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## Supporting Information

# Carbolithiation of *meso*-Aryl-Substituted 5,15-Diazaporphyrin Selectively Provides 3-Alkylated Diazachlorins

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**Table of Contents**

Instrumentation and Materials ..... S2
General Procedures and Compound Data ..... S2
NMR Spectra of Compounds ..... S8
Cyclic Voltammograms of **3a** and **4a** ..... S18
Theoretical Calculations ..... S19

**Instrumentation and Materials**

$^{1}$H NMR (500 MHz) and $^{13}$C NMR (126 MHz) were recorded on a Varian INOVA-500 spectrometer and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ ($\delta$ = 7.26 ppm) or $CD_2Cl_2$ ($\delta$ = 5.32 ppm) for $^{1}$H NMR and $CDCl_3$ ($\delta$ = 77.16 ppm) or $CD_2Cl_2$ ($\delta$ = 53.84 ppm) for $^{13}$C NMR. UV/vis absorption spectra were recorded on a Shimadzu UV-2550. Mass spectra were recorded on a Bruker microTOF using ESI-TOF method for *i*-PrOH solutions. X-ray data were taken on a Bruker SMART APEX X-Ray diffractometer equipped with a large area CCD detector. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

**General Procedures**

**Synthesis of $\beta$-Alkylated diazaporphyrin 3 and $\beta$-Alkylated diazachlorin 4**

A Schlenk tube containing **2** (15.1mg, 0.025 mmol) was evacuated and then refilled with nitrogen. To the tube, dry solvent (toluene or THF, 5 mL) was added. The mixture was cooled to –78 °C and stirred. To the mixture, RLi (0.20 mmol) was added dropwise over 5 min. The mixture was stirred at –78 °C for 3.5 h. After the reaction completed, water and EtOAc were added. The organic layer was separated, washed with water, and evaporated under reduced pressure to get a solid residue. The residue was subjected on silica gel column chromatography ($CHCl_3$ as an eluent) to afford **3** as a purple solid and **4** as a green solid.

**Synthesis of diazachlorin 5**

A two-necked round bottom flask containing **2** (15.3 mg, 0.025 mmol) was evacuated and then refilled with nitrogen. To the flask, *p*-tosylhydrazide (2 equiv.), potassium carbonate (5 equiv.), and pyridine (10 mL) was added. The mixture was heated to 100 °C and stirred for 1 h. Progress of the reaction was monitored by TLC. Additional sets of *p*-tosylhydrazide (2 equiv.) and potassium carbonate (5 equiv.) were added to the solution at hour intervals until the consumption of **2** was saturated. After the reaction was completed, the mixture was cooled to room temperature. After reaction was quenched by additions of a dilute aqueous HCl solution, the final mixture was

extracted with $CH_2Cl_2$. The organic layer was separated and dried over $Na_2SO_4$. The solvent was removed by a rotary evaporator and the solid residue was subjected on silica gel column chromatography (hexane/EtOAc as an eluent) to get **5** as a green solid (1.0 mg, 7%).

**Compound Data**

**3a**: $^1$H NMR (500 MHz, $CD_2Cl_2$): $\delta$ = 9.11–9.15 (m, 3H, $\beta$-H), 8.74–8.78 (m, 3H, $\beta$-H), 8.47 (m, 1H, $\beta$-H), 7.29 (s, 4H, Mes-*meta*), 3.44 (s, 3H, Me), 2.60 (s, 6H, Mes-*para*), 1.81 (s, 6H, Mes-*ortho*), 1.80 (s, 6H, Mes-*ortho*); $^{13}$C NMR (500 MHz, $CD_2Cl_2$): $\delta$ = 150.80, 150.71, 150.70, 150.52, 145.44, 144.79, 144.42, 143.56, 139.33, 139.31, 138.88, 138.84, 135.73, 135.69, 134.59, 133.85, 133.80, 133.46, 131.02, 130.94, 128.32, 121.58, 119.78, 21.56, 21.54, 21.51, 21.50, 13.81 ppm; $\lambda_{max}$ ($\varepsilon$ [$M^{-1}$ $cm^{-1}$]) = 375 (70000), 391 (91000), and 575 (65000) nm; HR-MS (ESI-MS): *m/z* = 619.2112, calcd. for $(C_{37}H_{32}N_6Ni)^+$ = 619.2126 [$(M + H)^+$]. Single crystals were obtained by slow vapor diffusion of acetonitrile into a 1,2-dichloroethane solution. $C_{37}H_{32}N_6Ni$, $M_w$ = 619.40, monoclinic, space group = $P2_1/c$, $a$ = 8.477(5), $b$ = 24.012(15), $c$ = 7.890(5) Å, $\beta$ = 110.629(10)°, $V$ = 1503.1(16) Å$^3$, $Z$ = 2, $D_{calc}$ = 1.369 g/cm$^3$, $T$ = 153(2) K, $R$ = 0.0444 ($I > 2.0\ \sigma(I)$), $R_w$ = 0.1359 (all data), GOF = 1.043.

**4a**: $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 8.68 (d, $J$ = 5.0 Hz, 1H, $\beta$-H), 8.58 (d, $J$ = 4.5 Hz, 1H, $\beta$-H), 8.38 (d, $J$ = 5.0 Hz, 1H, $\beta$-H), 8.29 (d, $J$ = 5.0 Hz, 1H, $\beta$-H), 8.21 (d, $J$ = 4.5 Hz, 1H, $\beta$-H), 8.02 (d, $J$ = 5.0 Hz, 1H, $\beta$-H), 7.21 (s, 1H, Mes-*meta*), 7.17 (s, 2H, Mes-*meta*), 7.16 (s, 1H, Mes-*meta*), 4.45–4.56 (m, 1H, sp$^3$-$\beta$), 4.06–4.11 (dd, $J$ = 17.5, 9.5 Hz, 1H, sp$^3$-$\beta$), 3.46–3.51 (dd, $J$ = 17.5, 4.5 Hz, 1H, sp$^3$-$\beta$), 2.54 (s, 3H, Mes-*para*), 2.51 (s, 3H, Mes-*para*), 1.93 (s, 3H, Mes-*ortho*), 1.87 (s, 3H, Mes-*ortho*), 1.81 (s, 3H, Mes-*ortho*), 1.81 (s, 3H, Mes-*ortho*), 1.77 (d, $J$ = 7.0 Hz, 3H, Me) ppm; $^{13}$C NMR ($CDCl_3$): $\delta$ = 166.26, 158.77, 152.40, 149.24, 148.27, 139.34, 138.55, 138.35, 138.12, 137.92, 137.80, 136.94, 135.99, 135.28, 135.05, 132.78, 130.85, 130.00, 129.03, 128.94, 128.91, 128.00, 127.44, 125.98, 114.99, 112.09, 40.84, 40.52, 29.94, 21.81, 21.51, 21.08, 20.96 ppm; $\lambda_{max}$ ($\varepsilon$ [$M^{-1}$ $cm^{-1}$]) = 350 (31000), 392 (54000), 486 (3000), 518 (6000), and 636 (37000) nm; HR-MS (ESI-MS): *m/z* = 621.2273, calcd. for $(C_{37}H_{34}N_6Ni)^+$ = 621.2282 [$(M + H)^+$]. Single

crystals were obtained by vapor diffusion of hexane into an EtOAc solution. $C_{74}H_{62}N_{10}Ni_2$, $M_w$ = 1208.76, triclinic, space group = $P1$ (No. 2), $a$ = 8.455(5), $b$ = 13.354(5), $c$ = 16.134(5) Å, $\alpha$ = 110.622(5), $\beta$ = 90.985(5)°, $\gamma$ = 96.490(5), $V$ = 1690.8(13) Å$^3$, $Z$ = 1, $D_{calc}$ = 1.187 g/cm$^3$, $T$ = 113 K, $R$ = 0.0504 ($I > 2.0\ \sigma(I)$), $R_w$ = 0.1322 (all data), GOF = 1.167.

**3b**: $^1$H NMR (500 MHz, $CD_2Cl_2$): $\delta$ = 9.12–9.16 (m, 3H, $\beta$-H), 8.74–8.78 (m, 3H, $\beta$-H), 8.47 (s, 1H, $\beta$-H), 7.32 (s, 1H, Mes-*meta*), 7.29 (s, 1H, Mes-*meta*), 7.29 (s, 2H, Mes-*meta*), 3.97 (t, $J$ = 8.0 Hz, 2H, *n*Bu), 2.61 (s, 3H, Mes-*para*), 2.60 (s, 3H, Mes-*para*), 2.21 (quintet, $J$ = 8.5 Hz, 2H, *n*Bu), 1.81 (s, 6H, Mes-*ortho*), 1.80 (s, 6H, Mes-*ortho*), 1.70 (sextet, $J$ = 7.5 Hz, 2H, *n*Bu), 1.09 (t, $J$ = 7.5 Hz, 3H, *n*Bu) ppm; $^{13}$C NMR (500 MHz, $CD_2Cl_2$): $\delta$ = 150.79, 150.70, 150.50, 150.67, 150.20, 144.81, 144.53, 143.54, 139.35, 139.32, 138.87, 138.81, 135.80, 135.72, 134.56, 133.90, 133.83, 133.59, 133.45, 133.43, 129.95, 128.37, 128.33, 121.53, 119.82, 33.84, 33.10, 28.12, 28.07, 23.39, 23.37, 21.59, 21.52, 14.32 ppm; $\lambda_{max}$ ($\varepsilon$ [M$^{-1}$ cm$^{-1}$]) = 376 (67000), 392 (89000), and 575 (62000) nm**;** HR-MS (ESI-MS): $m/z$ = 661.2565, calcd. for $(C_{40}H_{38}N_6Ni)^+$ = 661.2595 [$(M + H)^+$].

**4b**: $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 8.67 (d, $J$ = 5.0 Hz, 1H, $\beta$-H), 8.58 (d, $J$ = 4.5 Hz, 1H, $\beta$-H), 8.38 (d, $J$ = 4.5 Hz, 1H, $\beta$-H), 8.29 (d, $J$ = 5.0 Hz, 1H, $\beta$-H), 8.21 (d, $J$ = 5.0 Hz, 1H, $\beta$-H), 8.01 (d, $J$ = 4.5 Hz, 1H, $\beta$-H), 7.23 (s, 1H, Mes-*meta*), 7.18 (s, 1H, Mes-*meta*), 7.17 (s, 1H, Mes-*meta*), 7.15 (s, 1H, Mes-*meta*), 4.42–4.48 (m, 1H, sp$^3$-$\beta$), 4.00–4.05 (dd, $J$ = 17.75, 9.5 Hz, 1H, sp$^3$-$\beta$), 3.57 (dd, $J$ = 22.5, 9.0 Hz, 1H, sp$^3$-$\beta$), 2.54 (s, 3H, Mes-*para*), 2.52 (s, 3H, Mes-*para*), 2.36–2.42 (m, 2H, *n*-Bu), 1.97 (s, 3H, Mes-*ortho*), 1.90 (s, 3H, Mes-*ortho*), 1.80 (s, 3H, Mes-*ortho*), 1.77 (s, 3H, Mes-*ortho*), 1.51–1.56 (m, 2H, *n*Bu), 1.34–1.50 (m, 2H, *n*Bu), 0.88 (t, $J$ = 7.0 Hz, 3H, *n*Bu) ppm; $^{13}$C NMR (500 MHz, $CD_2Cl_2$): $\delta$ =139.29, 138.58, 138.55, 138.30, 138.10, 137.94, 137.74, 136.92, 135.99, 135.90, 135.28, 135.04, 132.74, 130.90, 130.83, 129.94, 129.04, 128.97, 128.91, 127.99, 127.49, 127.42, 125.90, 111.97, 45.80, 38.63, 36.04, 28.94, 22.91, 21.52, 21.49, 21.12, 21.07, 21.02, 20.95, 20.88, 14.51 ppm; $\lambda_{max}$ ($\varepsilon$ [M$^{-1}$ cm$^{-1}$]) = 351 (37000), 392 (65000), 487 (4000), 519 (7000), and 637 (46000) nm; HR-MS (ESI-MS): $m/z$ = 663.2764, calcd. for $(C_{40}H_{40}N_6Ni)^+$ = 663.2752 [$(M + H)^+$].

**3c**: $^{1}$H NMR (500 MHz, $CDCl_3$): $\delta$ = 9.14–9.17 (m, 3H, $\beta$-H), 8.79 (d, $J$ = 5.0 Hz, 1H, $\beta$-H), 8.78 (d, $J$ = 5.0 Hz, 1H, $\beta$-H), 8.74 (d, $J$ = 4.5 Hz, 1H, $\beta$-H), 8.41 (s, 1H, $\beta$-H), 7.28 (s, 2H, Mes-*meta*), 7.26 (s, 2H, Mes-*meta*), 4.60 (quartet, $J$ = 2.0 Hz, 1H, *s*Bu), 2.63 (s, 3H, Mes-*para*), 2.61 (s, 3H, Mes-*para*), 2.31 (quintet, $J$ = 2.0, 2.0 Hz, 1H, *s*Bu), 2.16 (quintet, $J$ = 2.0, 2.0 Hz, 1H, *s*Bu), 1.82 (s, 3H, Mes-*ortho*), 1.81 (s, 3H, Mes-*ortho*), 1.80 (s, 6H, Mes-*ortho*), 1.79 (d, $J$ = 7.0 Hz, 3H, *s*Bu), 1.10 (t, $J$ = 7.5 Hz, 3H, *s*Bu) ppm; $^{13}$C NMR ($CDCl_3$): $\delta$ = 155.42, 150.43, 150.35, 150.33, 149.60, 144.43, 144.17, 143.29, 143.22, 139.13, 139.12, 139.10, 138.47, 138.41, 135.64, 135.55, 134.24, 133.99, 133.58, 133.43, 133.28, 128.21, 128.13, 128.06, 121.17, 119.59, 34.12, 31.15, 21.92, 21.65, 21.62, 21.55, 12.32, 12.30 ppm; $\lambda_{max}$ ($\varepsilon$ [$M^{-1}$ $cm^{-1}$]) = 376 (64000), 392 (84000), and 575 (56000) nm; HR-MS (ESI-MS): $m/z$ = 661.2586, calcd for $(C_{40}H_{38}N_6Ni)^+$ = 661.2595 [$(M + H)^+$].

**4c**: $^{1}$H NMR (500 MHz, $CDCl_3$): $\delta$ = 8.68 (d, $J$ = 4.5 Hz, 1H, $\beta$-H), 8.59 (dd, $J$ = 1.0, 4.5 Hz, 1H, $\beta$-H), 8.38 (dd, $J$ = 1.0, 4.5 Hz, 1H, $\beta$-H), 8.30 (d, $J$ = 5.0 Hz, 1H, $\beta$-H), 8.22 (d, $J$ = 4.5 Hz, 1H, $\beta$-H), 8.01 (dd, $J$ = 6.0, 3.0 Hz, 1H, $\beta$-H), 7.24 (s, 1H, Mes-*meta*), 7.19 (s, 1H, Mes-*meta*), 7.16 (s, 1H, Mes-*meta*), 7.15 (s, 1H, Mes-*meta*), 4.52–4.65 (m, 1H, $sp^3$-$\beta$), 3.82–3.95 (octet, $J$ = 10.5, 18.0, 34.0 Hz, 1H, $sp^3$-$\beta$), 3.59–3.65 (m, 1H, $sp^3$-$\beta$), 2.74 (m, 1H, *s*Bu), 2.54 (s, 3H, Mes-*para*), 2.52 (s, 3H, Mes-*para*), 2.02 (d, 3H, Mes-*ortho*), 1.94 (d, 3H, Mes-*ortho*), 1.78 (d, 3H, Mes-*ortho*), 1.76 (d, 3H, Mes-*ortho*), 1.65 (m, 1H, *s*Bu), 1.48 (m, 1H, *s*Bu), 1.08 (t, 3H, *s*Bu), 0.72 (t, 3H, *s*Bu) ppm; $^{13}$C NMR ($CDCl_3$): $\delta$ = 165.77, 165.23, 160.04, 159.94, 152.35, 152.16, 149.43, 149.21, 148.18, 139.23, 138.59, 138.26, 138.08, 137.89, 137.72, 136.96, 135.92, 135.33, 135.03, 134.99, 132.70, 130.92, 129.91, 129.05, 128.95, 127.99, 125.79, 111.74, 50.95, 49.36, 39.33, 21.50, 21.05, 20.94, 20.81, 13.98, 12.26, 12.20 ppm; $\lambda_{max}$ ($\varepsilon$ [$M^{-1}$ $cm^{-1}$]) = 350 (33000), 392 (60000), 487 (4000), 519 (7000), and 636 (41000) nm; HR-MS (ESI-MS): $m/z$ = 663.2745, calcd. for $(C_{40}H_{40}N_6Ni)^+$ = 663.2752 [$(M + H)^+$].

**4d**: $^{1}$H NMR (500 MHz, $CDCl_3$): $\delta$ = 8.67 (d, $J$ = 4.5 Hz, 1H, $\beta$-H), 8.58 (d, $J$ = 4.5 Hz, 1H, $\beta$-H), 8.37 (d, $J$ = 4.5 Hz, 1H, $\beta$-H), 8.29 (d, $J$ = 4.5 Hz, 1H, $\beta$-H), 8.22 (d, $J$ = 4.5 Hz, 1H, $\beta$-H), 8.03 (d,

$J$ = 5.0 Hz, 1H, $\beta$-H), 7.27 (s, 1H, Mes-*meta*), 7.20 (s, 1H, Mes-*meta*), 7.13 (s, 1H, Mes-*meta*), 7.11 (s, 1H, Mes-*meta*), 4.28, 4.26 (dd, 1H, $J$ = 3.0, 10.0 Hz, $sp^3$-$\beta$), 4.03, 4.01 (dd, 1H, $J$ = 10.0, 18.3 Hz, $sp^3$-$\beta$), 3.75, 3.72 (dd, 1H, $J$ = 3.5, 18.3 Hz, $sp^3$-$\beta$), 2.54 (s, 3H, Mes-*para*), 2.51 (s, 3H, Mes-*para*), 2.17 (s, 3H, Mes-*ortho*), 1.99 (s, 3H, Mes-*ortho*), 1.72 (s, 3H, Mes-*ortho*), 1.60 (s, 3H, Mes-*ortho*), 1.00 (s, 9H, *t*Bu) ppm; $^{13}$C NMR ($CDCl_3$): $\delta$ = 163.54, 159.81, 151.38, 149.25, 149.21, 148.34, 139.05, 138.61, 138.59, 138.25, 138.07, 138.02, 137.80, 136.76, 135.91, 135.86, 135.32, 134.75, 132.37, 131.24, 131.19, 129.93, 129.04, 128.91, 128.74, 127.98, 127.57, 125.93, 111.01, 54.76, 36.31, 35.99, 27.18, 21.49, 20.92, 20.65 ppm; $\lambda_{max}$ ($\varepsilon$ [$M^{-1}$ $cm^{-1}$]) = 353 (34000), 393 (60000), 488 (4000), 519 (7000), and 638 (39000) nm; HR-MS (ESI-MS): $m/z$ = 663.2771, calcd. for $(C_{40}H_{40}N_6Ni)^+$ = 663.2752 [$(M + H)^+$].

**3e**: $^1$H NMR (500 MHz, $CD_2Cl_2$): $\delta$ = 9.20 (d, $J$ = 4.5 Hz, 1H, β-H), 9.14 (d, $J$ = 4.5 Hz, 2H, β-H), 8.90 (s, 1H, β-H), 8.77–8.79 (m, 3H, β-H), 8.75 (dd, 2H, $J$ = 7.8, 1.0 Hz, Ph-H), 7.73 (t, 2H, $J$ = 7.8 Hz, Ph-H), 7.58 (t, 1H, $J$ = 7.8 Hz, Ph-H), 7.31 (s, 2H, Mes-*meta*), 7.30 (s, 2H, Mes-*meta*), 2.62 (s, 3H, Mes-*para*), 2.61 (s, 3H, Mes-*para*), 1.84 (s, 6H, Mes-*ortho*), 1.82 (s, 6H, Mes-*ortho*) ppm; $^{13}$C NMR (500 MHz, $CD_2Cl_2$): $\delta$ = 151.21, 151.11, 150.92, 148.33, 145.55, 144.50, 144.20, 144.18, 143.37, 139.38, 139.31, 138.94, 135.60, 135.52, 135.40, 134.65, 134.33, 133.93, 133.89, 133.79, 133.74, 133.62, 133.57, 131.27, 1131.22, 29.79, 129.73, 129.06, 128.57, 128.42, 128.35, 121.44, 120.97, 21.62, 21.59, 21.56, 21.52 ppm; $\lambda_{max}$ ($\varepsilon$ [$M^{-1}$ $cm^{-1}$]) = 367 (63000), 396 (91000), and 583 (55000) nm; HR-MS (ESI-MS): $m/z$ = 681.2285, calcd for $(C_{42}H_{34}N_6Ni)^+$ = 681.2282 [$(M + H)^+$]. Single crystals were obtained by vapor diffusion of acetonitrile into a chloroform solution. $C_{86}H_{70}Cl_6N_8Ni_2$, $M_w$ = 1545.62, monoclinic, space group $P2(1)/c$, $a$ = 34.583(5), $b$ = 29.038(4), $c$ = 14.934(2) Å, $\beta$ = 94.398(3)°, $V$ = 14952(3) Å$^3$, $Z$ = 8, $D_{calc}$ = 1.421 g/cm$^3$, $T$ = 153 K, $R$ = 0.0739 ($I$ > 2.0 $\sigma(I)$), $R_w$ = 0.2023 (all data), GOF = 1.028.

**5**: $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 8.67 (d, $J$ = 4.5 Hz, 1H, $\beta$-H), 8.57 (d, $J$ = 5.0 Hz, 1H, $\beta$-H), 8.33 (d, $J$ = 4.5 Hz, 1H, $\beta$-H), 8.28 (d, $J$ = 5.0 Hz, 1H, $\beta$-H), 8.21 (d, $J$ = 5.0 Hz, 1H, $\beta$-H), 8.01 (d, $J$ = 5.0 Hz, 1H, $\beta$-H), 7.18 (s, 2H, Mes-*meta*), 7.17 (s, 2H, Mes-*meta*), 4.43–4.39 (m, 2H, $sp^3$-$\beta$),

3.86–3.89 (m, 2H, $sp^3$-$\beta$), 2.54 (s, 3H, Mes-*para*), 2.50 (s, 3H, Mes-*para*), 1.87 (s, 6H, Mes-*ortho*), 1.84 (s, 6H, Mes-*ortho*) ppm; $^{13}C$ NMR (500 MHz, $CD_2Cl_2$): $\delta$ = 163.15, 160.51,152.10, 149.65, 149.27, 148.25, 139.38, 138.54, 138.35, 138.13, 137.79, 136.98, 136.09, 135.22, 134.91, 132.82, 130.88, 130.80, 129.98, 129.10, 128.97, 128.00, 126.08, 111.99, 34.87, 32.21, 21.49, 21.45, 21.02, 20.97 ppm; $\lambda_{max}$ ($\varepsilon$ [$M^{-1}$ $cm^{-1}$]) = 349 (24000), 391 (45000), 487 (2923), 518 (4600), and 638 (31000) nm; HR-MS (ESI-MS): $m/z$ = 607.2147, calcd. for $(C_{36}H_{32}N_6Ni)^+$ = 607.2126 [$(M + H)^+$].

## NMR Spectra of Compounds

* = solvents and impurities

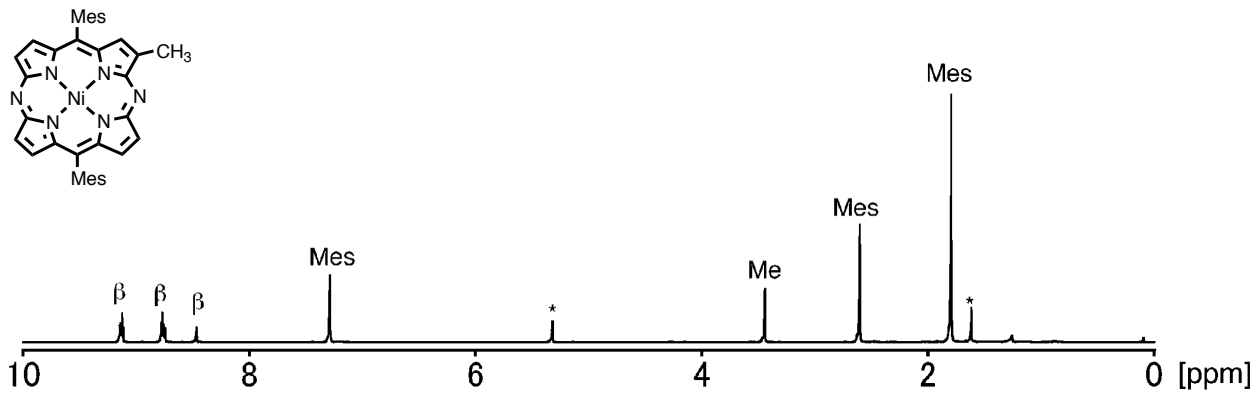


***Figure S1.*** $^{1}$H NMR spectrum of **3a** in $CD_2Cl_2$.

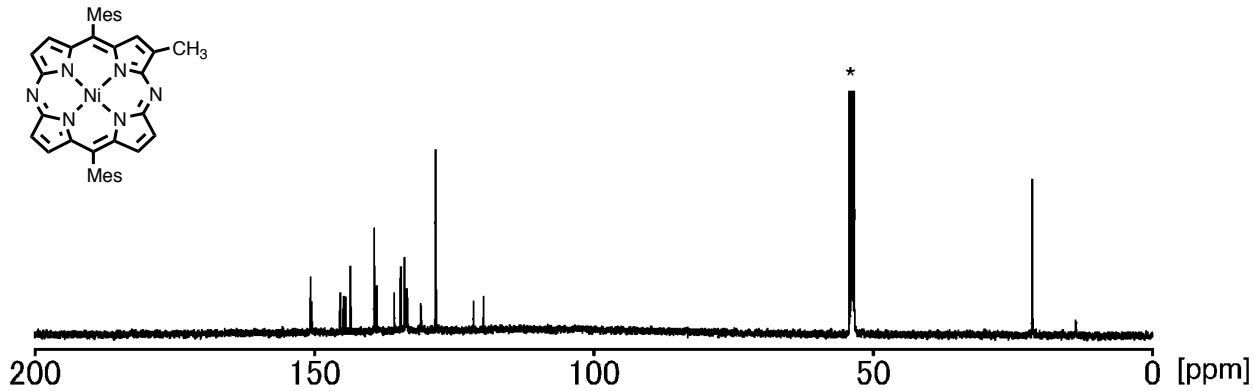


***Figure S2.*** $^{13}$C NMR spectrum of **3a** in $CD_2Cl_2$.

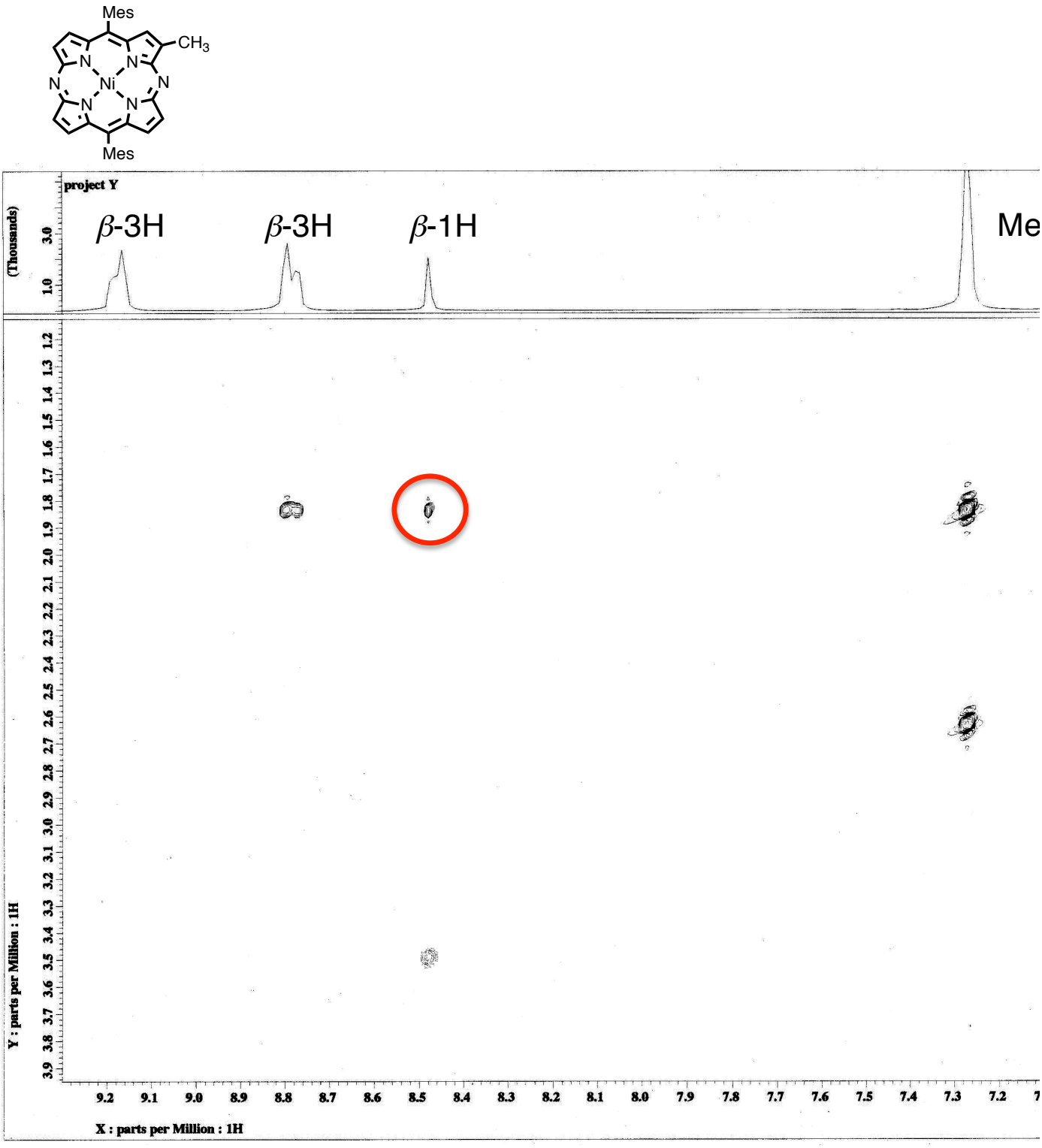


***Figure S3.*** $^{1}$H- $^{1}$H NOESY NMR spectrum of **3a** in $CDCl_3$.

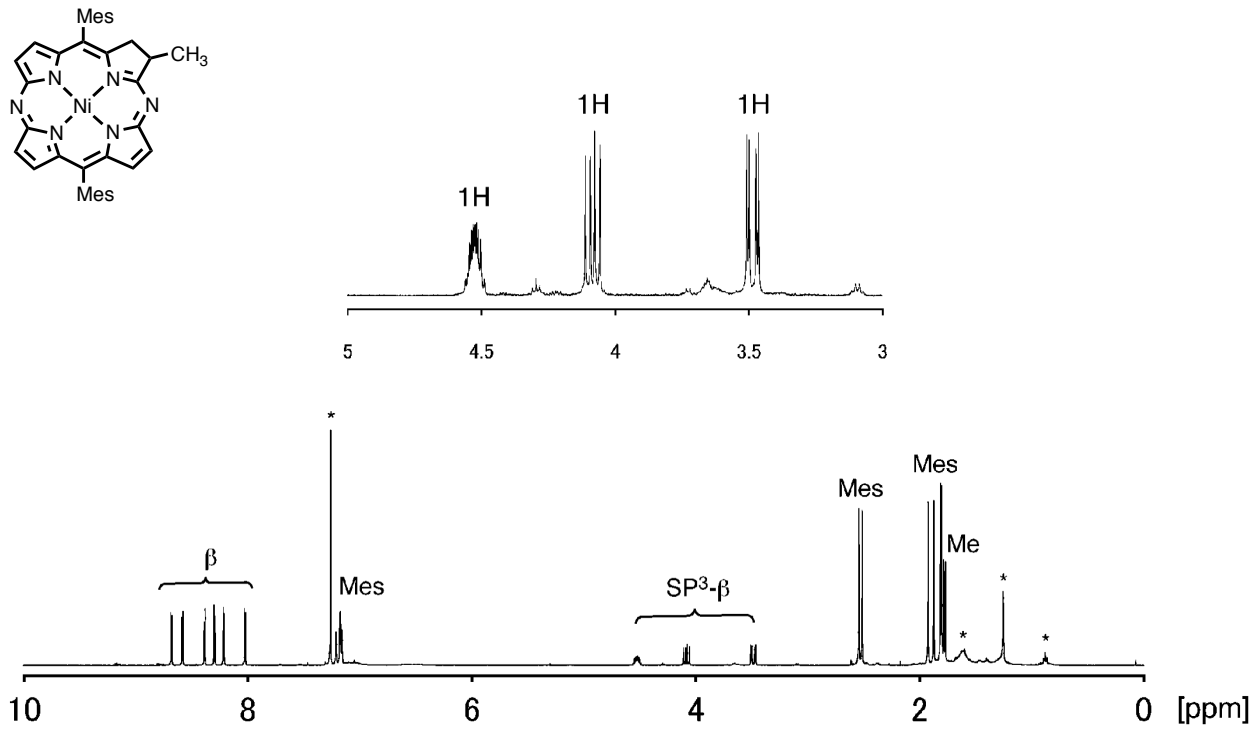


***Figure S4.*** $^{1}$H NMR spectrum of **4a** in $CDCl_3$.

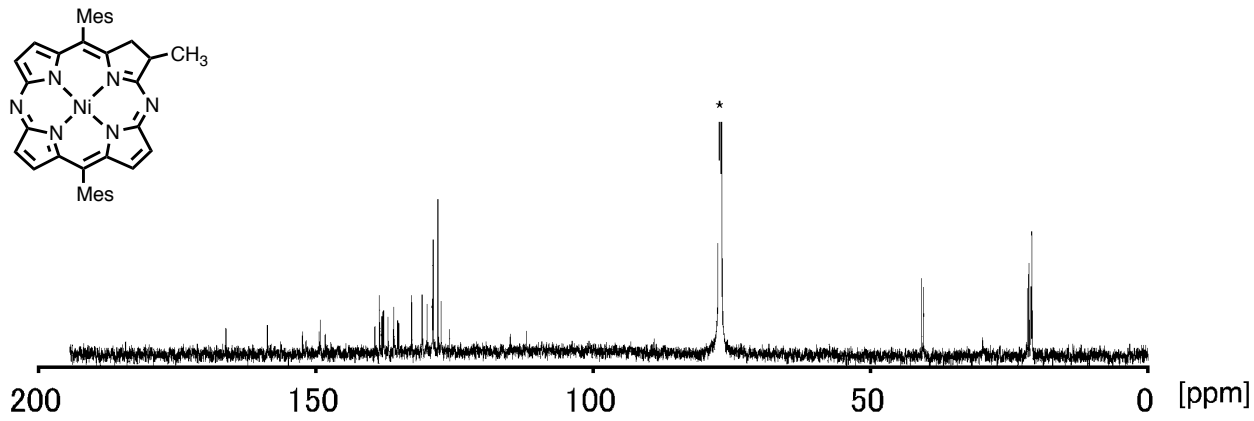


***Figure S5.*** $^{13}$C NMR spectrum of **4a** in $CDCl_3$.

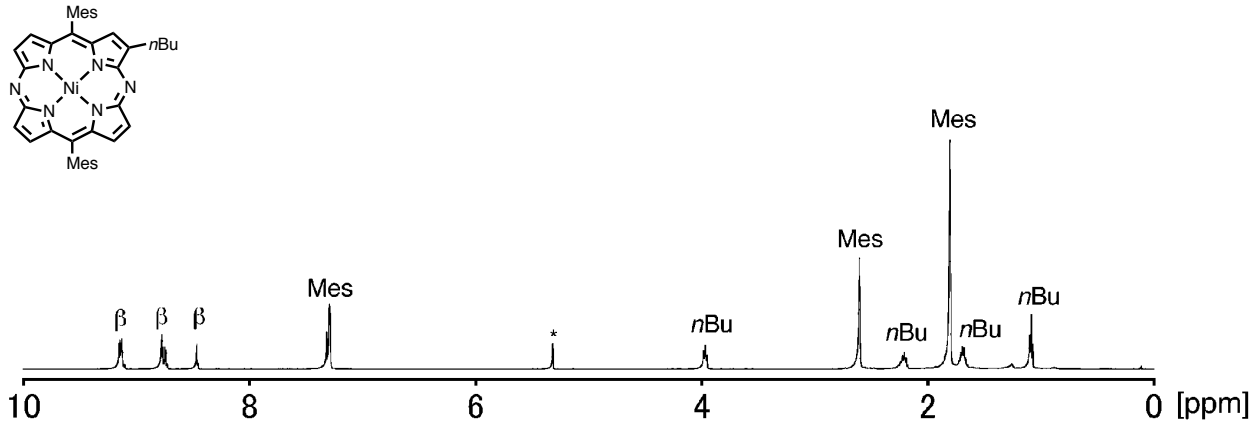


***Figure S6.*** $^{1}$H NMR spectrum of **3b** in $CD_2Cl_2$.

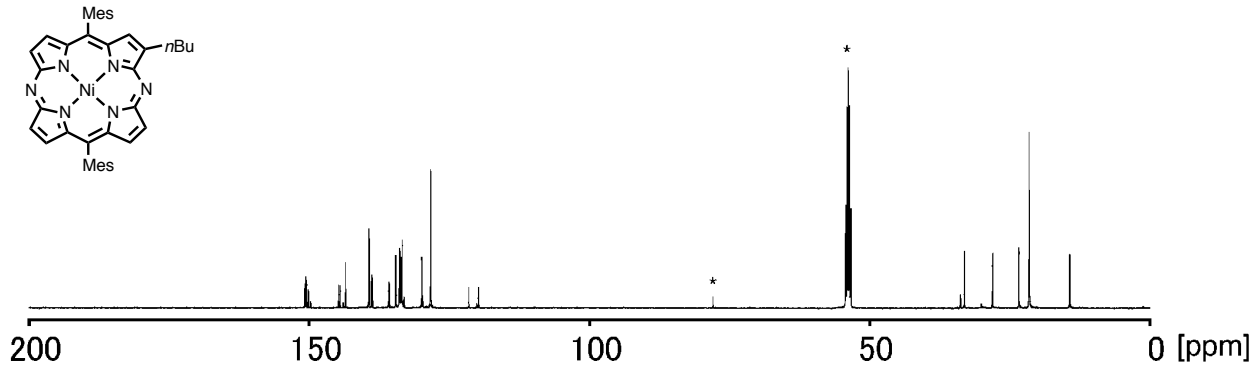


***Figure S7.*** $^{13}$C NMR spectrum of **3b** in $CD_2Cl_2$

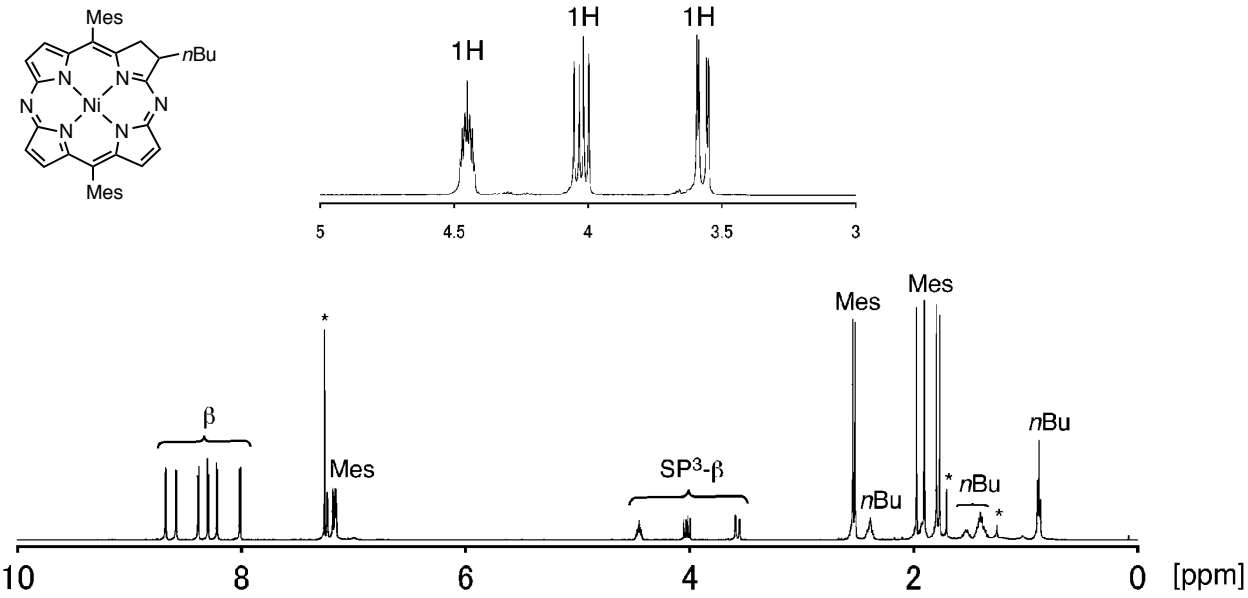


***Figure S8.*** $^{1}$H NMR spectrum of **4b** in $CDCl_3$.

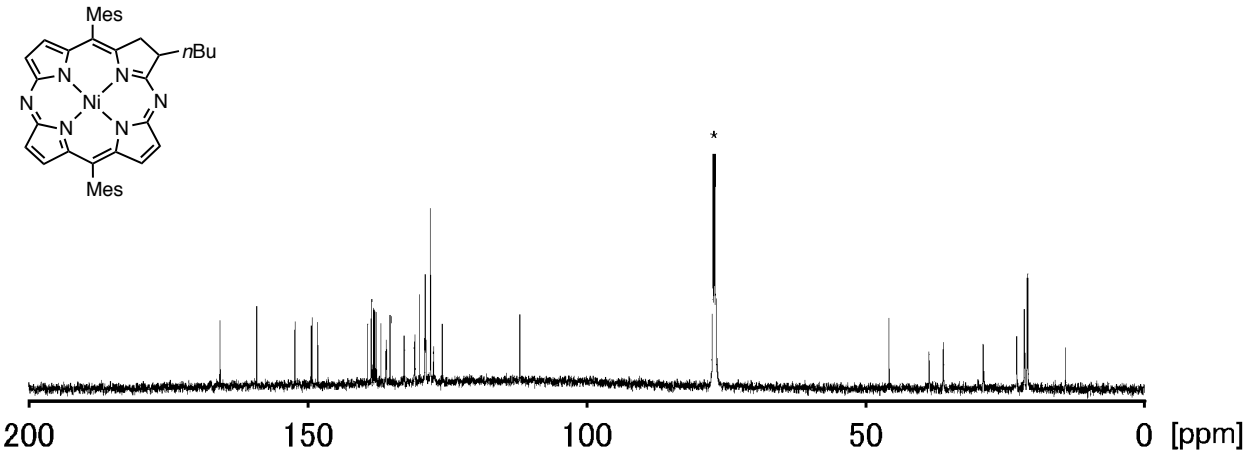


***Figure S9.*** $^{13}$C NMR spectrum of **4b** in $CDCl_3$.

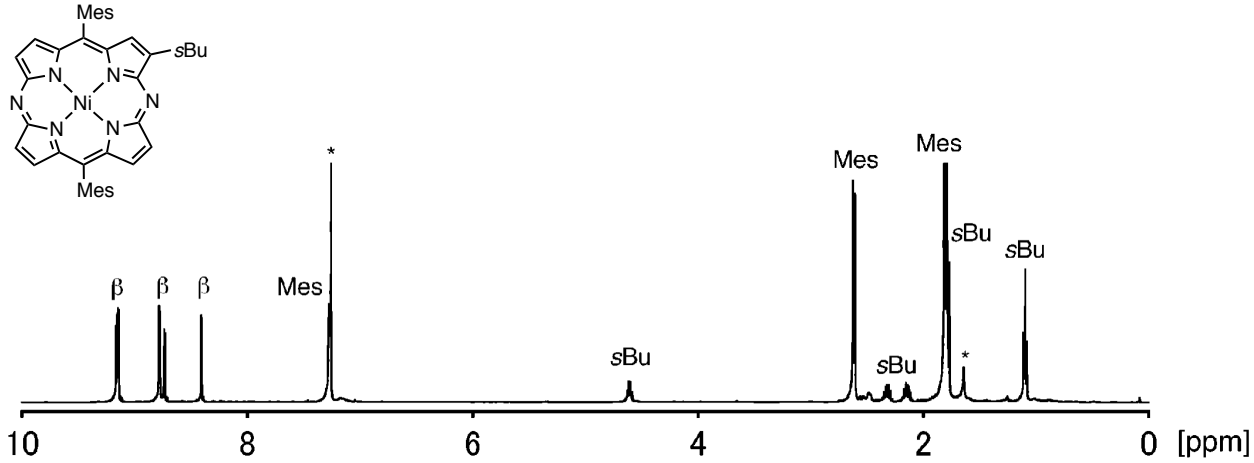


***Figure S10.*** $^{1}$H NMR spectrum of **3c** in $CDCl_3$.

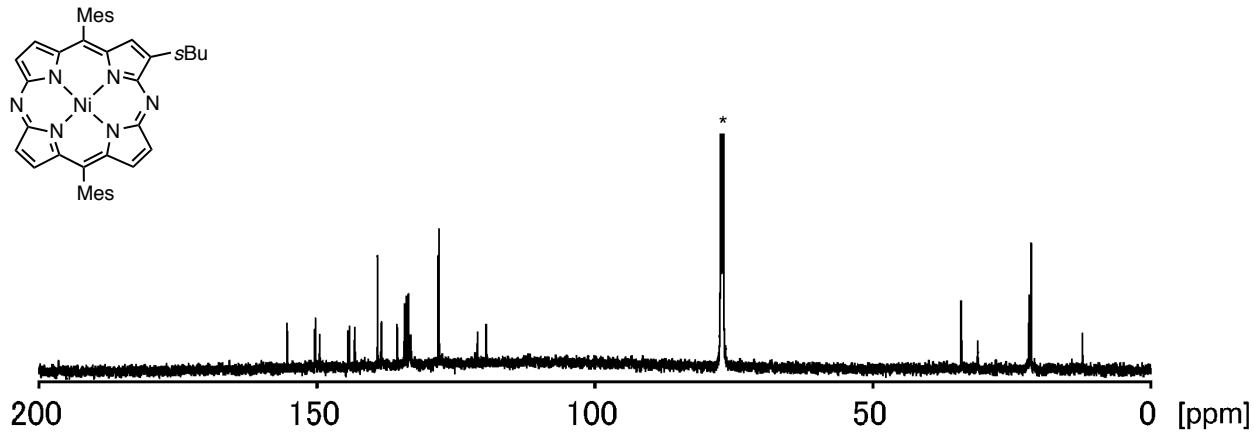


***Figure S11.*** $^{13}$C NMR spectrum of **3c** in $CDCl_3$.

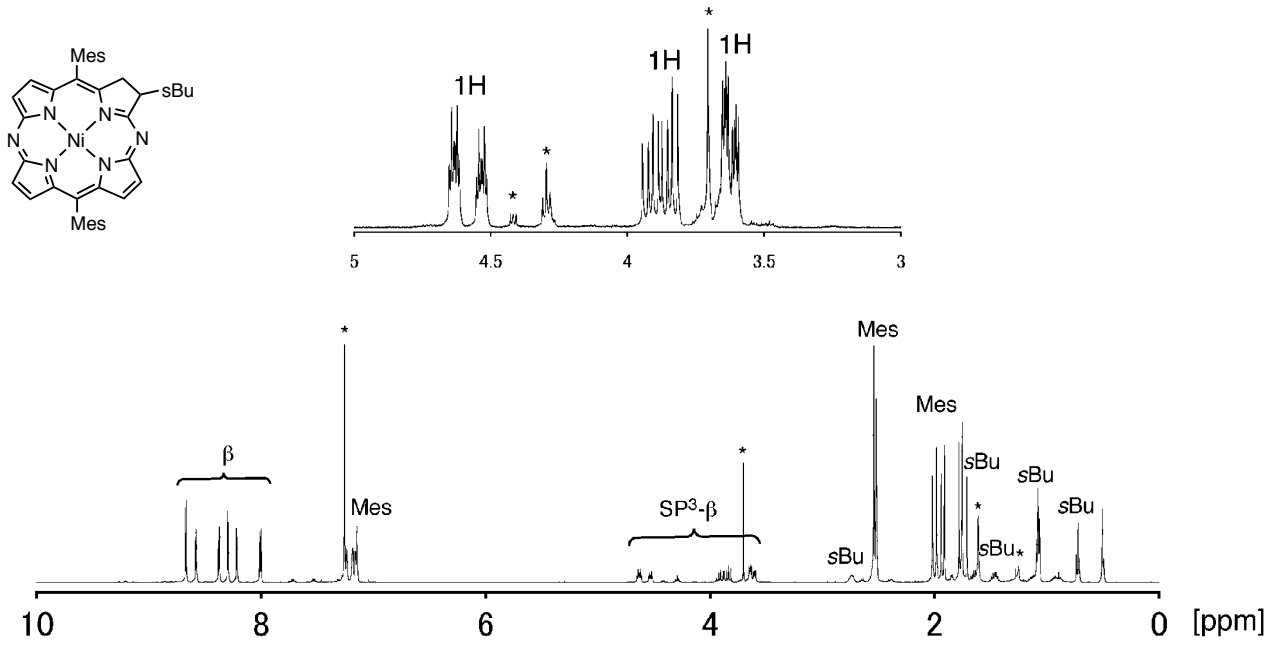


***Figure S12.*** $^{1}$H NMR spectrum of **4c** in $CDCl_3$.

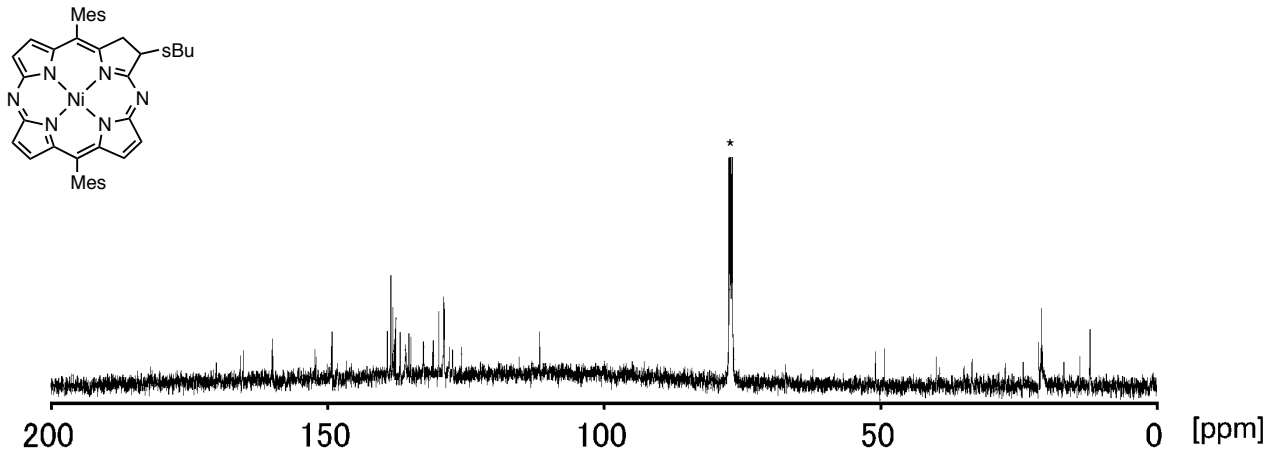


***Figure S13.*** $^{13}$C NMR spectrum of **4c** in $CDCl_3$.

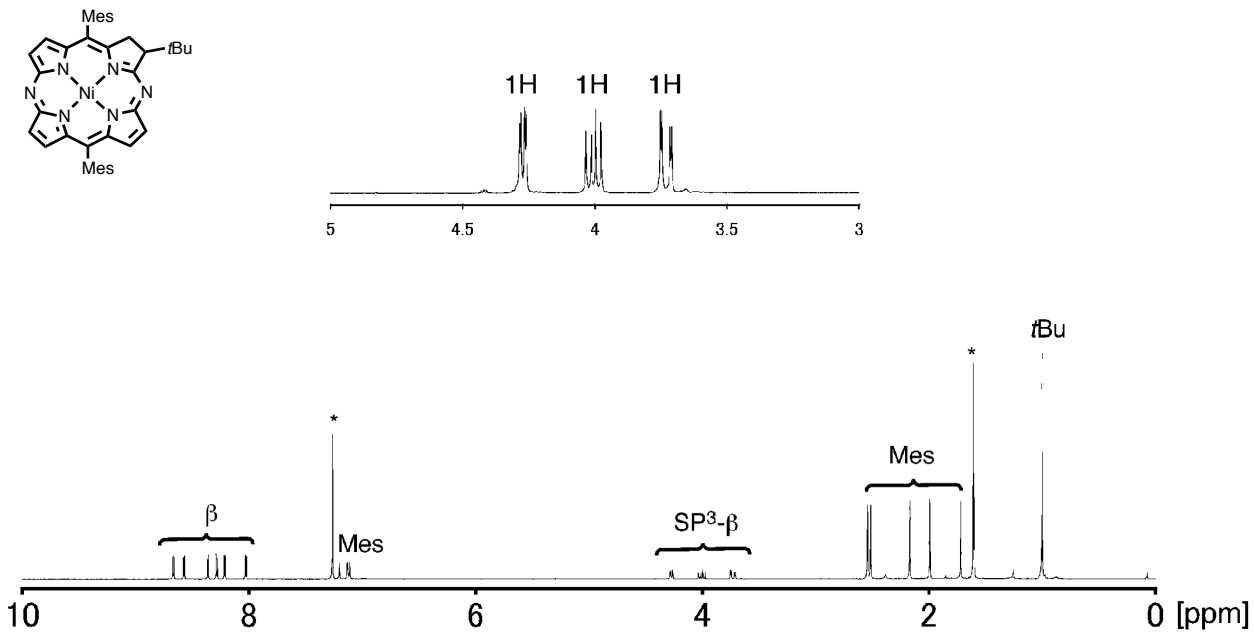


***Figure S14.*** $^{1}$H NMR spectrum of **4d** in $CDCl_3$.

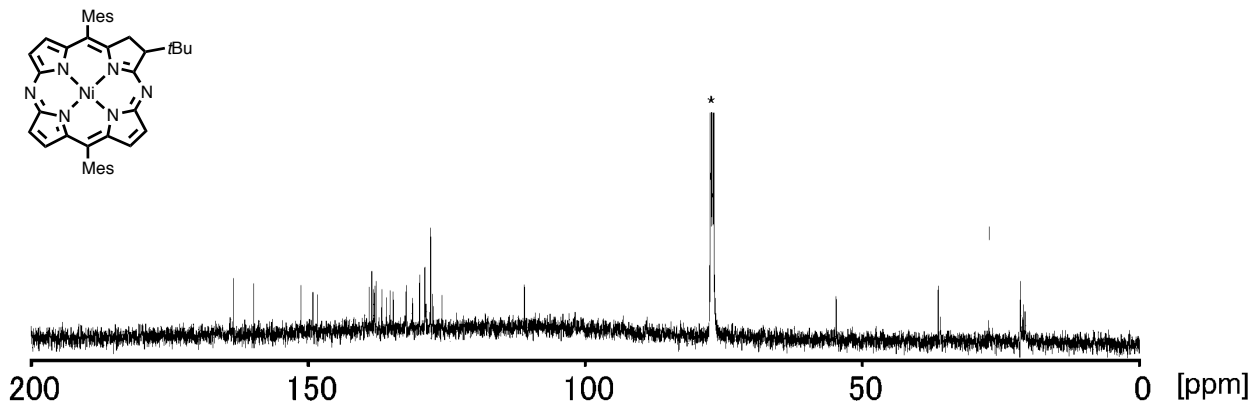


***Figure S15.*** $^{13}$C NMR spectrum of **4d** in $CDCl_3$.

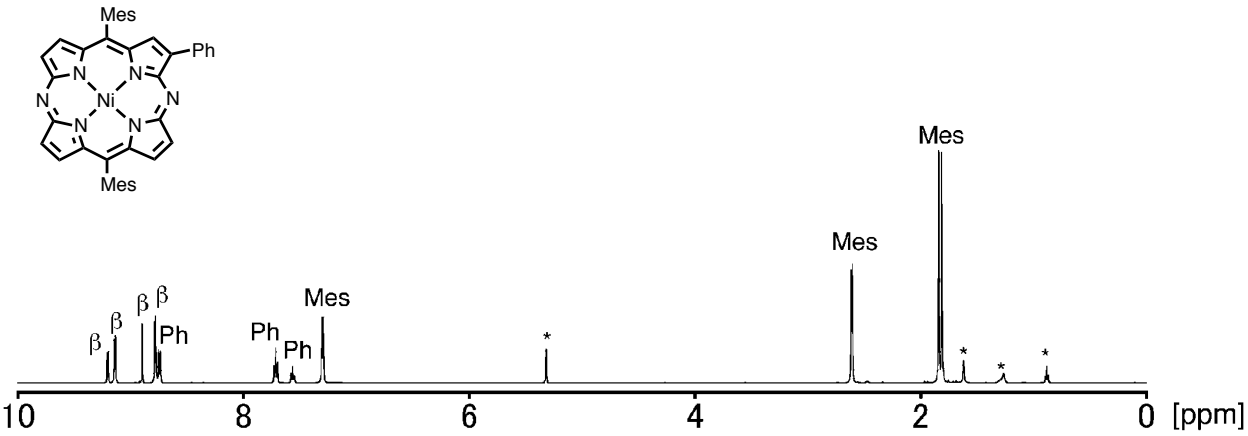


***Figure S16.*** $^{1}$H NMR spectrum of **3e** in $CD_2Cl_2$.

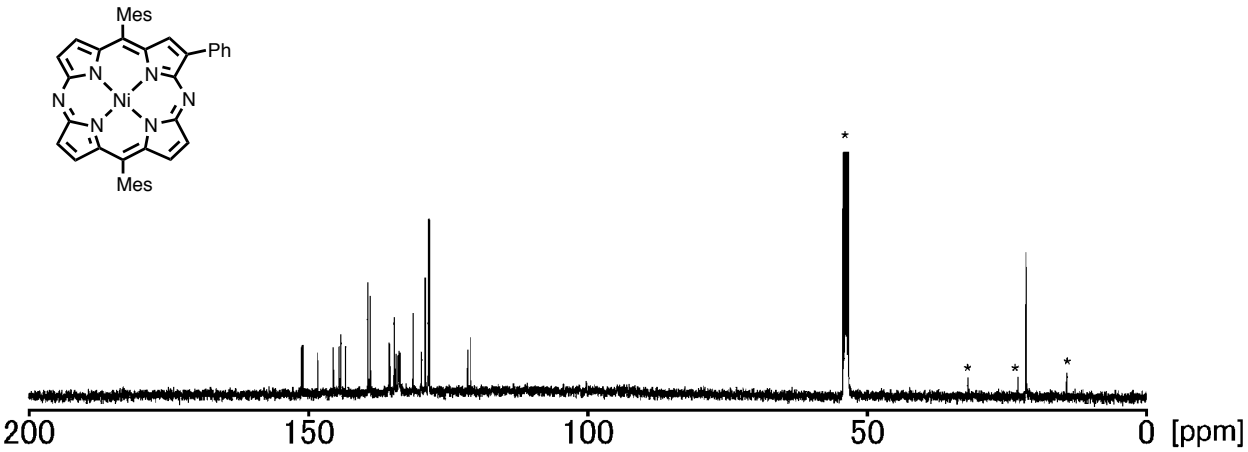


***Figure S17.*** $^{13}$C NMR spectrum of **3e** in $CD_2Cl_2$.

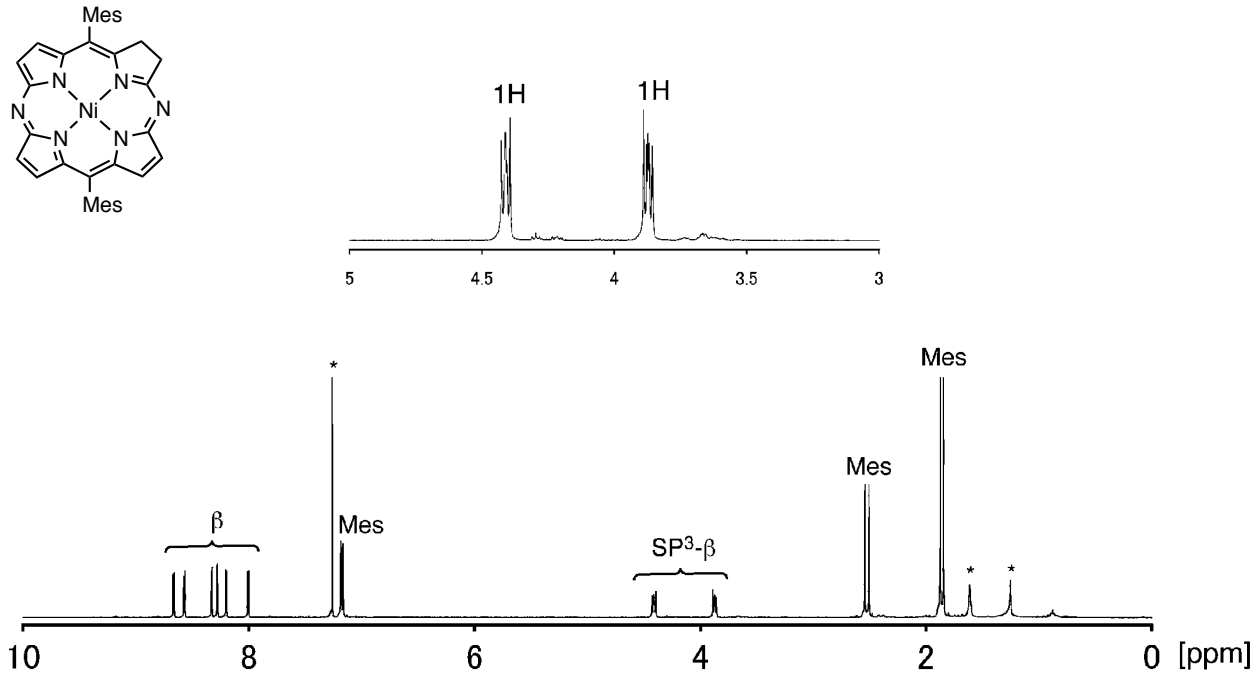


***Figure S18.*** $^{1}$H NMR spectrum of **5** in $CDCl_3$.

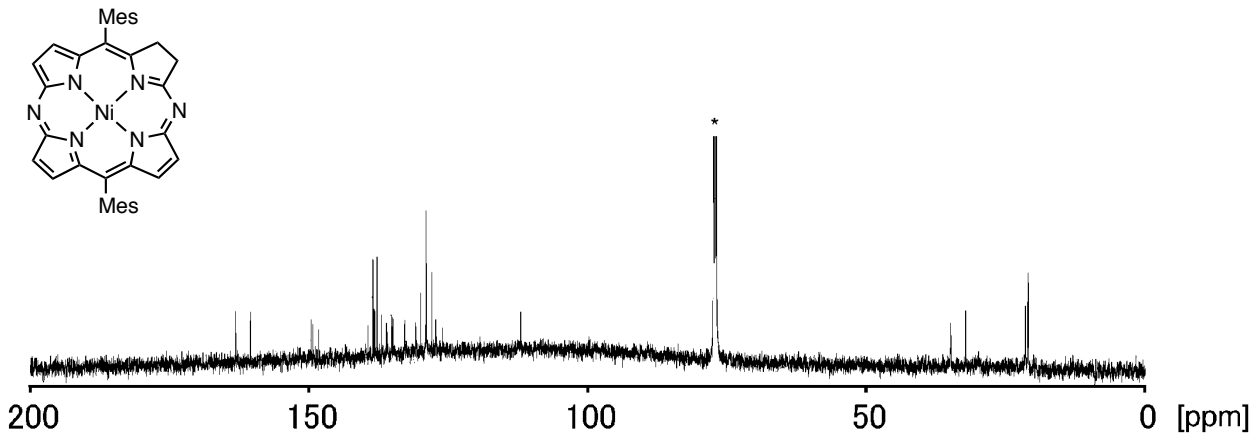


***Figure S19.*** $^{13}$C NMR spectrum of **5** in $CDCl_3$.

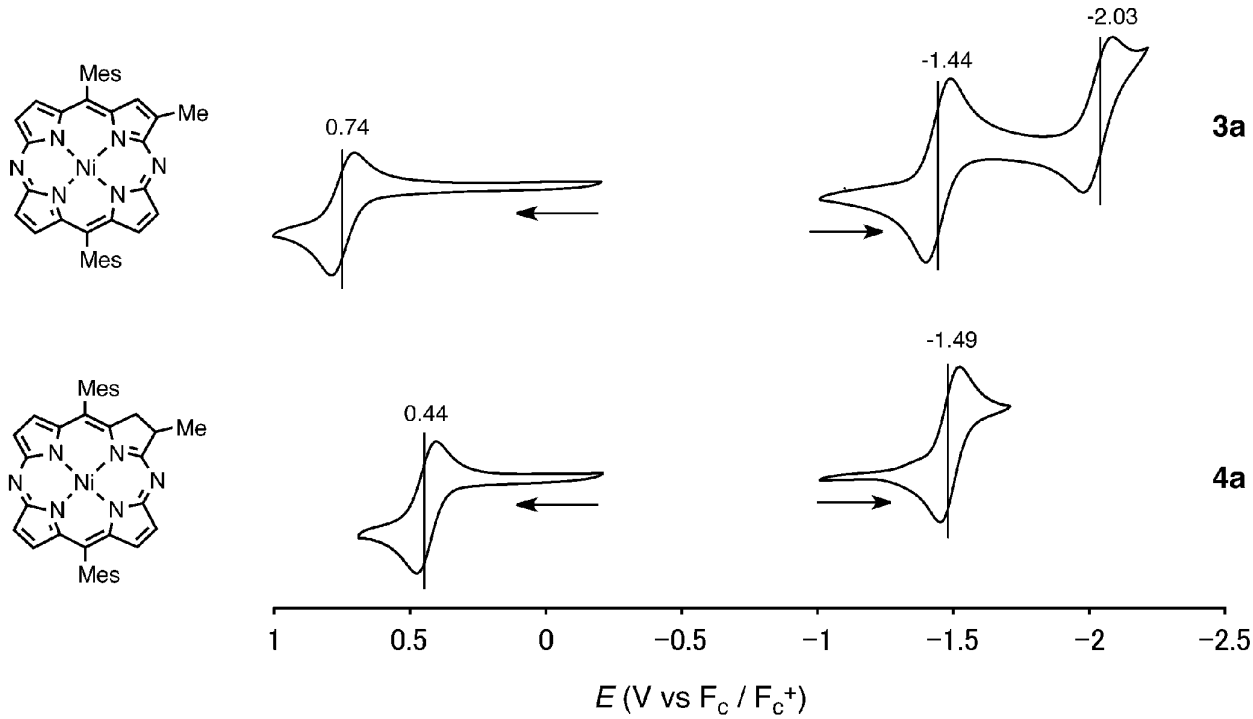


***Figure S20.*** Cyclic voltammograms (0.1 V•s$^{-1}$) of **3a** and **4a** in $CH_2Cl_2$ (0.1 M $TBAPF_6$). working electrode: Pt, counter electrode: Pt, reference electrode: Ag/$AgClO_4$.

## Theoretical calculations

All calculations were carried out using the *Gaussian 09* program.[1] Initial geometries of for **3a** and **4a** were obtained from their X-ray structures. Full optimizations were performed without any symmetry restriction with Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP)[2] and a basis set consisting of SDD[3] for Ni and 6-31G(d) for the rest (denoted as 631SDD).

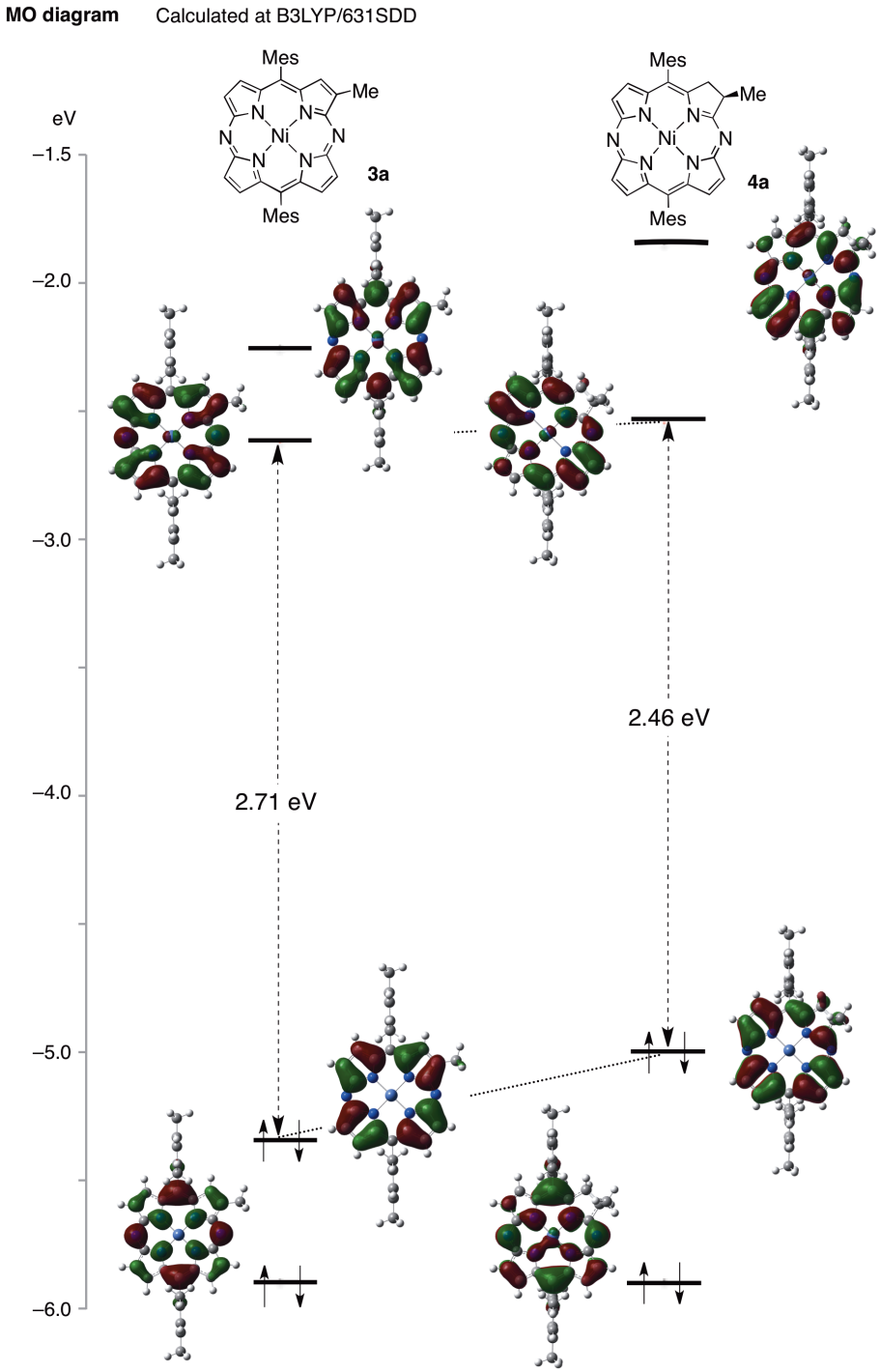


***Figure S21.*** MO diagram for **3a** and **4a** calculated at the B3LYP/631SDD level.

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2) (a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098. (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
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