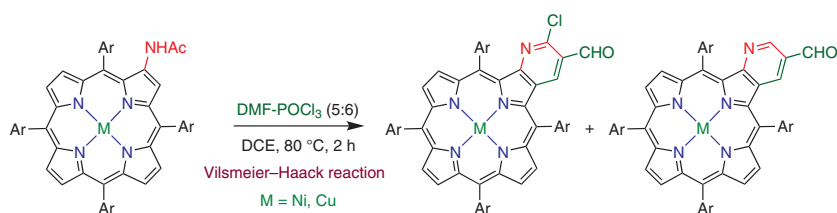


# A Modified Vilsmeier–Haack Strategy to Construct $\beta$ -Pyridine-Fused 5,10,15,20-Tetraarylporphyrins

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**Abstract** A modified Vilsmeier–Haack strategy has been developed to construct a novel series of  $\pi$ -extended nickel(II) or copper(II) complexes of 2-chloro-3-formyl- and 3-formylpyrido[2,3-*b*]porphyrins from 2-acetamido-*meso*-tetraarylporphyrins. After chromatographic purification and spectral characterization, nickel(II) complexes of 2-chloro-3-formyl- and 3-formylpyrido[2,3-*b*]porphyrins underwent reaction with malononitrile under Knoevenagel conditions to afford new porphyrins with extended  $\pi$ -conjugation in appreciable yields. On photophysical investigation, the newly prepared pyridoporphyryns displayed a significant redshift in their electronic absorption spectra as compared to simple *meso*-tetraarylporphyrin precursors.

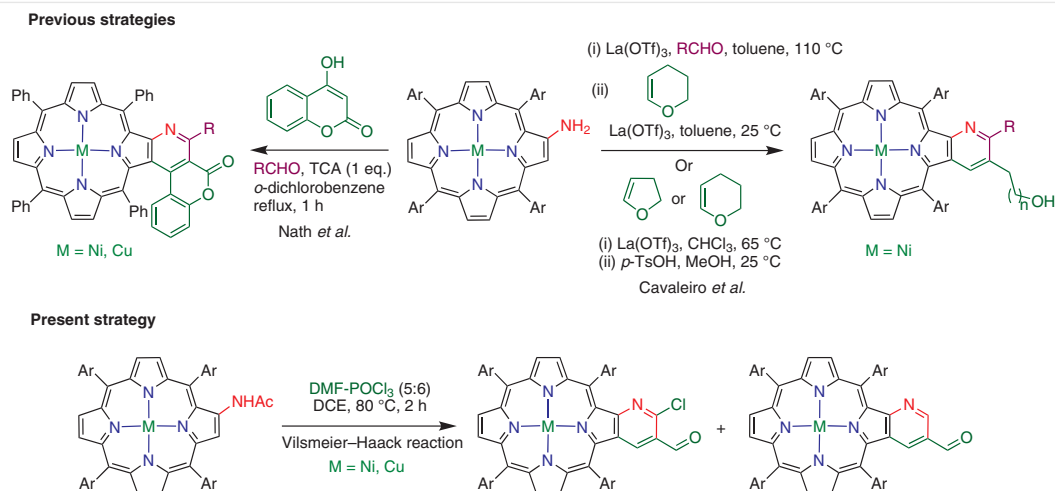
**Key words** 2-chloro-3-formylpyrido[2,3-*b*]porphyrins, 3-formylpyrido[2,3-*b*]porphyrins, Knoevenagel condensation, redshift, synthesis, Vilsmeier–Haack reaction

Porphyrin macrocycles are an important class of tetrapyrrolic systems that play key roles in diverse processes including photosynthesis,<sup>1</sup> oxygen transport,<sup>2</sup> and solar energy conservation.<sup>3,4</sup> Apart from naturally occurring porphyrins, a large number of artificial porphyrins have been constructed for various electronic applications due to their good thermal stabilities and  $\pi$ -electron conjugation.<sup>5–7</sup> Furthermore, the incorporation of electron-rich aromatic and heteroaromatic systems at the porphyrin periphery have led to the generation of molecules with extended  $\pi$ -systems. These porphyrins display a wide range of applications in diverse areas including molecular devices,<sup>8–12</sup> hybrid solar cells,<sup>13–17</sup> light-emitting diodes<sup>18,19</sup> and sensors.<sup>20–23</sup> Ef-

forts have also been made to synthesize a variety of  $\beta, \beta'$ -fused porphyrins decorated with different heterocyclic scaffolds<sup>24–29</sup> including pyrrole, pyrazole, triazole, imidazole, BODIPY, and pyrrolo[1,2-*a*]pyrazine to develop conjugated structures that demonstrate intense electronic absorption and fluorescence properties.

To this end, Cavaleiro and co-workers synthesized various pyridine-appended porphyrins through hetero-Diels–Alder reaction of nickel(II) complexes of 2-imino-*meso*-tetraphenylporphyrins with electron-rich dienophiles or one-pot reaction of 2-amino-*meso*-tetraarylporphyrins with cyclic enol ethers.<sup>30–32</sup> Recently, our group developed a simple one-pot strategy to generate densely  $\pi$ -conjugated coumarin-fused pyrido[2,3-*b*]porphyrins via a trichloroacetic acid accelerated reaction of 2-amino-5,10,15,20-tetraphenylporphyrins with aromatic aldehydes and 4-hydroxycoumarin.<sup>33</sup> On photophysical investigation, these pyrido[2,3-*b*]porphyrinoids have shown a significant bathochromic shift in their UV/Vis and emission spectra. Prompted by these results and in the context of our interest in developing convenient and alternate synthetic methods for diverse  $\beta, \beta'$ -fused porphyrins from easily accessible *meso*-tetraarylporphyrin precursors,<sup>34–36</sup> we report herein the synthesis of a new series of nickel(II) and copper(II) 2-chloro-3-formyl- and 3-formylpyrido[2,3-*b*]porphyrins by using a modified Vilsmeier–Haack strategy (Scheme 1). Although, the Vilsmeier–Haack protocol has been previously utilized to generate 2-formyl derivatives<sup>37</sup> of *meso*-tetraarylporphyrins, this methodology has not been explored for the synthesis of  $\beta$ -pyridine-fused *meso*-tetraarylporphyrinic systems. Hence, the current study further elaborates the scope of Vilsmeier–Haack reaction to generate conjugated porphyrin molecules.

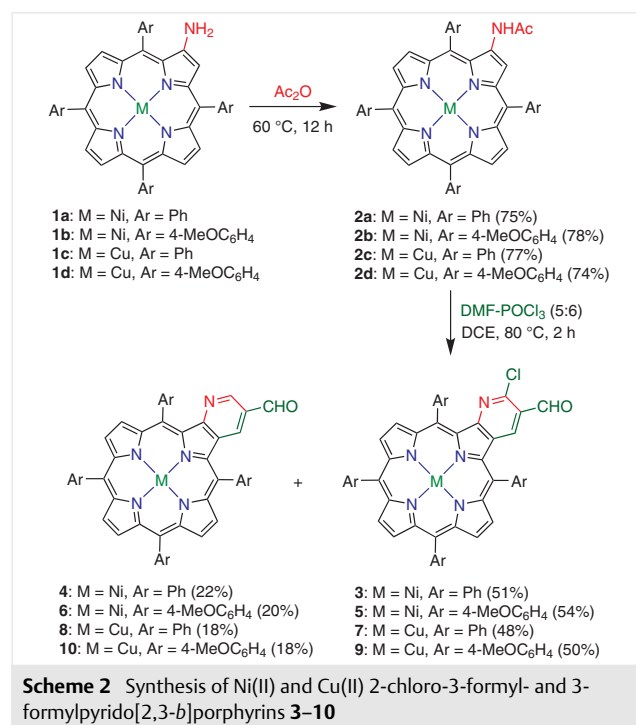
For the synthesis of the target pyridoporphyryns, nickel(II) and copper(II) 2-acetamido-5,10,15,20-tetraarylporphyrin precursors **2a–d** were synthesized in 74–78% yields



**Scheme 1** One-pot synthetic approaches to nickel(II) and copper(II) pyrido[2,3-*b*]porphyrins

through acetylation of the corresponding 2-aminoporphyrins **1a–d** using acetic anhydride at 60 °C (Scheme 2). Initially, nickel(II) 2-acetamido-5,10,15,20-tetraphenylporphyrin (**2a**) was selected as a model substrate to optimize the reaction conditions for the synthesis of the desired pyridoporphyrins **3** and **4**. In a typical experiment, **2a** was allowed to react with the Vilsmeier reagent (chloromethyleneiminium ion), generated in situ after mixing *N,N*-dimethylformamide (DMF) with phosphorus oxychloride in a ratio of 1:3 in 1,2-dichloroethane (DCE) at 80 °C (Table 1, entry 1). As indicated by TLC, the starting material was completely consumed within two hours and the reaction mixture turned green in color. The solvent was then evaporated under reduced pressure and the residue obtained was loaded onto neutral alumina and the desired green product was eluted using 40% chloroform in hexane to afford a mixture of nickel(II) 2-chloro-3-formylpyrido[2,3-*b*]porphyrin (**3**) and nickel(II) 3-formylpyrido[2,3-*b*]porphyrin (**4**). Efforts to separate these porphyrins by column chromatography failed because of their very similar  $R_f$  values. However, pyridoporphyrins **3** and **4** could be separated by silica gel preparative TLC using 65% chloroform in hexane as an eluent. The desired porphyrins **3** and **4** were obtained in moderate (37%) and poor (11%) isolated yields, respectively, and characterized by spectroscopic analysis. In the  $^1\text{H}$  NMR spectrum, porphyrin **3** showed a characteristic singlet at  $\delta = 9.23$  ppm for an aldehydic proton and a singlet at  $\delta = 8.95$  ppm for one proton of the pyridine ring. The IR spectrum showed a characteristic peak at  $1667\text{ cm}^{-1}$  due to the stretching of a C=O bond. ESI mass spectrometric analysis further supported the assigned structure of nickel(II) 2-chloro-3-formylpyrido[2,3-*b*]porphyrin (**3**), showing an  $[\text{M} + \text{H}]^+$  ion peak at  $m/z$  784.1409, corresponding to a molecu-

lar formula  $\text{C}_{48}\text{H}_{28}\text{ClN}_5\text{NiO}$ . In contrast, the proton NMR spectrum of nickel(II) 3-formylpyrido[2,3-*b*]porphyrin (**4**) showed two singlets for one proton each at  $\delta = 9.14$  and 9.00 ppm, corresponding to the two pyridine protons. In addition, a singlet at  $\delta = 9.22$  ppm for one proton confirmed the presence of an aldehydic proton in the molecule. Furthermore, IR spectroscopic and mass spectrometric data also support the formation of porphyrin **4**.



**Table 1** Optimization of Reaction Conditions for the Synthesis of Nickel(II)  $\beta$ -Pyridine-Fused Porphyrins **3** and **4**<sup>a</sup>

| Entry | Solvent     | Temp (°C) | DMF-POCl <sub>3</sub> | Yields (%) <sup>b</sup> |                |
|-------|-------------|-----------|-----------------------|-------------------------|----------------|
|       |             |           |                       | <b>3</b>                | <b>4</b>       |
| 1     | DCE         | 80        | 1:3                   | 37                      | 11             |
| 2     | DCE         | 80        | 1:5                   | – <sup>c</sup>          | – <sup>c</sup> |
| 3     | DCE         | 80        | 1:1                   | 42                      | 18             |
| 4     | DCE         | 80        | 2:1                   | 20                      | 8              |
| 5     | DCE         | 80        | 5:7                   | 45                      | 19             |
| 6     | DCE         | 80        | 5:6                   | 51                      | 22             |
| 7     | benzene     | 80        | 5:6                   | – <sup>c</sup>          | – <sup>c</sup> |
| 8     | 1,4-dioxane | 100       | 5:6                   | 32                      | 10             |
| 9     | DCE         | 60        | 5:6                   | – <sup>d</sup>          | – <sup>d</sup> |
| 10    | THF         | 60        | 5:6                   | – <sup>d</sup>          | – <sup>d</sup> |

<sup>a</sup> Reaction conditions: Nickel(II) 2-acetamido-5,10,15,20-tetraarylporphyrin (**2a**; 0.14 mmol), DMF/POCl<sub>3</sub> (28  $\mu$ L), solvent (35 mL), heat, 2 h.

<sup>b</sup> Isolated yield.

<sup>c</sup> Starting material was decomposed.

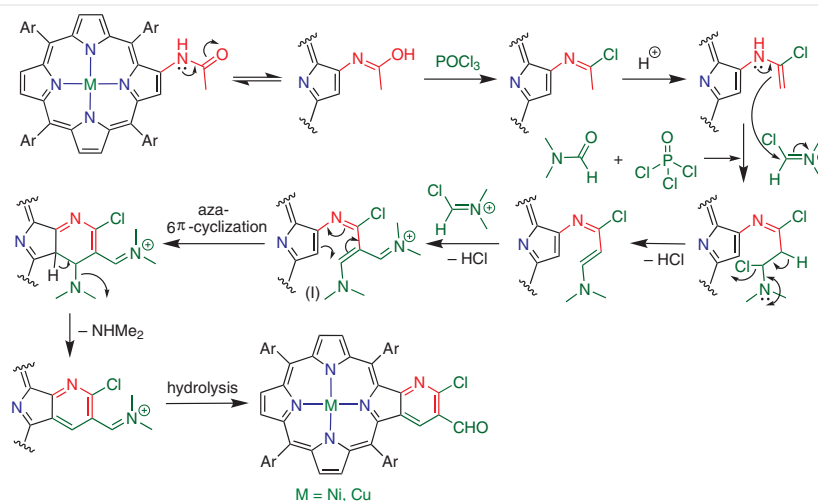
<sup>d</sup> Reaction did not proceed.

To improve the yields of porphyrins **3** and **4**, experiments were carried out by varying the ratio of DMF and POCl<sub>3</sub> in 1,2-dichloroethane (Table 1, entries 2–6). Increasing the ratio of POCl<sub>3</sub> to DMF to 5:1 caused complete decomposition of the starting material (entry 2). The yield of desired porphyrins (**3**; 42% and **4**; 18%) increased when the reaction was carried out in an equimolar mixture of DMF and POCl<sub>3</sub> (entry 3), and use of a slight excess of POCl<sub>3</sub> in DMF further improved the yields of the desired porphyrin products (entry 5). The best results were obtained when DMF and POCl<sub>3</sub> were used in a 5:6 ratio to afford the desired porphyrins **3** and **4** in 51 and 22% isolated yields, respectively (entry 6). Carrying out the reaction in refluxing ben-

zene did not provide any desired product and only decomposition of starting materials was observed (entry 7). The effect of temperature on the formation of porphyrins **3** and **4** was also studied by carrying out the reactions at 100 °C in 1,4-dioxane and at 60 °C in DCE or THF (entries 8–10). Increasing the reaction temperature from 80 to 100 °C afforded the desired porphyrins **3** and **4** in lower yields (entry 8); whereas decreasing the reaction temperature to 60 °C did not result in formation of the desired porphyrins, and unreacted starting material, 2-acetamidoporphyrin (**2a**) was recovered quantitatively. Hence, the use of DMF-POCl<sub>3</sub> (5:6) in DCE at 80 °C was considered to be the optimum condition for the synthesis of porphyrins **3** and **4**.

After establishing the optimized conditions, the protocol was further extended to construct various nickel(II) and copper(II) 2-chloro-3-formylpyrido[2,3-*b*]porphyrins **5**, **7**, and **9**, and 3-formylpyrido[2,3-*b*]porphyrins **6**, **8**, and **10** from the corresponding nickel(II) and copper(II) 2-acetamido-5,10,15,20-tetraarylporphyrins **2b–d** in moderate yields, as presented in Scheme 2.

Literature reports on the synthesis of 2-chloroquinoline-3-carbaldehydes<sup>38</sup> from acetanilides provided an insight into a possible mechanistic pathway for the formation of nickel(II) or copper(II) complexes of 2-chloro-3-formylpyrido[2,3-*b*]porphyrins **3**, **5**, **7**, and **9**. The reaction may proceed via formation of the corresponding imidoyl chloride<sup>38c</sup> from the 2-acetamido-5,10,15,20-tetraarylporphyrin in the presence of POCl<sub>3</sub>. In the next step, an enamine intermediate is formed under the acidic conditions<sup>38c</sup> and this undergoes electrophilic addition twice by reacting with chloromethyleneiminium cation (generated in situ from the reaction of DMF and POCl<sub>3</sub>). This will form methyleneiminium cation intermediate **I**, which, on aza-6 $\pi$ -cyclization followed by elimination of dimethylamine and hydrolysis, affords the desired 2-chloro-3-formylpyrido[2,3-*b*]porphyrins (Scheme 3). Similarly, a possible mechanism

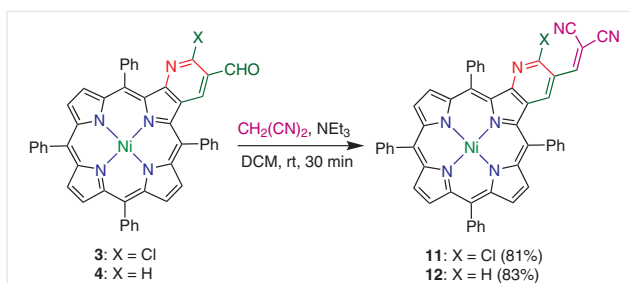

**Scheme 3** Plausible mechanism for the formation of Ni(II) and Cu(II) 2-chloro-3-formylpyrido[2,3-*b*]porphyrins **3**, **5**, **7**, and **9**

for the formation of nickel(II) and copper(II) complexes of 3-formylpyrido[2,3-*b*]porphyrins (**4**, **6**, **8**, and **10**) is shown in the Supporting Information (Figure S32).

The structures of the newly synthesized porphyrins were established on the basis of spectroscopic analyses and their characterization data are presented in the experimental section as well as in the Supporting Information.

For comparative UV/Vis studies, the  $\pi$ -conjugation of newly prepared pyridoporphyrins was further extended through the functionalization of the aldehydic moiety of porphyrins **3** and **4** using a Knoevenagel condensation strategy. Under typical Knoevenagel conditions, nickel(II) 2-chloro-3-formylpyrido[2,3-*b*]porphyrin (**3**) and nickel(II) 3-formylpyrido[2,3-*b*]porphyrin (**4**) were reacted separately with malononitrile in the presence of triethylamine in dichloromethane at ambient temperature to produce highly conjugated nickel(II) porphyrins **11** and **12** in 81 and 83% yields, respectively (Scheme 4). The IR spectra of porphyrins **11** and **12** showed a new peak at ca. 2224  $\text{cm}^{-1}$  due to the cyanide stretching and disappearance of the peak at ca. 1667  $\text{cm}^{-1}$  due to the C=O bond stretching, confirming the formation of the expected porphyrin molecules. Furthermore, the absence of a signal for the CHO proton at ca.  $\delta = 9.2$  ppm and the appearance of a characteristic signal for a vinylic proton at  $\delta = 7.13$  ppm and  $\delta = 7.08$  ppm in the  $^1\text{H}$  NMR spectra of porphyrins **11** and **12**, respectively, also supported the assigned structures of these porphyrin derivatives.

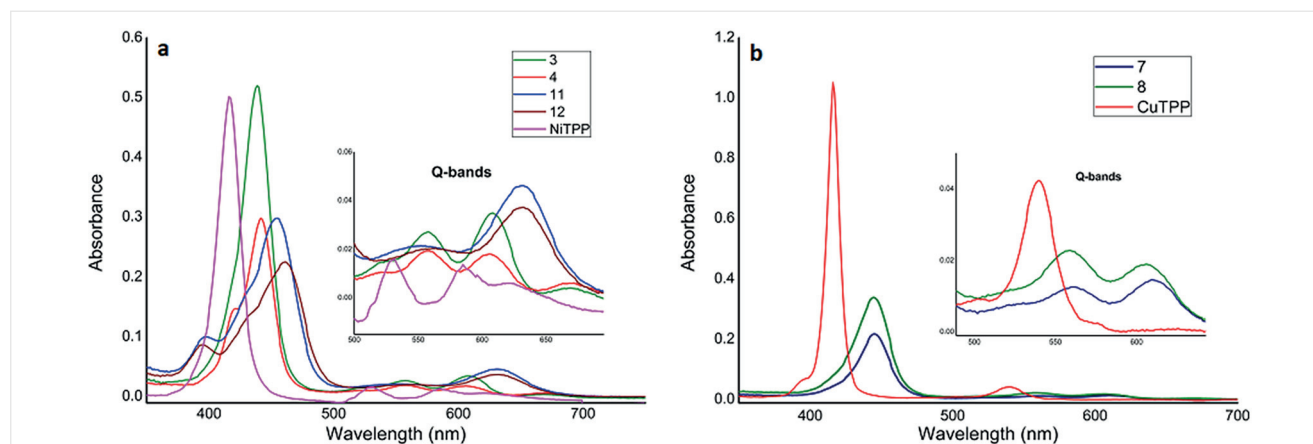
The electronic absorption spectra of the new porphyrins were recorded in  $\text{CHCl}_3$  ( $1 \times 10^{-6}$  M) at room temperature. The nickel(II) and copper(II) 2-acetamidoporphyrins **2a-d** absorbed in a similar region to their precursors nickel(II) *meso*-tetraphenylporphyrin (NiTPP) and copper(II) *meso*-tetraphenylporphyrin (CuTPP), and did not show any significant variation in their electronic absorption spectra, as presented in the Supporting Information Figure S33. However, UV/Vis studies of the newly formed nickel(II) and cop-



**Scheme 4** Synthesis of nickel(II) pyrido[2,3-*b*]porphyrins **11** and **12** under Knoevenagel conditions

per(II) pyridoporphyrin molecules did give very encouraging results. The electronic absorption spectra of nickel(II) 2-chloro-3-formylpyrido[2,3-*b*]porphyrin (**3**) and nickel(II) 3-formylpyrido[2,3-*b*]porphyrin (**4**) showed intense Soret bands at 439 and 442 nm, respectively, and two Q bands between 558 and 608 nm (Figure 1a). In contrast, nickel(II) porphyrins **11** and **12** displayed their Soret bands at 455 and 461 nm, respectively, and two Q bands between 552 and 632 nm (Figure 1a). However, the UV/Vis spectra of copper(II) 2-chloro-3-formylpyrido[2,3-*b*]porphyrin (**7**) and copper(II) 3-formylpyrido[2,3-*b*]porphyrin (**8**) exhibited Soret bands at 438 and 441 nm, respectively, and two Q bands between 559 and 610 nm (Figure 1b). The Soret and Q bands in all the newly prepared pyridoporphyrins are redshifted by ca. 20–45 nm compared to the simple *meso*-tetraphenylporphyrins such as NiTPP (Soret band at 417 nm and Q bands at 533 and 572 nm) and CuTPP (Soret band at 416 nm and Q bands at 540 and 569 nm).

In conclusion, Vilsmeier–Haack reaction conditions have been successfully applied to generate a novel series of  $\pi$ -extended nickel(II) and copper(II) 3-formylpyrido[2,3-*b*]porphyrin analogues from readily accessible 2-acetamido-*meso*-tetraarylporphyrins. In addition, the formyl moiety of two of these porphyrins has been functionalized by reaction with malononitrile under Knoevenagel reaction



**Figure 1** (a) Electronic absorption spectra of porphyrins **3**, **4**, **11**, **12** and NiTPP in  $\text{CHCl}_3$  ( $1 \times 10^{-6}$  mol  $\text{L}^{-1}$ ) at 298 K. (b) Electronic absorption spectra of porphyrins **7**, **8** and CuTPP in  $\text{CHCl}_3$  ( $1 \times 10^{-6}$  mol  $\text{L}^{-1}$ ) at 298 K. Inset shows Q-bands.

conditions to form highly conjugated pyridoporphyrin molecules. Preliminary UV/Vis studies of these new porphyrins reveal significant bathochromic shifts in their electronic absorption spectra due to the extended  $\pi$ -conjugation. The new pyridoporphyrins contain a formyl functionality that is an excellent site for future modifications to develop highly conjugated aromatic superstructures for various medicinal and material applications.

All the chemicals were purchased from Sigma–Aldrich and used without further purification. The progress of the reactions was monitored by thin-layer chromatography (TLC) using silica gel 60 F<sub>254</sub> (precoated aluminum sheets) from Merck. The synthesized products were purified by column as well as preparative thin-layer chromatography using neutral aluminum oxide (Brokmann grade I–II, Merck) and silica gel grade G. NMR spectra were obtained in CDCl<sub>3</sub> with a Jeol ECX 400P (400 MHz) NMR spectrometer using TMS as an internal standard. Chemical shifts are expressed in parts per million (ppm) relative to residual CHCl<sub>3</sub> ( $\delta$  = 7.26 ppm for <sup>1</sup>H NMR and  $\delta$  = 77.00 ppm for <sup>13</sup>C NMR) and coupling constants (*J*) are reported in hertz (Hz). Infrared spectra were recorded with a Bruker FTIR spectrometer and absorption maxima ( $\nu_{\max}$ ) are given in cm<sup>-1</sup>. Electronic absorption spectra were measured in CHCl<sub>3</sub> with an Analytik Jena Specord 250 UV/Vis spectrophotometer. Mass spectra (ESI-HRMS) were recorded with an LCMS–Waters SYNAPT G2 mass spectrometer. Melting points were determined with a Büchi M-560 melting point apparatus.

#### Nickel(II) or Copper(II) 2-Acetamido-5,10,15,20-tetraarylporphyrins (2a–d); General Procedure

A solution of nickel(II) or copper(II) 2-amino-5,10,15,20-tetraphenylporphyrin **1a–d** (0.15 mmol) in acetic anhydride (7 mL) was stirred at 60 °C for 12 hours, and progress of reaction was monitored by thin-layer chromatography. Upon completion of reaction, the mixture was evaporated to dryness. The viscous material thus obtained was dissolved in chloroform (25 mL) and washed twice with water (2 × 30 mL). The organic layer was then dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The crude products were purified over neutral alumina column using 40–50% chloroform in hexane as eluent to furnish the desired products **2a–d** in good yields. Characterization data of a representative porphyrin (**2a**) are given below.

#### Nickel(II) 2-Acetamido-5,10,15,20-tetraphenylporphyrin (2a)

Yield: 81 mg (75%); purple solid; mp >300 °C

UV:  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup>cm<sup>-1</sup>): 418 (47.72), 540 (2.99), 577 (0.99) nm.

IR (CHCl<sub>3</sub>): 3421, 3056, 3021, 2922, 2853, 1701, 1593, 1516, 1445, 1355, 1305, 1240, 1170, 1074, 1009, 835, 793, 750, 704 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.25 (s, 1 H,  $\beta$ -pyrrolic H), 8.75–8.70 (m, 5 H,  $\beta$ -pyrrolic H), 8.62 (d, *J* = 5.04 Hz, 1 H,  $\beta$ -pyrrolic H), 8.02–8.01 (m, 8 H, *meso*-ArH), 7.82–7.79 (m, 2 H, *meso*-ArH), 7.69–7.63 (m, 11 H, *meso*-ArH, NH), 1.82 (s, 3 H, CH<sub>3</sub>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 166.79, 143.00, 142.70, 142.35, 142.04, 141.90, 141.65, 140.56, 139.41, 139.38, 133.63, 133.58, 133.55, 132.78, 132.65, 132.44, 132.12, 131.99, 131.85, 131.15, 129.14, 128.35, 127.76, 127.02, 126.88, 120.33, 119.71, 118.94, 118.26, 115.06, 24.15.

HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>46</sub>H<sub>32</sub>N<sub>5</sub>NiO<sup>+</sup>: 728.1955; found: 728.1941.

#### Nickel(II) or Copper(II) 2-Chloro-3-formylpyrido[2,3-*b*]porphyrins **3**, **5**, **7** and **9**, and 3-Formylpyrido[2,3-*b*]porphyrins **4**, **6**, **8**, and **10**; General Procedure

To a solution of DMF (0.14 mmol) in 1,2-dichloroethane (5 mL), POCl<sub>3</sub> (0.17 mmol) was added dropwise and the reaction mixture was stirred at r.t. for 5–10 minutes. A solution of nickel(II) or copper(II) 2-acetamido-5,10,15,20-tetraarylporphyrin **2a–d** (0.14 mmol) in 1,2-dichloroethane (30 mL) was then added and the reaction mixture was stirred at 80 °C for 2 hours. Upon completion of reaction, the solvent was evaporated under reduced pressure. The solid residue was dissolved in chloroform (30 mL) and the resulting solution was washed twice with water (2 × 30 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude material was loaded on a neutral alumina column and a green band consisting of a mixture of two compounds was eluted with 40% chloroform in hexane. The two porphyrin analogues were separated on silica gel preparative TLC using 65% chloroform in hexane (for compounds **3–4** and **7–8**) and chloroform (for compounds **5–6** and **9–10**) as eluents to afford the desired 2-chloro-3-formylpyrido[2,3-*b*]porphyrins **3**, **5**, **7**, and **9**, and 3-formylpyrido[2,3-*b*]porphyrins **4**, **6**, **8**, and **10** in 18–54% isolated yields. Characterization data of representative porphyrins **3** and **4** are given below.

#### Nickel(II) Pyrido[2,3-*b*]porphyrin (3)

Yield: 55 mg (51%); purple solid; mp >300 °C.

UV:  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup>cm<sup>-1</sup>): 439 (51.99), 558 (2.71), 608 (3.49) nm.

IR (CHCl<sub>3</sub>): 3056, 3024, 2923, 2853, 1667, 1575, 1540, 1451, 1395, 1360, 1300, 1246, 1187, 1152, 1076, 1011, 966, 853, 790, 755, 705, 671 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.23 (s, 1 H, CHO), 8.95 (s, 1 H, pyridine H), 8.73–8.65 (m, 5 H,  $\beta$ -pyrrolic H), 8.60 (d, *J* = 5.08 Hz, 1 H,  $\beta$ -pyrrolic H), 8.00–7.88 (m, 7 H, *meso*-ArH), 7.80–7.64 (m, 11 H, *meso*-ArH), 7.21 (d, *J* = 8.52 Hz, 1 H, *meso*-ArH), 7.07 (d, *J* = 8.52 Hz, 1 H, *meso*-ArH).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 188.13, 156.79, 149.32, 144.42, 143.96, 142.47, 142.22, 142.12, 141.78, 139.91, 139.58, 139.29, 137.98, 136.23, 135.67, 134.87, 133.74, 133.52, 133.45, 133.25, 133.08, 132.66, 132.27, 131.98, 131.38, 128.87, 128.31, 128.14, 127.50, 127.18, 126.99, 123.05, 121.05, 120.39, 116.52, 115.94.

HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>48</sub>H<sub>29</sub>ClN<sub>5</sub>NiO<sup>+</sup>: 784.1409; found: 784.1407.

#### Nickel(II) Pyrido[2,3-*b*]porphyrin (4)

Yield: 23 mg (22%); purple solid; mp >300 °C.

UV:  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup>cm<sup>-1</sup>): 442 (29.84), 559 (1.95), 606 (1.82) nm.

IR (CHCl<sub>3</sub>): 3058, 2922, 2853, 1666, 1574, 1521, 1461, 1395, 1355, 1167, 1123, 1075, 1013, 941, 859, 789, 753, 704 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.23 (s, 1 H, CHO), 9.14 (s, 1 H, pyridine H), 9.01 (s, 1 H, pyridine H), 8.72–8.58 (m, 6 H,  $\beta$ -pyrrolic H), 7.99–7.64 (m, 18 H, *meso*-ArH), 7.22–7.18 (m, 1 H, *meso*-ArH), 7.06–6.99 (m, 1 H, *meso*-ArH).

HRMS (ESI): *m/z* [M + K]<sup>+</sup> calcd for C<sub>48</sub>H<sub>29</sub>N<sub>5</sub>KNiO<sup>+</sup>: 788.1357; found: 788.2294.

#### Nickel(II) Pyrido[2,3-*b*]porphyrins **11** and **12**

To a solution of nickel(II) 2-chloro-3-formylpyrido[2,3-*b*]porphyrin or nickel(II) 3-formylpyrido[2,3-*b*]porphyrin **3** or **4** (0.05 mmol) in dichloromethane (20 mL), malononitrile (0.4 mmol) and triethylamine (0.15 mmol) were added and the reaction mixture was stirred at r.t.

for 30 minutes. Upon completion of reaction, the mixture was diluted with chloroform (20 mL) and washed twice with water (2 × 40 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The crude porphyrin **11** was purified on neutral alumina column using 40% chloroform in hexane as eluent. However, porphyrin **12** was obtained in a sufficiently pure form by trituration of the crude solid with methanol. Characterization data of title porphyrins are given below.

#### Nickel(II) Pyrido[2,3-*b*]porphyrin (**11**)

Yield: 34 mg (81%); greenish-purple solid; mp >300 °C.

UV:  $\lambda_{\text{max}}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup>cm<sup>-1</sup>): 455 (29.84), 552 (2.15), 632 (4.62) nm.

IR (CHCl<sub>3</sub>): 3057, 3022, 2920, 2851, 2226, 1571, 1540, 1451, 1395, 1356, 1300, 1190, 1133, 1009, 969, 922, 847, 792, 752, 705, 670 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.34 (s, 1 H, pyridine H), 8.71–8.65 (m, 5 H,  $\beta$ -pyrrolic H), 8.60 (d, *J* = 4.96 Hz, 1 H,  $\beta$ -pyrrolic H), 7.99–7.93 (m, 4 H, *meso*-ArH), 7.89–7.79 (m, 5 H, *meso*-ArH), 7.76–7.68 (m, 9 H, *meso*-ArH), 7.24–7.20 (m, 1 H, *meso*-ArH), 7.13 (s, 1 H, vinylic H), 7.06–7.02 (m, 1 H, *meso*-ArH).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 156.92, 155.23, 149.49, 144.75, 144.51, 142.66, 141.92, 141.10, 139.35, 138.96, 138.87, 138.38, 136.08, 135.60, 135.06, 134.73, 133.99, 133.81, 133.43, 133.26, 132.80, 132.69, 132.53, 132.33, 131.32, 129.48, 128.97, 128.60, 128.22, 128.00, 127.81, 127.36, 127.24, 127.08, 123.18, 121.33, 120.60, 116.15, 114.08, 113.38.

HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>51</sub>H<sub>29</sub>ClN<sub>7</sub>Ni<sup>+</sup>: 832.1521; found: 832.1548.

#### Nickel(II) Pyrido[2,3-*b*]porphyrin (**12**)

Yield: 33 mg (83%); greenish-purple solid; mp >300 °C.

UV:  $\lambda_{\text{max}}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup>cm<sup>-1</sup>): 461 (22.56), 564 (2.05), 632 (3.73) nm.

IR (CHCl<sub>3</sub>): 3057, 3020, 2919, 2852, 2224, 1567, 1528, 1448, 1356, 1211, 1128, 1075, 1011, 915, 747 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.41 (s, 1 H, pyridine H), 9.35 (s, 1 H, pyridine H), 8.74–8.59 (m, 6 H,  $\beta$ -pyrrolic H), 7.97–7.68 (m, 18 H, *meso*-ArH), 7.23–7.20 (m, 1 H, *meso*-ArH), 7.08–7.03 (m, 2 H, *meso*-ArH, vinylic H).

HRMS (ESI): *m/z* [M + K]<sup>+</sup> calcd for C<sub>51</sub>H<sub>29</sub>N<sub>7</sub>KNi<sup>+</sup>: 836.1469; found: 836.2321.

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#### Supporting Information

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