Supporting Information

Carbazole-Containing Porphyrinoids and Its Oligomers

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Instrumentation and Materials

^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were taken on a Bruker AVANCE-500 spectrometer, and chemical shifts were reported as the delta scale in ppm. The residual peak of $CDCl_3$ was used as internal reference for ^{1}H NMR (δ = 7.26 ppm) and the solvent $CDCl_3$ was used as internal reference for ^{13}C NMR (δ = 77.16 ppm). UV/Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. IR spectra were recorded on a Nicolet 670 FTIR spectrometer. MALDI-TOF mass spectra were obtained with a Bruker ultrafleXtreme MALDI-TOF/TOF spectrometer with matrix. X-Ray data were taken on a Rigaku Supernova diffractometer equipped with a EOS S2 CCD detector. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Diboryltripyrrane **5** was systhesized as the procedure we reported before.[1]

Steady-state absorption spectra were measured on a UV/Vis/NIR spectrometer (Varian, Cary5000) and fluorescence spectra were measured on a fluorescence spectrophotometer (Hitachi, F-2500). Fluorescence spectra are spectrally corrected by using correction factor of the fluorescence spectrophotometer. HPLC-grade solvents were purchased from Sigma-Aldrich and used without further purification. For the steady-state fluorescence excitation anisotropy measurement,

Picosecond time-resolved fluorescence measurements.

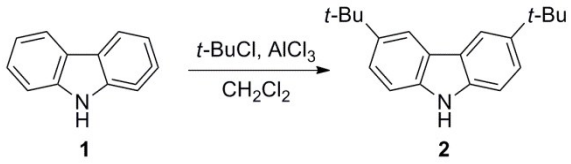
A time-correlated single-photon-counting (TCSPC) system was used for measurements of spontaneous fluorescence decay. As an excitation light source, we used a mode-locked Ti:sapphire laser (Spectra Physics, MaiTai BB) which provides ultrashort pulse (center wavelength of 800 nm with 80 fs at FWHM) with 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 measurements.

A femtosecond time-resolved transient absorption (TA) spectrometer used for this study consisted of a femtosecond optical parametric amplifier (Quantronix, Palitra-FS) pumped by a Ti:sapphire regenerative amplifier system (Quantronix, Integra-C) operating at 1 kHz repetition rate and an accompanying optical detection system. The generated OPA pulses had a pulse width of ~100 fs and an average power of 1 mW in the range 550 to 690 nm, which were used as pump pulses. White light continuum (WLC) probe pulses were generated using a sapphire window (2 mm

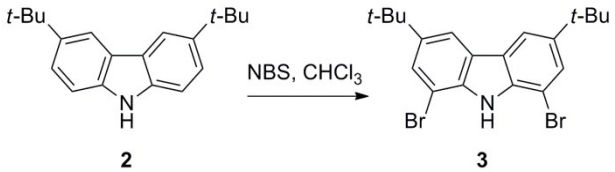
thick) by focusing of small portion of the fundamental 800 nm pulses, which were picked off by a quartz plate before entering into the OPA. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (Newport, ILS250). Intensities of the spectrally dispersed WLC probe pulses were monitored by 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 were used to excite samples and to obtain the 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 to prevent polarization-dependent signals. The cross-correlation FWHM in the pump-probe experiments was less than 200 fs, and chirp of WLC probe pulses was measured to be 800 fs in the 450-1300 nm regions. To minimize chirp, all reflection optics were used in the probe beam path, and a quartz cell of 2 mm path length was employed. After completing each set of fluorescence and TA experiments, the absorption spectra of all compounds were carefully checked to rule out the presence of artifacts or spurious signals arising from, for example, degradation or photo-oxidation of the samples in question.

General Procedures



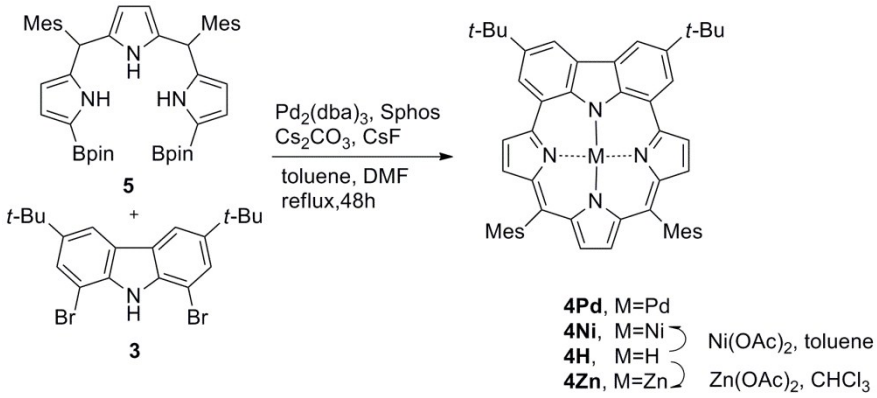
1 2

Synthesis of 2: In a 500 mL flask containing $AlCl_3$ (0.8 g, 6 mmol), **1** (1 g, 6 mmol) was dissolved in 20 mL dry CH_2Cl_2 and 4 mL solution of *t*-BuCl (1.32 mL, 12 mmol) in CH_2Cl_2 was added dropwise and the mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with CH_2Cl_2, washed with water, dried over anhydrous sodium sulfate, and recrystallization with *n*-hexane, **2** was obtained as white solid (1.4 g, 5 mmol, 83% yield).



2 3

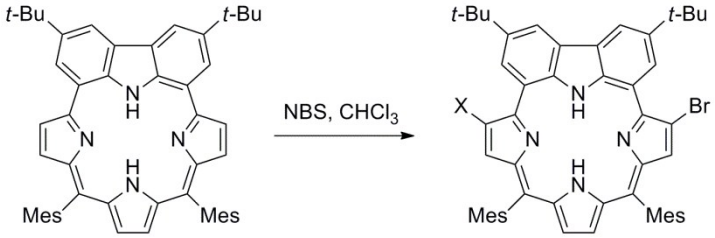
Synthesis of 3: In a 250 mL flask, **2** (500 mg, 1.8 mmol) was dissolved in 100 mL $CHCl_3$ and NBS (673 mg, 3.8 mmol) was added, the mixture was stirred at room temperature for 3.5 h. The reaction mixture was washed with water, dried over anhydrous sodium sulfate, Evaporation of the solvent and recrystallization with *n*-hexane, **3** was obtained as yellow solid (699 mg, 1.6 mmol, 89% yield).



Synthesis of 4H and **4Pd**: A toluene-DMF solution (2 mL/1 mL) of **3** (43.6 mg, 0.1 mmol), **5** (71.3 mg, 0.1 mmol), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol), Sphos (16.4 mg, 0.04 mmol), Cs_2CO_3 (65.2 mg, 0.2 mmol) and CsF (30.4 mg, 0.2 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 $CHCl_3$, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) and recrystallization with MeOH, **4H** was obtained as bluish violet solids (7.8 mg, 0.0106 mmol, 10.6% yield); **4Pd** was obtained as green solids (3.6 mg, 0.0043 mmol, 4.3% yield).

Synthesis of 4Zn: To a solution of **4H** (20 mg, 0.03 mmol) in $CHCl_3$/MeOH (5 mL/1 mL) was added (22 mg, 0.09 mmol) $Zn(OAc)_2 \cdot 2H_2O$ and then the mixture was stirred at room temperature for 5 h, the reaction mixture was passed through a short alumina column. Evaporation of the solvent and recrystallized from methanol, **4Zn** was obtained as a green solid (21 mg, 0.026 mmol, 96% yield).

Synthesis of 4Ni: To a solution of **4H** (20 mg, 0.027 mmol) in toluene (6 mL) was added (20 mg, 0.09 mmol) $Ni(OAc)_2 \cdot 4H_2O$ and then the mixture was stirred at reflux for 12 h, After cooling down to room temperature, the reaction mixture was passed through a short alumina column. Evaporation of the solvent and recrystallized from methanol, **4Ni** was obtained as a green solid (20 mg, 0.026 mmol, 96% yield).

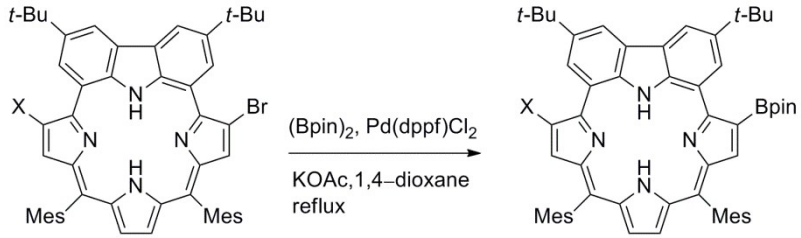


4H

4-2Br, X=Br
4-Br, X=H

Synthesis of 4-Br: A solution of **4H** (200 mg, 0.27 mmol) in $CHCl_3$ (250 mL) was cooled to 0 °C and a solution of NBS (42.7 mg, 0.24 mmol) in $CHCl_3$ (50 mL) was added dropwise. The mixture was washed with water, dried over anhydrous sodium sulfate. Evaporation of the solvent followed by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) and recrystallization with MeOH, **4-Br** was obtained as a green solid (165.6 mg, 0.2 mmol, 75% yield).

Synthesis of 4-2Br: **4H** (200 mg, 0.27 mmol) was dissolved in 250 mL $CHCl_3$ and a solution of NBS (178 mg1.0 mmol) in $CHCl_3$ (50 mL) was added dropwise at room temperature.The mixture was stirred at room temperature for another 3.5 h. The reaction mixture was washed with water, dried over anhydrous sodium sulfate. Evaporation of the solvent and recrystallization with *n*-hexane, **4-2Br** was obtained as green solid (240 mg, 0.27 mmol, 99% yield).



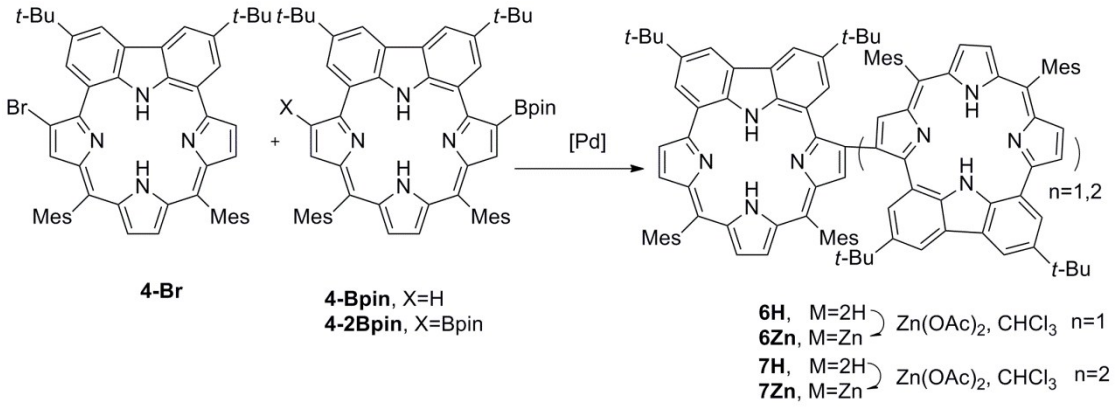
4-2Br, X=Br
4-Br, X=H

4-2Bpin, X=Bpin
4-Bpin, X=H

BPin = —B(O)(O)

Synthesis of 4-Bpin: A Schlenk tube containing **4-Br** (100 mg, 0.123 mmol), $(Bpin)_2$ (91.4 mg, 0.36 mmol), $Pd(dppf)Cl_2$ (4.4 mg, 0.006 mmol) and KOAc (23.5 mg, 0.24 mmol) was purged with argon, and then charged with 1,4-dioxane (5 mL). The resulting mixture was then stirred at reflux for 12 h, the reaction mixture was diluted with $CHCl_3$, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by GPC ($CHCl_3$ as an eluent) and recrystallization with MeOH, **4-Bpin** was obtained as green solid (95.5 mg, 0.111 mmol, 90% yield);

4-2Bpin: A Schlenk tube containing **4-2Br** (100 mg, 0.112 mmol), $(Bpin)_2$ (254 mg, 1.1 mmol), $Pd(dppf)Cl_2$ (7.3 mg, 0.01 mmol) and KOAc (43.2 mg, 0.44 mmol) was purged with argon, and then charged with 1,4-dioxane (5 mL). The resulting mixture was then stirred at reflux for 16 h, the reaction mixture was diluted with $CHCl_3$, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by GPC ($CHCl_3$ as an eluent) and recrystallization with MeOH, **4-2Bpin** was obtained as green solid (93.5 mg, 0.095 mmol, 85% yield).



Synthesis of 6H: A toluene-DMF solution (6 mL/3 mL) of **4-Br** (244.2 mg, 0.3 mmol), **4-Bpin** (258.3 mg, 0.3 mmol), $Pd_2(dba)_3$ (27.5 mg, 0.03 mmol), PPh_3 (31.5 mg, 0.12 mmol), Cs_2CO_3 (293.2mg, 0.9 mmol) and CsF (136.7 mg, 0.9 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 $CHCl_3$, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) and recrystallization with MeOH, **6H** was obtained as green solid (271.6 mg, 0.185 mmol, 62% yield).

Synthesis of 6Zn: To a solution of **6H** (20 mg, 0.0136 mmol) in $CHCl_3$/MeOH (5 mL/1 mL) was added (22 mg, 0.09 mmol) $Zn(OAc)_2 \cdot 2H_2O$ and then the mixture was stirred at room temperature for 5 h, the reaction mixture was passed through a short alumina column, evaporated of the solvent and recrystallized from methanol and dichloromethane. **6Zn** was obtained as agreen solid (20.6 mg, 0.013 mmol, 95% yield).

Synthesis of 7H: A toluene-DMF solution (6 mL/3 mL) of the mixture of **4-Br** (244.2 mg, 0.3 mmol), **4-2Bpin** (148 mg, 0.15 mmol), $Pd_2(dba)_3$ (27.5 mg, 0.03 mmol), PPh_3 (31.5 mg, 0.12 mmol), Cs_2CO_3 (293.2mg, 0.9 mmol) and CsF (136.7 mg, 0.9 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 $CHCl_3$, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) and recrystallization with MeOH, **7H** was obtained as green solid (267.4 mg, 0.12 mmol, 40.6% yield); **Synthesis of 7Zn**: To a solution of **7H** (20 mg, 0.009 mmol) in $CHCl_3$/MeOH (5 mL/1 mL) was added

(22 mg, 0.09 mmol) $Zn(OAc)_2 \cdot 2H_2O$ and then the mixture was stirred at room temperature for 5 h, the reaction mixture was passed through a short alumina column, evaporated of the solvent and recrystallized from methanol and dichloromethane. **6Zn** was obtained as agreen solid (20.4 mg, 0.0085 mmol, 95% yield).

Compound Data.

2: ^{1}H NMR (500 MHz, $CDCl_3$) : δ = 8.08 (d, *J* = 1.5 Hz, 2H, carbazole-H), 7.85 (s, 1H, N-H), 7.46 (dd, 2H, *J* = 8.5, 1.5 Hz, carbazole-H), 7.34 (d, *J* = 8.5 Hz, 2H, carbazole-H), 1.45 (s, 18H, *t*-Bu-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.35, 138.14, 123.65, 123.41, 116.29, 110.17, 34.83, 32.18 ppm.

3: ^{1}H NMR (500 MHz, $CDCl_3$) : δ = 8.13 (s, 1H, N-H), 7.97 (d, *J* = 1.5 Hz, 2H, carbazole-H), 7.64 (d, *J* = 1.5 Hz, 2H, carbazole-H), 1.44 (s, 18H, *t*-Bu-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.88, 136.44, 126.77, 124.94, 116.09, 104.14, 35.06, 32.05 ppm.

4H: ^{1}H NMR (500 MHz, $CDCl_3$) : δ = 9.03 (s, 2H, N-H), 8.79 (d, *J* = 1.0 Hz, 2H, carbazole-H*),* 8.72 (d, J = 1.0 Hz, 2H, carbazole-H), 8.03 (d, J = 4.5 Hz, 2H, pyrrole-β-H), 7.32 (d, *J* = 4.5 Hz, 2H, pyrrole-*β*-H), 7.05 (s, 4H, Ar-*m*-H), 6.67 (s, 2H, pyrrole-*β*-H), 2.45 (s, 6H, Me-H), 2.10 (s, 12H, Me-H), 1.68 (s, 18H, *t*-Bu-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.51, 152.48, 142.42, 137.8, 137.79, 136.17, 135.97, 135.78, 132.18, 128.03, 125.13, 124.63, 124.42, 122.27, 119.79, 114.58, 35.36, 32.52, 21.39, 20.57 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [M^{-1} cm^{-1}]) = 328 (33700), 386 (50400), 579 (19100), 629 (24200) nm; IR (KBr disk): ν = 3373, 2957, 2914, 2862, 1602, 1567, 1484, 1382, 1332, 1256, 1179, 932, 800 cm^{-1}; MALDI-TOF-MS (positive mode): m/z = 732.4056 $[M]^+$, calcd for $(C_{52}H_{52}N_4)^+$ = 732.4186.

4Pd: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.51 (s, 2H, carbazole-H), 9.34 (s, 2H, carbazole-H), 8.97 (d, *J* = 3.5 Hz, 2H, pyrrole-*β*-H), 8.10 (d, *J* = 3.5 Hz, 2H, pyrrole-*β*-H), 7.65 (s, 2H, pyrrole-*β*-H), 7.17 (s, 4H, Ar-*m*-H), 2.55 (s, 6H, Me-H), 2.01 (s, 12H, Me-H), 1.87 (s, 18H, *t*-Bu-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.06, 142.52, 140.17, 138.31, 138.29, 137.83, 137.24, 136.97, 133.24, 131.34, 128.06, 127.99, 126.53, 123.28, 122.07, 120.79, 112.58, 35.79, 32.69, 21.51, 20.98 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [M^{-1} cm^{-1}]) = 361 (22700), 427 (46200), 629 (14000), 660 (19200), 692 (37800) nm; IR (KBr disk): ν = 2956, 2911, 2860, 1607, 1549, 1462, 1356, 1322, 1234, 1196, 1005, 835, 790 cm^{-1}; MALDI-TOF-MS (positive mode): m/z = 832.2734 $[M]^+$, calcd for $(C_{52}H_{50}N_4Pd)^+$ = 832.3086.

4Zn: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.28 (s, 2H, carbazole-H), 9.21 (s, 2H, carbazole-H), 8.68 (d, *J* = 4.5 Hz, 2H, pyrrole-*β*-H), 7.87 (d, *J* = 4.5 Hz, 2H, pyrrole-*β*-H), 7.37 (s, 2H, pyrrole-*β*-H), 7.14 (s, 4H, Ar-*m*-H), 2.53 (s, 6H, Me-H), 2.07 (s, 12H, Me-H), 1.83 (s, 18H, *t*-Bu-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ =

162.16, 148.19, 147.22, 145.97, 141.21, 138.00, 137.52, 134.03, 133.03, 127.91, 127.29, 123.77, 122.85, 120.28, 112.86, 35.59, 32.74, 21.46, 20.86 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [M^{-1} cm^{-1}]) = 350 (26600), 410 (36200), 433 (38400), 633 (16800), 698 (36000) nm; IR (KBr disk): ν = 2955, 2918, 2860, 1593, 1543, 1477, 1342, 1308, 1259, 1236, 1080, 991, 959, 835, 790 cm^{-1}; MALDI-TOF-MS (positive mode): m/z = 794.3319 $[M]^+$, calcd for $(C_{52}H_{50}N_4Zn)^+$ = 794.3321.

4Ni: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.14 (s, 2H, carbazole-H), 9.04 (s, 2H, carbazole-H), 8.71 (d, *J* = 4.0 Hz, 2H, pyrrole-*β*-H), 7.96 (d, *J* = 4.0 Hz, 2H, pyrrole-*β*-H), 7.45 (s, 2H, pyrrole-*β*-H), 7.11 (s, 4H, Ar-*m*-H), 2.50 (s, 6H, Me-H), 1.99 (s, 12H, Me-H), 1.78 (s, 18H, *t*-Bu-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.53, 142.60, 139.81, 139.31, 138.05, 137.75, 136.30, 134.01, 129.49, 127.95, 127.91, 127.50, 122.63, 121.85, 119.88, 111.71, 35.53, 32.55, 21.45, 20.76 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [M^{-1} cm^{-1}]) = 356 (17500), 390 (18400), 439 (39700), 706 (20900) nm; IR (KBr disk): ν = 2956, 2914, 2858, 1626, 1574, 1474, 1357, 1224, 1192, 995, 836, 793 cm^{-1}; MALDI-TOF-MS (positive mode): m/z = 788.3121 $[M]^+$, calcd for $(C_{52}H_{50}N_4Ni)^+$ = 788.3383.

4-Br: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.91 (d, *J* = 1.5 Hz, 1H, carbazole-H), 8.87 (s, 1H, N-H), 8.81 (d, 1H, *J* = 1.5 Hz, carbazole-H), 8.80 (d, *J* = 1.5 Hz, 1H, carbazole-H), 8.76 (s, 1H, N-H), 8.72 (d, *J* = 1.5 Hz, 1H, carbazole-H), 8.05 (d, *J* = 4.5 Hz, 1H, pyrrole-*β*-H), 7.42 (s, 1H, pyrrole-*β*-H), 7.32 (d, *J* = 4.5 Hz, 1H, pyrrole-*β*-H), 7.05 (s, 4H, Ar-*m*-H), 6.73-6.71 (m, 1H, pyrrole-*β*-H), 6.68-6.66 (m, 1H, pyrrole-*β*-H), 2.45 (s, 6H, Me-H), 2.09 (s, 6H, Me-H), 2.08 (s, 6H, Me-H), 1.69 (s, 9H, *t*-Bu-H), 1.68 (s, 9H, *t*-Bu-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.97, 159.74, 153.28, 148.26, 142.56, 142.23, 139.06, 138.82, 138.01, 137.88, 137.78, 137.67, 136.84, 136.26, 135.94, 135.78, 135.45, 133.45, 131.58, 128.12, 125.84, 125.78, 124.97, 124.70, 124.42, 123.85, 122.06, 120.02, 119.77, 114.50, 35.73, 35.34, 32.57, 32.48, 21.38, 20.59, 20.53 ppm.

4-2Br: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.87 (s, 2H, carbazole-H), 8.80 (s, 2H, carbazole-H), 8.62 (s, 1H, N-H), 8.51 (s, 1H, N-H), 7.41 (s, 2H, pyrrole-*β*-H), 7.04 (s, 4H, Ar-*m*-H), 6.70 (s, 2H, pyrrole-*β*-H), 2.45 (s, 6H, Me-H), 2.07 (s, 12H, Me-H), 1.69 (s, 18H, *t*-Bu-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.37, 149.02, 142.35, 138.79, 138.18, 138.08, 137.64, 135.95, 135.39, 132.92, 128.20, 126.03, 124.76, 123.51, 120.00, 115.32, 114.37, 35.71, 32.53, 21.38, 20.54 ppm.

4-Bpin: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.55 (d, *J* = 1.5 Hz, 1H, carbazole-H), 9.07 (s, 1H, N-H), 9.05 (s, 1H, N-H), 8.77 (d, *J* = 1.5 Hz, 1H, carbazole-H), 8.74 (d, *J* = 1.5 Hz, 1H, carbazole-H), 8.67 (d, *J* = 1.5 Hz, 1H, carbazole-H), 8.01 (d, *J* = 4.5 Hz, 1H, pyrrole-*β*-H), 7.42 (s, 1H, pyrrole-*β*-H), 7.28 (d, *J* = 4.5 Hz, 1H, pyrrole-*β*-H), 7.04 (s, 4H, Ar-*m*-H), 6.62-6.61 (m, 1H, pyrrole-*β*-H), 6.59-6.57 (m, 1H, pyrrole-*β*-H),

2.46 (s, 3H, Me-H), 2.44 (s, 3H, Me-H), 2.09 (s, 6H, Me-H), 2.07 (s, 6H, Me-H), 1.71 (s, 9H, *t*-Bu-H), 1.67 (s, 9H, *t*-Bu-H). 1.44 (s, 12H, BPin-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.59, 167.80, 152.90, 151.27, 150.89, 142.28, 142.11, 138.44, 137.80, 137.72, 137.53, 136.50, 136.34, 135.71, 135.61, 135.51, 132.77, 131.66, 128.23, 128.07, 128.04, 125.51, 125.09, 124.28, 123.93, 123.16, 121.91, 119.64, 118.86, 116.62, 114.57, 84.10, 35.72, 35.29, 32.64, 32.49, 25.05, 21.42, 21.38, 20.64, 20.58 ppm.

4-2Bpin: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.41 (d, *J* = 1.5 Hz, 2H, carbazole-H), 9.07 (s, 1H, N-H), 9.04 (s, 1H, N-H), 8.72 (d, *J* = 1.5 Hz, 2H, carbazole-H), 7.87 (s, 2H, pyrrole-*β*-H), 7.02 (s, 4H, Ar-*m*-H), 6.53 (s, 2H, pyrrole-*β*-H), 2.44 (s, 6H, Me-H), 2.06 (s, 12H, Me-H), 1.69 (s, 18H, *t*-Bu-H). 1.42(s, 24H, BPin-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.05, 151.73, 150.51, 141.90, 138.23, 137.81, 137.56, 136.13, 135.96, 132.36, 128.09, 124.43, 122.76, 118.83, 116.60, 84.07, 35.64, 32.62, 25.04, 21.41, 20.65 ppm.

6H: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.09 (s, 2H, N-H), 9.00 (s, 2H, N-H), 8.68 (s, 2H, carbazole-H), 8.61 (s, 4H, carbazole-H), 8.33 (s, 2H, carbazole-H), 8.04 (d, *J* = 4.5 Hz, 2H, pyrrole-*β*-H), 7.35-7.32 (m, 4H, pyrrole-*β*-H), 7.09-7.05 (m, 6H, Ar-*m*-H), 6.96 (s, 2H, Ar-*m*-H), 6.69 (s, 2H, pyrrole-*β*-H), 6.65 (s, 2H, pyrrole-*β*-H), 2.47 (s, 6H, Me-H), 2.38 (s, 6H, Me-H), 2.20 (s, 6H, Me-H), 2.17 (s, 6H, Me-H), 2.14 (s, 6H, Me-H), 2.12 (s, 6H, Me-H), 1.62 (s, 18H, *t*-Bu-H), 0.67 (s, 18H, *t*-Bu-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.56, 165.91, 152.73, 150.45, 142.14, 141.87, 139.35, 138.24, 137.87, 137.83, 137.75, 137.73, 137.68, 137.62, 136.28, 136.12, 135.79, 135.71, 135.59, 132.44, 131.88, 128.07, 126.63, 125.31, 124.79, 124.23, 123.90, 122.64, 122.10, 119.57, 118.87, 115.24, 114.48, 35.25, 34.55, 32.45, 31.44, 21.42, 21.35, 20.82, 20.64 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [M^{-1} cm^{-1}]) = 329 (82200), 393 (121300), 597 (48800), 654 (70600) nm; IR (KBr disk): ν = 3381, 2957, 2911, 2858, 1600, 1566, 1483, 1383, 1333, 1255, 1176, 930, 828 cm^{-1}; MALDI-TOF-MS (positive mode): *m/z* = 1462.8171 $[M]^+$, calcd for $(C_{104}H_{102}N_8)^+$ =1462.8222.

6Zn: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.51 (d, *J* = 1.0 Hz, 2H, carbazole-H), 9.26 (d, *J* = 1.0 Hz, 2H, carbazole-H), 9.06 (d, *J* = 1.0 Hz, 2H, carbazole-H), 8.80 (d, *J* = 1.0 Hz, 2H, carbazole-H), 8.72 (d, *J* = 4.5 Hz, 2H, pyrrole-*β*-H), 7.92 (d, *J* = 4.5 Hz, 2H, pyrrole-*β*-H), 7.90 (s, 2H, pyrrole-*β*-H), 7.42 (d, *J* = 4.5 Hz, 2H, pyrrole-*β*-H), 7.37 (d, *J* = 4.5 Hz, 2H, pyrrole-*β*-H), 7.17 (2H, Ar-*m*-H), 7.15 (2H, Ar-*m*-H), 7.07 (s, 2H, Ar-*m*-H), 6.95 (s, 2H, Ar-*m*-H), 2.55 (s, 6H, Me-H), 2.36 (s, 6H, Me-H), 2.18 (s, 6H, Me-H), 2.13 (s, 6H, Me-H), 2.08-2.07 (m, 12H, Me-H), 1.77 (s, 18H, *t*-Bu-H), 0.49 (s, 18H, *t*-Bu-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.28, 160.07, 148.50, 148.48, 147.46, 146.03, 145.60, 141.19, 140.67, 138.14, 138.06, 137.99, 137.87, 137.65, 137.56, 137.49, 137.38, 135.65, 134.04, 132.98, 132.77, 128.16, 127.95, 127.83, 127.48, 127.42, 127.33, 126.73, 123.51, 123.01, 120.02, 119.50, 113.84, 112.80, 35.53, 34.60, 32.69, 31.45, 21.50, 21.32, 21.19, 21.15, 21.04, 20.94 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [M^{-1} cm^{-1}]) = 354 (68000), 415 (89500),

438 (101700), 656 (43000), 728 (113600) nm; IR (KBr disk): ν = 2954, 2914, 2861, 1589, 1536, 1445, 1339, 1287, 1260, 1232, 1204, 992, 951, 834, 792, 727 cm^{-1}; MALDI-TOF-MS (positive mode): *m/z* = 1586.6171 $[M]^+$, calcd for $(C_{104}H_{98}N_8Zn_2)^+$ = 1586.6492.

7H: ^1H NMR (500 MHz, $CDCl_3$): δ = 9.12-9.09 (m, , 2H, N-H), 9.06-8.94 (m, 4H, N-H), 8.80 (d, *J* = 1.5 Hz, 1H, carbazole-H), 8.75 (d, *J* = 1.5 Hz, 1H, carbazole-H), 8.70 (d, *J* = 1.0 Hz, 1H, carbazole-H), 8.68 (d, *J* = 1.0 Hz, 1H, carbazole-H), 8.67 (d, *J* = 1.0 Hz, 2H, carbazole-H), 8.66 (d, *J* = 1.0 Hz, 1H, carbazole-H),, 8.63 (d, *J* = 1.0 Hz, 1H, carbazole-H), 8.43 (d, *J* = 1.5 Hz, 1H, carbazole-H), 8.35 (d, *J* = 1.5 Hz, 1H, carbazole-H), 8.25 (d, *J* = 1.5 Hz, 1H, carbazole-H), 8.20 (d, *J* = 1.5 Hz, 1H, carbazole-H), 8.07-8.05 (m, 2H, pyrrole-*β*-H), 7.37-7.33 (m, 6H, pyrrole-*β*-H), 7.09-7.06 (m, 8H, Ar-*m*-H), 7.01-6.96 (m, 4H, Ar-*m*-H), 6.72-6.71 (m, 4H, pyrrole-*β*-H), 6.68-6.66 (s, 2H, pyrrole-*β*-H), 2.47 (s, 6H, Me-H), 2.43(s, 3H, Me-H), 2.40 (s, 6H, Me-H), 2.39 (s, 3H, Me-H), 2.29 (s, 3H, Me-H), 2.25 (s, 3H, Me-H), 2.21 (s, 12H, Me-H), 2.18 (s, 3H, Me-H), 2.17 (s, 6H, Me-H), 2.14 (s, 9H, Me-H),1.64 (s, 9H, *t*-Bu-H), 1.62 (s, 9H, *t*-Bu-H), 0.81 (s, 9H, *t*-Bu-H), 0.68 (s, 9H, *t*-Bu-H), 0.65 (s, 9H, *t*-Bu-H), 0.64 (s, 9H, *t*-Bu-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.58, 165.96, 165.92, 165.88, 165.74, 152.74, 150.70, 150.65, 150.48, 142.20, 142.13, 141.97, 141.94, 141.82, 141.70, 139.73, 139.68, 139.59, 139.57, 138.36, 138.28, 138.24, 137.92, 137.89, 137.83, 137.78, 137.73, 137.65, 136.37, 136.30, 136.23, 136.19, 136.16, 136.03, 135.88, 135.82, 135.79, 135.75, 135.67, 135.59, 132.46, 132.38, 132.08, 131.94, 131.92, 131.88, 128.08, 127.02, 126.82, 126.67, 126.54, 125.31, 124.87, 124.83, 124.29, 124.26, 124.21, 123.97, 123.91, 122.64, 122.61, 122.52, 122.11, 119.57, 118.86, 118.72, 115.38, 115.26, 115.23, 114.54, 114.50, 35.27, 35.25, 34.70, 34.58, 34.50, 34.47, 32.46, 32.45, 31.61, 31.42, 31.39, 21.41, 21.38, 21.35, 20.99, 20.90, 20.87, 20.82, 20.63 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [M^{-1} cm^{-1}]) = 332 (111800), 397 (161000), 607 (64000), 671 (82700) nm; IR (KBr disk): ν = 3379, 2956, 2923, 2858, 1602, 1567, 1383, 1332, 1259, 1194, 1129, 1048, 929, 827 cm^{-1}; MALDI-TOF-MS (positive mode): *m/z* = 2193.1797 $[M]^+$, calcd for $(C_{156}H_{152}N_{12})^+$ = 2193.2257.

7Zn: ^1H NMR (500 MHz, $CDCl_3$): δ = 9.52 (d, *J* = 1.0 Hz, 1H, carbazole-H), 9.51 (d, *J* = 1.0 Hz, 1H, carbazole-H), 9.48 (d, *J* = 1.0 Hz, 1H, carbazole-H), 9.41 (d, *J* = 1.0 Hz, 1H, carbazole-H), 9.26 (s, 2H, carbazole-H), 9.06 (s, 2H, carbazole-H), 8.80 (s, 2H, carbazole-H), 8.72 (d, *J* = 4.5 Hz, 2H, pyrrole-*β*-H), 8.67 (s, 1H, carbazole-H), 8.64 (s, 1H, carbazole-H), 8.02 (s, 1H, pyrrole-*β*-H), 7.99 (s, 2H, pyrrole-*β*-H), 7.97 (s, 1H, pyrrole-*β*-H), 7.92 (dd, *J* = 4.5, 1.5 Hz, 2H, pyrrole-*β*-H), 7.46 (s, 2H, pyrrole-*β*-H), 7.44-7.43 (m, 2H, pyrrole-*β*-H), 7.41-7.39 (m, 2H, pyrrole-*β*-H), 7.18 (s, 2H, Ar-*m*-H), 7.16 (s, 2H, Ar-*m*-H), 7.13-7.11 (m, 4H, Ar-*m*-H), 7.00 (s, 2H, Ar-*m*-H), 6.98 (s, 2H, Ar-*m*-H), 2.54 (s, 6H, Me-H), 2.41-2.39 (m, 12H, Me-H), 2.28 (s, 3H, Me-H), 2.21 (s, 3H), 2.17-2.16 (m, 15H, Me-H), 2.12 (s, 3H, Me-H), 2.10-2.09 (m, 12H, Me-H), 1.76 (s, 18H, *t*-Bu-H), 0.50 (s, 18H, *t*-Bu-H), 0.43 (s, 9H, *t*-Bu-H), 0.42 (s, 9H, *t*-Bu-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.38, 160.27, 160.20, 160.10, 148.95, 148.91, 148.59, 147.53, 146.05,

145.93, 145.69, 141.34, 140.87, 140.71, 138.16, 138.11, 138.04, 137.93, 137.68, 137.61, 137.47, 135.73, 134.11, 133.04, 132.76, 132.68, 132.56, 128.21, 127.98, 127.92, 127.71, 127.60, 127.51, 127.38, 126.79, 126.45, 123.53, 123.06, 120.08,119.51, 119.34, 113.88, 112.79, 35.54, 34.64, 34.61, 34.55, 34.51, 21.50, 21.36, 21.21, 20.95 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [M^{-1} cm^{-1}]) = 358 (89200), 441 (134400), 676 (56400), 715 (65600), 747 (140500) nm; IR (KBr disk): ν = 2954, 2911, 2859, 1590, 1536, 1446, 1384, 1339, 1261, 1232, 1201, 993, 948, 833 cm^{-1}; MALDI-TOF-MS (positive mode): *m/z* = 2378.9586 $[M]^+$, calcd for $(C_{156}H_{146}N_{12}Zn_3)^+$ = 2378.9662.

Spectra of Compounds

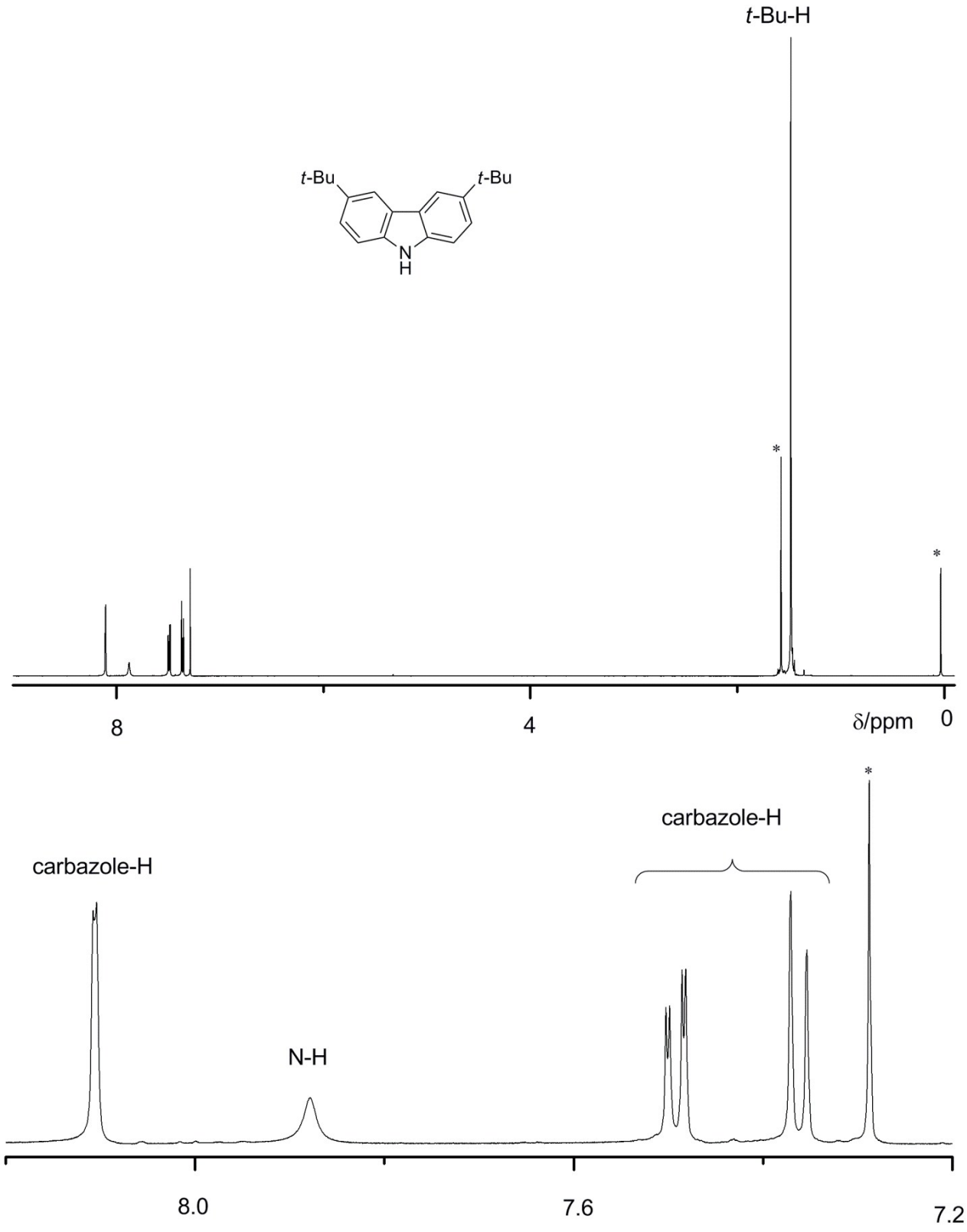


Figure S1. ^{1}H NMR spectrum of **2** in $CDCl_3$.

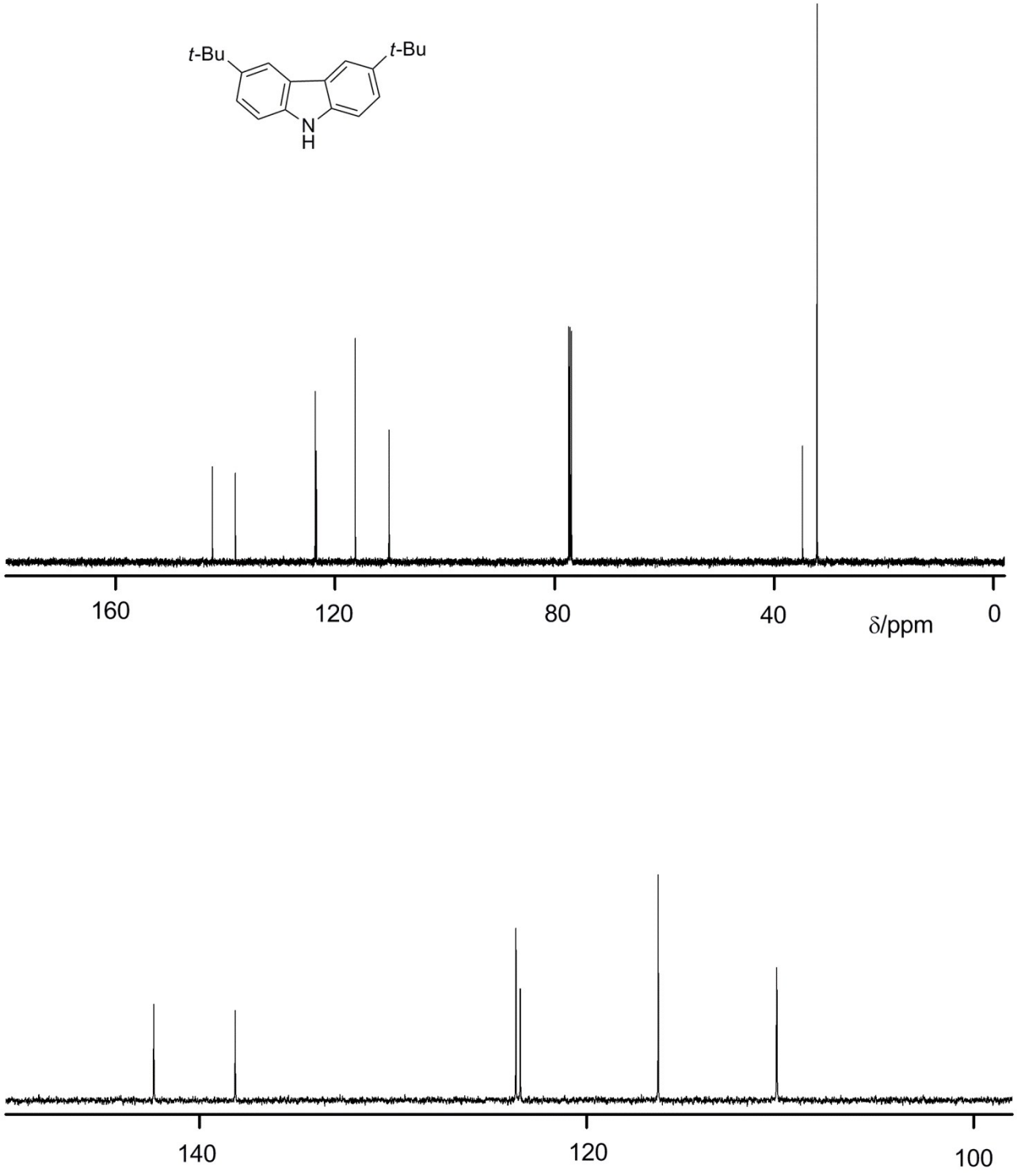


Figure S2 . ^{13}C NMR spectrum of **2** in $CDCl_3$.

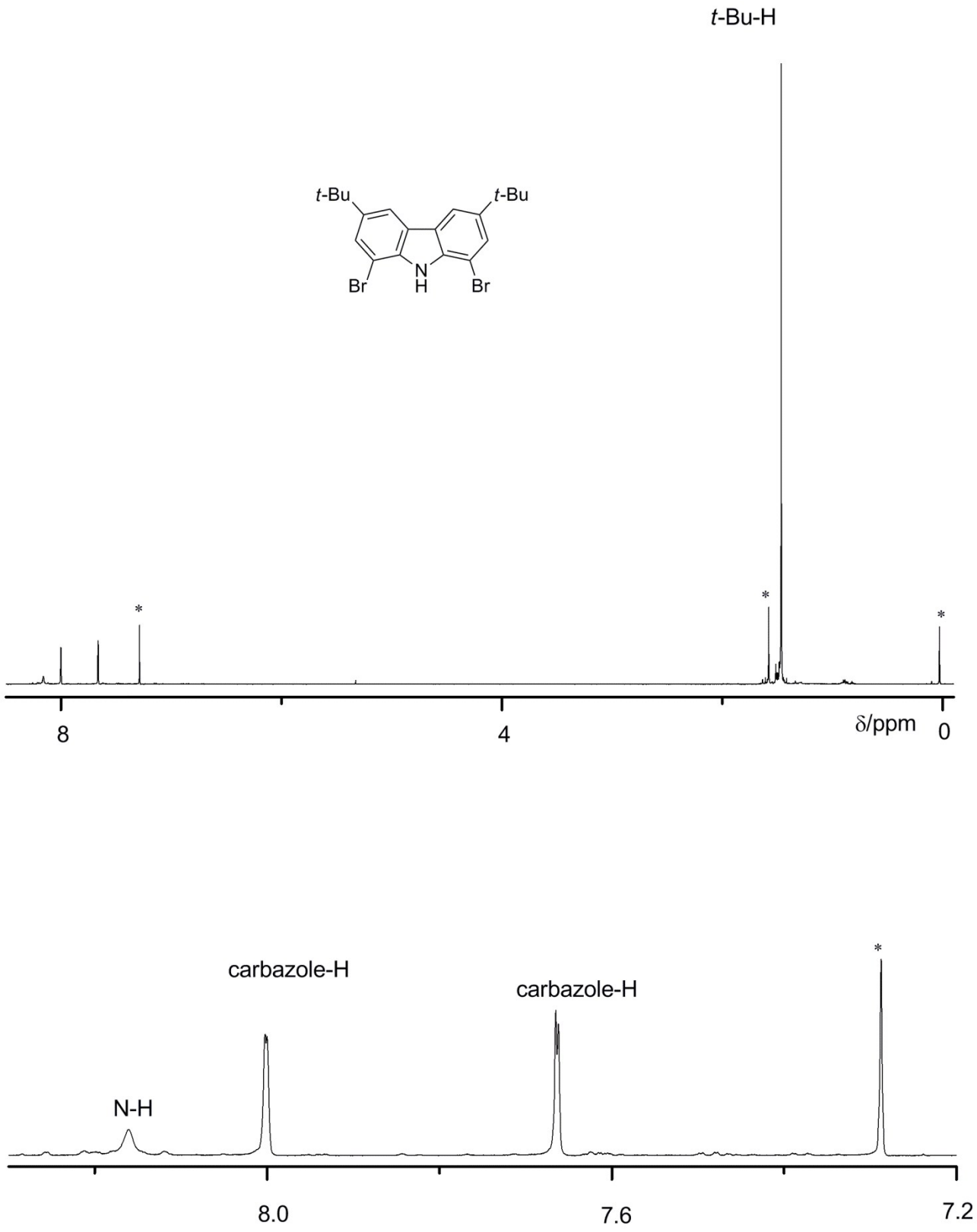


Figure S3. ^{1}H NMR spectrum of **3** in $CDCl_3$.

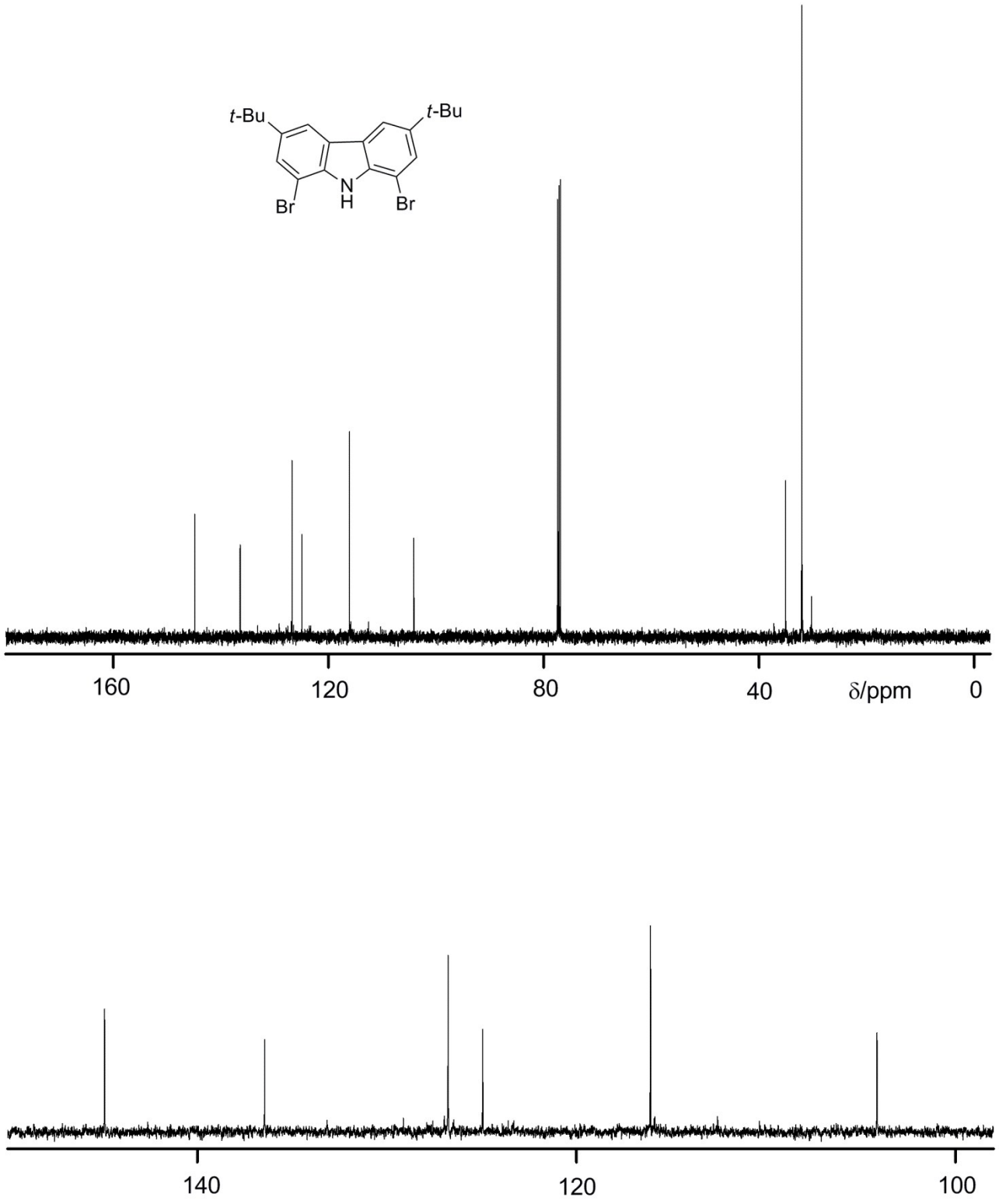


Figure S4. ^{13}C NMR spectrum of **3** in $CDCl_3$.

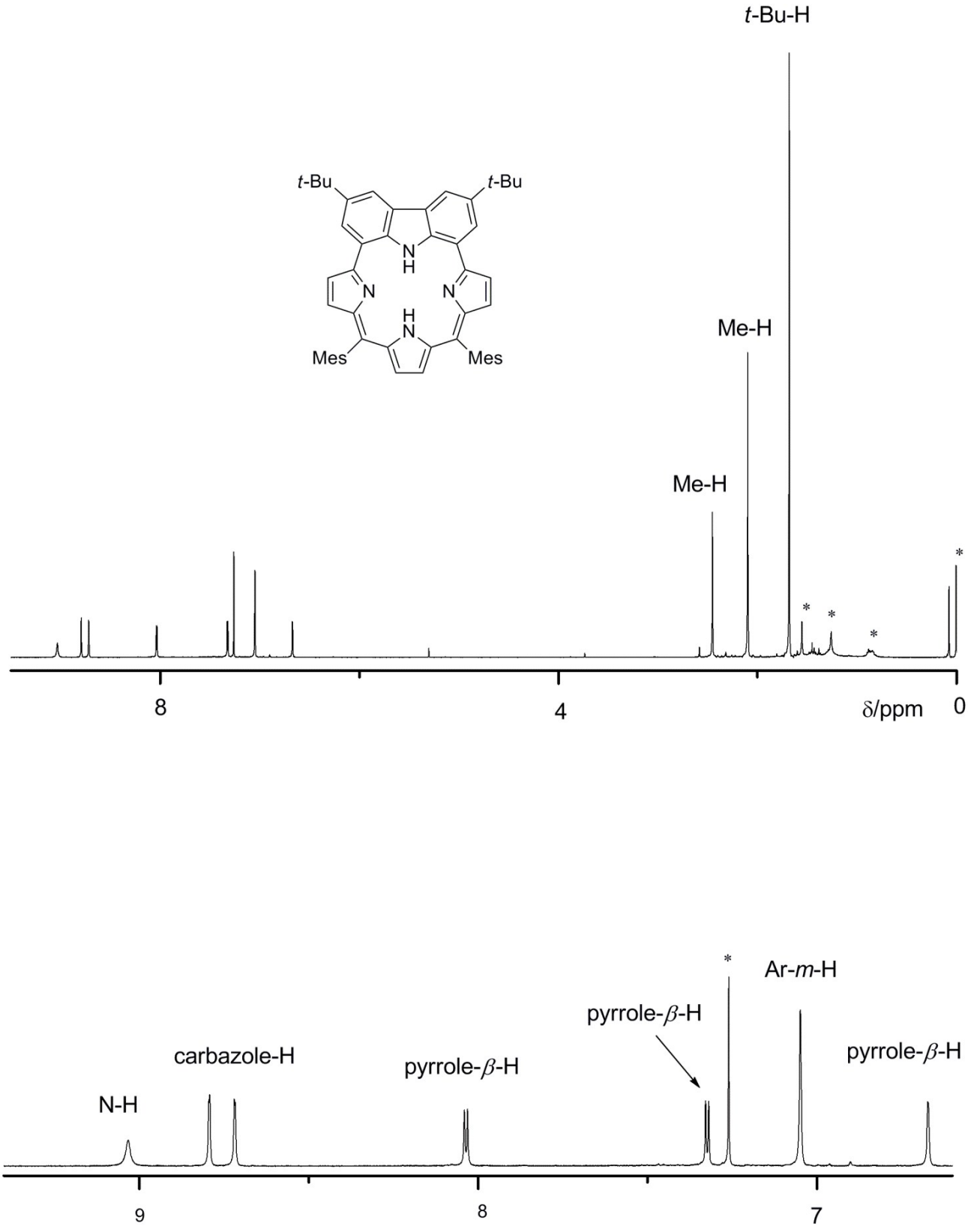


Figure S5. ^{1}H NMR spectrum of **4H** in $CDCl_3$.

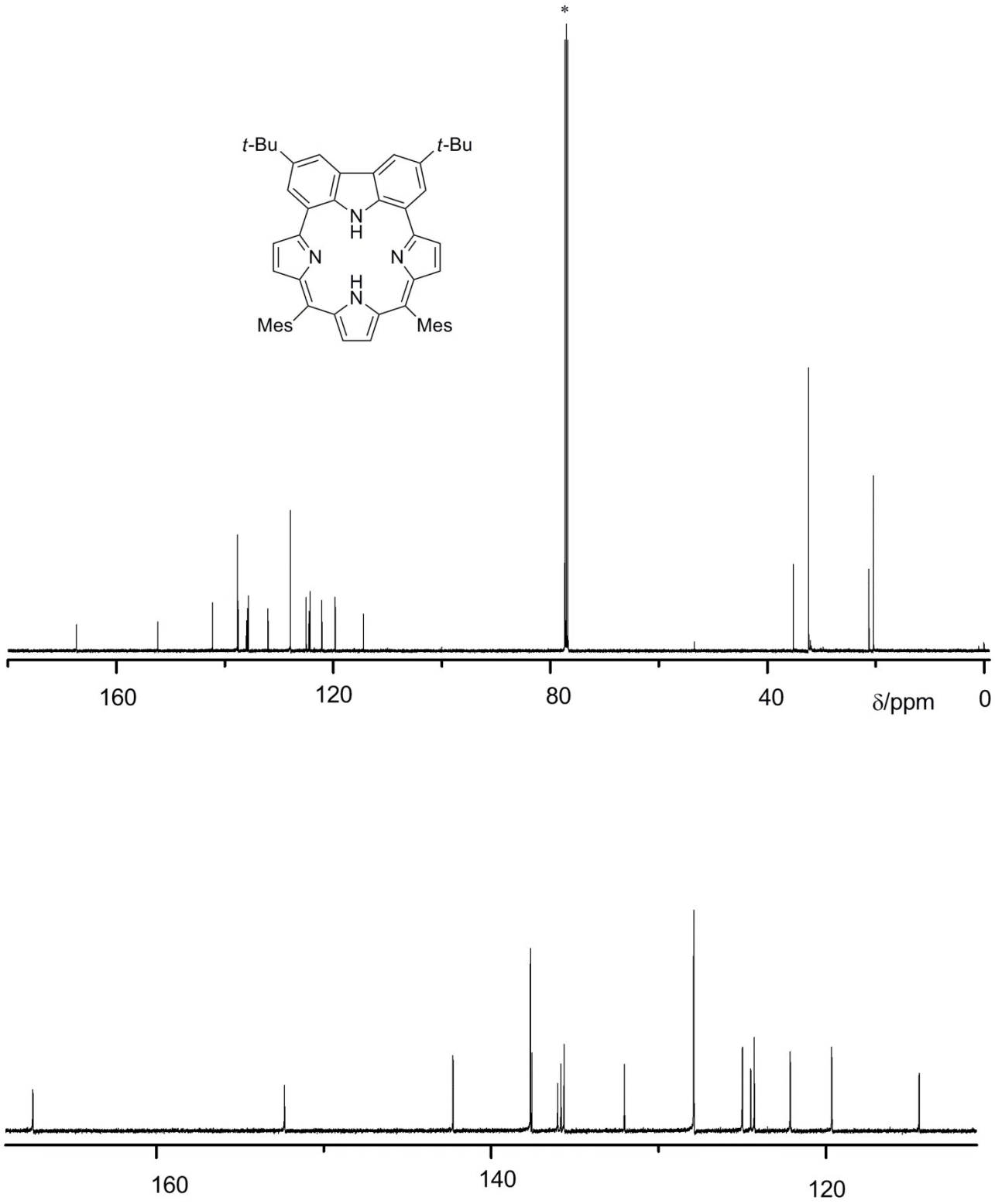


Figure S6. ^{13}C NMR spectrum of **4H** in $CDCl_3$.

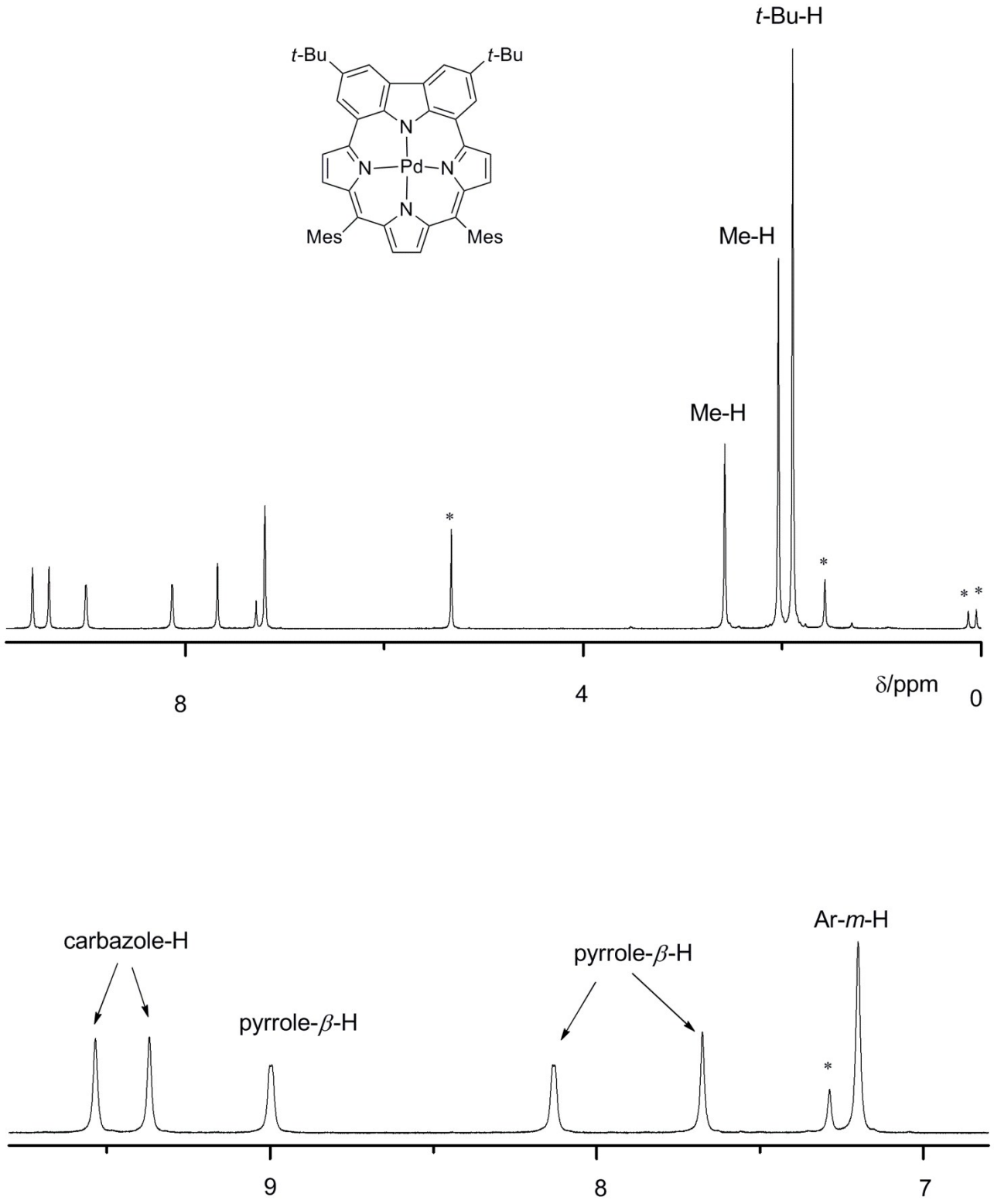


Figure S7. ^{1}H NMR spectrum of **4Pd** in $CDCl_3$.

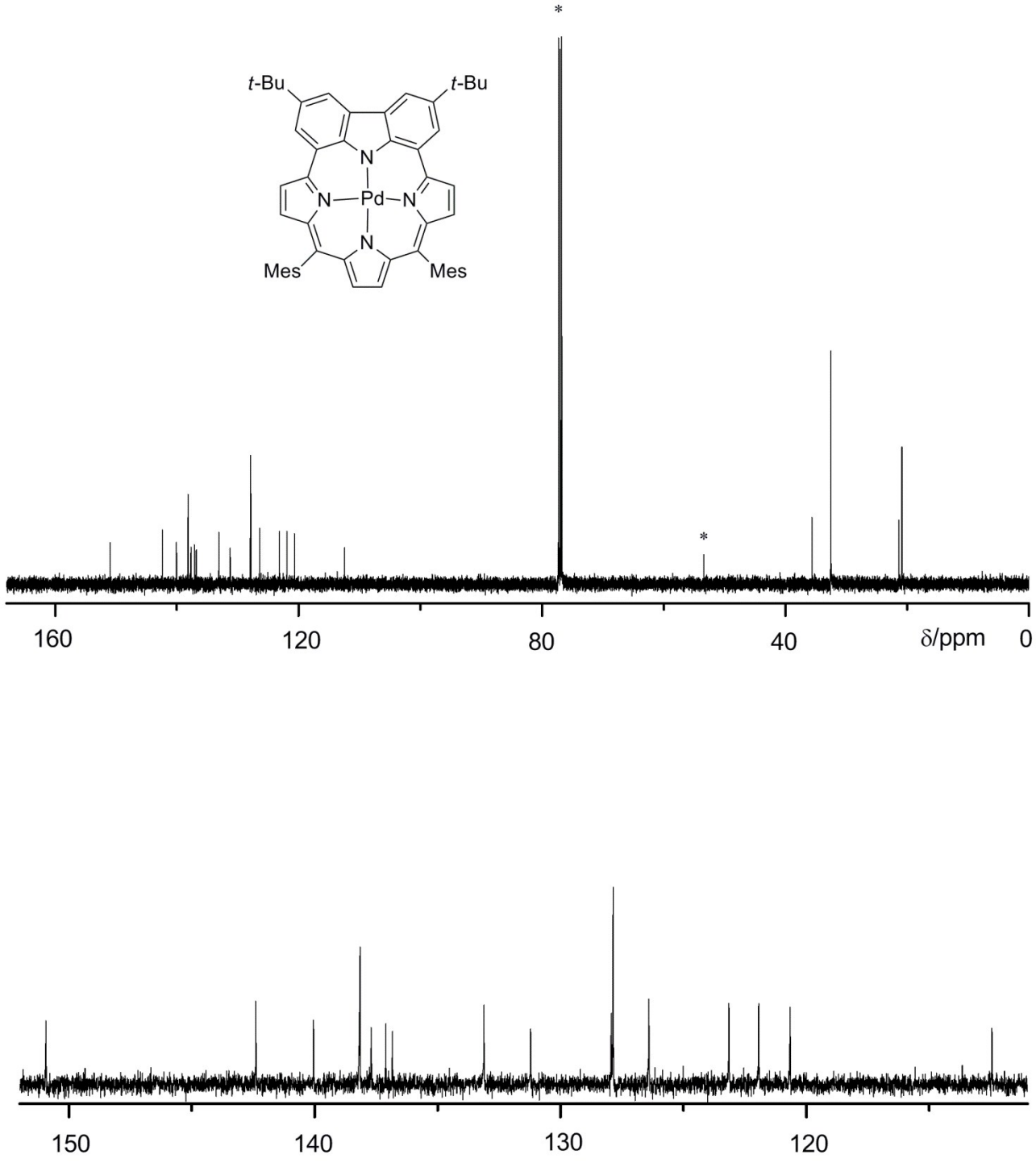


Figure S8. ^{13}C NMR spectrum of **4Pd** in $CDCl_3$.

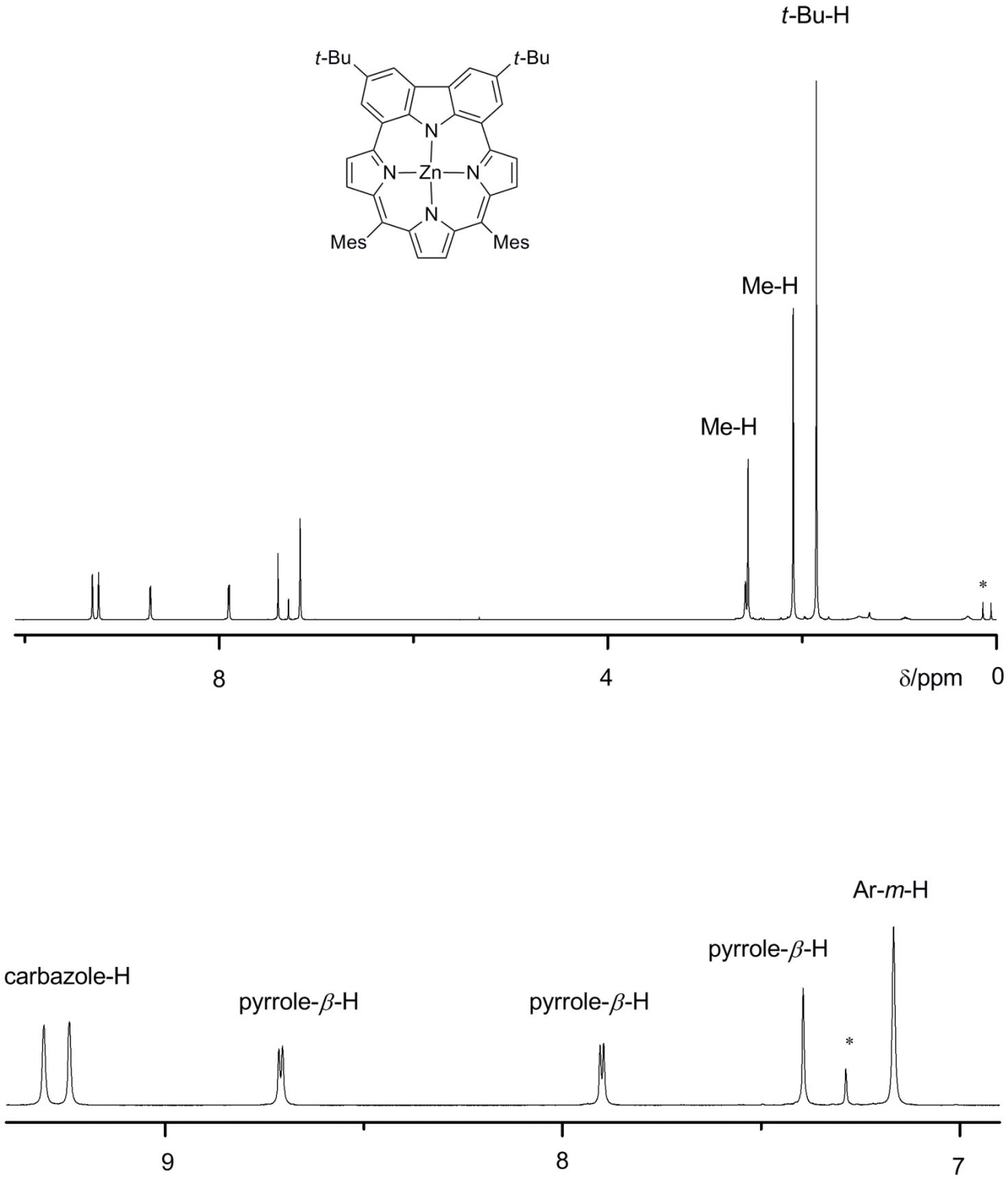


Figure S9. ^{1}H NMR spectrum of **4Zn** in $CDCl_3$.

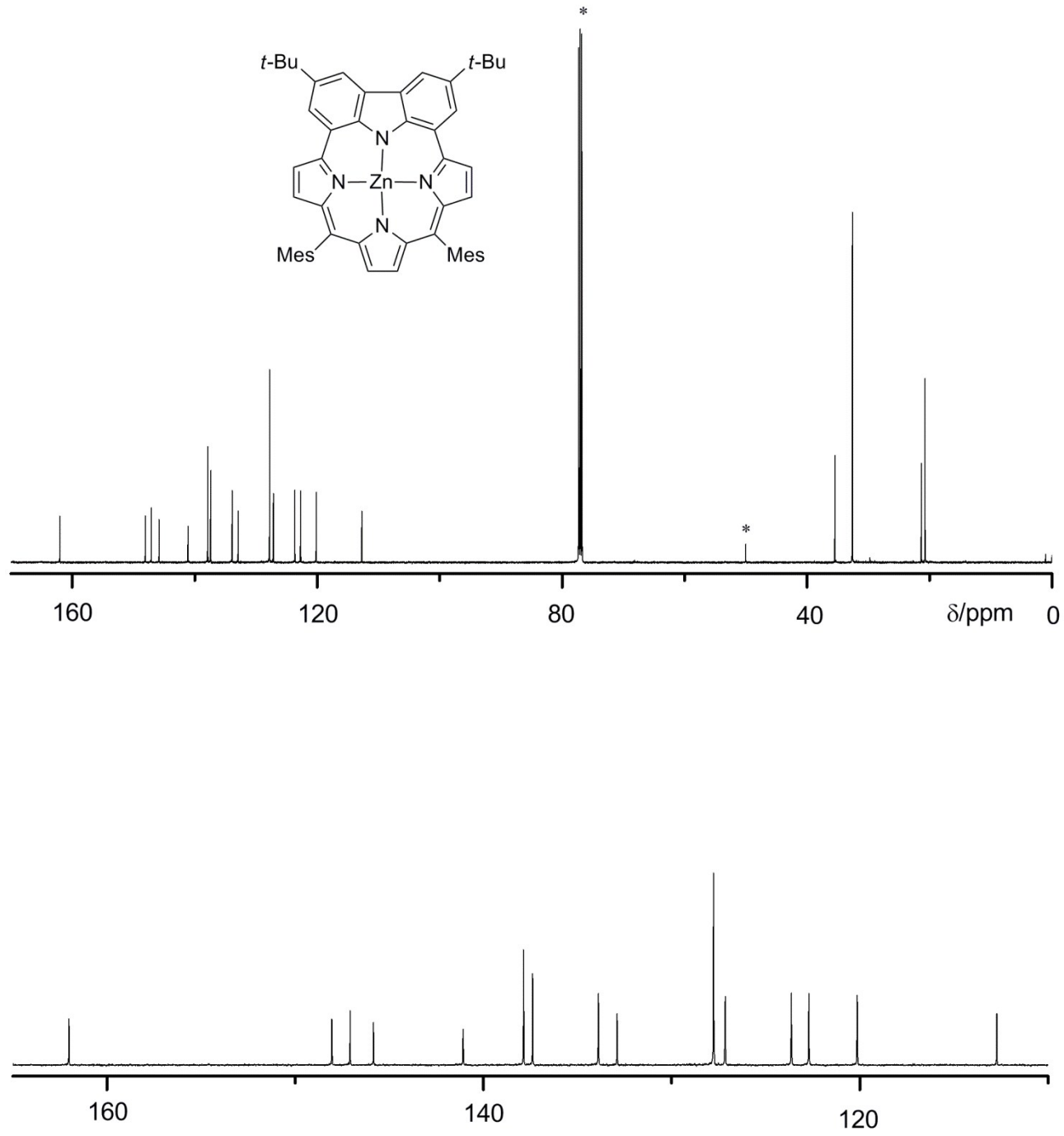


Figure S10. ^{13}C NMR spectrum of **4Zn** in $CDCl_3$.

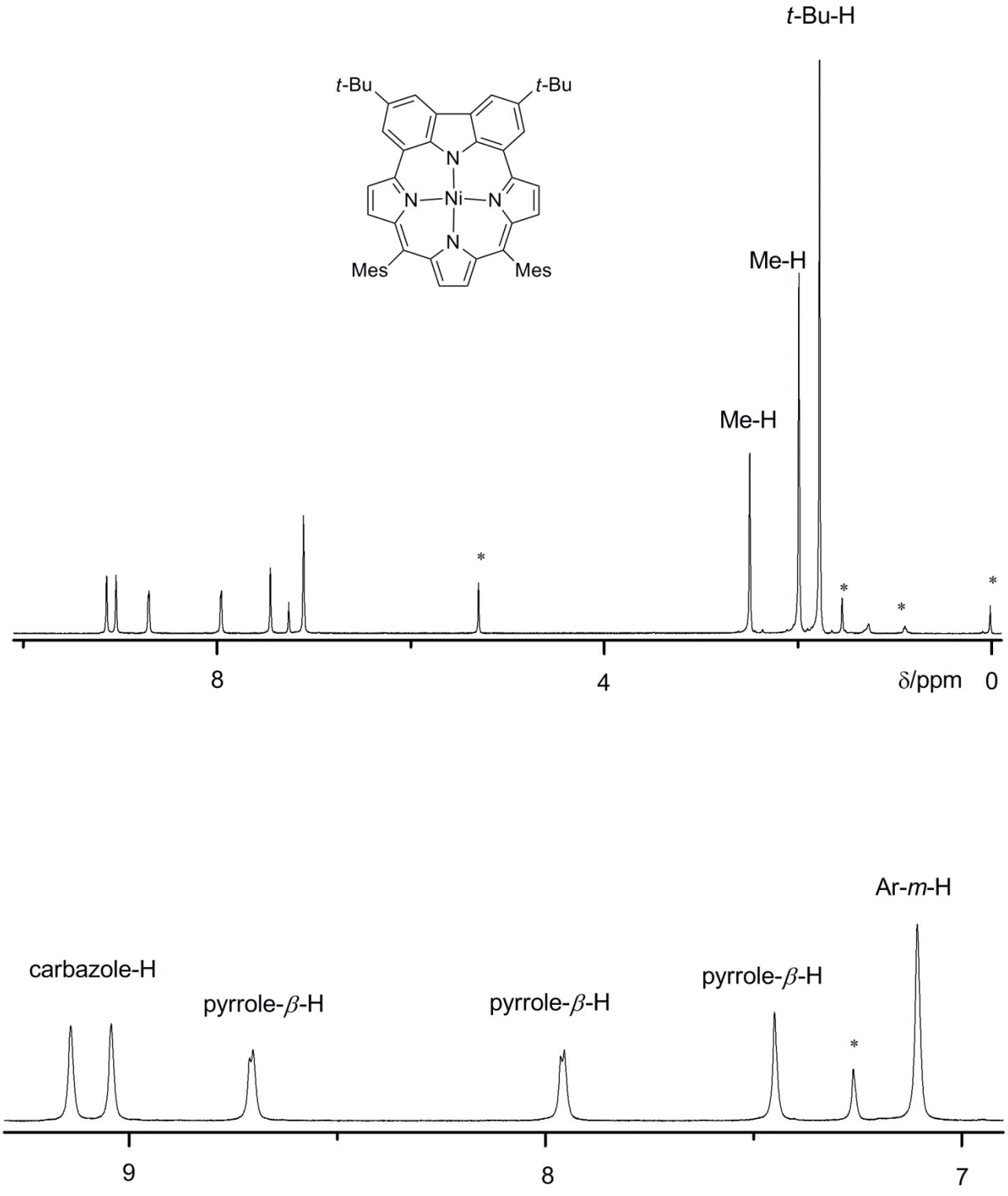


Figure S11. ^{1}H NMR spectrum of 4**Ni** in $CDCl_3$.

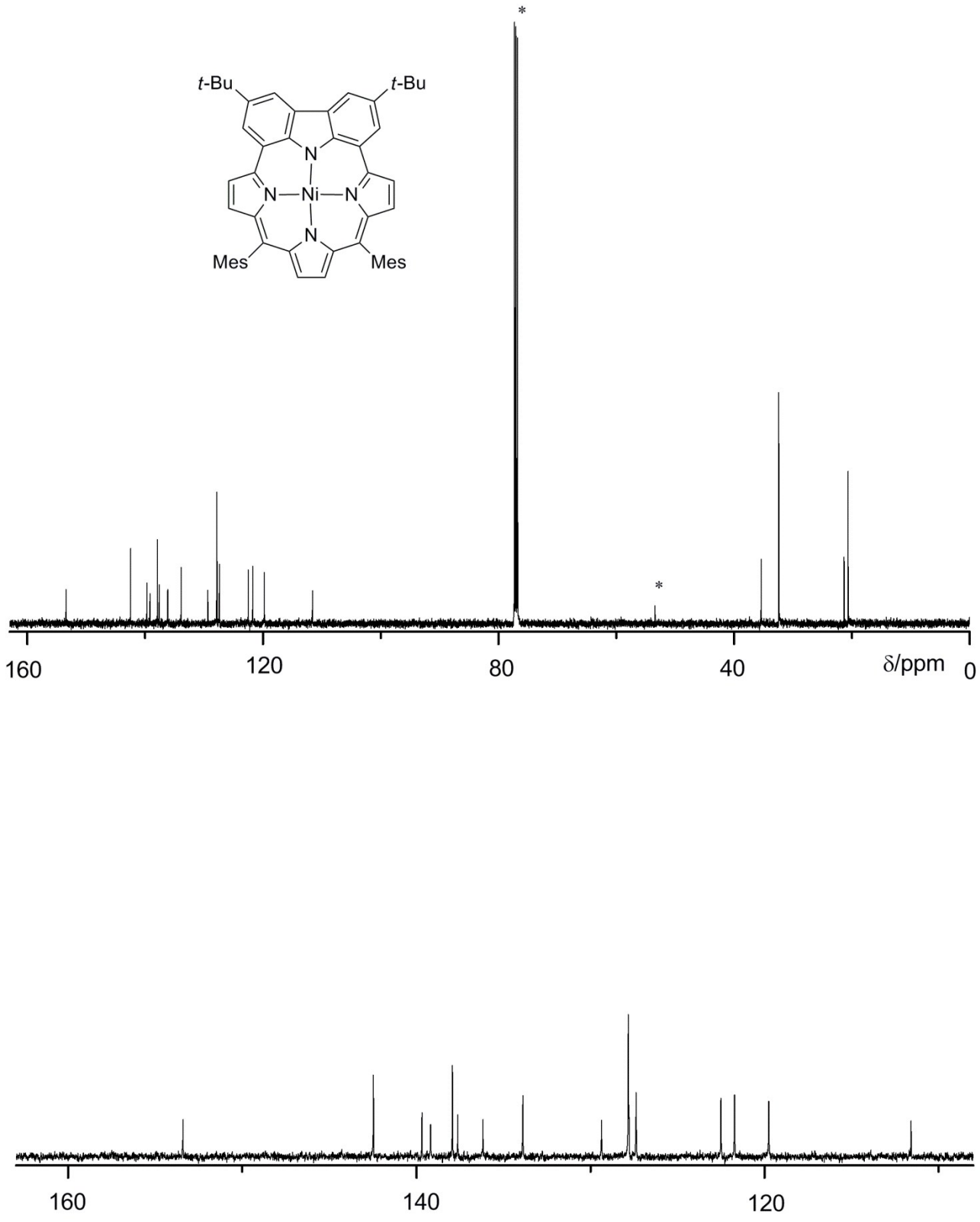


Figure S12. ^{13}C NMR spectrum of **4Ni** in $CDCl_3$.

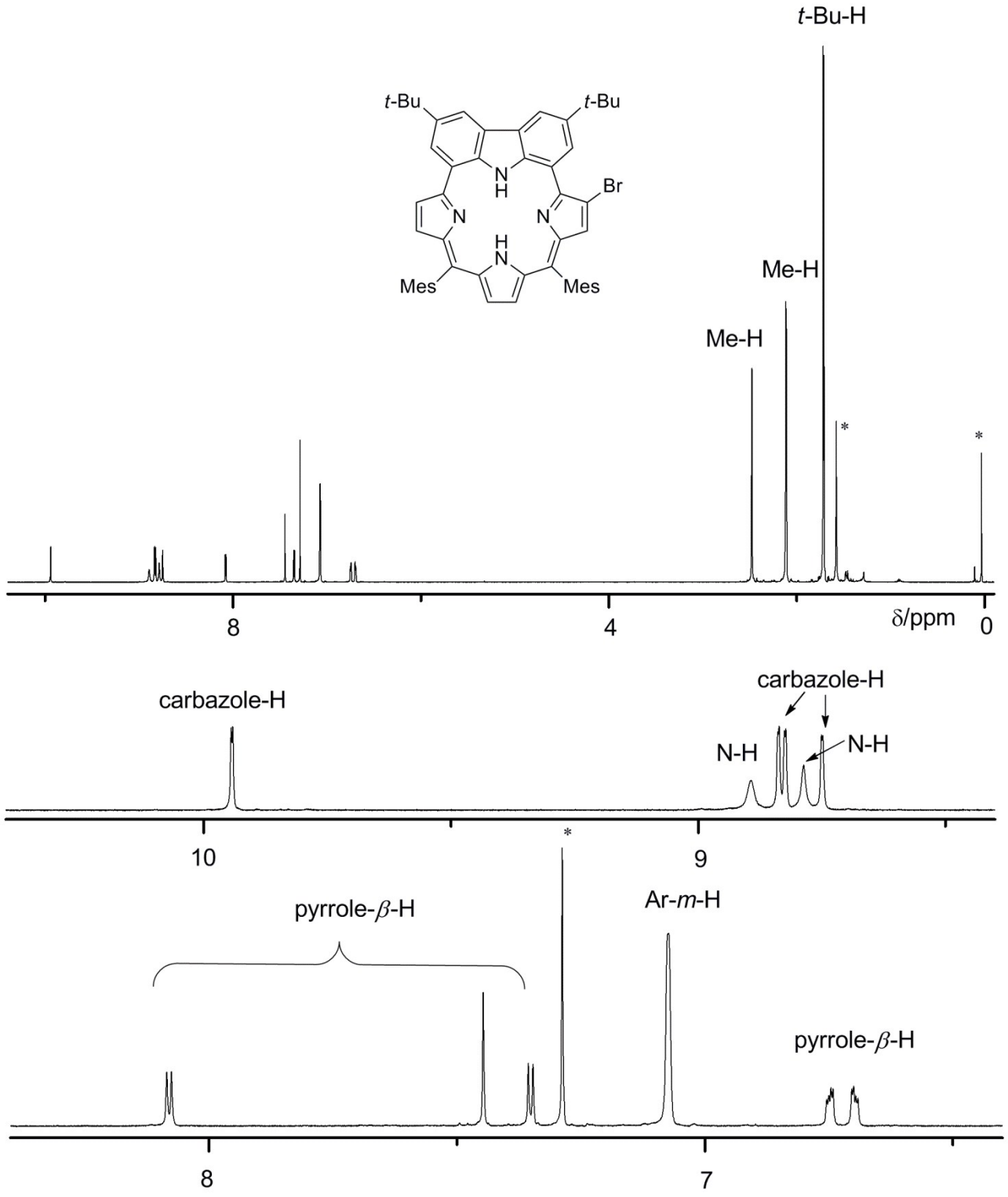


Figure S13. ^{1}H NMR spectrum of **4-Br** in $CDCl_3$.

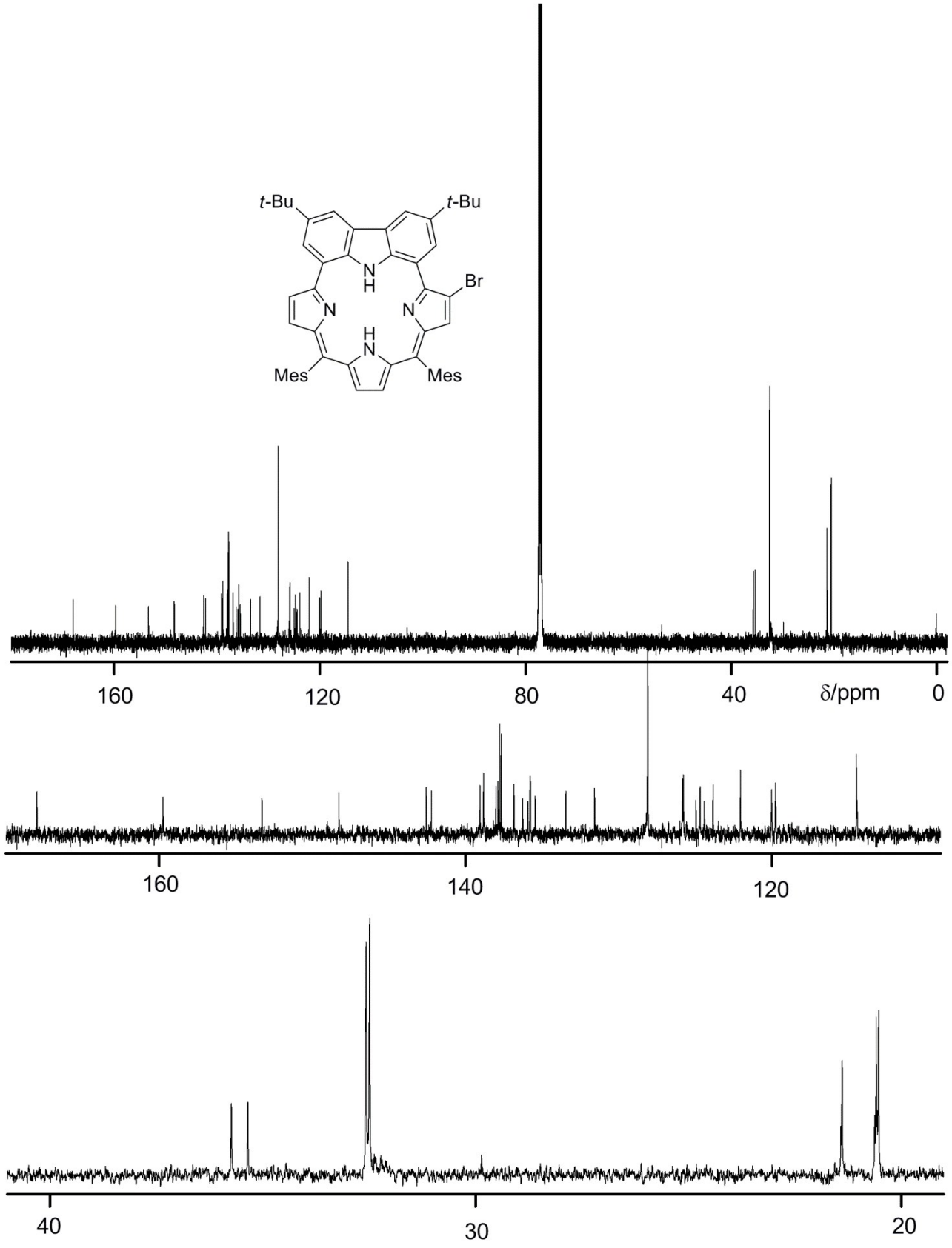


Figure S14. ^{13}C NMR spectrum of **4-Br** in $CDCl_3$.

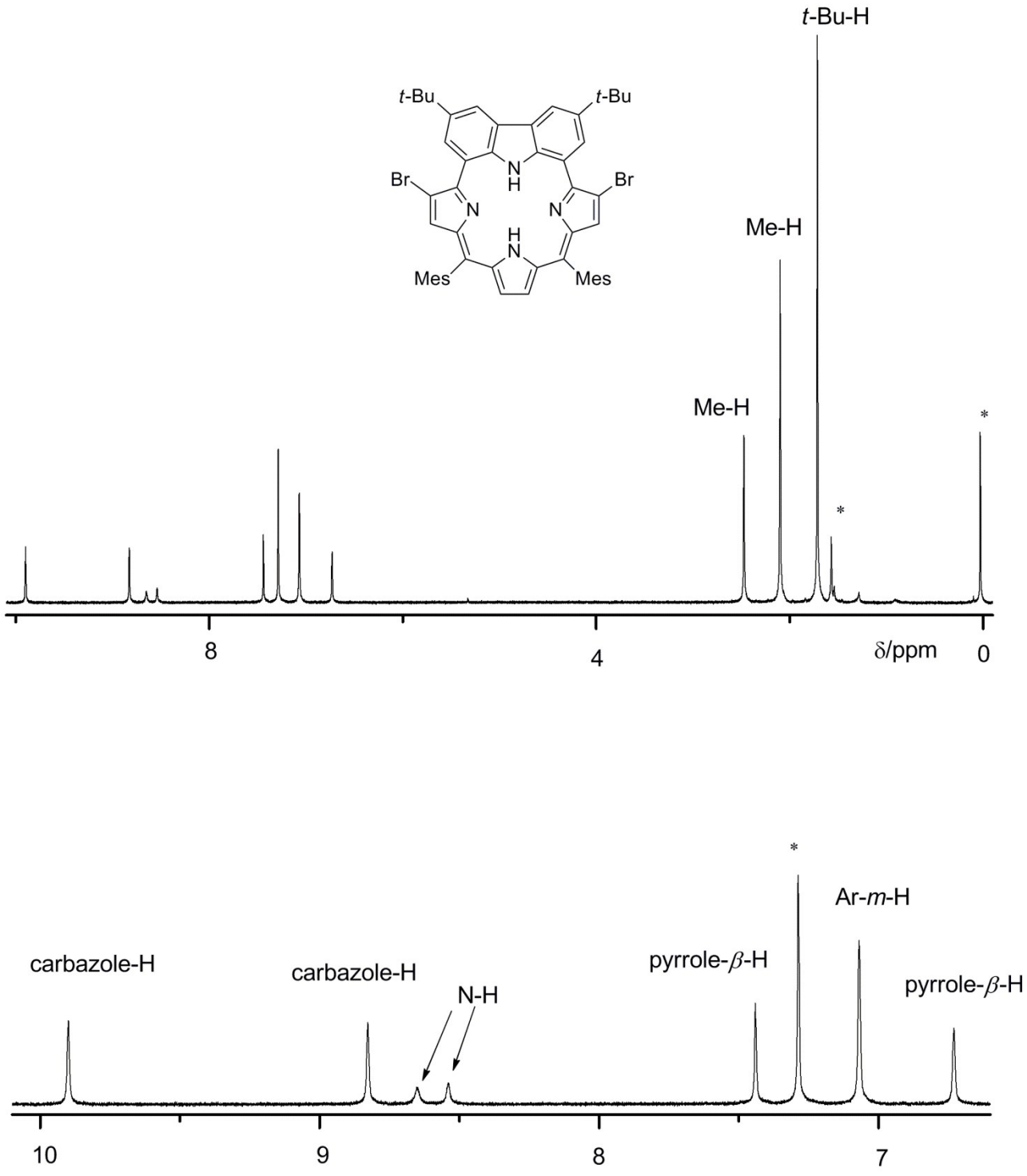


Figure S15. ^{1}H NMR spectrum of **4-2Br** in $CDCl_3$.

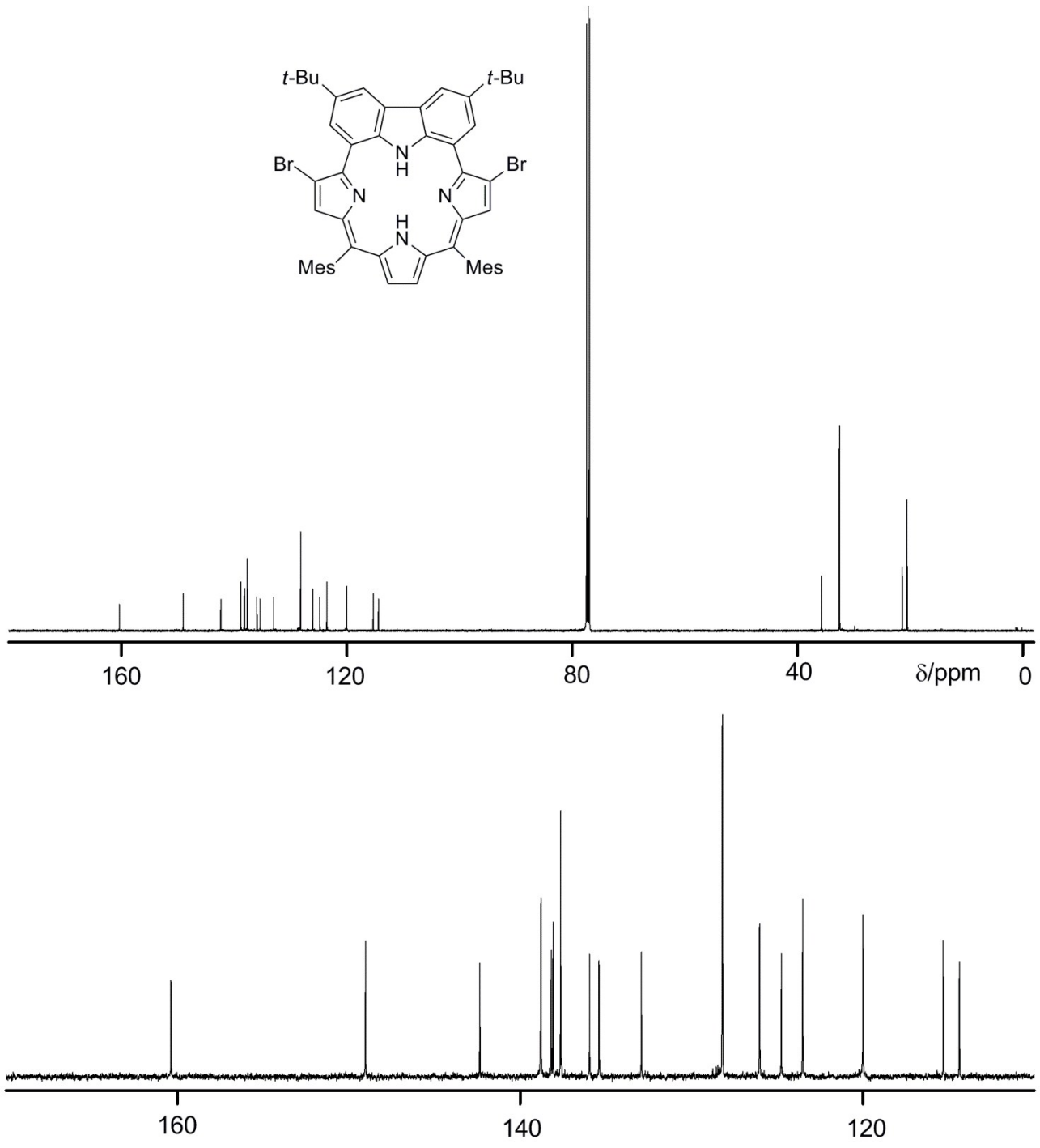


Figure S16. ^{13}C NMR spectrum of **4-2Br** in $CDCl_3$.

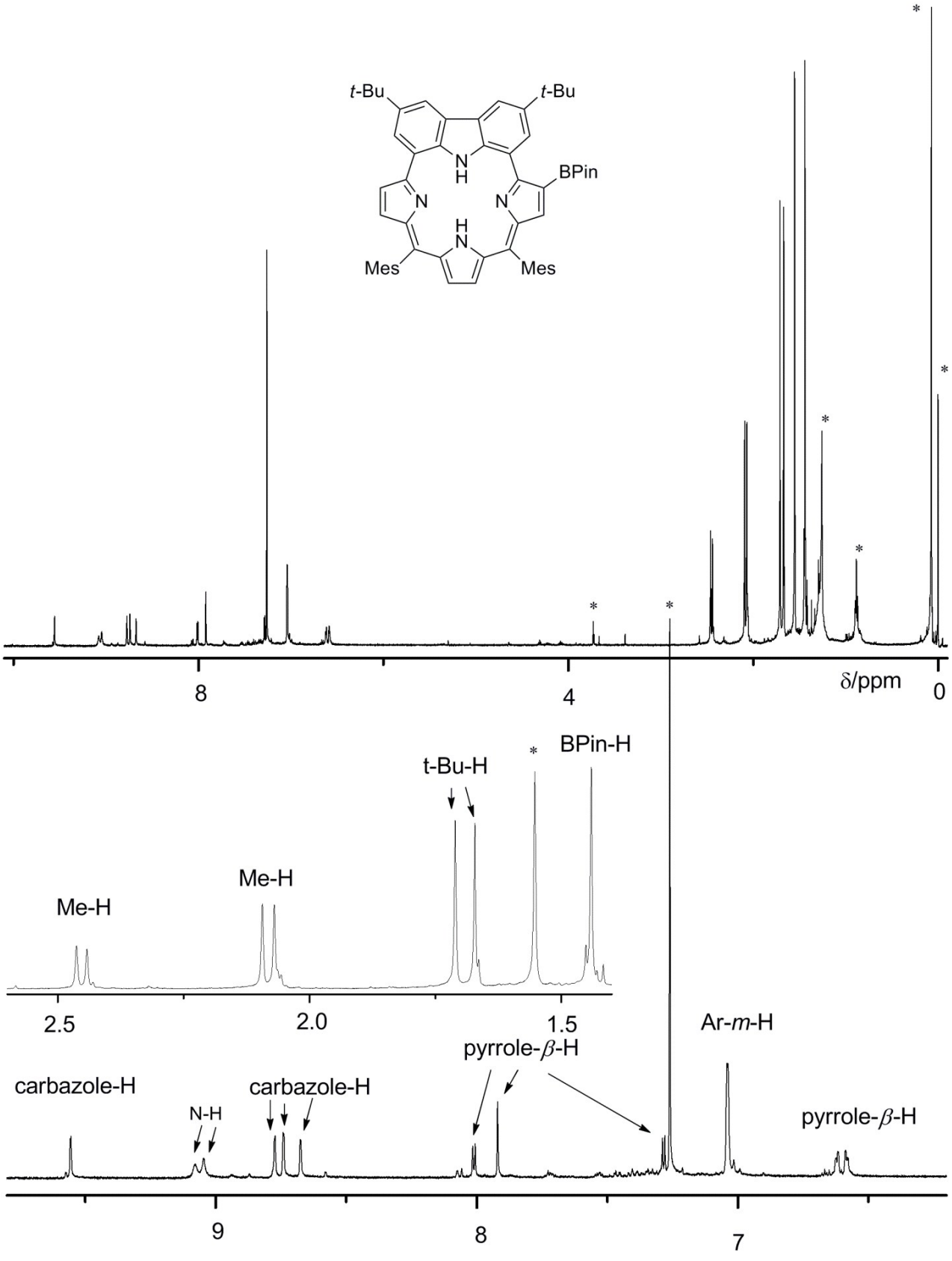


Figure S17. ^{1}H NMR spectrum of **4-Bpin** in $CDCl_3$.

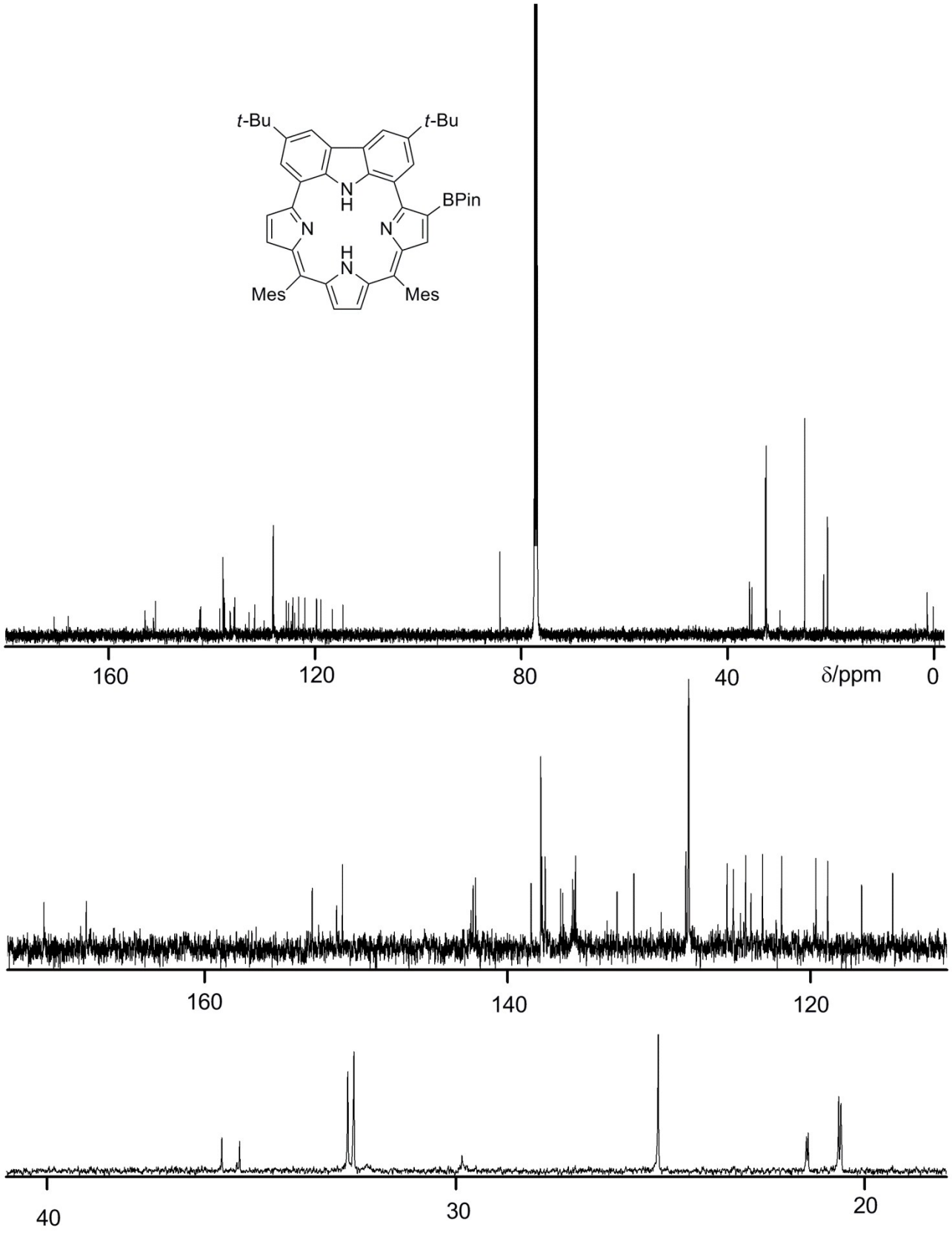


Figure S18. ^{13}C NMR spectrum of **4-Bpin** in $CDCl_3$.

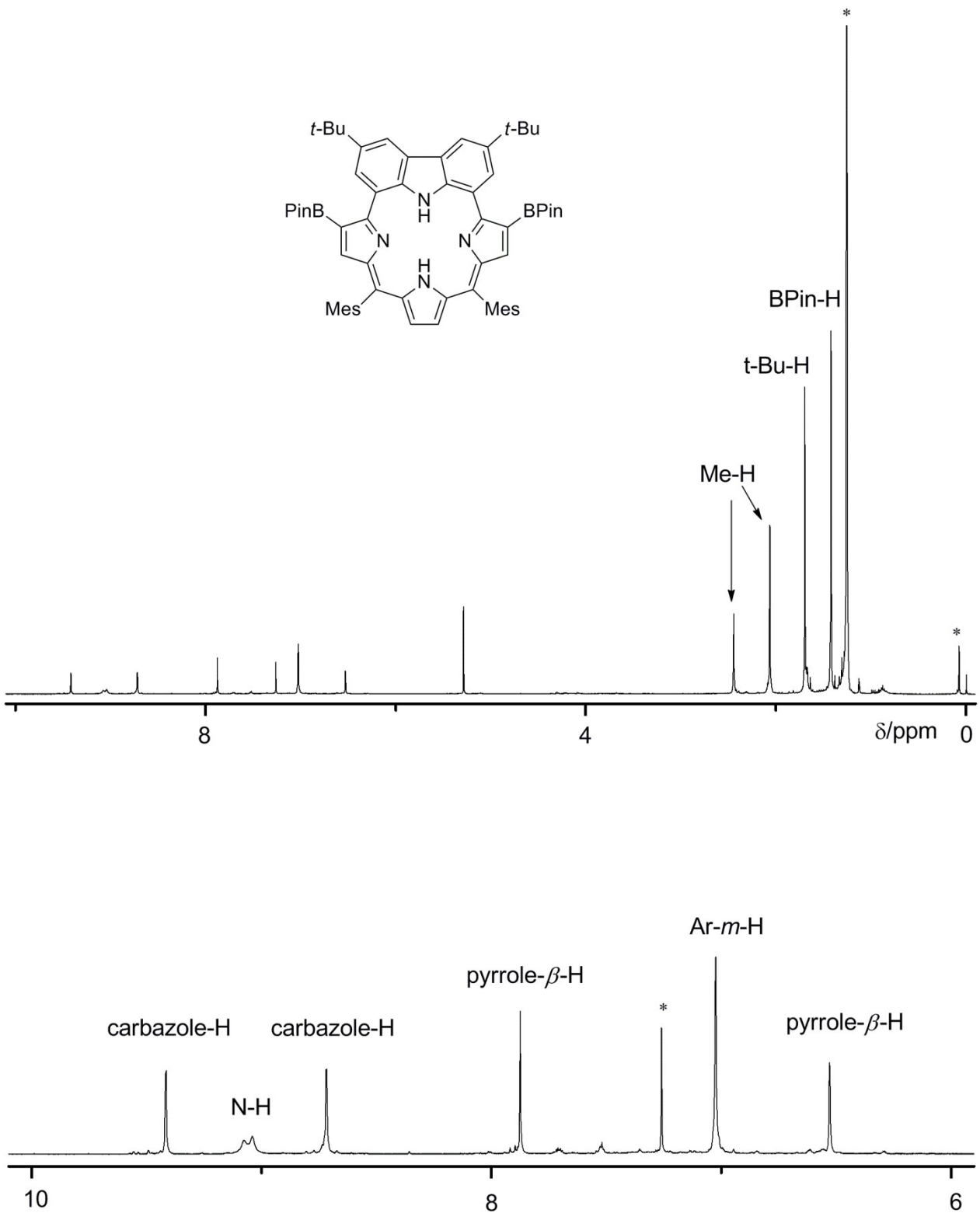


Figure S19. ^{1}H NMR spectrum of **4-2Bpin** in $CDCl_3$.

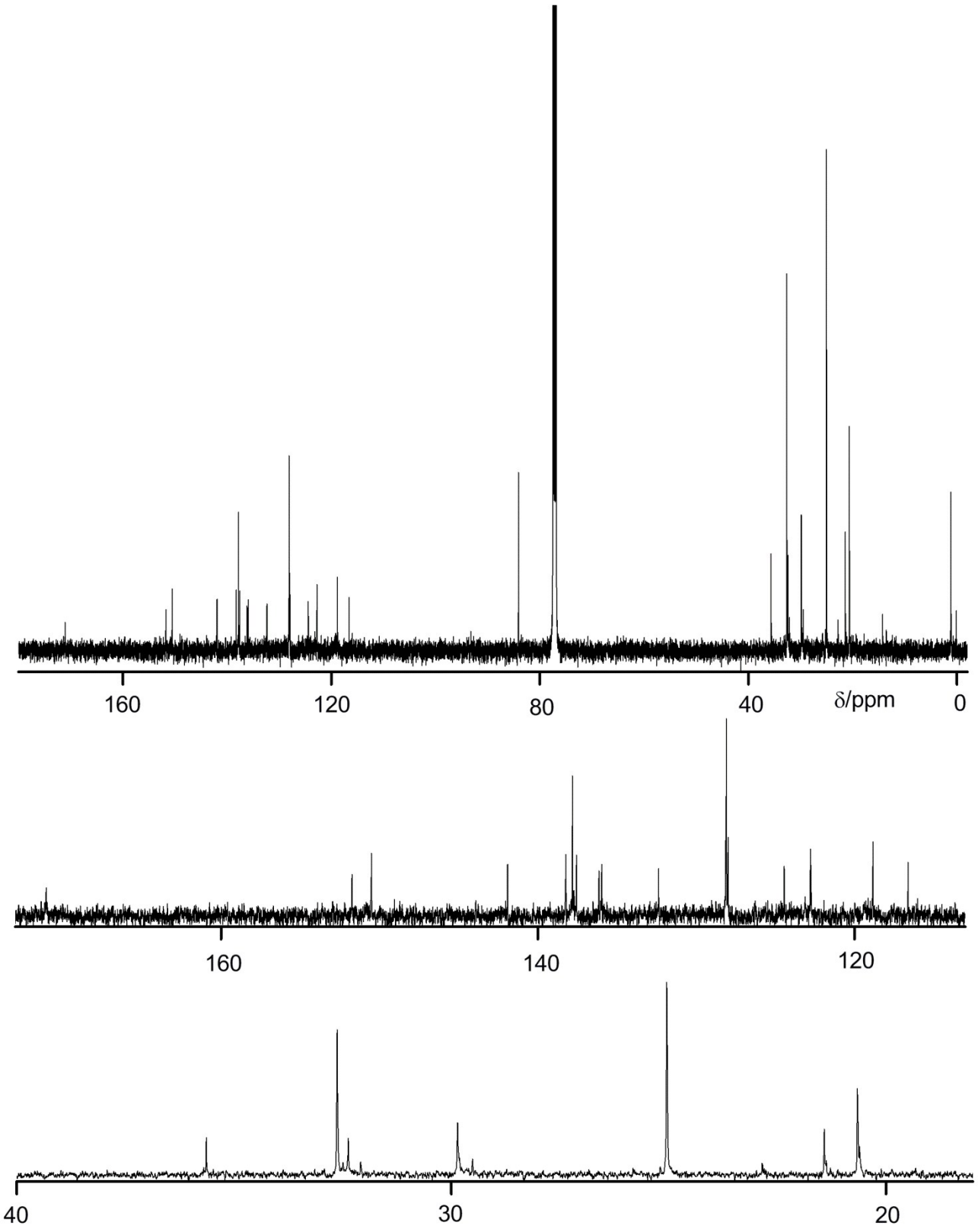


Figure S20 ^{13}C NMR spectrum of **4-2Bpin** in $CDCl_3$.

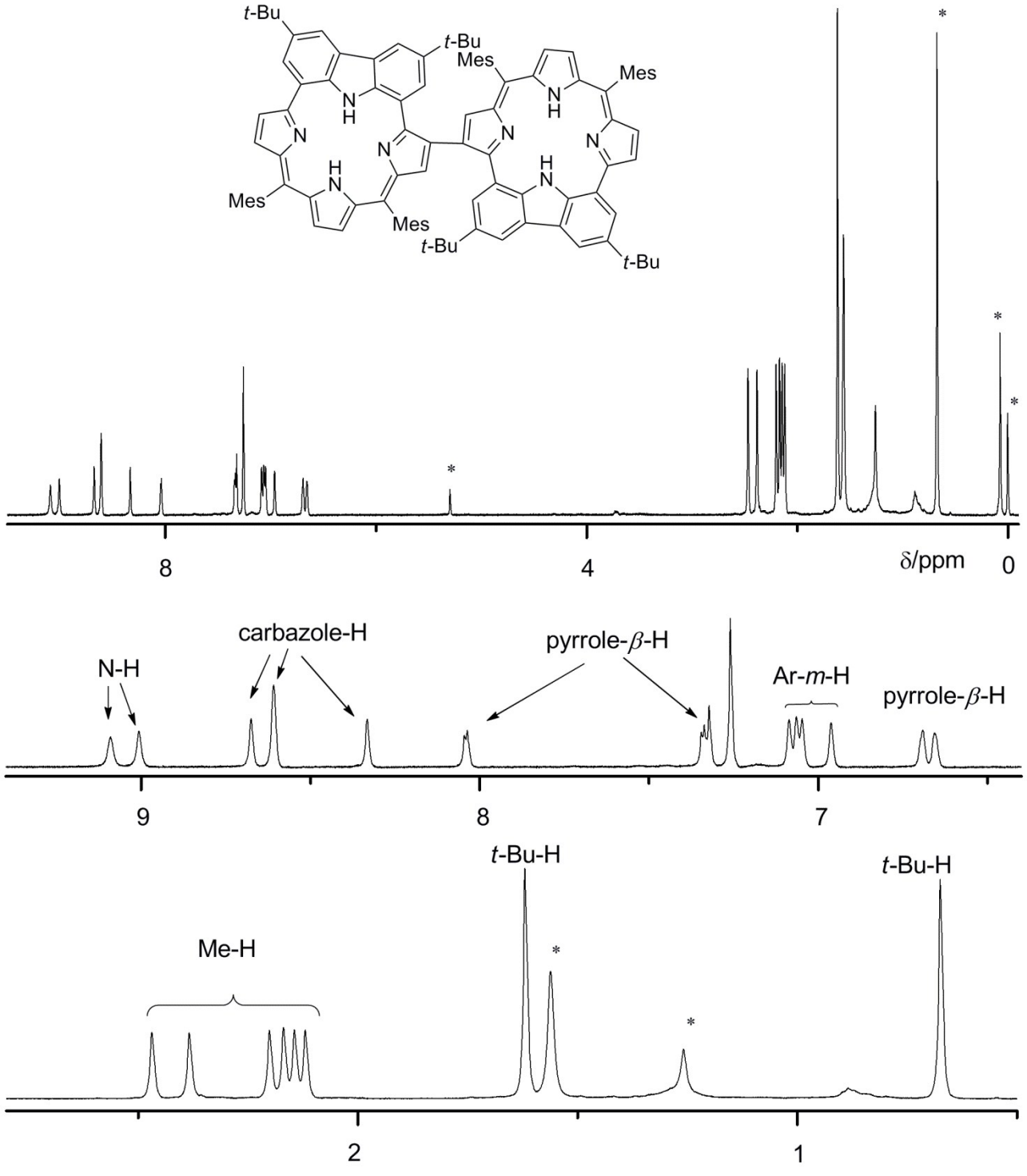


Figure S21. ^{1}H NMR spectrum of **6H** in $CDCl_3$.

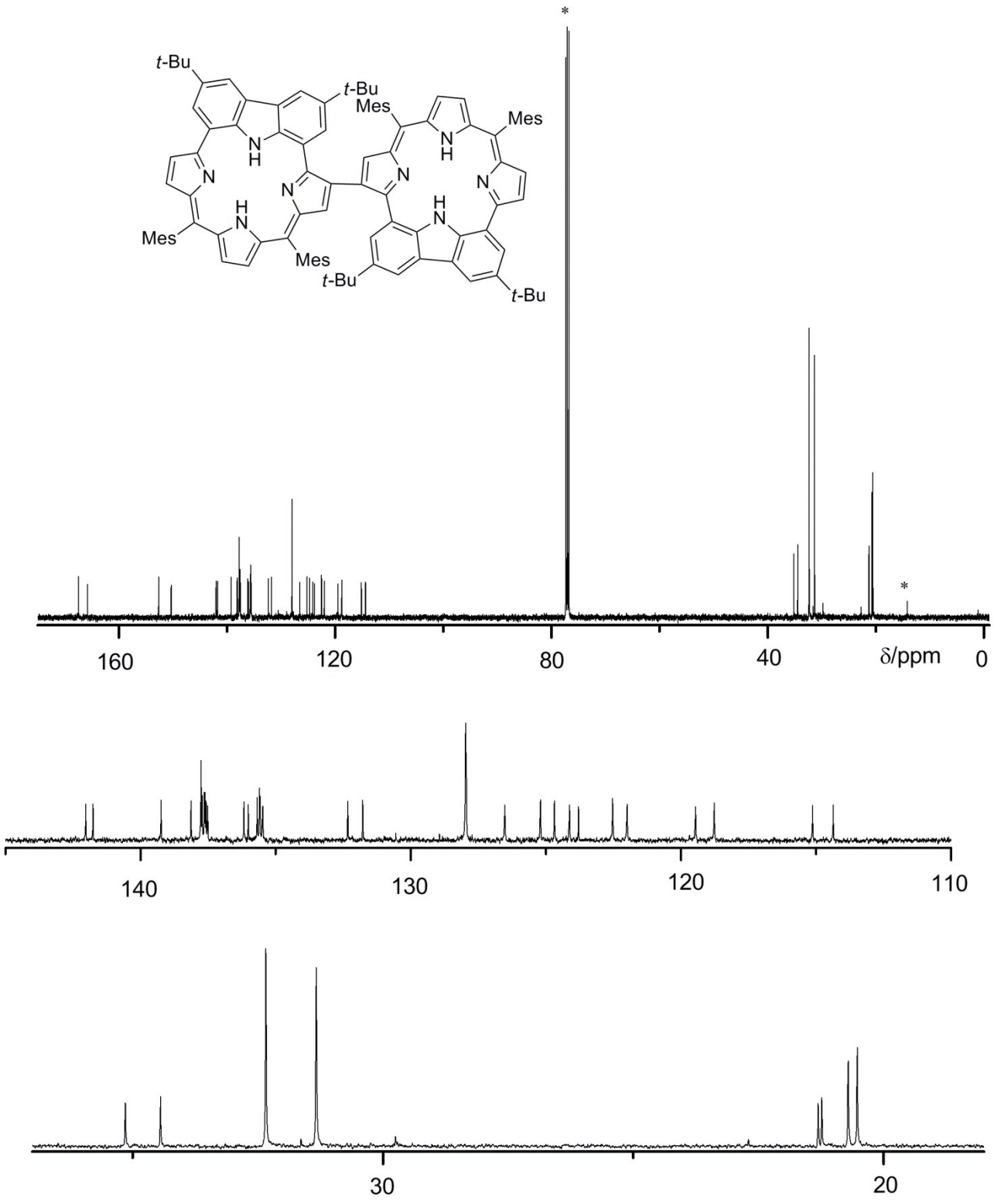


Figure S22. ^{13}C NMR spectrum of **6H** in $CDCl_3$.

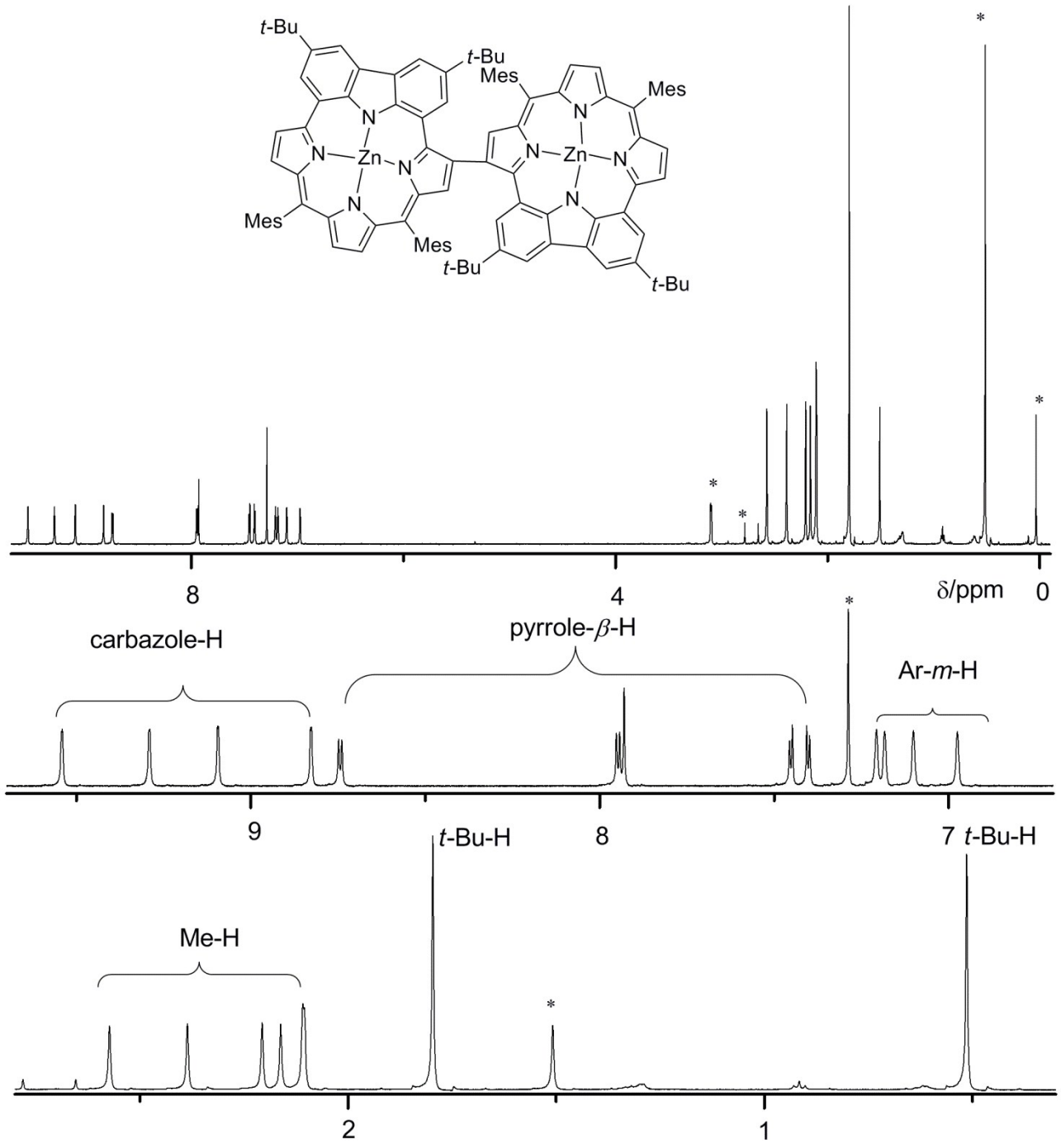


Figure S23. ^{1}H NMR spectrum of **6Zn** in $CDCl_3$.

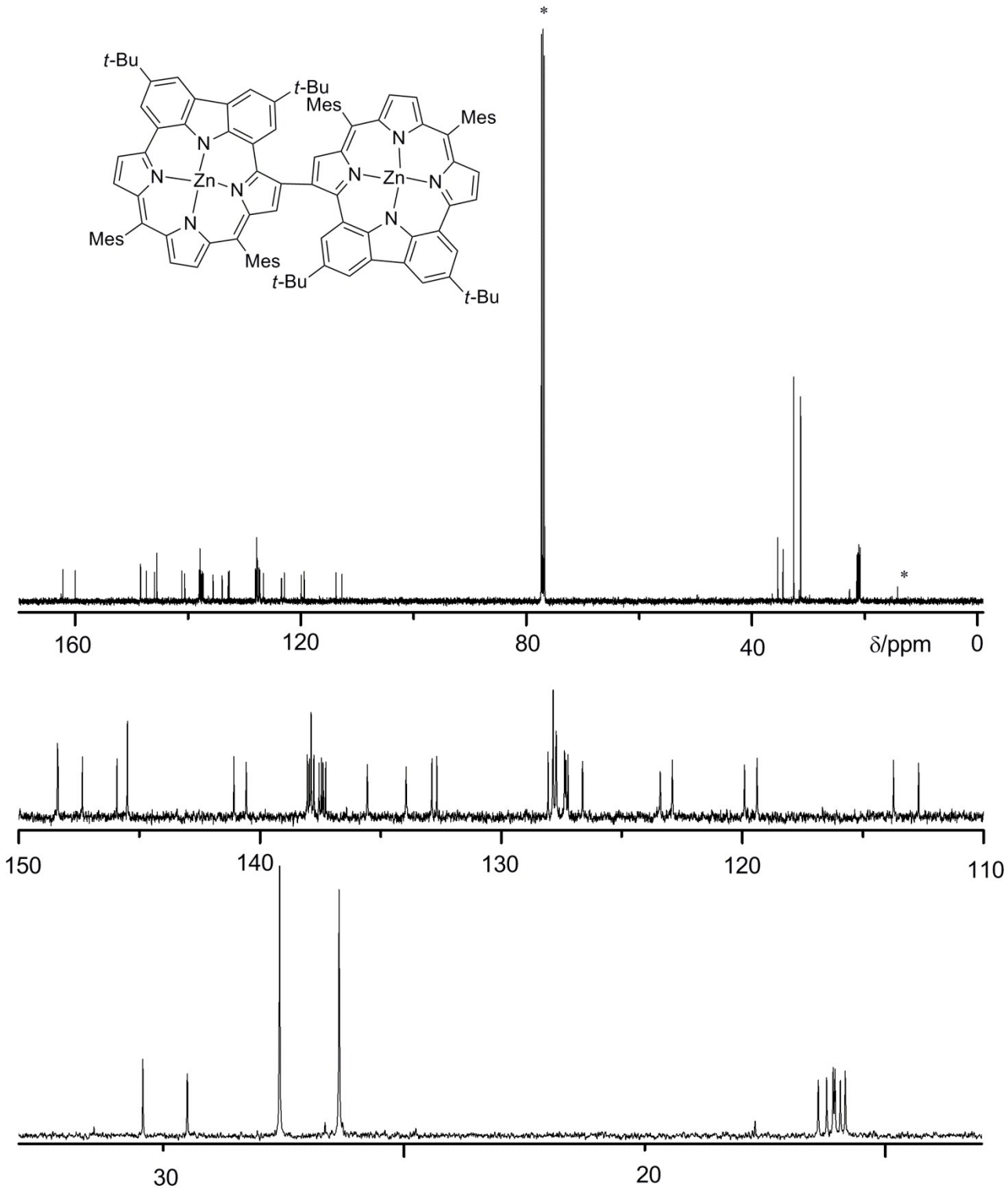


Figure S24. ^{13}C NMR spectrum of **6Zn** in $CDCl_3$.

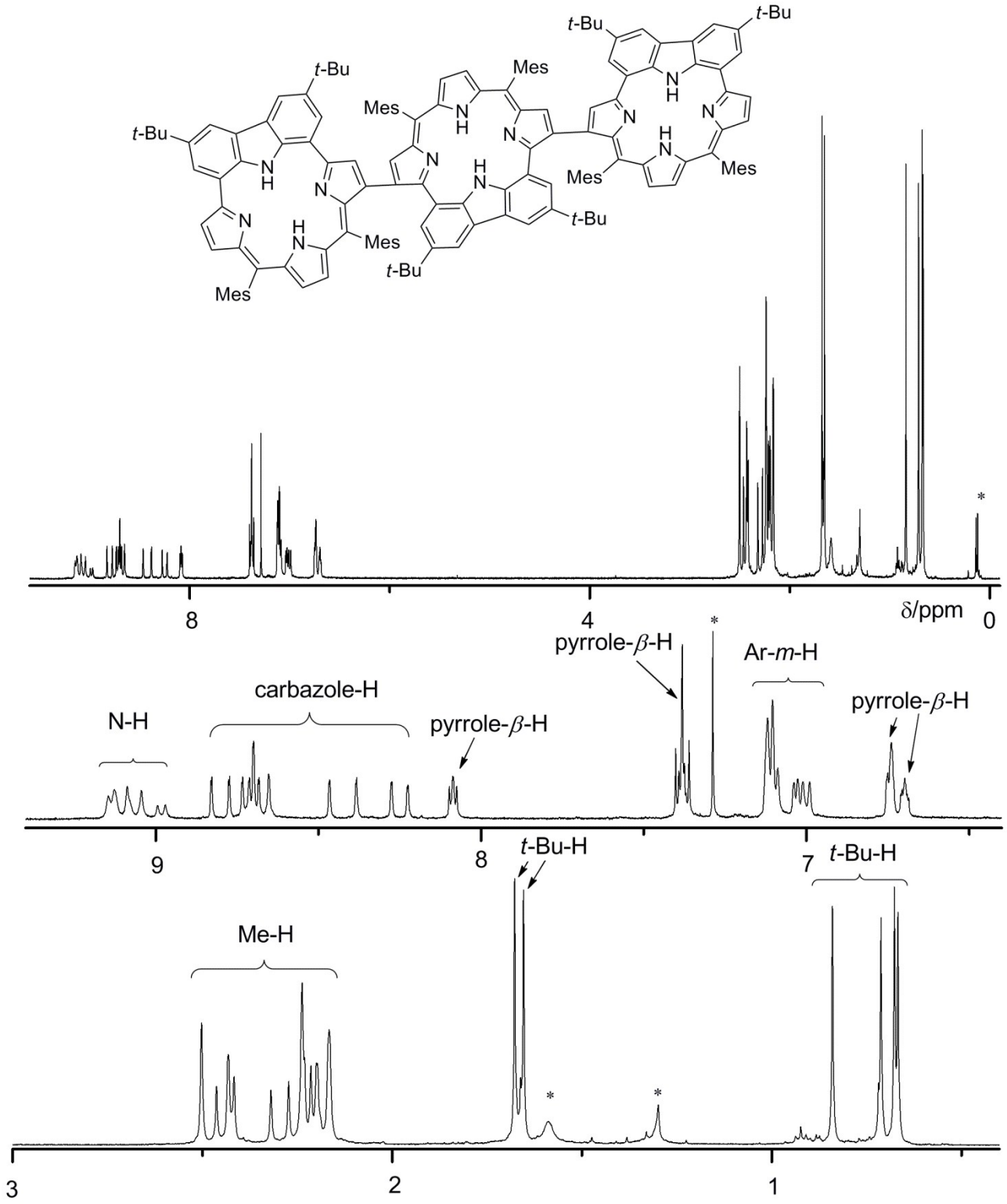


Figure S25. ^{1}H NMR spectrum of **7H** in $CDCl_3$.

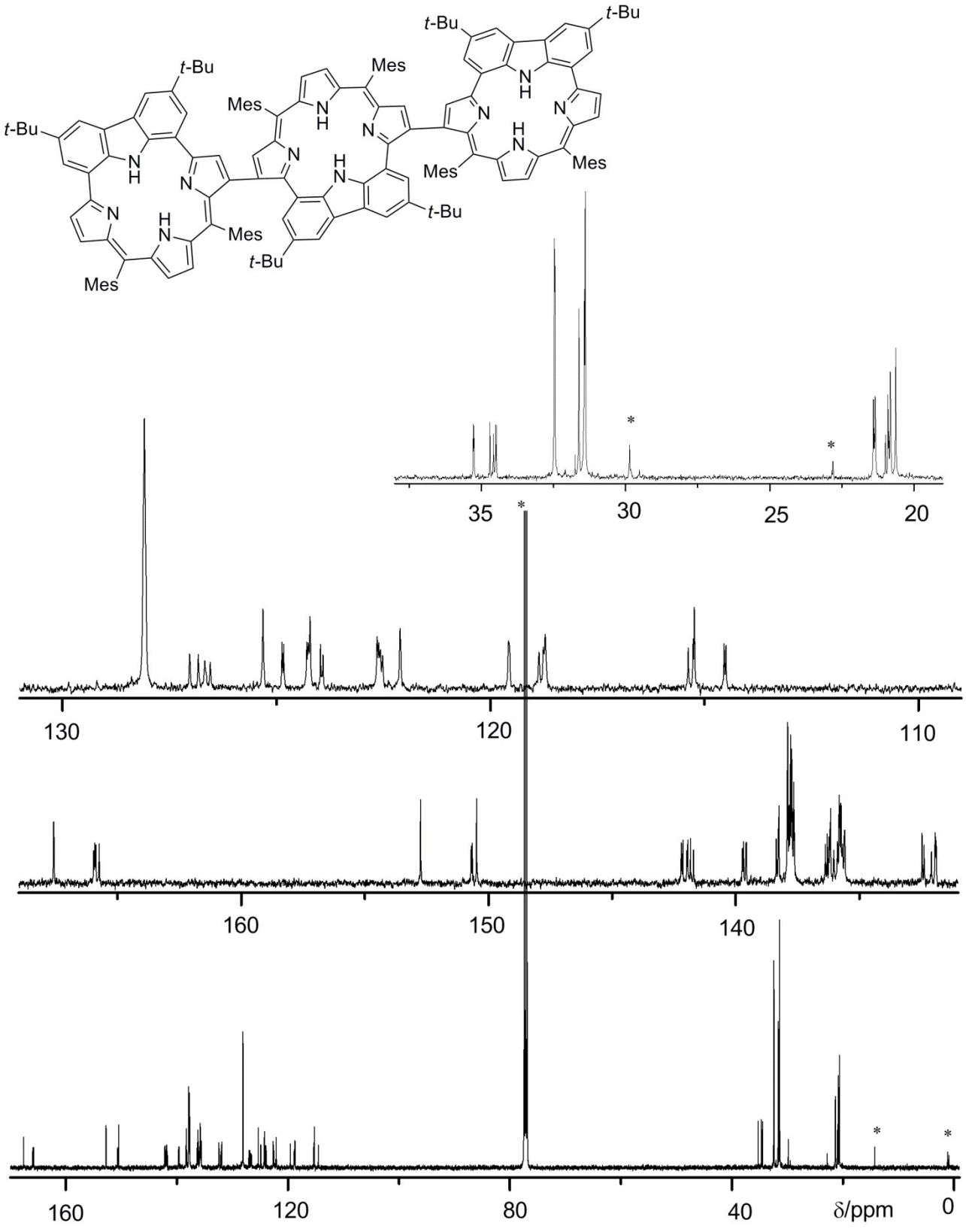


Figure S26. ^{13}C NMR spectrum of **7H** in $CDCl_3$.

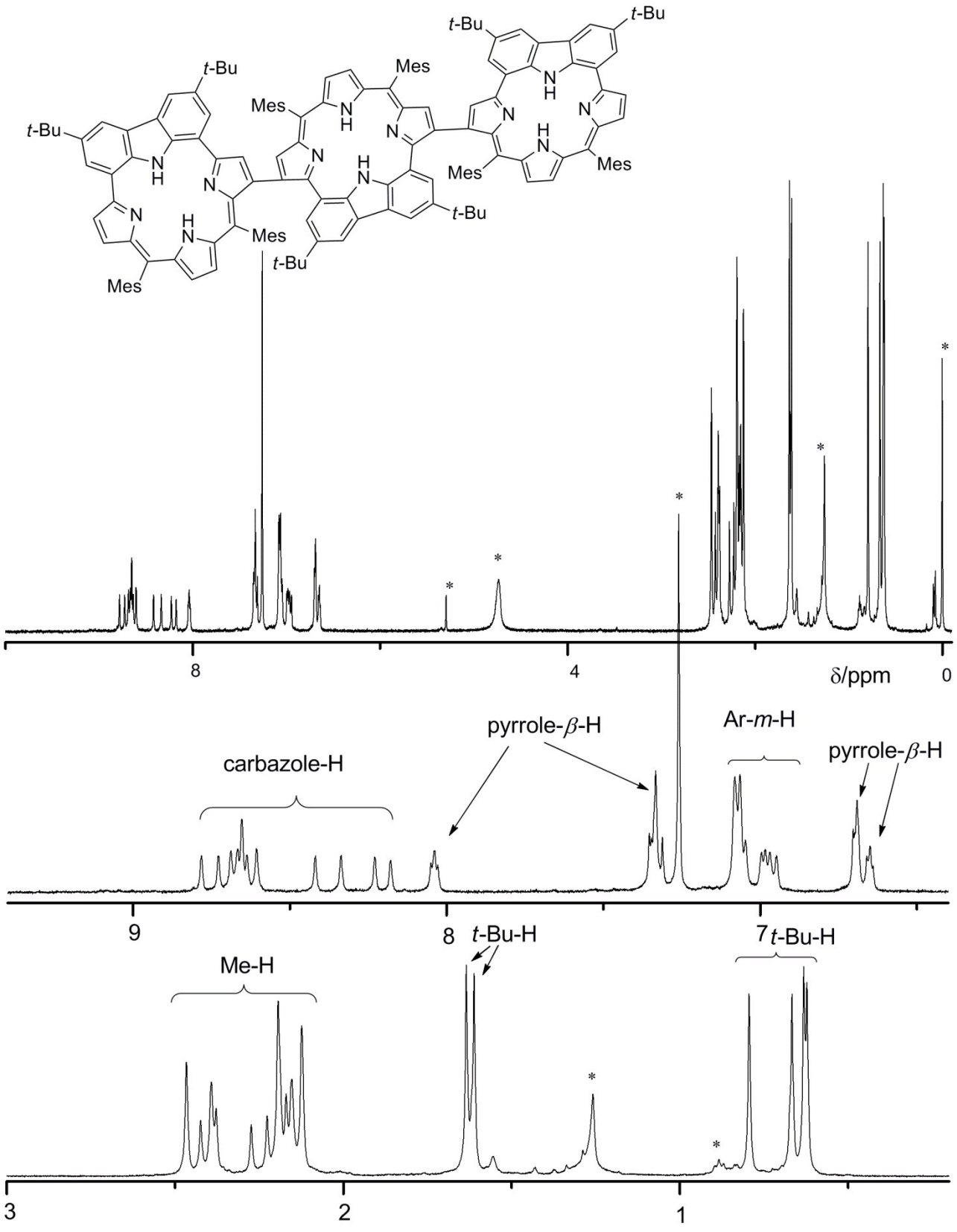


Figure S27. H-D exchanged ^{1}H NMR spectrum of **7H** in $CDCl_3$.

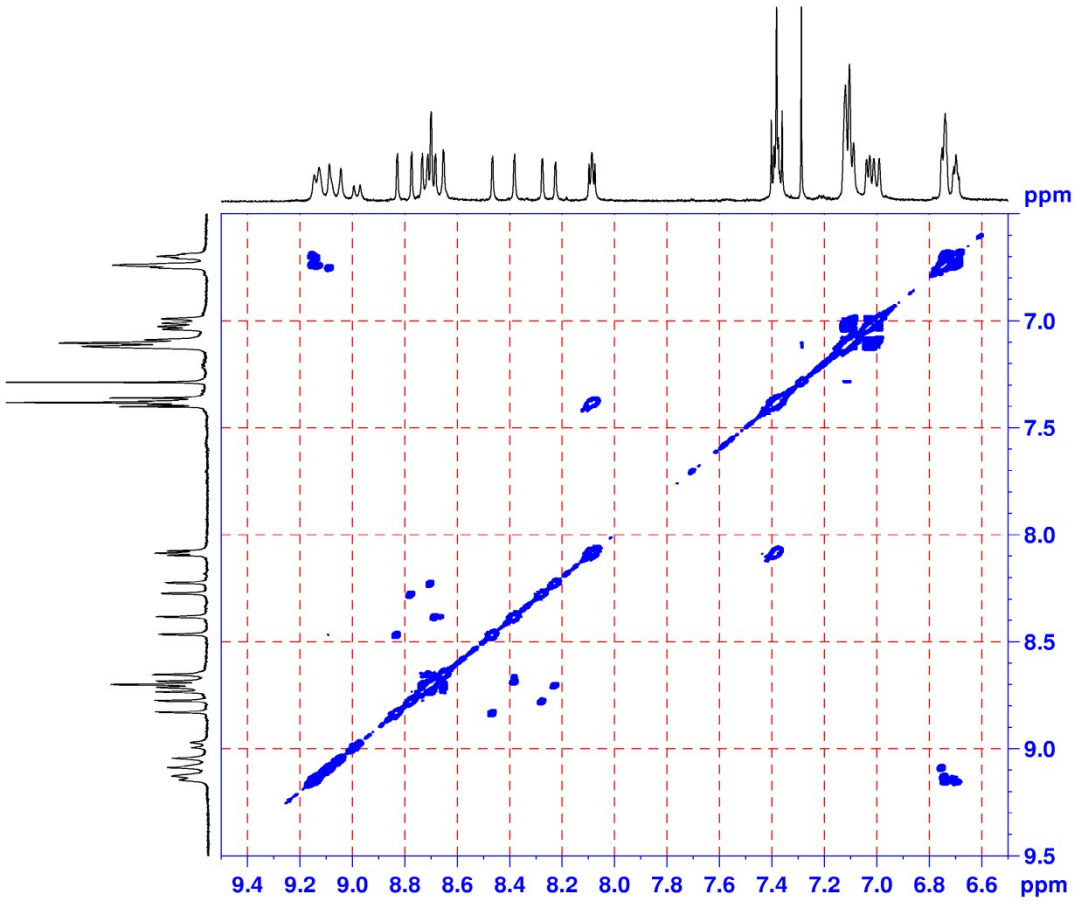


Figure S28. H-H COSY spectrum of **7H** in $CDCl_3$.

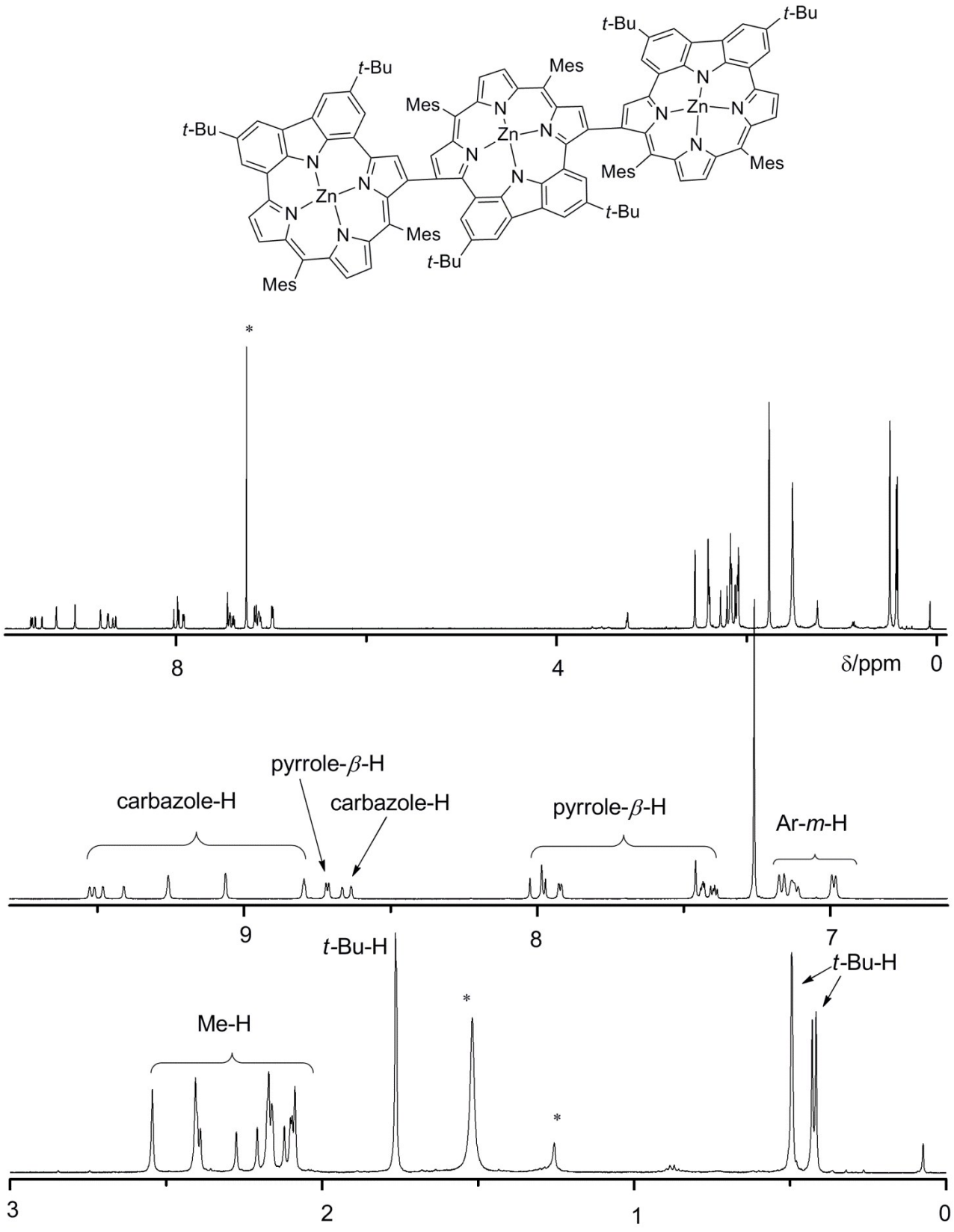


Figure S29. ^{1}H NMR spectrum of **7Zn** in $CDCl_3$.

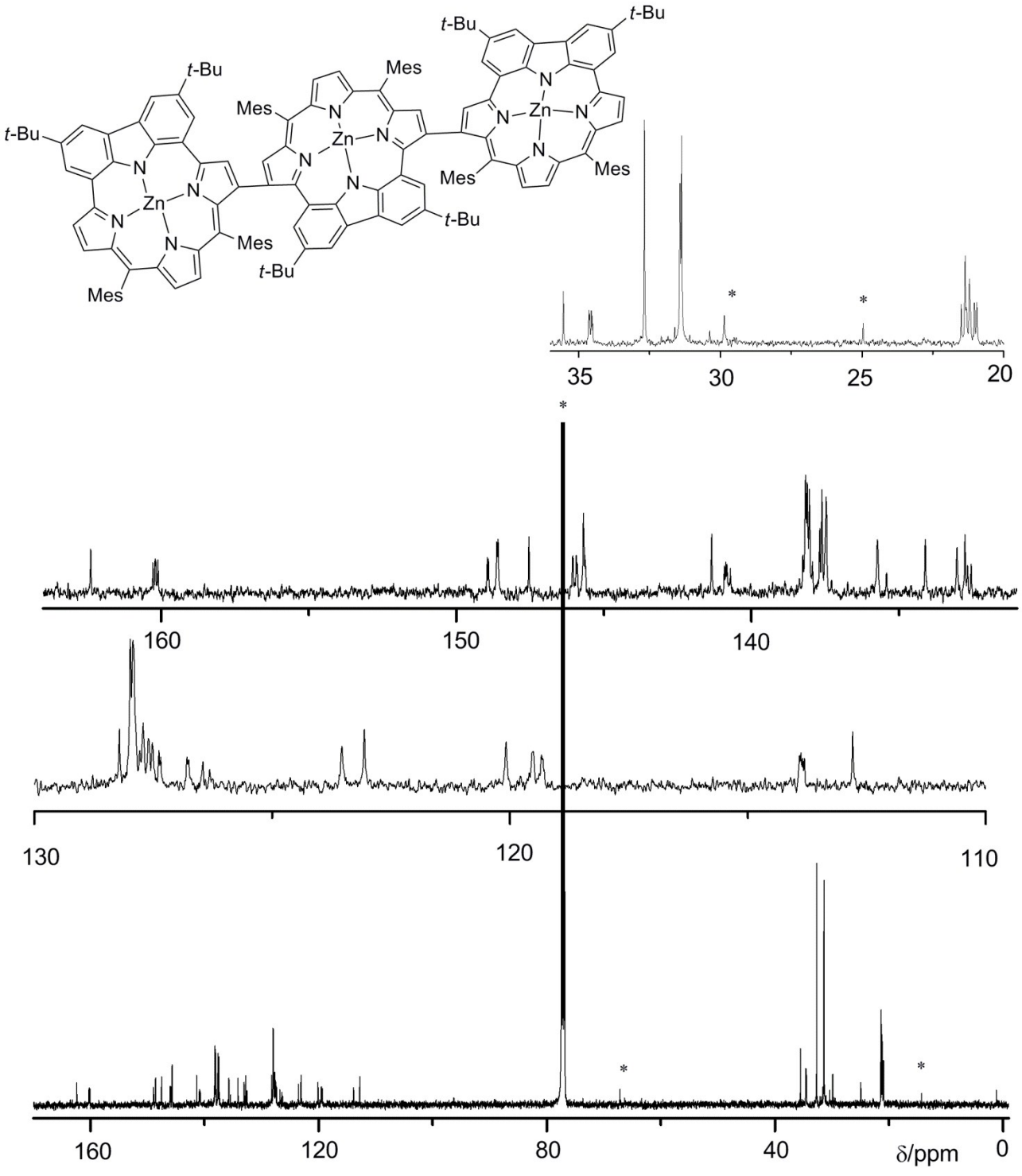


Figure S30. ^{13}C NMR spectrum of **7Zn** in $CDCl_3$.

Photophysical Properties

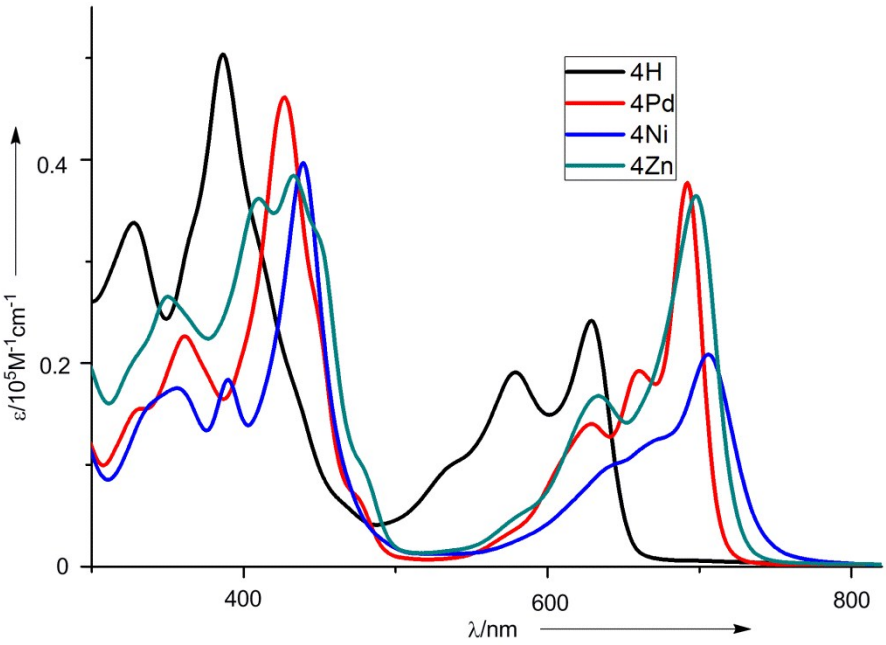


Figure S31. UV/Vis absorption spectra of **4H**, **4Pd**, **4Ni** and **4Zn** in CH_2Cl_2.

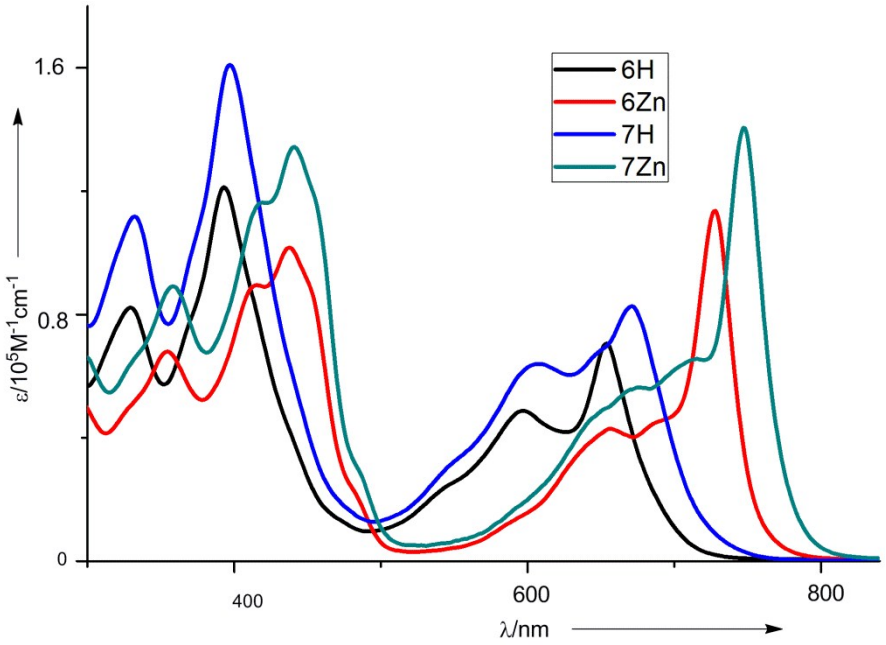


Figure S32. UV/Vis absorption spectra of **6H**, **6Zn**, **7H** and **7Zn** in CH_2Cl_2.

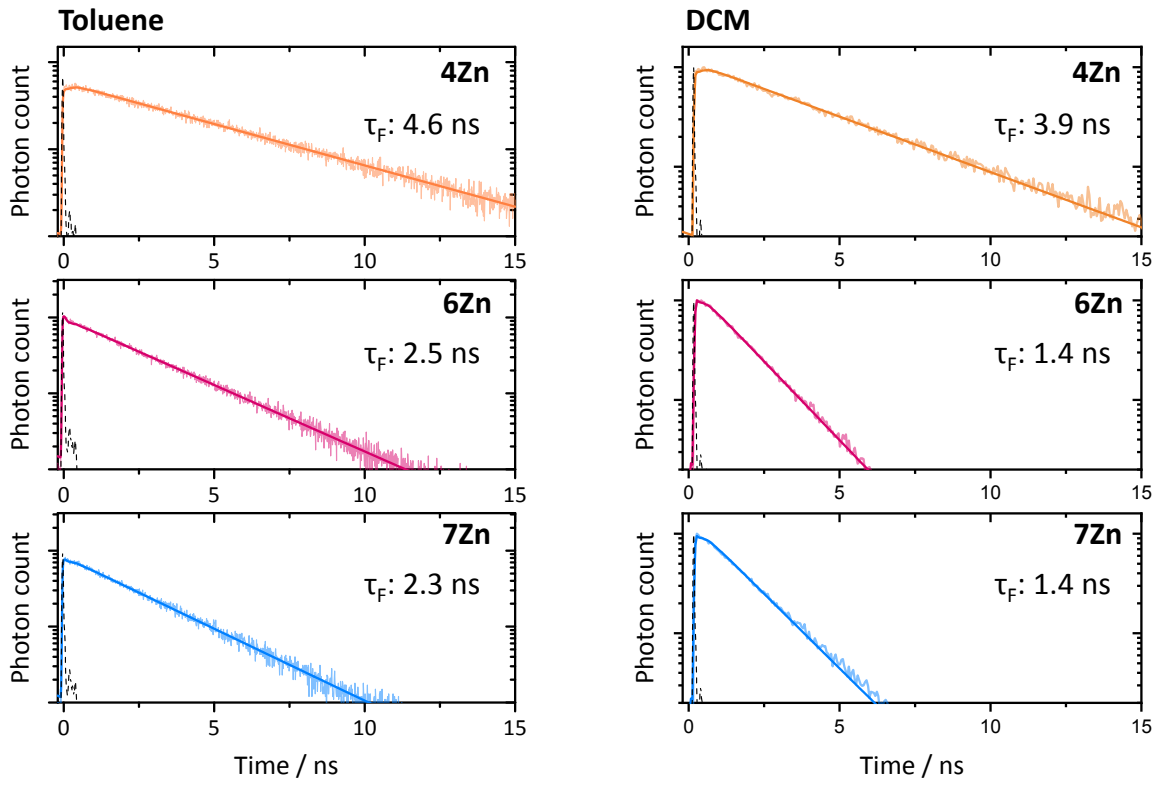


Figure S33. Fluorescence decay profiles of **4Zn**, **6Zn** and **7Zn** in toluene (left) and CH_2Cl_2 (right).

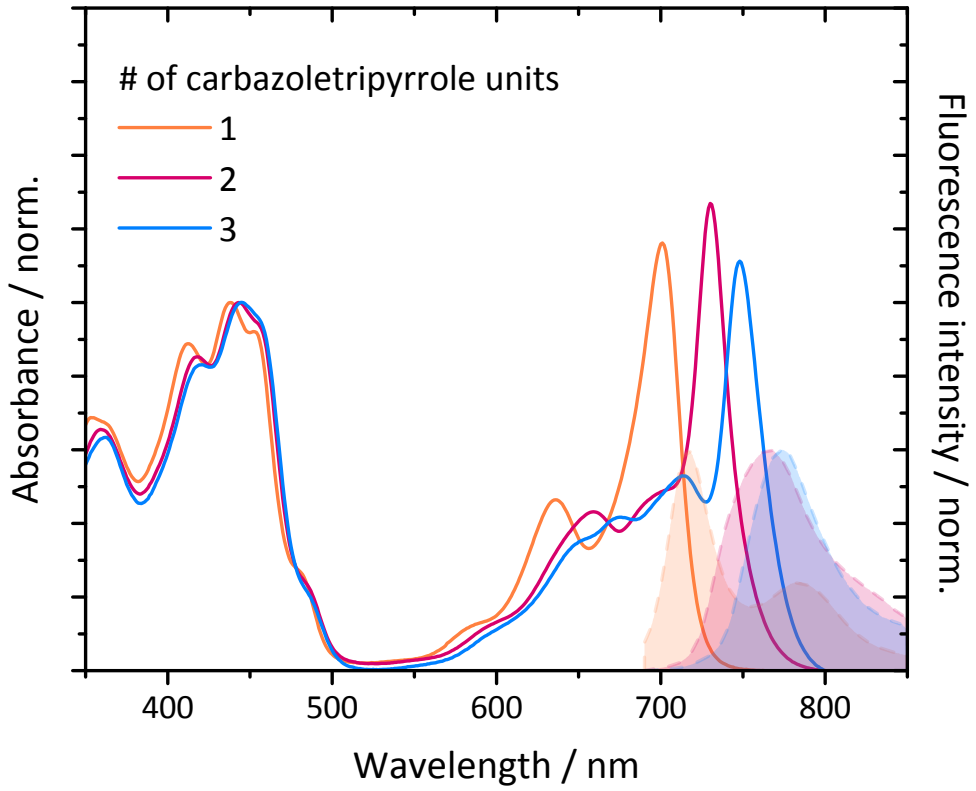


Figure S34. Absorption and fluorescence spectra of **4Zn**, **6Zn**, and **7Zn** in toluene.

Table S1. Fluorescence parameters of **4Zn**, **6Zn**, and **7Zn** in toluene and DCM.

Solvent	Compound	λ_{Fmax} (nm)	Φ_F	τ_F (ns)	k_r (s^{-1})	k_{nr} (s^{-1})
Toluene	**4Zn**	716	0.32	4.6	$7.0x10^7$	$1.5x10^8$
	6Zn	766	0.36	2.5	$1.4x10^8$	$2.6x10^8$
	7Zn	774	0.36	2.3	$1.6x10^8$	$2.7x10^8$
DCM	**4Zn**	716	0.14	3.9	$3.6x10^7$	$2.2x10^8$
	6Zn	743	0.10	1.4	$7.1x10^7$	$6.4x10^8$
	7Zn	770	0.19	1.4	$1.4x10^8$	$5.7x10^8$

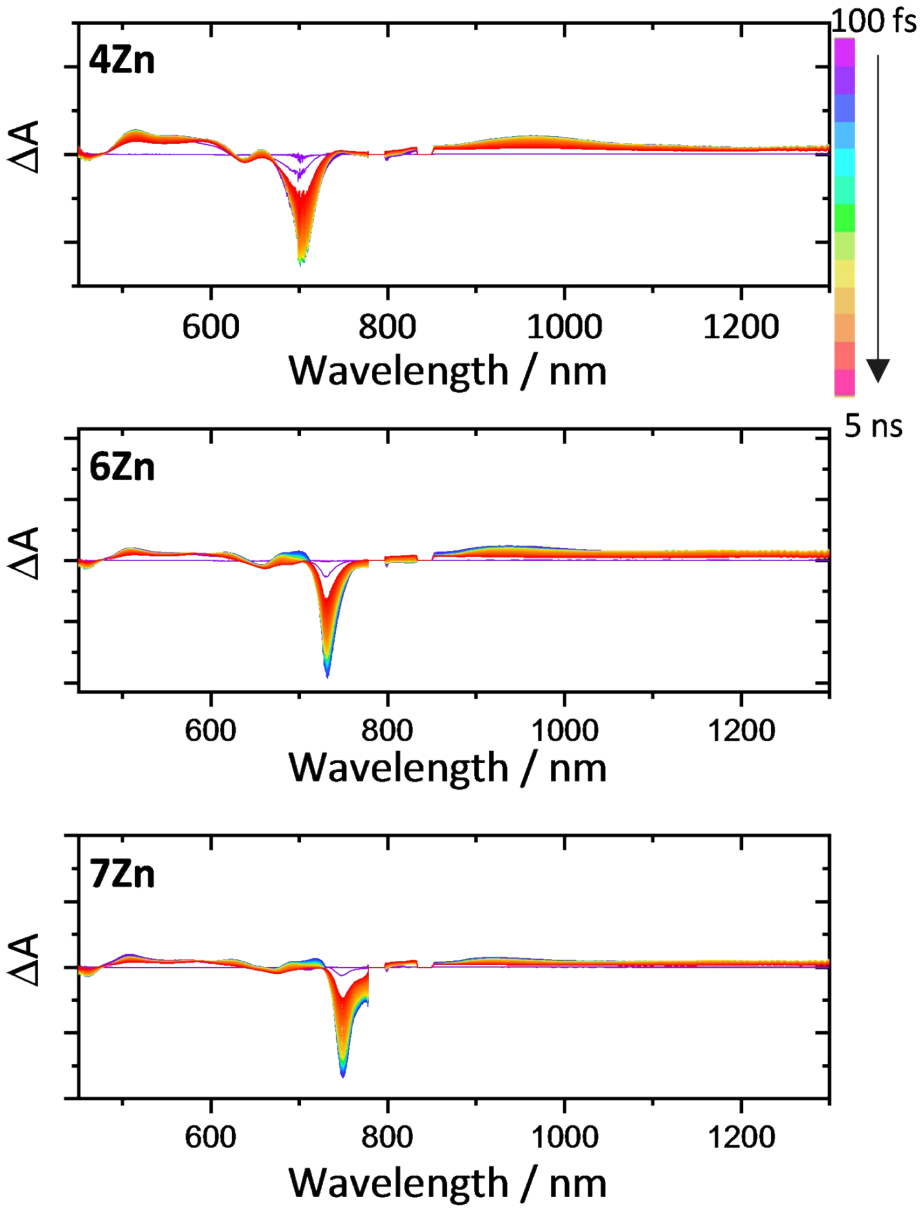


Figure S35. *Fs*-transient absorption (TA) spectra of **4Zn**, **6Zn**, and **7Zn** in toluene recorded during 5 ns.

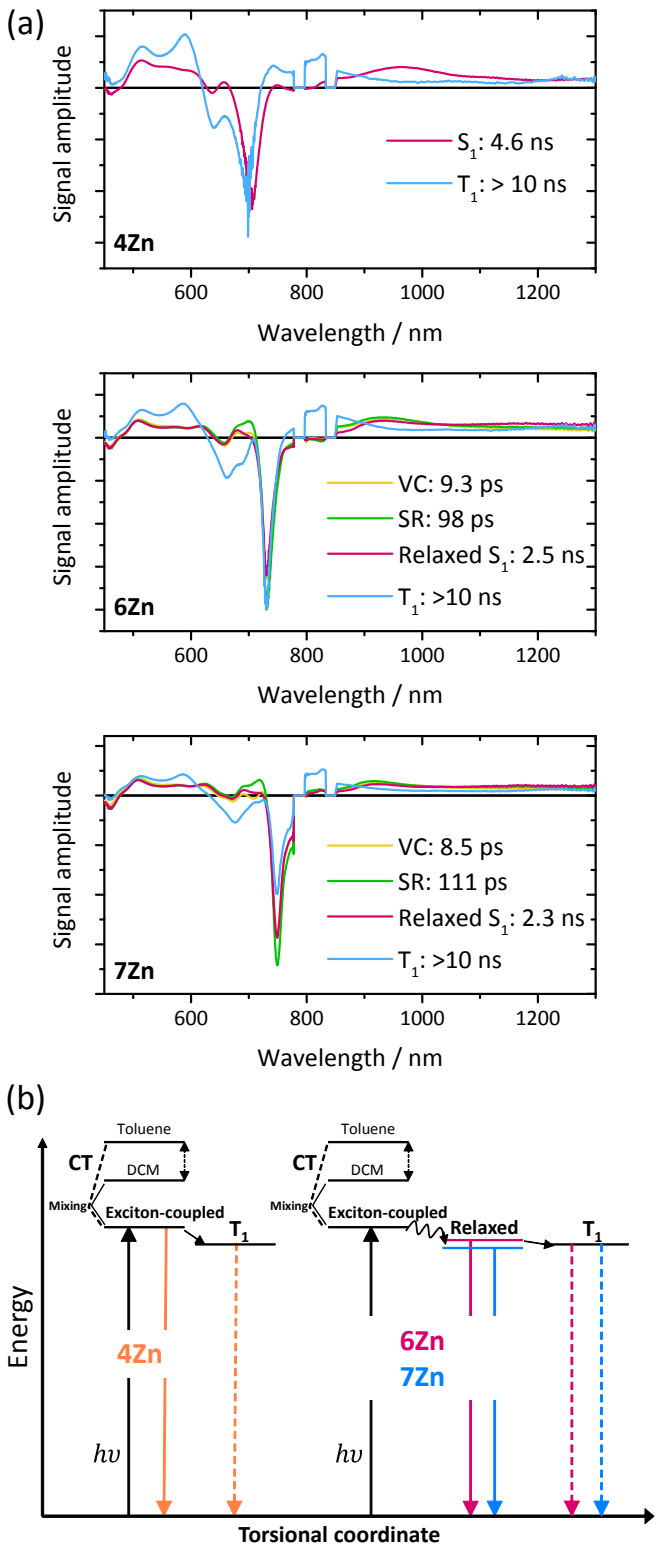


Figure S36. (a) Extracted species associated spectra (SAS) and (b) scheme of excited-state dynamics of **4Zn**, **6Zn**, **and 7Zn**

Quantum mechanical calculations

Quantum mechanical calculations were carried out with Gaussian 16 program suite.[2] Geometry optimization in ground state (S_0) was performed by density functional theory (DFT) and time-dependent DFT (TD-DFT), respectively, method with B3LYP,[3] employing a basis set consisting of 6-31G(d) for all atoms.[4]

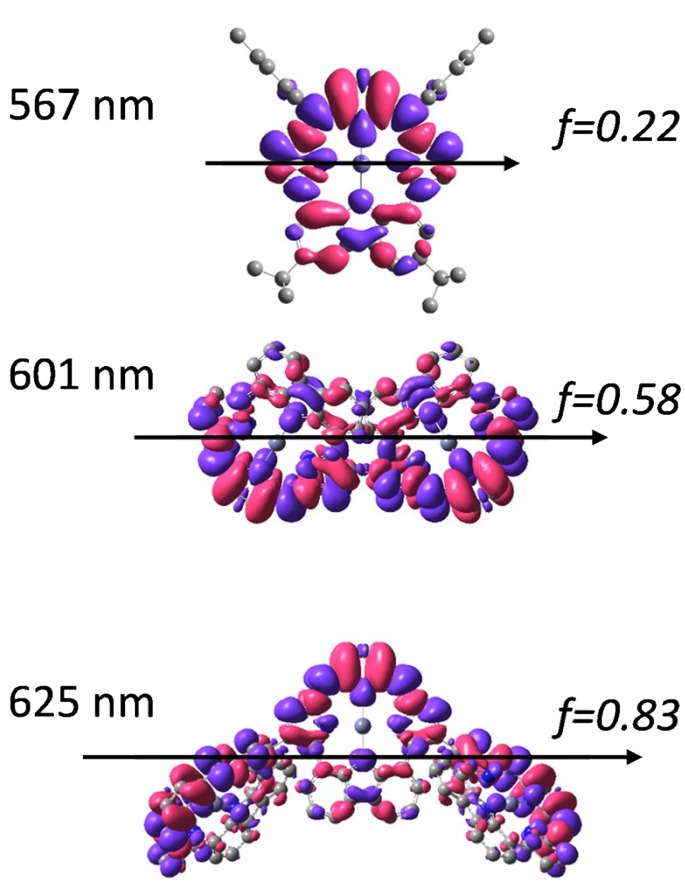


Figure S37. Electron density difference maps (EDDM) of S_0 to S_1 transition. Arrows indicate the direction of the transition dipole moment, *f* the oscillator strength, and wavenumbers (cm^{-1}) the lowest transition energy. Red: positive isovalue and purple for negative isovalue.

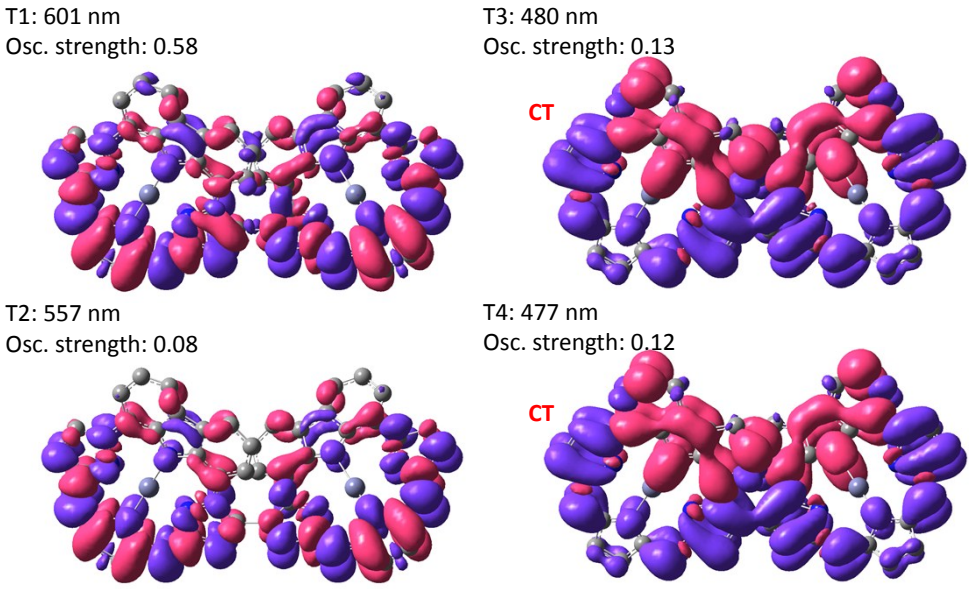


Figure S38. Electron density difference maps (EDDM) of four lowest transitions of **6Zn**

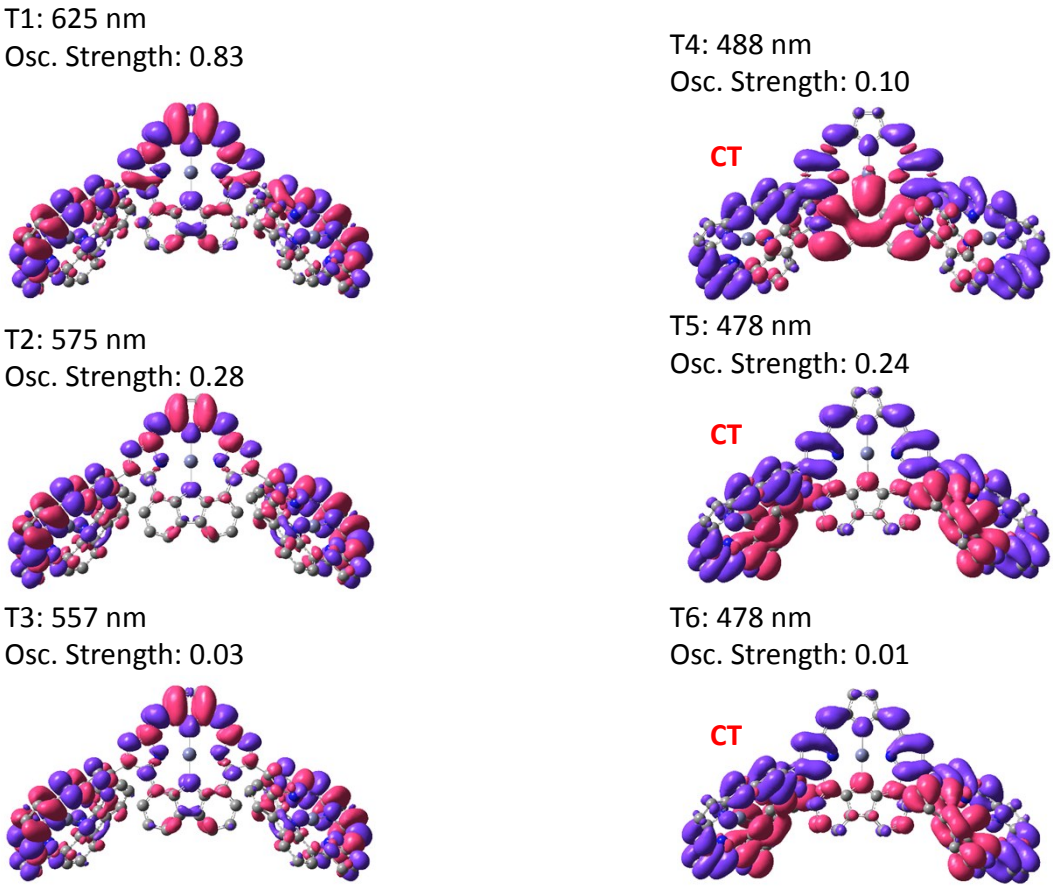
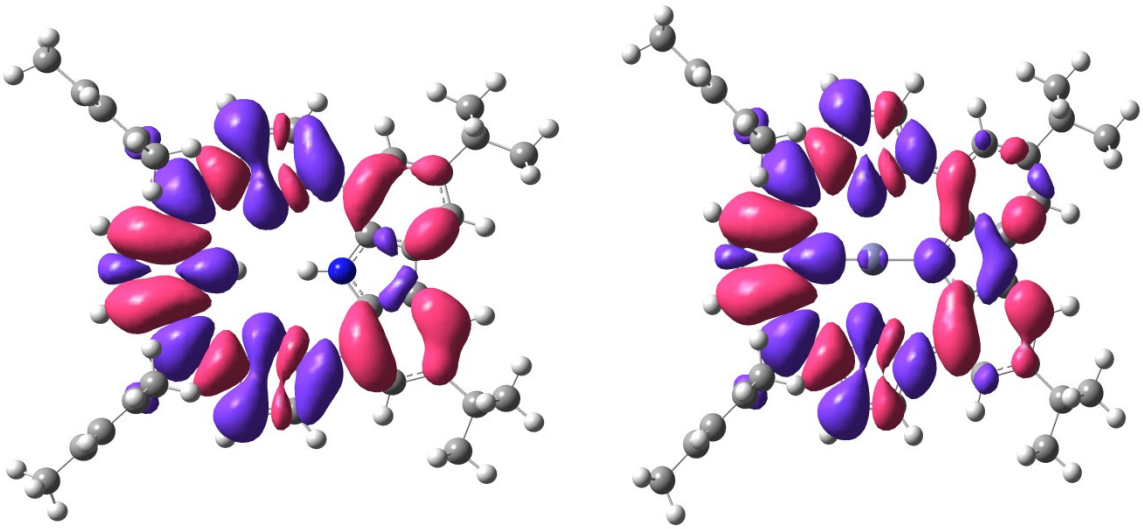


Figure S39. Electron density difference maps (EDDM) of six lowest transitions of **7Zn**.



Zn free monomer Zn monomer

Figure S40. Electron density difference map for the first electronic transitions.

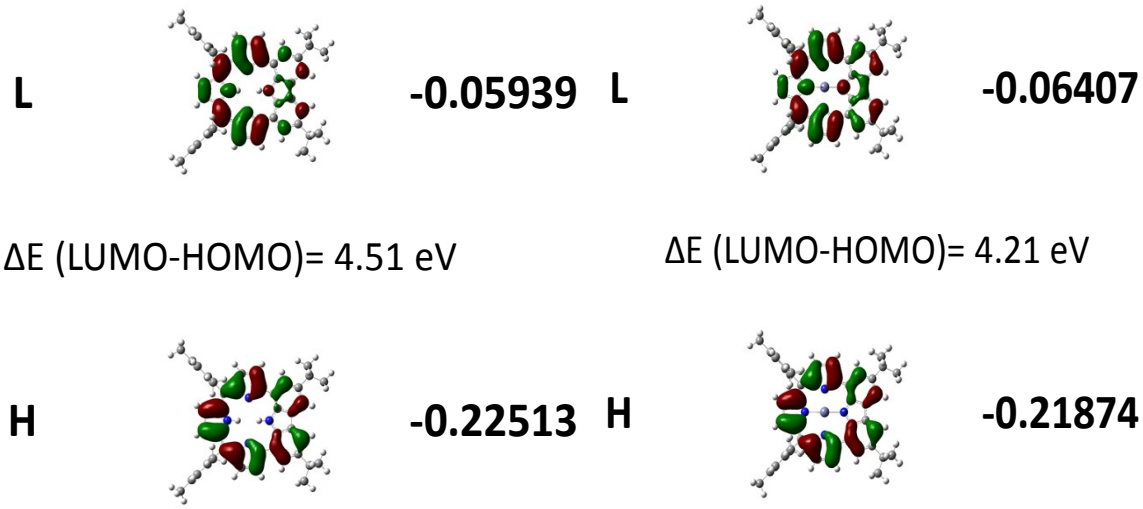


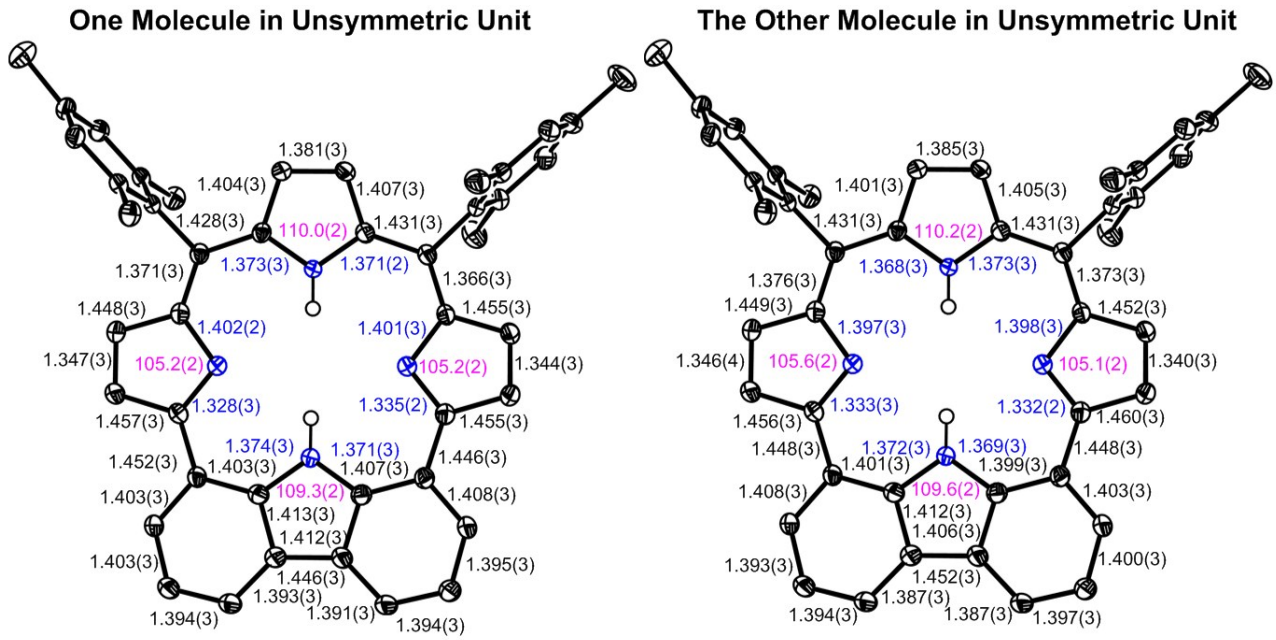
Figure S41. HOMO and LUMO of Zn-free (left) and Zn monomer (right).

X-ray crystal data

Table S2. Crystal data and structure refinement for **4H**

Empirical formula	$C_{52}H_{52}N_4$
Formula weight	732.42
Temperature(K)	100.01(10)
Wavelength(Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	a = 14.3365(2) Å α = 99.6885(12)°
	b = 16.9978(3) Å β = 106.9925(12)°
	c = 21.8178(3) Å γ = 99.9700(12)°
Volume(Å^3)	4870.73(13)
Z	2
Density(calc) (Mg/cm^3)	1.090
M(mm^{-1})	0.484
F(000)	1712.0
Crystal size(mm^3)	0.15 × 0.07 × 0.03
2θ for data collection	8.208 to 133.2°
Index ranges	-17 ≤ h ≤ 17, -20 ≤ k ≤ 20, -26 ≤ l ≤ 26
Reflections collected	17184
Independent reflections	17184 [R(int) = 0.0428]
Data/restraints/parameters	17184 / 42 / 1113
Goodness-of-fit on F^2	1.050
Final R indexes [I >= 2σ (I)]	R_1 = 0.0605, wR_2 = 0.1714
R indexes (all data)	R_1 = 0.0748, wR_2 = 0.1829
Largest diff. peak and hole(e Å^{-3})	0.88 and -0.54
CCDC No.	1921822

a)



b)

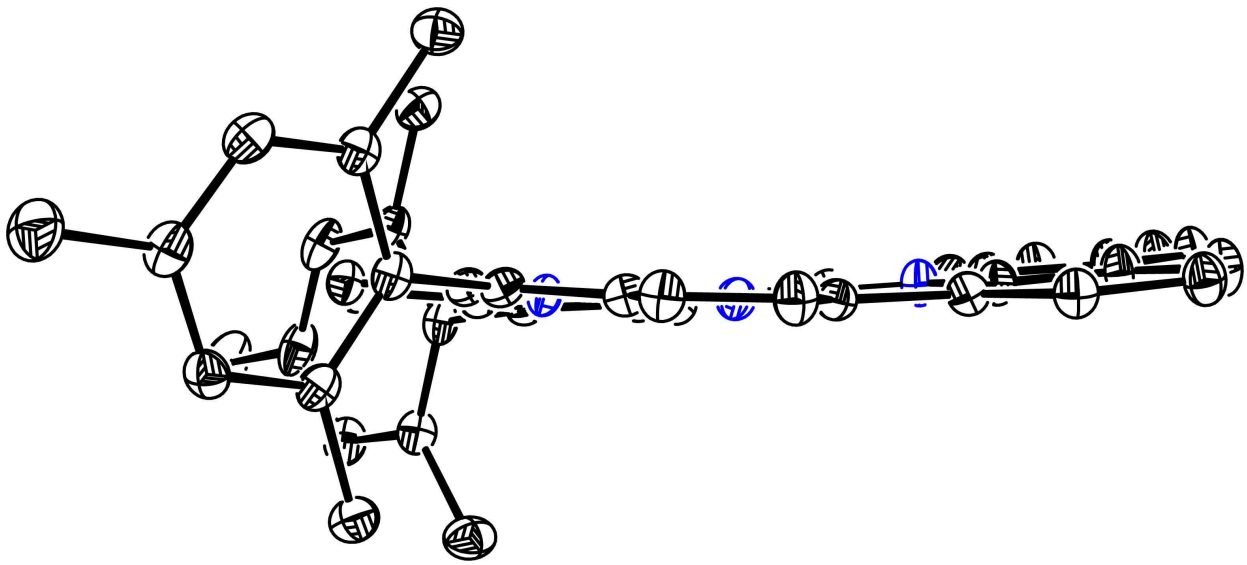
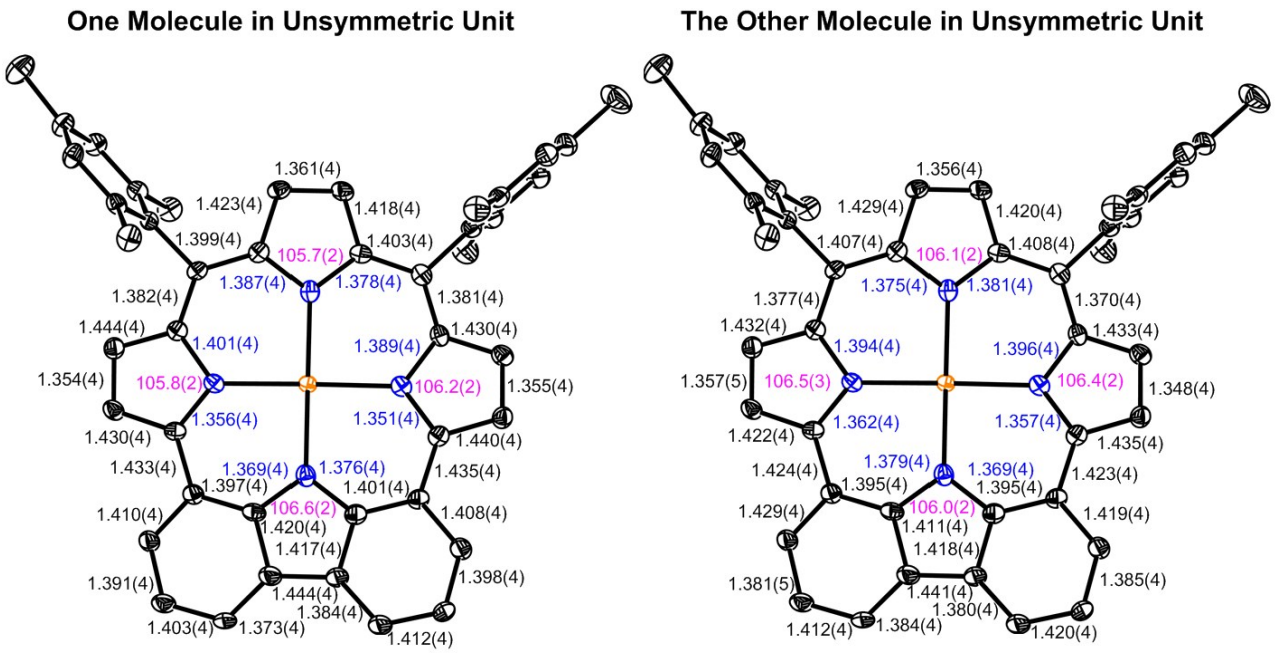


Figure S42. X-ray crystal structure of **4H**. (a) Top view, black figures indicate the C-C bond lengths (Å), blue figures indicate the C-C bond lengths (Å), pink figures indicate the C-N-C bond angles (°) (b) side view. The thermal ellipsoids are 50% probability level. Hydrogen atoms (except hydrogen atoms of nitrogen), *tert*-Butyl groups and solvent molecules are omitted for clarity.

Table S3. Crystal data and structure refinement for **4Pd**

Empirical formula	$C_{52}H_{50}N_4Pd$
Formula weight	837.36
Temperature(K)	99.99(10)
Wavelength(Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	a = 14.3716(2) Å α = 99.8281(10)°
	b = 16.9373(2) Å β = 106.8207(13)°
	c = 21.8677(2) Å γ = 100.5416(12)°
Volume(Å^3)	4865.73(12)
Z	2
Density(calc) (Mg/cm^3)	1.143
M(mm^{-1})	3.338
F(000)	1744.0
Crystal size(mm^3)	0.20 × 0.15 × 0.05
2θ for data collection	8.208 to 133.2°
Index ranges	$-17 \le h \le 17$, $-20 \le k \le 20$, $-27 \le l \le 27$
Reflections collected	66551
Independent reflections	17134 [R(int) = 0.0686]
Data/restraints/parameters	17134 / 0 / 1051
Goodness-of-fit on F^2	1.073
Final R indexes [$I >= 2\sigma$ (I)]	R_1 = 0.0492, wR_2 = 0.1336
R indexes (all data)	R_1 = 0.0545, wR_2 = 0.1382
Largest diff. peak and hole(e Å^{-3})	1.52 and -1.99
CCDC No.	1921946

a)



b)

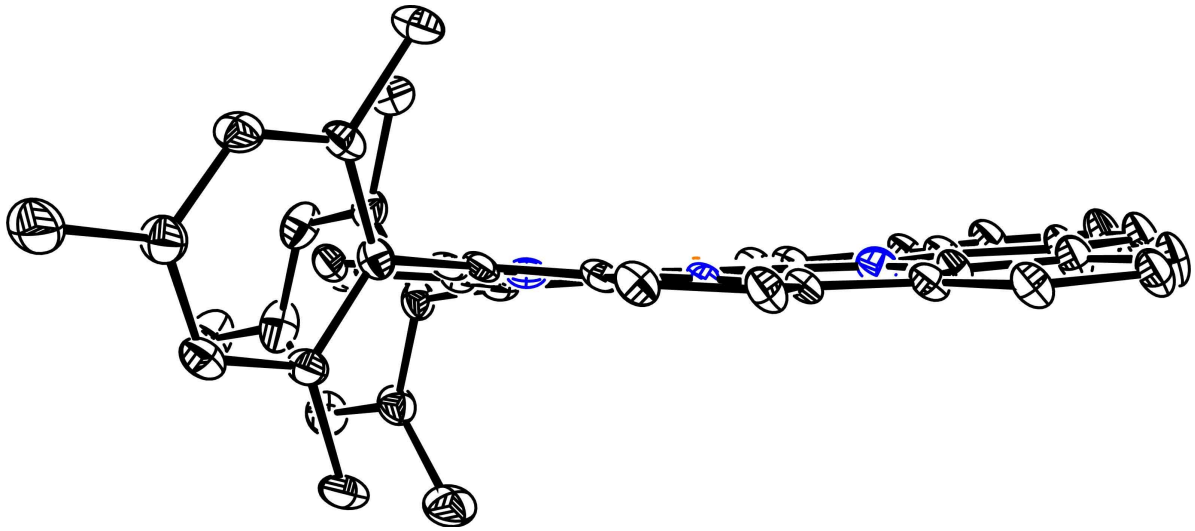
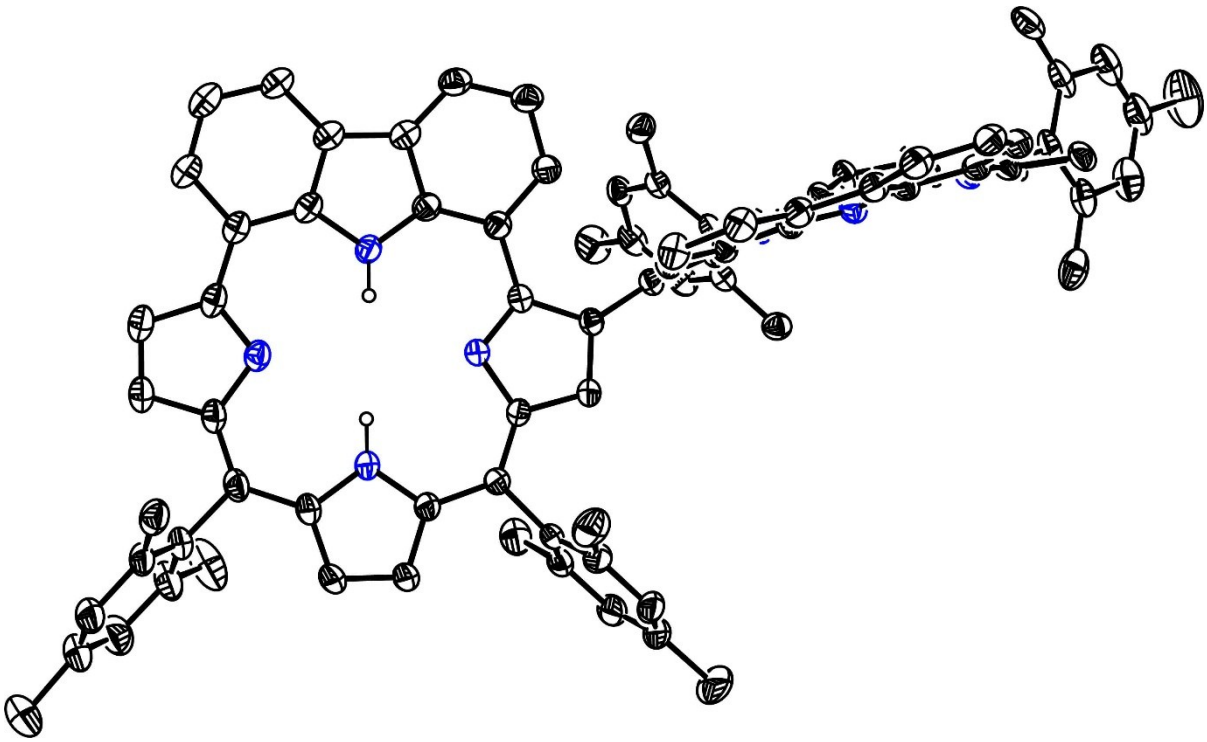


Figure S43. X-ray crystal structure of **4Pd**. (a) Top view, black figures indicate the C-C bond lengths (Å), blue figures indicate the C-C bond lengths (Å), pink figures indicate the C-N-C bond angles (°) (b) side view. The thermal ellipsoids are 50% probability level. Hydrogen atoms, *tert*-Butyl groups are omitted for clarity.

Table S4. Crystal data and structure refinement for **6H**

Empirical formula	$C_{104}H_{102}N_8$
Formula weight	1463.93
Temperature(K)	100.02(10)
Wavelength(Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	a = 14.9926(4) Å α = 88.588(2)°
	b = 19.2244(6) Å β = 88.777(2)°
	c = 19.7967(6) Å γ = 70.557(3)°
Volume($Å^3$)	5378.4(3)
Z	2
Density(calc) (Mg/cm^3)	0.904
M(mm^{-1})	0.402
F(000)	1564.0
Crystal size(mm^3)	0.6 × 0.2 × 0.15
Radiation	CuKα (λ = 1.54184)
2θ for data collection	9.124 to 133.2°
Index ranges	$-17 \le h \le 18$, $-23 \le k \le 23$, $-24 \le l \le 24$
Reflections collected	18980
Independent reflections	18980 [R(int) = 0.0621]
Data/restraints/parameters	18980/12/1033
Goodness-of-fit on F^2	1.105
R indexes [$I >= 2\sigma(I)$]	$R_1 = 0.0930$, $wR_2 = 0.2734$
R indexes (all data)	$R_1 = 0.1173$, $wR_2 = 0.2952$
Largest diff. peak and hole(e $Å^{-3}$)	0.67 and -0.49
CCDC No.	1921824

a)



b)

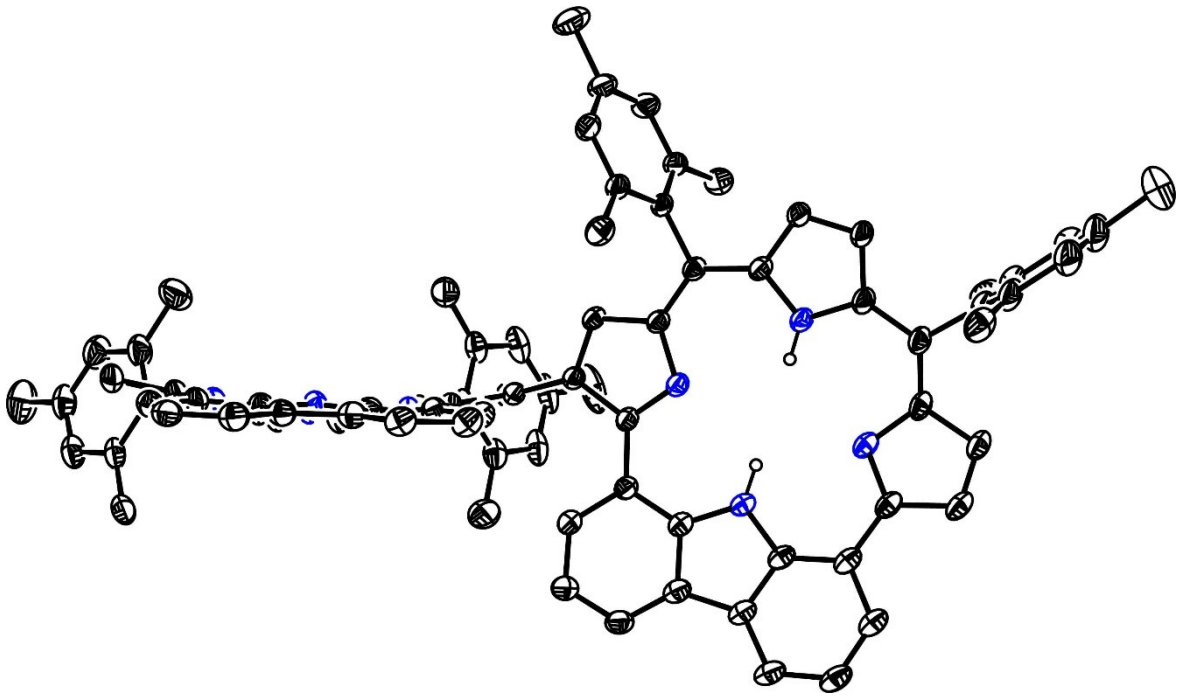


Figure S44. X-ray crystal structure of **6H**. The thermal ellipsoids are 30% probability level. (a) Top view, (b) side view. Hydrogen atoms (except hydrogen atoms of nitrogen) and *tert*-Butyl groups are omitted for clarity.

Table S5. Crystal data and structure refinement for **6Zn**

Empirical formula	$C_{108}H_{110}N_8O_2Zn_2$
Formula weight	1682.77
Temperature(K)	100.01(10)
Wavelength(Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 25.7916(8) Å α = 90°
	b = 12.9587(3) Å β = 106.236(3)°
	c = 36.5620(11) Å γ = 90°
Volume(Å^3)	11732.6(6)
Z	4
Density(calc) (Mg/cm^3)	0.953
M(mm^{-1})	0.830
F(000)	3560.0
Crystal size(mm^3)	0.3 × 0.3 × 0.06
Radiation	CuKα (λ = 1.54184)
2θ for data collection	7.14 to 133.2°
Index ranges	$-30 \le h \le 30$, $-15 \le k \le 13$, $-43 \le l \le 37$
Reflections collected	20751
Independent reflections	20751 [R(int) = 0.1037]
Data/restraints/parameters	20751/54/1114
Goodness-of-fit on F^2	0.888
Final R indexes [$I >= 2\sigma$ (I)]	R_1 = 0.0598, wR_2 = 0.1464
Final R indexes (all data)	R_1 = 0.0951, wR_2 = 0.1620
Largest diff. peak and hole(e Å^{-3})	0.83 and -0.49
CCDC No.	1921825

a)

b)

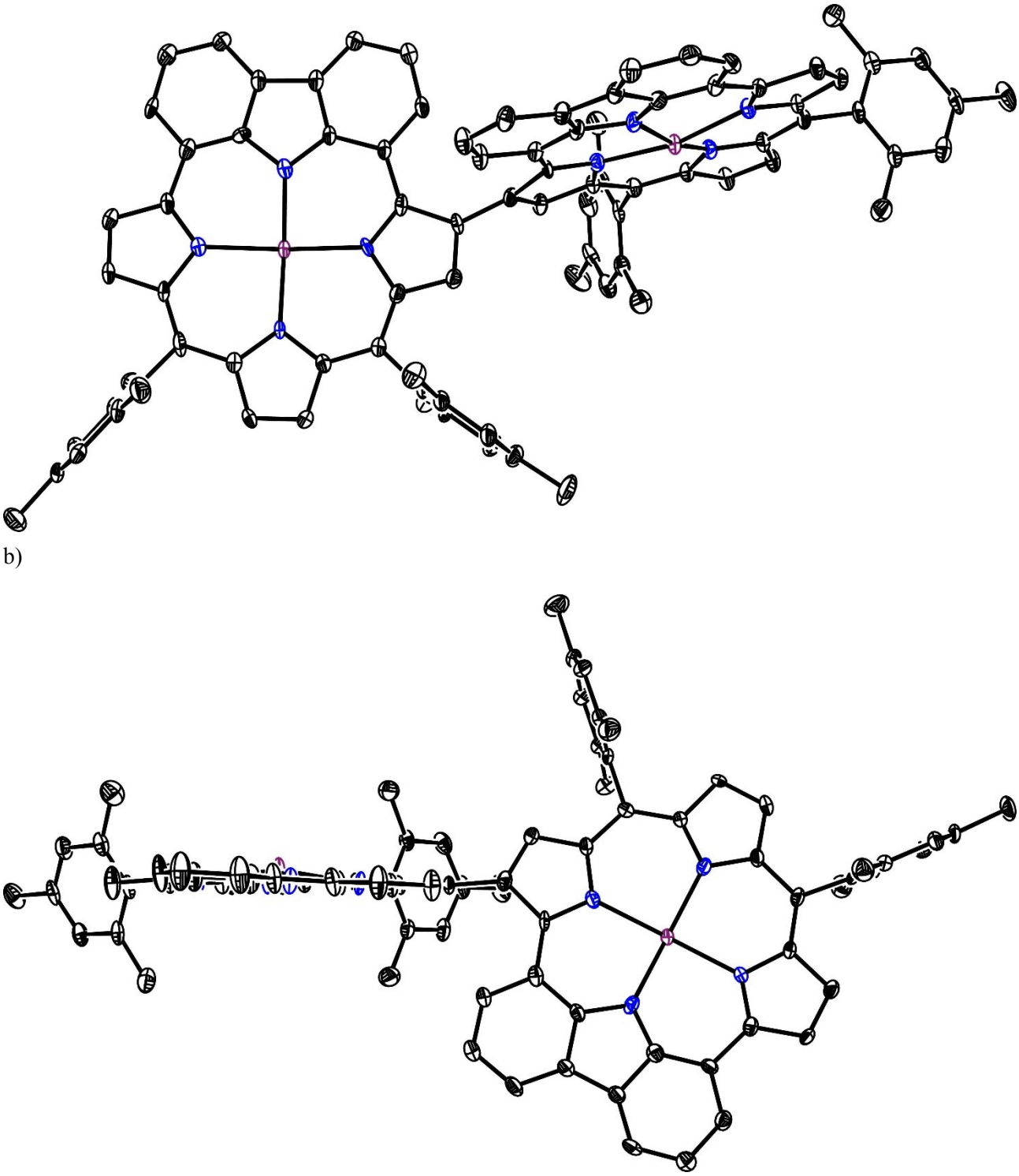


Figure S45. X-ray crystal structure of **6Zn**. (a) Top view, (b) side view. The thermal ellipsoids are 50% probability level. Hydrogen atoms, *tert*-Butyl groups, methanol and *i*-propanol coordinate to Zn are omitted for clarity.

Supporting Reference

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(3) T. Yanai, D. W. Tew, N. C. Handy, *Chem. Phys. Lett*. **2004**, *393*, 51.

(4) R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys*. **1971**, *54*, 724.