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COPPER-MEDIATED TRIFLUOROMETHYLATION OF BORYLPORPHYRINS USING AN IN SITU-GENERATED CF_3 RADICAL FROM $NaSO_2CF_3$ AND *tert*-BUTYL HYDROPEROXIDE

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Abstract – We developed a method for the copper-mediated reaction of borylated Ni(II) porphyrins using $NaSO_2CF_3$ (Langlois' reagent) and *tert*-butyl hydroperoxide (TBHP) to prepare trifluoromethylated Ni(II) porphyrins. Porphyrin trifluoromethylation can be carried out 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 accurately turned by modifying the steric and/or electronic characteristics of peripheral substituents on the porphyrin ring.[2] Currently, there are many methods for introducing various functional groups (e.g., amino, alkoxy, ester, boryl, silyl, C_6F_5, CN, and NO_2) onto porphyrins.[3] Trifluoromethyl group is one of the most important peripheral substituents owing to its strong electron-withdrawing nature, which can greatly affect the electronic properties of a porphyrin core.[4] Conventional approaches for synthesizing trifluoromethylated porphyrins involve multiple condensation reactions of trifluoromethyl dipyrromethane derivatives with aldehydes under acidic conditions, followed by the oxidation of resulting porphyrinogen intermediates.[4a,5] However, these multiple condensation methods suffer from low yields, many side products, and tedious chromatographic purification. The direct introduction of CF_3 group onto the porphyrin core using trifluoromethylation reagents, such as CF_3-$SR_2^+OTf^-$ (Umemoto's reagent) and $FSO_2CF_2CO_2Me$ (Chen's

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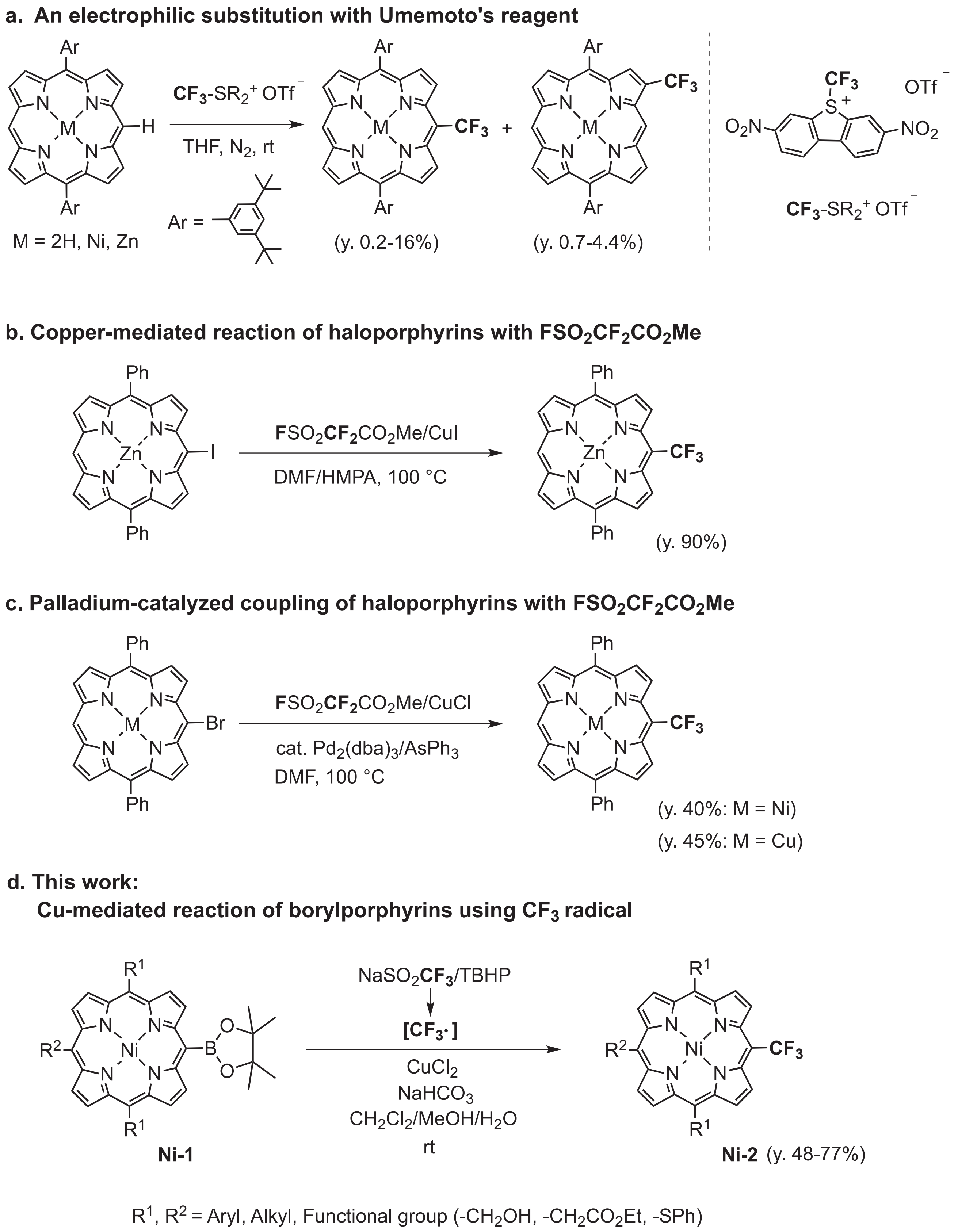
This work is dedicated to Professor Dr. Yasuyuki Kita on the occasion of his 77th birthday.



Scheme 1. Preparation of *mono*-trifluoromethylated porphyrins

reagent), has been reported.[6] However, the electrophilic substitution of porphyrins with Umemoto's reagent provides a mixture of *meso*- and β-CF_3 compounds in low yields (Scheme 1a).[6a] Copper-mediated reactions of Chen's reagent with halogenated porphyrins have a narrow substrate scope; to our knowledge, there is only one example of a 10-iodo-5,15-diphenylporphyrin Zn(II) complex (Scheme 1b).[6b] Palladium-catalyzed cross-coupling of Chen's reagent with bromoporphyrins requires a toxic arsenic compound ($AsPh_3$) as ligand (Scheme 1c).[6c] Therefore, the efficient introduction of trifluoromethyl group onto porphyrin core still remains a challenging and highly demanding task.

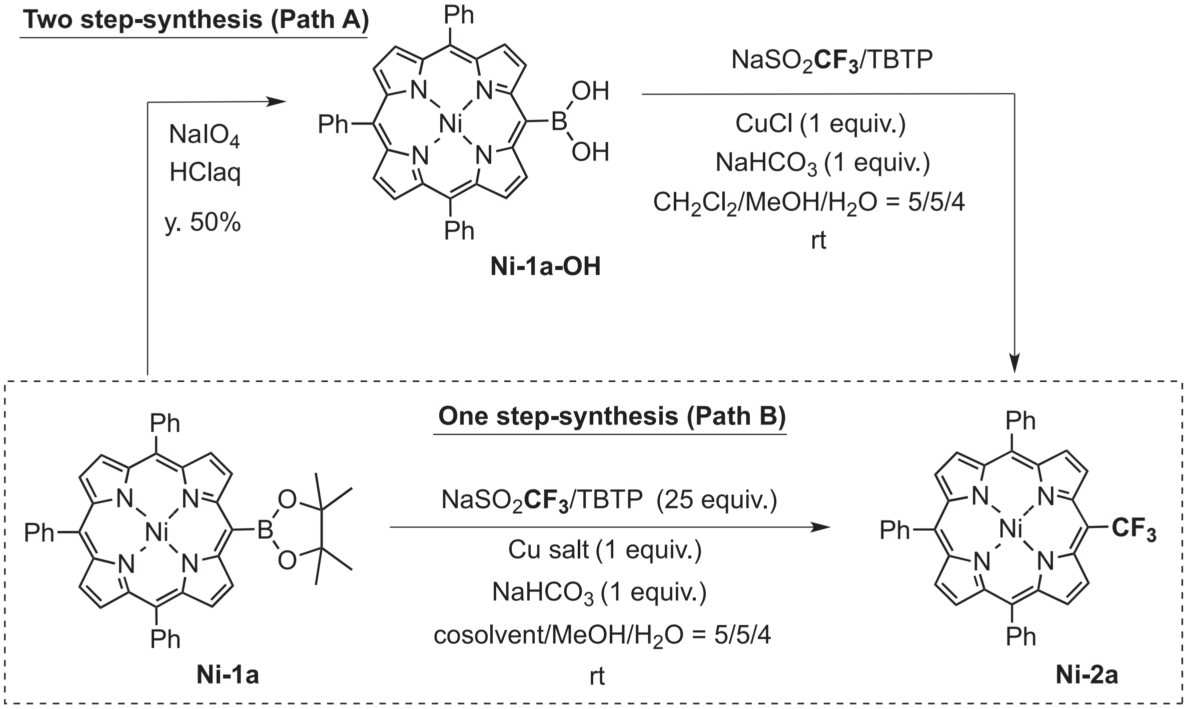
Here, we report an efficient method for synthesizing trifluoromethylated Ni(II) porphyrins via the Cu-mediated reaction of borylated Ni(II) porphyrins **Ni-1** using in situ-generated CF_3 radical from $NaSO_2CF_3$ (Langlois' reagent) and *tert*-butyl hydroperoxide (TBHP) (Scheme 1d). This trifluoromethylation can be carried out under mild conditions and is suitable not only for various borylporphyrins, such as *meso*-mono-, *meso*-di-, and β-mono-borylporphyrins, but also borylporphyrins bearing reactive functional groups such as ester, hydroxymethyl, and phenylthio groups.

RESULTS AND DISCUSSION

Recently, Sanford and coworkers have reported an efficient method for the copper-mediated trifluoromethylation of arylboronic acid with CF_3 radical derived from $NaSO_2CF_3$ and TBHP without an inert atmosphere and dry solvents.[7] Following the conditions developed by Sanford et al. for the trifluoromethylation of arylboronic acid, we examined the reaction of *meso*-dihydroxyborylated Ni(II) triphenylporphyrin **Ni-1a-OH** with 15 equiv. of $NaSO_2CF_3$ and TBHP in the presence of stoichiometric CuCl and $NaHCO_3$ in a 5:5:4 mixture of CH_2Cl_2, MeOH, and H_2O at 25 °C. Unfortunately, this Cu-mediated reaction yields only a trace amount of the desired *meso*-trifluoromethylated porphyrin **Ni-2a** (Table 1, entry 1). With an increase in the loading of $NaSO_2CF_3$ and TBHP to 25 equiv., the yield improved to 73% (Table 1, entry 2).

Dihydroxyborylated Ni(II) triphenylporphyrin **Ni-1a-OH** was provided in a 50% yield by treating pinacolatoborylated Ni(II) triphenylporphyrin **Ni-1a** with $NaIO_4$ and HCl(aq). Thus, the desired trifluoromethylporphyrin **Ni-2a** was obtained in only 37% yield using a boronic acid precursor **Ni-1a** (Table 1, path A). Therefore, we further investigated the trifluoromethylation of pinacolatoborylated Ni(II) triphenylporphyrin **Ni-1a** using a different combination of Cu salts and solvents (Table 1, path B). As shown in Table 1, pinacolatoborylated Ni(II) triphenylporphyrin **Ni-1a** was determined to be superior to dihydroxyborylated Ni(II) triphenylporphyrin **Ni-1a-OH** as a borylated substrate, and the combination of inexpensive $CuCl_2$ and CH_2Cl_2 as cosolvent was effective for the trifluoromethylation of **Ni-1a** and afforded the desired *meso*-trifluoromethylated porphyrin **Ni-2a** in an 80% isolated yield (entry 4).

Table 1. Reaction conditions screening for the trifluoromethylation of *meso*-borylated Ni(II) triphenylporphyrin **Ni-1** using $NaSO_2CF_3$ as the CF_3 source

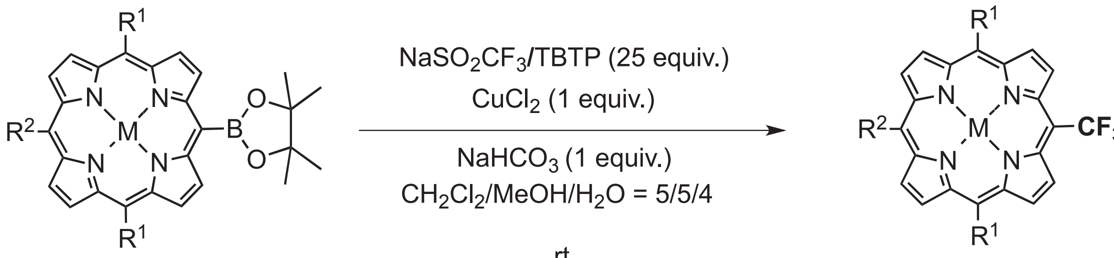


Entry	Substrates	$NaSO_2CF_3$/TBHP (equiv.)	Cu salt	Cosolvent	Yield (%) [a]
1	**Ni-1a-OH**	15	CuCl	CH_2Cl_2	15 (8 [b])
2	**Ni-1a-OH**	25	CuCl	CH_2Cl_2	73 (37 [b])
3	**Ni-1a**	25	CuCl	CH_2Cl_2	77
4	**Ni-1a**	25	$CuCl_2$	CH_2Cl_2	80
5	**Ni-1a**	25	$CuCl_2$	THF	trace
6	**Ni-1a**	25	$CuCl_2$	DMF	trace
7	**Ni-1a**	25	$CuCl_2$	toluene	8

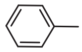
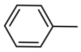
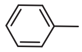
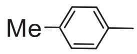
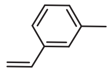
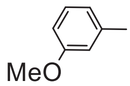
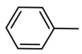
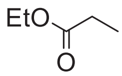
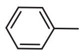
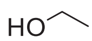
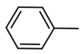
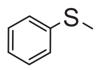
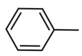
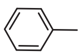
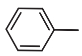
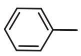
[a] Isolated yield. [b] Isolated yield that is based on **Ni-1a**.

The Cu-mediated trifluoromethylation presented here is applicable to an array of *meso*-borylated Ni(II) porphyrins **Ni-1** (Table 2). Under optimal reaction conditions, *meso*-borylated Ni(II) diaryl- and triarylporphyrins (**Ni-1a**–**Ni-1e**), such as those with aliphatic, vinyl, and alkoxy groups on their phenyl substituent, were converted to corresponding *meso*-trifluoromethylated Ni(II) complexes (**Ni-2a**–**Ni-2e**) with moderate to good yields (entries 1–5). Similarly, *meso*-borylated Ni(II) dialkylporphyrins **Ni-1f** underwent *meso*-trifluoromethylation, which produced the corresponding *meso*-trifluoromethyl-substituted Ni(II) dialkylporphyrin **Ni-2f** with a good yield (entry 6). Further reactions confirmed the functional group tolerance of trifluoromethylation. Of note, substrates bearing highly reactive groups (e.g., ester and hydroxymethyl groups) on the opposite side to the borylated *meso*

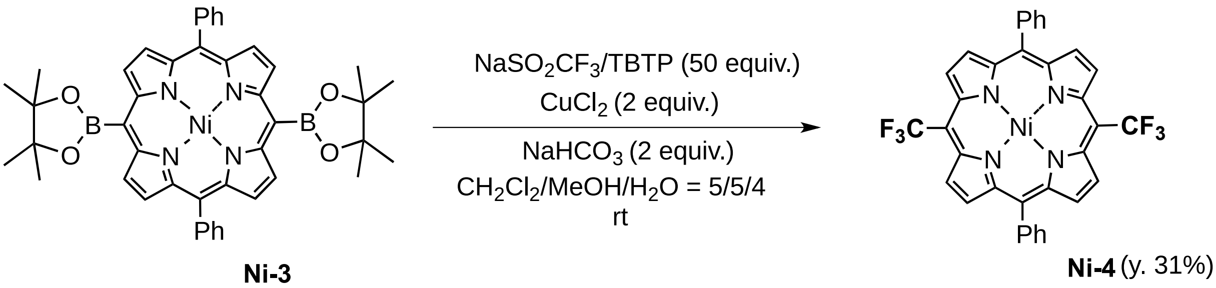
Table 2. Copper-mediated trifluoromethylation of *meso*-borylated Ni(II) triphenylporphyrin **Ni-1** using the $NaSO_2CF_3$/TBHP system



Ni-1 **Ni-2**

Entry	Substrates	M	R^1	R^2	Products	Yield (%)[a]
1	**Ni-1a**	Ni			**Ni-2a**	80
2	**Ni-1b**	Ni		H	**Ni-2b**	64
3	**Ni-1c**	Ni		H	**Ni-2c**	57
4	**Ni-1d**	Ni		H	**Ni-2d**	48
5	**Ni-1e**	Ni		H	**Ni-2e**	51
6	**Ni-1f**	Ni	*n*-Bu—	H	**Ni-2f**	50
7	**Ni-1g**	Ni			**Ni-2g**	77
8	**Ni-1h**	Ni			**Ni-2h**	50
9	**Ni-1i**	Ni			**Ni-2i**	53
10	**Zn-1a**	Zn			**Zn-2a**	trace
11	**H_2-1a**	2H			**H_2-2a**	trace

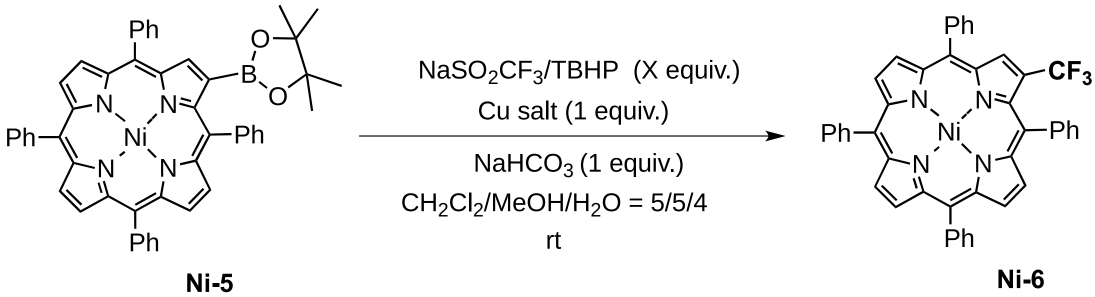
[a] Isolated yield.



Scheme 2. Preparation of bis(trifluoromethyl)porphyrin **Ni-4**

position were compatible with trifluoromethylation and afforded *meso*-trifluoromethyl-substituted Ni(II) porphyrins in acceptable to good yields (entries 7 and 8). The phenylthio substituent was also compatible with reaction conditions (entry 9). The central porphyrin Ni(II) ion was crucial for trifluoromethylation. The use of both Zn(II) porphyrin (**Zn-1a**) and free base porphyrin (**H_2-1a**) as substrates, resulted in a trace amount of desired trifluoromethylated products (**Zn-2a** and **H_2-2a**) in addition to recovered initial materials and deborylated products (entries 10 and 11). In addition, the reaction also occurred with diborylated Ni(II) porphyrin **Ni-3** to provide porphyrin **Ni-4**, which contained two trifluoromethyl substituents at the *meso* positions, in a 31% yield (Scheme 2).

Table 3. Preparation of β-trifluoromethyl-substituted porphyrin **Ni-6**



Entry	NaSO2CF3/TBHP (equiv.)	Cu salt	Yield (%)[a]
1	25	$CuCl_2$	28
2	75	$CuCl_2$	41
3	75	$CuBr_2$	50
4	75	CuCl	17
5	75	CuBr	32
6	75	-	trace

[a] Isolated yield.

Next, we focused on developing a direct method for introducing a CF_3 substituent onto the porphyrin core at the β position. Thus, we examined the direct conversion of β-borylated Ni(II) porphyrin **Ni-5** to the desired β-trifluoromethyl-substituted Ni(II) porphyrin **Ni-6** (Table 3). Although the standard reaction conditions using 25 equiv. of $NaSO_2CF_3$ and TBHP provided only a 28% yield of the desired product **Ni-6**, the yield of the β–CF_3 compound was improved to 41% by increasing the loading of $NaSO_2CF_3$ and TBHP to 75 equiv (entries 1 and 2). Further $CuBr_2$ was determined to be an efficient Cu salt (entries 2–5). Under these conditions, β-trifluoromethyl-substituted Ni(II) porphyrin **Ni-6** was obtained as the sole isolable product in a 50% yield (entry 3).

CONCLUSION

In summary, we developed an efficient method for the preparation trifluoromethylporphyrins via the Cu-mediated reaction of a borylated porphyrin Ni(II) complex using $NaSO_2CF_3$ and TBHP. This method is applicable to a broad spectrum of *meso*- and β-borylated Ni(II) porphyrins to produce sufficient yields of *meso*- and β-trifluoromethylated Ni(II) porphyrins. Further studies on this and related porphyrin ring functionalization reactions are currently underway.

EXPERIMENTAL

General ^{1}H-and ^{13}C-NMR spectra were recorded at rt on JEOL JNM AL-300, JEOL JNM AL-400, and JEOL JNM ECS-400 spectrometers using perdeuterated solvents as internal standards. The 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 coupling constants (J) are in Hz. The following abbreviations were used for signal multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; 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 JASCO FT/IR-4100 spectrophotometer. The mass spectroscopic data were obtained on JEOL JNM-DX302 spectrometer. The melting point data were not available for obtained porphyrin derivatives 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–**Ni-1a**,[8] and **Ni-5**[9]–were prepared according to methods described in the literature. Other chemicals were purchased from commercial sources and used as received unless stated otherwise.

General Procedure for the Preparation of Borylated Ni(II) Porphyrin 1. An oven-dried 50 mL sealable two-necked flask equipped with a magnetic stirring bar and rubber septa was charged with [bromoporphyrinato]nickel(II) (0.25 mmol) and $PdCl_2(PPh_3)_2$ (10 mg, 0.015 mmol, 6 mol%). The reaction vessel was evacuated and flushed with argon (three times), and 1,2-dichloroethane (15 mL) was added. Et_3N (0.5 mL, 3.25 mmol, 13 eq) and pinacolborane (0.72 mL, 5 mmol, 20 eq) were added to the solution by a syringe. The reaction mixture was heated under argon at 75 °C. After reaction completion (monitored by TLC), the solution was allowed to reach rt. The reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (CH_2Cl_2/*n*-hexane 1:3) followed by recrystallization from MeOH/CH_2Cl_2 yielded pure compound **1**.

[5,15-Diphenyl-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)porphyrinato]nickel(II) (**Ni-1b**). Prepared from (10-bromo-5,15-diphenylporphyrinato)nickel(II) **Ni-1b-Br**[10] (299 mg, 0.5 mmol) following the general procedure; Purple solid; 217.4 mg, 63%; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 9.81 (2H, d, J = 4.9 Hz), 9.74 (1H, s), 9.06 (2H, d, J = 4.8 Hz), 8.89 (2H, d, J = 4.9 Hz), 8.81 (2H, d, J = 4.8 Hz), 8.04–8.02 (4H, m), 7.73–7.67 (6H, m), 1.70 (12H, s); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 146.5, 142.9, 142.1, 141.8, 141.0, 133.8, 133.7, 132.9, 132.2, 131.9, 127.7, 126.8, 118.3, 105.7, 84.9, 25.2; IR (KBr): 3055, 3024, 2978, 2974, 1547, 1466, 1377, 1308, 1146, 1072, 1003, 791, 706 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 404.5 (5.4), 522.0 (4.2), 553.5 (3.9) nm; HRMS-FAB ([M]$^+$): Calcd for $C_{38}H_{31}BN_4NiO_2$: 644.1894; Found: 644.1895.

[10-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl)-5,15-di(*p*-tolyl)porphyrinato]nickel(II) (**Ni-1c**). Prepared from [10-bromo-5,15-di(*p*-tolyl)porphyrinato]nickel(II) **Ni-1c-Br**[3m] (157 mg, 0.25 mmol) following the general procedure; Purple solid; 107.7 mg, 64%; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 9.78 (1H, s), 9.75 (2H, d, J = 4.9 Hz), 9.08 (2H, d, J = 4.9 Hz), 8.88 (2H, d, J = 4.9 Hz), 8.83 (2H, d, J = 4.9 Hz), 7.89 (4H, d, J = 7.8 Hz), 7.48 (4H, d, J = 7.8 Hz), 2.65 (6H, s), 1.69 (12H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 146.4, 143.1, 142.3, 141.8, 138.0, 137.3, 133.7, 133.6, 133.0, 132.1, 132.0, 127.5, 118.4, 105.7, 84.9, 25.2, 21.5; IR (KBr): 3020, 2978, 2924, 2866, 1547, 1462, 1377, 1308, 1142, 1068, 1003, 852, 795 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 406.0 (5.4), 523.5 (4.2), 554.5 (4.0) nm; HRMS-FAB ([M]$^+$): Calcd for $C_{40}H_{35}BN_4NiO_2$: 672.2207; Found: 672.2201.

[10-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl)-5,15-bis(3-vinylphenyl)porphyrinato]nickel(II) (**Ni-1d**). Prepared from [10-bromo-5,15-bis(3-vinylphenyl)porphyrinato]nickel(II) **Ni-1d-Br**[3m] (164 mg, 0.25 mmol) following the general procedure; Purple solid; 73.7 mg, 42%; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 9.82 (1H, s), 9.77 (2H, d, J = 4.9 Hz), 9.11 (2H, d, J = 4.9 Hz), 8.88 (2H, d, J = 4.9 Hz), 8.83 (2H, d, J = 4.9 Hz), 8.06 (2H, t, J = 1.5 Hz), 7.91 (2H, dt, J = 7.6, 1.4 Hz), 7.76 (2H, dt, J = 7.6, 1.4 Hz), 7.64 (2H, t, J = 7.6 Hz), 6.93 (2H, dd, J = 17.4, 11.0 Hz), 5.90 (2H, d, J = 17.4 Hz), 5.36 (2H, d, J = 11.0 Hz), 1.69

(12H, s); ^{13}C-NMR ($CDCl_3$, 75 MHz) *δ*: 146.5, 142.9, 142.1, 141.9, 141.2, 136.8, 136.0, 133.8, 133.3, 132.9, 132.3, 132.0, 131.7, 127.0, 125.6, 118.1, 114.7, 105.8, 84.9, 25.2; IR (KBr): 3086, 3047, 2978, 2924, 1593, 1550, 1466, 1377, 1308, 1142, 1068, 1003, 795 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log *ε*) 407.0 (5.3), 524.5 (4.2), 556.0 (3.9) nm; HRMS-FAB ($[M]^+$): Calcd for $C_{42}H_{35}BN_4NiO_2$: 696.2207; Found: 696.2207.

[5,15-Bis(3-methoxyphenyl)-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)porphyrinato]nickel(II) (**Ni-1e**). Prepared from [10-bromo-5,15-bis(3-methoxyphenyl)porphyrinato]nickel(II) **Ni-1e-Br**[3m] (54.6 mg, 0.083 mmol) following the general procedure; Purple solid; 35.0 mg, 60%; ^{1}H-NMR ($CDCl_3$, 400 MHz) *δ*: 9.81 (1H, s), 9.76 (2H, d, *J* = 5.0 Hz), 9.10 (2H, d, *J* = 4.6 Hz), 8.90 (2H, d, *J* = 5.0 Hz), 8.86 (2H, d, *J* = 4.6 Hz), 7.62 (2H, dt, *J* = 7.4, 1.4 Hz), 7.57 (2H, dd, *J* = 7.9, 7.4 Hz), 7.56 (2H, dd, *J* = 2.5, 1.4 Hz), 7.26 (2H, ddd, *J* = 7.9, 2.5, 1.4 Hz), 3.93 (6H, s), 1.70 (12H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) *δ*: 158.1, 146.5, 142.8, 142.3, 142.0, 141.9, 133.7, 133.0, 132.2, 132.0, 127.7, 126.8, 119.6, 118.1, 113.6, 105.8, 84.9, 55.4, 25.2; IR (KBr): 3059, 2978, 2935, 2831, 1593, 1466, 1377, 1308, 1207, 1146, 1068, 791 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log *ε*) 405.0 (5.4), 523.5 (4.2), 554.5 (4.0) nm; HRMS-FAB ($[M]^+$): Calcd for $C_{40}H_{35}BN_4NiO_4$: 704.2105; Found: 704.2109.

[5,15-Di-*n*-butyl-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)porphyrinato]nickel(II) (**Ni-1f**). Prepared from [10-bromo-5,15-di(*n*-butyl)porphyrinato]nickel(II) **Ni-1f-Br**[3m] (50.2 mg, 0.09 mmol) following the general procedure; Purple solid; 32.0 mg, 59%; ^{1}H-NMR ($CDCl_3$, 300 MHz) *δ*: 9.84 (2H, d, *J* = 4.9 Hz), 9.49 (1H, s), 9.38 (2H, d, *J* = 4.9 Hz), 9.26 (2H, d, *J* = 4.8 Hz), 9.01 (2H, d, *J* = 4.8 Hz), 4.53 (4H, t, *J* = 8.0 Hz), 2.37–2.27 (4H, m), 1.73 (12H, s), 1.65–1.60 (4H, m), 1.06 (6H, t, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) *δ*: 145.4, 142.6, 141.7, 140.5, 134.1, 132.3, 130.1, 129.0, 117.3, 104.7, 84.7, 39.6, 33.8, 25.2, 23.4, 14.0; IR (KBr): 3109, 2958, 2927, 2862, 1547, 1462, 1377, 1308, 1146, 1065, 1007, 856, 783 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log *ε*) 408.0 (5.5), 528.0 (4.3), 560.0 (4.1), 685.0 (3.7) nm; HRMS-FAB ($[M]^+$): Calcd for $C_{34}H_{39}BN_4NiO_2$: 604.2520; Found: 604.2519.

Preparation of [5-(2-Ethoxycarbonylethyl)-10,20-diphenyl-15-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)porphyrinato]nickel(II) (**Ni-1g**). NBS (25 mg, 0.14 mmol) was added to a solution of 5-(2-ethoxycarbonylethyl)-10,20-diphenylporphyrin **H2-1g-H**[3r] (71.3 mg, 0.13 mmol) in $CHCl_3$ (50 mL) at 0 °C. The reaction mixture was stirred for 30 min. The solvent was evaporated to dryness. The resulting solid was purified by recrystallization from *n*-hexane/CH_2Cl_2 to afford the free base *meso*-bromoporphyrin. $Ni(OAc)_2 \cdot 4H_2O$ (124 mg, 0.5 mmol) was added to a solution of free base *meso*-bromoporphyrin in DMF (10 mL). The mixture was stirred at 160 °C for 1 h. After reaction completion (monitored by TLC), the solution was poured into water (25 mL). The resulting precipitate was collected and washed with water, which produced brominated Ni(II) porphyrin. An oven-dried 30 mL sealable two-necked flask equipped with a magnetic stirring bar and rubber septa was charged with brominated Ni(II) porphyrin and $PdCl_2(PPh_3)_2$ (5 mg, 0.007 mmol). The reaction vessel was evacuated and flushed with argon (three times), and 1,2-dichloroethane (10 mL) was added. Et_3N (0.25 mL, 1.7 mmol) and pinacolborane (0.36 mL, 2.5 mmol) were added to the solution via a syringe. The reaction mixture was heated under argon at 75 °C. After reaction completion (monitored by TLC), the solution was allowed to reach rt. The reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (CH_2Cl_2/*n*-hexane 1:3) followed by recrystallization from MeOH/CH_2Cl_2 yielded pure compound **Ni-1g** as a purple solid; 25.0 mg, 26%; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 9.70 (2H, d, J = 4.9 Hz), 9.30 (2H, d, J = 4.9 Hz), 8.75 (2H, d, J = 4.9 Hz), 8.72 (2H, d, J = 4.9 Hz), 7.96–7.94 (4H, m), 7.69–7.65 (6H, m), 5.51 (2H, s), 4.18 (2H, q, J = 7.1 Hz), 1.66 (12H, s), 1.18 (3H, t, J = 7.1 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 172.0, 146.9, 142.6, 141.8, 141.7, 140.7, 134.2, 133.7, 133.1, 132.4, 129.7, 127.7, 126.8, 118.5, 110.2, 84.8, 61.5, 39.9, 25.1, 14.2.; IR (KBr): 3109, 3051, 2978, 2935, 1728, 1550, 1462, 1373, 1311, 1265, 1146, 1072, 1011, 795, 706 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 413.0 (5.4), 532.0 (4.3), 574.5 (4.0) nm; HRMS (EI) *m*/*z*: Calcd for $C_{42}H_{37}BN_4NiO_4$: 730.2261; Found: 730.2264.

Preparation of [5-Hydroxymethyl-10,20-diphenyl-15-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)porphyrinato]nickel(II) (**Ni-1h**). DDQ (88 mg, 0.39 mmol) was added to a solution of [5,15-diphenyl-10-(trimethylsilyl)methylporphyrinato]nickel(II) **Ni-1h-Si**[3p] (78.7 mg, 0.13 mmol) in a mixed solution of H_2O/THF (1:10 55 mL) at rt. After being stirred for 1 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 = 1:5) followed by recrystallization from CH_2Cl_2/*n*-hexane afforded *meso*-hydroxymethylporphyrin. NBS (25 mg, 0.14 mmol) was added to a solution of *meso*-hydroxymethylporphyrin in $CHCl_3$ (50 mL) at 0 °C. The reaction mixture was stirred for 30 min. The solvent was evaporated to dryness. The resulting solid was purified by recrystallization from *n*-hexane/CH_2Cl_2 to afford *meso*-brominated Ni(II) porphyrin. An oven-dried 30 mL sealable two-necked flask equipped with a magnetic stirring bar and rubber septa was charged with [bromoporphyrinato]nickel(II) and $PdCl_2(PPh_3)_2$ (5 mg, 0.007 mmol). The reaction vessel was evacuated and flushed with argon (three times), and 1,2-dichloroethane (10 mL) was added. To this solution, Et_3N (0.25 mL, 1.7 mmol) and pinacolborane (0.36 mL, 2.5 mmol) were added via a syringe. The reaction mixture was heated under argon at 75 °C. After reaction completion (monitored by TLC), the solution was allowed to reach rt. The reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (CH_2Cl_2/*n*-hexane 1:3) followed by recrystallization from MeOH/CH_2Cl_2 yielded pure compound **Ni-1h** as a purple solid; 44.0 mg, 48%; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 9.73 (2H, d, J = 5.0

Hz), 9.40 (2H, d, J = 4.8 Hz), 8.773 (2H, d, J = 5.0 Hz), 8.768 (2H, d, J = 4.8 Hz), 7.96–7.94 (4H, m), 7.68–7.66 (6H, m), 6.49 (2H, d, J = 5.8 Hz), 2.52 (1H, t, J = 5.8 Hz), 1.66 (12H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 146.6, 142.7, 141.9, 141.5, 140.6, 134.3, 133.7, 133.1, 132.7, 129.2, 127.8, 126.9, 118.6, 114.9, 84.9, 63.4, 25.2.; IR (KBr): 3263, 3059, 3024, 2978, 2924, 1550, 1462, 1369, 1311, 1146, 1072, 1007, 795, 706 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 412.0 (5.4), 533.0 (4.3), 574.5 (4.0) nm; HRMS-FAB ([M]$^+$): Calcd for $C_{39}H_{33}N_4NiO_3$: 674.1999; Found: 674.2001.

Preparation of [5,15-Diphenyl-10-phenylsulfanyl-20-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)porphyrinato]nickel(II) (**Ni-1i**). NBS (25 mg, 0.14 mmol) was added to a solution of 5,15-diphenyl-10-phenylsulfanylporphyrin **H2-1i-H**[3q] (74.2 mg, 0.13 mmol) in $CHCl_3$ (50 mL) at 0 °C. The reaction mixture was stirred for 30 min. The solvent was evaporated to dryness. The resulting solid was purified by recrystallization from *n*-hexane/CH_2Cl_2 to afford free base *meso*-bromoporphyrin. The solution of free base *meso*-bromoporphyrin in DMF (10 mL) was added to $Ni(OAc)_2 \cdot 4H_2O$ (124 mg, 0.5 mmol). The mixture was stirred at 160 °C for 1 h. After reaction completion (monitored by TLC), the solution was poured into water (25 mL). The resulting precipitate was collected and washed with water, which produced brominated Ni(II) porphyrin. An oven-dried 30-mL sealable two-necked flask equipped with a magnetic stirring bar and rubber septa was charged with brominated Ni(II) porphyrin and $PdCl_2(PPh_3)_2$ (5 mg, 0.007 mmol). The reaction vessel was evacuated and flushed with argon (three times), and 1,2-dichloroethane (10 mL) was added. To this solution, Et_3N (0.25 mL, 1.7 mmol) and pinacolborane (0.36 mL, 2.5 mmol) were added via a syringe. The reaction mixture was heated under argon at 75 °C. After reaction completion (monitored by TLC), the solution was allowed to reach rt. The reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (CH_2Cl_2/*n*-hexane 1:3) followed by recrystallization from MeOH/CH_2Cl_2 yielded pure compound **Ni-1i** as a purple solid; 29.2 mg, 30%; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 9.73 (2H, d, J = 4.9 Hz), 9.68 (2H, d, J = 4.9 Hz), 8.77 (2H, d, J = 4.9 Hz), 8.70 (2H, d, J = 4.9 Hz), 7.96–7.95 (4H, m), 7.68–7.65 (6H, m), 6.97–6.88 (5H, m), 1.67 (12H, s); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 146.4, 146.1, 143.2, 142.4, 142.0, 140.5, 134.5, 133.8, 133.6, 133.0, 132.9, 128.7, 127.8, 126.9, 126.7, 125.0, 119.0, 107.6, 84.9, 25.1; IR (KBr): 3059, 3024, 2978, 2927, 1535, 1473, 1450, 1369, 1311, 1142, 1068, 1007, 795, 702 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 417.0 (5.3), 537.5 (4.2), 572.5 (4.1) nm; HRMS (EI) *m*/*z*: Calcd for $C_{44}H_{35}BN_4NiO_2S$: 752.1927; Found: 752.1927.

Preparation of [5,15-Diphenyl-10,20-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)porphyrinato]-nickel(II) (**Ni-3**). Prepared from (5,15-dibromo-10,20-diphenylporphyrinato)nickel(II) **Ni-3-Br**[11] (102 mg, 0.15 mmol) following the general procedure using $PdCl_2(PPh_3)_2$ (12 mg, 0.018 mmol, 12 mol%), Et_3N (0.6 mL, 3.9 mmol, 26 eq) and pinacolborane (1.7 mL, 12 mmol, 40 eq); Purple solid; 11.9 mg, 10%; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 9.77 (4H, d, J = 4.9 Hz), 8.80 (4H, d, J = 4.9 Hz), 8.01–8.00 (4H, m), 7.71–7.67 (6H, m), 1.68 (24H, s); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 145.7, 142.1, 140.9, 134.1, 133.7, 132.5, 127.6, 126.8, 118.4, 84.8, 25.1; IR (KBr): 3055, 2974, 2927, 2866, 1543, 1450, 1362, 1308, 1142, 1068, 1007, 849, 795, 706 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 411.0 (5.5), 532.5 (4.2), 575.0 (4.2) nm; HRMS-FAB ([M]$^{+}$): Calcd for $C_{44}H_{42}B_2N_4NiO_4$: 770.2746; Found: 770.2750.

General Procedure for the Copper-Mediated Trifluoromethylation of Borylporphyrins Using an in Situ-Generated CF_3 Radical From $NaSO_2CF_3$ and *tert*-Butyl Hydroperoxide. TBHP (70% solution in water, 0.09 mL 0.625 mmol, 25 equiv.) was slowly added with stirring to a solution of borylporphyrin (0.025 mmol), $CuCl_2$ (3.4 mg, 0.025 mmol, 1 equiv.), $NaHCO_3$ (2.1 mg, 0.025 mmol, 1 equiv.), and $NaSO_2CF_3$ (97.5 mg, 0.625 mmol, 25 equiv.) in a mixture of CH_2Cl_2/MeOH/H_2O (1.25 mL/1.25 mL/1 mL) at 0 °C. The reaction was allowed to warm to room temperature and then vigorously stirred for 12 h. The reaction was monitored using TLC (CH_2Cl_2/*n*-hexane 1:2). Saturated aqueous sodium bicarbonate was added, and the reaction mixture was stirred for 5 min. The mixture was diluted with CH_2Cl_2 and washed with saturated aqueous sodium bicarbonate. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (CH_2Cl_2/*n*-hexane 1:5) followed by recrystallization from MeOH/CH_2Cl_2 yielded pure compound **2**.

[5,10,15-Triphenyl-20-trifluoromethylporphyrinato]nickel(II) (**Ni-2a**). Prepared from *meso*-borylporphyrin **Ni-1a** (18.0 mg, 0.025 mmol) following the general procedure; Red purple solid; 13.3 mg, 80%; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 9.43 (2H, dq, J = 4.9, 2.8 Hz), 8.83 (2H, d, J = 4.9 Hz), 8.71 (2H, d, J = 4.9 Hz), 8.65 (2H, d, J = 4.9 Hz), 7.97–7.96 (6H, m), 7.70–7.64 (9H, m); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 143.5, 142.0, 141.3, 140.27, 140.25, 140.12, 140.10, 134.6, 133.6, 133.5, 133.3, 132.2, 131.4 (q, J = 4.7 Hz), 128.0, 127.6 (q, J = 274.8 Hz), 127.03, 126.98, 121.8, 119.7, 101.2 (q, J = 31.7 Hz); ^{19}F-NMR ($CDCl_3$, 376 MHz) δ: –39.8 (3F, s); IR (KBr): 3059, 3028, 1554, 1450, 1369, 1277, 1114, 1011, 790, 748, 705 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 413.5 (5.4), 535.5 (4.2), 573.5 (4.1) nm; HRMS (EI) *m*/*z*: Calcd for $C_{39}H_{23}F_3N_4Ni$: 662.1228; Found: 662.1223.

[5,15-Diphenyl-10-trifluoromethylporphyrinato]nickel(II) (**Ni-2b**). Prepared from *meso*-borylporphyrin **Ni-1b** (16.1 mg, 0.025 mmol) following the general procedure; Red purple solid; 9.1 mg, 64%; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 9.68 (1H, s), 9.41 (2H, dq, J = 5.1, 2.6 Hz), 9.03 (2H, d, J = 4.8 Hz), 8.82 (2H, d, J = 5.1 Hz), 8.74 (2H, d, J = 4.8 Hz), 7.96–7.94 (4H, m), 7.73–7.63 (6H, m); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 143.5, 141.9, 141.5, 140.2, 139.9 (q, J_{CF} = 1.9 Hz), 134.6, 133.7, 133.1, 132.6, 131.3 (q, J_{CF} = 5.0 Hz), 128.1, 127.7 (q, J_{CF}= 274.0 Hz), 127.1, 119.2, 106.9, 101.6 (q, J_{CF} = 31.5 Hz); ^{19}F-NMR ($CDCl_3$, 376 MHz) δ: –40.2 (3F, s); IR (KBr): 3154, 3116, 3078, 3028, 1597, 1554, 1462, 1389, 1331, 1269, 1107, 1003, 864, 787, 701 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 406.0 (5.3), 528.5 (4.1), 566.5 (4.1) nm; HRMS-FAB ([M]$^{+}$): Calcd for $C_{33}H_{19}F_3N_4Ni$: 586.0915; Found: 586.0912.

[5,15-Di(*p*-tolyl)-10-trifluoromethylporphyrinato]nickel(II) (**Ni-2c**). Prepared from *meso*-borylporphyrin **Ni-1c** (16.8 mg, 0.025 mmol) following the general procedure; Red purple solid; 8.8 mg, 57%; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 9.60 (1H, s), 9.39 (2H, dq, J = 4.9, 2.6 Hz), 8.96 (2H, d, J = 4.9 Hz), 8.82 (2H, d, J = 4.9 Hz), 8.70 (2H, d, J = 4.9 Hz), 7.76 (4H, d, J = 7.8 Hz), 7.44 (4H, d, J = 7.8 Hz), 2.63 (6H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 143.3, 141.6, 141.3, 139.5 (q, J_{CF} = 1.7 Hz), 137.7, 137.0, 134.6, 133.5, 132.9, 132.6, 131.1 (q, J_{CF} = 4.7 Hz), 127.7, 127.5 (q, J_{CF} = 273.9 Hz), 119.1, 106.7, 101.1 (q, J_{CF} = 31.4 Hz), 21.4; ^{19}F-NMR ($CDCl_3$, 376 MHz) δ: –40.1 (3F, s); IR (KBr): 3024, 2920, 2858, 1551, 1458, 1273, 1115, 1007, 791, 717 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 407.5 (5.5), 530.5 (4.3), 567.0 (4.3) nm; HRMS-FAB ([M]$^+$): Calcd for $C_{35}H_{23}F_3N_4Ni$: 614.1228; Found: 614.1226.

[10-Trifluoromethyl-5,15-bis(3-vinylphenyl)porphyrinato]nickel(II) (**Ni-2d**). Prepared from *meso*-borylporphyrin **Ni-1d** (17.4 mg, 0.025 mmol) following the general procedure; Red purple solid; 7.7 mg, 48%; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 9.62 (1H, s), 9.43 (2H, dq, J = 5.1, 2.6 Hz), 8.98 (2H, d, J = 4.8 Hz), 8.84 (2H, d, J = 5.1 Hz), 8.73 (2H, d, J = 4.8 Hz), 7.97 (2H, t, J = 1.6 Hz), 7.82–7.74 (4H, m), 7.61 (2H, t, J = 7.6 Hz), 6.91 (2H, dd, J = 17.6, 11.0 Hz), 5.90 (2H, d, J = 17.6 Hz), 5.38 (2H, d, J = 11.0 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 143.2, 141.7, 141.2, 140.2, 139.7, 136.6, 136.3, 134.6, 133.2, 133.0, 132.6, 131.5, 131.4 (q, J = 4.4 Hz), 127.5 (q, J = 274.0 Hz), 127.2, 125.8, 118.8, 115.0, 106.9, 101.4 (q, J = 31.7 Hz); ^{19}F-NMR ($CDCl_3$, 376 MHz) δ: –38.4 (3F, s); IR (KBr): 3151, 3086, 3055, 3012, 2927, 2862, 1724, 1570, 1462, 1381, 1269, 1107, 1007, 791, 717 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 407.0 (5.4), 529.5 (4.2), 566.0 (4.2) nm; HRMS-FAB ([M]$^+$): Calcd for $C_{37}H_{23}F_3N_4Ni$: 638.1228; Found: 638.1224.

[5,15-Bis(3-methoxyphenyl)-10-trifluoromethylporphyrinato]nickel(II) (**Ni-2e**). Prepared from *meso*-borylporphyrin **Ni-1e** (17.6 mg, 0.025 mmol) following the general procedure; Red purple solid; 8.3 mg, 51%; ^{1}H-NMR (CD_2Cl_2, 300 MHz) δ: 9.72 (1H, s), 9.43 (2H, dq, J = 5.3, 2.7 Hz), 9.07 (2H, d, J = 4.8 Hz), 8.90 (2H, d, J = 5.3 Hz), 8.80 (2H, d, J = 4.8 Hz), 7.63–7.50 (6H, m), 7.30–7.27 (2H, m), 3.94 (6H, s); ^{13}C-NMR (CD_2Cl_2, 75 MHz) δ: 158.7, 143.6, 142.2, 141.6, 141.5, 140.0 (q, J_{CF} = 1.9 Hz), 135.0, 133.6, 133.0, 131.3 (q, J_{CF} = 4.8 Hz), 128.3, 128.0 (q, J_{CF} = 274.0 Hz), 126.9, 120.0, 119.4, 114.0, 107.4, 101.4 (q, J_{CF} = 31.1 Hz), 55.8; ^{19}F-NMR ($CDCl_3$, 376 MHz) δ: –38.8 (3F, s); IR (KBr): 3059, 3001, 2927, 2854, 1592, 1462, 1273, 1130, 1061, 795, 706 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 407.0 (5.5), 530.0 (4.3), 567.0 (4.3) nm; HRMS-FAB ([M]$^+$): Calcd for $C_{35}H_{23}F_3N_4NiO_2$: 646.1127; Found: 646.1131.

[5,15-Di-*n*-butyl-10-trifluoromethylporphyrinato]nickel(II) (**Ni-2f**). Prepared from *meso*-borylporphyrin **Ni-1f** (15.1 mg, 0.025 mmol) following the general procedure; Red purple solid; 6.8 mg, 50%; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 9.35 (2H, dq, J = 5.2, 2.6 Hz), 9.23 (1H, s), 9.18 (2H, d, J = 5.1 Hz), 9.03 (2H, d, J = 4.8 Hz), 8.82 (2H, d, J = 4.8 Hz), 4.24 (4H, t, J = 8.1 Hz), 2.23–2.13 (4H, m), 1.59–1.47 (4H, m), 1.01 (6H, t, J = 7.3 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 142.8, 140.7, 140.3, 138.4 (q, J = 1.9 Hz), 133.0, 131.7, 131.3 (q, J = 4.8 Hz), 129.4, 127.6 (q, J = 274.6 Hz), 118.3, 105.8, 99.9 (q, J =

31.3 Hz), 39.6, 33.5, 23.3, 13.9; ^{19}F-NMR ($CDCl_3$, 376 MHz) δ: –38.6 (3F, s);IR (KBr): 2954, 2927, 2866, 1457, 1273, 1115, 779, 706 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 409.0 (5.3), 533.5 (4.1), 571.0 (4.0) nm; HRMS-FAB ([M]$^+$): Calcd for $C_{29}H_{27}F_3N_4Ni$: 546.1541; Found: 546.1545.

[5-(2-Ethoxycarbonylethyl)-10,20-diphenyl-15-trifluoromethylporphyrinato]nickel(II) (Ni-2g). Prepared from *meso*-borylporphyrin **Ni-1g** (18.3 mg, 0.025 mmol) following the general procedure; Red purple solid; 12.9 mg, 77%; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 9.31 (2H, dq, J = 4.9, 2.4 Hz), 9.23 (2H, d, J = 4.9 Hz), 8.74 (2H, d, J = 5.1 Hz), 8.66 (2H, d, J = 5.1 Hz), 7.90–7.89 (4H, m), 7.72–7.62 (6H, m), 5.37 (2H, s), 4.18 (2H, q, J = 7.1 Hz), 1.19 (3H, t, J = 7.1 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 171.6, 142.9, 141.8, 141.0, 139.9, 139.8, 134.7, 133.5, 133.0, 131.5 (q, J = 4.8 Hz), 130.7, 128.0, 127.3 (q, J = 272.1 Hz), 127.0, 119.4, 111.7, 101.1 (q, J = 34.2 Hz), 61.5, 39.6, 14.2; ^{19}F-NMR ($CDCl_3$, 376 MHz) δ: –39.2 (3F, s); IR (KBr): 3140, 3062, 3024, 2997, 2954, 2858, 1728, 1365, 1265, 1111, 1011, 756, 706 cm^{-1} UV/vis (CH_2Cl_2) λ_{max} (log ε) 413.0 (5.4), 536.5 (4.2), 577.0 (4.1) nm; HRMS (EI) m/z: Calcd for $C_{37}H_{25}F_3N_4NiO_2$: 672.1283; Found: 672.1278.

[5-Hydroxymethyl-10,20-diphenyl-15-trifluoromethylporphyrinato]nickel(II) (Ni-2h). Prepared from *meso*-borylporphyrin **Ni-1h** (16.9 mg, 0.025 mmol) following the general procedure; Red purple solid; 7.7 mg, 50%; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 9.35 (2H, d, J = 4.9 Hz), 9.33 (2H, dq, J = 4.9, 2.4 Hz), 8.76 (2H, d, J = 5.4 Hz), 8.72 (2H, d, J = 5.4 Hz), 7.91–7.90 (4H, m), 7.70–7.64 (6H, m), 6.40 (2H, d, J = 5.4 Hz), 2.52 (1H, t, J = 5.4 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 143.0, 141.6, 141.3, 139.8, 139.7, 134.7, 133.5, 133.3, 131.7 (q, J = 4.4 Hz), 130.2, 128.1, 127.3 (q, J = 271.5 Hz), 127.1, 119.5, 116.5, 101.6 (q, J = 33.1 Hz), 63.0; ^{19}F-NMR ($CDCl_3$, 376 MHz) δ: –39.1 (3F, s); IR (KBr): 3262, 3057, 3024, 2974, 2924, 1549, 1468, 1373, 1354, 1309, 1142, 1072, 1009, 854, 796, 702 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 416.0 (5.6), 541.0 (4.2), 577.0 (3.6) nm; HRMS-FAB ([M]$^+$): Calcd for $C_{34}H_{21}F_3N_4NiO$: 616.1021; Found: 616.1023.

[5,15-Diphenyl-10-phenylsulfanyl-20-trifluoromethylporphyrinato]nickel(II) (Ni-2i). Prepared from *meso*-borylporphyrin **Ni-1i** (18.8 mg, 0.025 mmol) following the general procedure; Red purple solid; 9.2 mg, 53%; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 9.62 (2H, d, J = 4.9 Hz), 9.34 (2H, dq, J = 5.0, 2.5 Hz), 8.75 (2H, d, J = 4.9 Hz), 8.64 (2H, d, J = 4.9 Hz), 7.91–7.89 (4H, m), 7.68–7.64 (6H, m), 6.96–6.89 (5H, m); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 145.9, 143.5, 141.7, 141.1, 139.6, 134.7, 133.9, 133.6, 133.5, 131.8 (q, J = 4.1 Hz), 128.9, 128.2, 128.2 (q, J = 273.9 Hz), 127.2, 127.10, 127.05, 125.4, 119.8, 110.1, 102.4 (q, J = 29.0 Hz); ^{19}F-NMR ($CDCl_3$, 376 MHz) δ: –39.2 (3F, s); IR (KBr): 3055, 2924, 2854, 1446, 1362, 1277, 1119, 1011, 791, 744, 702 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 418.5 (5.4), 545.5 (4.3), 584.5 (4.4) nm; HRMS (EI) m/z: Calcd for $C_{39}H_{23}F_3N_4NiS$: 694.0949; Found: 694.0943.

[5,15-Diphenyl-10,20-bis(trifluoromethyl)porphyrinato]nickel(II) Ni-4. Prepared from *meso*-diborylporphyrin **Ni-3** (19.3 mg, 0.025 mmol) following the general procedure using $CuCl_2$ (6.8 mg,

0.05 mmol, 2 equiv), $NaHCO_3$ (4.2 mg, 0.05 mmol, 2 equiv) and $NaSO_2CF_3$ (195 mg, 1.25 mmol, 50 equiv); Red purple solid; 5.1 mg, 31%; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 9.34 (4H, dq, J = 5.0, 2.5 Hz), 8.72 (4H, d, J = 5.1 Hz), 7.89–7.88 (4H, m), 7.74–7.62 (6H, m); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 142.1, 139.1, 138.9 (q, J = 1.9 Hz), 134.7, 133.4, 132.5 (q, J = 4.6 Hz), 128.3, 127.2, 126.8 (q, J = 274.0 Hz), 119.9, 103.7 (q, J = 32.9 Hz); ^{19}F-NMR ($CDCl_3$, 376 MHz) δ: –39.6 (3F, s); IR (KBr): 3151, 3058, 3028, 2927, 2854, 1550, 1362, 1269, 1122, 1049, 1011, 790, 706 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ε) 412.0 (5.4), 545.5 (4.2), 589.5 (4.5) nm; HRMS-FAB ($[M]^+$): Calcd for $C_{34}H_{18}F_3N_4Ni$: 654.0789; Found: 654.0789.
[5,10,15,20-Tetraphenyl-2-trifluoromethylporphyrinato]nickel(II) Ni-6. TBHP (70% solution in water, 0.09 mL 0.625 mmol, 25 equiv.) was slowly added with stirring to a solution of β-boryl-tetraphenylporphyrin **Ni-5** (19.9 mg, 0.025 mmol), $CuBr_2$ (3.4 mg, 0.025 mmol, 1 equiv.), $NaHCO_3$ (2.1 mg, 0.025 mmol, 1 equiv.), and $NaSO_2CF_3$ (292.5 mg, 1.875 mmol, 75 equiv.) in a mixture of CH_2Cl_2/MeOH/H_2O (1.25 mL/1.25 mL/1 mL) at 0 °C. The reaction was allowed to warm to room temperature and then vigorously stirred for 12 h. The reaction was monitored using TLC (CH_2Cl_2/*n*-hexane 1:2). Saturated aqueous sodium bicarbonate was added, and the reaction mixture was stirred for 5 min. The mixture was diluted with CH_2Cl_2 and washed with saturated aqueous sodium bicarbonate. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. Column chromatography on silica gel (CH_2Cl_2/*n*-hexane 1:5) followed by recrystallization from MeOH/CH_2Cl_2 yielded pure **6**[6c] as red purple solid; 9.2 mg, 50%.

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