introduced silylzinc halides (e.g., $R_3SiZnCl$) as new, efficient silicon nucleophiles that can participate in metal-catalyzed C–Si bond formation with inactive secondary alkyl bromides. Reactions such as this one were not achievable with other silicon nucleophiles, such as pinB-SiR_3.[7] Therefore, we selected $Ph_2MeSiZnCl$ (**2a**) as the Si source for porphyrin *meso*-silylation. Following the conditions developed by Fu et al., for the silylation of alkyl halides, we examined the cross-coupling of *meso*-brominated Ni(II) triphenylporphyrin (**1a**) with the silylating agent (**2a**) in the presence of substoichiometric $NiBr_2$·diglyme without ligands.[7] Unfortunately, this Ni(II)-catalyzed reaction yields only a trace amount of the desired *meso*-silylated porphyrin (**3aa**) along with a debrominated product (**4a**) and the recovered, initial porphyrin (**1a**) (Table 1, entry 1). However, we

found that bipyridyl-based ligands have a crucial impact on the outcome of the Ni(II)-catalyzed reaction (entries 2–6), as well as choosing the simple bipyridine (bpy) ligand, which gave the best result (entry 2). We also observed that the C–Si bond formation, at the *meso*-position, occurs in the reaction between *meso*-brominated Ni(II) porphyrin (**1a**) and the silyllithium reagent $PhMe_2SiLi$ (i.e., the silylzinc reagent precursor), in the absence of the Ni(II) catalyst, although the yield is quite low (entry 7).[8–10]

The catalytic silylation presented here is applicable to an array of *meso*-brominated Ni(II) porphyrins (**1**) (Table 2). Under optimal reaction conditions, *meso*-brominated Ni(II) diaryl- and triarylporphyrins (**1a-1h**), such as those with aliphatic, vinyl, and alkoxy groups on their phenyl substituent, were

Table 1. Ligand screening for the coupling between the *meso*-bromoporphyrin (**1a**) and the silylzinc reagent (**2a**)

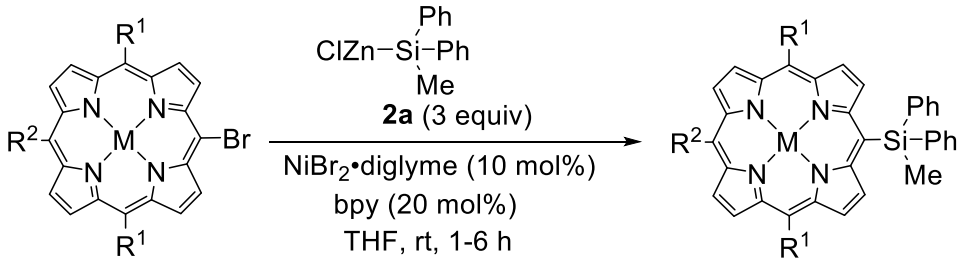


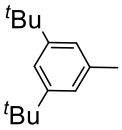
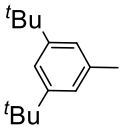
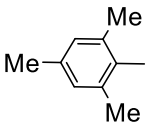
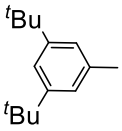
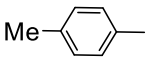
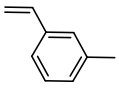
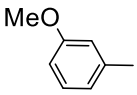


entry	ligand	yield[a] (%) of **3aa**	yield[a] (%) of **4a**	Recovery[a] (%) of **1a**
1	-	0	21	69
2	bpy	71	17	trace
3	6,6-dmbpy	23	39	24
4	dbbp	trace	47	31
5	phen	32	40	15
6	2,9-dmp	26	46	trace
7[b]	-	15	48	trace

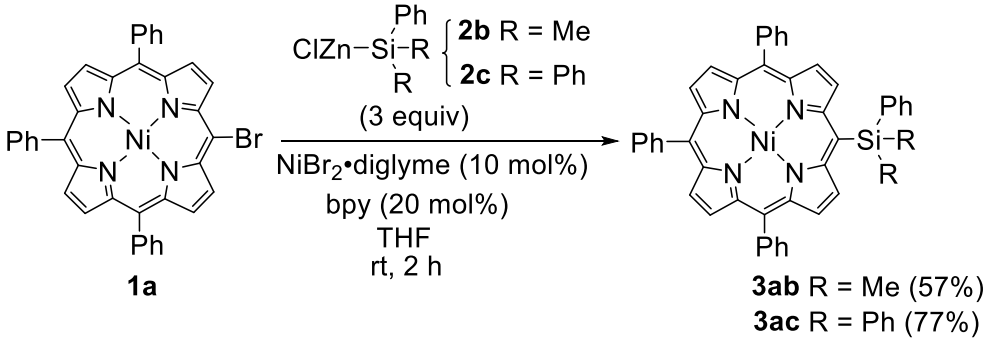
[a] Isolated yield. [b] Reaction was carried out using $Ph_2MeSiLi$ instead of $Ph_2MeSiZnCl$ without the Ni(II) catalyst.

Table 2. Coupling reactions between *meso*-bromoporphyrins (**1**) and $Ph_2MeSiZnCl$ (**2a**)



entry	substrates	R^1	R^2	M	time (h)	products	yield[a] (%)
1	**1a**	Ph	Ph	Ni	1	**3aa**	71
2	**1b**			Ni	5	**3ba**	57
3	**1c**	Ph	H	Ni	5	**3ca**	65
4	**1d**		H	Ni	6	**3da**	48
5	**1e**		H	Ni	2	**3ea**	52
6	**1f**		H	Ni	2	**3fa**	68
7	**1g**		H	Ni	3	**3ga**	55
8	**1h**		H	Ni	1	**3ha**	39
9	**1i**	Ph	C_6F_5	Ni	2	**3ia**	27
10	**1j**	^{n}Bu	H	Ni	4	**3ja**	52
11	**1k**	^{i}Bu	H	Ni	3	**3ka**	61
12	**Zn-1a**	Ph	Ph	Zn	1	**Zn-3aa**	trace
13	**H_2-1a**	Ph	Ph	2H	1	**H_2-3aa**	trace

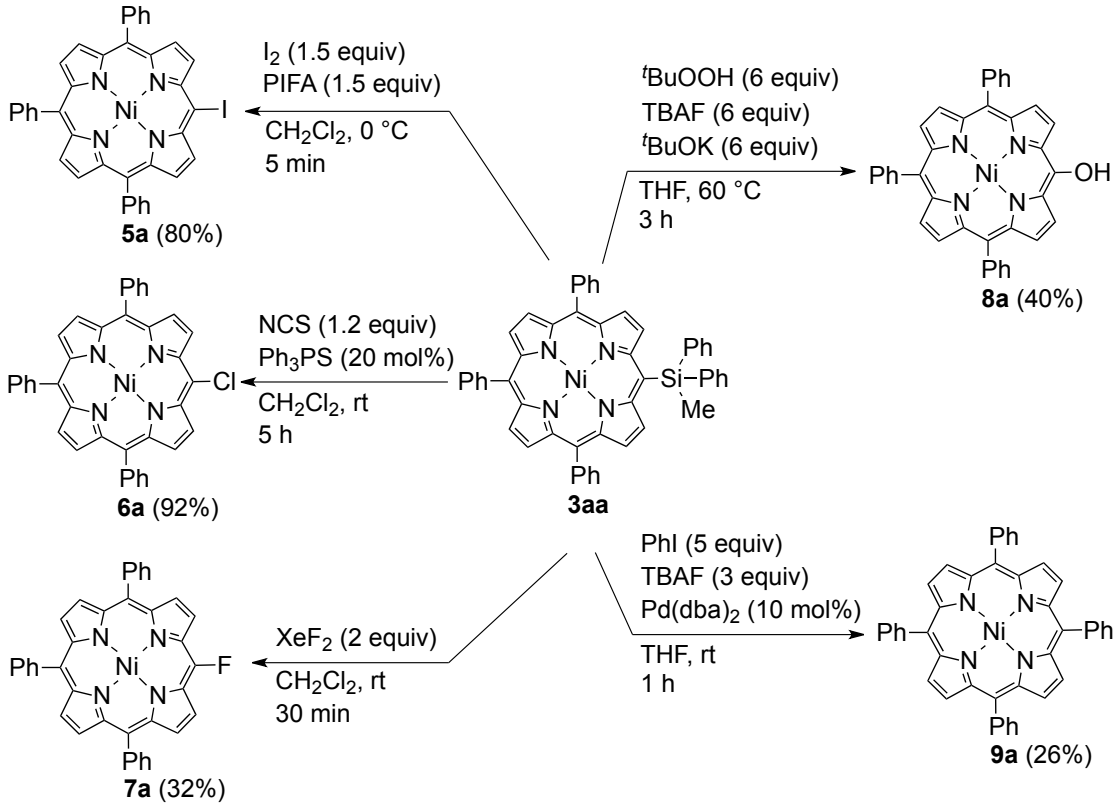
[a] Isolated yield.



Scheme 2. Porphyrin *meso*-silylation using a variety of silylzinc reagents (**2**)

converted to the corresponding *meso*-silylated Ni(II) complexes (**3aa-3ha**) with good to high yields (entries 1–8). Ni(II) porphyrin (**1i**), characterized by strong C_6F_5 group electron withdrawal, was also suitable for this catalytic silylation, allowing the corresponding *meso*-silylated derivative (**3ia**) to produce an appreciable yield (entry 9). Similarly, *meso*-brominated Ni(II) 5,15-dialkylporphyrins (**1j** and **1k**) underwent catalytic *meso*-silylation, producing the corresponding *meso*-silyl-substituted Ni(II) porphyrins (**3ja** and **3ka**) with good yields (entries 10 and 11). The central porphyrin Ni(II) ion was crucial for silylation. The use of both the Zn(II) porphyrin (**Zn-1a**) and the free base porphyrin (**H_2-1a**), as substrates, resulted in a trace amount of the desired silylated products (**Zn-3aa** and **H_2-3aa**), together with the recovered, initial materials and the debrominated products (entries 12 and 13). In addition to $Ph_2MeSiZnCl$ (**2a**), other silylzinc reagents, including $PhMe_2SiZnCl$ (**2b**) and $Ph_3SiZnCl$ (**2c**), were examined using *meso*-brominated Ni(II) triphenylporphyrin (**1a**) as the coupling partner under optimized conditions. As shown in Scheme 2, both silylzinc reagents (**2b** and **2c**) participated in the coupling reactions with *meso*-bromoporphyrin (**1a**), producing the corresponding *meso*-silylated derivatives (**3ab** and **3ac**) with good yields.

This Ni(II)-catalyzed cross-coupling provides rapid access to *meso*-silyl-substituted porphyrins that are useful in a variety of transformations (Scheme 3). For example, the iodination of *meso*-silylporphyrin (**3aa**) is easily accomplished using I_2/phenyliodine bis(trifluoroacetate) (PIFA). *meso*-Silylporphyrin (**3aa**) underwent chlorination with *N*-chlorosuccinimide (NCS), in the presence of a substoichiometric amount of Ph_3PS, producing high yields of *meso*-chloroporphyrin (**6a**). Treating porphyrin **3aa** with XeF_2 produced a 32% isolated yield of *meso*-fluorinated derivative (**7a**). The oxidation of *meso*-silylporphyrin **3aa** with a *t*-BuOOH/TBAF/*t*-BuOK system in THF at 60 °C produced a Ni(II) complex of *meso*-hydroxyporphyrin (**8a**) with a yield of 40%. Finally, we explored the effects of installing a carbon–carbon bond at the porphyrin's *meso*-position via the Hiyama coupling reaction. In the presence of TBAF, we performed the Pd-catalyzed reaction between *meso*-silylporphyrin **3aa** and iodobenzene, yielding 26% of the desired Hiyama couplingf product (**9a**).



Scheme 3. Functionalization of the *meso*-silylporphyrins **3aa**

CONCLUSION

In summary, we developed an efficient method to prepare *meso*-silylporphyrins via the Ni-catalyzed coupling of a *meso*-bromoporphyrin Ni(II) complex with silylzinc reagents. This method is applicable to a broad spectrum of *meso*-brominated Ni(II) porphyrins in order to produce sufficient yields of *meso*-silylated Ni(II) porphyrins. We also demonstrated the synthetic utility of *meso*-silylporphyrins, as a synthon for more complex porphyrin derivatives, by performing several transformations (e.g., cross-coupling reactions, halogenation, and oxidation) that convert C–Si bonds to C–C and C–heteroatom bonds. Further studies on this and the related porphyrin ring functionalization reactions are currently underway.

EXPERIMENTAL

General ^{1}H and ^{13}C NMR spectra were recorded at rt on a JEOL JNM AL-300, a JEOL JNM AL-400, a JEOL JNM ECS-400, and a JEOL JNM LA-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. $CDCl_3$ (δ = 7.24) and CD_2Cl_2 (δ = 5.32) for ^{1}H NMR and relative to the central resonance of $CDCl_3$ (δ = 77.0) and CD_2Cl_2 (δ = 53.8) for ^{13}C NMR. ^{19}F NMR spectra were recorded at rt on a JEOL JNM ECS-400 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 on a JASCO V-660 dual-beam grating spectrophotometer with a 1 cm quartz cell. IR spectra were recorded on a JASCO FT/IR-4100 spectrophotometer. The mass spectroscopic data were obtained on JEOL JNM-DX302 spectrometer. 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 atmosphere of argon using standard vacuum line techniques and glassware that was flame-dried and cooled under argon before use. Dry THF and dioxane were purchased for the reactions and used without further desiccation. Porphyrin derivatives—**1a**,[11a] **1c**,[11b] **Zn-1a**,[11c] and **H_2-1a**[3d]—were prepared according to methods described in the literature. Other chemicals were purchased from commercial sources and used as received unless otherwise stated.

General Procedure for Preparation of Porphyrins 1. A solution of a free base *meso*-bromoporphyrin **H_2-1** (0.89 mmol) in DMF (30 mL) was added to $Ni(OAc)_2 \cdot 4H_2O$ (885.8 mg, 3.6 mmol). The mixture was stirred at 140 °C for 2 h. After reaction completion (monitored by TLC), the solution was poured into water (80 mL). The resulting precipitate was collected and washed with water and MeOH, producing *meso*-brominated Ni(II) porphyrin (**1**).

[5-Bromo-10,15,20-tris(3,5-di-*t*-butylphenyl)porphynato]nickel(II) (1b). Prepared from *meso*-bromoporphyrin **H_2-1b**[12a] (359.0 mg, 0.38 mmol) following the general procedure; Red solid; 360.0 mg, 95% yield; R_f = 0.55 (1/2 toluene/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.50 (2H, d, *J* = 4.8 Hz), 8.82 (2H, d, *J* = 4.8 Hz), 8.75 (4H, s), 7.84 (6H, s), 7.73 (2H, s), 7.70 (1H, s), 1.48 (36H, s), 1.45 (18H, s); ^{13}C NMR ($CDCl_3$ 100 MHz) δ: 148.9, 148.8, 143.1, 142.9, 142.8, 142.0, 139.5, 139.4, 133.4, 132.7, 132.6, 128.6, 128.6, 128.4, 121.1, 121.0, 120.6, 120.5, 101.6, 34.8, 34.8, 31.5, 31.5; IR (KBr), 2958, 1593, 1470, 1362, 1300, 1011, 717 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε): 419 (5.4), 531 (4.2) nm; HRMS (EI) *m/z*: calcd for $C_{62}H_{71}BrN_4Ni$ 1008.4216, found 1008.4221.

[5-Bromo-10,20-bis(2,4,6-trimethylphenyl)porphynato]nickel(II) (1d). Prepared from *meso*-bromoporphyrin **H_2-1d**[3f] (140.0 mg, 0.22 mmol) following the general procedure; Red solid; 144.0 mg, 94% yield; R_f = 0.55 (1/2 toluene/hexane); ^{1}H NMR (CD_2Cl_2 400 MHz) δ: 9.80 (1H, s), 9.55 (2H, d, *J* = 4.9 Hz), 9.10 (2H, d, *J* = 4.9 Hz), 8.67 (4H, d, *J* = 4.9 Hz), 7.26 (4H, s), 2.59 (6H, s), 1.77 (12H, s).^{13}C NMR ($CDCl_3$, 100 MHz) δ: 143.8, 143.7, 143.3, 142.7, 139.5, 138.4, 137.4, 133.9, 133.3, 132.5, 132.4, 128.3, 118.1, 105.3, 103.0, 21.9 (2C) 21.8 (4C); IR (KBr) 2918, 2851, 1551, 1381, 1324, 1230, 1047, 858, 789, 694 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 409 (5.3), 525 (4.2) nm; HRMS-FAB$^+$ (M^+) calcd for $C_{38}H_{31}BrN_4Ni$ 680.1086, found 680.1081.

[5-Bromo-10,20-bis(3,5-di-*t*-butylphenyl)porphynato]nickel(II) (1e). Prepared from *meso*-bromoporphyrin **H_2-1e**[12b] (547.9 mg, 0.72 mmol) following the general procedure; Red solid; 522.7 mg, 89% yield; R_f = 0.66 (1/3 toluene/hexane); ^{1}H NMR ($CDCl_3$ 400 MHz) δ: 9.76 (1H, s), 9.55 (2H, d, *J* = 4.9 Hz), 9.07 (2H, d, *J* = 4.9 Hz), 8.87 (2H, d, *J* = 4.9 Hz), 8.86 (2H, d, *J* = 4.9 Hz), 7.86 (4H, s), 7.75 (2H, s), 1.49 (36H, s); ^{13}C NMR ($CDCl_3$ 100 MHz) δ: 149.3, 143.7, 143.3, 143.2, 142.2, 139.7, 133.6, 133.4, 133.1, 132.4, 129.0, 121.5, 120.6, 105.1, 102.8, 35.2, 31.9; IR (KBr), 2958, 2870, 1593, 1470, 1362, 1323, 1003, 717 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε): 412 (5.3), 526 (4.1) nm; HRMS (EI) *m/z*: calcd for $C_{48}H_{51}BrN_4Ni$ 820.2651, found 820.2656.

[5-Bromo-10,20-di(*p*-tolyl)porphynato]nickel(II) (1f). Prepared from *meso*-bromoporphyrin **H_2-1f**[3d] (255.0 mg, 0.45 mmol) following the general procedure; Red solid; 259.0 mg, 92% yield; R_f = 0.40 (1/2 toluene/hexane); ^{1}H NMR ($CDCl_3$ 400 MHz) δ: 9.62 (1H, s), 9.50 (2H, d, *J* = 4.9 Hz), 8.97 (2H, d, *J* = 4.9 Hz), 8.79 (4H, d, *J* = 4.9 Hz), 8.78 (4H, d, *J* = 4.9 Hz), 7.83 (4H, d, *J* = 7.8 Hz), 7.47 (4H, d, *J* = 7.8 Hz), 2.65 (6H, s); ^{13}C NMR ($CDCl_3$ 100 MHz) δ: 143.9, 143.5, 143.4, 142.5, 138.0, 138.0, 134.1, 133.6, 133.4, 133.4, 132.8, 128.1, 119.6, 105.4, 103.1, 22.0; IR (KBr), 3024, 2916, 1512, 1458, 1385, 1068, 791 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε): 410 (5.2), 526 (4.1) nm; HRMS (EI) *m/z*: calcd for $C_{34}H_{23}BrN_4Ni$ 624.0460, found 624.0456.

[5-Bromo-10,20-di(3-vinylphenyl)porphynato]nickel(II) (1g). Prepared from *meso*-bromoporphyrin **H_2-1g**[3d] (250.0 mg, 0.42 mmol) following the general procedure; Red solid; 237.0 mg, 87% yield; R_f = 0.35 (1/2 toluene/hexane); ^{1}H NMR ($CDCl_3$ 400 MHz) δ: 9.67 (1H, s), 9.53 (2H, d, *J* = 4.9 Hz), 9.01 (2H, d, *J* = 4.9 Hz), 8.80 (2H, d, *J* = 4.9 Hz), 8.80 (2H, d, *J* = 4.9 Hz), 8.01 (2H, s), 7.86 (2H, d, *J* = 7.3 Hz), 7.77 (2H, d, *J* = 7.8 Hz), 7.64 (2H, dd, *J* = 7.8, 7.3 Hz), 6.92 (2H, dd, *J* = 17.6, 10.7 Hz), 5.91 (2H, d, *J* = 17.6 Hz), 5.37 (2H, d, *J* = 10.7 Hz). ^{13}C NMR ($CDCl_3$ 100 MHz) δ: 143.3, 143.2, 142.8, 142.2, 140.8, 136.7, 136.2, 133.2, 133.2, 133.1, 132.9, 132.5, 131.6, 127.1, 125.7, 118.8, 114.9, 105.1, 102.9; IR (KBr): 3086, 3051, 1327, 1072, 1003, 791 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 410 (5.4), 525 (4.3), 556 (3.7) nm; HRMS-FAB$^+$ (M^+) Calcd for $C_{36}H_{23}BrN_4Ni$ 648.0460, found 648.0462.

[5-Bromo-10,20-di(3-methoxyphenyl)porphynato]nickel(II) (1h). Prepared from *meso*-bromoporphyrin **H_2-1h**[3d] (350.0 mg, 0.58 mmol) following the general procedure; Red solid; 363.0 mg, 95% yield; R_f = 0.16 (1/1 toluene/hexane); ^{1}H NMR(CD_2Cl_2 300 MHz) δ: 9.81 (1H, s), 9.58 (2H, d, *J* = 5.0 Hz), 9.12 (2H, d, *J* = 5.0 Hz), 8.88 (4H, d, *J* = 5.0 Hz), 7.63-7.62 (2H, m), 7.61 (2H, s), 7.58-7.54 (2H, m), 7.32-7.30 (2H, m), 3.95 (6H, s).^{13}C NMR ($CDCl_3$ 100 MHz) δ: 158.1, 143.2, 143.2, 142.8, 142.2, 141.8, 133.2, 133.1, 133.0, 132.5, 127.8, 126.8, 119.7, 118.8, 113.6, 105.1, 102.8, 55.5; IR (KBr): 3086, 3051, 1327, 1072, 1003, 791 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 410 (5.4), 525 (4.3), 556 (3.7) nm; HRMS-FAB$^+$ (M^+): Calcd for $C_{36}H_{23}BrN_4Ni$ 648.0460, found 648.0462.

[5-Bromo-10,20-di(*n*-butyl)porphynato]nickel(II) (1j). Prepared from *meso*-bromoporphyrin **H_2-1j**[3f]

(219.0 mg, 0.44 mmol) following the general procedure; Red solid; 225.0 mg, 92% yield; R_f = 0.60 (1/2 toluene/hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.46 (2H, d, *J* = 5.0 Hz), 9.40 (1H, s), 9.22 (4H, s), 8.96 (2H, d, *J* = 5.0 Hz), 4.44 (4H, t, *J* = 6.6 Hz), 2.29-2.19 (4H, m), 1.62-1.53 (4H, m), 1.04 (6H, t, *J* = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 142.8, 142.4, 141.8, 140.8, 133.2, 132.5, 130.2, 130.0, 118.1, 118.1, 103.9, 39.6, 33.8, 23.4, 14.0; IR (KBr): 2954, 2862, 1466, 1335, 1080, 1003, 779 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 412 (5.5), 529 (4.4) nm; HRMS (EI) *m/z*: Calcd for $C_{28}H_{27}BrN_4Ni$ 556.0773, found 556.0765.

[5-Bromo-10,20-di(*i*-butyl)porphynato]nickel(II) (1k). Prepared from *meso*-bromoporphyrin **H_2-1k**[3f] (190.0 mg, 0.38 mmol) following the general procedure; Red solid; 175.0 mg, 83% yield; R_f = 0.43 (1/3 toluene/hexane); ^{1}H NMR ($CDCl_3$ 400 MHz) δ: 9.48 (2H, d, *J* = 4.9 Hz), 9.42 (1H, s), 9.26 (2H, d, *J* = 4.9 Hz), 9.25 (2H, d, *J* = 4.9 Hz), 8.97 (2H, d, *J* = 4.9 Hz), 4.47 (4H, d, *J* = 6.3 Hz), 2.24-2.22 (2H, m), 0.86 (12H, d, *J* = 6.3 Hz); ^{13}C NMR ($CDCl_3$ 100 MHz) δ: 143.1, 142.8, 141.6, 140.6, 133.0, 132.3, 130.8, 130.6, 116.7, 103.7, 101.5, 42.1, 34.5, 22.8; IR (KBr): 2954, 2893, 1466, 1381, 1080, 1007, 775 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 412 (5.5), 531 (4.3) nm; HRMS (EI) *m/z*: calcd for $C_{28}H_{27}BrN_4Ni$ 556.0773, found 556.0775.

Preparation of [5-Bromo-10,20-diphenyl-15-pentafluorophenylporphynato]nickel(II) (1i). A solution of a [5,15-diphenyl-10-pentafluorophenylporphynato]nickel(II) **4i**[13] (110.0 mg, 0.16 mmol) in $CHCl_3$ (40 mL) was added to *N*-bromosuccinimide (NBS) (34.0 mg, 0.19 mmol) at 0 °C. The mixture was stirred for 2 h and quenched with acetone (10 mL). The solvent was evaporated to dryness. Column chromatography performed on a silica gel (1/2 toluene/hexane) followed by recrystallization from MeOH/CH_2Cl_2, produced the pure compound **1i** as a red solid. 104.0 mg, 85% yield; R_f = 0.50 (1/2 toluene/hexane); ^{1}H NMR ($CDCl_3$ 400 MHz) δ: 9.52 (2H, d, *J* = 5.1 Hz), 8.79 (2H, d, *J* = 5.1 Hz), 8.77 (2H, d, *J* = 5.1 Hz), 8.59 (2H, d, *J* = 5.1 Hz), 7.99-7.96 (4H, m), 7.74-7.66 (6H, m); ^{13}C NMR ($CDCl_3$ 100 MHz) δ: 146.1 (d, *J* = 253.0 Hz), 143.7, 143.0, 142.5, 142.4, 142.0 (, d, *J* = 257.8 Hz), 140.1, 137.5 (d, *J* = 248.2 Hz), 134.1, 133.8, 133.6, 133.6, 130.4, 128.1, 127.0, 120.1, 115.2 (t, *J* = 18.2 Hz), 103.9, 100.8; ^{19}F NMR ($CDCl_3$ 376 MHz) δ: -136.8 (2F, ddd, *J* = 26.0, 4.0, 2.0 Hz), -152.3 (1F, t, *J* = 20.7 Hz), -161.7 (2F, ddd, *J* = 21.8, 6.1, 3.1 Hz); IR (KBr): 3059, 1493, 1338, 1072, 945, 768, 729, 702 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 413 (5.2), 530 (4.1), 561 (3.7); HRMS (EI) *m/z*: Calcd for $C_{38}H_{18}BrF_5N_4Ni$ 761.9988, found 761.9982.

Preparation of Silylzinc Reagents (2). All silylzinc reagents **2** were prepared according to methods described in the literature.[7] A 20 mL oven-dried flask equipped with a magnetic stirring bar was charged with elemental lithium (196 mg, 28 mmol, 2.8 equiv) and washed in pentane. The reaction vessel was evacuated and flushed with argon (three times), and dry THF (10 mL) was added. The suspension was cooled to 0 °C. Chlorosilane (10 mmol, 1.0 equiv) was then added by a syringe, and the reaction mixture was sonicated in an ice/water bath for 1 h. The mixture was stirred under argon at 0 °C for 12 h. Next, the temperature of the vessel was increased to room temperature, and the supernatant (10 mL) was removed

from the residual lithium metal and transferred by a syringe to another oven-dried 30 mL flask, equipped with a magnetic stirring bar in an atmosphere of argon. Silyllithium was titrated against 0.1 M HCl according to Fleming's method.[14a] $ZnCl_2$ was dried using a heat gun under vacuum for 20 min. The dried $ZnCl_2$ (1.0–1.36 g: 1.0 equiv with respect to the titrated silyllithium) was then weighed quickly and placed into a 20 mL oven-dried flask. The reaction vessel was evacuated and flushed with argon (three times), and dry THF (10 mL) was added. The $ZnCl_2$ solution was added by a syringe to the solution of silyllithium at 0 °C, and the reaction mixture was stirred at 0 °C for 30 min. After attaining to room temperature, the mixture was filtered, in an argon atmosphere, by injecting it through a syringe filter directly into a 30 mL oven-dried flask equipped with a rubber septum. The silylzinc solution was titrated using Knochel's method.[14b]

General Procedure for the Nickel-Catalyzed Coupling of *meso*-Bromoporphyrins with Silylzinc Reagents. A 30 mL oven-dried two-necked flask equipped with a magnetic stirring bar and a rubber septum was charged with *meso*-brominated Ni(II) porphyrin **1** (0.1 mmol), $NiBr_2$·diglyme (3.5 mg, 10 μmol), and 2,2-bipyridyl (3.1 mg, 20 μmol). The reaction vessel was evacuated and flushed with argon (three times), and dry THF (20 mL) was added at room temperature, followed by stirring. A solution of silylzinc reagents **2** (1.15 mL, 0.26 M solution in THF, 0.3 mmol, 3 equiv) was added to this mixture at room temperature. The reaction mixture was stirred at room temperature for 1 h and was continually monitored using TLC (1/3 toluene/hexane). The reaction was quenched by the addition of aqueous NH_4Cl (1 mL), followed by stirring for 1 min. The resulting mixture was diluted with CH_2Cl_2 (50 mL) and washed with aqueous NH_4Cl, water, and brine. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatography performed on silica gel (1/3 toluene/hexane), followed by recrystallization from MeOH/CH_2Cl_2, yielded pure compound **3**.

[5,10,15-Triphenyl-20-((methyl)diphenylsilyl)porphyrinato]nickel(II) (3aa). Prepared from *meso*-brominated Ni(II) porphyrin **1a** (134.8 mg, 0.2 mmol) following the general procedure; red solid; 112.8 mg, 71% yield; R_f = 0.25 (1/3 toluene/hexane); ^{1}H NMR (CD_2Cl_2 400 MHz) δ: 8.93 (2H, d, J = 4.9 Hz), 8.70 (2H, d, J = 4.9 Hz), 8.64 (2H, d, J = 4.9 Hz), 8.52 (2H, d, J = 4.9 Hz), 7.99 (2H, dd, J = 7.6, 1.7 Hz), 7.93 (4H, dd, J = 7.6, 1.7 Hz), 7.69-7.62 (13H, m), 7.44-7.36 (6H, m), 1.26 (3H, s). ^{13}C NMR (CD_2Cl_2 100 MHz) δ: 146.6, 142.9, 141.8, 140.7, 140.6, 139.9, 135.6, 134.9, 134.2, 134.0, 134.0, 133.0, 132.9, 132.1, 129.9, 128.6, 128.2, 128.2, 127.4, 127.3, 127.3, 118.8, 108.4, 3.3; IR (KBr): 3057, 3020, 2949, 1440, 1347, 1110, 1010, 795, 751, 700, 670 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 419 (5.4), 536 (4.3) nm; HRMS-FAB$^+$ (M^+): calcd for $C_{51}H_{36}N_4NiSi$ 790.2063, found 790.2066.

[5,10,15-Tris(3,5-di-*tert*-butylphenyl)-20-((methyl)diphenylsilyl)porphyrinato]nickel(II) (3ba). Prepared from *meso*-brominated Ni(II) porphyrin **1b** (101.1 mg, 0.1 mmol) following the general procedure; red solid; 64.4 mg, 57% yield; R_f = 0.50 (1/2 toluene/hexane); ^{1}H NMR (CD_2Cl_2 400 MHz) δ: 8.91 (2H, d,

J = 4.9 Hz), 8.74 (2H, d, *J* = 4.9 Hz), 8.71 (2H, d, *J* = 4.9 Hz), 8.53 (2H, d, *J* = 4.9 Hz), 7.86 (2H, d, *J* = 2.0 Hz), 7.78 (4H, d, *J* = 2.0 Hz), 7.76 (1H, t, *J* = 1.5 Hz), 7.71 (4H, t, *J* = 1.5 Hz), 7.70 (2H, d, *J* = 1.5 Hz), 7.43 (2H, d, *J* = 7.3 Hz), 7.38 (4H, d, *J* = 7.3 Hz), 1.48 (18H, s), 1.44 (36H, s), 1.26 (3H, s).^{13}C NMR (CD_2Cl_2 100 MHz) δ: 149.6, 146.4, 143.0, 141.8, 140.8, 140.0, 139.7, 139.6, 135.6, 134.6, 133.3, 133.1, 132.1, 129.8, 129.0, 129.0, 128.9, 128.5, 121.9, 121.8, 121.8, 119.9, 107.7, 35.3, 35.2, 31.8, 31.7, 3.5; IR (KBr): 2962, 2904, 2867, 1593, 1428, 1294, 1011, 868, 710 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 423 (5.4), 541 (4.3) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{75}H_{84}N_4NiSi$ 1127.5897, found 1127.5892.

[5,15-Diphenyl-10-((methyl)diphenylsilyl)porphyrinato]nickel(II) (3ca). Prepared from *meso*-brominated Ni(II) porphyrin **1c** (59.8 mg, 0.1 mmol) following the general procedure; red solid; 46.5 mg, 65% yield; R_f = 0.36 (1/2 toluene/hexane); ^{1}H NMR (CD_2Cl_2 400 MHz) δ: 9.69 (1H, s), 9.06 (2H, d, *J* = 5.0 Hz), 9.00 (2H, d, *J* = 5.0 Hz), 8.75 (2H, d, *J* = 5.0 Hz), 8.56 (2H, d, *J* = 5.0 Hz), 7.93 (4H, dd, *J* = 7.8, 1.37 Hz), 7.71-7.62 (10H, m), 7.45-7.43 (2H, m), 7.36 (4H, t, *J* = 7.4 Hz), 1.29 (3H, s).^{13}C NMR (CD_2Cl_2 100 MHz) δ: 145.8, 142.5, 141.5, 140.4, 140.2, 139.5, 135.2, 134.4, 133.6, 132.6, 132.5, 132.0, 129.4, 128.1, 127.7, 126.9, 118.0, 108.4, 105.3, 3.1; IR (KBr): 3052, 3017, 1810, 1428, 1004, 856 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 413 (5.4), 533 (4.3) nm; HRMS-FAB$^+$ (M$^+$): calcd for $C_{45}H_{32}N_4NiSi$ 714.1750, found: 714.1744.

[5,15-Di(2,4,6-trimethylphenyl)-10-((methyl)diphenylsilyl)porphyrinato]nickel(II) (3da). Prepared from *meso*-brominated Ni(II) porphyrin **1d** (68.2 mg, 0.1 mmol) following the general procedure; red solid; 38.2 mg, 48% yield; R_f = 0.42 (1/2 toluene/hexane); ^{1}H NMR (CD_2Cl_2 400 MHz) δ: 9.70 (1H, s), 9.07 (2H, d, *J* = 4.9 Hz), 8.93 (2H, d, *J* = 4.9 Hz), 8.58 (2H, d, *J* = 4.9 Hz), 8.36 (2H, d, *J* = 4.9 Hz), 7.68 (4H, dd, *J* = 8.1, 1.2 Hz), 7.43-7.42 (2H, m), 7.35-7.33 (4H, m), 7.19 (4H, s), 2.54 (6H, s), 1.76 (12H, s), 1.26 (3H, s); ^{13}C NMR (CD_2Cl_2 100 MHz) δ: 146.5, 142.8, 142.1, 140.8, 140.1, 139.2, 138.3, 136.9, 135.7, 135.1, 133.2, 131.9, 131.4, 129.8, 128.5, 128.1, 116.8, 108.5, 105.5, 21.5, 21.4, 3.7; IR (KBr): 2916, 1428, 1063, 792 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 412 (5.3), 530 (4.1) nm; HRMS-FAB$^+$ (M$^+$): calcd for $C_{51}H_{44}N_4NiSi$ 798.2689, found 798.2693.

[5,15-Bis(3,5-di-*tert*-butylphenyl)-10-((methyl)diphenylsilyl)porphyrinato]nickel(II) (3ea). Prepared from *meso*-brominated Ni(II) porphyrin **1e** (82.2 mg, 0.1 mmol) following the general procedure; red solid; 49.2 mg, 52% yield; R_f = 0.61 (1/2 toluene/hexane); ^{1}H NMR (CD_2Cl_2 400 MHz) δ: 9.74 (1H, s), 9.12 (2H, d, *J* = 4.8 Hz), 8.97 (2H, d, *J* = 4.8 Hz), 8.86 (2H, d, *J* = 4.8 Hz), 8.58 (2H, d, *J* = 4.8 Hz), 7.81 (4H, d, *J* = 1.8 Hz), 7.74 (2H, t, *J* = 1.8 Hz), 7.70 (4H, dd, *J* = 8.0, 1.4 Hz), 7.45-7.43 (2H, m), 7.38-7.34 (4H, m), 1.46 (36H, s), 1.26 (3H, s); ^{13}C NMR (CD_2Cl_2 100 MHz) δ: 149.7, 146.0, 143.1, 141.8, 141.1, 140.0, 139.6, 135.7, 134.7, 133.4, 132.8, 132.6, 129.8, 129.0, 128.6, 121.8, 119.7, 108.4, 105.7, 35.3, 31.8, 3.6; IR (KBr): 2962, 2903, 1592, 1427, 1005, 790 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 415 (5.4), 534 (4.3) nm; HRMS-FAB$^+$ (M$^+$): calcd for $C_{61}H_{64}N_4NiSi$ 938.4254, found 938.4247.

[5,15-Di(*p*-tolyl)-10-((methyl)diphenylsilyl)porphyrinato]nickel(II) (3fa). Prepared from *meso*-brominated Ni(II) porphyrin **1f** (62.6 mg, 0.1 mmol) following the general procedure; red solid; 50.2 mg, 68% yield; R_f = 0.32 (1/2 toluene/hexane); ^{1}H NMR (CD_2Cl_2 400 MHz) δ: 9.73 (1H, s), 9.10 (2H, d, *J* = 4.9 Hz), 8.97 (2H, d, *J* = 4.9 Hz), 8.79 (2H, d, *J* = 4.9 Hz), 8.57 (2H, d, *J* = 4.9 Hz), 7.82 (4H, d, *J* = 7.8 Hz), 7.68 (4H, dd, *J* = 7.8, 1.5 Hz), 7.47 (4H, d, *J* = 7.8 Hz), 7.43-7.42 (2H, m), 7.37-7.33 (4H, m), 2.62 (6H, s), 1.27 (3H, s); ^{13}C NMR (CD_2Cl_2 100 MHz) δ: 146.2, 143.2, 141.9, 141.1, 140.0, 138.1, 137.7, 135.7, 134.8, 134.0 133.0, 132.9, 132.5, 129.8, 128.6, 128.1, 118.6, 108.7, 105.7, 21.5, 3.5; IR (KBr): 3022, 1491, 1380, 1107, 1005, 716 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 414 (5.3), 534 (4.2) nm; HRMS-FAB$^+$ (M^+): calcd for $C_{47}H_{36}N_4NiSi$ 742.2063, found 742.2069.

[5,15-Di(3-vinylphenyl)-10-((methyl)diphenylsilyl)porphyrinato]nickel(II) (3ga). Prepared from *meso*-brominated Ni(II) porphyrin **1g** (65.0 mg, 0.1 mmol) following the general procedure; red solid; 42.4 mg, 55% yield; R_f = 0.24 (1/3 toluene/hexane); ^{1}H NMR (CD_2Cl_2 400 MHz) δ: 9.67 (1H, s), 9.04 (2H, d, *J* = 4.9 Hz), 8.95 (2H, d, *J* = 4.9 Hz), 8.74 (2H, d, *J* = 4.9 Hz), 8.53 (2H, d, *J* = 4.9 Hz), 7.93 (2H, s), 7.81 (2H, d, *J* = 7.8 Hz), 7.71 (2H, d, *J* = 7.8 Hz), 7.65 (4H, dd, *J* = 7.8, 1.5 Hz), 7.57 (2H, t, *J* = 7.8 Hz), 7.41-7.37 (2H, m), 7.32-7.30 (4H, m), 6.87 (2H, dd, *J* = 17.6, 10.2 Hz), 5.84 (2H, dd, *J* = 17.6, 1.0 Hz), 5.31 (2H, dd, *J* = 10.7, 1.0 Hz), 1.24 (3H, s); ^{13}C NMR (CD_2Cl_2 100 MHz) δ: 146.3, 142.9, 142.0, 140.9, 140.9, 139.9, 137.1, 136.6, 135.6, 134.9, 133.5, 133.0, 133.0, 132.4, 131.8, 129.9, 128.6, 127.5, 126.0, 118.2, 114.9, 109.0, 105.8, 3.5; IR (KBr): 3047, 3007, 1596, 1428, 1004, 792 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 413 (5.4), 534 (4.2) nm; HRMS-FAB$^+$ (M^+): calcd for $C_{49}H_{36}N_4NiSi$ 766.2063, found 766.2057.

[5,15-Di(3-methoxyphenyl)-10-((methyl)diphenylsilyl)porphyrinato]nickel(II) (3ha). Prepared from *meso*-brominated Ni(II) porphyrin **1h** (32.9 mg, 0.05 mmol) following the general procedure using column chromatography on silica gel (1/2 CH_2Cl_2/cyclohexane); red solid; 15.3 mg, 39% yield; R_f = 0.14 (1/1 toluene/hexane); ^{1}H NMR (CD_2Cl_2 400 MHz) δ: 9.74 (1H, s), 9.11 (2H, d, *J* = 4.9 Hz), 8.98 (2H, d, *J* = 4.9 Hz), 8.82 (2H, d, *J* = 4.9 Hz), 8.59 (2H, d, *J* = 4.9 Hz), 7.68 (4H, dd, *J* = 7.32, 1.0 Hz), 7.56 (4H, d, *J* = 5.9 Hz), 7.47 (2H, s), 7.43-7.42 (2H, m), 7.37-7.33 (4H, m), 7.24-7.23 (2H, m), 3.90 (6H, s), 1.27 (3H, s); ^{13}C NMR (CD_2Cl_2 100 MHz) δ: 158.7, 146.3, 142.9, 142.0, 141.9, 140.8, 140.0, 135.6, 134.9, 133.0, 133.0, 132.5, 129.9, 128.6, 128.2, 126.9, 120.1, 118.2, 113.8, 108.9, 105.8, 55.8, 3.5; IR (KBr), 3099, 2949, 1597, 1584, 1329, 1282, 994, 782 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 411 (5.2), 530 (4.0) nm; HRMS-FAB$^+$ ([M+H]$^+$) calcd for $C_{47}H_{36}N_4NiO_2Si$ 775.2039, found 775.2045.

[5,10-Diphenyl-15-pentafluorophenyl-20-((methyl)diphenylsilyl)porphyrinato]nickel(II) (3ia). Prepared from *meso*-brominated Ni(II) porphyrin **1i** (76.4 mg, 0.1 mmol) following the general procedure using column chromatography on silica gel (1/5 CH_2Cl_2/hexane); red solid; 23.5 mg, 27% yield; R_f = 0.40 (1/2 toluene/hexane); ^{1}H NMR (CD_2Cl_2 400 MHz) δ: 8.96 (2H, d, *J* = 5.0 Hz), 8.73 (2H, d, *J* = 5.0 Hz),

8.63 (2H, d, *J* = 5.0 Hz), 8.54 (2H, d, *J* = 5.0 Hz), 7.93 (4H, dd, *J* = 7.8, 3.9 Hz), 7.68-7.65 (10H, m), 7.42-7.36 (6H, m), 1.26 (3H, s); ^{13}C NMR (CD_2Cl_2 100 MHz) δ: 146.7, 146.6 (d, *J* = 252.4 Hz), 143.2, 142.2 (d, *J* = 247.5 Hz), 141.5, 141.0, 140.2, 139.6, 138.0 (d, *J* = 250.8 Hz), 135.6, 135.5, 134.0, 133.6, 133.4, 130.9, 129.9, 128.6, 128.3, 127.4, 119.5, 115.5 (t, *J* = 22.8 Hz), 110.6, 101.3, 3.4; ^{19}F NMR (CD_2Cl_2 376 MHz) δ: -138.1 (2F, dd, *J* = 23.6, 7.5 Hz), -153.7 (1F, t, *J* = 20.7 Hz), -162.8 (2F, ddd, *J* = 22.1, 6.5, 3.3 Hz); IR (KBr): 3021, 2371, 1490, 987, 700 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 417 (5.3), 538 (4.1) nm; HRMS-FAB$^+$ (M^+): calcd for $C_{51}H_{31}F_5N_4NiSi$ 880.1592, found 880.1585.

[5,15-Di(*n*-butyl)-10-((methyl)diphenylsilyl)porphyrinato]nickel(II) (3ja). Prepared from *meso*-brominated Ni(II) porphyrin **1j** (55.8 mg, 0.1 mmol) following the general procedure; red solid; 35.4 mg, 52% yield; R_f = 0.48 (1/2 toluene/hexane); ^{1}H NMR (CD_2Cl_2 400 MHz) δ: 9.53 (1H, s), 9.27 (2H, d, *J* = 4.9 Hz), 9.09 (4H, d, *J* = 4.9 Hz), 8.96 (2H, d, *J* = 4.9 Hz), 7.69 (4H, dd, *J* = 7.8, 1.0 Hz), 7.47-7.43 (2H, m), 7.39-7.35 (4H, m), 4.45 (4H, t, *J* = 8.1 Hz), 2.21-2.13 (4H, m), 1.53-1.46 (4H, m), 1.24 (3H, s), 0.97 (6H, t, *J* = 7.3 Hz); ^{13}C NMR (CD_2Cl_2 100 MHz) δ: 145.2, 142.9, 140.9, 140.6, 140.1, 135.6, 135.0, 133.0, 130.5, 129.9, 129.8, 128.6, 117.8, 107.3, 104.8, 39.7, 33.7, 23.7, 14.1, 3.4; IR (KBr): 2954, 2865, 1470, 1259, 754 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 415 (5.4), 538 (4.2) nm; HRMS-FAB$^+$ (M^+): calcd for $C_{41}H_{40}N_4NiSi$ 674.2376, found 674.2374.

[5,15-Di(*i*-butyl)-10-((methyl)diphenylsilyl)porphyrinato]nickel(II) (3ka). Prepared from *meso*-brominated Ni(II) porphyrin **1k** (55.8 mg, 0.1 mmol) following the general procedure; red solid; 41.4 mg, 61% yield; R_f = 0.30 (1/3 toluene/hexane); ^{1}H NMR (CD_2Cl_2 400 MHz) δ: 9.55 (1H, s), 9.29 (2H, d, *J* = 5.0 Hz), 9.11 (2H, d, *J* = 5.0 Hz), 9.09 (2H, d, *J* = 5.0 Hz), 8.95 (2H, d, *J* = 5.0 Hz), 7.67 (4H, dd, *J* = 7.9, 1.5 Hz), 7.47-7.42 (2H, m), 7.38-7.33 (4H, m), 4.47 (4H, d, *J* = 7.2 Hz), 2.14-2.05 (2H, m), 1.21 (3H, s), 0.75 (12H, d, *J* = 6.6 Hz); ^{13}C NMR (CD_2Cl_2 100 MHz) δ: 144.9, 143.3, 141.0, 140.8, 140.0, 135.6, 135.0, 133.0, 131.4, 130.6, 129.8, 128.5, 116.6, 107.2, 104.8, 42.1, 34.5, 22.9, 3.3; IR (KBr): 2954, 2865, 1458, 1326, 1002, 757 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 415 (5.2), 539 (4.0) nm; HRMS-FAB$^+$ (M^+): calcd for $C_{41}H_{40}N_4NiSi$ 674.2376, found 674.2380.

[5,10,15-Triphenyl-20-(dimethyl(phenyl)silyl)porphyrinato]nickel(II) (3ab). Prepared from *meso*-brominated Ni(II) porphyrin **1a** (67.4 mg, 0.1 mmol) following the general procedure using column chromatography on silica gel (1/5 CH_2Cl_2/cyclohexane); red solid; 41.7 mg, 57% yield; R_f = 0.30 (1/5 CH_2Cl_2/cyclohexane); ^{1}H NMR (CD_2Cl_2 400 MHz) δ: 9.17 (2H, d, *J* = 5.0 Hz), 8.68 (2H, d, *J* = 5.0 Hz), 8.65 (2H, d, *J* = 5.0 Hz), 8.62 (2H, d, *J* = 5.0 Hz), 7.97-7.93 (6H, m), 7.72 (2H, t, *J* = 6.0 Hz), 7.66 (10H, t, *J* = 6.0 Hz), 7.38-7.35 (2H, m), 1.06 (6H, s); ^{13}C NMR (CD_2Cl_2 100 MHz) δ: 146.3, 142.8, 142.1, 141.8, 140.8, 140.7, 140.7, 134.7, 134.4, 134.1, 134.0, 134.0, 133.2, 132.8, 132.1, 129.5, 128.5, 128.2, 128.2, 127.3, 120.3, 118.8, 110.6, 4.4; IR (KBr): 3052, 1598, 1439, 1009, 700 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 419 (5.4), 536 (4.1), 578 (3.7) nm; HRMS-FAB$^+$ (M^+): calcd for $C_{46}H_{34}N_4NiSi$ 728.1906, found 728.1908.

[5,10,15-Triphenyl-20-(triphenylsilyl)porphyrinato]nickel(II) (3ac). Prepared from *meso*-brominated Ni(II) porphyrin **1a** (67.4 mg, 0.1 mmol) following the general procedure; red solid; 65.4 mg, 77% yield; R_f = 0.34 (1/2 toluene/hexane); ^{1}H NMR (CD_2Cl_2 400 MHz) δ: 8.83 (2H, d, *J* = 4.9 Hz), 8.72 (2H, d, *J* = 4.9 Hz), 8.65 (2H, d, *J* = 4.9 Hz), 8.42 (2H, d, *J* = 4.9 Hz), 8.00 (2H, dd, *J* = 7.3, 2.0 Hz), 7.91 (4H, dd, *J* = 7.3, 1.5 Hz), 7.75 (6H, dd, *J* = 8.1, 1.2 Hz), 7.72-7.66 (3H, m), 7.65-7.59 (6H, m), 7.43-7.41 (3H, m), 7.35-7.32 (6H, m); ^{13}C NMR (CD_2Cl_2 100 MHz) δ: 147.2, 143.1, 141.8, 140.8, 140.6, 140.5, 137.9, 136.8, 135.6, 134.0, 133.9, 133.0, 132.9, 132.1, 129.9, 128.5, 128.3, 128.2, 127.4, 127.3, 120.9, 119.0, 106.0; IR (KBr): 3050, 1428, 1104, 1009, 751 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 420 (5.4), 539 (4.2), 579 (3.8) nm; HRMS-FAB$^+$ (M^+): calcd for $C_{56}H_{38}N_4NiSi$ 852.2219, found 852.2219.

Preparation of [5-Iodo-10,15,20-triphenylporphyrinato]nickel(II) (5a). A solution of *meso*-silyl-porphyrin **3aa** (39.6 mg, 50 μmol) in CH_2Cl_2 (5 mL) was slowly added dropwise to a mixed solution of [bis(trifluoroacetoxy)iodo]benzene (32 mg, 75 μmol, 1.5 equiv) and iodine (9.5 mg, 75 μmol, 1.5 equiv) in CH_2Cl_2 (5 mL) at 0 °C. The mixture was stirred at 0 °C for 5 min and was continually monitored with TLC (1/2 toluene/hexane). The reaction mixture was diluted with CH_2Cl_2 and washed with aqueous $Na_2S_2O_3$, water, and brine. The organic layer was dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. Column chromatography performed on silica gel (1/2 toluene/hexane), followed by recrystallization from MeOH/CH_2Cl_2, yielded pure compound **5a**[15] (27 mg, 80%) as a red solid. R_f = 0.43 (1/2 toluene/hexane); ^{1}H NMR ($CDCl_3$ 500 MHz) δ: 9.50 (2H, d, *J* = 4.9 Hz), 8.74 (2H, d, *J* = 4.9 Hz), 8.69 (2H, d, *J* = 4.9 Hz), 8.67 (2H, d, *J* = 4.9 Hz), 7.98-7.96 (6H, m), 7.69-7.66 (9H, m); HRMS (EI) *m/z*: calcd for $C_{38}H_{23}IN_4Ni$ 720.0321, found 720.0318.

Preparation of [5-Chloro-10,15,20-triphenylporphyrinato]nickel(II) (6a). A solution of *meso*-silyl-porphyrin **3aa** (39.6 mg, 50 μmol) in CH_2Cl_2 (1.5 mL) was added to a mixed solution of *N*-chlorosuccinimide (8.0 mg, 60 μmol, 1.2 equiv) and Ph_3PS (2.9 mg, 10 μmol, 20 mol%) in CH_2Cl_2 (1.5 mL) at room temperature. The mixture was stirred at room temperature for 1.5 h and was continually monitored with TLC (1/3 toluene/hexane). The solvent was evaporated to dryness. Column chromatography performed on silica gel (1/4 to 1/1 toluene/hexane), followed by recrystallization from MeOH/CH_2Cl_2, yielded pure **6a**[16] (29.2 mg, 92%) as a red solid. R_f = 0.41 (1/3 toluene/hexane); ^{1}H NMR ($CDCl_3$ 400 MHz) δ: 9.49 (2H, d, *J* = 5.0 Hz), 8.80 (2H, d, *J* = 5.0 Hz), 8.69 (4H, s), 7.99-7.97 (6H, m), 7.72-7.66 (9H, m); HRMS (EI) *m/z*: calcd for $C_{38}H_{23}ClN_4Ni$ 628.0965, found 628.0964.

Preparation of [5-Fluoro-10,15,20-triphenylporphyrinato]nickel(II) (7a). A solution of *meso*-silyl-porphyrin **3aa** (79.2 mg, 100 μmol) in CH_2Cl_2 (20 mL) was slowly added dropwise to a solution of XeF_2 (33.9 mg, 200 μmol, 2 equiv) in CH_2Cl_2 (10 mL) at room temperature. The mixture was stirred at room temperature for 30 min and was monitored by TLC (1/3 toluene/hexane). The reaction was quenched with aqueous $NaHCO_3$. The reaction mixture was diluted with CH_2Cl_2 and washed with brine. The organic

layer was dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. Column chromatography on silica gel (1/3 toluene/hexane), followed by recrystallization from MeOH/CH_2Cl_2, gave the pure compound **7a** (19.2 mg, 32%) as a red solid. R_f = 0.30 (1/3 toluene/hexane); ^{1}H NMR ($CDCl_3$ 300 MHz) δ: 9.36 (2H, dd, *J* = 5.0, 1.7 Hz), 8.79 (2H, d, *J* = 5.0 Hz), 8.74 (2H, d, *J* = 4.8 Hz), 8.70 (2H, d, *J* = 4.8 Hz), 8.02-7.96 (6H, m), 7.71-7.66 (9H, m); ^{13}C NMR ($CDCl_3$ 75 MHz) δ: 143.8, 143.1, 143.0, 142.8, 142.0 (d, *J* = 237.3 Hz), 141.0, 140.9, 133.9, 133.8, 133.0, 132.2, 131.9, 128.0, 127.9, 127.1, 127.0, 126.3, 119.6, 118.5; ^{19}F NMR ($CDCl_3$ 376 MHz) δ: -133.9; IR (KBr): 3062, 3031, 2372, 1801, 1589, 1465, 1358, 1169, 1072, 837, 702 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 409 (5.3), 523 (4.3) nm; HRMS (EI) *m/z*: calcd for $C_{38}H_{23}FN_4Ni$ 612.1260, found 612.1269.

Preparation of [5-Hydroxy-10,15,20-triphenylporphyrinato]nickel(II) (8a). A 30 mL oven-dried two-necked flask equipped with a magnetic stirring bar and a rubber septum was charged with *t*-BuOK (33.7 mg, 0.3 mmol, 6 equiv). The reaction vessel was evacuated and flushed with argon (three times), and then dry THF (0.4 mL) and *t*-butyl hydroperoxide (0.06 mL of a 6 M solution in THF, 0.3 mmol, 6 equiv) were added at 0 °C. After 10 min, a solution of *meso*-silylporphyrin **3aa** (39.6 mg, 50 μmol) in THF (10 mL) was added to the resulting mixture. A solution of tetrabutylammonium fluoride (0.3 mL, 1 M solution in THF, 0.3 mmol, 6 equiv) was added afterwards to the resulting solution. The reaction mixture was stirred at 70 °C for 1 h and was continually monitored with TLC (1/3 THF/hexane). The reaction mixture was then cooled, and aqueous $Na_2S_2O_3$ (5 mL, 1.3 M solution in water) was added. The mixture was stirred for 30 min and 5 mL of saturated aqueous NH_4Cl was added. The resulting solution was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic fractions were washed with 5% citric acid, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried over anhydrous $MgSO_4$, and concentrated in vacuo. Column chromatography performed on silica gel (1/5 CH_2Cl_2/hexane), followed by recrystallization from MeOH/CH_2Cl_2, yielded pure **8a**[17] (12.3 mg, 40%) as a red solid. R_f = 0.14 (1/3 THF/hexane); ^{1}H NMR ($CDCl_3$ 400 MHz) δ: 9.44 (2H, d, *J* = 4.9 Hz), 8.75 (2H, d, *J* = 4.9 Hz), 8.67 (2H, d, *J* = 4.9 Hz), 8.64 (2H, d, *J* = 4.9 Hz), 7.96-7.95 (6H, m), 7.66-7.64 (9H, m); HRMS-FAB$^+$ (M^+): calcd for $C_{38}H_{24}N_4NiO$ 610.1304, found 610.1302.

Preparation of [5,10,15,20-Tetraphenylporphyrinato]nickel(II) (9a). A 20 mL oven-dried two-necked flask equipped with a magnetic stirring bar and a rubber septum was charged with *meso*-silylporphyrin **3aa** (39.6 mg, 50 μmol) and $Pd(dba)_2$ (2.9 mg, 5 μmol, 10 mol%). The reaction vessel was evacuated and flushed with argon (three times), and then dry THF (10 mL), tetrabutylammonium fluoride (0.15 mL of a 1 M solution in THF, 0.15 mmol, 3 equiv), and iodobenzene (28 μL, 0.25 mmol, 5 equiv) were added to the reaction vessel. The mixture was stirred at 60 °C for 1 h and was continually monitored with TLC (1/3 toluene/hexane). The solvent was evaporated to dryness. Column chromatography performed on silica gel (1/5 $CHCl_3$/hexane), followed by recrystallization from MeOH/CH_2Cl_2, yielded pure **9a**[18] (8.8 mg, 26%)

as a red solid. R_f = 0.26 (1/3 toluene/hexane); ^{1}H NMR ($CDCl_3$ 300 MHz) δ: 8.74 (8H, s), 8.01 (8H, dd, *J* = 7.3, 2.0 Hz), 7.68 (12H, d, *J* = 6.4 Hz); HRMS (EI) *m/z*: calcd for $C_{44}H_{28}N_4Ni$ 670.1667, found 670.1664.

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