COPPER-MEDIATED TRIFLUOROMETHYLATION OF BORYLPORPHYRINS USING AN IN SITU-GENERATED CF₃ RADICAL FROM NaSO₂CF₃ AND tert-BUTYL HYDROPEROXIDE

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Abstract – We developed a method for the copper-mediated reaction of borylated Ni(II) porphyrins using NaSO₂CF₃ (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. 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. Currently, there are many methods for introducing various functional groups (e.g., amino, alkoxy, ester, boryl, silyl, C₆F₅, CN, and NO₂) onto porphyrins. 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. 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. However, these multiple condensation methods suffer from low yields, many side products, and tedious chromatographic purification. The direct introduction of CF₃ group onto the porphyrin core using trifluoromethylation reagents, such as CF₃-SR₂⁺OTf⁻ (Umemoto’s reagent) and FSO₂CF₂CO₂Me (Chen’s

This work is dedicated to Professor Dr. Yasuyuki Kita on the occasion of his 77th birthday.
a. An electrophilic substitution with Umemoto's reagent

\[
\begin{align*}
\text{Ar} & \quad \text{CF}_3\text{-SR}_2^{+}\text{OTf}^- \\
\text{M} = 2\text{H}, \text{Ni}, \text{Zn} \\
\text{Ar} & \quad \text{CF}_3
\end{align*}
\]
(y. 0.2-16%)
(y. 0.7-4.4%)

b. Copper-mediated reaction of haloporphyrins with FSO$_2$CF$_2$CO$_2$Me

\[
\begin{align*}
\text{Ph} & \quad \text{FSO}_2\text{CF}_2\text{CO}_2\text{Me}/\text{CuI} \\
\text{DMF}/\text{HMPA, } 100 \text{ °C} \\
\text{Ph} & \quad \text{CF}_3
\end{align*}
\]
(y. 90%)

(c) Palladium-catalyzed coupling of haloporphyrins with FSO$_2$CF$_2$CO$_2$Me

\[
\begin{align*}
\text{Ph} & \quad \text{FSO}_2\text{CF}_2\text{CO}_2\text{Me}/\text{CuCl} \\
\text{cat. Pd}_2(\text{dba})_3/\text{AsPh}_3 \\
\text{DMF, } 100 \text{ °C} \\
\text{Ph} & \quad \text{CF}_3
\end{align*}
\]
(y. 40%: M = Ni)
(y. 45%: M = Cu)

d. This work:
Cu-mediated reaction of borylporphyrins using CF$_3$ radical

\[
\begin{align*}
\text{Ni-1} & \quad \text{NaSO}_2\text{CF}_3/\text{TBHP} \\
\quad & \quad \text{CuCl}_2 \\
\quad & \quad \text{NaHCO}_3 \\
\quad & \quad \text{CH}_2\text{Cl}_2/\text{MeOH/H}_2\text{O} \\
\quad & \quad \text{rt} \\
\text{Ni-2} & \quad \text{CF}_3
\end{align*}
\]
(y. 48-77%)

R$_1$, R$_2$ = Aryl, Alkyl, Functional group (-CH$_2$OH, -CH$_2$CO$_2$Et, -SPh)

**Scheme 1. Preparation of mono-trifluoromethylated porphyrins**
reagent), has been reported. 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). 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). Palladium-catalyzed cross-coupling of Chen’s reagent with bromoporphyrins requires a toxic arsenic compound (AsPh$_3$) as ligand (Scheme 1c). 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$_2$CF$_3$ (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$_2$CF$_3$ and TBHP without an inert atmosphere and dry solvents. 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$_2$CF$_3$ and TBHP in the presence of stoichiometric CuCl and NaHCO$_3$ in a 5:5:4 mixture of CH$_2$Cl$_2$, MeOH, and H$_2$O 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$_2$CF$_3$ 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$_2$Cl$_2$ 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$_2$CF$_3$ as the CF$_3$ source

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrates</th>
<th>NaSO$_2$CF$_3$/TBHP (equiv.)</th>
<th>Cu salt</th>
<th>Cosolvent</th>
<th>Yield (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni-1a-OH</td>
<td>15</td>
<td>CuCl</td>
<td>CH$_2$Cl$_2$</td>
<td>15 (8$^b$)</td>
</tr>
<tr>
<td>2</td>
<td>Ni-1a-OH</td>
<td>25</td>
<td>CuCl</td>
<td>CH$_2$Cl$_2$</td>
<td>73 (37$^b$)</td>
</tr>
<tr>
<td>3</td>
<td>Ni-1a</td>
<td>25</td>
<td>CuCl</td>
<td>CH$_2$Cl$_2$</td>
<td>77</td>
</tr>
<tr>
<td>4</td>
<td>Ni-1a</td>
<td>25</td>
<td>CuCl$_2$</td>
<td>CH$_2$Cl$_2$</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>Ni-1a</td>
<td>25</td>
<td>CuCl$_2$</td>
<td>THF</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>Ni-1a</td>
<td>25</td>
<td>CuCl$_2$</td>
<td>DMF</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>Ni-1a</td>
<td>25</td>
<td>CuCl$_2$</td>
<td>toluene</td>
<td>8</td>
</tr>
</tbody>
</table>

$^a$ 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

![Diagram of Ni-1 and Ni-2]

**Table 2.** Copper-mediated trifluoromethylation of meso-borylated Ni(II) triphenylporphyrin Ni-1 using the NaSO$_2$CF$_3$/TBHP system

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrates</th>
<th>M</th>
<th>R$^1$</th>
<th>R$^2$</th>
<th>Products</th>
<th>Yield (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni-1a</td>
<td>Ni</td>
<td></td>
<td></td>
<td>Ni-2a</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>Ni-1b</td>
<td>Ni</td>
<td></td>
<td>H</td>
<td>Ni-2b</td>
<td>64</td>
</tr>
<tr>
<td>3</td>
<td>Ni-1c</td>
<td>Ni</td>
<td>Me</td>
<td>H</td>
<td>Ni-2c</td>
<td>57</td>
</tr>
<tr>
<td>4</td>
<td>Ni-1d</td>
<td>Ni</td>
<td></td>
<td>H</td>
<td>Ni-2d</td>
<td>48</td>
</tr>
<tr>
<td>5</td>
<td>Ni-1e</td>
<td>Ni</td>
<td></td>
<td>MeO</td>
<td>Ni-2e</td>
<td>51</td>
</tr>
<tr>
<td>6</td>
<td>Ni-1f</td>
<td>Ni</td>
<td>n-Bu</td>
<td>H</td>
<td>Ni-2f</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>Ni-1g</td>
<td>Ni</td>
<td></td>
<td>EtO</td>
<td>Ni-2g</td>
<td>77</td>
</tr>
<tr>
<td>8</td>
<td>Ni-1h</td>
<td>Ni</td>
<td></td>
<td>HO</td>
<td>Ni-2h</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
<td>Ni-1i</td>
<td>Ni</td>
<td></td>
<td>S</td>
<td>Ni-2i</td>
<td>53</td>
</tr>
<tr>
<td>10</td>
<td>Zn-1a</td>
<td>Zn</td>
<td></td>
<td></td>
<td>Zn-2a</td>
<td>trace</td>
</tr>
<tr>
<td>11</td>
<td>H$_2$-1a</td>
<td>2H</td>
<td></td>
<td></td>
<td>H$_2$-2a</td>
<td>trace</td>
</tr>
</tbody>
</table>

$a$ Isolated yield.
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**

<table>
<thead>
<tr>
<th>Entry</th>
<th>NaSO$_2$CF$_3$/TBHP (equiv.)</th>
<th>Cu salt</th>
<th>Yield (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>CuCl$_2$</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>75</td>
<td>CuCl$_2$</td>
<td>41</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>CuBr$_2$</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>CuCl</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>75</td>
<td>CuBr</td>
<td>32</td>
</tr>
<tr>
<td>6</td>
<td>75</td>
<td>-</td>
<td>trace</td>
</tr>
</tbody>
</table>

$^a$ Isolated yield.
Next, we focused on developing a direct method for introducing a CF₃ 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 NaSO₂CF₃ and TBHP provided only a 28% yield of the desired product Ni-6, the yield of the β–CF₃ compound was improved to 41% by increasing the loading of NaSO₂CF₃ and TBHP to 75 equiv (entries 1 and 2). Further CuBr₂ 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 NaSO₂CF₃ 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 ¹H-and ¹³C-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 ¹H- and ¹³C-spectra are given in ppm relative to residual protiated solvent and relative to the solvent, respectively. CDCl₃ (δ = 7.24) and CD₂Cl₂ (δ = 5.32) for ¹H-NMR and relative to the central resonance of CDCl₃ (δ = 77.0) and CD₂Cl₂ (δ = 53.8) for ¹³C-NMR. ¹⁹F-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-5⁹–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$_3$N (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$_2$Cl$_2$ and washed with water. The organic layer was dried over anhydrous MgSO$_4$ and concentrated in vacuo. Column chromatography on silica gel (CH$_2$Cl$_2$/n-hexane 1:3) followed by recrystallization from MeOH/CH$_2$Cl$_2$ 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, 1466, 1377, 1308, 1146, 1072, 1003, 791, 706 cm$^{-1}$; UV/vis (CH$_2$Cl$_2$) 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$_4$NiO$_2$: 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$_2$Cl$_2$) 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$_4$NiO$_2$: 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: 164.5, 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, 2914, 1593, 1550, 1466, 1377, 1308, 1142, 1068, 1003, 795 cm$^{-1}$; UV/vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\varepsilon$) 407.0 (5.3), 524.5 (4.2), 556.0 (3.9) nm; HRMS-FAB ([M$^+$]): Calcd for C$_{42}$H$_{35}$BN$_4$NiO$_2$: 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$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\varepsilon$) 405.0 (5.4), 523.5 (4.2), 554.5 (4.0) nm; HRMS-FAB ([M$^+$]): Calcd for C$_{40}$H$_{35}$BN$_4$NiO$_4$: 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$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\varepsilon$) 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$_4$NiO$_2$: 604.2520; Found: 604.2519.

Preparation of [5-(2-Ethoxycarboxylethyl)-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-ethoxycarboxylethyl)-10,20-diphenylporphyrin H$_2$-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$_2$Cl$_2$ to afford the free base meso-bromoporphyrin. Ni(OAc)$_2$·4H$_2$O (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 PdCl₂(PPh₃)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. Et₃N (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 CH₂Cl₂ and washed with water. The organic layer was dried over anhydrous MgSO₄ and concentrated in vacuo. Column chromatography on silica gel (CH₂Cl₂/n-hexane 1:3) followed by recrystallization from MeOH/CH₂Cl₂ yielded pure compound Ni-1g as a purple solid; 25.0 mg, 26%; ¹H-NMR (CDCl₃, 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); ¹³C-NMR (CDCl₃, 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 (CH₂Cl₂) λmax (log ε) 413.0 (5.4), 532.0 (4.3), 574.5 (4.0) nm; HRMS (EI) m/z: Calcd for C₄₂H₃₇B₄N₄NiO₄: 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-Si₃p (78.7 mg, 0.13 mmol) in a mixed solution of H₂O/THF (1:10 55 mL) at rt. After being stirred for 1 h, the reaction was quenched with Et₃N (1 mL). Then, the mixture was diluted with CH₂Cl₂ (100 mL) and washed with water and brine. The organic layer was dried over MgSO₄ and concentrated in vacuo. Column chromatography on silica gel (n-hexane/CH₂Cl₂ = 1:5) followed by recrystallization from CH₂Cl₂/n-hexane afforded meso-hydroxymethylporphyrin. NBS (25 mg, 0.14 mmol) was added to a solution of meso-hydroxymethylporphyrin in CHCl₃ (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/CH₂Cl₂ 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 PdCl₂(PPh₃)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, Et₃N (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 CH₂Cl₂ and washed with water. The organic layer was dried over anhydrous MgSO₄ and concentrated in vacuo. Column chromatography on silica gel (CH₂Cl₂/n-hexane 1:3) followed by recrystallization from MeOH/CH₂Cl₂ yielded pure compound Ni-1h as a purple solid; 44.0 mg, 48%; ¹H-NMR (CDCl₃, 400 MHz) δ: 9.73 (2H, d, J = 5.0 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); ¹³C-NMR (CDCl₃, 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 (CH₂Cl₂) λmax (log ε) 413.0 (5.4), 532.0 (4.3), 574.5 (4.0) nm; HRMS (EI) m/z: Calcd for C₄₂H₃₇B₄N₄NiO₄: 730.2261; Found: 730.2264.
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 = 4.8 Hz), 1.66 (12H, s); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$: 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, 795, 706 cm$^{-1}$; UV/vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log $\varepsilon$) 412.0 (5.4), 533.0 (4.3), 574.5 (4.0) nm; HRMS-FAB ([M]$^+$): Calcd for C$_{39}$H$_{33}$N$_4$NiO$_3$: 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 H$_2$-1i-H$_3$q (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$_2$Cl$_2$ to afford free base meso-bromoporphyrin. The solution of free base meso-bromoporphyrin in DMF (10 mL) was added to Ni(OAc)$_2$·4H$_2$O (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$_3$N (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$_2$Cl$_2$ and washed with water. The organic layer was dried over anhydrous MgSO$_4$ and concentrated in vacuo. Column chromatography on silica gel (CH$_2$Cl$_2$/n-hexane 1:3) followed by recrystallization from MeOH/CH$_2$Cl$_2$ yielded pure compound Ni-1i as a purple solid; 29.2 mg, 30%; $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$: 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) $\delta$: 146.4, 146.1, 143.2, 142.4, 142.0, 140.5, 134.5, 133.8, 133.6, 133.0, 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$_2$Cl$_2$) $\lambda_{max}$ (log $\varepsilon$) 417.0 (5.3), 537.5 (4.2), 572.5 (4.1) nm; HRMS (EI) $m/z$: Calcd for C$_{44}$H$_{35}$BN$_4$NiO$_2$S: 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$_3$N (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) $\delta$: 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) $\delta$: 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$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\varepsilon$) 411.0 (5.5), 532.5 (4.2), 575.0 (4.2) nm; HRMS-FAB ([M]$^+$): Calcd for C$_{44}$H$_{42}$B$_2$N$_4$NiO$_4$: 770.2746; Found: 770.2750.

**General Procedure for the Copper-Mediated Trifluoromethylation of Borylporphyrins Using an in Situ-Generated CF$_3$ Radical From NaSO$_2$CF$_3$ 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$_2$CF$_3$ (97.5 mg, 0.625 mmol, 25 equiv.) in a mixture of CH$_2$Cl$_2$/MeOH/H$_2$O (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$_2$Cl$_2$/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$_2$Cl$_2$ 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$_2$Cl$_2$/n-hexane 1:5) followed by recrystallization from MeOH/CH$_2$Cl$_2$ 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) $\delta$: 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) $\delta$: 143.5, 142.0, 141.3, 140.2, 140.1, 134.6, 133.6, 133.5, 133.2, 13.14 (q, $J = 4.7$ Hz), 128.0, 127.6 (q, $J = 24.8$ Hz), 127.03, 126.98, 121.8, 119.7, 101.2 (q, $J = 31.7$ Hz); $^{19}$F-NMR (CDCl$_3$, 376 MHz) $\delta$: –39.8 (3F, s); IR (KBr): 3059, 3028, 1597, 1554, 1462, 1389, 1331, 1269, 1107, 1003, 864, 787, 705 cm$^{-1}$; UV/vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\varepsilon$) 413.5 (5.4), 535.5 (4.2), 573.5 (4.1) nm; HRMS (EI) m/z: Calcd for C$_{39}$H$_{23}$F$_3$N$_4$Ni: 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) $\delta$: 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) $\delta$: 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, $J_{CF} = 24.0$ Hz), 127.1, 119.2, 106.9, 101.6 (q, $J_{CF} = 31.5$ Hz); $^{19}$F-NMR (CDCl$_3$, 376 MHz) $\delta$: –40.2 (3F, s); IR (KBr): 3154, 3116, 3078, 3028, 1597, 1554, 1462, 1389, 1331, 1269, 1107, 1003, 864, 787, 705 cm$^{-1}$; UV/vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\varepsilon$) 406.0 (5.3), 528.5 (4.1), 566.5 (4.1) nm; HRMS-FAB ([M]$^+$): Calcd for C$_{33}$H$_{16}$F$_3$N$_4$Ni: 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) \(\delta\): 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) \(\delta\): 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) \(\delta\): –40.1 (3F, s); IR (KBr): 3024, 2920, 2858, 1551, 1458, 1273, 1115, 1007, 791, 717 cm\(^{-1}\); UV/vis (CH\(_2\)Cl\(_2\)) \(\lambda_{max}\) (log \(\varepsilon\)) 407.5 (5.5), 530.5 (4.3), 567.0 (4.3) nm; HRMS-FAB ([M]+): Calcd for C\(_{35}H\(_{23}\)F\(_{3}\)N\(_{4}\)Ni: 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) \(\delta\): 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) \(\delta\): 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) \(\delta\): –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\(_2\)Cl\(_2\)) \(\lambda_{max}\) (log \(\varepsilon\)) 407.0 (5.4), 529.5 (4.2), 566.0 (4.2) nm; HRMS-FAB ([M]+): Calcd for C\(_{37}H\(_{23}\)F\(_{3}\)N\(_{4}\)Ni: 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\(_2\)Cl\(_2\), 300 MHz) \(\delta\): 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), \(J_{CF} = 1.9\) Hz), 3.94 (6H, s); \(^{13}C\)-NMR (CD\(_2\)Cl\(_2\), 75 MHz) \(\delta\): 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) \(\delta\): –38.8 (3F, s); IR (KBr): 3059, 3001, 2927, 2854, 1592, 1462, 1273, 1130, 1061, 795, 706 cm\(^{-1}\); UV/vis (CH\(_2\)Cl\(_2\)) \(\lambda_{max}\) (log \(\varepsilon\)) 407.0 (5.5), 530.0 (4.3), 567.0 (4.3) nm; HRMS-FAB ([M]+): Calcd for C\(_{35}H\(_{23}\)F\(_{3}\)N\(_{4}\)O\(_{2}\): 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) \(\delta\): 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) \(\delta\): 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; 19F-NMR (CDCl₃, 376 MHz) δ: −38.6 (3F, s); IR (KBr): 2954, 2927, 2866, 1457, 1273, 1115, 779, 706 cm⁻¹; UV/vis (CH₂Cl₂) λ_max (log ε) 409.0 (5.3), 533.5 (4.1), 571.0 (4.0) nm; HRMS-FAB ([M]+): Calcd for C₂₉H₂₇F₃N₄Ni: 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%; 1H-NMR (CDCl₃, 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); 13C-NMR (CDCl₃, 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; 19F-NMR (CDCl₃, 376 MHz) δ: −38.6 (3F, s); IR (KBr): 3140, 3062, 3024, 2997, 2954, 2858, 1728, 1365, 1265, 1111, 1011, 756, 706 cm⁻¹; UV/vis (CH₂Cl₂) λ_max (log ε) 413.0 (5.4), 536.5 (4.2), 577.0 (4.1) nm; HRMS (EI) m/z: Calcd for C₃₇H₂₅F₃N₄NiO₂: 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%; 1H-NMR (CDCl₃, 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); 13C-NMR (CDCl₃, 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; 19F-NMR (CDCl₃, 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 (CH₂Cl₂) λ_max (log ε) 416.0 (5.6), 541.0 (4.2), 577.0 (3.6) nm; HRMS-FAB ([M]+): Calcd for C₃₄H₂₁F₃N₄NiO: 616.1021; Found: 616.1023.

[5,15-Diphenyl-10-phenylsulfanyl-20-trifluoromethylporphyrinato]nickel(II) (Ni-2i). Prepared from meso-borylporphyrin Ni-1i (16.9 mg, 0.025 mmol) following the general procedure; Red purple solid; 9.2 mg, 53%; 1H-NMR (CDCl₃, 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); 13C-NMR (CDCl₃, 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); 19F-NMR (CDCl₃, 376 MHz) δ: −39.2 (3F, s); IR (KBr): 3055, 2924, 2854, 1446, 1362, 1277, 1119, 1011, 791, 744, 702 cm⁻¹; UV/vis (CH₂Cl₂) λ_max (log ε) 418.5 (5.4), 545.5 (4.3), 584.5 (4.4) nm; HRMS (EI) m/z: Calcd for C₃₉H₂₃F₃N₄NiS: 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 CuCl₂ (6.8 mg,
0.05 mmol, 2 equiv), NaHCO$_3$ (4.2 mg, 0.05 mmol, 2 equiv) and NaSO$_2$CF$_3$ (195 mg, 1.25 mmol, 50 equiv); Red purple solid; 5.1 mg, 31%; $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$: 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) $\delta$: 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) $\delta$: –39.6 (3F, s); IR (KBr): 3151, 3058, 3028, 2927, 2854, 1550, 1362, 1269, 1049, 1011, 790, 706 cm$^{-1}$; UV/vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\varepsilon$) 412.0 (5.4), 545.5 (4.2), 589.5 (4.5) nm; HRMS-FAB ([M]$^+$): Calcd for C$_{34}$H$_{18}$F$_3$N$_4$Ni: 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$_2$CF$_3$ (292.5 mg, 1.875 mmol, 75 equiv.) in a mixture of CH$_2$Cl$_2$/MeOH/H$_2$O (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$_2$Cl$_2$/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$_2$Cl$_2$ 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$_2$Cl$_2$/n-hexane 1:5) followed by recrystallization from MeOH/CH$_2$Cl$_2$ yielded pure 6$^6$c as red purple solid; 9.2 mg, 50%.

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REFERENCES


