

# Fusion and Desulfurization Reactions of Thiomorpholinochlorins

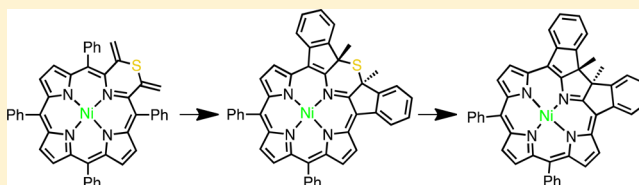
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**S** Supporting Information

**ABSTRACT:** An unusually nonplanar, ruffled structure that had been suspected for the previously reported [2,3-bismethylenethiomorpholinochlorinato]nickel(II) complex was confirmed by determination of its crystal structure. Treatment of this thiomorpholinochlorin with acid converts the exocyclic double bonds to direct links to the *ortho*-positions of both adjacent *meso*-phenyl groups. The crystal structure of this product indicated that the introduction of these linkages did not change the overall conformation of the macrocycle. The reactivity of the bis-linked thiomorpholine moiety with respect to Raney-nickel-induced (hydro)desulfurization reactions was probed, forming a bis-phenyl-linked 2,3-dimethylchlorin, also characterized by X-ray diffraction, and a bis-indene-annulated porphyrin. We also report on the synthesis of the oxygen analogue to the bis-linked thiomorpholine by reaction of a secochlorin bisketone nickel complex with Woollins' reagent. We thus introduce novel methodologies toward the synthesis of porphyrinoids carrying  $\beta$ -to-*ortho*-phenyl fusions and expand on the scope and limits of the chemistry and interconversion of pyrrole-modified porphyrins.

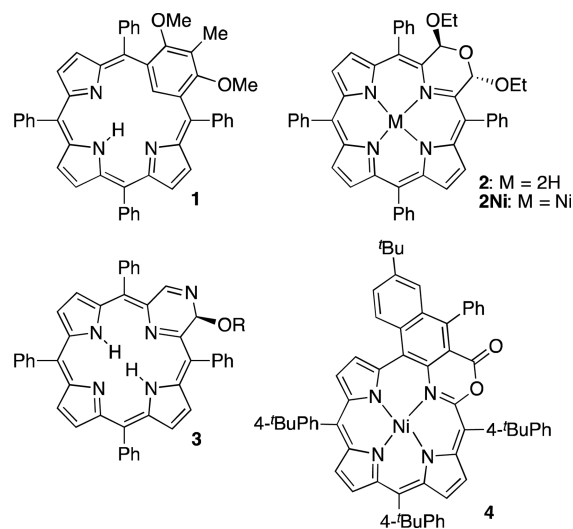


## INTRODUCTION

Synthetic chlorins and their analogues are of potential utility in a number of medical and technical applications, including as photochemotherapeutics,<sup>1</sup> optical labels,<sup>2</sup> imaging agents,<sup>3</sup> components in functional devices,<sup>4</sup> light-harvesting dyes,<sup>5</sup> or catalysts.<sup>6</sup> In most of these applications, it is desirable to possess the ability to tune the optical properties of the porphyrinoid of choice. This tuning can be accomplished, for instance, by the modification of the chromophore periphery with  $\pi$ -conjugated substituents,<sup>7</sup> their conversion to hydro-porphyrins,<sup>8</sup> or by adjustment of the planarity of the chromophore—nonplanar chromophores generally absorb at longer wavelengths than their planar analogues.<sup>9</sup>

We and others have achieved the synthesis of porphyrinoids by formal replacement of a pyrrole in porphyrins by a six-membered ring.<sup>8b,10–14</sup> Examples of such porphyrin or chlorin analogues are the carbaporphyrinoid benzporphyrin **1**<sup>10a,14</sup> or the pyrrole-modified porphyrinoids morpholinochlorin **2**/**2Ni**<sup>12</sup> or pyrazinoporphyrin **3**.<sup>13</sup> Compound **1** was synthesized from monopyrrolic precursors.<sup>11</sup> Oxypyriporphyrins can be accessed using either total synthesis or porphyrin modification methodologies,<sup>10,14,15</sup> whereas access to pyrazinoporphyryns<sup>13,16</sup> and morpholinochlorins<sup>12,17</sup> is exclusively along porphyrin modification strategies. Other examples, such as lactone **4**, were discovered as fortuitous products along nongeneralizable reaction pathways.<sup>18</sup> Lactone **4** is also an example for porphyrinoids containing a nonpyrrolic heterocycle and a covalent linkage to a neighboring *meso*-aryl group.<sup>10,17</sup>

We introduced 2,3-dimethylenethiomorpholinochlorin as its nickel(II) complex **8Ni**.<sup>15d</sup> It was prepared by reaction of the bisketone-substituted secochlorin **6Ni** with Lawesson's reagent<sup>19</sup> (Scheme 1). The secochlorin was made by oxidative

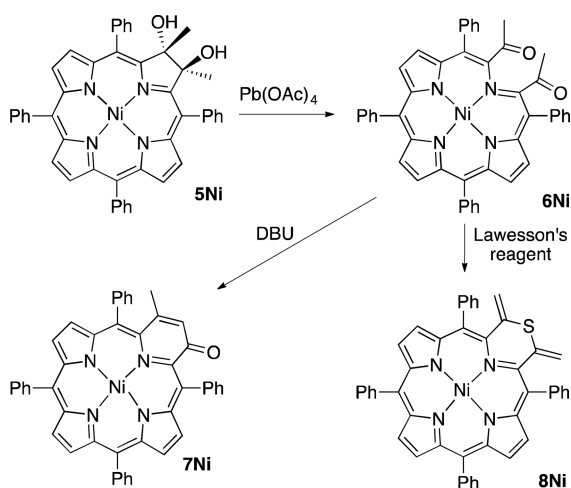


diol cleavage of diol **5Ni**, itself available by MeMgBr addition to well-known *meso*-tetraphenyl-2,3-dioxochlorin.<sup>20</sup>

Contrary to the well-studied benzporphyrins,<sup>10a</sup> we note that only little of the chemistry of the porphyrinoids containing six-membered heterocycles was reported.<sup>10–14</sup> We detail here our investigation into the conversions of thiomorpholinochlorins with respect to the formation of linkages to the *ortho*-position of the flanking *meso*-phenyl groups and (hydro)desulfurization reactions, leading to the formation of a number of novel porphyrinoids.

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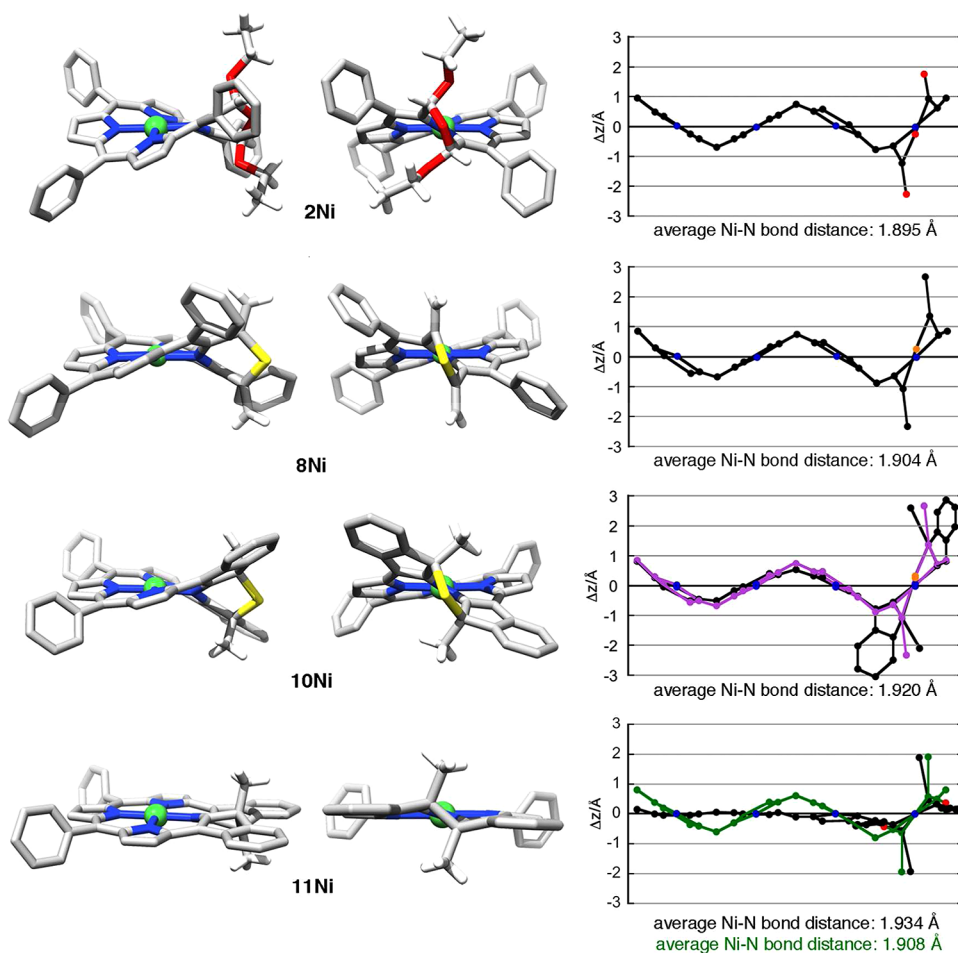
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Scheme 1. Known Synthesis of Thiomorpholinochlorin 8Ni<sup>15d</sup>

## RESULTS AND DISCUSSION

**X-ray Crystal Structure of [2,3-Dimethylene-thiomorpholinochlorinato]nickel(II) 8Ni.** We were now able to grow crystals of the nickel complex of 2,3-dimethylene-thiomorpholinochlorin 8Ni suitable for X-ray diffraction analysis (Figure 1). Its considerably ruffled conformation (of helimeric chirality) is comparable to that observed in morpholinochlorin 2Ni.<sup>12</sup> At first glance, the minimal conformational effects that the presence of the ring sulfur and the two  $\text{sp}^2$ -ring carbons in the thiomorpholine moiety elicit, when compared to the conformation of the morpholinochlorin nickel complex 2Ni bearing the smaller ring oxygen and two  $\text{sp}^3$ -ring carbons in the morpholine moiety, are surprising. However, this highlights once again that the conformations of these classes of porphyrinoids are largely determined by their coordination to the relatively small low-spin nickel(II) ion.<sup>12,21</sup> Correspondingly, the average Ni–N bond distances are similarly short in both molecules.

**Acid-Induced Ring-Closure Reaction of Thiomorpholinochlorin 8Ni.** Treatment of the thiomorpholinochlorin 8Ni with 3.3% TFA/ $\text{CH}_2\text{Cl}_2$  at ambient temperature converted the olive-green-colored, nonpolar starting material in good yield



**Figure 1.** Stick representation of the single-crystal X-ray structure of the compounds indicated: left column, oblique view; middle column, front view. Only one of the two enantiomers present in the crystals of the racemic mixture of the compounds is shown, and for 11Ni, only one of two independent molecules is shown. The hydrogen atoms on the *meso*-phenyl groups and the  $\beta$ -positions, all disorder, and solvent molecules are omitted for clarity. For details, see Supporting Information. Right column: Out-of-plane displacement plots of the chlorin macrocycle of the experimentally determined conformations of the compounds indicated. The plot for 10Ni (black) is overlaid with the out-of-plane displacement plot for 8Ni (pink); the plot for 11Ni (black) is overlaid with the out-of-plane displacement plot for 5Ni (green).

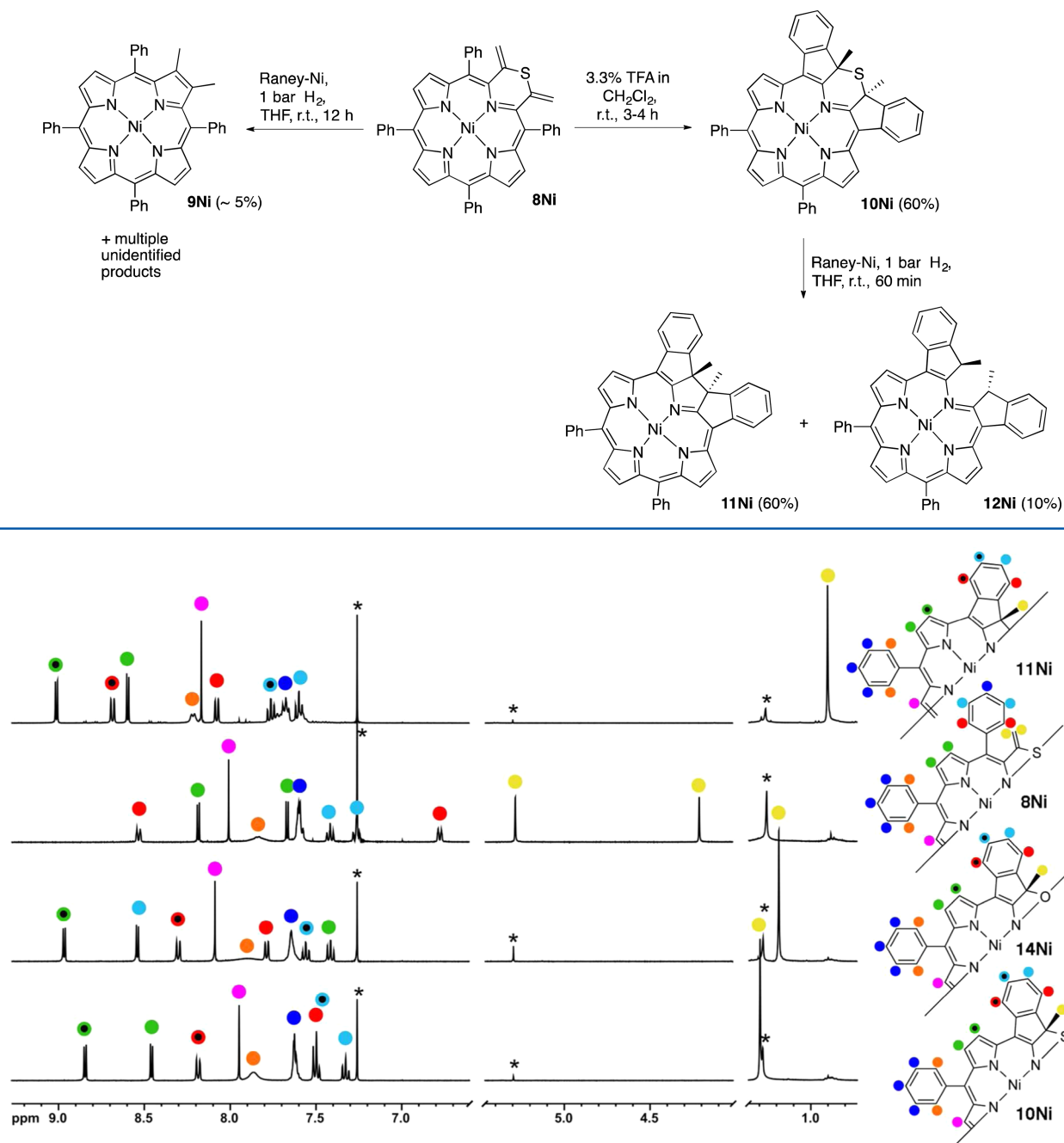
Scheme 2. Transformations of Thiomorpholinochlorin **8Ni**

Figure 2.  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ , 298 K) of the compounds indicated; \* = solvent peak.

into a dark green, nonpolar product, **10Ni** (Scheme 2). The composition of **10Ni** (as per ESI+ HR-MS,  $\text{C}_{46}\text{H}_{30}\text{N}_4\text{NiS}$  for  $[\text{M}^+]$ ) was identical to that of the starting material, indicating that merely an isomerization had taken place. The  $^1\text{H}$  NMR spectrum of the product showed that the two-fold symmetry of **8Ni** was retained; the methylene protons were replaced by methyl groups, and the diagnostic shifts and pattern for the presence of a  $\beta$ -to-*ortho*-phenyl linkage became evident (Figure 2). This suggested a bis-phenyl-linked connectivity. Connectivity and relative *trans*-stereochemistry of the morpholine methyl groups in **10Ni** were confirmed by X-ray diffractometry (Figure 1).

The establishment of two linkages with the two  $\beta$ -methyl groups in a *trans*-configuration can be rationalized by a

Markovnikov addition of a proton to the exocyclic double bond, followed by a Friedel–Crafts-type alkylation of the *ortho*-positions of the flanking *meso*-phenyl groups in the twisted conformation of the ring fusions. Irrespective of the ring fusions that took place, the conformation of the macrocycle of **10Ni** is nearly identical to that of its parent compound **8Ni** (Figure 1). Nonetheless, a slight lengthening of the Ni–N bond distances is observed, a sign of some in-plane distortions imposed by the fusions. Overall, the conformation highlights again the enormous influence the central nickel ion possesses on the conformation of these porphyrinoids.<sup>12,21</sup>

The UV–vis spectrum of **10Ni** is metallochlorin-like, but compared to the spectrum of **8Ni**, the Soret band is 14 nm red-shifted and the Q-band region is significantly broadened

(Figure 3). We attribute this to the electronic effects of the coplanar annulated *meso*-phenyl groups. A number of

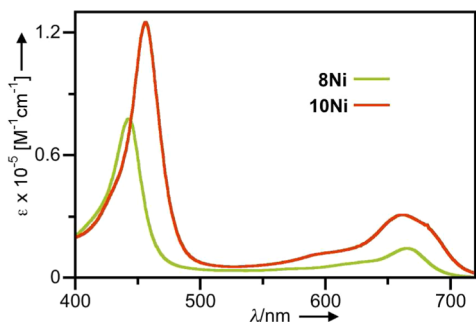


Figure 3. UV-vis spectra ( $\text{CH}_2\text{Cl}_2$ ) of the compounds indicated.

precedents of such intramolecular ring fusions were described for porphyrins, in general,<sup>7a</sup> and for morpholinochlorins, in particular.<sup>12</sup> These examples already illustrated the only modest electronic influences of one or two idealized coplanar *meso*-phenyl groups linked to the  $\beta$ -position.

**Reaction of [Thiomorpholinochlorinato]nickel(II) 8Ni with Raney Nickel.** Raney nickel is well-known to induce hydrodesulfurization reactions.<sup>22</sup> When 2,3-dimethylenethiomorpholinochlorin 8Ni is treated with Raney nickel in THF at ambient temperature and 1 bar  $\text{H}_2$  pressure, a multitude of porphyrinic products were formed. We isolated and identified a red-colored compound, 9Ni, with a regular metalloporphyrin-like UV-vis spectrum (see the Supporting Information) in low (~5%) yields (Scheme 2). The HR-MS (ESI+ 100%  $\text{CH}_3\text{CN}$ ) analysis indicated the loss of the sulfur and that a formal hydrogenation had taken place. Its  $^1\text{H}$  NMR spectrum suggested a [*meso*-tetraphenyl-2,3-dimethylporphyrinato]-nickel(II) structure for 9Ni. While this synthesis of a  $\beta,\beta'$ -dimethylporphyrin has no practical value,<sup>23</sup> from a fundamental point of view, the outcome was encouraging. It demonstrated that thiomorpholinochlorin 8Ni is susceptible to Raney-nickel-induced reduction and desulfurization reactions while maintaining the porphyrin framework. We rationalize the formation of the many reaction products with the convolution of three functional groups that are affected by the reaction conditions. This assessment proved to be correct, as indicated by the (hydro)desulfurization experiments on thiomorpholine derivative 10Ni lacking the exocyclic double bonds.

**Raney-Nickel-Induced Desulfurization Reactions of Bis-Fused [Morpholinochlorinato]nickel(II) 10Ni.** On reacting bis-fused thiomorpholinochlorin 10Ni with Raney nickel and  $\text{H}_2$  at ambient conditions (Scheme 2), a mixture of two nonpolar compounds was formed, 11Ni (major product, 60% yield) and 12Ni (minor product, 10% yield). The composition of both compounds, as per HR-MS (for  $[\text{M}]^+$ ), was  $\text{C}_{46}\text{H}_{30}\text{N}_4\text{Ni}$  and  $\text{C}_{46}\text{H}_{32}\text{N}_4\text{Ni}$ , respectively, indicating the absence of sulfur, identical C and N atom counts as found in the starting material, and their difference by 2H atoms. The  $^1\text{H}$  NMR spectra of both products showed significant chemical shift differences, but both exhibited two-fold symmetry, the retention of the *ortho*-linked phenyl groups, and the presence of two  $\text{sp}^3$ -hybridized carbons, one of which belonged to a methyl group (Figure 2 and Supporting Information). Two significant differences are that the two equivalent methyl groups in 11Ni appear as a singlet, while those of 12Ni are coupled with a proton at 5.4 ppm, and 11Ni possesses a near-regular

metallochlorin UV-vis spectrum, but the spectrum for 12Ni is very red-shifted and broadened (Figure 4). We thus assigned 11Ni and 12Ni the bis-phenyl-linked 2,3-*trans*-dimethylchlorin and bisindene-annulated structures, respectively.

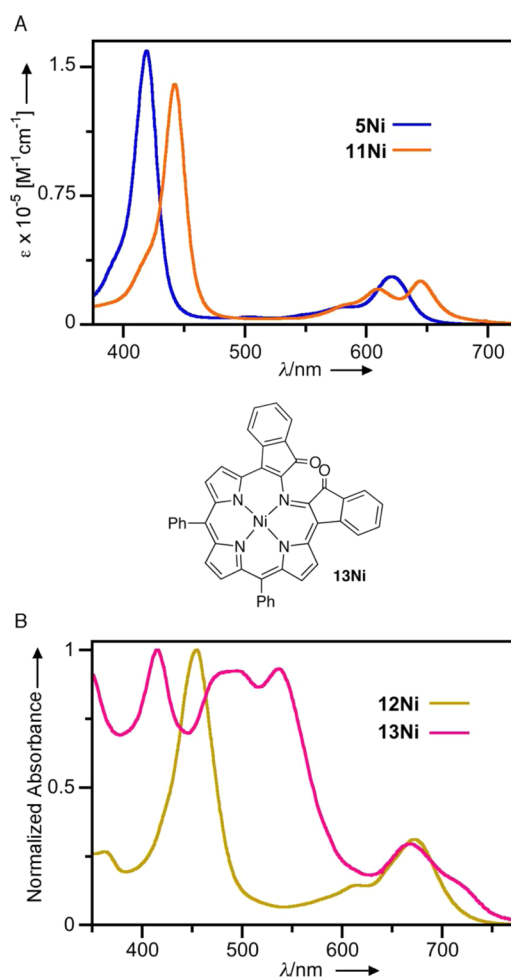


Figure 4. UV-vis spectra ( $\text{CH}_2\text{Cl}_2$ ) of the compounds indicated.

The connectivity of the dimethylchlorin nickel complex 11Ni could be confirmed by single-crystal X-ray diffraction (Figure 1). Using the Ni–N bond distances as a measure of planarity,<sup>24</sup> this nickel chlorin is, with a relatively long average Ni–N bond distance of 1.934 Å, significantly more planar than the nickel chlorin analogues discussed above and  $\beta,\beta'$ -dihydroxydimethylmetallochlorin 5Ni (average Ni–N bond distance of 1.908 Å)<sup>15d</sup> lacking the fusions to the phenyl groups. As a result of the fusions to the phenyl groups, chlorin 11Ni is similarly planar like the metalloporphyrin [*meso*-tetraphenylporphyrinato]nickel(II) (1.931 Å).<sup>25</sup>

Despite its more planar structure, the UV-vis spectrum of bis-fused  $\beta,\beta'$ -dimethylmetallochlorin 11Ni is very red-shifted compared to that of the nonfused metallochlorin 5Ni (Figure 4A). We attribute this to the electronic effects of the coplanar phenyl groups and possibly its inherent strain. The UV-vis spectrum of indene-annulated porphyrin nickel complex 12Ni is a broadened nickel chlorin-like spectrum. In comparison, the UV-vis spectrum of indaphyrin nickel complex 13Ni, an analogue of 12Ni in which the methyl moieties are replaced by carbonyl groups, is much distorted and falls into its own category (Figure 4B).<sup>7c,26</sup> This highlights the enormous

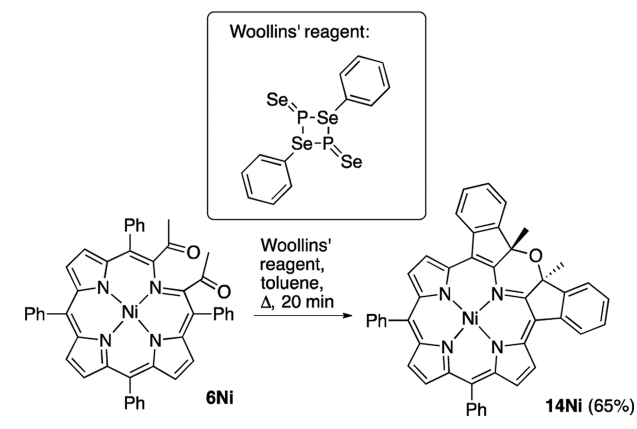
influence the conjugated ketone functionalities have on the chromophore. While we previously suspected this influence of the keto groups,<sup>7c,26</sup> this is the first direct evidence. Unlike the chemically very fragile nickel indaphyrin **13Ni**,<sup>7c</sup> its indene analogue **12Ni** appears to be more stable. However, due to its low yield and the great difficulty separating it from **11Ni** because of their similar  $R_f$  values, only small amounts of this material became available.

#### Reaction of Secochlorin **6Ni** with Woollins' Reagent.

We previously showed that an aldol condensation of bisketone **6Ni** resulted in the formation of oxyppyriporphyrin **7Ni** (Scheme 1).<sup>15d</sup> Thus, the reactivity of the carbonyl groups of secochlorinato nickel complex **6Ni** suggests that it possesses potential for the synthesis of other novel porphyrinoids containing nonpyrrolic heterocycles.

Woollins' reagent is the selenium analogue to Lawesson's reagent. It has been used to selenate carboxylic acids, alkenes, alkynes, and nitriles.<sup>27</sup> We reacted Woollins' reagent with brown-colored secochlorin bisketone **6Ni** in the hopes to generate a selenomorpholinochlorin analogue to thiomorpholinochlorin **8Ni** (Scheme 3). The reaction rapidly formed a

**Scheme 3.** Reaction of Secochlorin **8Ni** with Woollins' Reagent

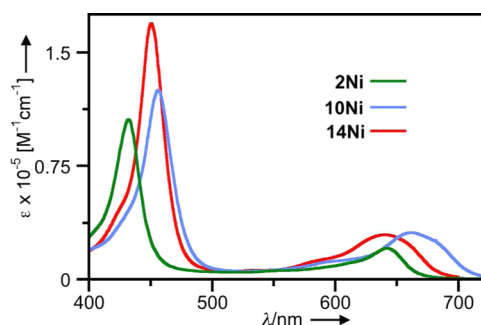


dark green and nonpolar compound **14Ni** that could be isolated in good yield. HR-MS (ESI+ 100%  $\text{CH}_3\text{CN}$ ) indicated it possessed a molecular formula of  $\text{C}_{46}\text{H}_{30}\text{N}_4\text{NiO}$  (for  $[\text{M}^+]$ ); that is, no selenium was incorporated into the product. Compared to the composition of the starting material, the product lost the elements of one molecule of  $\text{H}_2\text{O}$ . The absence of a carbonyl group was confirmed by its IR and  $^{13}\text{C}$  NMR spectra. The  $^1\text{H}$  NMR spectrum of product **14Ni** indicated the two-fold symmetry of the product and the hallmarks for the presence of an *ortho*-linked phenyl group (Figure 2). Thus, we derive the bis-fused morpholinochlorin structure **14Ni** shown.

The mechanism of formation of **14Ni** is not known, but several nucleophile-induced secochlorin bicarbonyl-to-morpholinochlorin reactions involving a number of nucleophiles are reported<sup>12</sup> as are intramolecular Friedel–Crafts-type mono- and bisbenzylations of the *ortho*-positions of the *meso*-phenyl groups in morpholinochlorins.<sup>12,17</sup> This methodology to access the bis-linked morpholinochlorin nickel complex **14Ni** is superior to that for the acid-induced cyclization of **2Ni** described previously.<sup>12</sup> With **14Ni** in hand, we now also found small amounts of this product in the Lawesson's-reagent-

induced formation of **10Ni**, suggesting that the reaction is not specific to the selenium-based reagent.

Structurally, we predict **14Ni** to be similar to its sulfur analogue **10Ni** but perhaps slightly less nonplanar. Correspondingly, the  $^1\text{H}$  NMR spectra of **10Ni** and **14Ni** resemble each other, but the metallochlorin-like UV–vis spectrum of the oxygen analogue **14Ni** is (24 nm for  $\lambda_{\text{max}}$ ) blue-shifted (Figure 5). The red shifts of the spectrum of **14Ni** relative to the spectrum of **2Ni** illustrate the electronic effects of the two ring fusions.



**Figure 5.** UV–vis spectra ( $\text{CH}_2\text{Cl}_2$ ) of the compounds indicated.

## CONCLUSIONS

In conclusion, our investigations detailed the conversions of thiomorpholinochlorins along chemical pathways hitherto uncharted for pyrrole-modified porphyrins, leading to the formation of novel porphyrinoids with broadly varying frameworks and optical properties. The ruffled conformations of many of the derivatives prepared were largely controlled by the presence of the small nickel(II) ion in the center of the macrocycles. Also considering the possible subsequent interconversion reactions of pyrrole-modified porphyrins that are possible, this work further highlights the plasticity of the “breaking and mending of porphyrins” approach toward the synthesis of chlorin analogues containing nonpyrrolic building blocks. The unconventional paths toward the generation of bis-phenyl-fused morpholinochlorins reported here are superior to alternate ring-closure methods previously applied.

## EXPERIMENTAL SECTION

**Materials.** All solvents and reagents were used as received. [Secochlorinato]nickel **6Ni** and [thiomorpholinochlorinato]nickel **8Ni** were prepared as described in the literature.<sup>15d</sup> Raney nickel was purchased as a 50% slurry in water at basic pH.

**Warning:** Raney nickel is potentially pyrophoric, should be kept wet, and needs to be disposed of properly.

**Preparation of Compounds.** [*meso*-Tetraphenyl-2,3-dimethylporphyrinato]nickel(II) (**9Ni**). To a solution of [*meso*-tetraphenyl-2,3-dimethylene-2a-thio-2a-homoporphyrinato]nickel(II) **8Ni** (25 mg,  $3.43 \times 10^{-5}$  mol) in THF (10 mL) was added Raney-Ni (~2.0 mL of a 50% slurry in  $\text{H}_2\text{O}$ ), and the reaction mixture was stirred for 12 h at rt under a  $\text{H}_2$  atmosphere (provided by balloon). After the starting material was consumed (reaction monitored by TLC), the catalyst was filtered off by gravity filtration. The organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and evaporated to dryness by rotary evaporation. The crude product was purified by preparative TLC plates (20 × 20 cm, 500  $\mu\text{m}$  silica–1:3  $\text{CH}_2\text{Cl}_2$ /hexanes) to provide a red-colored product **9Ni** in low yield ~5% (1–2 mg). **9Ni**: MW = 699.48 g/mol;  $R_f$  = 0.34 (silica–1:3  $\text{CH}_2\text{Cl}_2$ /hexanes);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 300 K)  $\delta$  8.67 (s, 2H), 8.62 (s, 4H), 7.99–7.97 (m, 4H), 7.87–7.85 (m, 4H), 7.66–7.60

(m, 12H), 2.23 (s, 6H) ppm; UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 442 (1.00), 587 (sh), 609 (4.31), 644 (4.40) nm; HR-MS (ESI+, 100%  $\text{CH}_3\text{CN}$ , TOF) calcd for  $\text{C}_{46}\text{H}_{32}\text{N}_4\text{Ni}$  ( $[\text{M}]^+$ ) 698.1980, found 698.1978.

[*meso*-Tetraphenyl-2,3-dimethyl-2a-thio-2a-homoporphyrinato]nickel(III) (**10Ni**). To a solution of [*meso*-tetraphenyl-2,3-dimethylene-2a-thio-2a-homoporphyrinato]nickel(II) **8Ni** (20 mg,  $2.74 \times 10^{-5}$  mol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added TFA (2.5 mL of a 10% solution in  $\text{CH}_2\text{Cl}_2$ ), and the reaction mixture was stirred at ambient conditions. The progress of the reaction was monitored by TLC. Once the starting material was exhausted (4 h), the excess acid was quenched by adding  $\text{Et}_3\text{N}$  (2 mL) and the organic layer was washed with water ( $3 \times 10$  mL). The organic layer was isolated, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and evaporated to dryness by rotary evaporation. The crude product was purified by preparative TLC (20  $\times$  20 cm, 500  $\mu\text{m}$  silica-1:1  $\text{CH}_2\text{Cl}_2$ /hexanes), providing **10Ni** as a green powder in a yield of 60% (12 mg). **10Ni**: MW = 729.53 g/mol;  $R_f$  = 0.75 (silica-1:1  $\text{CH}_2\text{Cl}_2$ /hexanes);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 320 K)  $\delta$  8.85 (d,  $J$  = 4.9 Hz, 2H), 8.46 (d,  $J$  = 4.8 Hz, 2H), 8.19 (d,  $J$  = 7.5 Hz, 2H), 7.95 (s, 2H), 7.86 (br s, 4H), 7.63–7.60 (m, 6H), 7.50 (t,  $J$  = 7.1 Hz, 4H), 7.33 (t,  $J$  = 7.2 Hz, 2H), 1.30 (s, 6H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 300 K)  $\delta$  154.2, 145.8, 143.0, 142.9, 139.5, 139.48, 138.6, 135.4, 132.8, 129.5, 128.7, 128.0, 127.2, 126.6, 126.3, 124.9, 122.9, 110.5, 29.9 ppm; UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 456 (5.10), 596 (sh), 661 (4.49) nm; HR-MS (ESI+, 100%  $\text{CH}_3\text{CN}$ , TOF) calcd for  $\text{C}_{46}\text{H}_{30}\text{N}_4\text{NiS}$  ( $[\text{M}]^+$ ) 728.1545, found 728.1550.

Bisphenyl-Linked [*meso*-Tetraphenyl-2,3-dimethylchlorinato]nickel(III) (**11Ni**) and [*meso*-Tetraphenyl-2,3-dimethylindeno-phyrinato]nickel(III) (**12Ni**). To a solution of [*meso*-tetraphenyl-2,3-dimethyl-2a-thio-2a-homoporphyrinato]nickel(II) **10Ni** (25 mg,  $3.43 \times 10^{-5}$  mol) in THF (10 mL) was added Raney-Ni ( $\sim 1.0$  mL of a 50% slurry of Raney-Ni in  $\text{H}_2\text{O}$ ), and the reaction mixture was stirred for 1 h at rt under a  $\text{H}_2$  atmosphere (provided by balloon). After the starting material was consumed (reaction monitored by TLC), the catalyst was filtered off by gravity filtration. The organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and evaporated to dryness by rotary evaporation. The crude products were purified by preparative HPTLC plates (10  $\times$  10 cm, with 2.5  $\times$  10 cm concentration zone, silica-1:9  $\text{CH}_2\text{Cl}_2$ /petroleum ether 30-60) to yield **11Ni** in 50–60% yield (12–14 mg) and **12Ni** in 8–10% yield (2 mg). **11Ni**: MW = 697.47 g/mol;  $R_f$  = 0.40 (silica-1:9  $\text{CH}_2\text{Cl}_2$ /petroleum ether 30-60);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 300 K)  $\delta$  9.01 (d,  $J$  = 4.9 Hz, 2H), 8.69 (d,  $J$  = 7.7 Hz, 2H), 8.60 (d,  $J$  = 4.8 Hz, 2H), 8.22 (d,  $J$  = 7.1 Hz, 2H), 8.17 (s, 2H), 8.08 (d,  $J$  = 7.0 Hz, 2H), 7.76 (dd,  $J$  = 7.6, 6.5 Hz, 2H), 7.69–7.66 (m, 4H), 7.62–7.58 (m, 4H), 0.90 (s, 6H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 300 K)  $\delta$  170.2, 146.8, 145.0, 144.4, 142.4, 140.9, 139.5, 134.0, 133.2, 133.0, 129.3, 128.6, 127.7, 126.9, 125.7, 125.4, 124.6, 123.4, 122.6, 109.0, 66.5, 22.2 ppm; UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 442 (5.15), 587 (sh), 609 (4.31), 644 (4.40) nm; HR-MS (ESI+, 100%  $\text{CH}_3\text{CN}$ , TOF) calcd for  $\text{C}_{46}\text{H}_{30}\text{N}_4\text{Ni}$  ( $[\text{M}]^+$ ) 696.1824, found 696.1816. **12Ni**: MW = 699.48 g/mol;  $R_f$  = 0.36 (silica-1:9  $\text{CH}_2\text{Cl}_2$ /petroleum ether 30-60);  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K)  $\delta$  8.81 (d,  $J$  = 4.8 Hz, 2H), 8.41 (d,  $J$  = 4.8 Hz, 2H), 7.99 (d,  $J$  = 7.7 Hz, 2H), 7.91 (s, 2H), 7.84 (br s, 2H), 7.63–7.60 (m, 6H), 7.48 (d,  $J$  = 7.4 Hz, 2H), 7.43 (t,  $J$  = 7.6 Hz, 2H), 7.25 (t,  $J$  = 7.4 Hz, 2H), 5.43 (q,  $J$  = 7.4 Hz, 2H), 0.96 (d,  $J$  = 7.5 Hz, 6H) ppm; UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 454 (4.61), 615 (sh), 672 (4.11) nm; HR-MS (ESI+, 100%  $\text{CH}_3\text{CN}$ , TOF) calcd for  $\text{C}_{46}\text{H}_{32}\text{N}_4\text{Ni}$  ( $[\text{M}]^+$ ) 698.1980, found 698.1993.

[*meso*-Tetraphenyl-2,3-dimethylene-2a-oxo-2a-homoporphyrinato]nickel(III) (**14Ni**). To a solution of [*meso*-tetraphenyl-1,4-diacetyl-chlorophinato]nickel(II) **6Ni** (25 mg,  $3.42 \times 10^{-5}$  mol) in toluene (10 mL) was added Woollins' reagent (72 mg,  $1.36 \times 10^{-4}$  mol). The reaction mixture was stirred for 20 min at ambient temperature and then gradually heated to reflux. The color of the solution turned from dark brown to green over the course of the reaction. After the starting material was consumed (reaction control by TLC, silica gel- $\text{CH}_2\text{Cl}_2$ ), the reaction was cooled and filtered through a short plug of silica gel. The solvent was removed by rotary evaporation, and the crude product was purified by preparative TLC

(20  $\times$  20 cm, 500  $\mu\text{m}$  silica- $\text{CH}_2\text{Cl}_2$ ). **14Ni** was isolated as a bright green powder in 65% yield (16 mg). **14Ni**: MW = 713.47 g/mol;  $R_f$  = 0.63 (silica-1:1  $\text{CH}_2\text{Cl}_2$ /hexanes);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 320 K)  $\delta$  8.97 (d,  $J$  = 4.9 Hz, 2H), 8.54 (d,  $J$  = 4.9 Hz, 2H), 8.30 (d,  $J$  = 7.6 Hz, 2H), 8.09 (s, 2H), 7.90 (br s, 2H), 7.79 (dd,  $J$  = 7.35, 0.40 Hz, 2H), 7.64 (m, 6H), 7.56 (td,  $J$  = 7.6, 1.1 Hz, 2H), 7.41 (td,  $J$  = 7.4, 0.8 Hz, 2H), 1.19 (s, 6H) ppm;  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 300 K)  $\delta$  152.3, 145.6, 143.1, 142.2, 140.24, 140.1, 139.3, 135.1, 133.1, 130.1, 129.6, 128.1, 127.2, 127.1, 125.4, 125.0, 123.6, 122.8, 109.6, 82.3, 25.9 ppm; UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 451 (5.23), 588 (sh), 641 (4.47) nm; HR-MS (ESI+, 100%  $\text{CH}_3\text{CN}$ , TOF) calcd for  $\text{C}_{46}\text{H}_{30}\text{N}_4\text{NiO}$  ( $[\text{M}]^+$ ) 712.1773, found 712.1780.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02383.

Reproduction of the  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, and IR spectra of all obtained compounds and all experimental details of the crystal structure determinations (PDF)

X-ray data for **11Ni** (CIF)

X-ray data for **10Ni** (CIF)

X-ray data for **8Ni** (CIF)

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) (a) Bonnett, R. *Chem. Soc. Rev.* **1995**, *24*, 19–33. (b) Pandey, R. K.; Zheng, G. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 6, pp 157–230. (c) Brandis, A. S.; Salomon, Y.; Scherz, A. In *Chlorophylls and Bacteriochlorophylls*; Grimm, B., Porra, R. J., Rüdinger, W., Scheer, H., Eds.; Springer: Dordrecht, The Netherlands, 2006; pp 485–494.
- (2) de Haas, R. R.; van Gijlswijk, R. P. M.; van der Tol, E. B.; Zijlmans, H. J. M. A. A.; Bakker-Schut, T.; Bonnet, J.; Verwoerd, N. P.; Tanke, H. J. *J. Histochem. Cytochem.* **1997**, *45*, 1279–1292.
- (3) (a) Schäferling, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 3532–3554. (b) Huang, H.; Song, W.; Rieffel, J.; Lovell, J. F. *Front. Phys.* **2015**, *3*, 23.
- (4) Jurow, M.; Schuckman, A. E.; Batteas, J. D.; Drain, C. M. *Coord. Chem. Rev.* **2010**, *254*, 2297–2310.
- (5) (a) Grätzel, M. *J. Photochem. Photobiol., C* **2003**, *4*, 145–153. (b) Lindsey, J. S.; Mass, O.; Chen, C.-Y. *New J. Chem.* **2011**, *35*, 511–516.
- (6) (a) Suslick, K. S. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, CA, 2000;

- Vol. 4, pp 41–63. (b) Meunier, B.; Robert, A.; Pratiel, G.; Bernadou, J. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 4, pp 119–187. (c) Marchon, J.-C.; Ramasseul, R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, CA, 2003; Vol. 11, pp 75–132. (d) Ruppel, J. V.; Fields, K. B.; Snyder, N. L.; Zhang, X. P. In *Handbook of Porphyrin Science*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; World Scientific: River Edge, NY, 2010; Vol. 10, pp 1–182.
- (7) (a) Fox, S.; Boyle, R. W. *Tetrahedron* **2006**, *62*, 10039–10054. (b) Akhigbe, J.; Luciano, M.; Zeller, M.; Brückner, C. *J. Org. Chem.* **2015**, *80*, 499–511. (c) Götz, D. C. G.; Gehrold, A. C.; Dorazio, S. J.; Daddario, P.; Samankumara, L.; Bringmann, G.; Brückner, C.; Bruhn, T. *Eur. J. Org. Chem.* **2015**, *2015*, 3913–3922.
- (8) (a) Brückner, C.; Samankumara, L.; Ogikubo, J. In *Handbook of Porphyrin Science*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; World Scientific: River Edge, NY, 2012; Vol. 17, pp 1–112. (b) Taniguchi, M.; Lindsey, J. S. *Chem. Rev.* **2016**, DOI: [10.1021/acs.chemrev.5b00696](https://doi.org/10.1021/acs.chemrev.5b00696). (c) Lindsey, J. S. *Chem. Rev.* **2015**, *115*, 6534–6620.
- (9) (a) Shelnut, J. A.; Song, X.-Z.; Ma, J.-G.; Jentzen, W.; Medforth, C. J. *Chem. Soc. Rev.* **1998**, *27*, 31–41. (b) Lebedev, A. Y.; Filatov, M. A.; Cheprakov, A. V.; Vinogradov, S. A. *J. Phys. Chem. A* **2008**, *112*, 7723–7733.
- (10) (a) Lash, T. D. *Org. Biomol. Chem.* **2015**, *13*, 7846–7878. (b) Arnold, L.; Müllen, K. J. *Porphyrins Phthalocyanines* **2011**, *15*, 757–779. (c) Brückner, C.; Akhigbe, J.; Samankumara, L. In *Handbook of Porphyrin Science*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; World Scientific: River Edge, NY, 2014; Vol. 31, pp 1–276. (d) Szyszko, B.; Latos-Grażyński, L. *Chem. Soc. Rev.* **2015**, *44*, 3588–3616. (e) Costa, L. D.; Costa, J. I.; Tome, A. C. *Molecules* **2016**, *21*, 320. (f) Brückner, C. *Acc. Chem. Res.* **2016**, *49*, 1080–1092.
- (11) Szymanski, J. T.; Lash, T. D. *Tetrahedron Lett.* **2003**, *44*, 8613–8616.
- (12) (a) Daniell, H. W.; Brückner, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 1688–1691. (b) Brückner, C.; Götz, D. C. G.; Fox, S. P.; Ryppa, C.; McCarthy, J. R.; Bruhn, T.; Akhigbe, J.; Banerjee, S.; Daddario, P.; Daniell, H. W.; Zeller, M.; Boyle, R. W.; Bringmann, G. *J. Am. Chem. Soc.* **2011**, *133*, 8740–8752.
- (13) Head, M. L.; Zarate, G.; Brückner, C. *Eur. J. Org. Chem.* **2016**, *2016*, 992–998.
- (14) Lash, T. D. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 2, pp 125–199.
- (15) (a) Adams, K. R.; Bonnett, R.; Burke, P. J.; Salgado, A.; Valles, M. A. *J. Chem. Soc., Chem. Commun.* **1993**, 1860–1861. (b) Adams, K. R.; Bonnett, R.; Burke, P. J.; Salgado, A.; Valles, M. A. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1769–1772. (c) Ryppa, C.; Niedzwiedzki, D.; Morozowich, N. L.; Srikanth, R.; Zeller, M.; Frank, H. A.; Brückner, C. *Chem. – Eur. J.* **2009**, *15*, 5749–5762. (d) Banerjee, S.; Zeller, M.; Brückner, C. *J. Porphyrins Phthalocyanines* **2012**, *16*, 576–588.
- (16) Akhigbe, J.; Brückner, C. *Eur. J. Org. Chem.* **2013**, *2013*, 3876–3884.
- (17) Samankumara, L. P.; Wells, S.; Zeller, M.; Acuña, A. M.; Röder, B.; Brückner, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 5757–5760.
- (18) Callot, H. J.; Schaeffer, E. *Tetrahedron* **1978**, *34*, 2295–2300.
- (19) Jesberger, M.; Davis, T. P.; Barner, L. *Synthesis* **2003**, 1929–1958.
- (20) (a) Crossley, M. J.; King, L. G. *J. Chem. Soc., Chem. Commun.* **1984**, 920–922. (b) Daniell, H. W.; Williams, S. C.; Jenkins, H. A.; Brückner, C. *Tetrahedron Lett.* **2003**, *44*, 4045–4049.
- (21) Brückner, C.; Hyland, M. A.; Sternberg, E. D.; MacAlpine, J.; Rettig, S. J.; Patrick, B. O.; Dolphin, D. *Inorg. Chim. Acta* **2005**, *358*, 2943–2953.
- (22) Yamamura, S.; Nishiyama, S. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, UK, 1991; Vol. 8, pp 307–325.
- (23) Dolphin, D. *J. Heterocycl. Chem.* **1970**, *7*, 275–283.
- (24) Barkigia, K. M.; Renner, M. W.; Furenlid, L. R.; Medforth, C. J.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* **1993**, *115*, 3627–3635.
- (25) Maclean, A. L.; Foran, G. J.; Kennedy, F. J.; Turner, P.; Hambley, T. W. *Aust. J. Chem.* **1996**, *49*, 1273–1278.
- (26) McCarthy, J. R.; Hyland, M. A.; Brückner, C. *Org. Biomol. Chem.* **2004**, *2*, 1484–1491.
- (27) Hua, G.; Woollins, J. D. *Angew. Chem., Int. Ed.* **2009**, *48*, 1368–1377.