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PALLADIUM-CATALYZED [3+2] ANNULATION OF *meso*-BROMOPORPHYRINS WITH SILYLACETYLENES AND DESILYLATION OF 8^a-SILYL-7,8-DEHYDROPURPURIN

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Abstract – Palladium-catalyzed [3+2] annulation of *meso*-bromoporphyrins with trimethylsilyl-, *tert*-butyldimethylsilyl-, and triisopropylsilylacetylenes afforded 8^a-silyl-7,8-dehydropurpurins. Protodesilylation of 8^a-trimethylsilyl-7,8-dehydropurpurin resulted in the first synthesis of an 8^a,8^b-unsubstituted 7,8-dehydropurpurin.

INTRODUCTION

The electronic nature of a porphyrin ring is susceptible to modifications through fusion of π-conjugated segments at the periphery. Chemists have hence devoted much time to the design and synthesis of novel π-extended fused porphyrins.[1,2] Among them, 7,8-dehydropurpurins are intriguing porphyrinoids that bear a fused five-membered ring that includes a vinylene moiety bridging across the *meso* and *β* positions.[3–7] They exhibit largely altered absorption reaching out to the near infrared region due to their forbidden HOMO–LUMO transition with a narrow energy gap. These properties arise from the presence of dual 18π- and 20π-electronic circuits that resonate in the conjugated macrocycles.[3] Today, a variety of 7,8-dehydropurpurin derivatives have been synthesized, which contain various substituents like aryl,[4] alkynyl,[5] and porphyrinyl[5,6] groups at their 8^a- and 8^b-positions. In addition, fused π-segments such as phenylene[7] and thienylene[3] also behave as bridging vinylene moieties. However, 8^a,8^b-unsubstituted 7,8-

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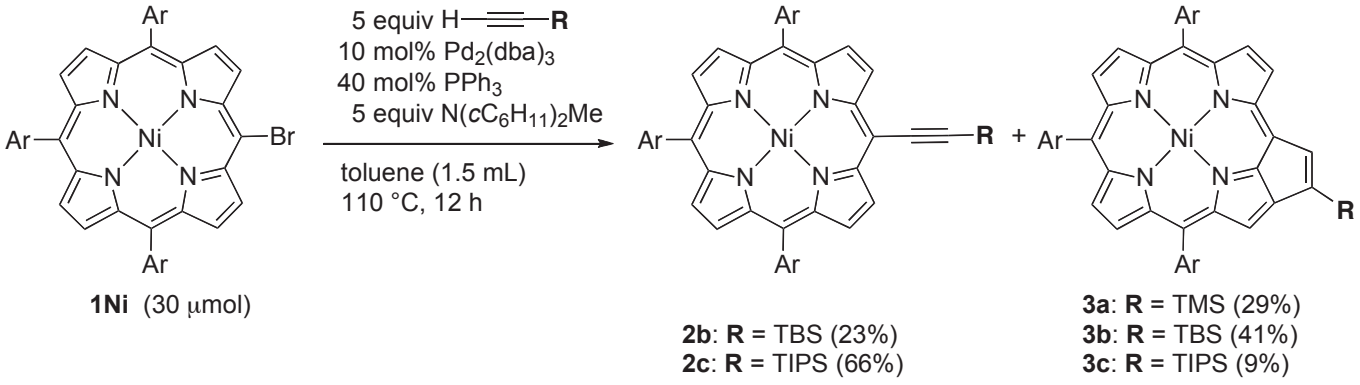
This paper is dedicated to Professor Isao Kuwajima on the occasion of his 77th birthday.

dehydropurpurin has been unexplored. Our continuing interest in porphyrin π-systems encouraged us to envisage synthesizing a 7,8-dehydropurpurin having no substituent at the bridging vinylene moiety. Investigation into the 8[a],8[b]-unsubstituted 7,8-dehydropurpurin should be helpful to elucidate the intrinsic nature of its attractive π-system.

Recently, we reported the facile synthesis of 7,8-dehydropurpurin derivatives *via* Pd-catalyzed [3+2] annulation of *meso*-bromoporphyrin with diphenylacetylene.[4,8] According to this procedure, we have synthesized 8[a]-silyl-7,8-dehydropurpurins by replacement of diphenylacetylene with terminal trimethylsilyl- (TMS-), *tert*-butyldimethylsilyl- (TBS-), and triisopropylsilyl- (TIPS-) acetylenes. Desilylation reaction of 8[a]-TMS-7,8-dehydropurpurin led to the first synthesis of an 8[a],8[b]-unsubstituted 7,8-dehydropurpurin.

RESULTS AND DISCUSSION

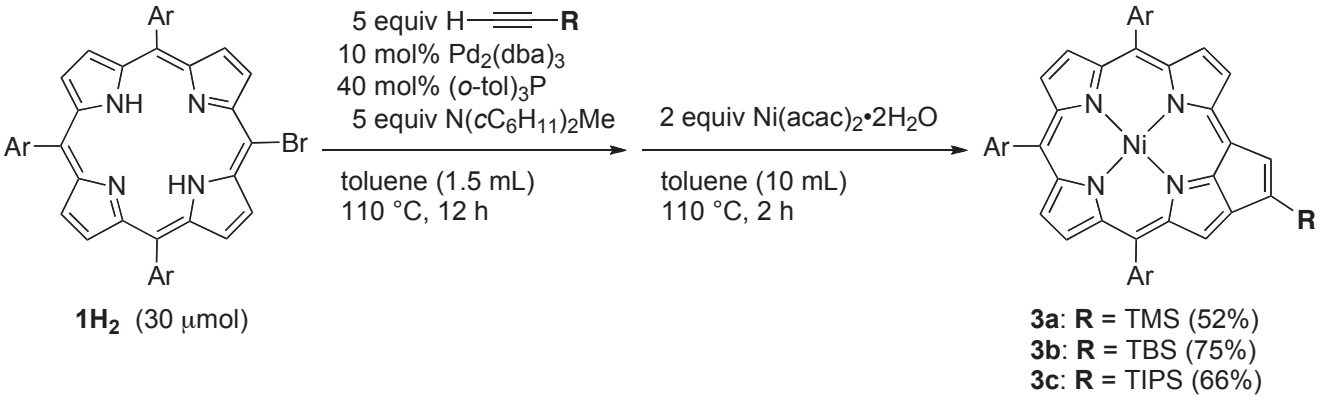
Initially, we performed Pd-catalyzed [3+2] annulation of Ni^{II} *meso*-bromoporphyrin **1Ni** with TMS-, TBS-, and TIPS-acetylenes in the presence of catalytic amount of $Pd_2(dba)_3$ and PPh_3 (Scheme 1). The reaction of **1Ni** with TMS-acetylene afforded the expected 8[a]-TMS-7,8-dehydropurpurin **3a** in low yield (29%) with some side products. In the case of a bulkier TBS group, Sonogashira coupling[9] competed with the desired [3+2] annulation to provide TBS-ethynylporphyrin **2b** and 8[a]-TBS-7,8-dehydropurpurin **3b** in 23% and 41% yields, respectively. Such competitive Sonogashira coupling has been reported in the Pd-catalyzed [3+2] annulation reactions of 9-bromoanthracene with terminal acetylenes.[10] The steric hinderance caused by the bulkiest TIPS group prevented the desired [3+2] annulation to afford a small amount of 8[a]-TIPS-7,8-dehydropurpurin **3c** (9%) and a good yield of TIPS-ethynylporphyrin **2c** (66%).



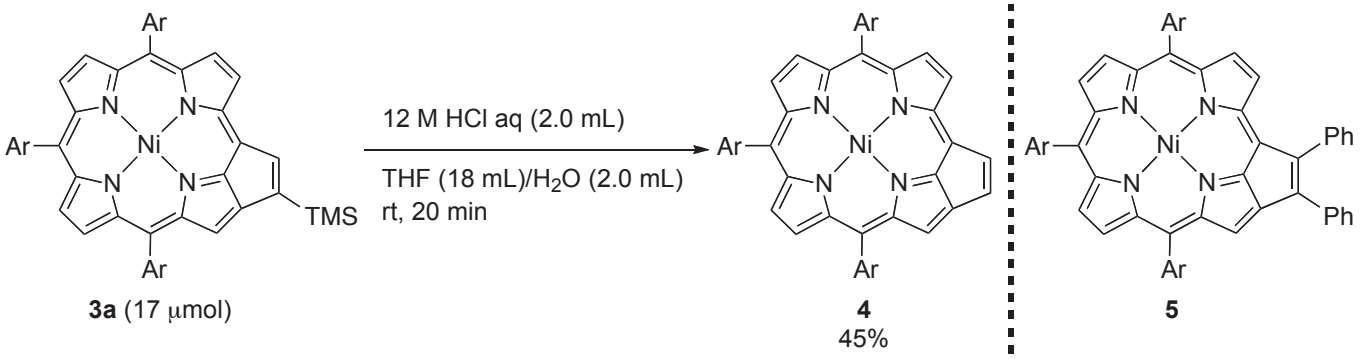
Scheme 1. Pd-Catalyzed [3+2] annulation of **1Ni** with silylacetylenes. Ar = 3,5-di-*tert*-butylphenyl

After extensive screening of porphyrin substrates and reaction conditions, we found that utilization of free base *meso*-bromoporphyrin $\mathbf{1H_2}$ as a starting material and $(o\text{-tol})_3P$ as a ligand is more effective for annulation (Scheme 2). The Pd-catalyzed [3+2] annulation of $\mathbf{1H_2}$ with TMS-acetylene followed by

nickel metalation furnished **3a** in 52% yield as a sole isomer without any alkynylporphyrins. By considering the previously reported reaction of 9-bromoanthracene with TMS-acetylene,[10,11] the carbopalladation of porphyrinylpalladium to the C–C triple bond occurred to minimize steric hinderance, providing the 8[a]-silylated compound selectively. Even in the cases of bulkier silyl groups like TBS and TIPS groups, the [3+2] annulation reactions also proceeded smoothly and gave **3b** and **3c** in 75% and 66% yields, respectively.



Scheme 2. Pd-Catalyzed [3+2] annulation of $\mathbf{1H_2}$ with silylacetylenes. Ar = 3,5-di-*tert*-butylphenyl



Scheme 3. Protodesilylation of **3a** and structure of **5**. Ar = 3,5-di-*tert*-butylphenyl

Protodesilylation of **3a** with hydrochloric acid in aqueous THF afforded unsubstituted 7,8-dehydropurpurin **4** in 45% yield (Scheme 3). The ^{1}H NMR spectrum of **4** in $CDCl_3$ showed two upfield-shifted doublet signals owing to the two protons at the bridging vinylene moiety at 6.80 and 5.96 ppm (J = 5.5 Hz). In the case of pyracylene, which had dual 10π- and 12π- electronic circuits, the paramagnetic ring current also resulted in relatively high field-shifted signals at 6.01 and 6.52 ppm in CCl_4.[12] The ^{13}C–^{1}H COSY measurement revealed the ^{13}C signals of the fused five-membered ring at 139.35 and 126.18 ppm (Supporting Information, Figure S13). Unfortunately, compared with the previously reported 8[a],8[b]-substituted 7,8-dehydropurpurin derivatives,[3–7] **4** was less stable in solution and gradually decomposed to a complicated mixture. Probably, the substituents at the fused five-membered

rings kinetically supressed their oxidative decomposition processes despite its inherent instability caused by the contribution of 20π-antiaromatic conjugations.

The UV-visible absorption spectra of **3a–c**, **4**, and 8[a],8[b]-diphenyl-7,8-dehydropurpurin **5**[4,6] in CH_2Cl_2 are shown in Figure 1. These absorption spectra have characteristic split Soret bands located at 350–500 nm, almost featureless Q-like bands around 580 nm, and weak and extremely broad bands almost reaching 1000 nm. The absorption spectra of **3a–c** and **4** are almost similar because of the exiguous perturbations of the silyl groups to 7,8-dehydropurpurin π-systems. Compared with **5**, **4** has slightly blue-shifted absorption bands in the overall region. Although the phenyl groups at the 8[a]- and 8[b]- positions of **5** were twisted out of the porphyrin plane,[4,6] they could contribute to the π-extension of the 7,8-dehydropurpurin π-system to a small degree.

Figure 1. UV-Visible absorption spectra of (a) **3a–c** and (b) **4** and **5** in CH_2Cl_2

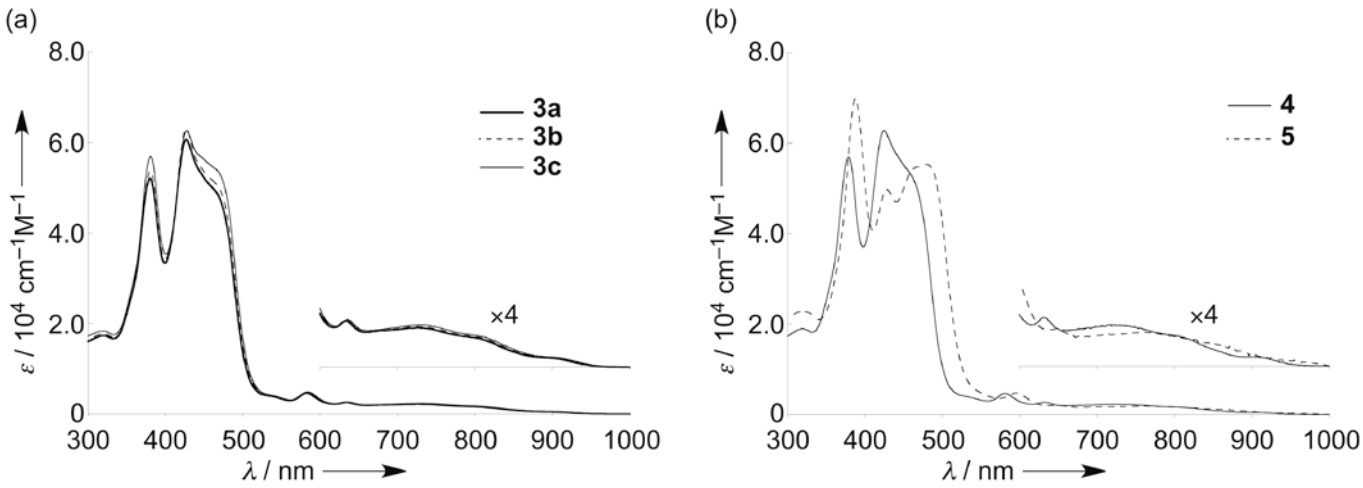


Table 1. Redox potentials of **2a–c**, **4** and **5**[a]

	oxidation (V)		reduction (V)		$E^{1/2}_{ox1} - E^{1/2}_{red1}$
	$E^{1/2}_{ox1}$	$E^{1/2}_{ox2}$	$E^{1/2}_{red1}$	$E^{1/2}_{red2}$	(eV)
3a	0.24	0.71	–1.51	–2.04[b]	1.75
3b	0.24	0.75	–1.51	—	1.75
3c	0.24	0.74	–1.53	—	1.77
4	0.24[b]	—	–1.51	—	1.75
5	0.19	0.64	–1.47	–1.90	1.66

[a] The redox potentials were measured by cyclic voltammetry in anhydrous CH_2Cl_2 with 0.1 M Bu_4NPF_6 as a supporting electrolyte, and $Ag/AgClO_4$ as a reference electrode. Ferrocene/ferrocenium ion couple was used as an external reference. [b] Irreversible peak.

The electrochemical properties of **3a–c**, **4** and **5** were studied by cyclic voltammetry (CV) in CH_2Cl_2 (Table 1). 8[a]-Silyl-7,8-dehydropurpurins **3a–c** exhibited two reversible oxidation waves and one reversible reduction wave. Unsubstituted 7,8-dehydropurpurin **4** displayed a similar reversible reduction wave, but its first oxidation wave became irreversible. Lack of kinetically protecting groups at fused five-membered ring destabilized the radical cation and triggered off the decomposition of **4**. Compared with **3a–c** and **4**, **5** exhibited a slightly smaller electrochemical HOMO–LUMO gap because of the contribution of phenyl groups to the π-extension.

In conclusion, Pd-catalyzed [3+2] annulation of free base *meso*-bromoporphyrin $\mathbf{1H_2}$ with three terminal silylacetylenes furnished 8[a]-silyl-7,8-dehydropurpurins **3a–c**. Protodesilylation of **3a** with hydrochloric acid resulted in the first synthesis of an unsubstituted 7,8-dehydropurpurin **4**. By comparing the characters of unsubstituted **4** and substituted **5**, the substituents at the fused five-membered rings of previously reported 7,8-dehydropurpurin derivatives have some contribution to their stability and π-extension.

EXPERIMENTAL

^{1}H NMR (600 MHz), ^{13}C NMR (151 MHz), and ^{13}C–^{1}H COSY spectra were taken on a JEOL ECA-600 spectrometer. Chemical shifts are reported on a delta scale in ppm relative to residual $CHCl_3$ (δ = 7.26 ppm) for ^{1}H NMR and to $CDCl_3$ (δ = 77.16 ppm) for ^{13}C NMR. Spectroscopic grade solvents were used for all spectroscopic studies without further purification. UV-visible absorption spectra were recorded on a Shimadzu UV-3600PC spectrometer. APCI-TOF-MS spectra were recorded on a Bruker micrOTOF instrument using a negative-ion mode. Redox potentials were measured by cyclic voltammetry on an ALS electrochemical analyzer model 660. Preparative separations were performed by silica gel chromatography (Wako gel C-200, C-300, or C-400). Toluene was distilled from CaH_2. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Pd-Catalyzed [3+2] Annulation of Ni^{II} *meso*-Bromoporphyrins with Silylacetylenes: The reaction of Ni^{II} *meso*-bromoporphyrin **1Ni** with TBS-acetylene is representative: Ni^{II} *meso*-bromoporphyrin **1Ni** (30 μmol, 30 mg), $Pd_2(dba)_3$ (3.0 μmol, 2.8 mg), and PPh_3 (12 μmol, 3.2 mg) were placed in a reaction flask under argon. Toluene (1.5 mL), TBS-acetylene (0.15 mmol, 28 μL), and *N*,*N*-dicyclohexylmethylamine (0.15 mmol, 32 μL) were added, and the whole mixture was heated at 110 °C for 12 h. The resulting mixture was allowed to cool to ambient temperature, diluted with CH_2Cl_2, and filtered through a small plug of silica gel with copious washings (CH_2Cl_2). After removal of the solvent *in vacuo*, the residue was purified by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization of the each separated solids from CH_2Cl_2/MeCN gave **2b** (6.9 μmol, 7.4 mg, 23%) and **3b** (12 μmol, 12.9 mg, 41%), respectively.

2b: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.52 (d, 2H, J = 5.0 Hz, β), 8.83 (d, 2H, J = 5.0 Hz, β), 8.76–8.72 (m, 4H, β), 7.85 (d, 4H, J = 1.9 Hz, Ar-*o*), 7.84 (d, 2H, J = 1.9 Hz, Ar-*o*), 7.73 (t, 2H, J = 1.9 Hz, Ar-*p*), 7.71 (t, 1H, J = 1.9 Hz, Ar-*p*), 1.49 (s, 36H, *tert*-butyl), 1.46 (s, 18H, *tert*-butyl), 1.25 (s, 9H, TBS), 0.48 (s, 6H, TBS); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.14, 149.09, 145.21, 143.49, 142.82, 142.75, 139.96, 139.87, 133.37, 132.66, 132.30, 131.43, 128.80, 128.70, 121.90, 121.36, 121.31, 121.10, 106.28, 100.34, 98.51, 35.14 (overlap), 31.84, 31.81, 26.67, 17.39, –4.09 ppm; UV-vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 426 (250000), 540 (17000), 573 nm (9600); MS (APCI, negative): m/z = 1068.5941. Calcd for $C_{70}H_{86}N_4{}^{58}NiSi$: 1068.5981 [$M$]$^-$.

2c: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.55 (d, 2H, J = 4.6 Hz, β), 8.82 (d, 2H, J = 4.6 Hz, β), 8.75–8.71 (m, 4H, β), 7.86–7.83 (m, 6H, Ar-*o*), 7.72 (d, 2H, J = 1.9 Hz, Ar-*p*), 7.70 (t, 1H, J = 1.9 Hz, Ar-*p*), 1.48 (s, 36H, *tert*-butyl), 1.46 (s, 18H, *tert*-butyl), 1.40–1.36 (m, 21H, TIPS); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.12, 149.08, 145.31, 143.48, 142.87, 142.77, 140.01, 139.92, 133.39, 132.64, 132.27, 131.45, 128.71 (overlap), 121.87, 121.37, 121.30, 121.08, 107.51, 98.88, 98.55, 35.15 (overlap), 31.85, 31.82, 19.21, 11.96 ppm; UV-vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 427 (270000), 541 (17000), 573 nm (9800); MS (APCI, negative): m/z = 1110.6415. Calcd for $C_{73}H_{92}N_4{}^{58}NiSi$: 1110.6450 [$M$]$^-$.

Pd-Catalyzed [3+2] Annulation of Free Base *meso*-Bromoporphyrins with Silylacetylenes: The reaction of free base *meso*-bromoporphyrin **1H$_2$** with TMS-acetylene is representative: Free base *meso*-bromoporphyrin **1H$_2$** (30 μmol, 28.6 mg), $Pd_2(dba)_3$ (3.0 μmol, 2.8 mg), and (*o*-tol)$_3$P (12 μmol, 3.7 mg) were placed in a reaction flask under argon. Toluene (1.5 mL), TMS-acetylene (0.15 mmol, 21 μL), and *N*,*N*-dicyclohexylmethylamine (0.15 mmol, 32 μL) were added, and the whole mixture was heated at 110 ˚C for 12 h. The resulting mixture was allowed to cool to ambient temperature, diluted with CH_2Cl_2, and filtered through a small plug of silica gel with copious washings (CH_2Cl_2). After removal of the solvent *in vacuo*, the residue was dissolved in toluene (10 mL). After addition of Ni(acac)$_2$•2H$_2$O (60 μmol, 15.4 mg), the mixture was stirred for 2 h at 110 ˚C. After removal of the solvent *in vacuo*, the residue was purified by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization of the separated solids from CH_2Cl_2/MeCN gave **3a** (15.5 μmol, 15.9 mg, 52%) of high purity.

3a: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.35 (d, 1H, J = 5.0 Hz, β), 8.33 (d, 1H, J = 5.0 Hz, β), 8.10 (d, 1H, J = 5.0 Hz, β), 8.07 (d, 1H, J = 5.0 Hz, β), 8.04 (d, 1H, J = 5.0 Hz, β), 8.01 (d, 1H, J = 5.0 Hz, β), 7.69–7.67 (m, 6H, Ar-*o*), 7.64 (t, 1H, J = 1.9 Hz, Ar-*p*), 7.63 (t, 1H, J = 1.9 Hz, Ar-*p*), 7.62 (t, 1H, J = 1.9 Hz, Ar-*p*), 7.13 (s, 1H, β), 7.05 (s, 1H, fused five-membered ring), 1.47 (s, 18H, *tert*-butyl), 1.45 (s, 18H, *tert*-butyl), 1.43 (s, 18H, *tert*-butyl), 0.35 (s, 9H, TMS) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.29, 154.73, 149.24, 149.19, 149.17, 148.35, 147.41 (overlap), 146.89, 145.10, 143.79, 143.52, 142.55, 140.11, 139.92, 139.76, 138.18, 135.17, 133.09, 130.93, 129.85, 129.54, 128.93, 128.33, 127.81, 127.26, 126.71, 126.37, 126.02, 121.27, 121.11 (overlap), 120.29, 115.53, 35.11, 35.08 (overlap), 31.80, 31.77 (overlap),

–0.92 ppm; UV-vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 380 (52000), 427 (61000), 583 nm (4600); MS (APCI, negative): *m*/*z* = 1026.5488. Calcd for $C_{67}H_{80}N_4{}^{58}NiSi$: 1026.5511 [*M*]$^-$.

3b: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.37 (d, 1H, *J* = 5.0 Hz, β), 8.34 (d, 1H, *J* = 5.0 Hz, β), 8.12–8.09 (m, 2H, β), 8.05 (d, 1H, *J* = 5.0 Hz, β), 8.02 (d, 1H, *J* = 5.0 Hz, β), 7.69–7.67 (m, 6H, Ar-*o*), 7.64 (t, 1H, *J* = 1.9 Hz, Ar-*p*), 7.63–7.61 (m, 2H, Ar-*p*), 7.12 (s, 1H, β), 7.05 (s, 1H, fused five-membered ring), 1.46 (s, 18H, *tert*-butyl), 1.45 (s, 18H, *tert*-butyl), 1.42 (s, 18H, *tert*-butyl), 1.10 (s, 9H, TBS), 0.29 (s, 6H, TBS) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.15, 155.49, 149.29, 149.25, 149.21, 148.94, 148.33, 147.40, 146.89, 145.18, 143.84, 143.55, 142.48, 139.97, 139.81, 138.15, 137.91, 135.15, 133.07, 130.91, 129.90, 129.58, 129.03, 128.35, 127.83, 127.64, 127.32, 126.40, 126.01, 121.30, 121.18, 121.13, 120.35, 115.53, 35.11 (overlap), 31.81, 31.78 (overlap), 26.99, 17.08, –5.63 ppm; UV-vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 381 (54000), 427 (63000), 583 nm (4700); MS (APCI, negative): *m*/*z* = 1068.5956. Calcd for $C_{70}H_{86}N_4{}^{58}NiSi$: 1068.5981 [*M*]$^-$.

3c: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.38 (d, 1H, *J* = 5.0 Hz, β), 8.34 (d, 1H, *J* = 5.0 Hz, β), 8.12 (d, 1H, *J* = 5.0 Hz, β), 8.09 (d, 1H, *J* = 5.0 Hz, β), 8.06 (d, 1H, *J* = 5.0 Hz, β), 8.01 (d, 1H, *J* = 5.0 Hz, β), 7.69–7.66 (m, 6H, Ar-*o*), 7.65 (t, 1H, *J* = 1.9 Hz, Ar-*p*), 7.64–7.61 (m, 2H, Ar-*p*), 7.10 (s, 1H, β), 7.08 (s, 1H, fused five-membered ring), 1.46 (s, 18H, *tert*-butyl), 1.45 (s, 18H, *tert*-butyl), 1.42 (s, 18H, *tert*-butyl), 1.40-1.30 (m, 3H, TIPS), 1.28-1.24 (m, 18H, TIPS) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.20, 155.99, 149.69, 149.24, 149.20, 149.15, 148.20, 147.35, 146.84, 145.16, 143.77, 143.48, 142.24, 139.93, 139.76, 138.11, 135.33, 135.12, 133.04, 130.89, 129.91, 129.56, 129.11, 128.35, 127.87, 127.82, 127.25, 126.33, 126.04, 121.27, 121.13, 121.10, 120.29, 115.72, 35.09 (overlap), 31.80, 31.78, 31.75, 19.08, 11.68 ppm; UV-vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 381 (57000), 428 (63000), 584 nm (4900); MS (APCI, negative): *m*/*z* = 1110.6405. Calcd for $C_{73}H_{92}N_4{}^{58}NiSi$: 1110.6450 [*M*]$^-$.

Protodesilylation of 8^a-Trimethylsilyl-7,8-dehydropurpurin 3a: 8^a-Trimethylsilyl-7,8-dehydropurpurin **3a** (17.8 μmol, 16.5 mg) was placed in a reaction flask, and dissolved in THF (18 mL) and H_2O (2.0 mL). After the addition of conc. HCl aqueous solution (12 M, 2.0 mL), the mixture was stirred at room temperature for 20 min. Then, the reaction was quenched by the addition of a saturated aqueous $NaHCO_3$ aqueous solution, and the product was extracted with CH_2Cl_2 (3×25 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was purified by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization of the separated solids from CH_2Cl_2/MeOH gave **4** (7.4 μmol, 7.1 mg, 45%) of high purity.

4: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.33–8.28 (m, 2H, β), 8.09 (d, 1H, *J* = 4.8 Hz, β), 8.04–8.00 (m, 2H, β), 7.98 (d, 1H, *J* = 4.8 Hz, β), 7.67 (d, 2H, *J* = 1.9 Hz, Ar-*o*), 7.65 (d, 2H, *J* = 1.9 Hz, Ar-*o*), 7.65–7.62 (m, 3H, Ar-*o*+Ar-*p*), 7.63–7.60 (m, 2H, Ar-*p*), 7.08 (s, 1H, β), 6.80 (d, 1H, *J* = 5.5 Hz, fused five-membered ring), 5.96 (d, 1H, *J* = 5.5 Hz, fused five-membered ring), 1.44 (s, 36H, *tert*-butyl), 1.41

(s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 156.48, 150.95, 149.27, 149.21, 149.11, 148.51, 147.09 (overlap), 144.99, 144.04, 143.63, 142.54, 139.87, 139.68, 139.35, 138.12, 137.64, 135.19, 133.19, 130.99, 129.96, 129.41, 128.31, 128.25, 127.78, 127.49, 126.55, 126.35, 126.18, 121.34, 121.28, 121.11, 120.04, 114.57, 35.07 (overlap), 31.79, 31.78, 31.76 ppm; UV-vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 379 (57000), 425 (63000), 581 nm (4700); MS (APCI, negative): *m/z* = 954.5075. Calcd for $C_{64}H_{72}N_4{}^{58}Ni$: 954.5116 [*M*]$^-$.

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