Supporting Information

Meso-to-meso Pyrrole-Bridged Porphyrin Arrays

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Instrumentation and Materials

^{1}H NMR (500 MHz) spectra were taken on a Bruker AVANCE-500 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ as internal reference for ^{1}H NMR (δ = 7.260 ppm). UV/Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. Fluorescence emission spectra were recorded on a HITACHI F-4500 spectrometer and absolute fluorescence quantum yields were measured by a photon-counting method by using an integration sphere on a Hamamatsu Photonics C9920-02 spectrometer. MALDI-TOF mass spectra were obtained with a Bruker ultrafleXtreme MALDI-TOF/TOF spectrometer with matrix. X-Ray data were taken on a Bruker SMART APEX II X-Ray diffractometer equipped with a large area CCD detector. Redox potentials were measured by cyclic voltammetry on a CHI900 scanning electrochemical microscope. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Time-resolved fluorescence decay measurements

A time-correlated single-photon-counting (TCSPC) system was used for measurements of spontaneous fluorescence decay. As an excitation light source, we used a mode-locked Ti:sapphire laser (Spectra Physics, MaiTai BB) which provides ultrashort pulse (center wavelength of 800 nm with 80 fs at FWHM) with high repetition rate (80 MHz). This high repetition rate was reduced to 800 kHz by using homemade pulse-picker. The pulse-picked output was frequency doubled by a 1-mm-thick BBO crystal (type-I, θ = 29.2°, EKSMA). The fluorescence was collected by a microchannel plate photomultiplier (MCP-PMT, Hamamatsu, R3809U-51) with a thermoelectric cooler (Hamamatsu, C4878) connected to a TCSPC board (Becker & Hickel SPC-130). The overall instrumental response function was about 25 ps (FWHM). A vertically polarized pump pulse by a Glan-laser polarizer was irradiated to samples, and a sheet polarizer set at an angle complementary to the magic angle (54.7°), was placed in the fluorescence collection path to obtain polarization-independent fluorescence decays.

Femtosecond transient absorption and transient absorption anisotropy measurements

The femtosecond time-resolved transient absorption (TA) spectrometer consisted of Optical Parametric Amplifiers (Palitra, Quantronix) pumped by a Ti:sapphire regenerative amplifier system (Integra-C) operating at 1 kHz repetition rate and an optical detection system. The generated OPA pulses had a pulse width of approximately 100fs and an average power of 1 mW in the range 280-2700 nm which were used as pump pulses. White light continuum (WLC) probe pulses were generated using a sapphire window (3 mm of thickness) by focusing of small portion of the fundamental 800 nm pulses. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (ILS250, Newport). Intensities of the spectrally dispersed WLC probe pulses are monitored by a High Speed spectrometer (Ultrafast Systems). To obtain the time-resolved transient absorption difference signal (ΔA) at a specific time, the pump pulses were chopped at 500 Hz and absorption spectra intensities were saved alternately with or without pump pulse. Typically, 4000 pulses excite samples to obtain the fs-TA spectra at

a particular delay time. The polarization angle between pump and probe beam was set at the magic angle (54.7°) using a Glan-laser polarizer with a half-wave retarder in order to prevent polarization-dependent signals. Cross-correlation fwhm in pump-probe experiments was less than 200 fs and chirp of WLC probe pulses was measured to be 800 fs in the 400-800 nm regions. To minimize chirp, all reflection optics in probe beam path and 2 mm path length of quartz cell were used. After the fs-TA experiments, we carefully checked absorption spectra of all compounds to detect if there were artifacts due to degradation and photo-oxidation of samples.

General Procedures

Synthesis of 2H and 3H: A toluene–DMF solution (4 mL/2 mL) of **1**-bromoporphyrin (150 mg, -1Br ca 75%, -2Br ca 24%), 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole (35.1 mg, 0.11 mmol), $Pd_2(dba)_3$ (10.07 mg, 0.011 mmol), PPh_3 (11.53 mg, 0.044 mmol), Cs_2CO_3 (71.5 mg, 0.22 mmol), and CsF (33.44 mg, 0.22 mmol) was degassed through three freeze-pump-thaw cycles, and the reaction flask was purged with argon. The resulting mixture was stirred at reflux for 48 h. The reaction mixture was diluted with CH_2Cl_2, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by silica-gel column chromatography (CH_2Cl_2–hexane as an eluent) and recrystallization with CH_2Cl_2/MeOH, **2H** obtained as a dark red solid(79 mg, 0.0549 mmol, 50% yield), while **3H** was obtained as a dark green solid (30 mg, 0.0137 mmol, 18% yield).

Synthesis of 2H-1Br: To a solution of **2H** (150 mg, 0.104 mmol) in $CHCl_3$ (300 ml) in a 500 ml of flask was added dropwise at 0 ^oC a solution of NBS (18.5 mg, 0.104 mmol) in $CHCl_3$. Until complete consumption of starting material as monitored by TLC, quenched with acetone. Evaporation of the solvent followed by silica-gel column chromatography (CH_2Cl_2–hexane as an eluent) and recrystallization with CH_2Cl_2/MeOH, **2H-1Br** obtained as a dark green solid (94.6 mg, 0.0624 mmol, 60% yield).

Synthesis of 4H: A toluene–DMF solution (4 mL/2 mL) of **2H-1Br** (100 mg, 0.066 mmol), 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole (10.53 mg, 0.033 mmol), $Pd_2(dba)_3$ (3.02 mg, 0.0033 mmol), PPh_3 (3.46 mg, 0.0132 mmol), Cs_2CO_3 (21.45 mg, 0.066 mmol), and CsF (10.03 mg, 0.066 mmol) was degassed through three freeze-pump-thaw cycles, and the reaction flask was purged with argon. The reaction mixture was diluted with CH_2Cl_2, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by silica-gel column chromatography (CH_2Cl_2–hexane as an eluent) and recrystallization with CH_2Cl_2/MeOH, **4H** obtained as a dark green solid (67.8 mg, 0.023 mmol, 70% yield).

Synthesis of Boc-3H: A mixture of **3H** (100 mg, 0.0457 mmol), DMAP (8.4 mg, 0.0685 mmol), and $(Boc)_2O$ (100 mg, 0.457 mmol) in THF (5mL) was stirred under Ar atmosphere for 2 h. Evaporation of the solvent followed by recrystallization from CH_2Cl_2/MeOH . **Boc-3H** was obtained quantitatively.

Synthesis of Boc-4H: A mixture of **4H** (150 mg, 0.051 mmol), DMAP (9.4 mg, 0.0765 mmol), and $(Boc)_2O$ (111 mg, 0.51 mmol) in THF (6mL) was stirred under Ar atmosphere for 2 h. Evaporation of the solvent followed by recrystallization from CH_2Cl_2/MeOH. **Boc-4H** was obtained quantitatively.

Synthesis of Boc-3H-1Br: To a solution of **Boc-3H** (100 mg, 0.0424 mmol) in $CHCl_3$ (300 ml) in a 500 ml of flask was added dropwise at 0 °C a solution of NBS (7.56 mg, 0.0424 mmol) in $CHCl_3$. After the reaction was quenched with acetone. Evaporation of the solvent followed by silica-gel column chromatography (CH_2Cl_2–hexane as an eluent) and recrystallization with CH_2Cl_2/MeOH, **Boc-3H-1Br** obtained as a dark red solid (57.8 mg, 0.0237 mmol, 56% yield).

Synthesis of Boc-4H-1Br: To a solution of **Boc-4H** (150 mg, 0.047 mmol) in $CHCl_3$ (300 ml) in a 500 ml of flask was added dropwise at 0 °C a solution of NBS (8.4 mg, 0.047 mmol) in $CHCl_3$. After the reaction was quenched with acetone. Evaporation of the solvent followed by silica-gel column chromatography (CH_2Cl_2–hexane as an eluent) and recrystallization with CH_2Cl_2/MeOH, **Boc-4H-1Br** obtained as a dark red solid(86.01 mg, 0.0263 mmol, 56% yield).

Synthesis of Boc-5H: A toluene–DMF solution (4 mL/2 mL) of **2H-1Br** (92.48 mg, 0.061 mmol), **Boc-3H-1Br** (150 mg, 0.061 mmol), 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole (19.46 mg, 0.061 mmol), $Pd_2(dba)_3$ (5.58 mg, 0.0061 mmol), PPh_3 (6.39 mg, 0.0244 mmol), Cs_2CO_3 (39.65 mg, 0.122 mmol), and CsF (18.54 mg, 0.122 mmol) was degassed through three freeze-pump-thaw cycles, and the reaction flask was purged with argon. The resulting mixture was stirred at reflux for 48 h. The reaction mixture was poured to water and the products were extracted with CH_2Cl_2. The organic extracts were combined, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by GPC and silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) and recrystallization with CH_2Cl_2/MeOH, **Boc-5H** (65 mg, 0.016 mmol, 26.1% yield) was obtained as a dark red solids.

Synthesis of Boc-6H: A toluene–DMF solution (3 mL/1.5 mL) of **Boc-3H-1Br** (100 mg, 0.041 mmol), 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole (6.54 mg, 0.0205 mmol), $Pd_2(dba)_3$ (1.86 mg, 0.00205 mmol), PPh_3 (2.1 mg, 0.0082 mmol), Cs_2CO_3 (13.33 mg, 0.041 mmol), and CsF (6.23 mg, 0.041 mmol) was degassed through three freeze-pump-thaw cycles, and the reaction flask was purged with argon. The reaction mixture was diluted with CH_2Cl_2, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by GPC and silica-gel column chromatography (CH_2Cl_2–hexane as an eluent) and recrystallization with CH_2Cl_2/MeOH, **Boc-6H** obtained as a dark red solid (64 mg, 0.013 mmol, 63% yield).

Synthesis of Boc-8H: A toluene–DMF solution (2 mL/1 mL) of **Boc-4H-1Br** (100 mg, 0.0306 mmol), 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole (4.88 mg, 0.0153 mmol), $Pd_2(dba)_3$ (1.4 mg, 0.00153 mmol), PPh_3 (1.6 mg, 0.0612 mmol), Cs_2CO_3 (9.94 mg, 0.0306 mmol), and CsF (4.65 mg, 0.0306 mmol) was degassed through three freeze-pump-thaw cycles, and the reaction flask was purged with argon. The reaction mixture was diluted with CH_2Cl_2, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by silica-gel column chromatography (CH_2Cl_2–hexane as an eluent) and recrystallization with CH_2Cl_2/MeOH, **Boc-8H** obtained as a dark red solid (67 mg, 0.01 mmol, 66% yield).

Synthesis of 5H, 6H, and 8H: **Boc-5H**, **Boc-6H,** and **Boc-8H** was added to a flask containing a magnetic

bar, and dissolved in para-xylene. The reaction was stirred for 72 h at 140 ^{o}C . Evaporation of the solvent followed by recrystallization with CH_2Cl_2/MeOH, **5H, 6H,** and **8H** was obtained quantitatively.

Synthesis of 2Zn, 3Zn, 4Zn, 5Zn, 6Zn, and 8Zn: Zn(II) porphyrin arrays **2Zn, 3Zn, 4Zn, 5Zn, 6Zn,** and **8Zn** were obtained quantitatively by treatment of **2H, 3H, 4H, 5H, 6H,** and **8H**, respectively, with $Zn(OAc)_2 \cdot 2H_2O$ in CH_2Cl_2/MeOH.

Synthesis of 2Ni, 3Ni, 4Ni, 5Ni, 6Ni and 8Ni: **2H** (20 mg, 0.0139 mmol), **3H** (20 mg, 0.0091 mmol), 4H (20 mg, 0.0068 mmol), **5H** (20 mg, 0.0054 mmol), **6H** (20 mg, 0.0045 mmol) and **8H** (20 mg, 0.0031 mmol) was added to a round-bottomed 50-mL flask with a magnetic bar, and dissolved in toluene. Excess nickel(II) acetylacetonate was added. After stirring for 24 h, the reaction mixture was passed through alumina column, evaporated and recrystallized from methanol and dichloromethane. **2Ni**, **3Ni**, **4Ni**, **5Ni,** and **6Ni** was obtained quantitatively.

Compound Data

2H: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.44 (s, 1H, Pyrrole-*N*H), 10.24 (s, 2H, *meso*-H), 9.72 (d, 4H, J = 5.0 Hz, *β*-H), 9.37 (d, 4H, J = 5.0 Hz, *β*-H), 9.12 (d, 4H, J = 5.0 Hz, *β*-H), 9.10 (d, 4H, J = 5.0 Hz, *β*-H), 8.16 (d, 8H, J = 1.5 Hz, Ar-*o*-H), 7.86 (m, 4H, Ar-*p*-H), 7.82 (d, 2H, J = 2.5 Hz, Pyrrole-*β*-H), 1.56 (s, 72H, *t*-Bu-H), and -2.73 (s, 4H, NH) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 411 (341000), 511 (30000), 576 (20000), 654 (12000) nm; HR-MS (MALDI-TOF-MS): *m/z* = 1436.8811, calcd for $(C_{100}H_{109}N_9)^+$ = 1436.8832 ([*M*]$^+$). Fluorescence (CH_2Cl_2, λ_{ex} = 417 nm): λ_{max} = 684 nm, Φ_F = 1.2 %.

2Zn: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.38 (s, 1H, Pyrrole-*N*H), 10.28 (s, 2H, *meso*-H), 9.82 (d, 4H,J = 5.0 Hz, *β*-H), 9.42 (d, 4H, J = 5.0 Hz, *β*-H), 9.20 (d, 4H, J = 5.0 Hz, *β*-H), 9.17 (d, 4H, J = 5.0 Hz, *β*-H), 8.13 (d, 8H, J = 1.5 Hz, Ar-*o*-H), 7.83 (m, 4H, Ar-*p*-H), 7.76 (d, 2H, J = 2.5 Hz, Pyrrole-*β*-H), and 1.54 (s, 72H, *t*-Bu-H) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 412 (337000), 546 (33000), 600 (15000) nm; HR-MS (MALDI-TOF-MS): *m/z* = 1563.7013, calcd for $(C_{100}H_{150}N_9Zn_2)^+$ = 1563.7032 ([*M*]$^+$). Fluorescence (CH_2Cl_2, λ_{ex} = 417 nm): λ_{max} = 653 nm, Φ_F = 3.6 %.

2Ni: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.82 (s, 2H, *meso*-H), 9.77 (s, 1H, Pyrrole-*N*H), 9.47 (d, 4H, J = 5.0 Hz, *β*-H), 9.13 (d, 4H, J = 5.0 Hz, *β*-H), 8.93 (d, 4H, J = 5.0 Hz, *β*-H), 8.92 (d, 4H, J = 5.0 Hz, *β*-H), 7.90 (d, 8H, J = 1.5 Hz, Ar-*o*-H), 7.75 (m, 4H, Ar-*p*-H), 7.56 (d, 2H, J = 2.5Hz, Pyrrole-*β*-H), and 1.55 (s, 72H, *t*-Bu-H) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 409 (205000), 528 (32000), 580 (12000) nm; HR-MS (MALDI-TOF-MS): *m/z* = 1549.7180, calcd for $(C_{100}H_{105}N_9Ni_2)^+$ = 1549.7158 ([*M*]$^+$).

2H-1Br: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.36 (s, 1H, Pyrrole-*N*H), 10.23 (s, 1H, *meso*-H), 9.67 (d, 2H, J = 5.0 Hz, *β*-H), 9.64 (d, 2H, J = 5.0 Hz, *β*-H), 9.60 (s, 2H, *β*-H), 9.35 (d, 2H, J = 5.0 Hz, *β*- H), 9.08 (m, 4H, *β*-H), 8.97 (d, 2H, J = 5.0 Hz, *β*-H), 8.94 (d, 2H, J = 5.0 Hz, *β*-H), 8.13 (d, 4H, J = 1.5 Hz, Ar-*o*-H), 8.07 (d, 4H, J = 1.5 Hz, Ar-*o*-H), 7.82 (d, 4H, J = 1.5 Hz, Ar-*p*-H), 7.77 (m, 2H, Pyrrole-*β*-H), 1.54 (s, 36H, *t*-Bu-H), 1.53 (s, 36H, *t*-Bu-H), -2.50 (s, 2H, NH), and -2.78 (s, 2H, NH) ppm.

3H: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.43 (s, 2H, Pyrrole-*N*H), 10.25 (s, 2H, *meso*-H), 9.70 (d, 4H, J = 5.0 Hz, *β*-H), 9.67 (d, 4H, J = 5.0 Hz, *β*-H), 9.37 (d, 4H, J = 5.0 Hz, *β*-H), 9.12 (d, 4H, J = 5.0 Hz, *β*-H), 9.10 (d, 4H, J = 5.0 Hz, *β*-H), 9.05 (d, 4H, J = 5.0 Hz, *β*-H), 8.16 (d, 8H, J = 1.5 Hz, Ar-*o*-H), 8.14 (d, 4H, J = 1.5 Hz, Ar-*o*-H), 7.86 (m, 4H, Ar-*p*-H), 7.84 (m, 2H, Ar-*p*-H), 7.83 (d, 4H, J = 2.5Hz, Pyrrole-*β*-H), 1.56 (s, 72H, *t*-Bu-H), 1.53 (s, 36H, *t*-Bu-H), -2.29 (s, 2H, NH), and -2.73 (s, 2H, NH) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 412 (456000), 514 (47000), 586 (37000), 670 (21000), 780 (15000) nm; HR-MS (MALDI-TOF-MS): *m/z* = 2186.3269, calcd for $(C_{152}H_{164}N_{14})^+$ = 2186.3290 ([*M*]$^+$). Fluorescence (CH_2Cl_2, λ_{ex} = 417 nm): λ_{max} = 713 nm, Φ_F = 0.53 %.

3Zn: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.38 (s, 2H, Pyrrole-*N*H), 10.28 (s, 2H, *meso*-H), 9.82 (d, 4H, J = 5.0 Hz, *β*-H), 9.79 (d, 4H, J = 5.0 Hz, *β*-H), 9.42 (d, 4H, J = 5.0 Hz, *β*-H), 9.19 (d, 4H, J = 5.0 Hz, *β*-H), 9.16 (d, 4H, J = 5.0 Hz, *β*-H), 9.15 (d, 4H, J = 5.0 Hz, *β*-H), 8.13 (d, 12H, J = 1.5 Hz, Ar-*o*-H), 7.82 (m, 6H, Ar-*p*-H), 7.76 (d, 4H, J = 2.5Hz, Pyrrole-*β*-H), 1.54 (s, 72H, *t*-Bu-H), and 1.52 (s, 36H, *t*-Bu-H) ppm; UV/Vis

(CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 413 (498000), 548 (57000), 619 (37000) nm; HR-MS (MALDI-TOF-MS): *m/z* = 2377.0671, calcd for $(C_{152}H_{158}N_{14}Zn_3)^+$ = 2377.0683 ([*M*]$^+$). Fluorescence (CH_2Cl_2, λ_{ex} = 417 nm): λ_{max} = 674 nm, Φ_F = 1.9 %.

3Ni: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.84 (s, 2H, *meso*-H), 9.77 (s, 2H, Pyrrole-*N*H), 9.48 (d, 4H, *J* = 5.0 Hz, *β*-H), 9.43 (d, 4H, *J* = 5.0 Hz, *β*-H), 9.15 (d, 4H, *J* = 5.0 Hz, *β*-H), 8.95 (m, 8H, *β*-H), 8.89 (d, 4H, *J* = 5.0 Hz, *β*-H), 7.92 (d, 8H, *J* = 1.5 Hz, Ar-*o*-H), 7.89 (d, 4H, *J* = 1.5 Hz, Ar-*o*-H), 7.76 (m, 4H, Ar-*p*-H), 7.74 (m, 2H, Ar-*p*-H), 7.59 (d, 4H, *J* = 2.5Hz, Pyrrole-*β*-H), 1.50 (s, 72H, *t*-Bu-H), and 1.47 (s, 36H, *t*-Bu-H) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 410 (286000), 532 (47000), 596 (22000) nm; HR-MS (MALDI-TOF-MS): *m/z* = 2356.0900, calcd for $(C_{152}H_{158}N_{14}Ni_3)^+$ = 2356.0866 ([*M*]$^+$).

Boc-3H: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.24 (d, 2H, *J* = 5.0 Hz, *meso*-H), 9.54 (m, 4H, *β*-H), 9.50 (s, 4H, *β*-H), 9.36 (m, 4H, *β*-H), 9.10 (m, 8H, *β*-H), 9.04 (d, 4H, *J* = 5.0 Hz, *β*-H), 8.25 (s, 1H, Ar-*o*-H), 8.20 (d, 4H, *J* = 1.5 Hz, Ar-*o*-H), 8.12 (d, 2H, *J* = 1.5 Hz, Ar-*o*-H), 8.08 (s, 2H, Ar-*o*-H), 8.06 (s, 2H, Ar-*o*-H), 7.97(s, 1H, Ar-*o*-H), 7.83 (m, 6H, Ar-*p*-H), 7.63 (m, 4H, Pyrrole-*β*-H), 1.54 (s, 72H, *t*-Bu-H), 1.53 (s, 36H, *t*-Bu-H), -0.75 (s, 9H, Boc-*t*-Bu-H), -0.81 (s, 9H, Boc-*t*-Bu-H), -2.30 (s, 2H, *N*H), and -2.70 (s, 4H, *N*H) ppm.

Boc-3H-1Br: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.24 (d, 1H, *J* = 5.0 Hz, *meso*-H), 9.71 (m, 2H, *β*-H), 9.56 (s, 2H, *β*-H), 9.52 (s, 2H, *β*-H), 9.47 (s, 4H, *β*-H), 9.36 (m, 2H, *β*-H), 9.11 (m, 4H, *β*-H), 9.05 (m, 4H, *β*-H), 8.98 (m, 4H, *β*-H), 8.27 (m, 1H, Ar-*o*-H), 8.22 (m, 2H, Ar-*o*-H), 8.15 (m, 2H, Ar-*o*-H), 8.13 (d, 2H, *J* = 1.5 Hz, Ar-*o*-H), 8.10 (m, 2H, Ar-*o*-H), 8.04 (m, 2H, Ar-*o*-H), 7.99 (m, 1H, Ar-*o*-H), 7.85 (m, 6H, Ar-*p*-H), 7.61 (m, 4H, Pyrrole-*β*-H), 1.54 (s, 36H, *t*-Bu-H), 1.53 (s, 72H, *t*-Bu-H), -0.69 (s, 5H, Boc-*t*-Bu-H), -0.73 (s, 9H, Boc-*t*-Bu-H), -0.80 (s, 4H, Boc-*t*-Bu-H), -2.30 (s, 2H, *N*H), -2.45 (s, 2H, *N*H), and -2.69 (s, 2H, *N*H) ppm.

4H: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.42 (s, 2H, Pyrrole-*N*H), 10.41 (s, 1H, Pyrrole-*N*H), 10.23 (s, 2H, *meso*-H), 9.69 (d, 4H, *J* = 5.0 Hz, *β*-H), 9.65 (d, 4H, *J* = 5.0 Hz, *β*-H), 9.64 (d, 4H, *J* = 5.0 Hz, *β*-H), 9.36 (d, 4H, *J* = 5.0 Hz, *β*-H), 9.11 (d, 4H, *J* = 5.0 Hz, *β*-H), 9.09 (d, 4H, *J* = 5.0 Hz, *β*-H), 9.04 (d, 8H, *J* = 5.0 Hz, *β*-H), 8.15 (d, 8H, *J* = 1.5 Hz, Ar-*o*-H), 8.13 (d, 8H, *J* = 1.5 Hz, Ar-*o*-H), 7.85 (m, 4H, Ar-*p*-H), 7.82 (m, 10H, 4H for Ar-*p*-H and 6H for Pyrrole-*β*-H), 1.56 (s, 72H, *t*-Bu-H), 1.53 (s, 72H, *t*-Bu-H), -2.30 (s, 4H, NH), and -2.74 (s, 4H, NH) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 413 (492000), 515 (54000), 588 (51000), 676 (32000), 781 (15000) nm; HR-MS (MALDI-TOF-MS): *m/z* = 2936.7752, calcd for $(C_{204}H_{219}N_{19})^+$ = 2936.7779 ([*M*]$^+$); Fluorescence (CH_2Cl_2, λ_{ex} = 417 nm): λ_{max} = 718 nm, Φ_F = 0.43 %.

4Zn: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.37 (s, 3H, Pyrrole-*N*H), 10.28 (s, 2H, *meso*-H), 9.81 (d, 4H, *J* = 5.0 Hz, *β*-H), 9.78 (m, 8H, *β*-H), 9.42 (d, 4H, *J* = 5.0 Hz, *β*-H), 9.19 (d, 4H, *J* = 5.0 Hz, *β*-H), 9.16 (d, 4H, *J* = 5.0 Hz, *β*-H), 9.15 (d, 8H, *J* = 5.0 Hz, *β*-H), 8.13 (d, 8H, *J* = 1.5 Hz, Ar-*o*-H), 8.12 (d, 8H, *J* = 1.5 Hz, Ar-*o*-H), 7.81 (m, 8H, Ar-*p*-H), 7.76 (d, 6H, *J* = 2.5 Hz, Pyrrole-*β*-H), 1.54 (s, 72H, *t*-Bu-H), and 1.52 (s, 72H, *t*-Bu-H) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 414 (556000), 549 (57000), 623 (55000) nm; HR-MS (MALDI-TOF-MS): *m/z* = 3190.4233, calcd for $(C_{204}H_{211}N_{19}Zn_4)^+$ = 3190.4253 ([*M*]$^+$); Fluorescence (CH_2Cl_2, λ_{ex} = 417 nm): λ_{max} = 683 nm, Φ_F = 1.2 %.

4Ni: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.82 (s, 2H, *meso*-H), 9.75 (s, 2H, Pyrrole-*N*H), 9.73 (s, 1H, Pyrrole-*N*H), 9.46 (d, 4H, J = 5.0 Hz, β-H), 9.41 (d, 4H, J = 5.0 Hz, β-H), 9.39 (d, 4H, J = 5.0 Hz, β-H), 9.13 (d, 4H, J = 5.0 Hz, β-H), 8.94 (d, 4H, J = 5.0 Hz, β-H), 8.93 (d, 4H, J = 5.0 Hz, β-H), 8.86 (m, 8H, β-H), 7.90 (d, 8H, J = 1.5 Hz, Ar-*o*-H), 7.87 (d, 8H, J = 1.5 Hz, Ar-*o*-H), 7.74 (m, 4H, Ar-*p*-H), 7.72 (m, 4H, Ar-*p*-H), 7.57 (d, 6H, J = 2.5Hz, Pyrrole-β-H), 1.48 (s, 72H, *t*-Bu-H), and 1.45 (s, 72H, *t*-Bu-H) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 412 (323000), 533 (61000), 595 (33000) nm. HR-MS (MALDI-TOF-MS): *m/z* = 3162.4550, calcd for $(C_{204}H_{211}N_{19}Ni_4)^+$ = 3162.4522 ([*M*]$^+$).

Boc-4H: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.23 (m, 2H, *meso*-H), 9.54 (m, 4H, β-H), 9.50 (s, 8H, β-H), 9.35 (m, 4H, β-H), 9.10 (m, 8H, β-H), 9.04 (m, 4H, β-H), 8.25 (s, 2H, Ar-*o*-H), 8.20 (s, 4H, Ar-*o*-H), 8.13 (m, 4H, Ar-*o*-H), 8.08 (m, 4H, Ar-*o*-H), 7.99 (m, 2H, Ar-*o*-H), 7.83(m, 8H, Ar-*p*-H), 7.61 (m, 6H, Pyrrole-β-H), 1.54 (s, 72H, *t*-Bu-H), 1.53 (s, 72H, *t*-Bu-H), -0.78 (m, 27H, Boc-*t*-Bu-H), -2.31 (s, 4H, *N*H), and -2.71 (s, 4H, *N*H) ppm.

Boc-4H-1Br: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.24 (m, 1H, *meso*-H), 9.68 (m, 2H, β-H), 9.50 (m, 12H, β-H), 9.36 (m, 2H, β-H), 9.11-8.96 (m, 16H, β-H), 8.25-7.97 (m, 16H, Ar-*o*-H), 7.83 (m, 8H, Ar-*p*-H), 7.61 (m, 6H, Pyrrole-β-H), 1.54 (s, 72H, *t*-Bu-H), 1.53 (s, 72H, *t*-Bu-H), -0.76 (m, 27H, Boc-*t*-Bu-H), -2.32 (s, 4H, *N*H), -2.50 (s, 2H, *N*H), and -2.72 (s, 2H, *N*H) ppm.

5H: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.41 (s, 2H, Pyrrole-*N*H), 10.40 (s, 2H, Pyrrole-*N*H), 10.22 (s, 2H, *meso*-H), 9.67 (d, 4H, J = 5.0 Hz, β-H), 9.62 (m, 12H, β-H), 9.35 (d, 4H, J = 5.0 Hz, β-H), 9.09 (d, 4H, J = 5.0 Hz, β-H), 9.07 (d, 4H, J = 5.0 Hz, β-H), 9.02 (d, 12H, J = 5.0 Hz, β-H), 8.13 (m, 20H, Ar-*o*-H), 7.82 (m, 18H, 10H for Ar-*p*-H and 8H for Pyrrole-β-H), 1.54 (s, 72H, *t*-Bu-H), 1.51 (s, 108H, *t*-Bu-H), -2.32 (s, 6H, NH), and -2.77 (s, 4H, NH) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 413 (385000), 516 (50000), 590 (41000), 678 (28000) nm; HR-MS (MALDI-TOF-MS): *m/z* = 3686.2212, calcd for $(C_{256}H_{274}N_{24})^+$ = 3686.2237 ([*M*]$^+$); Fluorescence (CH_2Cl_2, λ_{ex} = 417 nm): λ_{max} = 721 nm, Φ_F = 0.24 %.

5Zn: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.38 (s, 4H, Pyrrole-*N*H), 10.28 (s, 2H, *meso*-H), 9.82 (d, 4H, J = 5.0 Hz, β-H), 9.79 (m, 12H, β-H), 9.43 (d, 4H, J = 5.0 Hz, β-H), 9.20 (d, 4H, J = 5.0 Hz, β-H), 9.16 (m, 16H, β-H), 8.13 (m, 20H, Ar-*o*-H), 7.83 (m, 10H, Ar-*p*-H), 7.77 (d, 8H, J = 2.5 Hz, Pyrrole-β-H), 1.55 (s, 72H, *t*-Bu-H), and 1.53 (s, 108H, *t*-Bu-H) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 414 (484000), 550 (63000), 624 (58000) nm; HR-MS (MALDI-TOF-MS): *m/z* = 4003.7823, calcd for $(C_{256}H_{264}N_{24}Zn_5)^+$ = 4003.7847 ([*M*]$^+$); Fluorescence (CH_2Cl_2, λ_{ex} = 417 nm): λ_{max} = 681 nm, Φ_F = 1.2 %.

5Ni: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.82 (s, 2H, *meso*-H), 9.74 (s, 4H, Pyrrole-*N*H), 9.46 (d, 4H, J = 5.0 Hz, β-H), 9.40 (m, 12H, β-H), 9.13 (d, 4H, J = 5.0 Hz, β-H), 8.94 (m, 8H, β-H), 8.85 (s, 12H, β-H), 7.89 (s, 8H, Ar-*o*-H), 7.87 (s, 12H, Ar-*o*-H), 7.73 (s, 4H, Ar-*p*-H), 7.71 (s, 6H, Ar-*p*-H), 7.57 (d, 8H, J = 2.5Hz, Pyrrole-β-H), 1.47 (s, 72H, *t*-Bu-H), and 1.44 (s, 108H, *t*-Bu-H) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 413 (272000), 535 (51000), 600 (32000) nm; HR-MS (MALDI-TOF-MS): *m/z* = 3969.8202, calcd for $(C_{256}H_{264}N_{24}Ni_5)^+$ = 3969.8174 ([*M*]$^+$).

Boc-5H: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.26 (m, 2H, *meso*-H), 9.57 (s, 4H, *β*-H), 9.53 (s, 12H, *β*-H),9.38 (m, 4H, *β*-H), 9.13 (m, 12H, *β*-H), 9.08 (m, 8H, *β*-H), 8.29-8.01 (m, 20H, Ar-*o*-H), 7.86 (m, 10H, Ar-*p*-H), 7.65 (m, 8H, Pyrrole-*β*-H), 1.54 (s, 72H, *t*-Bu-H), 1.53 (s, 108H, *t*-Bu-H), -0.73 (m, 36H, Boc-*t*-Bu-H), -2.28 (s, 6H, *N*H), and -2.69 (s, 4H, *N*H) ppm.

6H: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.41 (m, 5H, Pyrrole-*N*H), 10.22 (s, 2H, *meso*-H), 9.66 (d, 4H, J = 5.0 Hz, *β*-H), 9.62 (m, 20H, *β*-H), 9.35 (d, 4H, J = 5.0 Hz, *β*-H), 9.09 (d, 4H, J = 5.0 Hz, *β*-H), 9.07 (d, 4H, J = 5.0 Hz, *β*-H), 9.01 (d, 16H, J = 5.0 Hz, *β*-H), 8.12 (m, 24H, Ar-*o*-H), 7.80 (m, 22H, 12H for Ar-*p*-H and 10H for Pyrrole-*β*-H), 1.54 (s, 72H, *t*-Bu-H), 1.51 (s, 144H, *t*-Bu-H), -2.33 (s, 8H, NH), and -2.78 (s, 4H, NH) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 415 (214000), 513 (81000), 593 (51000), 684 (46000) nm; HR-MS (MALDI-TOF-MS): m/z = 4436.6701, calcd for $(C_{308}H_{329}N_{29})^+$ = 4436.6726 ([M]$^+$); Fluorescence (CH_2Cl_2, λ_{ex} = 417 nm): λ_{max} = 722 nm, Φ_F = 0.23 %.

6Zn: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.36 (m, 5H, Pyrrole-*N*H), 10.28 (s, 2H, *meso*-H), 9.81 (d, 4H, J = 5.0 Hz, *β*-H), 9.79 (m, 16H, *β*-H), 9.42 (d, 4H, J = 5.0 Hz, *β*-H), 9.19 (d, 4H, J = 5.0 Hz, *β*-H), 9.16 (m, 20H, *β*-H), 8.13 (m, 24H, Ar-*o*-H), 7.82 (m, 12H, Ar-*p*-H), 7.76 (d, 10H, J = 2.5 Hz, Pyrrole-*β*-H), 1.54 (s, 72H, *t*-Bu-H), and 1.51 (s, 144H, *t*-Bu-H) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 415 (311000), 552 (41000), 630 (40000) nm; HR-MS (MALDI-TOF-MS): m/z = 4817.1421, calcd for $(C_{308}H_{317}N_{29}Zn_6)^+$ = 4817.1442 ([M]$^+$); Fluorescence (CH_2Cl_2, λ_{ex} = 417 nm): λ_{max} = 685 nm, Φ_F = 0.92 %.

6Ni: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.82 (s, 2H, *meso*-H), 9.74 (m, 5H, Pyrrole-*N*H), 9.45 (d, 4H, J = 5.0 Hz, *β*-H), 9.40 (d, J = 5.0 Hz, 4H, *β*-H), 9.38 (d, J = 5.0 Hz, 12H, *β*-H), 9.12 (d, 4H, J = 5.0 Hz, *β*-H), 8.92 (m, 8H, *β*-H), 8.85 (m, 16H, *β*-H), 7.89 (d, 8H, J = 1.5 Hz, Ar-*o*-H), 7.86 (m, 16H, Ar-*o*-H), 7.73 (m, 4H, Ar-*p*-H), 7.70 (m, 8H, Ar-*p*-H), 7.56 (d, 10H, J = 2.5Hz, Pyrrole-*β*-H), 1.47 (s, 72H, *t*-Bu-H), and 1.44 (s, 144H, *t*-Bu-H) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 414 (148000), 536 (32000), 607 (21000) nm; HR-MS (MALDI-TOF-MS): m/z = 4776.1880, calcd for $(C_{308}H_{317}N_{29}Ni_6)^+$ = 4776.1835 ([M]$^+$).

Boc-6H: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.25 (m, 2H, *meso*-H), 9.55 (s, 4H, *β*-H), 9.51 (s, 16H, *β*-H), 9.36 (m, 4H, *β*-H), 9.10 (m, 8H, *β*-H), 9.06 (s, 16H, *β*-H), 8.27-8.00 (m, 24H, Ar-*o*-H), 7.84 (m, 12H, Ar-*p*-H), 7.63 (m, 10H, Pyrrole-*β*-H), 1.55 (s, 72H, *t*-Bu-H), 1.54 (s, 144H, *t*-Bu-H), -0.76 (m, 45H, Boc-*t*-Bu-H), -2.29 (s, 8H, *N*H), and -2.70 (s, 4H, *N*H) ppm.

8H: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.41 (s, 7H, Pyrrole-*N*H), 10.22 (s, 2H, *meso*-H), 9.66 (d, 4H, J = 5.0 Hz, *β*-H), 9.61 (m, 24H, *β*-H), 9.35 (d, 4H, J = 5.0 Hz, *β*-H), 9.09 (m, 8H, *β*-H), 9.01 (m, 24H, J = 5.0, *β*-H), 8.13 (m, 32H, Ar-*o*-H), 7.82 (m, 30H, 16H for Ar-*p*-H and 14H for Pyrrole-*β*-H), 1.56 (s, 72H, *t*-Bu-H), 1.54 (s, 216H, *t*-Bu-H), -2.33 (s, 12H, NH), and -2.77 (s, 4H, NH) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 416 (428000), 602 (104800), 679 (94000) nm; HR-MS (MALDI-TOF-MS): m/z = 5936.5645, calcd for $(C_{412}H_{439}N_{39})^+$ = 5936.5673 ([M]$^+$); Fluorescence (CH_2Cl_2, λ_{ex} = 417 nm): λ_{max} = 723nm, Φ_F = 0.15 %.

8Zn: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.36 (s, 7H, Pyrrole-*N*H), 10.28 (s, 2H, *meso*-H), 9.81 (d, 4H, J = 5.0 Hz, *β*-H), 9.79 (m, 24H, *β*-H), 9.42 (d, 4H, J = 5.0 Hz, *β*-H), 9.19 (d, 4H, J = 5.0 Hz, *β*-H), 9.16 (m, 28H,

β-H), 8.13 (m, 32H, Ar-*o*-H), 7.82 (m, 16H, Ar-*p*-H), 7.76 (s, 14H, Pyrrole-*β*-H), 1.54 (s, 72H, *t*-Bu-H), and 1.51 (s, 216H, *t*-Bu-H) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 416 (616000), 557 (80000), 632 (87200) nm; HR-MS (MALDI-TOF-MS): *m/z* = 6443.8586, calcd for $(C_{412}H_{423}N_{39}Zn_8)^+$ = 6443.8629 ([*M*]$^+$); Fluorescence (CH_2Cl_2, λ_{ex} = 417 nm): λ_{max} = 685 nm, Φ_F = 0.88 %.

8Ni: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.82 (s, 2H, *meso*-H), 9.74 (m, 7H, Pyrrole-*N*H), 9.45 (d, 4H, *J* = 5.0 Hz, *β*-H), 9.39 (m, 24H, *β*-H), 9.12 (d, 4H, *J* = 5.0 Hz, *β*-H), 8.92 (m, 8H, *β*-H), 8.85 (d, *J* = 5.0 Hz, 24H, *β*-H), 7.89 (s, 8H, Ar-*o*-H), 7.86 (s, 24H, Ar-*o*-H), 7.73 (s, 4H, Ar-*p*-H), 7.70 (s, 12H, Ar-*p*-H), 7.56 (s, 14H, Pyrrole-*β*-H), 1.47 (s, 108H, *t*-Bu-H), and 1.44 (s, 180H, *t*-Bu-H) ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 416 (281000), 536 (60000), 608 (43000) nm; HR-MS (MALDI-TOF-MS): *m/z* = 6389.9208, calcd for $(C_{308}H_{317}N_{29}Ni_6)^+$ = 6389.9148 ([*M*]$^+$).

Boc-8H: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.24 (m, 2H, *meso*-H), 9.54-9.36 (m, 32H, *β*-H), 9.10-9.05 (m, 32H, *β*-H), 8.26-7.99 (m, 32H, Ar-*o*-H), 7.83 (s, 16H, Ar-*p*-H), 7.62 (m, 14H, Pyrrole-*β*-H), 1.55 (s, 72H, *t*-Bu-H), 1.54 (s, 216H, *t*-Bu-H), -0.76 (m, 63H, Boc-*t*-Bu-H), -2.31 (s, 12H, *N*H), and -2.72 (s, 4H, *N*H) ppm.

^{1}H NMR Spectra

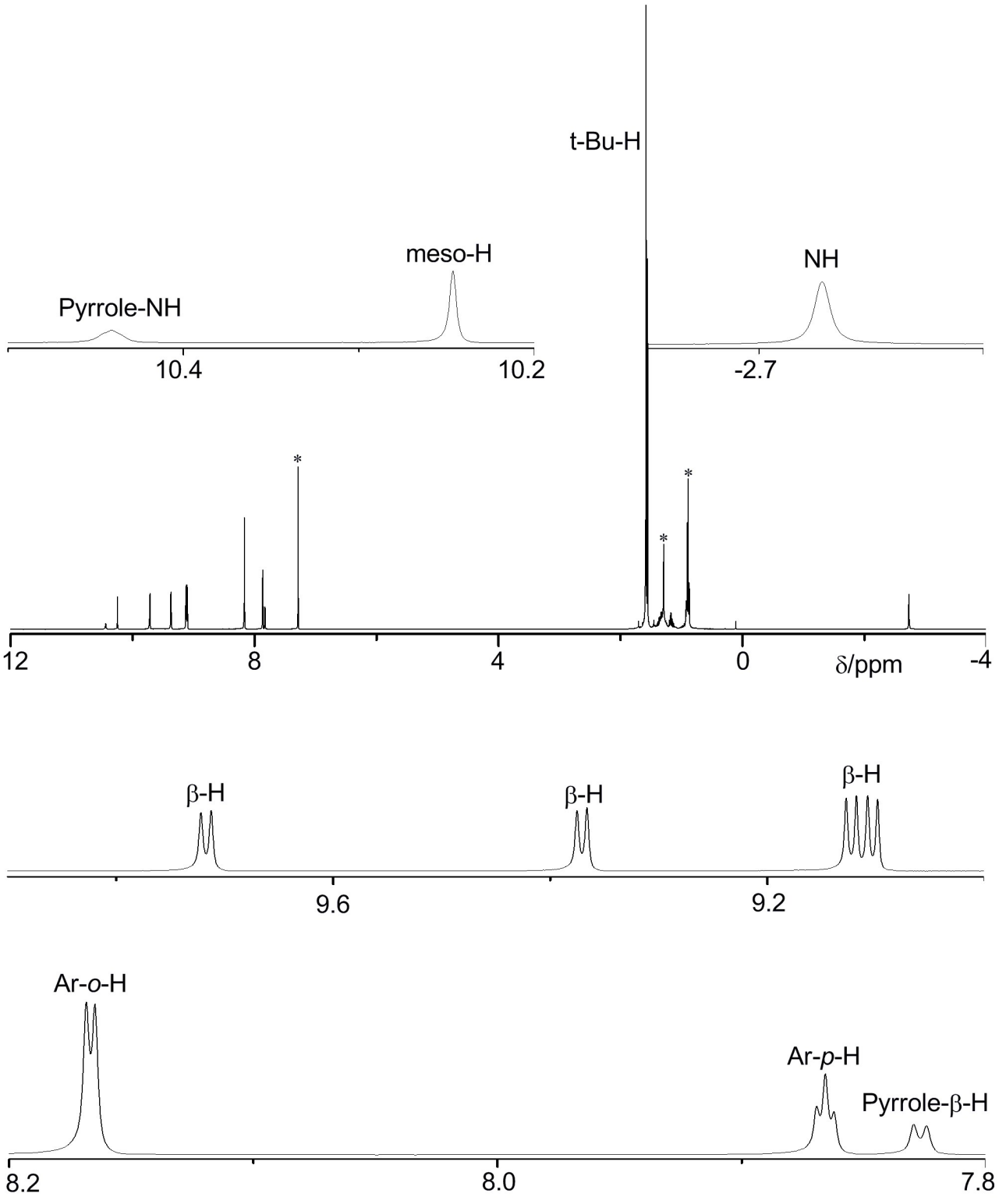

Figure S1. ^{1}H NMR spectrum of **2H** in $CDCl_3$.

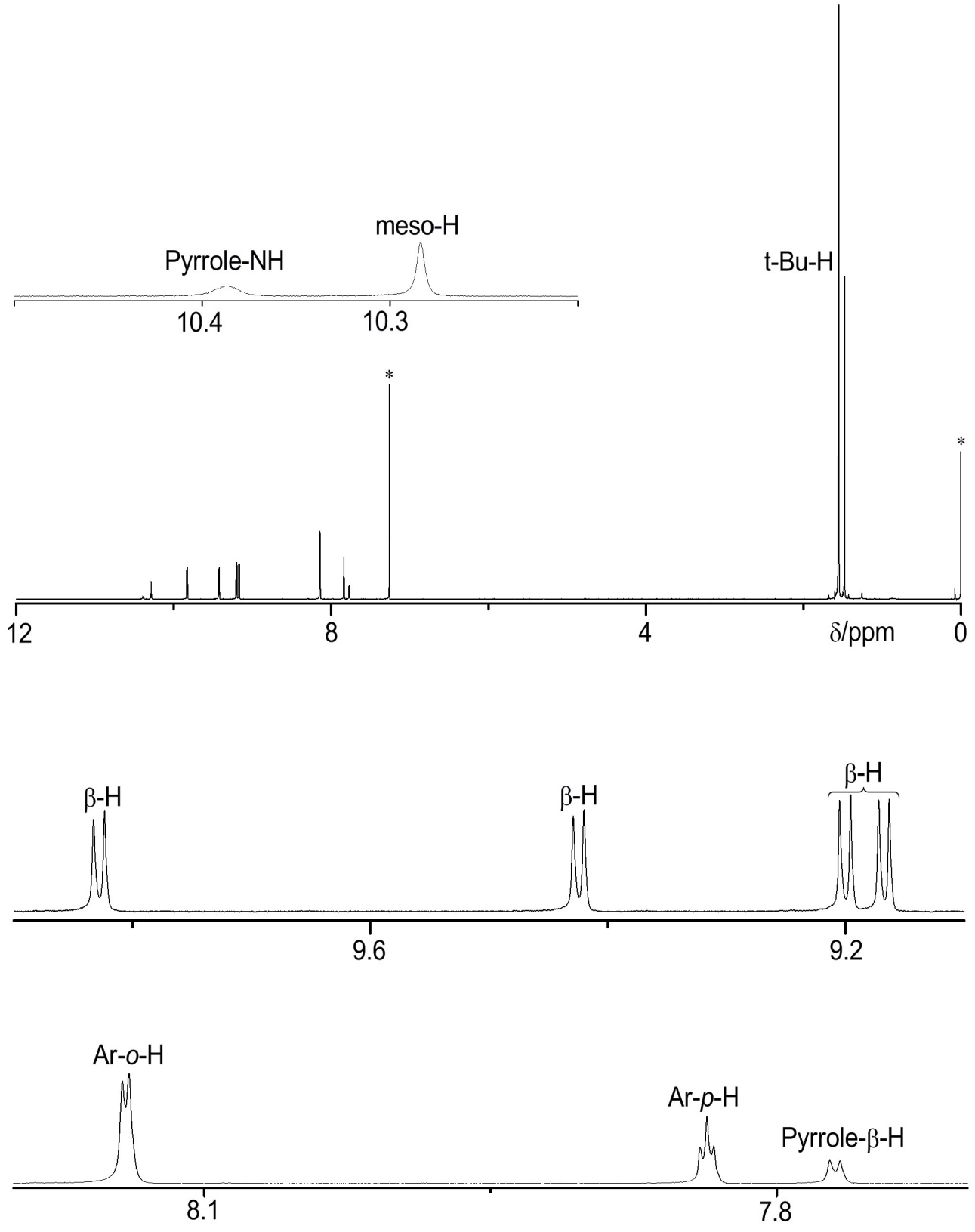

Figure S2. ^{1}H NMR spectrum of **2Zn** in $CDCl_3$.

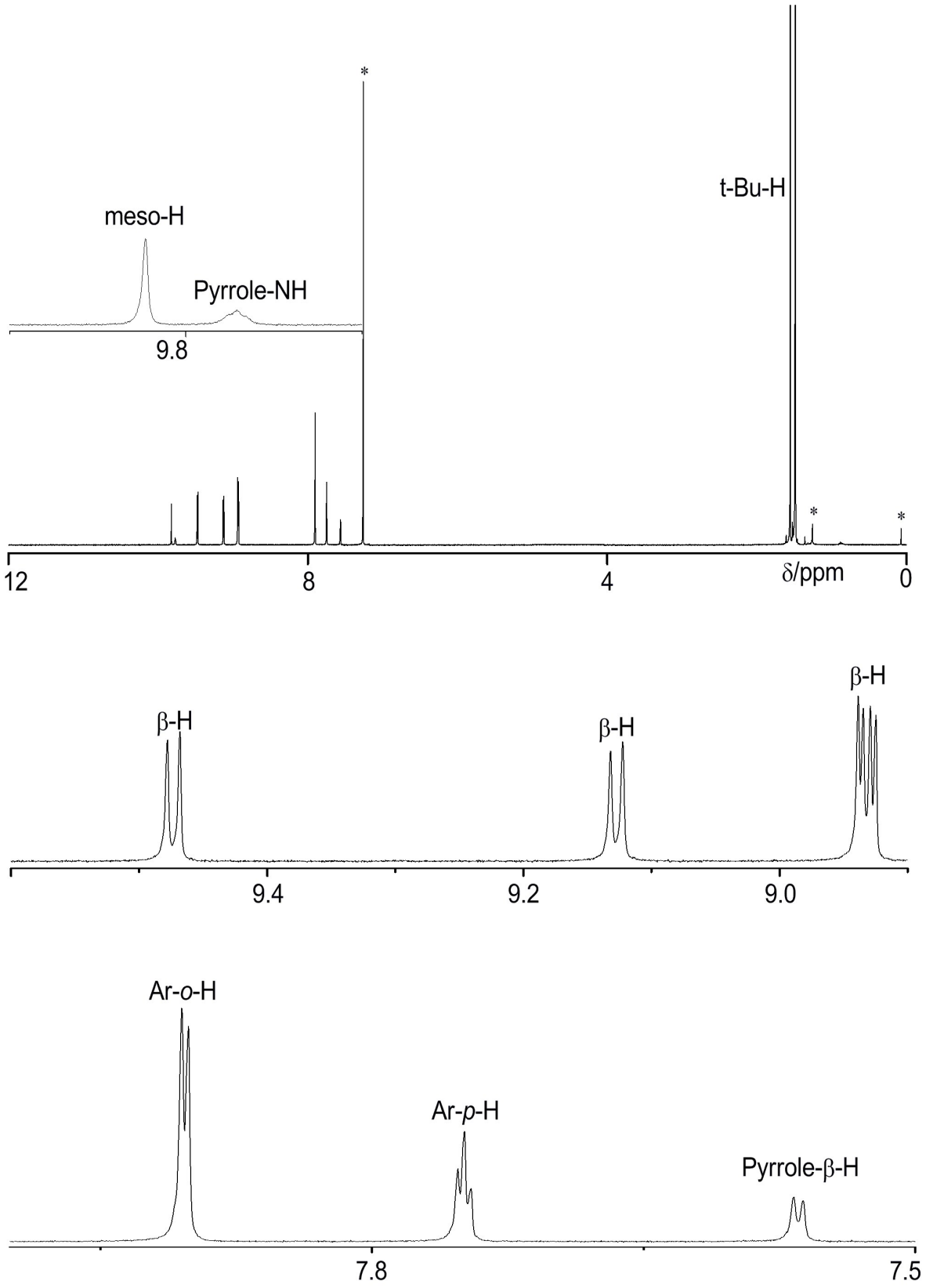

Figure S3. ^{1}H NMR spectrum of **2Ni** in $CDCl_3$.

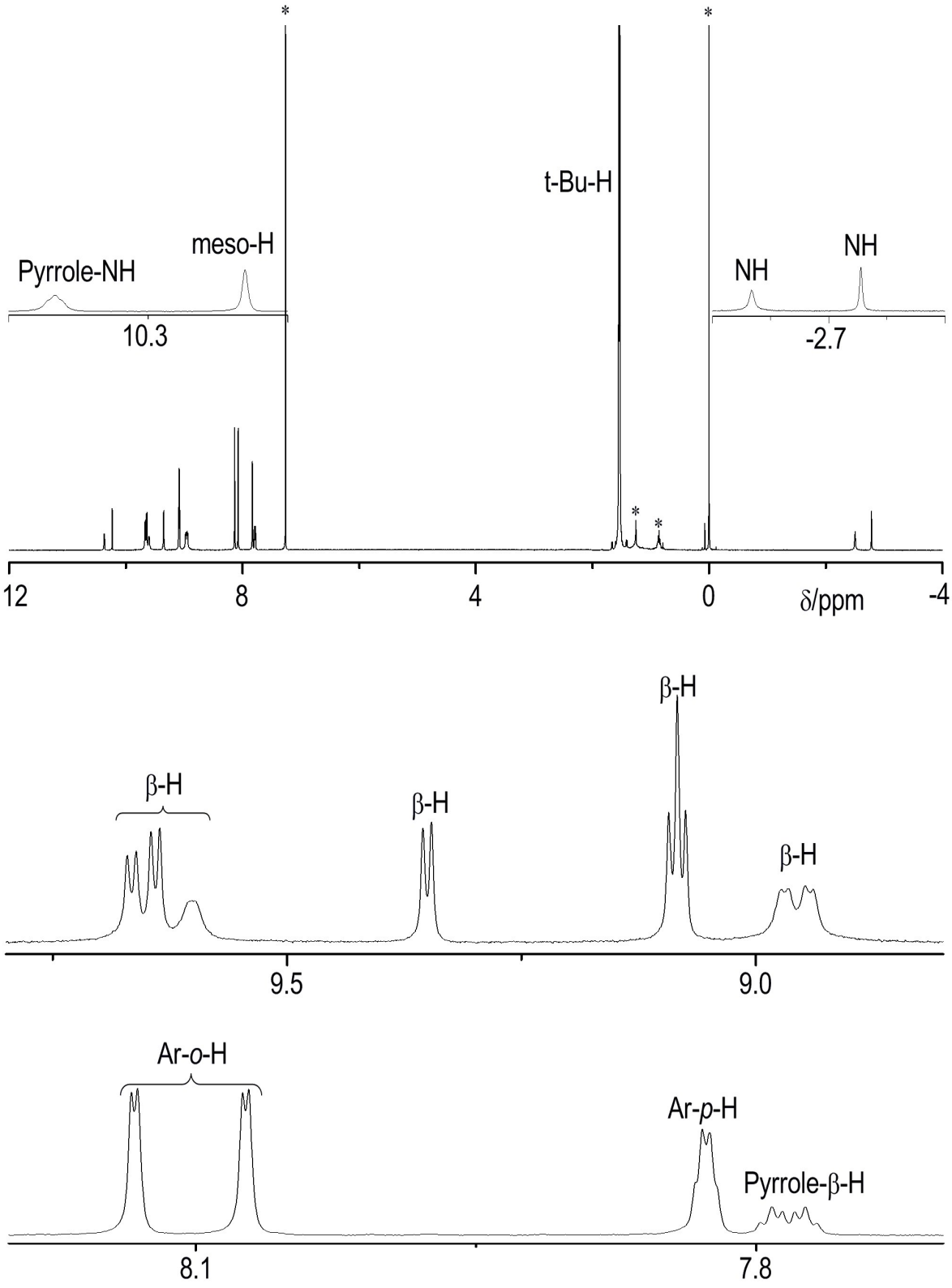

Figure S4. ^{1}H NMR spectrum of **2H-1Br** in $CDCl_3$.

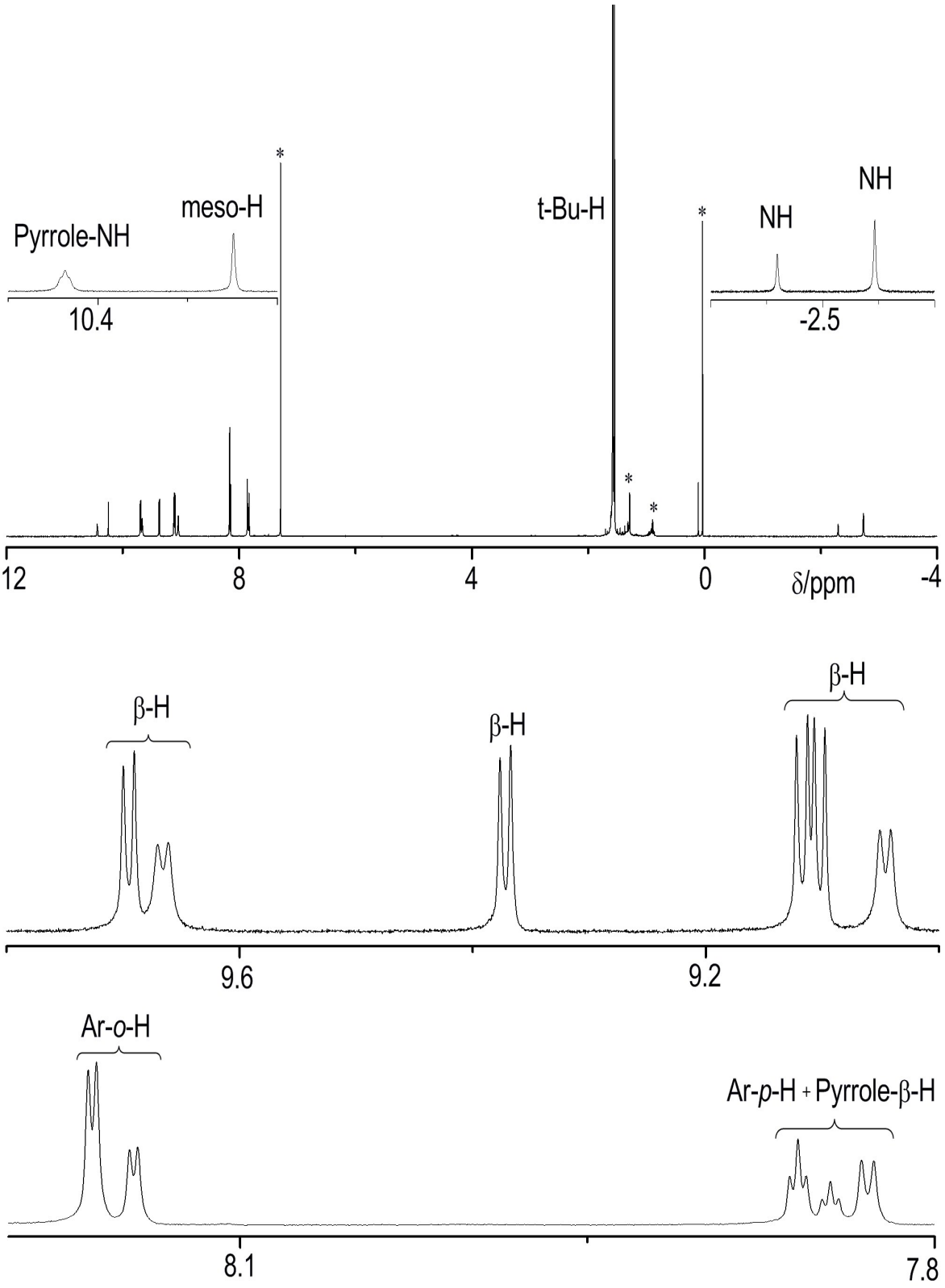

Figure S5. ^{1}H NMR spectrum of **3H** in $CDCl_3$.

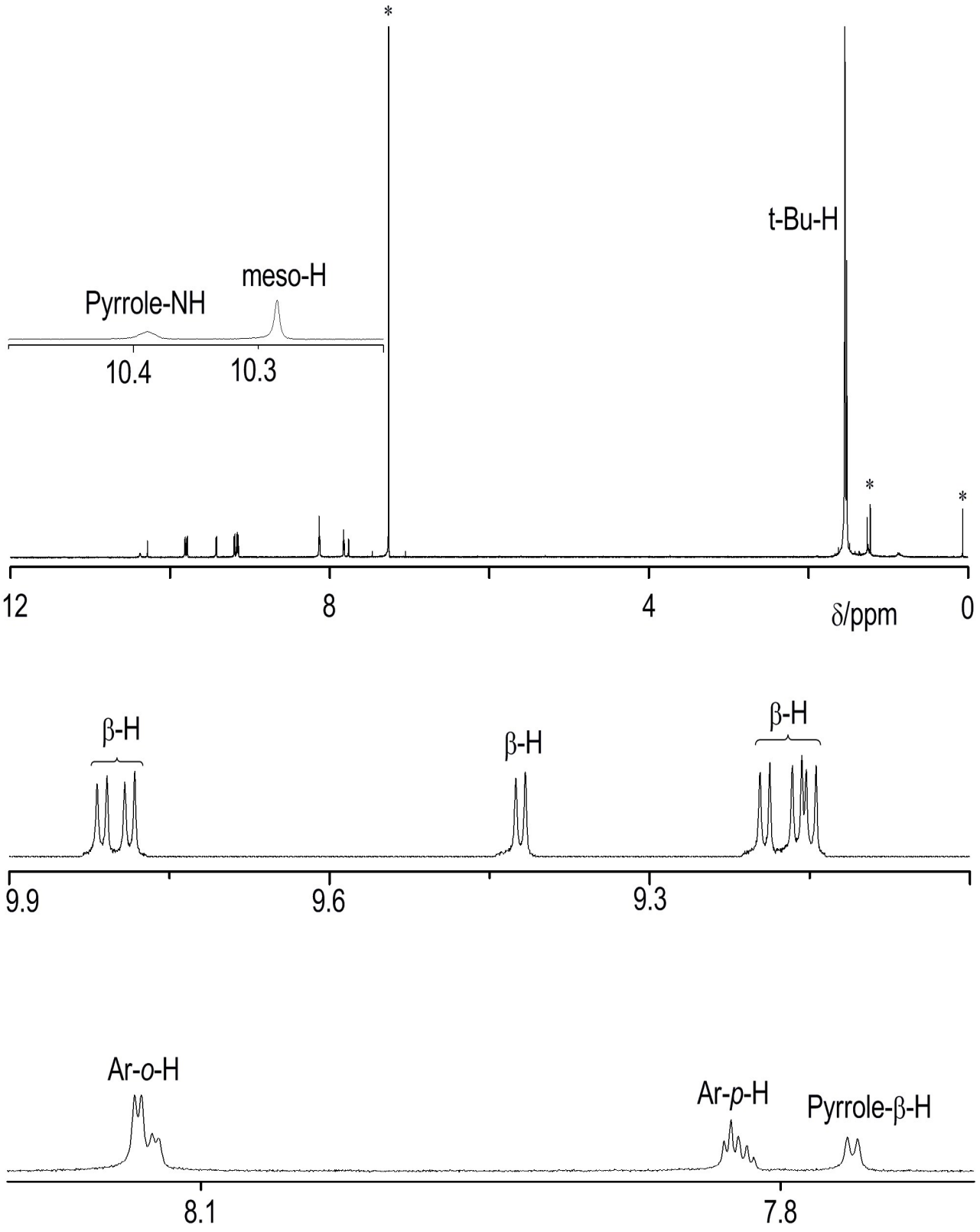

Figure S6. ^{1}H NMR spectrum of **3Zn** in $CDCl_3$.

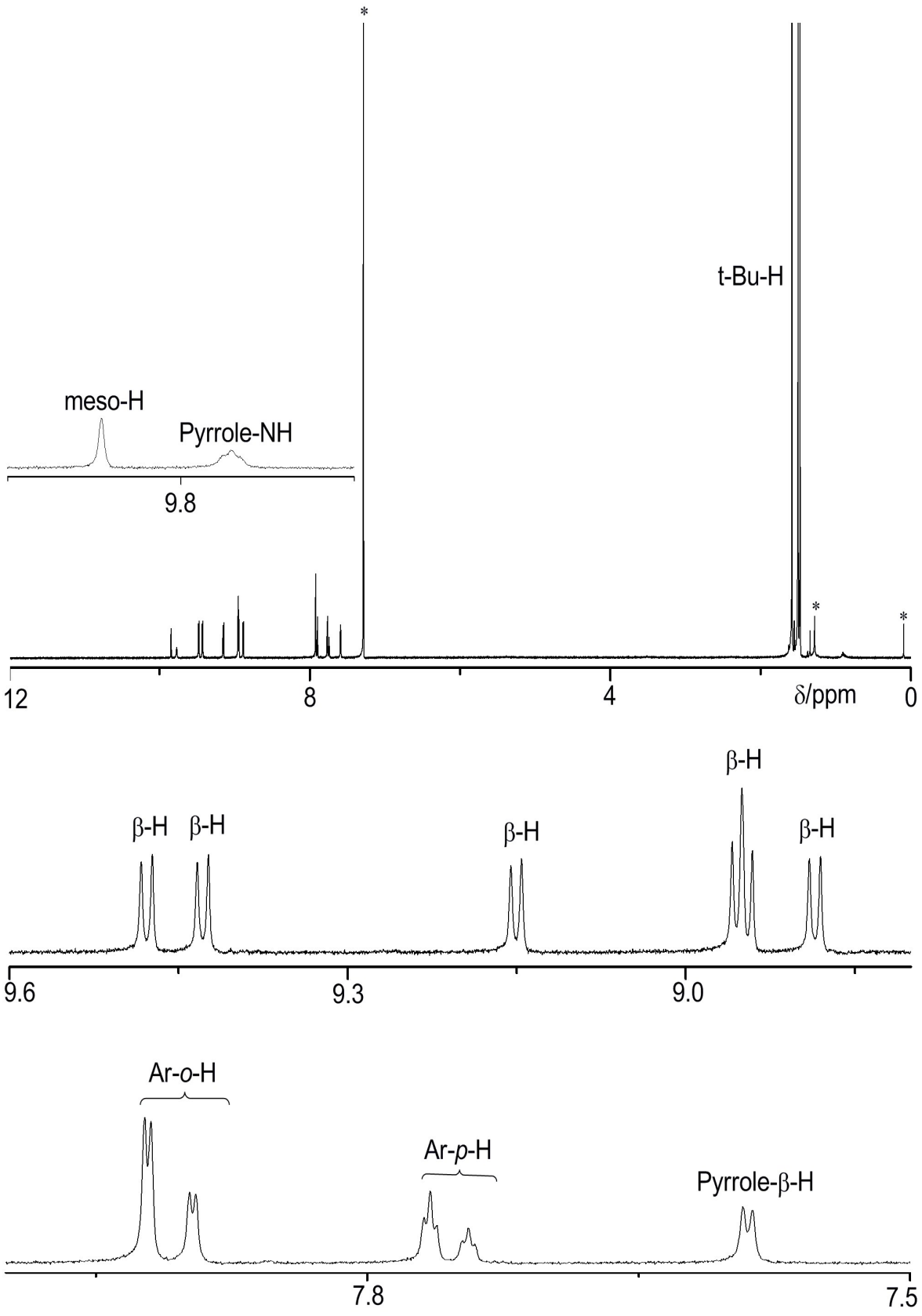

Figure S7. ^{1}H NMR spectrum of **3Ni** in $CDCl_3$.

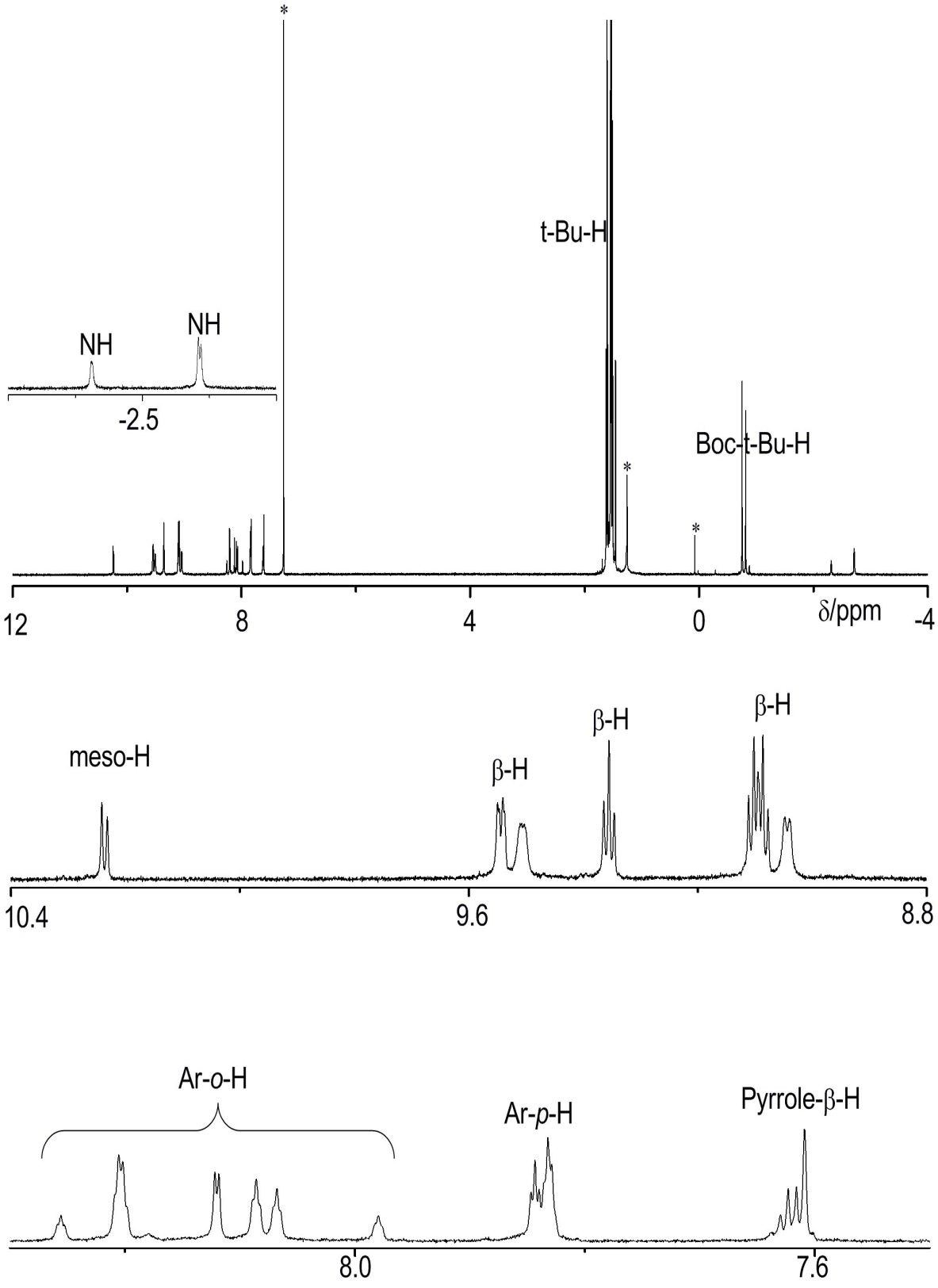

Figure S8. ^{1}H NMR spectrum of **Boc-3H** in $CDCl_3$.

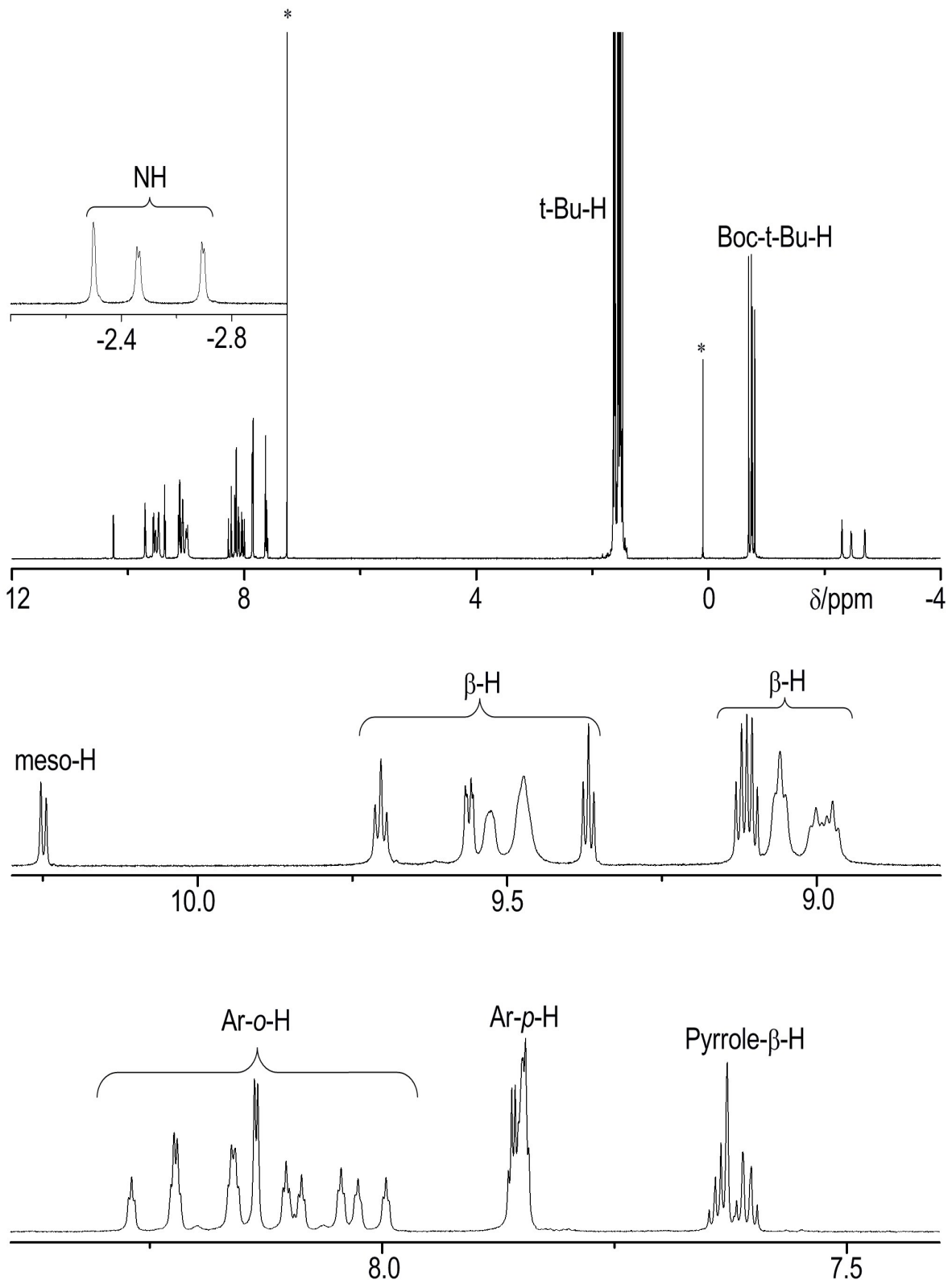

Figure S9. ^{1}H NMR spectrum of **Boc-3H-1Br** in $CDCl_3$.

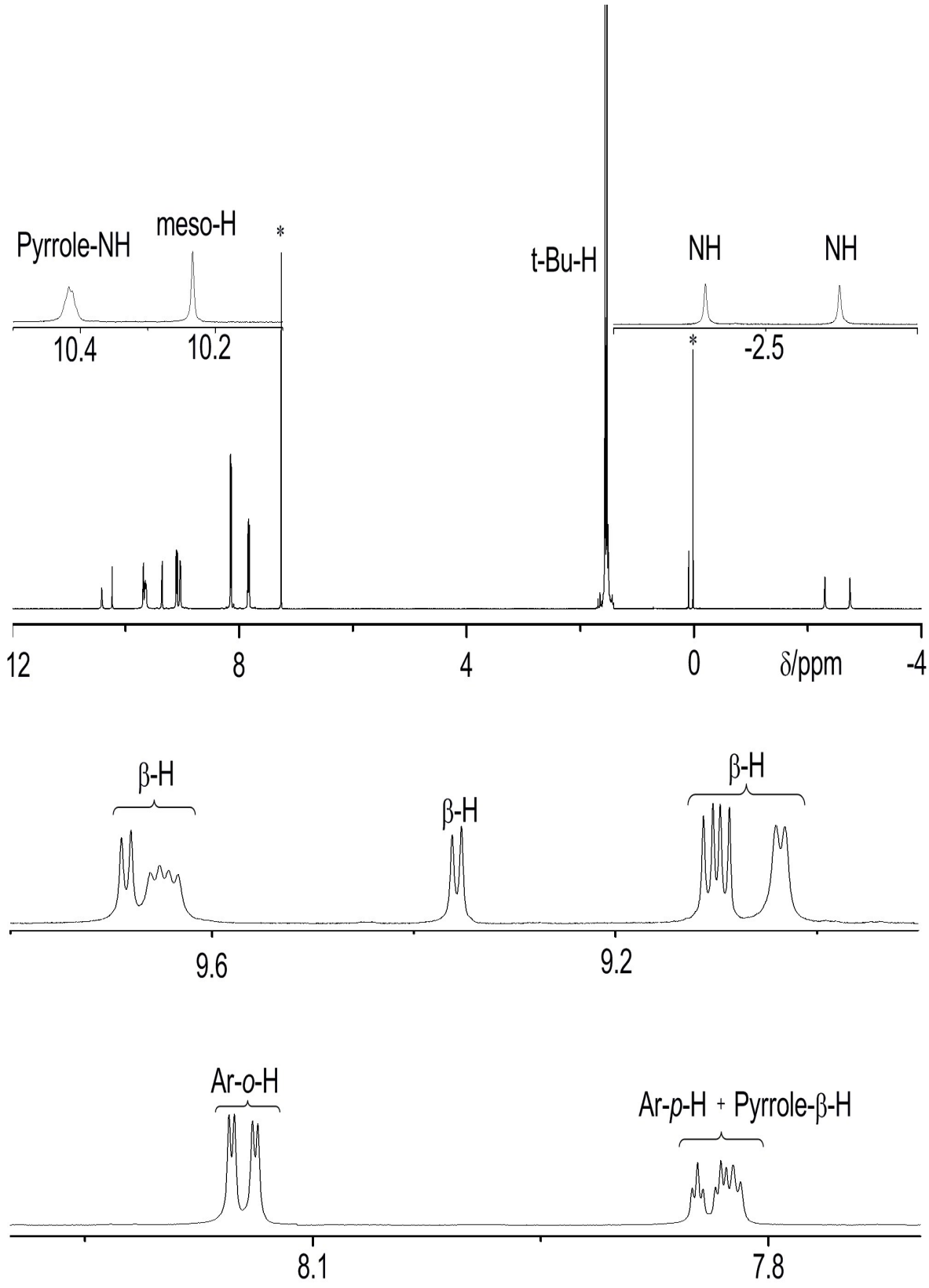

Figure S10. ^{1}H NMR spectrum of **4H** in $CDCl_3$.

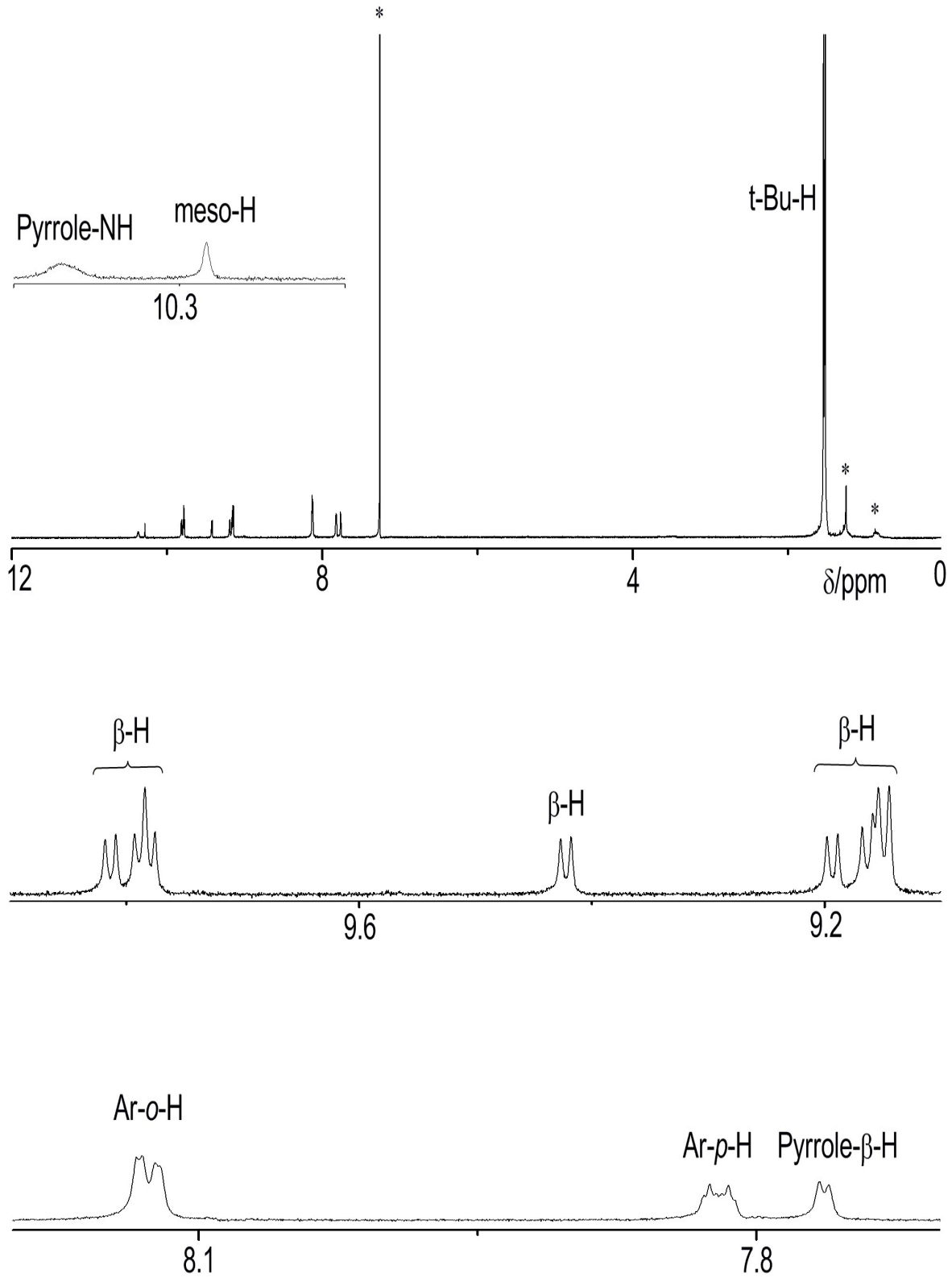

Figure S11. ^{1}H NMR spectrum of **4Zn** in $CDCl_3$.

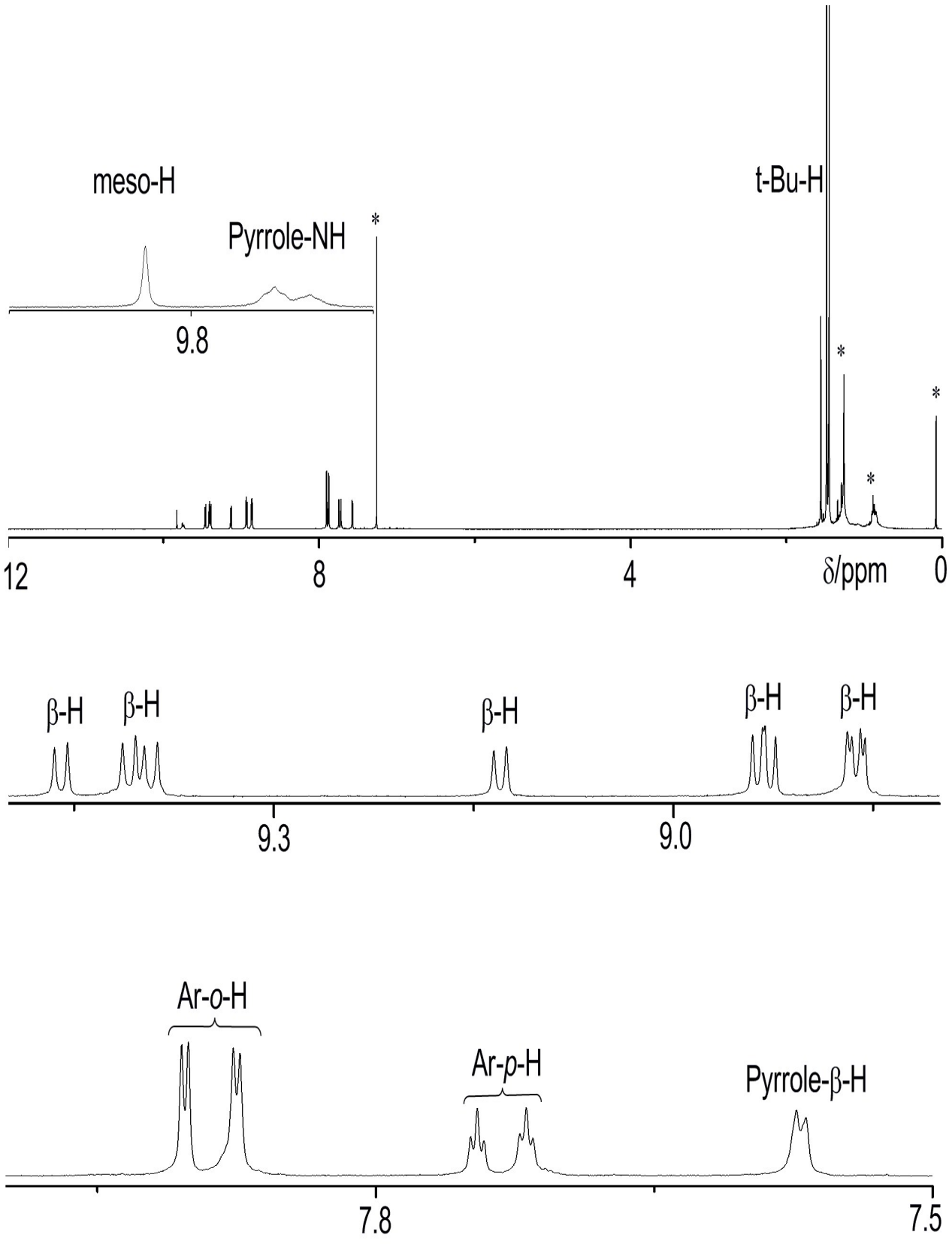

Figure S12. ^{1}H NMR spectrum of **4Ni** in $CDCl_3$.

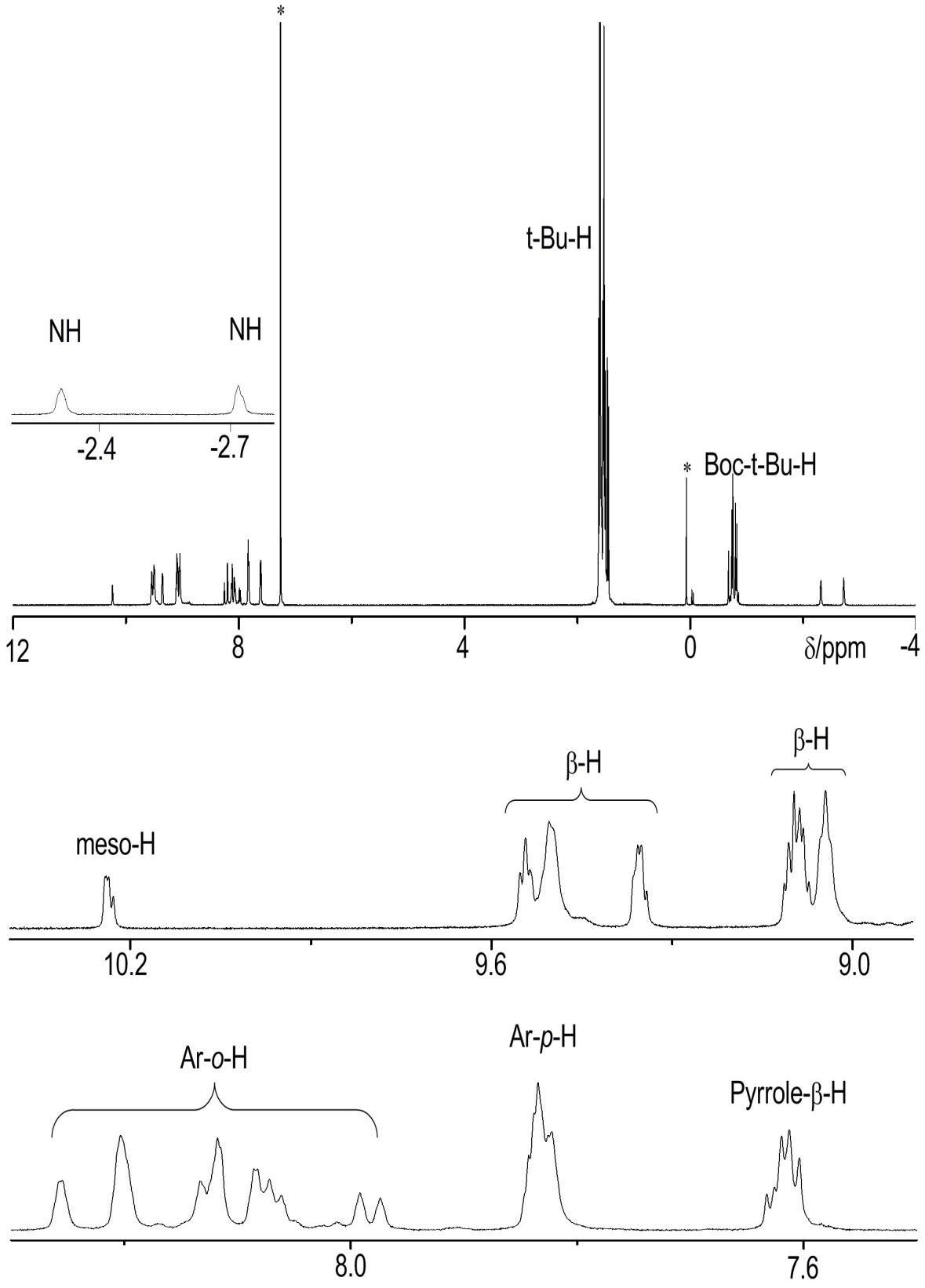

Figure S13. ^{1}H NMR spectrum of **Boc-4H** in $CDCl_3$.

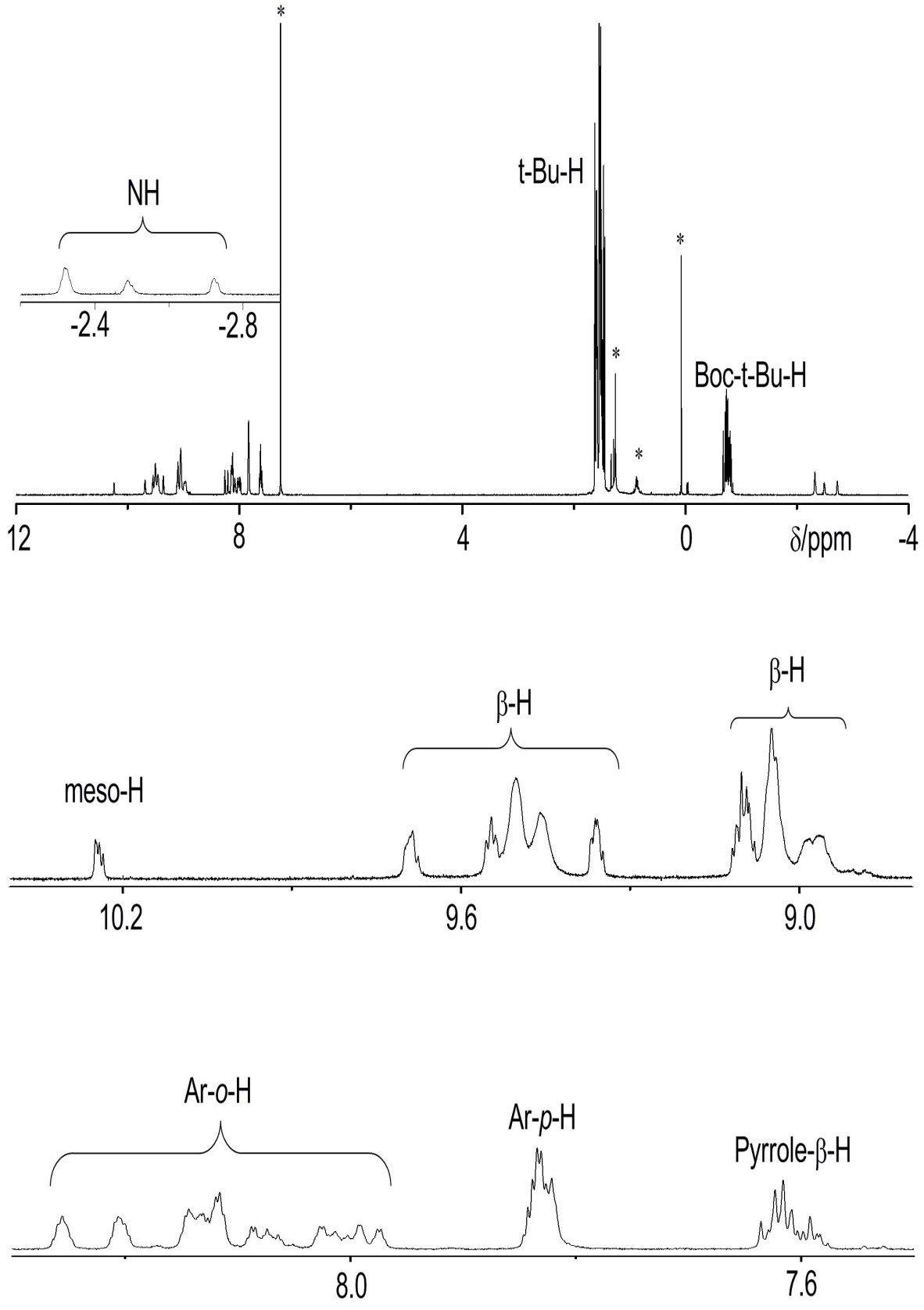

Figure S14. ^{1}H NMR spectrum of **Boc-4H-1Br** in $CDCl_3$.

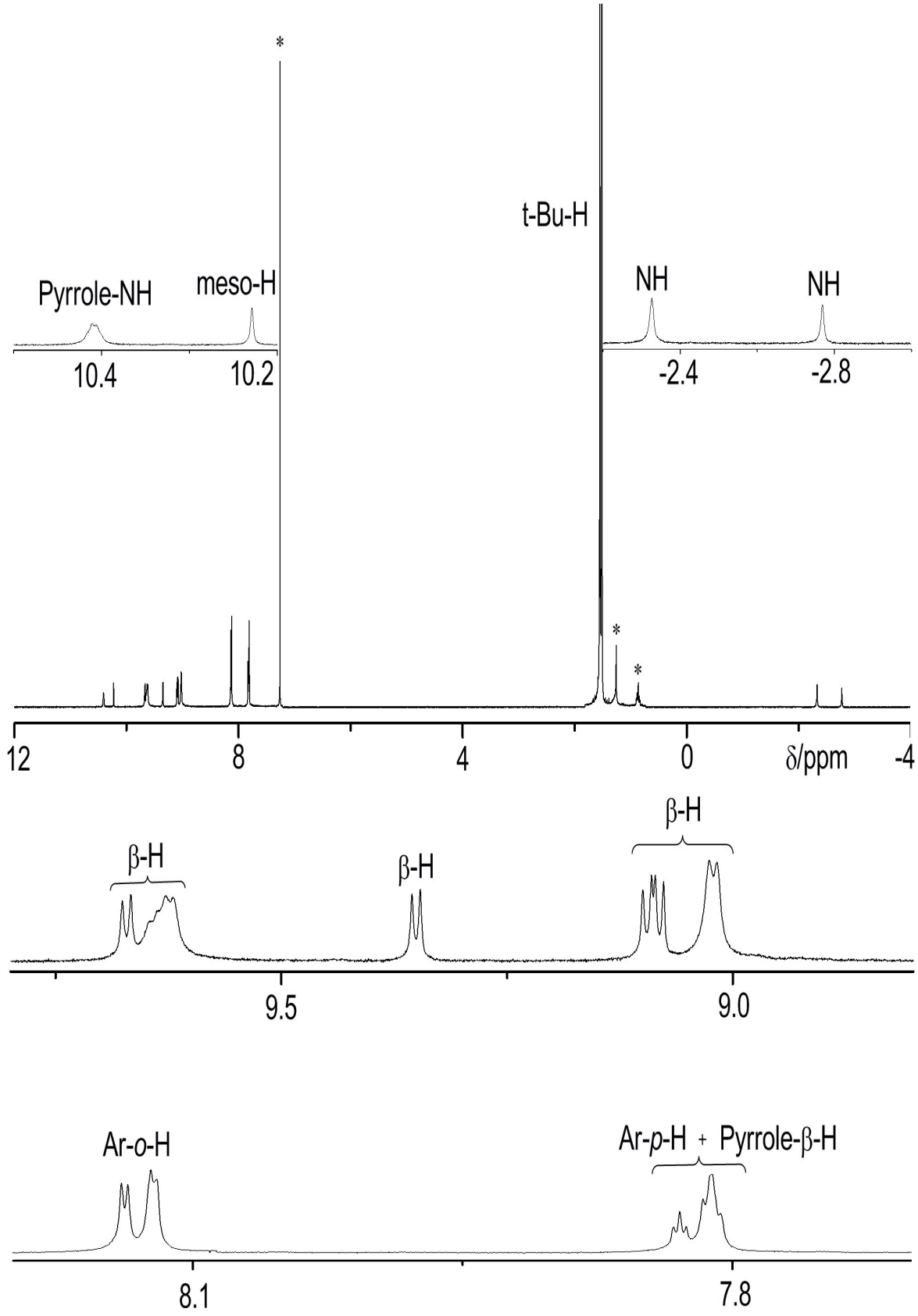

Figure S15. ^{1}H NMR spectrum of **5H** in $CDCl_3$.

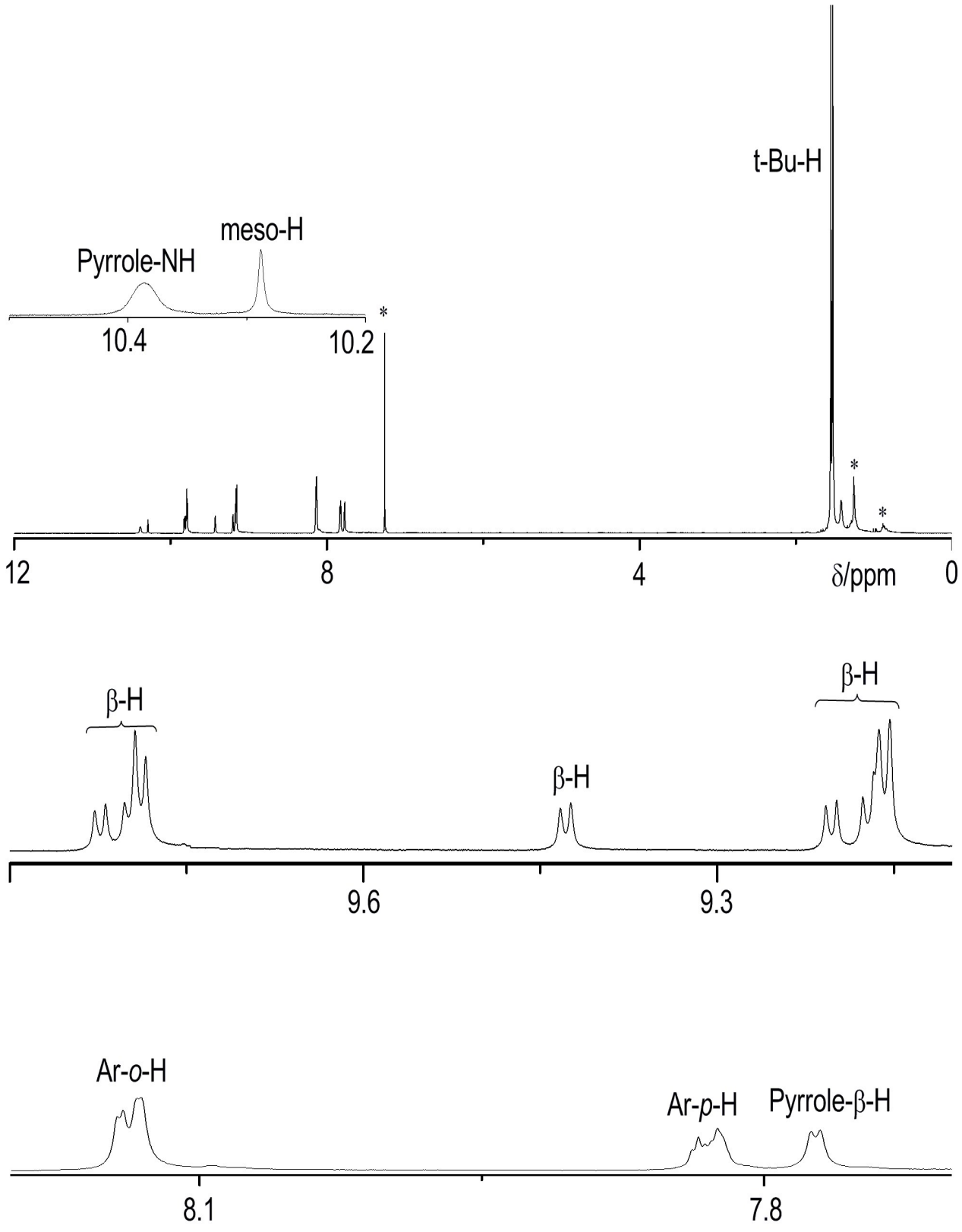

Figure S16. ^{1}H NMR spectrum of **5Zn** in $CDCl_3$.

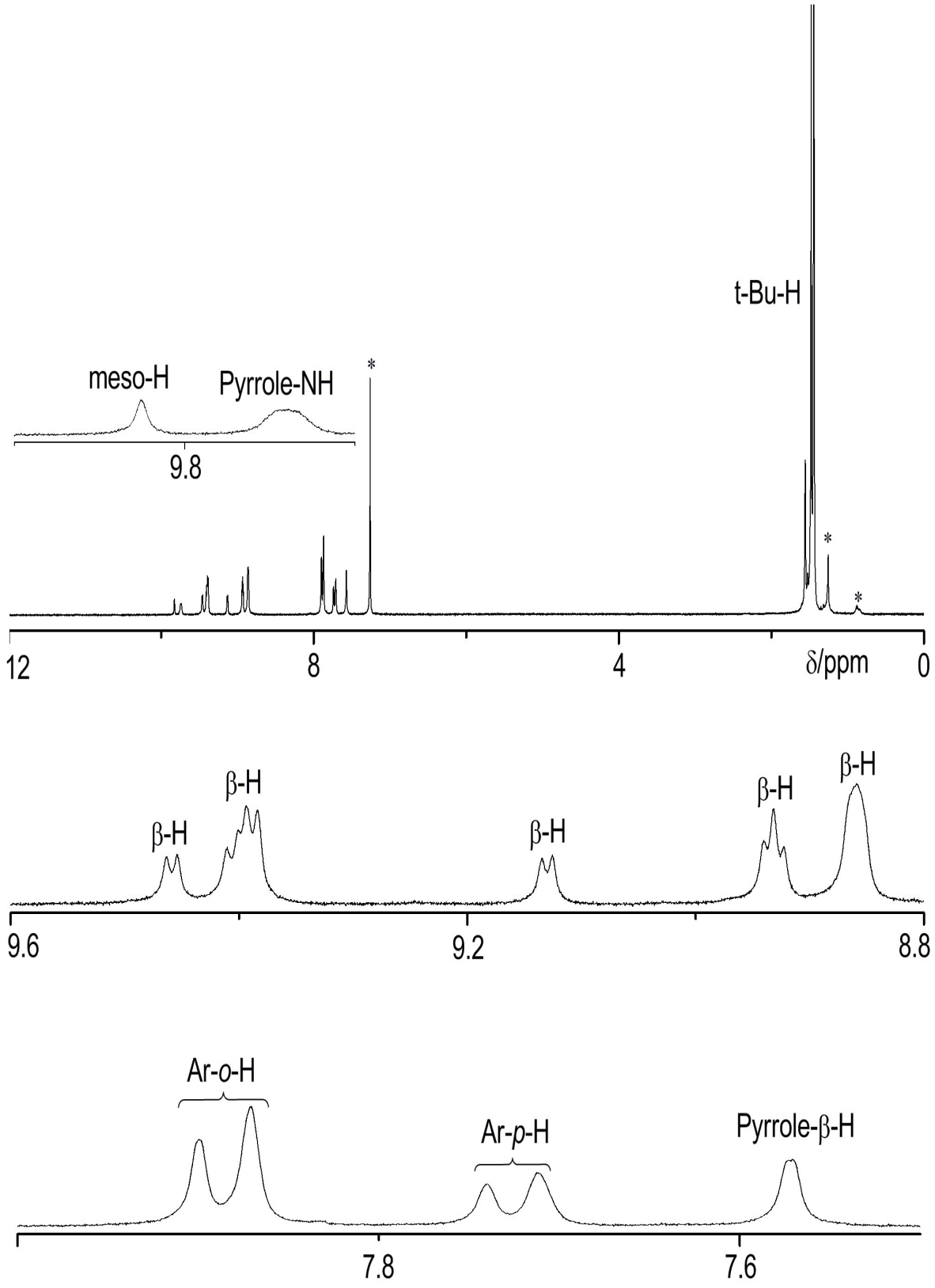

Figure S17. ^{1}H NMR spectrum of **5Ni** in $CDCl_3$.

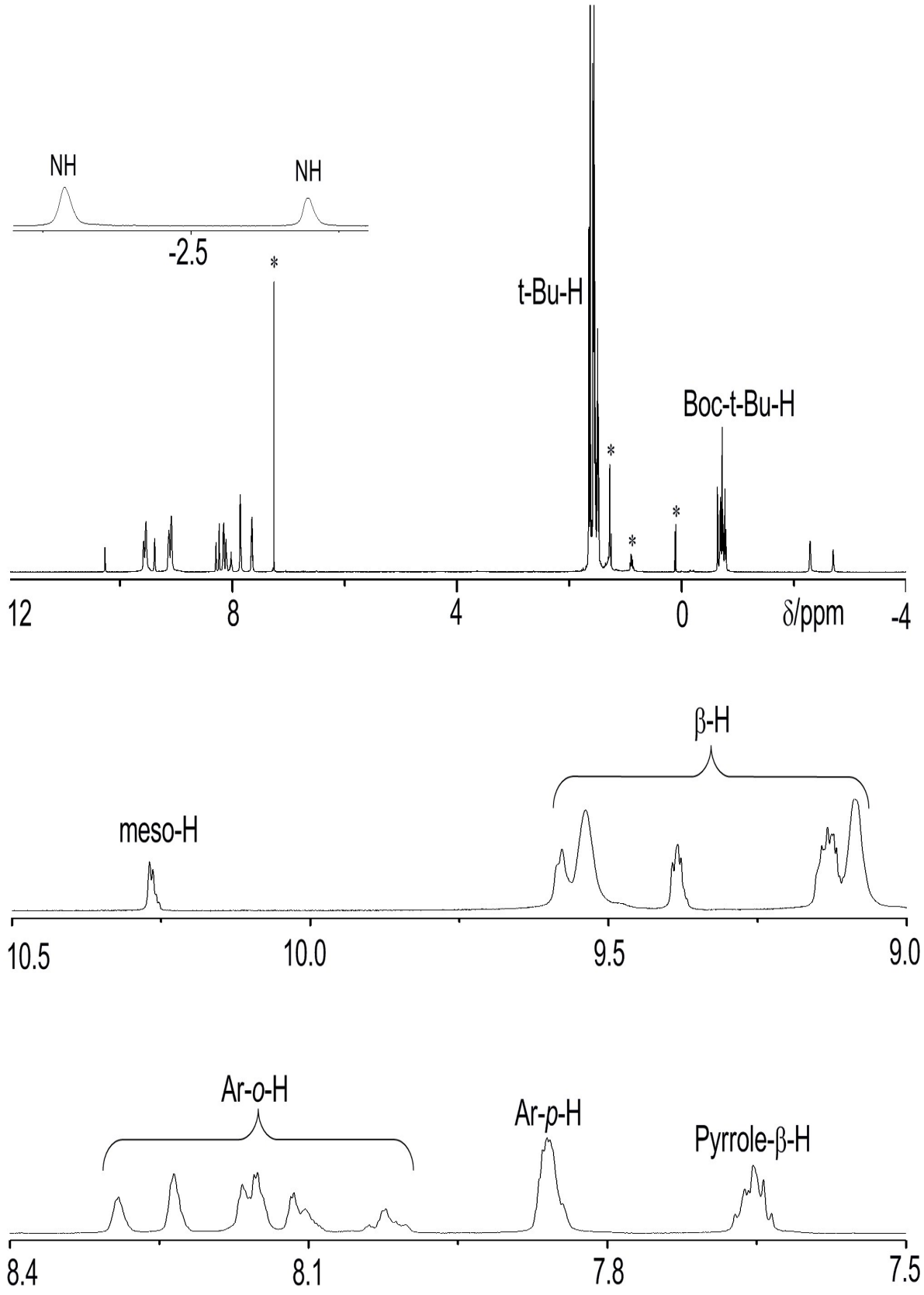

Figure S18. ^{1}H NMR spectrum of **Boc-5H** in $CDCl_3$.

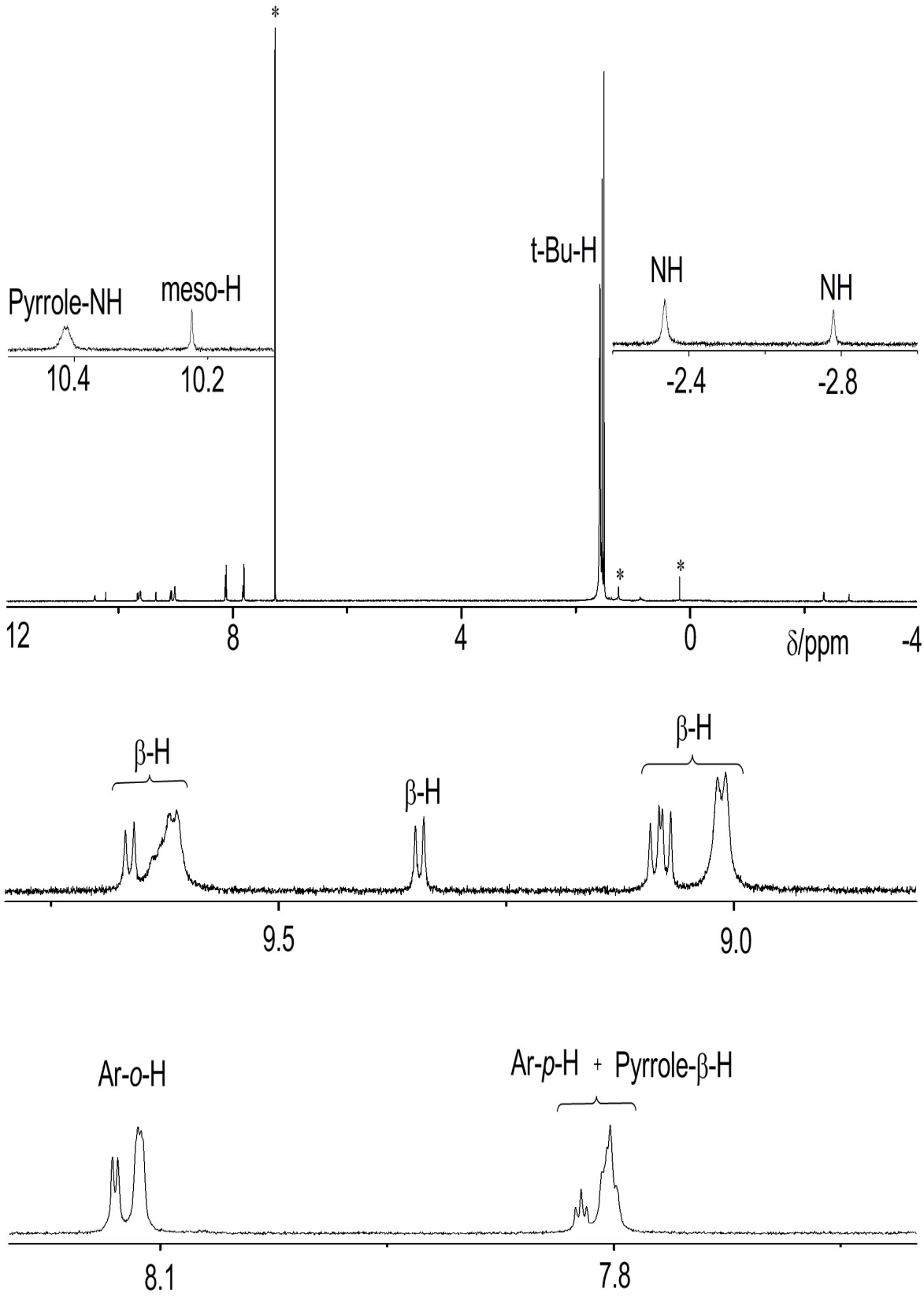

Figure S19. ^{1}H NMR spectrum of **6H** in $CDCl_3$.

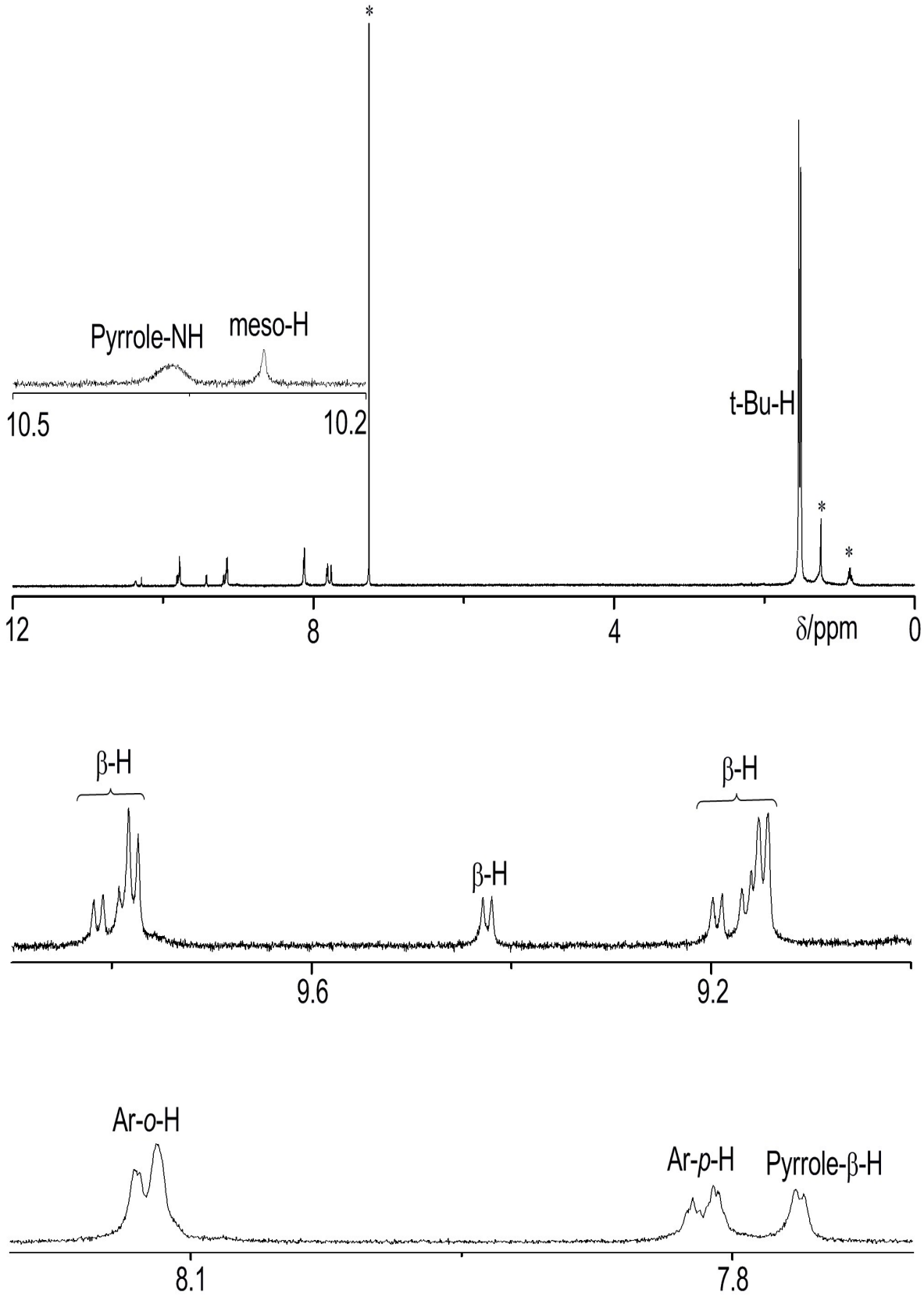

Figure S20. ^{1}H NMR spectrum of **6Zn** in $CDCl_3$.

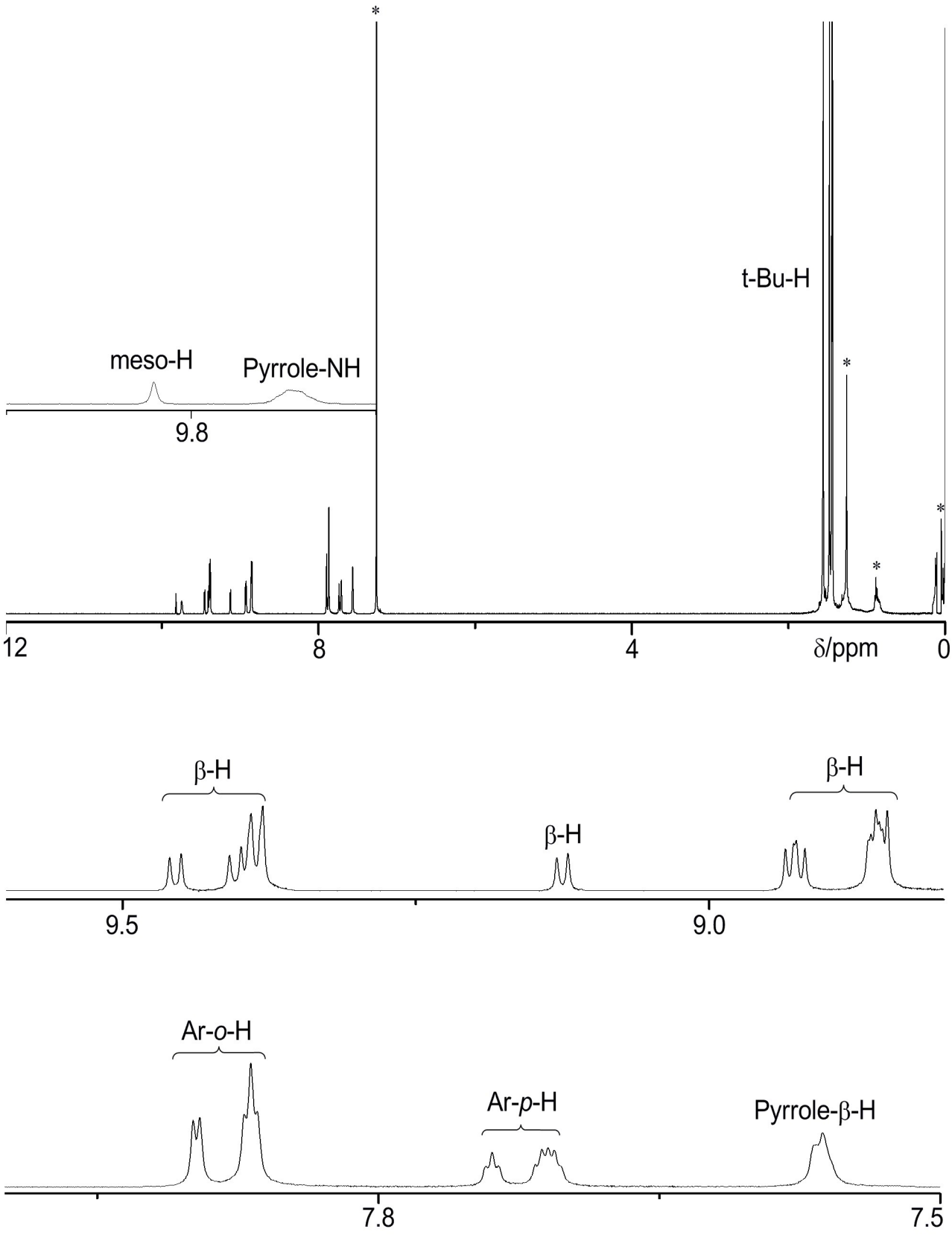

Figure S21. ^{1}H NMR spectrum of **6Ni** in $CDCl_3$.

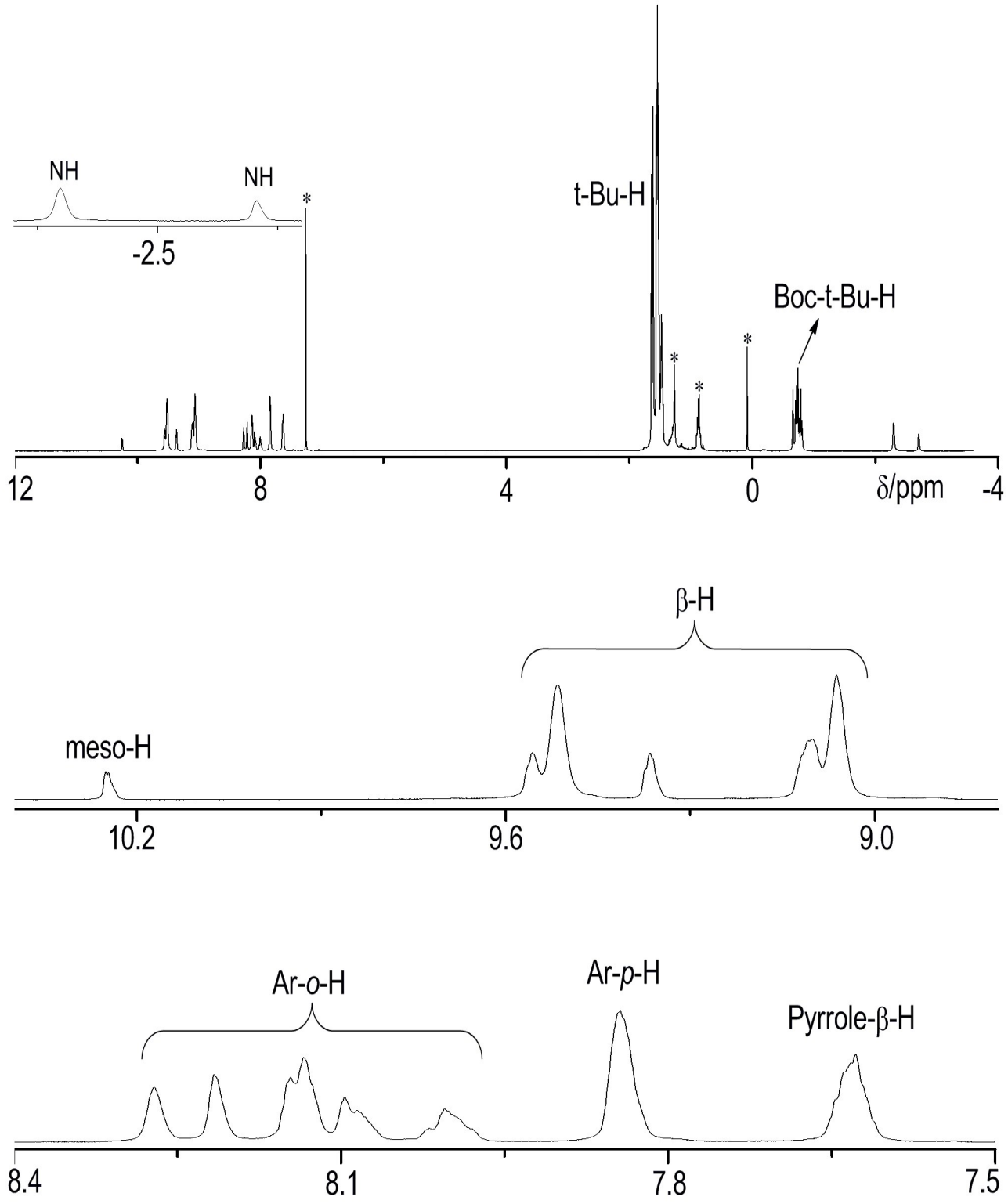

Figure S22. ^{1}H NMR spectrum of **Boc-6H** in $CDCl_3$.

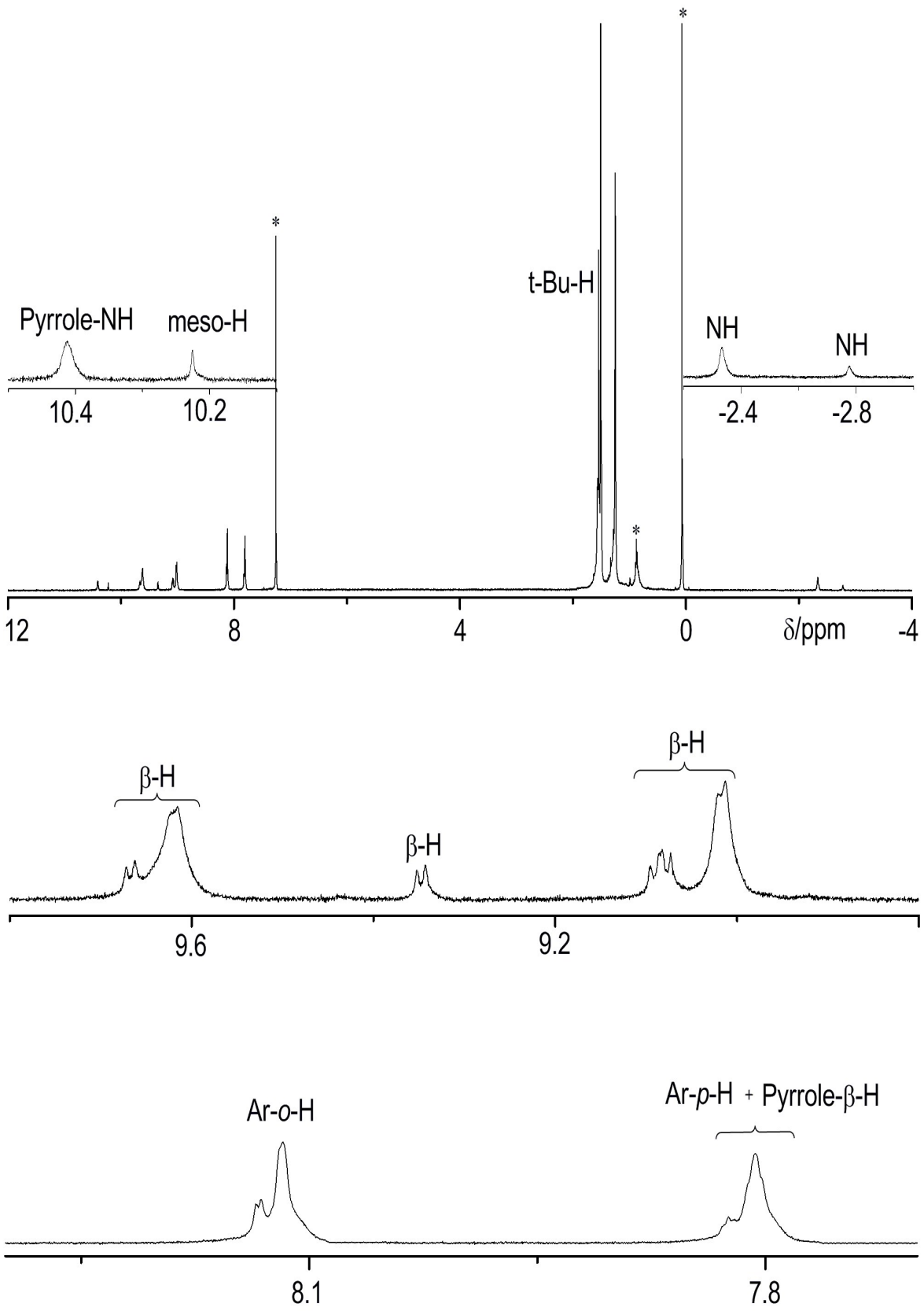

Figure S23. ^{1}H NMR spectrum of **8H** in $CDCl_3$.

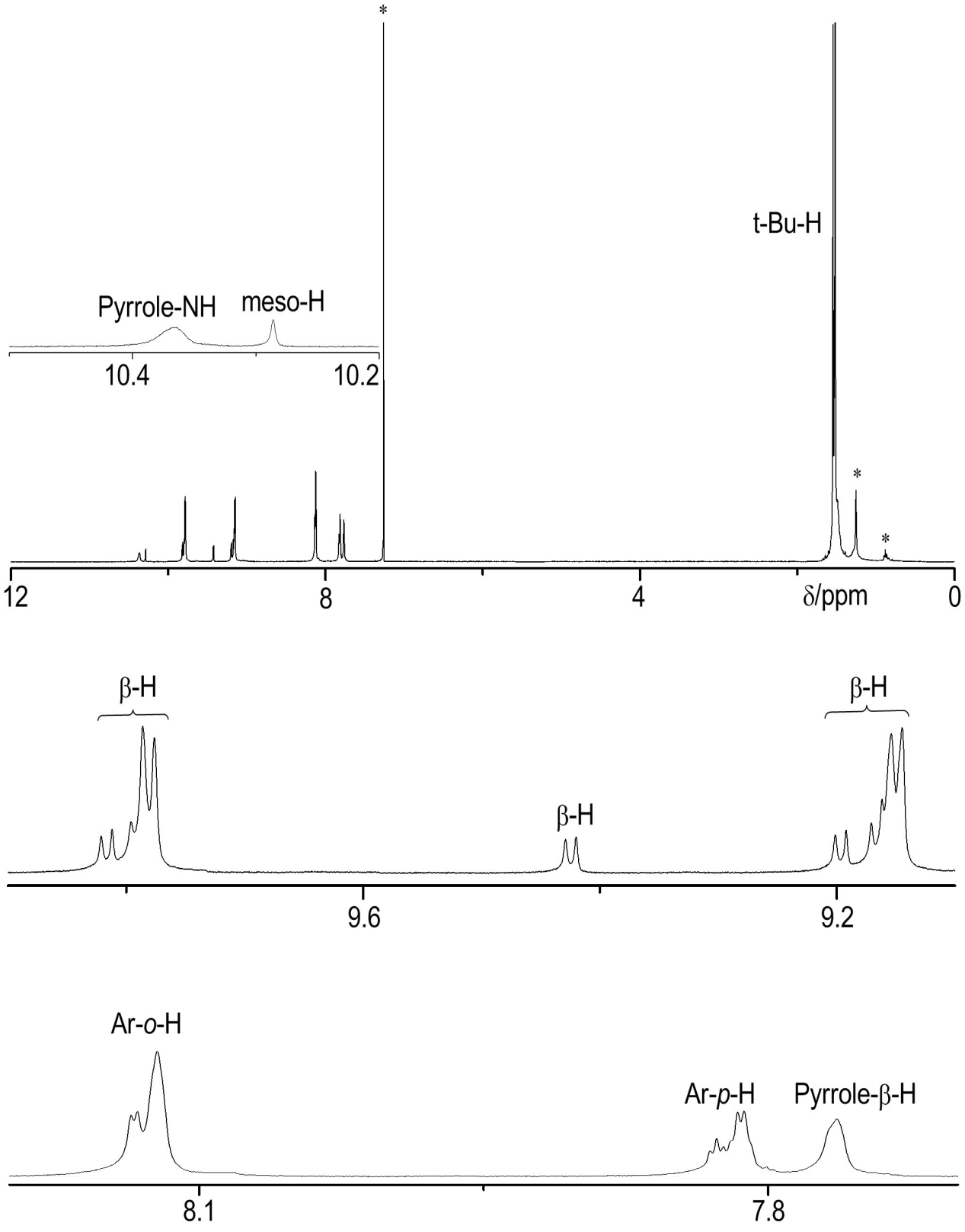

Figure S24. ^{1}H NMR spectrum of **8Zn** in $CDCl_3$.

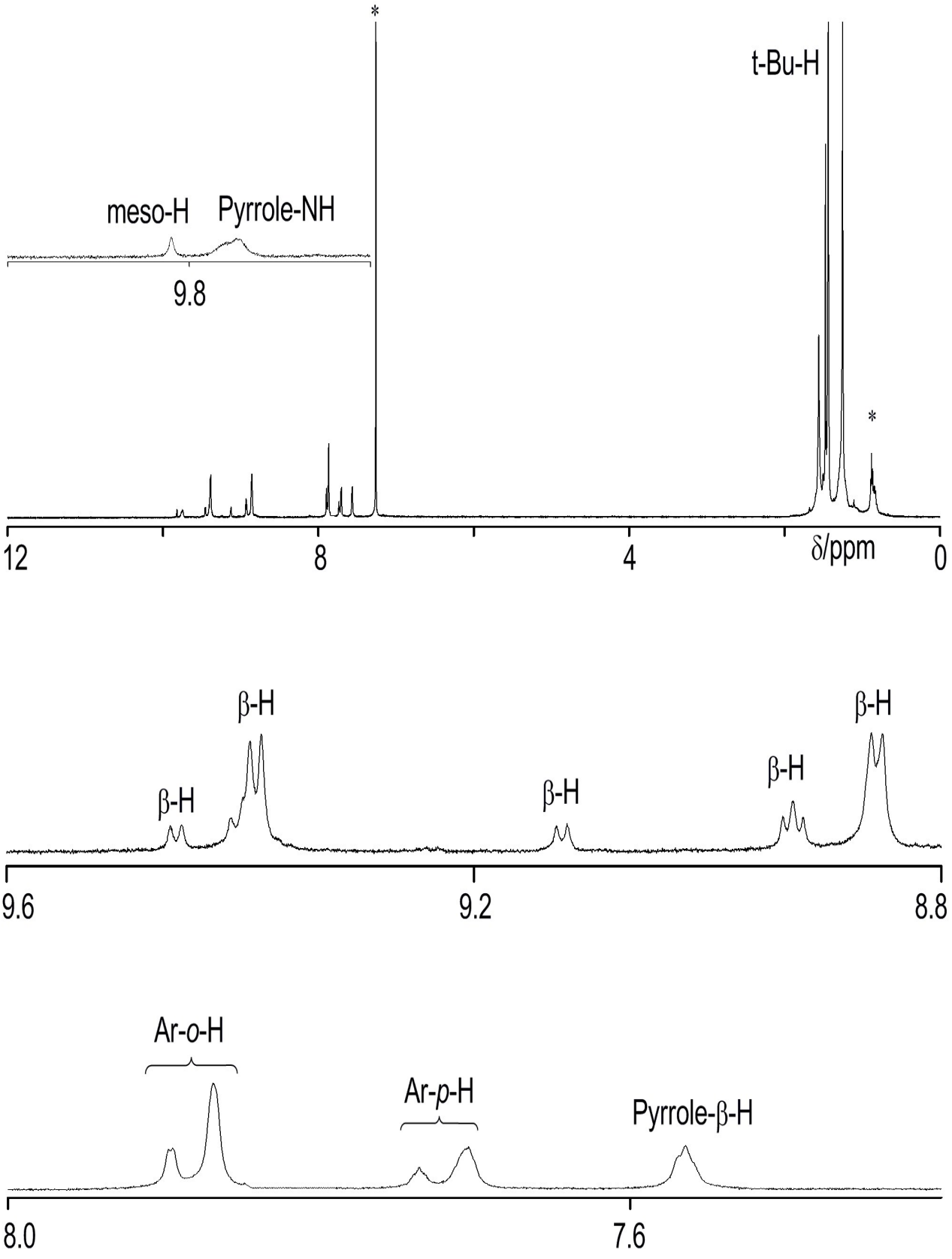

Figure S25. ^{1}H NMR spectrum of **8Ni** in $CDCl_3$.

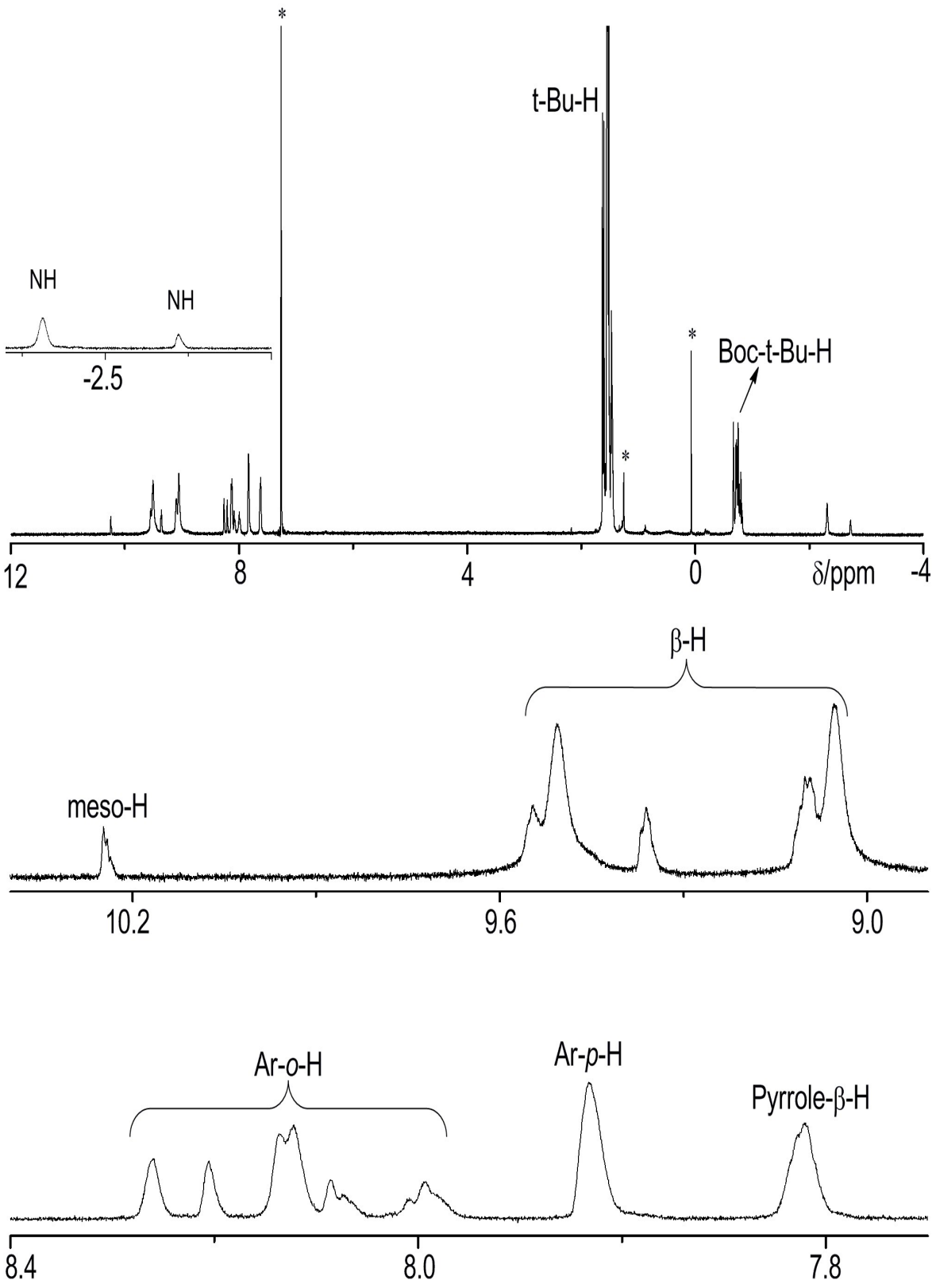

Figure S26. ^{1}H NMR spectrum of **Boc-8H** in $CDCl_3$.

Photophysical Properties

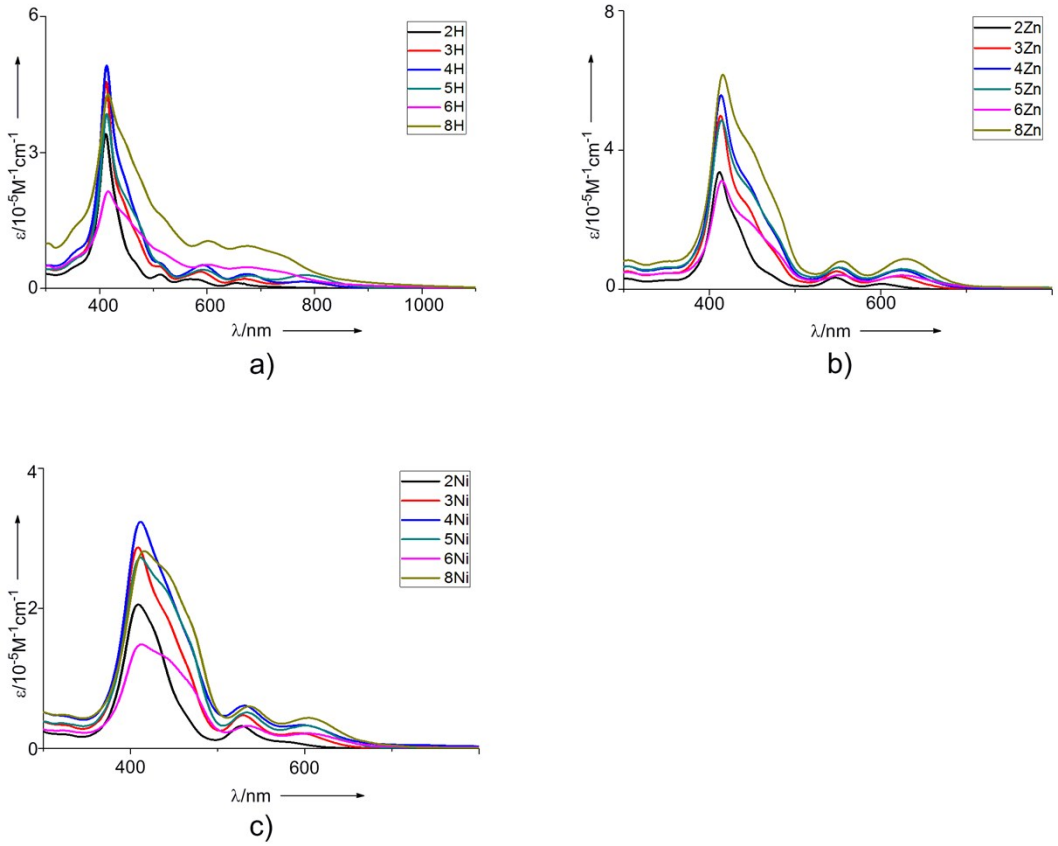

Figure S27. UV/vis absorption spectra of (a) **2H** (black line), **3H** (red line), **4H** (blue line), **5H** (dark cyan line), **6H** (magenta line), and **8H** (dark yellow line) and (b) **2Zn** (black line), **3Zn** (red line), **4Zn** (blue line), **5Zn** (dark cyan line), **6Zn** (magenta line), and **8Zn** (dark yellow line) and (c) **2Ni** (black line), **3Ni** (red line), **4Ni** (blue line), **5Ni** (dark cyan line), **6Ni** (magenta line) and **8Ni** (dark yellow line) in CH_2Cl_2.

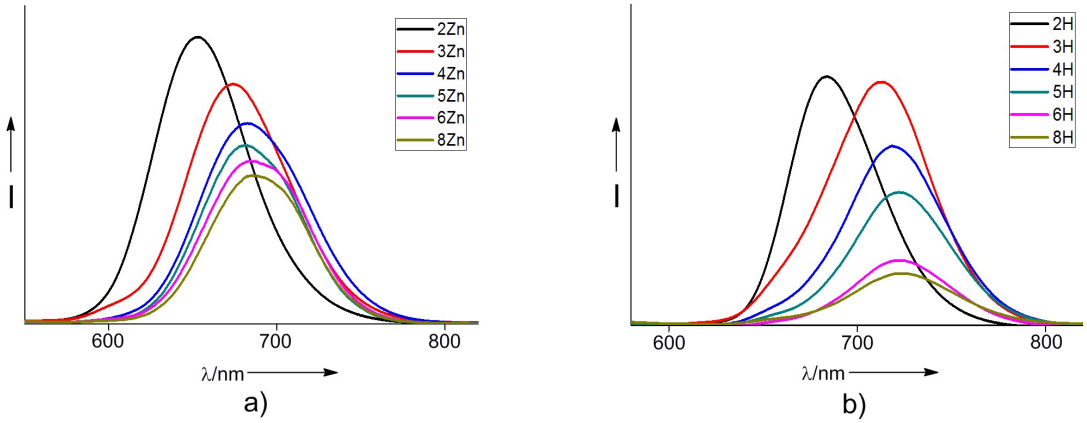

Figure S28. Fluorescence emission spectra of (a) **2Zn** (black line), **3Zn** (red line), **4Zn** (blue line), **5Zn** (dark cyan line), **6Zn** (magenta line), and **8Zn** (dark yellow line) and (b) **2H** (black line), **3H** (red line), **4H** (blue line), **5H** (dark cyan line), **6H** (magenta line), and **8H** (dark yellow line) in CH_2Cl_2.

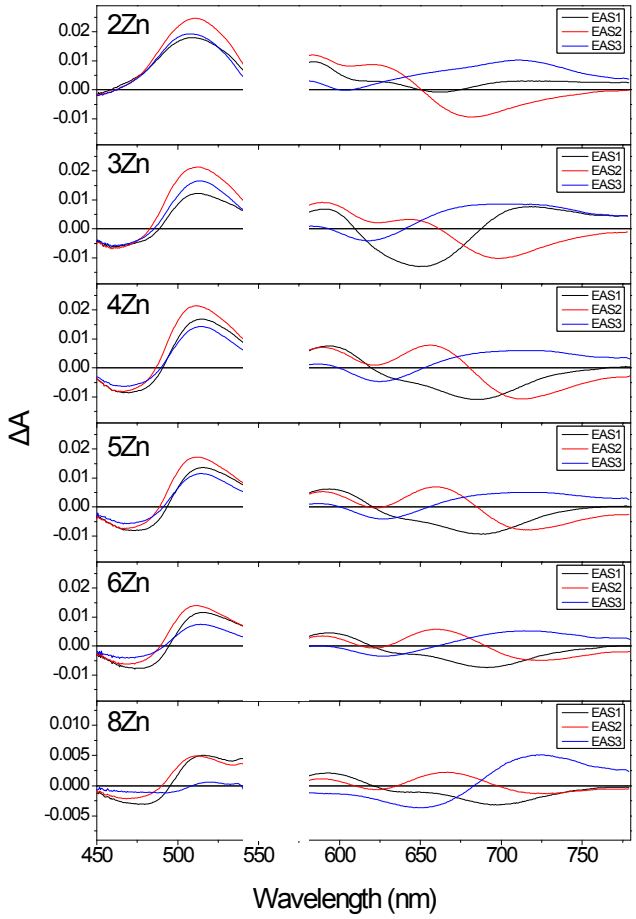

Figure S29. Evolution associated spectra (EAS) of **2Zn-8Zn** obtained from *fs*-trasient absorption measurements in toluene.

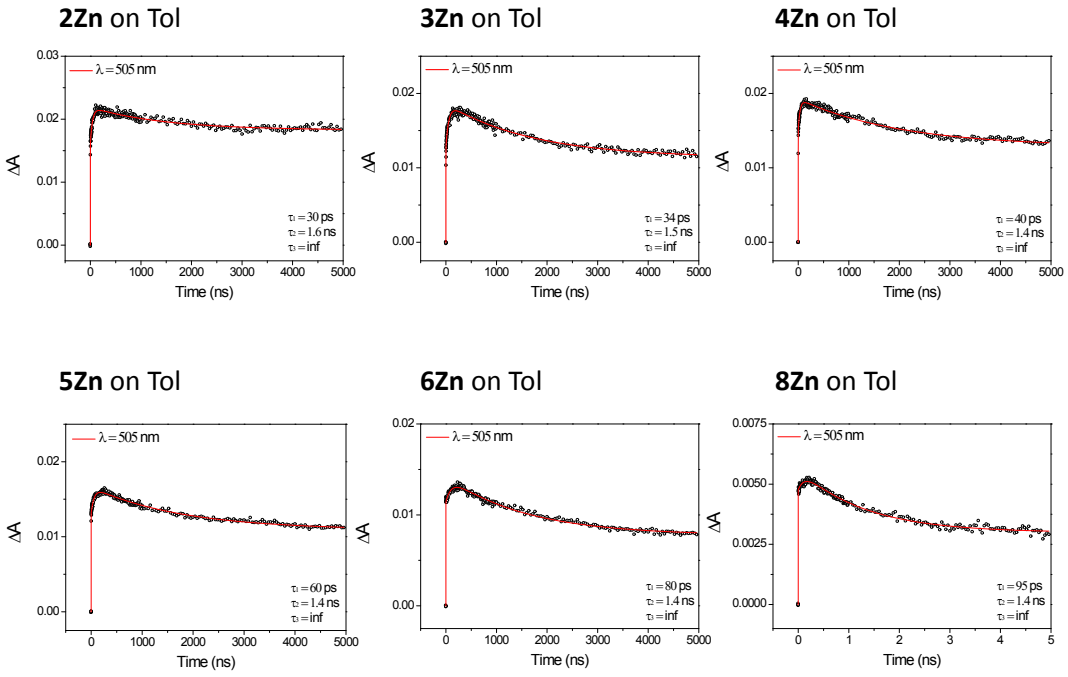

Figure S30. Decay profile of **2Zn-8Zn** obtained from *fs*-trasient absorption measurements in toluene.

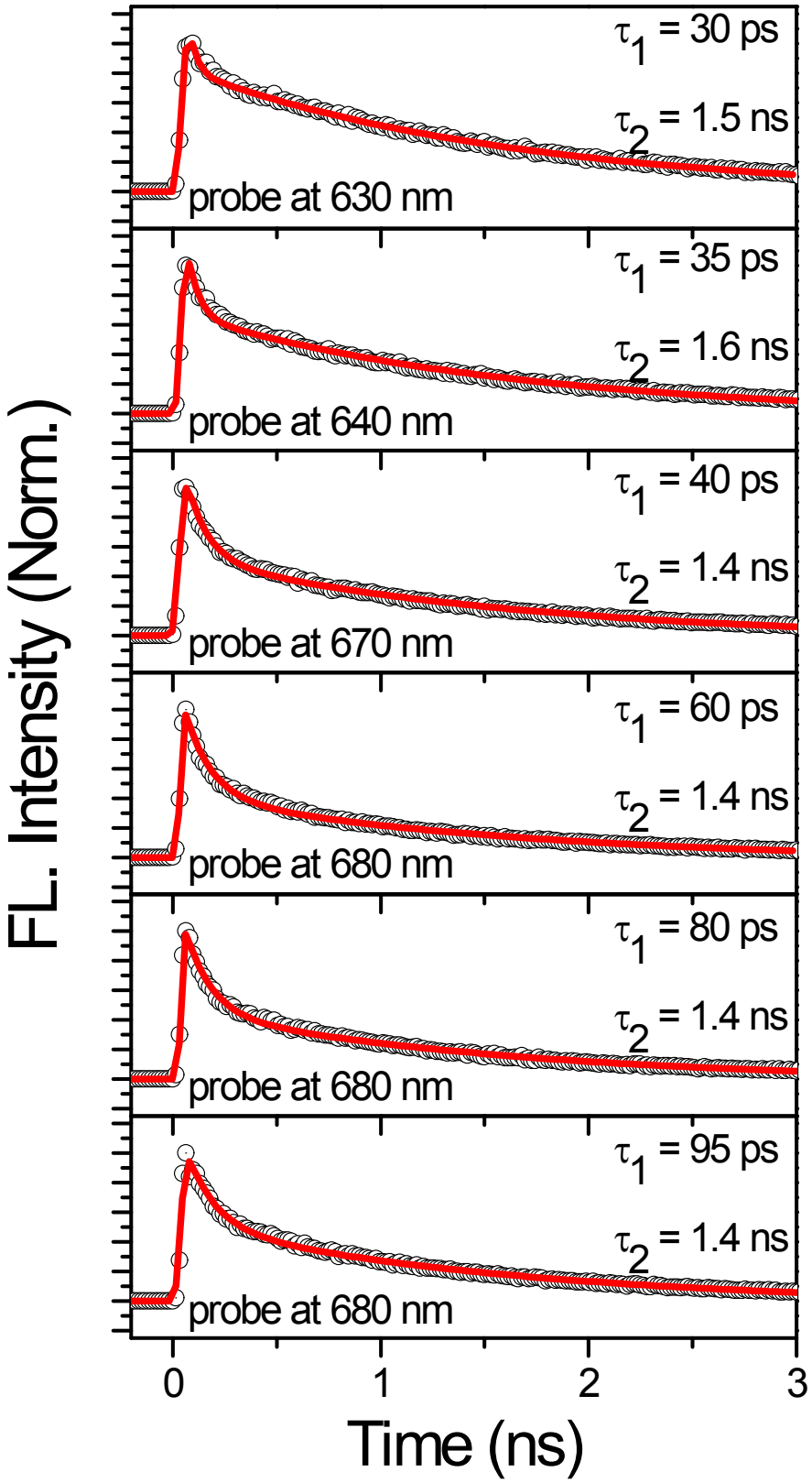

Figure S30. Decay profile of **2Zn-8Zn** obtained from TCSPC measurements in toluene.

Theoretical Calculations

All of the substituents of **[n]Zn** are substituted with H atoms to reduce computational cost when geometry optimization calculations are conducted. Models with 2 to up to 8 monomers were considered. The structures of these models were fully optimized using DFT B3LYP [S1,S2] exchange-correlation energy density functionals. A compound basis set was employed with Pople's 6-311G(d) basis set for Zn, 6-31G(d) for C and H elements, and 6-311+G(d) for N element [S3]. All computations were performed with Gaussian package version 09E01 [S4] with tight SCF convergence and ultrafine integration grids.

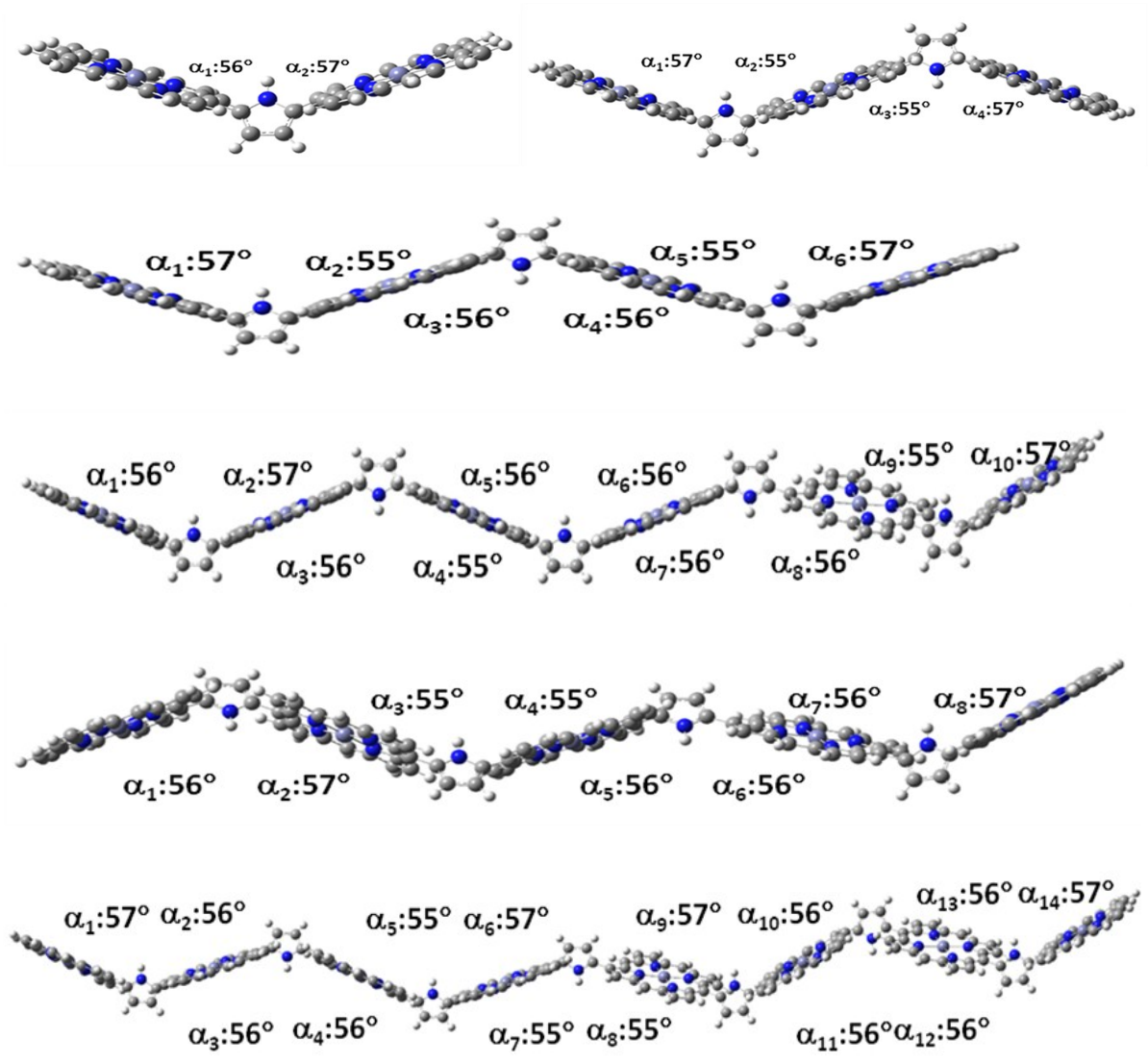

Figure S31. Optimized ground state geometry of **2Zn-8Zn**.

α_n denotes dihedral angles between pophyrin and neighboring pyrrole linker.

X-Ray Crystal Data

Table S1. Crystal data and structure refinement for dimer.

Identification code	song11
Empirical formula	C110 H115 N11 Zn2
Formula weight	1721.87
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	I b a 2
Unit cell dimensions	a = 24.0135(16) Å α= 90°.
b = 27.685(2) Å	β= 90°.
c = 41.457(3) Å	γ = 90°.
Volume	27561(3) $Å^3$
Z	8
Density (calculated)	0.830 Mg/m^3
Absorption coefficient	0.385 mm^{-1}
F(000)	7296
Crystal size	0.2 x 0.2 x0.3 mm^3
Theta range for data collection	1.12 to 25.00°.
Index ranges	-28<=h<=27, -32<=k<=29, -48<=l<=29
Reflections collected	53949
Independent reflections	20147 [R(int) = 0.0724]
Completeness to theta = 25.00°	98.2 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	20147 / 1827 / 1070
Goodness-of-fit on F^2	1.004
Final R indices [I>2sigma(I)]	R1 = 0.0734, wR2 = 0.1443
R indices (all data)	R1 = 0.1574, wR2 = 0.1637
Absolute structure parameter	0.51(2)
Largest diff. peak and hole	1.222 and -1.120 $e.Å^{-3}$
CCDC number	1565076

The contributions to the scattering arising from the presence of the disordered solvents in the crystal were removed by use of the utility SQUEEZE3 in the PLATON software package.[S5]

Table S2. Crystal data and structure refinement for trimer

Identification code	exp_19_1_smart_sq	
Empirical formula	C81 H84 N8 Zn1.50	
Formula weight	1267.61	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.3496(4) Å	α= 95.630(3)°.
	b = 15.1615(5) Å	β= 95.061(3)°.
	c = 30.0085(12) Å	γ = 104.331(3)°.
Volume	4073.6(3) $Å^3$	
Z	2	
Density (calculated)	1.033 Mg/m^3	
Absorption coefficient	0.891 mm^{-1}	
F(000)	1342	
Crystal size	0.2 x 0.3 x0.4 mm^3	
Theta range for data collection	4.510 to 67.399°.	
Index ranges	-9<=h<=11, -18<=k<=16, -35<=l<=35	
Reflections collected	43065	
Independent reflections	14618 [R(int) = 0.0694]	
Completeness to theta = 67.399°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14618 / 6 / 835	
Goodness-of-fit on F^2	1.095	
Final R indices [I>2sigma(I)]	R1 = 0.1137, wR2 = 0.3150	
R indices (all data)	R1 = 0.1742, wR2 = 0.3688	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.298 and -0.476 e.$Å^{-3}$	
CCDC number	1565075	

The contributions to the scattering arising from the presence of the disordered solvents in the crystal were removed by use of the utility SQUEEZE3 in the PLATON software package.[S5]

[S1] A. D. Becke, J. Chem. Phys. 98, 1372 (1993).

[S2] C. T. Lee, W. T. Yang, and R. G. Parr, Phys. Rev. B 37, 785 (1988).

[S3] R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys. 54, 724 (1971).

[S4] M.J. Frisch, G.W. Trucks, H.B. Schlegel, et al., GAUSSIAN 09, Revision E.01, Gaussian, Inc., Wallingford CT, 2009

[S5] Squeeze-Platon: (a) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool; Utrecht, The Netherlands, **2005**; (b) P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* 1990, **46**, 194.