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One-pot Synthesis of Functionalized Asymmetric 5,10,15,20-Substituted Porphyrins from 5,15-Diaryl- or -Dialkyl-porphyrins

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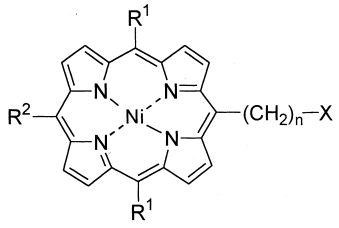
Abstract—Reaction of easily available (5,15-dialkyl/arylporphyrinato)nickel(II) with RLi under anhydrous conditions affords 5,10,15-trisubstituted porphyrin anions that can be used as in situ nucleophiles for reaction with alkyl iodide reagents. After oxidation with atmospheric oxygen, 5,10,15,20-tetrasubstituted porphyrins are obtained in good yields. This method permits introduction of all base-stable functional groups into the *meso* position of porphyrins.

Functionalized asymmetric 5,10,15,20-tetrasubstituted porphyrins like **1**, whose *meso* substituents contain chemically reactive groups such as halogens, alcohols, esters, or pseudohalogens, would present suitable precursors for the synthesis of more complicated porphyrin systems with special physical and chemical properties or those that could be easily transformed into amphiphilic porphyrins. However, it is extremely difficult to directly introduce such functional groups into the intact porphyrin skeleton to yield compounds like **1**. Normally, these porphyrins have been synthesized either through laborious multi-step total syntheses[1,2] or one-pot mixed condensations requiring tedious chromatographic separation.[3] Existing methods for a direct introduction of functional groups utilized halogenated or formylated porphyrins as starting material.[4–6]



R^1 = alkyl or aryl
R^2 = alkyl or aryl
X = Hal, OH, COOR, CN

1

In this context, we have reported on the reaction of porphyrins with organolithium reagents.[7–9] A reaction sequence of addition of RLi, hydrolysis with water, and subsequent oxidation with DDQ allowed the convenient and often quantitative preparation of porphyrins with various types and numbers of *meso* substituents.[7,9] However, the use of this method requires that potentially chemically reactive groups such as those in **1** must be protected at first and then refunctionalized due to the presence of RLi. Thus, synthesis of porphyrins like **1** using this method is complicated and limited by the fact that only one substituent is introduced in a given reaction sequence.

During more detailed mechanistic investigations of the reaction of RLi with (5,15-diphenylporphyrinato)nickel(II) **2**, we found that the addition of electrophilic reagents like alkyl iodide after the "hydrolysis step," followed by oxidation with atmospheric oxygen, permits the facile preparation of functionalized asymmetric 5,10,15,20-tetrasubstituted porphyrins in good yields. The use of an electrophile stemmed from the proposed mechanism for the reaction of porphyrins with RLi (Scheme 1). The mechanism entails formation of a monoanion after attack of the carbanion.

According to our postulation, the porphyrin anion **3** may possess a Meisenheimer-type structure in which the negative charge is partly located at the 20-position of the Ni(II)porphyrin after the addition of organolithium reagent at the 10-position. Thus, trapping of this anion with electrophiles should be possible in a manner akin to the reductive methylation described by Buchler,[10,11] who prepared porphyrin dianions by reduction with sodium anthracenide in an anhydrous atmosphere and showed that they can easily react as nucleophiles with methyl iodide. The porphyrin monoanion **3** generated through the reaction (Scheme 1) should react directly with electrophilic reagents like alkyl iodides and give novel porphodimethenes **4** with four

Keywords: porphyrins and analogues; lithium and compounds; substitution; alkyl halides.

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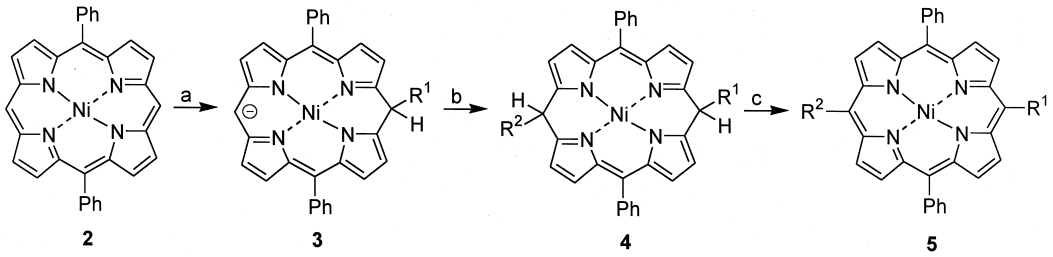


Scheme 1. a=LiR[1] in THF; b=R[2]I; c=O_2.

substituents at the *meso* positions. In contrast to the reductive alkylation mentioned above, this should allow the introduction of two different *meso* substituents. Subsequent oxidation with DDQ would then yield the corresponding porphyrins with three different types of *meso* substituents **5** in a one-pot reaction.

In addition, we found that the reaction mixture of free base porphyrin plus RLi after hydrolysis with dilute HCl turned blue-green at once, whereas the corresponding nickel(II)-complex became deep red. The different UV/Vis spectra are shown in Fig. 1. The protonated intermediate of the porphyrin free base product exhibits a spectrum typical for a phlorin with a broad absorption above 700 nm while the Ni(II)complex spectroscopically behaves like a porphodimethene. Thus, protonation at the 20-position of the intermediate occurs only in the nickel(II)complex, but not in the free base. In other words, the 20-position of the Ni(II)-porphyrin anion possesses a nucleophilic reactivity much higher than the one of the porphyrin free base, where the negative charge may be located more on the nitrogen atoms. This explains the formation of the phlorin isolated by Callot et al.[12,13] through the reaction of 5,10,15,20-tetraphenylporphyrin free base with *n*-BuLi and the porphodimethenes described by us as products of the reaction of (5,10,15,20-tetrabutylporphyrinato)nickel(II) under similar reaction conditions.[7]

Initially, (5,15-diphenylporphyrinato)nickel(II) **2** was made to react with excess *n*-butyl iodide. As expected, the porphyrins **7** and **8** were obtained quantitatively when either

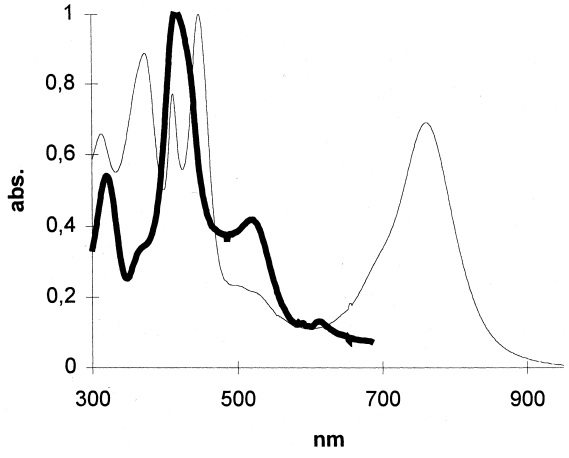


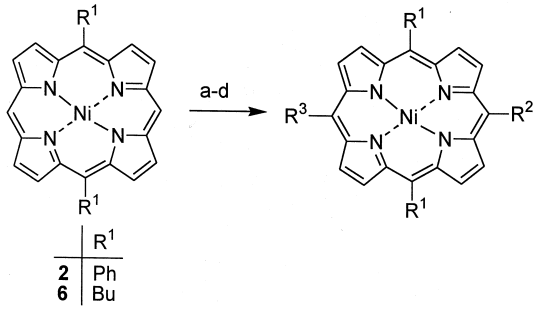
Figure 1. UV/Vis spectra of the intermediates obtained from the reaction of free base 5,15-diphenylporphyrin (thin line) and nickel(II)complex **2** (bold line) after addition of BuLi and hydrolysis with dilute HCl.

BuLi or PhLi was used as the organometallic reagent. The use of the respective free base under similar reaction conditions gave 5,10,15-trisubstituted porphyrins as the sole product, similar to the standard reaction sequence (Porphyrin+RLi+H_2O+DDQ) without use of butyl iodide.[9]

Further, the utility of alkyl iodide reagents with functional groups such as –I, –OH, –Br, –COOR, and –CN was investigated (Scheme 2). As these groups are prone to react with RLi at room temperature (RT), excess organolithium reagent from the first reaction step has to be eliminated before addition of the alkyl iodide, without destruction of the porphyrin monoanion. During the investigation of the reaction mechanism (Scheme 1) with **2** we found that the UV/Vis spectrum of the intermediate monoanion did not change significantly after the addition of water. Thus, the monoanions of these compounds are relatively stable against hydrolysis. An equilibrium between the monoanion and porphodimethene through a protonation and deprotonation sequence is possible, too. With that consideration in mind, the alkyl iodide reagents were added after the "hydrolysis-step," whose sole purpose now is destruction of any excess RLi. After the addition of RI, the color of the reaction mixture slowly changed from brown to red, and subsequent oxidation with air overnight and chromatographic separation with alumina gave the porphyrins **7**–**13** in yields from 50 to 90% (not optimized).

In principle, almost any alkyl RI compounds with reactive functional groups that are stable in basic medium at RT can be used. Additionally, the reaction is not limited to 5,15-diarylporphyrins but proceeds as well with 5,15-dialkylporphyrins. For example, (5,15-dibutylporphyrinato)nickel(II) **6** and 4-iodobutyronitrile, after initial reaction with phenyl lithium, gave the expected porphyrin **14** in 62% yield. The reactivity of the intermediates with alkyl bromides was investigated, too. The reaction of (5,15–diphenylporphyrinato)nickel(II) with phenyllithium and 1,4-dibromobutane gave the desired porphyrin **15**, albeit in low yield (24%).

As shown by the analytical data listed later the compounds presented in this study exhibit rather similar spectroscopic characteristics. However, the presence of different functional groups conveniently allow further transformations. Functional groups such as –CN can easily be transformed to $-CH_2NH_2$ and –COOH, or –I to $-N(C_2H_5)_3^+I^-$ through the reaction with triethylamine, allowing an entry into water soluble amphiphilic porphyrins. The methodology presented constitutes a convenient synthesis of functionalized porphyrins and provides the possibility to utilize



	R^1	R^2	R^3	yield (%)
7	Ph	Bu	Bu	92
8	Ph	Ph	Bu	90
9	Ph	Bu	$CH_2CH_2CH_2CH_2I$	79
10	Ph	Ph	$CH_2CH_2CH_2CH_2I$	71
11	Ph	Bu	$CH_2CH_2CH_2CH_2OH$	48
12	Ph	Ph	$CH_2CH_2CH_2COOEt$	52
13	Ph	Ph	$CH_2CH_2CH_2CN$	80
14	Bu	Ph	$CH_2CH_2CH_2CN$	62
15	Ph	Ph	$CH_2CH_2CH_2CH_2Br$	24

Scheme 2. a=LiR^2; b=H_2O; c=R^3I; d=air.

simple asymmetric porphyrins for biological studies. In addition, the porphyrins **7**–**15** can be used as suitable precursors in subsequent coupling reactions for complex systems with special chemical and physical properties. Such studies are currently under way in our laboratory.

Experimental

General

All chemicals used were of analytical grade and were purified before use by distillation. THF was dried before use by distillation with sodium. All reactions with organolithium reagents were performed under a purified argon atmosphere. Melting points were measured on a Büchi melting point apparatus and are uncorrected. Neutral or basic alumina (Alfa) (usually Brockmann Grade III, i.e. deactivated with 7% water) was used for column chromatography. Analytical thin-layer chromatography was carried out using Merck silica gel 60 plates or alumina 60 (neutral, fluorescence indicator F_{254}) plates. ^{1}H NMR spectra were recorded at a frequency of 250 MHz (AC 250). All chemical shifts are given in ppm, referenced on the δ scale downfield from the TMS signal as internal standard. Electronic absorption spectra were recorded with a Specord S10 (Carl Zeiss) spectrophotometer using dichloromethane as the solvent. Mass spectra were recorded with a Varian MAT 711 mass spectrometer using the EI technique with a direct insertion probe and an excitation energy of 80 eV.

Syntheses of 5,15-diphenylporphyrin, 5,15-dibutylporphyrin, their nickel(II)complexes and the alkyl iodide compounds that were commercially not available were performed using procedures described in the literature.[14–16]

General procedure of the reaction of porphyrins with organolithium reagents and alkyl iodide

A Schlenk flask was charged with 0.1 mmol of the porphyrin (ca. 50 mg) dissolved in 30 ml THF under an Argon atmosphere and the solution was cooled to −70°C (for BuLi) or 0°C (for PhLi). Within 15 min, RLi (0.6 mmol, 0.3 ml of a 2 M solution in cyclohexane) was added dropwise. After the removal of the cold bath, the reaction mixture was stirred for 15 min and 0.5 ml water in 5 ml THF was added. After 10 min, 10–20 equiv. of the alkyl iodide were added. The reaction mixture was stirred for 60 min at RT under argon and oxidized overnight with atmospheric O_2. Finally, the mixture was filtered through neutral alumina and subjected to column chromatography on neutral alumina (Alfa) with *n*-hexane/ethyl acetate followed by recrystallization from CH_2Cl_2/*n*-hexane.

(5,15-Dibutyl-10,20-diphenylporphyrinato)nickel(II) (7). Chromatography eluting with ethyl acetate/*n*-hexane (1:100, v/v); yield 55 mg (92%); mp 270°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.00 (t, ^3J=7.5 Hz, 6H, $CH_2CH_2CH_2CH_3$), 1.45–1.60 (m, 4H, $CH_2CH_2CH_2CH_3$), 2.25–2.40 (m, 4H, $CH_2CH_2CH_2CH_3$), 4.55 (t, ^3J=7.8 Hz, 4H, $CH_2CH_2CH_2CH_3$), 7.65–7.75, 7.95–8.05 (each m, 10H, H_{Ph}), 8.65, 9.35, (each d, ^3J=4.8 Hz, 8H, H_β); UV/Vis (CH_2Cl_2): λ_{max} (log ϵ)=417 nm (5.30), 536 (3.81); MS (80 eV); *m*/*z* (%): 630 (100) [M^+], 315 (17) [M^{2+}]; HRMS [$C_{36}H_{30}N_4$]: calcd 630.2293, found 630.2263.

(5-Butyl-10,15,20-triphenylporphyrinato)nickel(II) (8). Chromatography eluting with ethyl acetate/*n*-hexane (1:100, v/v); yield 56 mg (90%); mp >300°C; ^{1}H NMR (250 MHz, $CDCl_3$): 1.05 (t, ^3J=7.5 Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.55–1.65 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.25–2.40 (m, 2H, $CH_2CH_2CH_2CH_3$), 4.65 (t, ^3J=7.5 Hz, 2H, $CH_2CH_2CH_2CH_3$), 7.55–7.70, 7.95–8.05 (each m, 15H, H_{Ph}), 8.65 (s, 4H, H_β), 8.80, 9.35, (each d, ^3J=4.8 Hz, 4H, H_β); UV/Vis (CH_2Cl_2): λ_{max} (log ϵ)=414 nm (5.32), 529 (3.95); MS (80 eV); *m*/*z* (%): 650 (100) [M^+], 325 (4) [M^{2+}]; HRMS [$C_{42}H_{32}N_4Ni$]: calcd 650.1980, found 650.1946.

{5-Butyl-15-(4-iodobutyl)-10,20-diphenylporphyrinato}-nickel(II) (9). Chromatography eluting with ethyl acetate/*n*-hexane (1:100, v/v); yield 57 mg (79%); mp 193°C; ^{1}H NMR (250 MHz, $CDCl_3$): 1.05 (t, ^3J=7.5 Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.45–1.65 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.75–1.95 (m, 2H, $CH_2CH_2CH_2CH_2I$), 2.25–2.40 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.40–2.50 (m, 2H, $CH_2CH_2CH_2CH_2I$), 3.20 (t, ^3J=7.2 Hz, 2H, $CH_2CH_2CH_2CH_2I$), 4.45–4.55 (m, 4H, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2I$), 7.55–7.70, 7.95–8.05 (each m, 10H, H_{Ph}), 8.75, 9.20, 9.25, (each d, ^3J=4.8 Hz, 8H, H_β); UV/Vis (CH_2Cl_2): λ_{max} (log ϵ)=415 nm (5.31), 531 (4.17); MS (80 eV); *m*/*z* (%): 756 (100) [M^+], 378 (8) [M^{2+}]; HRMS [$C_{40}H_{35}N_4NiI$]: calcd 756.1259, found 756.1255.

{5-(4-Iodobutyl)-10,15,20-triphenylporphyrinato}nickel(II) (10). Chromatography eluting with ethyl acetate/*n*-hexane (1:100, v/v); yield 52 mg (71%); mp >300°C; ^{1}H NMR (250 MHz, $CDCl_3$): 1.85–2.05 (m, 2H, $CH_2CH_2CH_2CH_2I$),

2.35–2.50 (m, 2H, $CH_2CH_2CH_2CH_2I$), 3.20 (t, ^3J=7.2 Hz, 2H, $CH_2CH_2CH_2CH_2I$), 4.60 (t, ^3J=7.5 Hz, 2H, $CH_2CH_2CH_2CH_2I$), 7.65–7.75, 7.85–7.95 (each m, 15H, H_{Ph}), 8.65 (s, 4H, H_β), 8.80, 9.35, (each d, ^3J=4.8 Hz, 4H, H_β); UV/Vis (CH_2Cl_2): λ_{max} (log ϵ)=414 nm (5.32), 529 (4.24); MS (80 eV); *m*/*z* (%): 776 (100) [M^+]; HRMS [$C_{42}H_{31}N_4NiI$]: calcd 776.0946, found 776.0944.

{5-Butyl-15-(4-hydroxybutyl)-10,20-diphenylporphyrinato}-nickel(II) (11). Chromatography eluting with ethyl acetate/*n*-hexane (1:1, v/v); yield 30 mg (48%); mp 206°C; ^{1}H NMR (250 MHz, $CDCl_3$): 1.05 (t, ^3J=7.5 Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.50–1.65 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.75–1.85 (m, 2H, $CH_2CH_2CH_2CH_2OH$), 2.25–2.40 (m, 4H, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2OH$), 3.20 (t, ^3J=7.2 Hz, 2H, $CH_2CH_2CH_2CH_2OH$), 4.45–4.55 (m, 4H, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2OH$), 7.65–7.75, 7.90–8.05 (each m, 10H, H_{Ph}), 8.75, 9.25, (each d, ^3J=4.8 Hz, 8H, H_β); UV/Vis (CH_2Cl_2): λ_{max} (log ϵ)=417 nm (5.20), 532 (4.01); MS (80 eV); *m*/*z* (%): 646 (100) [M^+], 323 (1.7) [M^{2+}]; HRMS [$C_{40}H_{36}ON_4Ni$]: calcd 646.2243, found 646.2242.

{5-(4-Ethoxycarbonylbutyl)-10,15,20-triphenylporphyrinato}nickel(II) (12). Chromatography eluting with ethyl acetate/*n*-hexane (1:10, v/v); yield 36 mg (52%); mp >300°C; ^{1}H NMR (250 MHz, $CDCl_3$): 1.25 (t, ^3J=7.5 Hz, 3H,OCH_2CH_3), 1.70–1.80 (m, 2H, $CH_2CH_2CH_2CH_2COOEt$), 1.80-1.95 (m, 2H, $CH_2CH_2CH_2CH_2COOEt$), 2.25 (t, ^3J=7.5 Hz, 2H, $CH_2CH_2CH_2CH_2COOEt$), 4.15 (t, ^3J= 7.4 Hz, 2H, OCH_2CH_3), 4.60 (t, ^3J=7.5 Hz, 2H, $CH_2CH_2CH_2CH_2COOEt$), 7.65–7.75, 7.90–8.05 (each m, 15H, H_{Ph}), 8.65 (s, 4H, H_β), 8.80, 9.35, (each d, ^3J= 4.8 Hz, 4H, H_β); UV/Vis (CH_2Cl_2): λ_{max} (log ϵ)=414 nm (5.19), 529 (4.14); MS (80 eV); *m*/*z* (%): 722 (100) [M^+], 361 (1.8) [M^{2+}]; HRMS [$C_{45}H_{36}O_2N_4Ni$]: calcd 722.2192, found 722.2198.

{5-(4-Cyanobutyl)-10,15,20-triphenylporphyrinato}-nickel(II) (13). Chromatography eluting with ethyl acetate/*n*-hexane (1:5, v/v); yield 51 mg (80%)**;** mp >300°C; ^{1}H NMR (250 MHz, $CDCl_3$): 2.20 (t, ^3J=7.5 Hz, 2H, $CH_2CH_2CH_2CN$), 2.45–2.55 (m, 2H, $CH_2CH_2CH_2CN$), 4.60 (t, ^3J=7.5 Hz, 2H, $CH_2CH_2CH_2CN$), 7.55–7.65, 7.85–7.95 (each m, 15H, H_{Ph}), 8.65 (s, 4H, H_β), 8.75, 9.20, (each d, ^3J=4.8 Hz, 4H, H_β); UV/Vis (CH_2Cl_2): λ_{max} (log ϵ)=414 nm (5.33), 529 (4.18); MS (80 eV); *m*/*z* (%): 661 (100) [M^+], 331 (9) [M^{++}]; HRMS [$C_{42}H_{29}N_5Ni$]: calcd 661.1776, found 661.1770.

{5,15-Dibutyl-10-(4-cyanobutyl)-20-phenylporphyrinato}-nickel(II) (14). Chromatography eluting with ethyl acetate/*n*-hexane (1:5, v/v); yield 37 mg (62%); mp 153°C; ^{1}H NMR (250 MHz, $CDCl_3$): 1.05 (t, ^3J=7.5 Hz, 6H, $CH_2CH_2CH_2CH_3$), 1.45–1.65 (m, 4H, $CH_2CH_2CH_2CH_3$), 2.20–2.50 (m, 6H, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CN$), 2.45–2.55 (m, 2H, $CH_2CH_2CH_2CN$), 4.45 (t, ^3J=7.5 Hz, 4H, $CH_2CH_2CH_2CH_3$)4.70 (t, ^3J=7.5 Hz, 2H, $CH_2CH_2CH_2CN$), 7.65–7.75, 7.85–7.95 (each m, 5H, H_{Ph}), 8.65, 9.15, 9.25, 9.35 (each d, ^3J=4.8 Hz, 8H, H_β); UV/Vis (CH_2Cl_2): λ_{max} (log ϵ)=417 nm (5.32), 536 (3.84); MS (80 eV); *m*/*z* (%): 621 (100) [M^+], 311 (6) [M^{++}]; HRMS [$C_{42}H_{29}N_5Ni$]: calcd 621.2402, found 621.2405.

{5-(4-Bromobutyl)-15-butyl-10,20-diphenylporphyrinato}-nickel(II) (15). Chromatography eluting with ethyl acetate/*n*-hexane (1:100, v/v); yield 16 mg (24%); mp 203°C; ^{1}H NMR (250 MHz, $CDCl_3$): 1.05 (t, ^3J=7.5 Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.45–1.65 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.80–1.20 (m, 2H, $CH_2CH_2CH_2CH_2Br$), 2.20–2.35 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.40–2.50 (m, 2H, $CH_2CH_2CH_2CH_2Br$), 3.40 (t, ^3J=7.2 Hz, 2H, $CH_2CH_2CH_2CH_2Br$), 4.45–4.65 (m, 4H, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2I$), 7.55–7.70, 7.85–8.05 (each m, 10H, H_{Ph}), 8.75, 9.20, 9.25, (each d, ^3J=4.8 Hz, 8H, H_β); UV/Vis (CH_2Cl_2): λ_{max} (log ϵ)=416 nm (5.27), 532 (3.84); MS (80 eV); *m*/*z* (%): 710 (100) [M^+], 355 (4) [M^{2+}]; HRMS [$C_{40}H_{35}N_4BrNi$]: calcd 708.1399, found 708.1396.

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