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Efficient Synthesis and Versatile Reactivity of Porphyrinyl Grignard Reagents**

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Iodine-magnesium exchange between iodoporphyrins and *i*PrMgCl•LiCl successfully proceeded without decomposition of the porphyrin core. The resulting porphyrinyl Grignard reagents are nucleophilic enough to react with various carbonyl compounds, such as aldehyde, ketone, and amide. Furthermore, the porphyrinyl Grignard reagents underwent transmetalation to afford porphyrinyl copper and zinc species of mild and unique reactivity, which engaged in 1,4-addition and Negishi coupling, respectively.

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Introduction

Porphyrins are an important class of heteroaromatic compounds that play a wide variety of roles in nature such as oxygen transport and photosynthesis.[1] Significant attention has been paid to development of new porphyrins that exhibit interesting and useful properties in catalysis, biological applications, and material sciences. Peripheral functionalizations of porphyrin cores definitely represent an effective process to synthesize porphyrins that have altered properties.

Metalation of the periphery of porphyrins is regarded to be a key step for peripheral functionalization since the resulting carbon–metal bond is reactive to experience various transformations.[2] Direct mercuration is historically important as the first peripheral metalation.[3] Although the resulting carbon–mercury bonds were usefully convertible, the toxicity of mercury would impede the practical applications. In contrast, borylated porphyrins are easily accessible and safely underwent useful transformations,[4] such as Suzuki-Miyaura cross-coupling, oxidative hydroxylation, and halogenation.[5]

Considering the importance of these borylated porphyrins, we expected that peripherally magnesiated porphyrins should also be fascinating synthetic intermediates because of their higher nucleophilicity to achieve a wider variety of efficient bond-forming processes.[6] However, synthesis and reactions of magnesiated porphyrins have been still unexplored. Chen *et al.* reported the only one example of generation of a porphyrinyl Grignard reagent from *meso*-bromoporphyrin.[7] However, commercially available magnesium turnings did not serve, and preparation of active Rieke magnesium in situ from $MgCl_2$, KI, and extremely reactive metallic potassium was indispensable. The Grignard reagent reacted with aromatic aldehydes in only low yields and with ketones to anomalously form α-porphyrinylated ketones, the scope of electrophiles thus being extremely limited and unusual. These results indicate that the formation of the Grignard reagent is inefficient and accompanied by side reactions. In addition, the reactions should be performed in a Barbier fashion to avoid decomposition of the Grignard reagent. We thus assumed that the efficient generation of the porphyrinyl Grignard reagent was difficult since a porphyrin skeleton is susceptible to nucleophilic attack,[8] single electron transfer,[9] and reductive demetalation[10] under Chen's conditions.

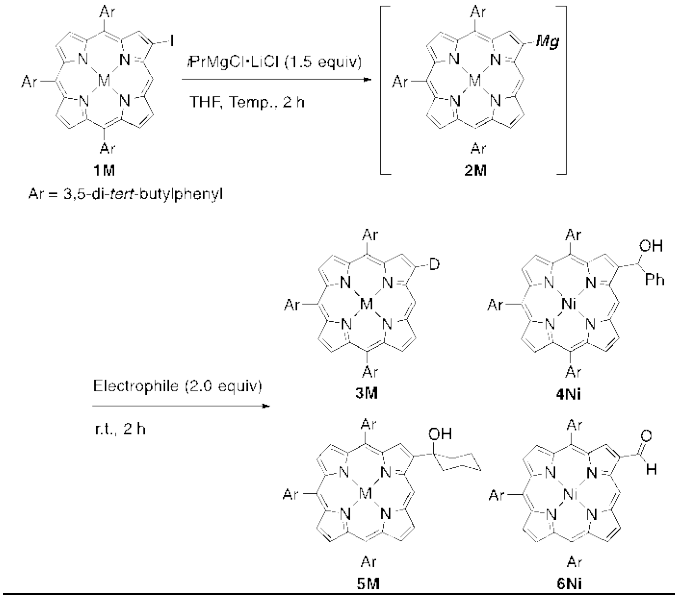
Preparation of functionalized Grignard reagents is rather difficult since the insertion of magnesium metal to a carbon–halogen bond does not work under cryogenic conditions and many functional groups are incompatible under noncryogenic conditions. In 2004, Knochel *et al.* developed *i*PrMgCl•LiCl as a powerful tool for smooth halogen-magnesium exchange.[11] This breakthrough has realized preparation of a variety of functionalized aryl and heteroaryl Grignard reagents at low temperatures, thereby considerably advancing organic synthesis. We envisioned that porphyrinyl Grignard reagents could be efficiently synthesized at a low temperature through iodine-magnesium exchange with *i*PrMgCl•LiCl. This was indeed the case and here we wish to report the first efficient synthesis of porphyrinyl Grignard reagents and their versatile reactivity.

Results and Discussion

Firstly, we aimed to identify formation of porphyrinyl Grignard reagent **2Ni** prepared through the iodine-magnesium exchange reaction of Ni^{II} β-iodoporphyrin **1Ni**[5l] (Table 1, Ar = 3,5-di-tert-butylphenyl and ***Mg*** that is located at the periphery denotes MgCl•LiCl throughout the manuscript.). After treatment of **1Ni** with *i*PrMgCl•LiCl in THF at –40 ºC for 2 h, D_2O was added to the resulting reaction mixture to afford β-deuterioporphyrin **3Ni** in 95% yield. This result suggests that the iodine-magnesium exchange reaction provided **2Ni** without any significant side reactions. Indeed, **2Ni** showed typical behavior in the reactions with carbonyl compounds, such as benzaldehyde, cyclohexanone, and dimethylformamide (DMF) to give **4Ni**, **5Ni**, and **6Ni**[12] in 78%, 71%, and 70% yields, respectively. Iodine-magnesium

exchange reaction of the zinc analogue **1Zn** was carried out at a lower temperature because zinc porphyrins were more labile under the reaction conditions. The formation of Zn^{II} porphyrinyl Grignard reagent **2Zn** was also confirmed by the reaction with D_2O to give **3Zn** in 90% yield. Nucleophilic addition of **2Zn** with cyclohexanone also took place cleanly to provide **5Zn** in 68% yield.

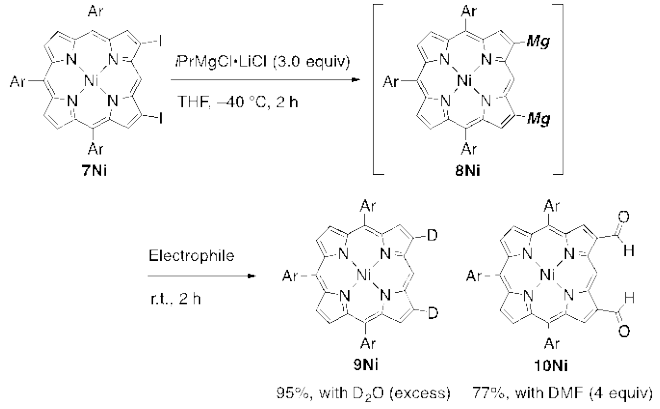
Table 1. Preparations and reactions of β-magnesiated porphyrins **2M**



Entry	Substrate	Temp. [ºC]	Electrophile	Product	Yield [%]
1	**1Ni**	–40	D_2O	**3Ni**	95[a]
2	**1Ni**	–40	PhCHO	**4Ni**	78
3	**1Ni**	–40	cyclohexanone	**5Ni**	70
4	**1Ni**	–40	DMF	**6Ni**	71
5	**1Zn**	–80	D_2O	**3Zn**	90[a]
6	**1Zn**	–80	cyclohexanone	**5Zn**	68

[a] With an excess amount of D_2O for 5 min.

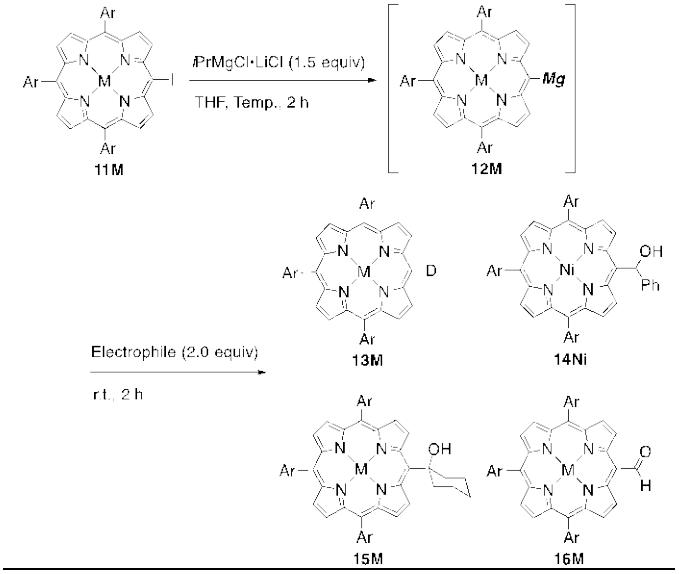
Scheme 1. Dimagnesiation of β,β'-diiodoporphyrin **7Ni**



We also attempted two-fold iodine-magnesium exchange of Ni^{II} β,β'-diiodoporphyrin **7Ni**[5l] with *i*PrMgCl•LiCl in THF at –40 ºC (Scheme 1). The iodine-magnesium exchange was successful, and the resulting dimagnesiated complex **8Ni** was trapped with D_2O or DMF to furnish β,β'-dideuterio- or diformylporphyrin **9Ni** or **10Ni** in 95% or 77% yields, respectively.

Encouraged by the success in the reactions of β-iodoporphyrins, we next tried to apply these procedures to *meso*-iodoporphyrins **11M**[13] (Table 2). Similar deuterium labelling experiments strongly suggest quantitative formation of the corresponding Grignard reagent **12M** via iodine-magnesium exchange (entries 1 and 5). *meso*-Magnesiated porphyrin **12Ni** also reacted with benzaldehyde to give **14Ni** in a reasonable yield of 68%. Unfortunately, the reactions with DMF required long times and furnished **16M** in moderate yields because of the low nucleophilicity of the sterically hindered *meso*-carbon. The reactions with cyclohexanone provided **15M**[12] in low yields due to competitive protonation of **12M** with the α-protons of cyclohexanone.

Table 2. Preparations and reactions of *meso*-magnesiated porphyrins **12M**



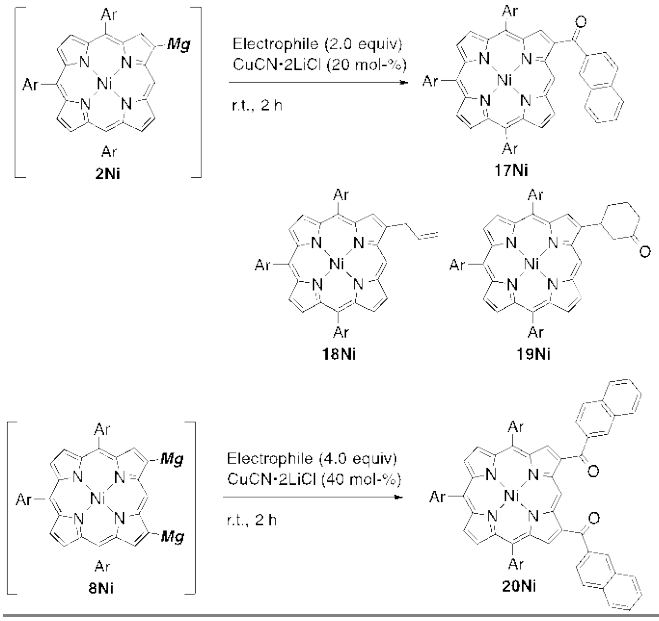
Entry	Substrate	Temp. [ºC]	Electrophile	Product	Yield [%]
1	**11Ni**	–40	D_2O	**13Ni**	94[a]
2	**11Ni**	–40	PhCHO	**14Ni**	68
3	**11Ni**	–40	cyclohexanone	**15Ni**	39
4	**11Ni**	–40	DMF	**16Ni**	50[b]
5	**11Zn**	–80	D_2O	**13Zn**	92[a]
6	**11Zn**	–80	cyclohexanone	**15Zn**	18
7	**11Zn**	–80	DMF	**16Zn**	53[b]

[a] With an excess amount of D_2O for 5 min. [b] For 24 h.

We then envisioned that the utility of the porphyrinyl Grignard reagents could be extended through transmetalation with other metal salts. Indeed, porphyrinyl copper was generated from the corresponding porphyrinyl magnesium and exhibited desired reactivities (Table 3). In the presence of a catalytic amount of CuCN•2LiCl,[11a] porphyrinyl Grignard reagents **2Ni** and **8Ni** reacted with 2-naphthoyl chloride to give β-(2-naphthoyl)porphyrins **17Ni** and **20Ni**[12] in 72% and 62% yields, respectively. An S_N2' reaction with allyl bromide also proceeded to yield β-allylporphyrin **18Ni** efficiently. In the presence of chlorotrimethylsilane,[14] 1,4-addition to 2-cyclohexen-1-one occurred to provide desired adduct **19Ni** in 68% yield. On the other hand, the reaction of porphyrinyl magnesium **2Ni** with 2-cyclohexen-1-one without CuCN•2LiCl gave a rather complicated and inseparable mixture. APCI-TOF MS analysis of the mixture tentatively implied that the mixture included not only β-unsubstituted porphyrin and **19Ni** but also considerable amounts of

β-phenylporphyrin and β-(1,3-cyclohexadienyl)porphyrin, which would result from 1,2-addition to 2-cyclohexen-1-one.

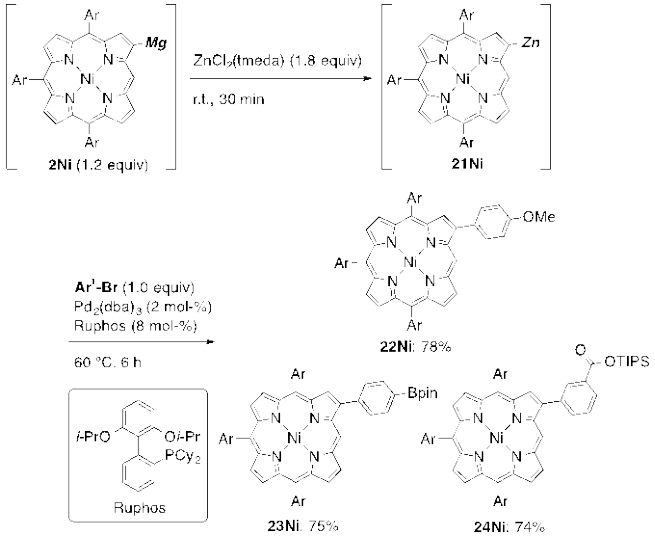
Table 3. Reactions of porphyrinyl copper



Entry	Substrate	Electrophile	Product	Yield [%]
1	**2Ni**	2-naphthoyl chloride	**17Ni**	72
2	**2Ni**	allyl bromide	**18Ni**	80
3	**2Ni**	2-cyclohexen-1-one	**19Ni**	68[a]
4	**8Ni**	2-naphthoyl chloride	**20Ni**	62

[a] With Me_3SiCl (2 equiv).

Scheme 2. Negishi cross-coupling reactions of **21Ni**



We finally examined Negishi cross-coupling reaction of porphyrinyl zinc species (Scheme 2). Porphyrinyl zinc **21Ni** was prepared through transmetalation of porphyrinyl Grignard reagent **2Ni** with $ZnCl_2$(tmeda) (tmeda = *N*,*N*,*N*',*N*'-tetramethylethylenediamine). In the presence of $Pd_2(dba)_3$/2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (Ruphos) catalyst,[15] Negishi cross-coupling reactions of **21Ni** with 4-bromoanisole gave β-(4-anisyl)porphyrin **22Ni** in 78% yield. The high reactivity of organozinc reagents in transmetalation with an aryl palladium halide allows activator-free cross-coupling. With this advantage, 4-bromophenylboronate reacted chemoselectively to yield **23Ni** whereas the boronate moiety remained untouched. Furthermore, the low nucleophilicity of organozinc reagents toward carbonyl groups enabled the cross-coupling reaction of **21Ni** with triisopropylsilyl 3-bromobenzoate without any observable nucleophilic attack.

Conclusions

We have successfully achieved the efficient synthesis of peripherally magnesiated porphyrins through iodine-magnesium exchange between iodoporphyrins with *i*PrMgCl•LiCl under mild conditions. The porphyrinyl Grignard reagents reacted with various carbonyl compounds as powerfully as the typical aryl Grignard reagents. Furthermore, transmetalation of the porphyrinyl Grignard reagents with copper and zinc salts efficiently proceeded. The resulting porphyrinyl copper and zinc were employed for their specific reactions, such as 1,4-addition to enone and Negishi cross-coupling reaction, respectively. Further applications of the Grignard reagents to synthesize novel porphyrinoids are underway in our laboratory.

Experimental Section

Preparation of *i*PrMgCl·LiCl (1.0 M in THF)[11a]: A flask containing magnesium turnings (0.67 g, 27.5 mmol) and anhydrous LiCl (1.06 g, 25 mmol) was dried in vacuum (1–3 torr) for 3 h at 150 ºC, and then purged with argon. After the flask was cooled to room temperature, dry THF (12 mL) and 1,2-dibromoethane (0.05 mL) were added. A solution of *i*PrCl (2.28 mL, 25 mmol) in dry THF (12 mL) was then slowly added at room temperature. The reaction started within a few minutes. After the completion of the addition, the reaction mixture was stirred further for 12 h at room temperature. The resulting gray solution of *i*PrMgCl·LiCl was cannulated into another argon-filled Schlenk tube, being free from the remaining magnesium metal. The solution was stored at –20 ºC and kept for at least 1 month without significant decomposition.

Synthesis of 3Ni–6Ni: A Schlenk tube containing Ni^{II} β-iodoporphyrin **1Ni** (106 mg, 100 μmol) was purged with argon, and then charged with dry THF (2.0 mL). After the solution was cooled to –40 ºC, *i*PrMgCl·LiCl (1.0 M solution in THF, 0.15 mL, 150 μmol) was slowly added, and then the reaction mixture was stirred for 2 h at –40 ºC. To the resulting red solution, an electrophile (200 μmol) was added. After being stirred for 2 h at room temperature, the reaction mixture was quenched with a sufficient amount of NH_4Cl solution, extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **4Ni**–**6Ni**. For the synthesis of **3Ni**, D_2O (ca. 0.05 mL) was added as an electrophile and the resulting mixture was stirred for 5 min.

3Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.83 (s, 1H, *meso*), 9.13 (d, *J* = 4.6 Hz, 1H, β), 8.93 (m, 2H, β), 8.83 (m, 4H, β), 7.90 (d, *J* = 1.8 Hz, 4H, Ar-*o*), 7.87 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.74 (t, *J* = 1.8 Hz, 2H, Ar-*p*), 7.71 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 1.49 (s, 36H, *tert*-butyl), and 1.46 (s, 18H, *tert*-butyl) ppm; APCI-TOF-MS: *m/z* = 931.5174. Calcd for $C_{62}H_{71}DN_4{}^{58}Ni$: 931.5168 $[M]^-$.

4Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 60 °C): δ = 9.91 (s, 1H, *meso*), 9.04 (d, *J* = 5.0 Hz, 1H, β), 8.86 (d, *J* = 5.0 Hz, 1H, β), 8.78 (s, 4H, β), 8.75 (s, 1H, β), 7.88 (d, *J* = 1.9 Hz, 2H, Ar-*o*), 7.87 (br-s, 2H, Ar-*o*), 7.85 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.78 (d, *J* = 7.8 Hz, 2H, Ph), 7.75 (t, *J* = 1.9 Hz, 1H, Ar-*p*), 7.73

(t, *J* = 1.8 Hz, 1H, Ar-*p*), 7.71 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 7.40 (m, 3H, Ph and benzyl), 7.32 (t, *J* = 7.8 Hz, 1H, Ph), 2.80 (d, *J* = 4.1Hz, 1H, OH), 1.49 (s, 18H, *tert*-butyl) and 1.47 (s, 36H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.11, 149.03, 146.49, 143.80, 143.23, 143.19, 143.05, 142.69, 141.16, 140.39, 140.20, 140.06, 139.96, 132.88, 132.51, 132.45, 132.33, 132.29, 131.07, 129.22, 128.92, 128.83, 128.05, 127.32, 121.24, 121.23, 120.89, 120.12, 120.09, 102.36, 72.04, 35.16, 35.14, 31.85, and 31.83 ppm; APCI-TOF-MS: *m/z* = 1036.5531. Calcd for $C_{69}H_{78}ON_4{}^{58}Ni$: 1036.5524 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 413 (2.6×10^5) and 525 (1.9×10^4).

5Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 60 °C): δ = 10.58 (s, 1H, *meso*), 9.14 (d, *J* = 4.6 Hz, 1H, β), 8.88 (d, *J* = 4.6 Hz, 1H, β), 8.77 (m, 5H, β), 7.90 (m, 4H, Ar-*o*), 7.87 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.75 (m, 2H, Ar-*p*), 7.72 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 2.72 (d, *J* = 13.3 Hz, 2H, cyclohexyl), 2.55–2.49 (m, 2H, cyclohexyl), 2.49 (s, 1H, OH), 2.19–2.13 (m, 2H, cyclohexyl), 1.93–1.85 (m, 3H, cyclohexyl), 1.59–1.52 (m, 1H, cyclohexyl), 1.51 (s, 18H, *tert*-butyl), 1.50 (s, 18H, *tert*-butyl), and 1.47 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 151.76, 149.13, 149.10, 149.02, 143.03, 142.93, 142.88, 142.54, 142.49, 142.43, 140.64, 140.52, 140.28, 140.23, 140.12, 132.74, 132.55, 132.43, 132.26, 132.21, 129.28, 128.92, 128.83, 121.24, 121.18, 121.11, 120.49, 119.92, 119.40, 104.83, 73.12, 40.80, 35.19, 35.16, 35.13, 31.87, 31.84, 26.11, and 22.76 ppm; APCI-TOF-MS: *m/z* = 1028.5846. Calcd for $C_{68}H_{82}ON_4{}^{58}Ni$: 1028.5837 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 413 (2.6×10^5) and 524 (1.9×10^4).

6Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 11.01 (s, 1H, formyl), 10.69 (s, 1H, *meso*), 9.37 (s, 1H, β), 9.17 (d, *J* = 4.6 Hz, 1H, β), 8.86 (d, *J* = 4.6 Hz, 1H, β), 8.78 (m, 3H, β), 8.74 (d, *J* = 4.9 Hz, 1H, β), 7.88 (s, 2H, Ar-*o*), 7.86 (s, 2H, Ar-*o*), 7.83 (s, 2H, Ar-*o*), 7.78 (s, 1H, Ar-*p*), 7.74 (s, 1H, Ar-*p*), 7.72 (s, 1H, Ar-*p*), 1.50 (s, 18H, *tert*-butyl), 1.49 (s, 18H, *tert*-butyl), and 1.46 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ =188.04, 149.31, 149.21, 144.72, 144.64, 144.41, 143.75, 143.50, 142.76, 140.20, 139.77, 139.63, 139.52, 139.47, 139.34, 137.32, 134.00, 133.50, 133.46, 133.21, 133.06, 132.54, 128.87, 128.72, 122.99, 121.79, 121.43, 121.22, 119.84, 104.71, 35.18, 35.17, 35.14, 31.83, and 31.80 ppm; APCI-TOF-MS: *m/z* = 958.5080. Calcd for $C_{63}H_{72}ON_4{}^{58}Ni$: 958.5054 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 426 (2.1×10^5), 535 (1.3×10^4), and 577 (1.2×10^4).

Synthesis of 3Zn and 5Zn: This procedure is similar to that for the synthesis of **3Ni**–**6Ni** except that iodine-magnesium exchange of **1Zn** was performed at –80 ºC. Recrystallization from CH_2Cl_2/methanol gave **3Zn** (85 mg, 90 μmol, 90%) and **5Zn** (70 mg, 68 μmol, 68%).

3Zn: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 10.27 (s, 1H, *meso*), 9.42 (d, *J* = 4.7 Hz, 1H, β), 8.93 (m, 2H, β), 9.06 (d, *J* = 4.6 Hz, 2H, β), 9.03 (d, *J* = 4.6 Hz, 2H, β), 8.12 (d, *J* = 1.9 Hz, 4H, Ar-*o*), 8.09 (d, *J* = 2.0 Hz, 2H, Ar-*o*), 7.82 (t, *J* = 1.9 Hz, 2H, Ar-*p*), 7.79 (t, *J* = 2.0 Hz, 1H, Ar-*p*), 1.55 (s, 36H, *tert*-butyl) and 1.52 (s, 18H, *tert*-butyl) ppm; APCI-TOF-MS: *m/z* = 937.5120. Calcd for $C_{62}H_{71}DN_4{}^{64}Zn$: 937.5106 $[M]^-$.

5Zn: ^{1}H NMR (600 MHz, $CDCl_3$, 60 °C): δ = 10.84 (s, 1H, *meso*), 9.41 (d, *J* = 4.6 Hz, 1H, β), 9.11 (d, *J* = 4.6 Hz, 1H, β), 9.03 (m, 3H, β), 8.99 (d, *J* = 4.6 Hz, 1H, β), 8.85 (s, 1H, β), 8.12 (m, 4H, Ar-*o*), 8.09 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.83 (m, 2H, Ar-*p*), 7.81 (br-s, 1H, Ar-*p*), 2.72 (d, *J* = 13.3 Hz, 2H, cyclohexyl), 2.55–2.49 (m, 2H, cyclohexyl), 2.43 (s, 1H, OH), 2.14–2.09 (m, 2H, cyclohexyl), 1.94–1.86 (m, 3H, cyclohexyl), 1.58 (s, 18H, *tert*-butyl), 1.56 (s, 18H, *tert*-butyl), and 1.54 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 60 °C): δ = 150.76, 150.68, 150.30, 150.14, 149.71, 148.91, 148.88, 148.78, 148.31, 147.78, 142.39, 142.22, 142.13, 132.60, 132.40, 132.27, 132.20, 132.08, 131.93, 130.37, 129.85, 129.74, 129.27, 122.84, 122.17, 121.67, 121.02, 120.99, 120.81, 106.14, 73.24, 41.07, 35.31, 35.28, 35.21, 32.00, 21.97, 26.13, and 22.79 ppm; APCI-TOF-MS: *m/z* = 1034.5788. Calcd for $C_{68}H_{82}ON_4{}^{64}Zn$: 1034.5775 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 418 (6.1×10^5) and 545 (2.4×10^4).

Synthesis of 9Ni and 10Ni: A Schlenk tube containing Ni^{II} β,β'-diiodoporphyrin **7Ni** (118 mg, 100 μmol) was purged with argon, and then charged with dry THF (2.0 mL). After the solution was cooled to –40 ºC, *i*PrMgCl·LiCl (1.0 M solution in THF, 0.30 mL, 300 μmol) was slowly added, and then the reaction mixture was stirred for 2 h at –40 ºC. To the resulting red solution, DMF (32 μL, 400 μmol) was added. After being stirred for 2 h at room temperature, the reaction mixture was quenched with a sufficient amount of NH_4Cl solution, extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **10Ni** (76 mg, 77 μmol, 77%). For the synthesis of **9Ni** (88 mg, 94 μmol, 94%), D_2O (ca. 0.1 mL) was added instead of DMF and the resulting mixture was stirred for 5 min.

9Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.83 (s, 1H, *meso*), 8.93 (s, 2H, β), 8.83 (m, 4H, β), 7.90 (d, *J* = 1.8 Hz, 4H, Ar-*o*), 7.87 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.74 (t, *J* = 1.8 Hz, 2H, Ar-*p*), 7.71 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 1.49 (s, 36H, *tert*-butyl) and 1.46 (s, 18H, *tert*-butyl) ppm; APCI-TOF-MS: *m/z* = 932.5235. Calcd for $C_{62}H_{70}D_2N_4{}^{58}Ni$: 932.5231 $[M]^-$.

10Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 11.38 (s, 1H, *meso*), 11.16 (s, 1H, formyl), 9.38 (s, 2H, β), 8.77 (d, *J* = 4.6 Hz, 2H, β), 8.75 (d, *J* = 4.6 Hz, 2H, β), 7.84 (d, *J* = 1.8 Hz, 4H, Ar-*o*), 7.81 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.73 (t, J = 1.8 Hz, 2H, Ar-*p*), 7.73 (t, J = 1.8 Hz, 1H, Ar-*p*), 1.50 (s, 36H, *tert*-butyl), and 1.46 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 187.45, 149.54, 149.41, 144.83, 144.15, 140.90, 140.10, 139.59, 139.32, 139.00, 138.76, 133.81, 133.59, 128.84, 128.64, 122.85, 122.02, 121.69, 103.76, 35.19, 35.16, 31.82 and 31.80 ppm; APCI-TOF-MS: *m/z* = 986.5032. Calcd for $C_{64}H_{72}O_2N_4{}^{58}Ni$: 986.5003 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 441 (2.0×10^5), 551 (1.4×10^4), and 592 (1.1×10^4).

Synthesis of 13Ni–16Ni: This procedure is similar to that for the synthesis of **3Ni**–**6Ni** except for the starting material.

13Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.14 (d, *J* = 4.6 Hz, 2H, β), 8.93 (d, *J* = 4.6 Hz, 2H, β), 8.84 (m, 4H, β), 7.90 (d, *J* = 1.8 Hz, 4H, Ar-*o*), 7.88 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.74 (t, *J* = 1.8 Hz, 2H, Ar-*p*), 7.71 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 1.49 (s, 36H, *tert*-butyl) and 1.46 (s, 18H, *tert*-butyl) ppm; APCI-TOF-MS: *m/z* = 931.5196. Calcd for $C_{62}H_{71}DN_4{}^{58}Ni$: 931.5168 $[M]^-$.

14Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.28 (d, *J* = 5.0 Hz, 2H, β), 8.76 (m, 4H, β), 8.74 (d, *J* = 4.6 Hz, 2H, β), 8.01 (d, *J* = 3.7 Hz, 1H, benzyl), 7.83 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.81 (d, *J* = 1.3 Hz, 4H, Ar-*o*), 7.69 (s, 3H, Ar-*p*), 7.57 (d, *J* = 7.8 Hz, 2H, Ph), 7.28 (d, *J* = 7.8 Hz, 2H, Ph), 7.23 (d, *J* = 7.8 Hz, 1H, Ph), 3.36 (d, *J* = 3.7 Hz, 1H, OH), and 1.45 (s, 54H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.12, 147.02, 142.81, 142.40, 142.02, 141.82, 139.3, 133.63, 132.83, 132.44, 130.62, 128.70, 128.26, 126.82, 126.51, 121.31, 120.85, 120.04, 116.58, 75.13, 35.12, and 31.80 ppm; APCI-TOF-MS: *m/z* = 1036.5546. Calcd for $C_{64}H_{72}O_2N_4{}^{58}Ni$: 1036.5524 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 418 (2.5×10^5) and 533 (1.7×10^4).

15Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.67 (d, *J* = 5.0 Hz, 2H, β), 8.67 (m, 4H, β), 8.60 (d, *J* = 5.0 Hz, 2H, β), 7.79 (br-s, 2H, Ar-*o*), 7.76 (br-s, 4H, Ar-*o*), 7.67 (m, 3H, Ar-*p*), 3.37 (m, 2H, cyclohexyl), 2.46 (d, *J* = 14.2 Hz, 2H, cyclohexyl), 2.14–2.06 (m, 2H, cyclohexyl), 2.01 (br-d, 1H, cyclohexyl), 1.91 (m, 2H, cyclohexyl), 1.76 (m, 1H, cyclohexyl), 1.58 (s, 1H, OH), 1.45 (s, 36H, *tert*-butyl), and 1.43 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.10, 141.99, 141.45, 139.90, 139.61, 139.47, 139.42, 133.66, 132.68, 132.63, 132.04, 128.62, 122.53, 121.18, 120.34, 119.20, 44.86, 35.10, 31.79, 25.77, and 23.18 ppm; APCI-TOF-MS: *m/z* = 1028.5865. Calcd for $C_{68}H_{82}ON_4{}^{58}Ni$: 1028.5837 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 419 (2.4 x 10^5) and 533 (1.6 x 10^4).

16Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 12.05 (s, 1H, formyl), 9.79 (d, *J* = 5.3 Hz, 2H, β), 8.88 (d, *J* = 5.3 Hz, 2H, β), 8.69 (d, *J* = 4.7 Hz, 2H, β), 8.62 (d, *J* = 4.6 Hz, 2H, β), 7.80 (m, 6H, Ar-*o*), 7.73 (t, *J* = 1.8 Hz, 2H,

Ar-*p*), 7.73 (t, *J* = 1.9 Hz, 1H, Ar-*p*), 1.47 (s, 36H, *tert*-butyl), and 1.45 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 192.89, 149.39, 149.31, 144.75, 144.54, 142.08, 141.16, 139.16, 135.83, 133.69, 132.25, 130.63, 128.61, 128.49, 124.94, 122.39, 121.66, 105.87, 35.15, 31.80, and 31.78 ppm; APCI-TOF-MS: *m/z* = 958.5072. Calcd for $C_{63}H_{72}ON_4{}^{58}Ni$: 958.5054 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 427 (2.1×10^5), 554 (1.0×10^4), and 596 (1.5×10^4).

Synthesis of 13Zn, 15Zn and 16Zn: This procedure is similar to that for the synthesis of **3Zn** and **5Zn** except for the starting material.

13Zn: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.42 (d, *J* = 4.7 Hz, 1H, β), 9.15 (d, *J* = 4.7 Hz, 2H, β), 9.06 (d, *J* = 4.6 Hz, 2H, β), 9.03 (d, *J* = 4.6 Hz, 2H, β), 8.12 (d, *J* = 1.9 Hz, 4H, Ar-*o*), 8.09 (d, *J* = 2.0 Hz, 2H, Ar-*o*), 7.82 (t, *J* = 1.9 Hz, 2H, Ar-*p*), 7.79 (t, *J* = 2.0 Hz, 1H, Ar-*p*), 1.55 (s, 36H, *tert*-butyl) and 1.52 (s, 18H, *tert*-butyl) ppm; APCI-TOF-MS: *m/z* = 937.5133. Calcd for $C_{62}H_{71}DN_4{}^{64}Zn$: 937.5106 $[M]^-$.

15Zn: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 10.08 (d, *J* = 4.6 Hz, 2H, β), 8.90 (d, *J* = 4.6 Hz, 2H, β), 8.84 (m, 4H, β), 8.04 (d, *J* = 1.9 Hz, 2H, Ar-*o*), 8.03 (d, *J* = 1.9 Hz, 4H, Ar-*o*), 7.78 (br-s, 2H, Ar-*p*), 7.75 (br-s, 1H, Ar-*p*), 3.83 (m, 2H, cyclohexyl), 2.76 (d, *J* = 14.7 Hz, 2H, cyclohexyl), 2.34 (s, 1H, OH), 2.30 (m, 2H, cyclohexyl), 2.12 (m, 1H, cyclohexyl), 2.05 (m, 2H, cyclohexyl), 1.96 (m, 1H, cyclohexyl), 1.53 (s, 36H, *tert*-butyl), and 1.51 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 150.33, 150.00, 149.07, 148.90, 148.86, 148.65, 142.23, 141.89, 132.17, 131.76, 130.93, 129.70, 129.63, 122.98, 122.22, 121.00, 79.35, 46.27, 35.25, 31.97, 31.94, 25.88, and 23.80 ppm; APCI-TOF-MS: *m/z* = 1034.5760. Calcd for $C_{68}H_{82}ON_4{}^{64}Zn$: 1034.5775 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 424 (4.0×10^5) and 557 (1.8×10^4).

16Zn: ^{1}H NMR (600 MHz, $CDCl_3$, 60 °C): δ = 12.28–12.20 (br-s, 1H, formyl), 9.93 (br-s, 2H, β), 9.07 (d, *J* = 5.0 Hz, 2H, β), 8.90 (d, *J* = 4.6 Hz, 2H, β), 8.84 (d, *J* = 4.6 Hz, 2H, β), 8.03 (d, *J* = 1.9 Hz, 4H, Ar-*o*), 8.01 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.81 (br-s, 2H, Ar-*p*), 7.78 (br-s, 1H, Ar-*p*), 1.53 (s, 36H, *tert*-butyl), and 1.50 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 60 °C): δ = 195.23, 153.35, 152.29, 149.66, 149.26, 148.88, 148.74, 141.45, 141.32, 135.08, 133.40, 131.77, 129.51, 129.44, 128.76, 128.53, 125.42, 121.29, 35.20, 35.14, 31.93, and 31.83 ppm; APCI-TOF-MS: *m/z* = 964.5010. Calcd for $C_{63}H_{72}ON_4{}^{64}Zn$: 964.4992 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 429 (4.3×10^5), 560 (1.5×10^4), and 604 (2.1×10^4).

Preparation of CuCN·2LiCl (0.2 M in THF)[16]: A Schlenk tube containing CuCN (36 mg, 0.40 mmol) and anhydrous LiCl (34 mg, 0.80 mmol) was dried in vacuum (1−3 torr) for 3 h at 150 ºC, and then purged with argon. After the flask was cooled to room temperature, THF (2.0 mL) was added. After the reaction mixture was stirred for 30 min at room temperature, a yellow solution of CuCN•2LiCl was obtained.

Synthesis of 17Ni and 18Ni: After **2Ni** was generated as described in the synthesis of **3Ni**–**6Ni**, CuCN•2LiCl (0.2 M solution in THF, 0.10 mL, 20 μmol) and an electrophile (200 μmol) were sequentially added. After being stirred for 2 h at room temperature, the reaction mixture was quenched with an NH_4Cl solution, extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After evaporation, the residue was purified on silica gel eluting with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **17Ni** (78 mg, 72 μmol, 72%) and **18Ni** (78 mg, 80 μmol, 80%).

17Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 10.56 (s, 1H, *meso*), 9.16 (m, 2H, β), 8.88 (d, *J* = 4.6 Hz, 1H, β), 8.81 (m, 3H, β), 8.78 (d, *J* = 4.8 Hz, 1H, β), 8.71 (s, 1H, naphthyl), 8.38 (d, *J* = 8.2 Hz, 1H, naphthyl), 8.06 (d, *J* = 8.2 Hz, 1H, naphthyl), 7.98 (d, *J* = 8.2 Hz, 1H, naphthyl), 7.92 (d, *J* = 8.2 Hz, 1H, naphthyl), 7.90 (d, 2H, *J* = 1.9 Hz, Ar-*o*), 7.90 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.90 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.74 (t, *J* = 1.9 Hz, 1H, Ar-*p*), 7.72 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 7.65 (t, *J* = 8.7 Hz, 1H, naphthyl), 7.63 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 7.56 (t, *J* = 8.7 Hz, 1H, naphthyl), 1.49 (s, 18H, *tert*-butyl), 1.47 (s, 18H, *tert*-butyl), and 1.41 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ =193.40, 149.27, 149.16, 144.27, 143.97, 143.33, 142.73, 142.82, 141.05, 139.94, 139.76, 139.63, 139.18, 138.06, 137.61, 137.50, 135.60, 133.96, 133.25, 132.94, 132.65, 132.50, 132.41, 129.90, 128.93, 128.84, 128.76, 128.59, 128.52, 127.99, 126.86, 126.15, 122.25, 121.53, 121.41, 120.97, 119.82, 105.19, 35.17, 35.15, 35.08, 31.84, 31.82, and 31.79 ppm; APCI-TOF-MS: *m/z* = 1084.5533. Calcd for $C_{73}H_{78}ON_4{}^{58}Ni$: 1084.5524 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 427 (2.0×10^5), 534 (1.5×10^4), and 574 (1.1×10^4).

18Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.83 (s, 1H, *meso*), 9.12 (d, *J* = 5.0 Hz, 1H, β), 8.92 (d, *J* = 5.0 Hz, 1H, β), 8.83–8.79 (m, 4H, β), 8.68 (s, 1H, β), 7.89 (m, 4H, Ar-*o*), 7.88 (d, *J* = 1.9 Hz, 2H, Ar-*o*), 7.73 (m, 2H, Ar-*p*), 7.71 (t, *J* = 1.9 Hz, 1H, Ar-*p*), 6.59–6.52 (m, 1H, allyl), 5.45 (d, *J* = 16.9 Hz, 1H, allyl), 5.31 (d, *J* = 8.7 Hz, 1H, allyl), 4.70 (d, *J* = 6.0 Hz, 2H, allyl), 1.50 (s, 18H, *tert*-butyl), 1.49 (s, 18H, *tert*-butyl), and 1.46 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.08, 148.97, 143.45, 143.18, 142.88, 142.69, 142.56, 142.38, 142.15, 142.10, 140.37, 140.29, 140.23, 137.36, 132.77, 132.44, 132.17, 132.09, 131.78, 131.14, 129.19, 128.94, 128.84, 121.22, 121.16, 121.08, 120.82, 120.19, 119.15, 116.70, 101.48, 35.17, 35.14, 32.94, and 31.86 ppm; APCI-TOF-MS: *m/z* = 970.5442. Calcd for $C_{65}H_{76}N_4{}^{58}Ni$: 970.5418 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 411 (2.4×10^5) and 523 (1.7×10^4).

Synthesis of 19Ni: After **2Ni** was generated as described in the synthesis of **3Ni**–**6Ni**, CuCN•2LiCl (0.2 M solution in THF, 0.10 mL, 20 μmol), 2-cyclohexen-1-one (19 μL, 200 μmol) and trimethylchlorosilane (25 μL, 200 μmol) were successively added. After the mixture was stirred for 2 h at room temperature, 3 M HCl was added to deprotect the resulting silyl ether. The organic layer was extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. Concentration followed by chromatographic purification eluting with CH_2Cl_2/hexane afforded a solid. Recrystallization from CH_2Cl_2/methanol gave **19Ni** (70 mg, 68 μmol, 68%).

19Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.76 (s, 1H, *meso*), 9.12 (d, *J* = 4.6 Hz, 1H, β), 8.92 (d, *J* = 4.6 Hz, 1H, β), 8.81–8.78 (m, 4H, β), 8.69 (s, 1H, β), 7.90–7.84 (brs, 6H, Ar-*o*), 7.74 (t, *J* = 1.9 Hz, 2H, Ar-*p*), 7.73 (t, *J* = 1.9 Hz, 2H, Ar-*p*), 7.70 (t, *J* = 1.9 Hz, 1H, Ar-*p*), 4.72 (m, 1H, cyclohexyl), 3.29 (m, 1H, cyclohexyl), 3.06 (t, *J* = 12.84 Hz, 1H, cyclohexyl), 2.78 (m, 1H, cyclohexyl), 2.69 (m, 1H, cyclohexyl), 2.64 (m, 1H, cyclohexyl), 2.40 (m, 2H, cyclohexyl), 2.22 (m, 1H, cyclohexyl), 1.50 (s, 18H, *tert*-butyl), 1.49 (s, 18H, *tert*-butyl), and 1.46 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 211.17, 149.12, 149.01, 148.07, 143.25, 143.02, 142.80, 142.64, 142.52, 140.68, 140.22, 140.15, 140.06, 132.60, 132.28, 132.26, 132.00, 129.24, 128.91, 128.83, 128.49, 121.29, 121.22, 121.17, 120.89, 120.28, 119.31, 100.76, 49.86, 41.70, 38.11, 35.18, 35.16, 35.13, 34.02, 31.85, 31.82, 25.87 ppm; APCI-TOF-MS: *m/z* = 1026.5703. Calcd for $C_{68}H_{80}ON_4{}^{58}Ni$: 1026.5680 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 412 (2.6×10^5) and 524 (1.9×10^4).

Synthesis of 20Ni: After **2Ni** was generated as described in the synthesis of **9Ni** and **10Ni**, CuCN•2LiCl (0.2 M solution in THF, 0.20 mL, 40 μmol) and 2-naphthoyl chloride (76 mg, 400 μmol) were added. The resulting mixture was stirred for 2 h at room temperature and then was quenched with an NH_4Cl solution The organic compounds were extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **20Ni** (77 mg, 62 μmol, 62%).

20Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 11.11 (s, 1H, *meso*), 9.13 (s, 2H, β), 8.81 (d, *J* = 5.0 Hz, 2H, β), 8.79 (d, *J* = 5.0 Hz, 2H, β), 8.68 (s, 2H, naphthyl), 8.35 (d, *J* = 8.7 Hz, 2H, naphthyl), 8.00 (d, *J* = 8.7 Hz, 2H, naphthyl), 7.94 (d, *J* = 8.3 Hz, 2H, naphthyl), 7.89 (d, *J* = 8.7 Hz, 2H, naphthyl), 7.88 (d, *J* = 1.9 Hz, 4H, Ar-*o*), 7.85 (d, *J* = 1.9 Hz, 2H, Ar-*o*), 7.73 (t, *J* = 1.8 Hz, 2H, Ar-*p*), 7.64 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 7.62 (t, *J* = 8.3 Hz, 2H, naphthyl), 7.53 (t, *J* = 8.3 Hz, 2H, naphthyl), 1.47 (s, 18H, *tert*-

butyl), and 1.42 (s, 36H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 192.65, 149.33, 144.22, 143.82, 141.64, 140.34, 140.20, 139.64, 139.29, 137.35, 137.14, 135.63, 133.34, 133.23, 132.61, 132.50, 129.90, 128.83, 128.70, 128.49, 128.46, 127.98, 126.75, 126.17, 121.92, 121.67, 121.54, 121.33, 105.87, 35.16, 35.10, 31.82, and 31.79 ppm; APCI-TOF-MS: *m/z* = 1238.5948. Calcd for $C_{84}H_{84}O_2N_4{}^{58}Ni$: 1238.5942 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 439 (2.1×10^5), 544 (1.8×10^4), and 580 (9.5×10^3).

Synthesis of 22Ni–24Ni: Porphyrinyl Grignard reagent **2Ni** was generated as described in the synthesis of **3Ni**–**6Ni**. To the resulting red solution, $ZnCl_2$(tmeda) (38 mg, 150 μmol) was added. After stirring for 30 min at room temperature, $Pd_2(dba)_3$ (1.5 mg, 1.7 μmol), Ruphos (3.1 mg, 6.7 μmol), and aryl bromide (83 μmol) were added, and then the reaction mixture was stirred for 6 h at 60 ºC. The reaction mixture was quenched with water, extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with CH_2Cl_2/hexane. Recrystallization from CH_2Cl_2/methanol gave **22Ni**–**24Ni**.

22Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.83 (s, 1H, *meso*), 9.05 (d, *J* = 4.6 Hz, 1H, β), 8.90 (d, *J* = 4.6 Hz, 1H, β), 8.86 (s, 1H, β), 8.82 (m, 4H, β), 8.01 (d, *J* = 8.7 Hz, 2H, 4-OMe-Ph), 7.91 (d, *J* = 2.0 Hz, 2H, Ar-*o*), 7.89 (d, *J* = 1.9 Hz, 2H, Ar-*o*), 7.88 (d, *J* = 1.9 Hz, 2H, Ar-*o*), 7.73 (m, 2H, Ar-*p*), 7.71 (t, *J* = 1.9 Hz, 1H, Ar-*p*), 7.28 (d, *J* = 8.7 Hz, 2H, 4-OMe-Ph), 4.01 (s, 3H, OMe), 1.48 (s, 36H, *tert*-butyl), and 1.46 (s, 18H, *tert*-butyl) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 159.63, 149.10, 149.01, 145.54, 143.26, 143.15, 143.05, 142.77, 142.71, 142.66, 141.76, 140.91, 140.28, 140.23, 140.12, 132.76, 132.55, 132.33, 132.31, 132.24, 132.03, 130.09, 129.20, 128.98, 128.94, 128.85, 121.22, 121.21, 120.59, 120.15, 119.40, 114.65, 104.35, 55.67, 35.15, 35.14, and 31.86 ppm; APCI-TOF-MS: *m/z* = 1036.5531. Calcd for $C_{69}H_{78}ON_4{}^{58}Ni$: 1036.5524 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 415 (2.5×10^5) and 526 (2.0×10^4).

23Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.85 (s, 1H, *meso*), 9.03 (d, *J* = 4.6 Hz, 1H, β), 8.96 (s, 1H, β), 8.89 (d, *J* = 4.6 Hz, 1H, β), 8.82 (m, 4H, β), 8.18 (d, *J* = 8.3 Hz, 2H, 4-Bpin-Ph), 8.11 (d, *J* = 8.3 Hz, 2H, 4-Bpin-Ph), 7.92 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.89 (d, *J* = 1.9 Hz, 2H, Ar-*o*), 7.88 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.73 (m, 2H, Ar-*p*), 7.71 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 1.48 (s, 36H, *tert*-butyl), 1.46 (s, 18H, *tert*-butyl), and 1.45 (s, 12H, Bpin) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 149.16, 149.12, 149.02, 145.48, 143.28, 143.15, 142.97, 142.79, 141.51, 140.67, 140.24, 140.14, 140.08, 139.46, 135.47, 132.83, 132.55, 132.45, 132.34, 132.23, 130.77, 130.64, 129.07, 128.95, 128.85, 121.26, 121.21, 120.65, 120.12, 119.72, 104.30, 84.14, 35.18, 35.16, 35.14, 31.85, and 25.13 ppm; APCI-TOF-MS: *m/z* = 1132.6261. Calcd for $C_{74}H_{87}O_2N_4{}^{11}B^{58}Ni$: 1132.6282 $[M]^-$;UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 416 (2.1×10^5) and 526 (1.9×10^4).

24Ni: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.81 (s, 1H, *meso*), 9.03 (d, *J* = 4.6 Hz, 1H, β), 8.96 (s, 1H, β), 8.90 (d, *J* = 4.6 Hz, 1H, β), 8.82 (m, 4H, β), 8.80 (s, 1H, 3-CO_2TIPS-Ph), 8.31 (d, *J* = 7.8 Hz, 1H, 3-CO_2TIPS-Ph), 8.27 (d, *J* = 7.8 Hz, 1H, 3-CO_2TIPS-Ph), 7.90 (d, *J* = 1.9 Hz, 2H, Ar-*o*), 7.89 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.87 (d, *J* = 1.8 Hz, 2H, Ar-*o*), 7.82 (t, *J* = 7.8 Hz, 1H, 3-CO_2TIPS-Ph), 7.74 (m, 2H, Ar-*p*), 7.71 (t, *J* = 1.8 Hz, 1H, Ar-*p*), 1.49 (s, 18H, *tert*-butyl), 1.48 (s, 18H, *tert*-butyl), 1.46 (s, 18H, *tert*-butyl), 1.45 (m, *J* = 7.3 Hz, 3H, TIPS), and 1.16 (d, *J* = 7.3 Hz, 18H, TIPS) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 166.47, 149.14, 149.05, 144.44, 143.27, 143.20, 143.10, 142.99, 142.82, 142.78, 141.36, 140.41, 140.17, 140.04, 140.03, 136.98, 135.58, 132.69, 132.64, 132.60, 132.97, 132.51, 132.48, 132.44, 132.33, 130.95, 129.42, 129.22, 128.95, 128.84, 128.80, 121.41, 121.30, 121.25, 120.73, 120.12, 119.75, 103.95, 35.17, 31.86, 31.83, 18.09, and 12.28 ppm; APCI-TOF-MS: *m/z* = 1206.6636. Calcd for $C_{78}H_{96}O_2N_4{}^{58}NiSi$: 1206.6651 $[M]^-$; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 415 (2.4×10^5) and 527 (1.8×10^4).

Crystal Data:

6Ni: $C_{64}H_{74}ON_4Cl_2Ni$; M_r = 1044.88; monoclinic; space group *C 2/c* (No. 15); *a* = 36.906(12), *b* = 15.540(4), *c* = 25.945(8) Å; β = 131.579(5)º; *V* = 11131(6) Å^3; *Z* = 8; ρ_{calcd} = 1.247 g/cm^3; *T* = 93 K; R_1 = 0.0564 [I>2σ(I)]; R_w = 0.1554 (all data); GOF = 1.043. Crystals were grown from CH_2Cl_2/MeOH.

15Ni: $C_{74.51}H_{89.22}O_{1.19}N_4Ni$; M_r = 1118.71; monoclinic; space group *C 2/c* (No. 15); *a* = 39.08(3), *b* = 9.117(5), *c* = 38.96(3) Å; β = 116.07(2)º; *V* = 12471(15) Å^3; *Z* = 8; ρ_{calcd} = 1.192 g/cm^3; *T* = 93 K; R_1 = 0.1049 [I>2σ(I)]; R_w = 0.2909 (all data); GOF = 1.092. Crystals were grown from toluene/MeOH.

20Ni: $C_{87}H_{84}O_2N_{4.84}Cl_{3.49}Ni$; M_r = 1411.70; triclinic, space group *P*-1 (No. 2); *a* = 13.491(5), *b* = 17.043(4), *c* = 17.188(4) Å; α = 102.5100(14), β = 92.344(9), γ = 106.854(8)º; *V* = 3669.7(17) Å^3; *Z* = 2; ρ_{calcd} = 1.278 g/cm^3; *T* = 93 K; R_1 = 0.0697 [I>2σ(I)]; R_w = 0.2269 (all data); GOF = 1.057. Crystals were grown from $CHCl_3$/MeCN.

CCDC 991731 (**6Ni**), CCDC 991732 (**15Ni**), and CCDC 991733 (**20Ni**) contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Experimental details, copies of the ^{1}H NMR, ^{13}C NMR, and HR-MS spectra of all compounds, and X-ray crystal structure of **6Ni**, **15Ni**, and **20Ni**.

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[12] The structures of **6Ni**, **15Ni**, and **20Ni** were confirmed by X-ray crystallographic analysis (Figures S61−63 in the Supporting Information).

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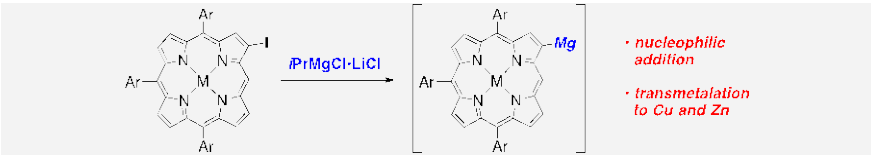

Keisuke Fujimoto, Hideki Yorimitsu,* and Atsuhiro Osuka* ……..... Page No. – Page No.

Efficient Synthesis and Versatile Reactivity of Porphyrinyl Grignard Reagents

Iodine-magnesium exchange between iodoporphyrins and *i*PrMgCl•LiCl has realized the formation of porphyrinyl Grignard reagents for the first time. Thanks to the high reactivity, the resulting porphyrinyl Grignard reagents do not only react with various carbonyl compounds but also undergo transmetalation to afford porphyrinyl copper and zinc species, which participate in 1,4-addition and Negishi coupling, respectively.

Keywords: porphyrin / iodine-magnesium exchange / Grignard reagent / transmetalation