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General methods and instrumentation

Commercial reagents were used without further purification. Solvents were freshly distilled from the appropriate drying agents or purified under nitrogen with the mBraun MBSPS-800 before use. The analytical TLCs were performed with silica gel 60 F254 plates. Column chromatography was performed by using silica gel 60 (200-300 mesh ASTM). The NMR spectra were recorded on a Bruker Avance II spectrometer, operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C or a Bruker Avance II spectrometer operating at 600 MHz for ^{1}H and 150 MHz for ^{13}C. TMS was used as an internal reference for ^{1}H and ^{13}C chemical shifts and $CDCl_3$ was used as solvent. Standard pulse programs from the Bruker library were used for homo- and heteronuclear 2D experiments. Mass spectrometry measurements were conducted by using the electrospray ionization technique on Finnigan LCQ Advantage MAX mass spectrometer (APCI) or Bruker apex ultra FT-ICR (ESI). Absorption UV/Vis/NIR spectra were recorded by using a Varian Cary 50 Bio and Jasco V-770 spectrophotometers. Circular dichroism spectra were recorded by means of Jasco J-1500 spectropolarimeter. Enantiomers resolutions were performed by means of HPLC on a chiral stationary phase analytical column Chirex 3010 (25x0.46 cm) with Merck/Hitachi chromatograph equipped with an optical flow cell mounted on the Jasco CD spectrophotometer. Electrochemical measurements were performed by means of Autolab (Metrohm) potentiostat/galvanostat system for dichloromethane solutions with a glassy carbon, a platinum wire, and Ag/Ag^{+} as the working, auxiliary, and reference electrodes, respectively. Tetrabutylammonium hexafluorophosphate was used as a supporting electrolyte. The potentials were referenced with the ferrocene/ferrocenium couple used as an internal standard. X-ray diffraction data are summarized in Tables S14-S16. The structures were solved by direct methods with SHELXS97[1] and refined by the full-matrix least-squares method on all F^2 data by using the SHELXL-2016/6 incorporated in the shelXle program[1,2]. All hydrogen atoms, including those located in the difference density map, were placed in calculated positions and refined as the riding model.

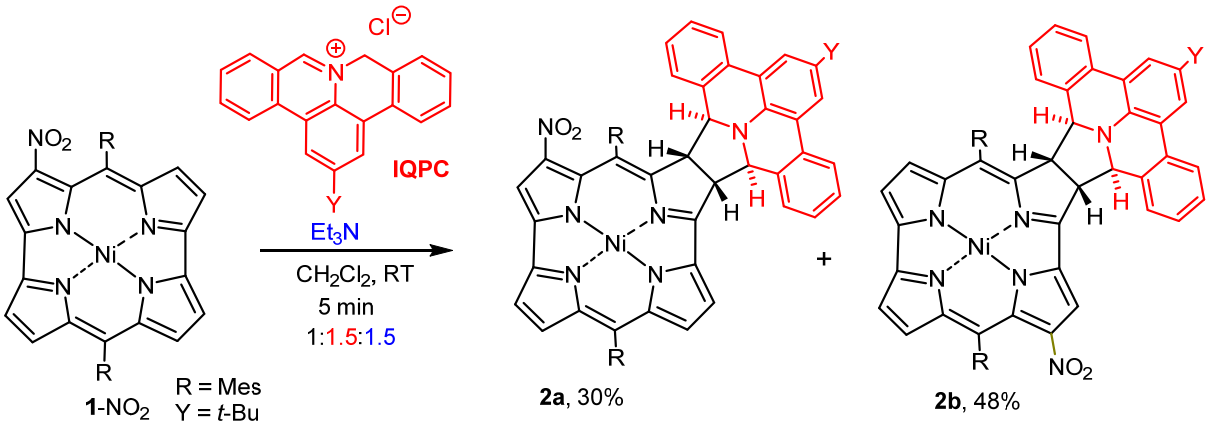
Computational methods

Density functional theory (DFT) calculations were performed by using the Gaussian 09 program[3]. DFT geometry optimizations were carried out in the unconstrained C_1 symmetry by using the X-ray structures, molecular mechanics, or semiempirical models as starting geometries. DFT geometries were refined to meet standard convergence criteria, and the existence of a local minimum was verified by a normal mode frequency calculation. DFT calculations were performed by using the hybrid B3LYP functional,[4-6] and the 6-31G(d,p) basis set. The electronic spectra were simulated by means of time-dependent density functional theory (TD-DFT) using the Tamm-Dancoff approximation for 50 states. For TD calculations, the polarizable continuum model of solvation was used (PCM, standard chloroform parametrization). The electronic transitions and UV/Vis/NIR spectra were analyzed by means of the GaussSum program.[7] The transitions were convoluted by Gaussian curves with 2000 cm^{-1} half line width. ^{1}H and ^{13}C NMR chemical shifts as well as nucleus-independent chemical shifts (NICS(–1,0,1)) were calculated by means of GIAO/B3LYP/6-31G(d,p) procedure included in the Gaussian program.

Syntheses and characterizations

Synthesis of the precursors. Starting norkorrolatonickel(II) complex **1**-H and its 3-nitro-derivative **1**-NO_2 were obtained as described previously.[8,9] Azomethine ylide (2-(*tert*-butyl)-8*H*-isoquinolino[4,3,2-*de*]phenanthridin-9-ium chloride, **IQPC** was synthesized by the literature method.[10]

Synthesis of 2a and 2b



In a 25 mL round bottom flask the 3-nitro-norcorrolatonickel(II) (**1**-NO_2, 31 mg, 0.05 mmol) and azomethine ylide (2-(*tert*-butyl)-8*H*-isoquinolino[4,3,2-*de*]phenanthridin-9-ium chloride, **IQPC**, 27 mg, 0.075 mmol) were dissolved in CH_2Cl_2 (6 mL) and triethylamine (11 μL, 0.075 mmol) was added in one shot. The reaction mixture was stirred at room temperature for several minutes until the complete consumption of **1**-NO_2. The reaction mixture was then passed through a short silica gel column with CH_2Cl_2 as eluent and all the movable fractions were collected together, then the solvent was evaporated under vacuum. The residue was purified by silica preparative thin layer plate (1 mm, 20 x 20 cm) with petroleum ether CH_2Cl_2 (*v*/*v* = 1:1.5) as eluent to afford product **2a** and **2b.**

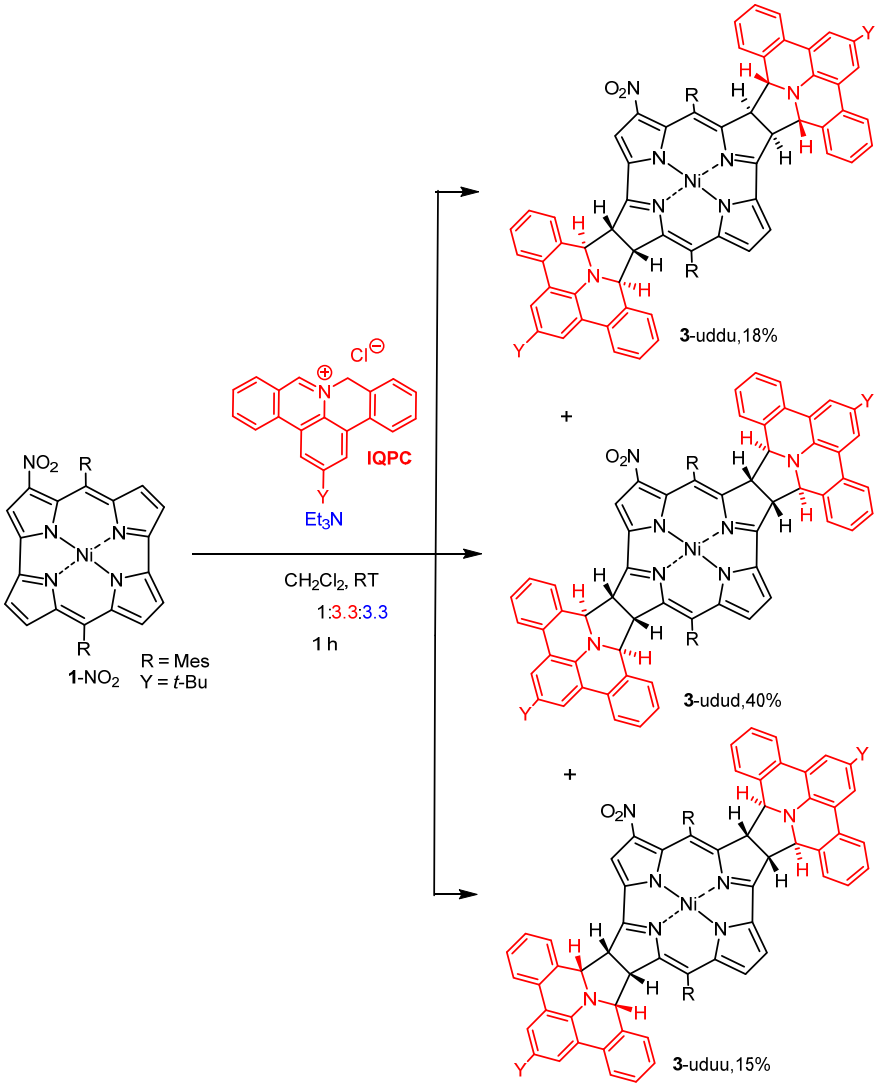
Selected data:

2a: yield 23 mg (48%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.63 (d, ^3J = 7.5 Hz, 1H, 6'), 7.56 (d, ^4J = 2.0 Hz, 1H, 9'), 7.49 (d, ^4J = 2.0 Hz, 1H, 11'), 7.27 (d, ^3J = 7.9 Hz, 1H, 14'), 7.26 (td, ^3J = 7.6 Hz, ^4J = 1.0 Hz, 1H, 5'), 7.03 (td, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 1H, 15'), 7.00 (td, ^3J = 7.6 Hz, ^4J = 1.0 Hz, 1H, 4'), 6.79 (dd, ^3J = 7.5 Hz, ^4J = 0.8 Hz, 1H, 3'), 6.71 (s, 1H, 14-*m*-Mes), 6.69 (td, ^3J = 7.5 Hz, ^4J = 1.0 Hz, 1H, 16'), 6.64 (s, 1H, 14-*m*-Mes), 6.50 (dd, ^3J = 7.6 Hz, ^4J = 0.8 Hz, 1H, 17'), 6.24 (s, 1H, 5-*m*-Mes), 6.11 (s, 1H, 5-*m*-Mes), 5.23 (s, 1H, 8-pyrr), 4.76 (d, ^3J = 4.9 Hz, 1H, 12-pyrr), 4.60 (d, ^3J = 4.9 Hz, 1H, 11-pyrr), 4.59 (d, ^3J = 4.0 Hz, 1H, 17-pyrr), 4.13 (d, ^{3}J = 4.0 Hz, 1H, 16-pyrr), 3.759 (d, ^3J = 8,6 Hz, 1H, 19'), 3.756 (d, ^3J = 8,2 Hz, 1H, 1'), 2.65 (t, ^3J = 8,2 Hz, 1H, 2), 2.61 (s, 3H, 14-*o*-Me), 2.43 (t, ^3J = 8,6 Hz, 1H, 3), 2.36 (s, 3H, 5-*o*-Me), 2.29 (s, 3H, 14-*o*-Me), 2.14 (s, 3H, 14-*p*-Me), 1.94 (s, 3H, 5-*o*-Me), 1.91 (s, 3H, 5-*p*-Me), 1.37 (s, 9H, 10'-*t*Bu). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ: 179.5, 171.5, 146.04, 145.6, 145.2, 144.5, 144.2,

144.0, 143.1, 140.2, 139.2, 138.2, 137.9, 136.1, 136.0, 135.64, 135.59, 134.9, 133.8, 130.9, 130.6, 130.1, 129.7, 129.3, 129.03, 128.95, 128.5, 128.3, 128.3, 127.57, 127.54, 127.1, 126.9, 126.8, 126.2, 122.8, 122.0, 121.4, 120.7, 120.5, 120.3, 120.0, 116.8, 64.4, 63.8, 59.1, 54.4, 34.4, 31.4, 20.88, 20.86, 20.0, 19.9, 19.7, 19.0. UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 272 (4.71), 295 (4.60), 346 (4.50), 432 (4.46), 485 (4.27). ESI-HRMS calc. for $C_{60}H_{49}N_6NiO_2^+$ $[M-H]^+$: 943.3265, Found: 943.3270.

2b: yield 14 mg (30%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.62 (d, ^3J = 8.0 Hz, 1H, 6'), 7.57 (s, 1H, 9'), 7.53 (s, 1H, 11'), 7.36 (d, ^3J = 8.0 Hz, 1H, 14'), 7.26 (t, ^3J = 7.7 Hz, 1H, 5'), 7.07 (t, ^3J = 7.5 Hz, 1H, 4'), 6.97 (t, ^3J = 7.7 Hz, 1H, 15'), 6.91 (d, ^3J = 7.7 Hz, 1H, 3'), 6.598 (s, 1H, 14-*m*-Mes), 6.592 (s, 1H, 14-*m*-Mes), 6.54 (s, 1H, 5-*m*-Mes), 6.51 (t, ^3J = 7.5 Hz, 1H, 16'), 6.28 (s, 1H, 5-*m*-Mes), 6.15 (d, ^3J = 7.7 Hz, 1H, 17'), 4.93 (s, 1H, 17-pyrr), 4.64 (d, ^3J = 5.0 Hz, 1H, 11-pyrr), 4.63 (d, ^3J = 4.0 Hz, 1H, 8-pyrr), 4.60 (d, ^3J = 5.0 Hz, 1H, 12-pyrr), 3.77 (d, ^3J = 8.0 Hz, 1H, 1'), 3.74 (d, ^3J = 8.0 Hz, 1H, 19'), 3.63 (d, ^3J = 4.0 Hz, 1H, 7-pyrr), 2.63 (s, 3H, 14-*o*-Me), 2.57 (t, ^3J = 8.0 Hz, 1H, 2), 2.45 (t, ^3J = 8.0 Hz, 1H, 3), 2.38 (s, 3H, 5-*o*-Me), 2.25 (s, 3H, 14-*o*-Me), 2.19 (s, 3H, 5-*o*-Me), 2.10 (s, 3H, 14-*p*-Me), 2.02 (s, 3H, 5-*p*-Me), 1.34 (s, 9H, 10'-*t*Bu). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ: 177.4, 172.2, 151.0, 149.1, 144.0, 141.6, 141.1, 140.6, 140.1, 139.8, 137.1, 136.9, 136.0, 135.8, 135.4, 134.8, 134.3, 130.4, 130.05, 130.03, 129.5, 129.4, 129.3, 129.2, 128.4, 128.0, 127.61, 127.55, 127.4, 127.09, 127.05, 126.9, 123.3, 122.7, 122.1, 122.0, 121.9, 121.4, 120.4, 120.2, 118.3, 117.3, 65.8, 64.8, 59.0, 54.8, 34.4, 31.4, 21.0, 20.7, 19.8, 19.7, 19.6, 19.5. UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 270 (4.62), 295 (4.53), 341 (4.44), 432 (4.27), 485 (4.22). ESI-HRMS calc. for $C_{60}H_{49}N_6NiO_2^+$ $[M-H]^+$: 943.3265, Found: 943.3274.

Synthesis of 3-uddu, 3-udud, and 3-uduu



In a 25 mL round bottom flask, **1**-NO_2 (31 mg, 0.05 mmol) and azomethine ylide **IQPC** (59 mg, 0.165 mmol) were dissolved in CH_2Cl_2 (10 mL) and triethylamine (23 μL, 0.165 mmol) was added in one shot. The reaction mixture was stirred at room temperature for one hour. Then, the reaction mixture was passed through a short silica gel column with CH_2Cl_2 as eluent and all the movable fractions were collected together, and then the solvent was evaporated under vacuum. The residue was subjected to separation on a silica preparative thin layer plate (1 mm, 20 x 20 cm) with petroleum ether/CH_2Cl_2 (*v*/*v* = 1:1.5) as eluent to afford stereomeric products **3**-uddu, **3**-udud, and **3**-uduu.

Selected data:

3-duud: yield 11 mg (18%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.692 (d, ^3J = 7.9 Hz, 1H, 6'), 7.685 (d, ^3J = 7.9 Hz, 1H, 6"), 7.64 (s, 3H, 9' + 9" + 11") 7.59 (s, 1H, 11'), 7.51 (d, ^3J = 8.0 Hz, 1H, 14"), 7.36 (m, 2H, 14' + 5"), 7.33 (t, ^3J = 7.2 Hz, 1H, 5'), 7.24 (m, 1H, 3"), 7.20 (t, ^3J = 7.2 Hz, 1H, 4"), 7.12 (d, ^3J = 7.2

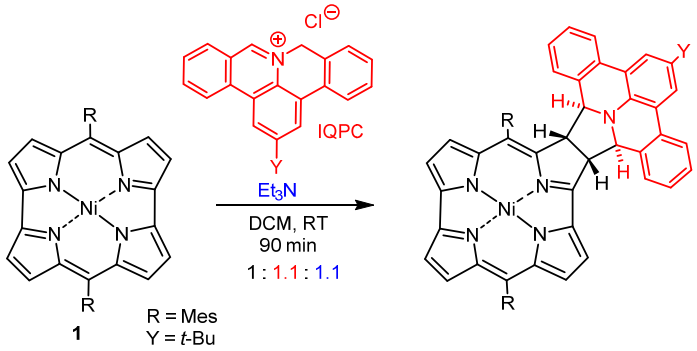
Hz, 1H, 3'), 7.08 (m, 3H, 4', 15', 15"), 6.86 (s, 1H, 5-*m*-Mes), 6.67 (t, ^{3}J = 7.5 Hz, 1H, 16'), 6.62 (s, 1H, 5-*m*-Mes), 6.50 (d, ^{3}J = 7.5 Hz, 1H, 16"), 6.43 (s, 1H, 14-*m*-Mes), 6.31 (s, 1H, 14-*m*-Mes), 6.28 (d, ^{3}J = 7.5 Hz, 1H, 17'), 5.65 (s, 1H, 8-pyrr), 5.45 (d, ^{3}J = 7.5 Hz, 1H, 17"), 5.44 (d, ^{3}J = 4.0 Hz, 1H, 17-pyrr), 4.49 (d, ^{3}J = 4.0 Hz, 1H, 16-pyrr), 4.11 (d, ^{3}J = 6.7 Hz, 1H, 19"), 4.09 (d, ^{3}J = 7.8 Hz, 1H, 1"), 4.07 (d, ^{3}J = 7.7 Hz, 1H, 1'), 3.99 (d, ^{3}J = 8.3 Hz, 1H, 19'), 3.30 (t, ^{3}J = 8.3 Hz, 2H, 2 + 11), 3.25 (d, ^{3}J = 6.7 Hz, 1H, 12), 3.15 (t, ^{3}J = 8.3 Hz, 1H, 3), 2.46 (s, 3H, 14-*o*-Me), 2.28 (s, 3H, 5-*o*-Me), 2.27 (s, 3H, 14-*p*-Me), 2.09 (s, 3H, 14-*o*-Me), 2.05 (s, 3H, 5-*p*-Me), 1.99 (s, 3H, 5-*o*-Me), 1.38 (s, 9H, 10'-*t*Bu), 1.39 (s, 9H, 10"-*t*Bu). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ: 176.4, 176.2, 148.8, 146.7, 144.0, 143.1, 142.4, 139.4, 137.8, 137.4, 137.3, 136.7, 136.5, 136.0, 135.8, 135.6, 134.9, 131.3, 131.0, 130.51, 130.47, 130.3, 129.72, 129.67, 129.6, 129.3, 129.2, 129.1, 128.5, 127.7, 127.5, 127.34, 127.32, 127.25, 126.9, 126.8, 126.7, 124.1, 124.0, 123.1, 122.8, 122.4, 122.2, 122.1, 121.9, 121.8, 121.1, 120.8, 120.3, 120.2, 120.1, 118.8, 116.9, 66.9, 66.3, 65.5, 65.0, 58.3, 58.1, 56.7, 34.5, 31.49, 31.45, 21.1, 20.39, 20.35, 20.1, 19.5. UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 273 (4.81), 295 (sh), 353 (4.56), 432 (4.38), 489 (4.17), 609(sh). ESI-HRMS calc. for $C_{84}H_{71}N_7NiO_2Na^+$ $[M+Na]^+$: 1290.4915, Found: 1290.4919.

3-ududd: yield 25 mg (40%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.77 (d, ^{3}J = 8.0 Hz, 1H, 6"), 7.74 (d, ^{3}J = 8.0 Hz, 1H, 6'), 7.71 (d, ^{4}J = 2.0 Hz, 1H, 9"), 7.65 (d, ^{4}J = 2.0 Hz, 1H, 9'), 7.57 (d, ^{4}J = 2.0 Hz, 1H, 11"), 7.50 (d, ^{4}J = 2.0 Hz, 1H, 11'), 7.41 (d, ^{3}J = 8.0 Hz, 1H, 14"), 7.36 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.0 Hz, 1H, 5"), 7.34 (td, ^{3}J = 8.0 Hz, ^{4}J = 1.0 Hz, 1H, 5'), 7.30 (d, ^{3}J = 8.0 Hz, 1H, 14'), 7.243 (t, ^{3}J = 7.5 Hz, 1H, 4"), 7.15 (m, 2H, 4' + 3"), 7.10 (m, 2H, 15' + 3'), 7.06 (t, ^{3}J = 7.7 Hz, 1H, 15"), 6.96 (d, ^{3}J = 7.6 Hz, 1H, 17"), 6.82 (m, 2H, 16' + 17'), 6.78 (t, ^{3}J = 7.6 Hz, 1H, 16"), 6.52 (s, 1H, 14-*m*-Mes), 6.38 (s, 1H, 14-*m*-Mes), 6.22 (s, 1H, 5-*m*-Mes), 6.14 (s, 1H, 5-*m*-Mes), 6.13 (s, 1H, 8-pyrr), 5.68 (d, ^{3}J = 4.0 Hz, 1H, 17-pyrr), 4.67 (d, ^{3}J = 4.0 Hz, 1H, 16-pyrr), 4.58 (m, 1H, 19"), 4.34 (d, ^{3}J = 8.0 Hz, 1H, 1"), 4.19 (d, ^{3}J = 7.8 Hz, 1H, 1'), 4.14 (m, 1H, 19'), 3.29 (t, ^{3}J = 8.0 Hz, 1H, 11), 3.25 (t, ^{3}J = 7.8 Hz, 1H, 2), 3.02 (t, ^{3}J = 8.5 Hz, 1H, 12), 2.97 (t, ^{3}J = 8.5 Hz, 1H, 3), 2.27 (s, 3H, 14-*o*-Me), 2.05 (s, 3H, 14-*p*-Me), 2.04 (s, 3H, 5-*o*-Me), 2.02 (s, 3H, 14-*o*-Me), 1.95 (s, 3H, 5-*p*-Me), 1.91 (s, 3H, 5-*o*-Me), 1.38 (s, 9H, *t*Bu), 1.37 (s, 9H, *t*Bu). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ: 174.6, 149.1, 145.7, 143.8, 143.2, 140.4, 139.0, 137.4, 137.0, 136.7, 136.6, 136.1, 135.7, 135.5, 134.8, 134.2, 131.9, 131.1, 131.0, 130.8, 130.7, 130.4, 130.3, 129.8, 129.6, 129.3, 129.1, 128.9, 128.6, 128.0, 127.7, 127.6, 127.53, 127.48, 127.3, 127.2, 127.0, 124.3, 124.1, 122.80, 122.75, 122.1, 122.3, 121.97, 121.6, 121.5, 121.4, 120.5, 120.4, 120.3, 119.9, 118.9, 117.1, 67.4, 67.2, 65.4, 64.6, 59.7, 58.7, 55.0, 54.5, 34.5, 34.4, 31.47, 31.44, 21.0, 20.91, 20.86, 20.7, 20.4, 19.7. UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 273 (4.86), 295 (sh), 352 (4.63), 429 (4.35), 484 (sh). ESI-HRMS calc. for $C_{84}H_{70}N_7NiO_2^+$ $[M-H]^+$: 1266.4939, Found: 1266.4957.

3-uduu: yield 9 mg (15%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.43 (s, 1H, 11"), 7.96 (s, 1H, 9"), 7.85 (d, ^{3}J = 7.8 Hz, 1H, 14"), 7.69 (d, ^{3}J = 8.0 Hz, 1H, 6'), 7.65 (d, ^{3}J = 7.8 Hz, 1H, 6"), 7.59 (s, 1H, 9'), 7.49 (s,

1H, 11'), 7.43 (t, ^{3}J = 7.6 Hz, 1H, 15"), 7.31 (m, 3H, 5' + 14' + 5"), 7.23 (t, ^{3}J = 7.6 Hz, 1H, 4"), 7.12 (m, 3H, 15' + 3" + 4'), 7.04 (d, ^{3}J = 7.8 Hz, 1H, 3'), 7.02 (t, ^{3}J = 7.5 Hz, 1H, 16"), 6.91 (t, ^{3}J = 7.5 Hz, 16'), 6.78 (s, 1H, 14-*m*-Mes), 6.77 (d, 1H, 17'), 6,50 (s, 1H, 14-*m*-Mes), 6.21 (d, ^{3}J = 7.8 Hz, 1H, 17"), 6.17 (s, 2H, 5-*m*-Mes), 5.53 (d, ^{3}J = 4.0 Hz, 1H, 17-pyrr), 4.68 (s, 1H, 8-pyrr), 4.55 (d, ^{3}J = 4.0 Hz, 1H, 16-pyrr), 4.27 (d, ^{3}J = 6.5 Hz, 1H, 1"), 4.18 (d, ^{3}J = 8.2 Hz, 1H, 19"), 3.97 (d, ^{3}J = 7.7 Hz, 1H, 1'), 3.72 (d, ^{3}J = 9.0 Hz, 1H, 19'), 3.37 (t, ^{3}J = 6.5 Hz, 1H, 11), 3.19 (t, ^{3}J = 7.8 Hz, 1H, 12), 3.12 (t, ^{3}J = 7.8 Hz, 1H, 2), 2.86 (t, ^{3}J = 8.7 Hz, 1H, 3), 2.25 (s, 15H, 14-*o*-Me + 14-*p*-Me + 10"-*t*Bu), 2.15 (s, 3H, 5-*o*-Me), 1.95 (s, 3H, 5-*p*-Me), 1.76 (s, 3H, 5-*o*-Me), 1.35 (s, 9H, 10'-*t*Bu), 1.11 (s, 3H, 14-*o*-Me). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ: 174.4, 174.1, 148.1, 145.5, 144.4, 143.8, 142.1, 141.2, 139.8, 138.7, 138.0, 137.1, 136.7, 136.4, 136.1, 135.3, 135.2, 134.7, 134.6, 133.1, 132.6, 131.7, 131.3, 130.5, 130.4, 130.1, 129.8, 129.7, 129.4, 129.0, 128.8, 128.6, 128.3, 128.2, 128.1, 127.8, 127.6, 127.5, 127.4, 127.2, 127.2, 127.1, 126.6, 123.9, 123.7, 123.3, 122.77, 122.76, 122.72, 122.6, 122.15, 122.08, 121.7, 121.4, 120.4, 120.0, 119.0, 118.5, 116.4, 67.5, 67.1, 64.7, 63.8, 58.8, 58.6, 54.7, 50.7, 35.5, 34.4, 32.6, 31.4, 21.0, 20.9, 20.2, 19.9, 19.5. UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 273 (4.83), 295 (4.60), 354 (4.54), 432 (4.31), 482 (4.16). ESI-HRMS calc. for $C_{84}H_{71}N_7NiO_2Na^+$ $[M+Na]^+$: 1290.4915, Found: 1290.4896.

Synthesis of 4



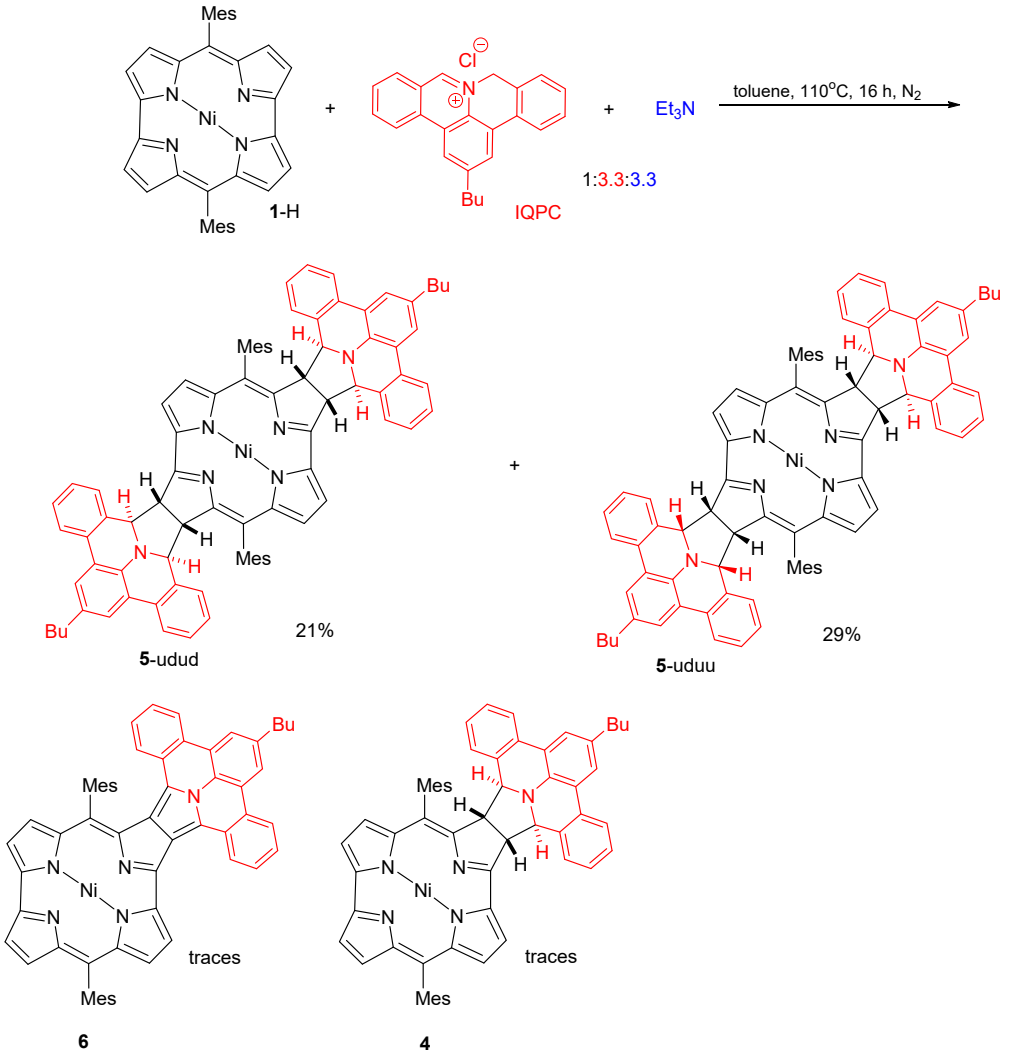
In a 25 mL round bottom flask the norcorrolatonickel(II) (**1**, 31 mg, 0.05 mmol) and azomethine ylide (2-(*tert*-butyl)-8*H*-isoquinolino[4,3,2-*de*]phenanthridin-9-ium chloride, **IQPC**, 20 mg, 0.055 mmol) were dissolved in CH_2Cl_2 (6 mL) and triethylamine (8 μL, 0.055 mmol) was added in one shot. The reaction mixture was stirred at room temperature for 90 minutes. The reaction mixture was then passed through a short silica gel column with CH_2Cl_2 as eluent and all the movable fractions were collected together, then the solvent was evaporated under vacuum. The residue was purified by silica preparative thin layer plate (1 mm, 20 x 20 cm) with petroleum ether CH_2Cl_2 (*v*/*v* = 1:1.5) as eluent to afford product **4.**

Selected data:

4: yield 22 mg (50%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.53 (d, ^3J = 7.8 Hz, 1H, 6'), 7.48 (d, ^4J = 1.5 Hz, 1H, 9'), 7.44 (d, ^4J = 1.5 Hz, 1H, 11'), 7.25 (m, 1H, 14'), 7.14 (td, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 1H, 5'), 6.89 (td, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 1H, 15'), 6.86 (td, ^3J = 7.5 Hz, ^4J = 1.0 Hz, 1H, 4'), 6.61 (m, 1H, 3'), 6.60 (s, 1H, 14-*m*-Mes), 6.47 (m, 2H, 16' + 14-*m*-Mes), 6.33 (s, 1H, 5-*m*-Mes), 6.19 (s, 1H, 5-*m*-Mes), 6.15 (d, ^3J = 7.8 Hz, 1H, 17'), 3.81 (d, ^3J = 4.9 Hz, 1H, 12-pyrr), 3.77 (d, ^3J = 3.9 Hz, 1H, 8-pyrr), 3.72 (d, ^3J = 4.9 Hz, 1H, 11-pyrr), 3.67 (d, ^3J = 3.9 Hz, 1H, 17-pyrr), 3.36 (d, ^3J = 8.4 Hz, 1H, 19'), 3.34 (d, ^3J = 8,4 Hz, 1H, 1'), 3.15 (d, ^3J = 3.9 Hz, 1H, 16-pyrr), 2.93 (s, 3H, 14-*o*-Me), 2.81 (d, ^3J = 3.9 Hz, 1H, 7-pyrr), 2.39 (s, 3H, 5-*o*-Me), 2.28 (s, 3H, 5-*o*-Me), 2.21 (s, 3H, 14-*o*-Me), 2.03 (s, 3H, 14-*p*-Me), 1.98 (t, ^3J = 8,5 Hz, 1H, 2), 1.91 (s, 3H, 5-*p*-Me), 1.79 (t, ^3J = 8,5 Hz, 1H, 3), 1.31 (s, 9H, 10'-*t*Bu). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ: 175.7, 173.3, 150.2, 147.8, 147.0, 146.0, 143.4, 141.8, 140.9, 139.2, 138.3, 137.0, 136.09, 136.07, 135.7, 135.4, 134.8, 134.3, 130.8, 130.3, 129.6, 129.11, 129.06, 128.7, 128.4, 128.1, 128.0, 127.2, 127.0, 126.94, 126.85, 126.7, 126.6, 122.3, 121.9, 121.6, 121.3, 121.2, 120.1, 120.0, 119.5, 119.1, 117.6, 116.1, 65.2, 63.8, 57.6, 53.3, 34.4, 31.4, 20.8, 20.6, 19.54, 19.45. UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 269 (4.53), 293 (sh), 317 (4.34), 342 (sh), 389 (4.31), 428 (4.36), 464 (sh), 518 (3.82), 553 (sh), 613 (3.34), 646 (sh), 681 (sh), 811 (3.15). ESI-HRMS calc. for $C_{60}H_{51}N_5NiNa^+$ $[M+Na]^+$: 922.3390, Found: 922.3409.

Due to retro-cycloaddition reaction, the spectra indicate the presence of starting norcorrole **1** in the amount up to 20% appearing shortly after dissolving an analytically (TLC) pure sample.

Synthesis of 5-uduu and 5-udud



In a 50 mL round bottom flask the norcorrole **1**-H (87 mg, 0.15 mmol) and azomethine ylide (177 mg, 0.50 mmol) were dissolved in toluene (30 mL) and triethylamine (69 μL, 0.50 mmol) was added in one shot. The reaction was stirred at 110°C for 16 h under the blanked of N_2. After that, the reaction mixture was passed through a short silica gel column with CH_2Cl_2:MeOH (99:1 v/v) as eluent and all the movable fraction was collected together, then the solvent was evaporated under vacuum. The components of the residue were separated by silica preparative thin layer plate (1 mm, 20 x 20 cm) with petroleum ether/CH_2Cl_2 (*v*/*v* = 1.5:1) as eluent to afford product **5**-uduu, **5**-udud, and traces of **4** and **6** in an order: first yellow band, norcorrole **1**-H; second purple band, **6**; third green band, **4**; forth yellow band, **5**-uduu; fifth brown band, **5**-udud.

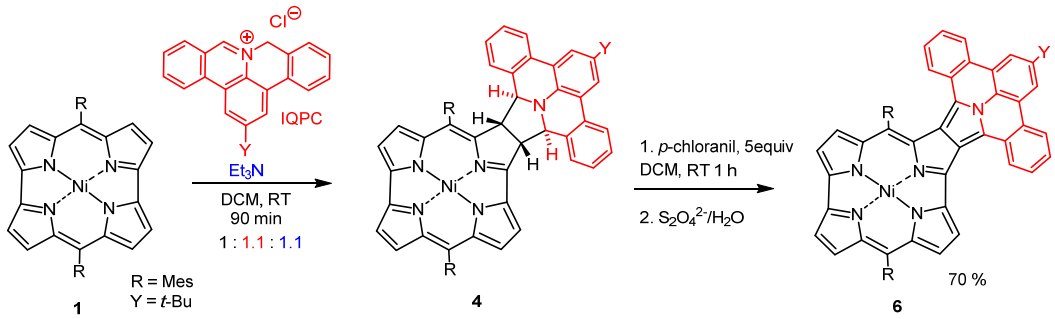
Selected data:

5-uduu: yield (53 mg) 29%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.66 (d, ^4J = 2.0 Hz, 1H, 11”), 7.97 (d, ^4J = 2.0 Hz, 1H, 9”), 7.95 (d, ^3J = 7.8 Hz, 1H, 14”), 7.64 (d, ^3J = 7.8 Hz, 1H, 6’), 7.58 (d, ^3J = 8.0 Hz, 1H, 6”), 7.56 (d, ^4J = 2.0 Hz, 1H, 9’), 7.49 (d, ^4J = 2.0 Hz, 1H, 11’), 7.42 (td, ^3J = 7.5 Hz, ^4J = 1.0 Hz, 1H, 15”), 7.33

(d, ^{3}J = 7.5 Hz, 1H, 14'), 7.24 (m, 1H, 5'), 7.15 (td, ^{3}J = 7.5, ^{4}J = 1.0 Hz, 1H, 5"), 7.07 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.0 Hz, 1H, 4"), 7.02 (m, 3H, 3" + 4' + 15'), 6.95 (m, 2H, 3' + 16"), 6.73 (s, 1H, 14-*m*-Mes), 6.70 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.0 Hz, 1H, 16'), 6.57 (d, ^{3}J = 7.5 Hz, 1H, 17'), 6.45 (s, 1H, 14-*m*-Mes), 6.42 (s, 1H, 5-*m*-Mes), 6.23 (s, 1H, 5-*m*-Mes), 6.11 (d, ^{3}J = 7.0 Hz, 1H, 17"), 5.08 (d, ^{3}J = 3.9 Hz, 1H, 17-pyrr), 4.12 (d, ^{3}J = 3.9 Hz, 1H, 16-pyrr), 4.07 (d, ^{3}J = 6.3 Hz, 1H, 1"), 4.04 (d, ^{3}J = 8.5 Hz, 1H, 19"), 3.78 (d, ^{3}J = 8.5 Hz, 1H, 1'), 3.77 (d, ^{3}J = 3.9 Hz, 1H, 7-pyrr), 3.67 (d, ^{3}J = 3.9 Hz , 1H, 8-pyrr), 3.64 (d, ^{3}J = 8.5 Hz, 1H, 19'), 3.09 (t, ^{3}J = 6.3 Hz, 1H, 11), 2.85 (dd, ^{3}J = 8.5, 6.5 Hz, 1H, 12), 2.80 (t, J = 8.3 Hz, 1H, 2), 2.52 (t, ^{3}J = 8.3 Hz, 1H, 3), 2.40 (s, 9H, 10"-*t*Bu), 2.38 (s, 3H, 14-*o*-Me), 2.23 (s, 3H, 5-*o*-Me), 2.21 (s, 3H, 14-*p*-Me), 1.98 (s, 3H, 5-*p*-Me), 1.91 (s, 3H, 5-*o*-Me), 1.33 (s, 9H, 10'-*t*Bu), 1.07 (s, 3H, 14-*o*-Me). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ: 171.7, 170.6, 147.9, 145.2, 143.2, 143.1, 139.9, 139.7, 139.1, 138.8, 137.4, 136.6, 136.4, 136.0, 135.7, 135.1, 134.4, 133.6, 132.9, 131.7, 131.3, 130.9, 130.39, 130.36, 130.2, 129.6, 129.4, 128.9, 128.7, 128.6, 128.4, 128.0, 127.8, 127.7, 127.6, 127.5, 127.2, 126.9, 126.8, 126.6, 126.5, 123.2, 122.7, 122.4, 122.0, 121.7, 121.3, 120.5, 120.1, 119.6, 115.0, 114.2, 66.9, 65.0, 64.3, 63.4, 57.7, 57.0, 54.2, 50.8, 35.6, 34.4, 32.7, 31.5, 29.7, 21.0, 20.7, 20.5, 20.1, 19.6, 19.3. UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 274 (4.71), 295 (4.49), 347 (4.44), 381 (4.42), 401 (4.41), 519 (3.60). ESI-HRMS calc. for $C_{84}H_{72}N_6Ni^+$ $[M]^+$: 1222.5166, Found: 1222.5127 and for $C_{84}H_{73}N_6Ni^+$ $[M+H]^+$: 1223.5245, Found: 1223.5165.

5-udud: yield 38 mg (21%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.68 (d, ^{3}J = 8.0 Hz, 2H, 6' + 6"), 7.71 (d, ^{4}J = 2.0 Hz, 2H, 9' + 9"), 7.53 (d, ^{4}J = 2.0 Hz, 2H, 11' + 11"), 7.36 (d, ^{3}J = 8.0 Hz, 2H, 14' + 14"), 7.28 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.5 Hz, 2H, 5' + 5"), 7.08 (td, ^{3}J = 7.2 Hz, ^{4}J = 0.8 Hz, 2H, 4' + 4"), 7.04 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.3 Hz, 2H, 3' + 3"), 7.01 (td, ^{3}J = 7.6 Hz, ^{4}J = 1.3 Hz, 2H, 15' + 15"), 6.70 (td, ^{3}J = 7.5 Hz, ^{4}J = 0.9 Hz, 2H, 16' + 16"), 6.64 (d, ^{3}J = 7.5 Hz, 2H, 17' + 17"), 6.49 (s, 2H, 14-*m*-Mes), 6.30 (s, 2H, 5-*m*-Mes), 5.17 (d, ^{3}J = 4.0 Hz, 2H, 8,17-pyrr), 4.20 (d, ^{3}J = 4.0 Hz, 2H, 7,16-pyrr), 3.99 (d, ^{3}J = 7.4 Hz, 2H, 1' + 1"), 3.97 (d, ^{3}J = 8.8 Hz, 2H, 19' + 19"), 2.94 (t, ^{3}J = 8.4 Hz, 2H, 2 + 11), 2.68 (t, ^{3}J = 8.5 Hz, 2H, 3 + 12), 2.32 (s, 6H, 14-*o*-Me), 2.06 (s, 6H, 5-*o*-Me), 2.01 (s, 6H, 5-p-Me + 14-p-Me), 1.35 (s, 18H, 10'-*t*Bu). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 171.4, 150.6, 143.3, 141.5, 137.6, 136.9, 136.5, 136.0, 134.6, 131.7, 131.2, 130.9, 130.5, 129.4, 129.1, 128.7, 127.8, 127.5, 127.4, 127.2, 126.9, 126.8, 124.0, 122.4, 122.1, 121.7, 121.3, 120.2, 119.9, 115.8, 66.7, 65.2, 57.7, 54.6, 34.4, 31.5, 20.7, 20.6, 19.8. UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 274 (4.81), 295 (4.63), 355 (4.57), 378 (4.61), 395 (4.59), 519 (3.64). ESI-HRMS calc. for $C_{84}H_{72}N_6Ni^+$ $[M]^+$: 1222.5166, Found: 1222.5205 and for $C_{84}H_{73}N_6Ni^+$ $[M+H]^+$: 1223.5245, Found: 1223.5254.

Synthesis of 6

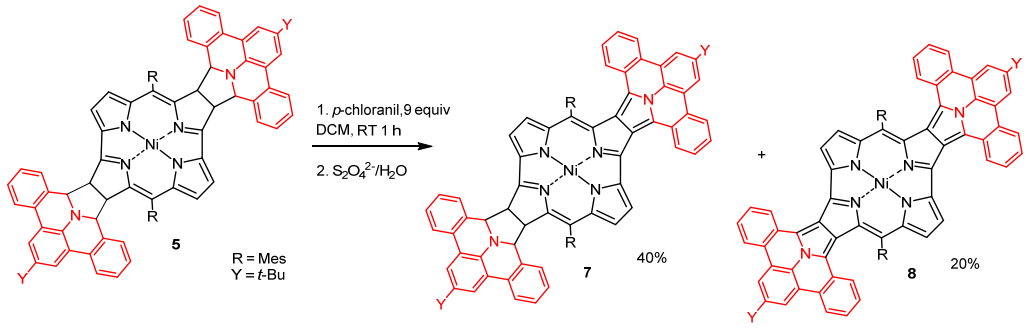


In a 25 mL round bottom flask the norcorrolatonickel(II) (**1**, 31 mg, 0.05 mmol) and azomethine ylide (2-(*tert*-butyl)-8*H*-isoquinolino[4,3,2-*de*]phenanthridin-9-ium chloride, **IQPC** 20 mg, 0.055 mmol) were dissolved in CH_2Cl_2 (6 mL) and triethylamine (8 μL, 0.055 mmol) was added in one shot. The reaction mixture was stirred at room temperature for 90 minutes. After that time, *p*-chloranil (63 mg, 0.25 mmol) was added and the stirring was continued for one hour. Then, 50 mg of zinc and 5 mL of saturated aqueous $Na_2S_2O_4$ solution were added and allowed to contact with the organic layer for about 20 minutes by vigorous stirring. Water layer was then removed by pipette and organic layer was washed by several 5-mL-portions of water. The organic layer was separated, dried with anhydrous sodium sulfate and filtered with a cotton pad. The components of the filtrate was separated by silica preparative thin layer plate (1 mm, 20 x 20 cm) with hexane/CH_2Cl_2 (*v*/*v* = 1.5:1) as eluent to afford product **6.**

Selected data:

6: yield 31 mg (70%) ^{1}H NMR (500MHz, $CDCl_3$, 298 K) δ: 7.95 (d, ^3J = 7.8 Hz, 1H, 6'), 7.94 (s, 1H, 9'), 7.90 (d, ^4J = 1.5 Hz, 1H, 11'), 7.71 (d, ^3J = 7.5 Hz, 1H, 14'), 7.26 (t, ^3J = 7.5 Hz, 1H, 5'), 6.97 (m, 2H, 15' + 4'), 6.48 (s, 2H, 14-*m*-Mes), 6.315 (s, 2H, 5-*m*-Mes), 6.30 (m, 2H, 16' + 3'), 5.38 (d, ^3J = 8.0 Hz, 1H, 17'), 3.70 (d, ^3J = 4.0 Hz, 1 H, 17-pyrr), 3.30 (d, ^3J = 4.8 Hz, 1 H, 12-pyrr), 3.14 (d, ^3J = 4.8 Hz, 1 H, 11-pyrr), 3.07 (d, ^3J = 3.7 Hz, 1 H, 8-pyrr), 2.83 (d, ^3J = 4.0 Hz, 1 H, 16-pyrr), 2.71 (s, 6H, 14-*o*-Me), 2.41 (s, 6H, 5-*o*-Me), 2.38 (d, ^3J = 3.7 Hz, 1 H, 7-pyrr), 1.99 (s, 3H, 14-*p*-Me), 1.90 (5-*p*-Me), 1.37 (s, 9H, 10'-*t*Bu). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 174.3, 166.9, 150.4, 148.9, 147.5, 146.8, 145.6, 137.8, 137.1, 136.8, 136.2, 131.1, 128.9, 128.0, 127.9, 127.6, 127.3, 126.2, 126.1, 126.0, 123.6, 123.3, 123.2, 122.9, 122.5, 122.1, 121.4, 121.1, 120.4, 119.9, 119.5, 118.7, 118.7, 118.3, 117.8, 117.0, 116.0, 37.1, 31.9, 31.5, 22.7, 20.73, 20.69, 19.1, 18.5, 14.1. UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 255 (4.64), 285 (4.47), 320 (4.37), 354 (4.31), 432 (4.24), 490 (4.19), 520 (4.25), 621 (4.01), 661 (4.01). ESI-HRMS calc. for $C_{60}H_{47}N_5Ni^+$ $[M]^+$: 895.3179, Found: 895.3179.

Synthesis of 7 and 8



In a 25 mL round bottom flask a mixture of stereomers of **5** (40 mg, 0.033 mmol) and *p*-chloranil (75 mg, 0.300 mmol) were dissolved in 5 mL of dichloromethane. The reaction mixture was stirred at room temperature for 1 h. Then, 50 mg of zinc and 5 mL of saturated aqueous $Na_2S_2O_4$ solution were added and allowed to contact with the organic layer for about 20 minutes by vigorous stirring. Water layer was then removed by pipette and organic layer was washed by several 5-mL-portions of water. The organic layer was separated, dried with anhydrous sodium sulfate and filtered with a cotton pad. The components of the filtrate was separated by silica preparative thin layer plate (1 mm, 20 x 20 cm) with hexane/CH_2Cl_2 (*v*/*v* = 1.5:1) as eluent giving rise to a blue-purple band containing product **7** and a green band of product **8**. The bands were then removed from the plate and extracted with dichloromethane, filtered by a cotton pad and crystallized with hexane.

Selected data:

7: yield 16 mg (40%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8,103 (d, 1H, 6”), 8,097 (s, 1H, 9”), 8,05 (d, ^4J = 1,4 Hz, 1H, 11”), 7,85 (d, ^3J = 8.0 Hz, 1H, 14”), 7,64 (d, ^3J = 7.8 Hz, 1H, 6’), 7,57 (d, ^4J = 2.0 Hz, 1H, 9’), 7,50 (d, ^4J = 2.0 Hz, 1H, 11’), 7,43 (d, ^3J = 8.0 Hz, 1H, 3”), 7,38 (d, ^3J = 7.8 Hz, 1H, 5”), 7,34 (d, ^3J = 8.0 Hz, 1H, 14’), 7,23 (m, 2H, 5’ + 4”), 7,06 (td, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H, 15”), 7,02 (t, ^3J = 7.5 Hz, 1H, 4’), 6,99 (t, ^3J = 7.8 Hz, 1H, 15’), 6,92 (d, ^3J = 7.5 Hz, 1H, 3’), 6,76 (s, 1H, 14-*m*-Mes), 6,66 (t, ^3J = 7.5 Hz, 1H, 16’), 6,51 (d, ^3J = 7.5 Hz, 1H, 17’), 6,48 (t, ^3J = 7.5 Hz, 1H, 16”), 6,47 (s, 1H, 5-*m*-Mes), 6,30 (s, 1H, 5-*m*-Mes), 6,24 (s, 1H, 14-*m*-Mes), 6,02 (d, ^3J = 8.0 Hz, 1H, 17”), 5,44 (d, ^3J = 4.0 Hz, 1H, 8-pyrr), 4,66 (d, ^3J = 4.0 Hz, 1H, 17-pyrr), 3,91 (d, ^3J = 4.0 Hz, 1H, 7-pyrr), 3,84 (d, ^3J = 4.0 Hz, 1H, 16-pyrr), 3,76 (d, ^3J = 8.5 Hz, 1H, 1’), 3,74 (d, ^3J = 8.5 Hz, 1H, 19’), 2,64 (t, ^3J = 8.5 Hz, 1H, 2), 2,380 (s, 3H, 5-*o*-Me), 2,377 (m, 1H, 3), 2,35 (s, 3H, 14-*o*-Me), 2,23 (s, 3H, 5-*o*-Me), 2,18 (s, 3H, 14-*o*-Me), 2,04 (s, 3H, 14-*p*-Me), 2,01 (s, 3H, 5-*p*-Me), 1,43 (s, 9H, 10”-*t*Bu), 1,35 (s, 9H, 10’-*t*Bu). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 172.6, 163.4, 149.8, 149.5, 147.3, 143.3, 140.1, 138.8, 138.3, 137.1, 136.5, 136.4, 136.2, 135.9, 134.7, 133.0, 131.6, 131.0, 130.9, 130.5, 129.3, 129.14, 129.07, 128.6, 128.4, 128.1, 127.9, 127.6, 127.5, 127.4, 127.2, 127.1, 126.8, 126.7, 126.4, 126.34, 126.27, 126.0, 125.4, 123.8, 123.7, 122.8, 122.5, 122.3, 122.2, 122.0, 121.7, 121.6, 121.5, 121.3, 121.2, 121.02, 120.98, 120.2, 120.1, 119.3, 118.3, 117.9,

117.0, 115.3, 66.1, 64.7, 57.5, 54.1, 35.1, 34.4, 31.6, 31.5, 20.8, 20.7, 20.1, 19.9, 19.8, 19.7. UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 255 (4.95), 273 (4.86), 341 (4.69), 400 (4.52), 427 (4.43), 565 (4.41), 600 (4.42), 680 (3.67). ESI-HRMS calc. for $C_{84}H_{68}N_6Ni^+$ $[M]^+$: 1218.4853, Found: 1218.4795 and for $C_{84}H_{69}N_6Ni^+$ $[M+H]^+$: 1219.4932, Found: 1219.4862.

8: yield 8 mg (20%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.08 (s, 2H, 9' + 9"), 8.07 (d, 2H, 6' + 6"), 8.03 (d, ^4J = 1.6 Hz, 2H, 11' + 11"), 7.82 (d, ^3J = 8.1 Hz, 2H, 14' + 14"), 7.32 (m, 2H, 5' + 5"), 7.13 (m, 4H, 4' + 4" + 3' + 3"), 7.00 (td, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 2H, 15' + 15"), 6.47 (s, 4H, 5-*m*-Mes + 14-*m*-Mes), 6.40 (t, ^3J = 7.5 Hz, 2H, 16' + 16"), 5.89 (dd, ^3J = 8.2 Hz, ^4J = 1.1 Hz, 2H, 17' + 17"), 4.92 (d, ^3J = 4.0 Hz, 2H, pyrr), 3.63 (d, ^3J = 4.0 Hz, 2H, pyrr), 2.36 (s, 12H, 5-*o*-Me + 14-*o*-Me), 2.01 (s, 6H, 5-*p*-Me + 14-*p*-Me), 1.42 (s, 18H, 10'-*t*Bu). UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 307 (4.41), 341 (4.03), 427 (3.83), 472 (sh), 499 (sh), 612 (sh), 672 (3.95), 807 (sh), 896 (sh). ESI-HRMS calc. for $C_{84}H_{64}N_6Ni^+$ $[M]^+$: 1215.4619, Found: 1215.4589 and for $C_{84}H_{65}N_6Ni^+$ $[M+H]^+$: 1214.4540, Found: 1214.4555.

Due to a spontaneous precipitation of the compound, we were unable to record a ^{13}C NMR spectrum.

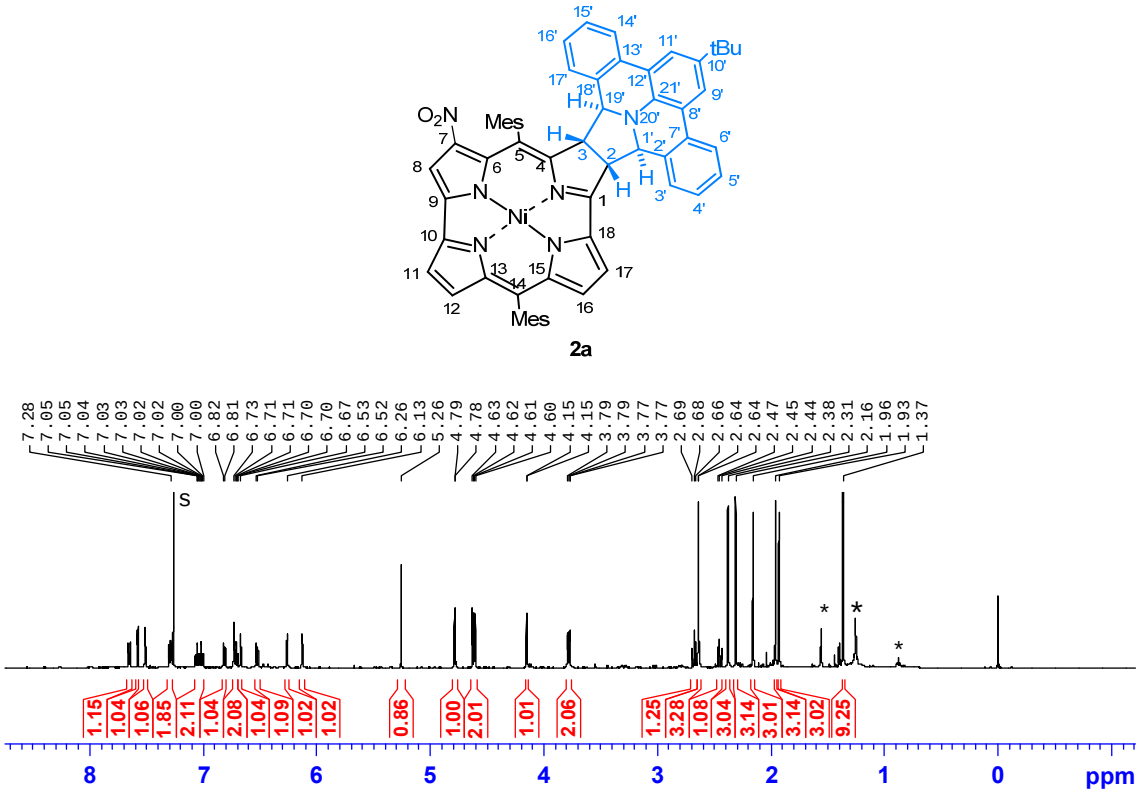


Figure S1. ^{1}H NMR spectrum of **2a** (500 MHz, 298 K, $CDCl_3$).

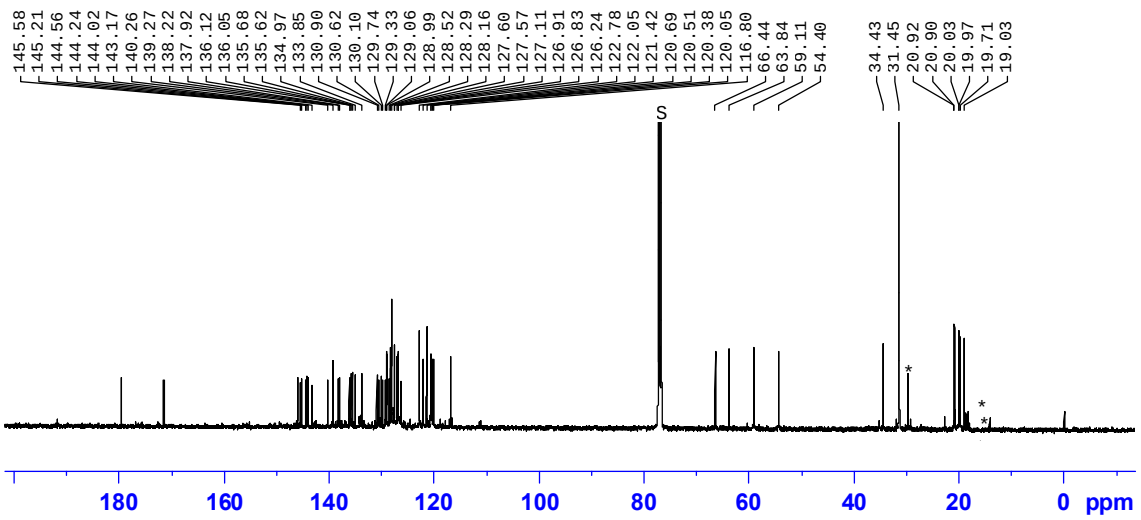


Figure S2. ^{13}C NMR spectrum of **2a** (125 MHz, 298 K, $CDCl_3$).

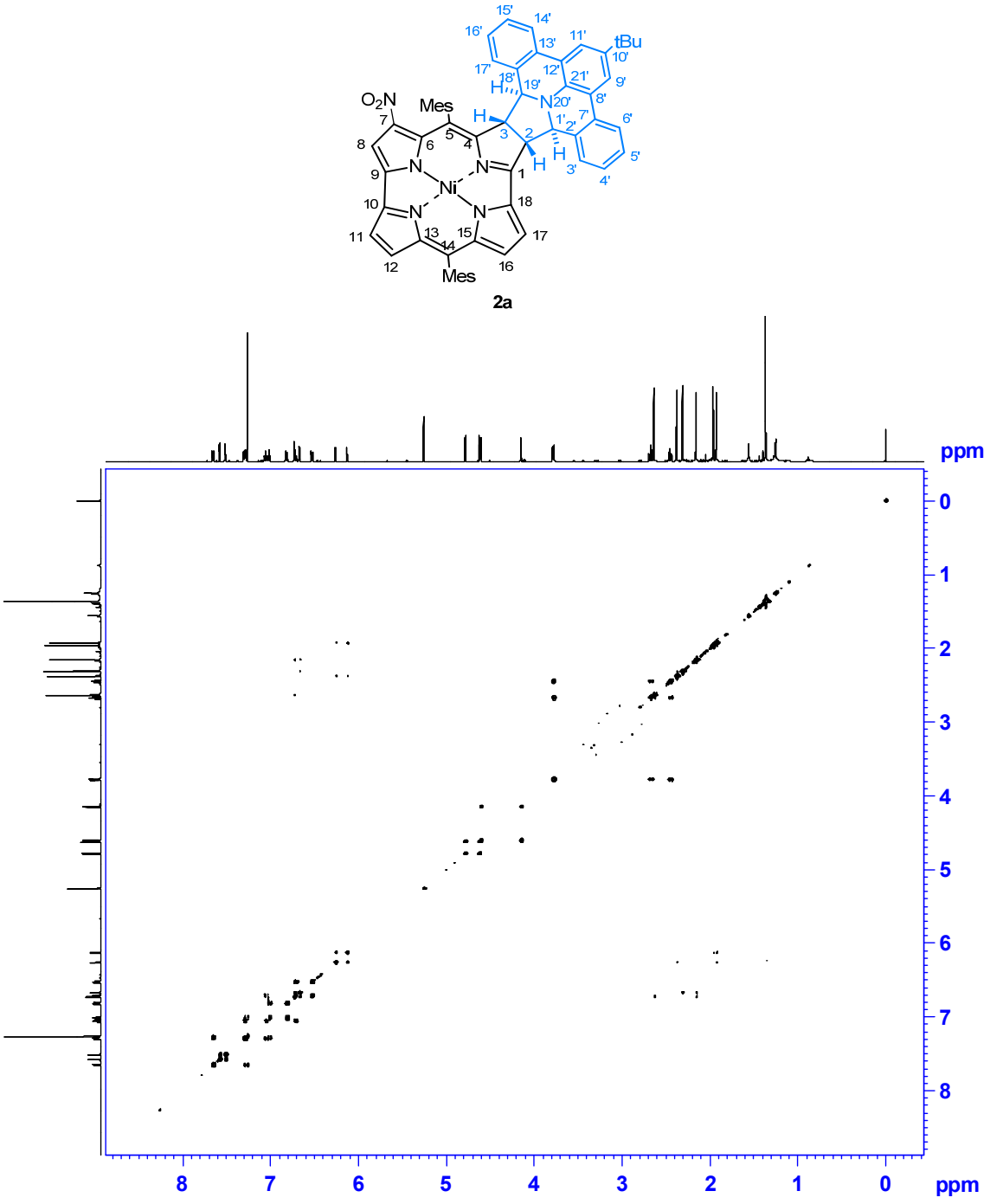


Figure S3. ^{1}H, ^{1}H COSY spectrum of **2a** (500 MHz, 298 K, $CDCl_3$).

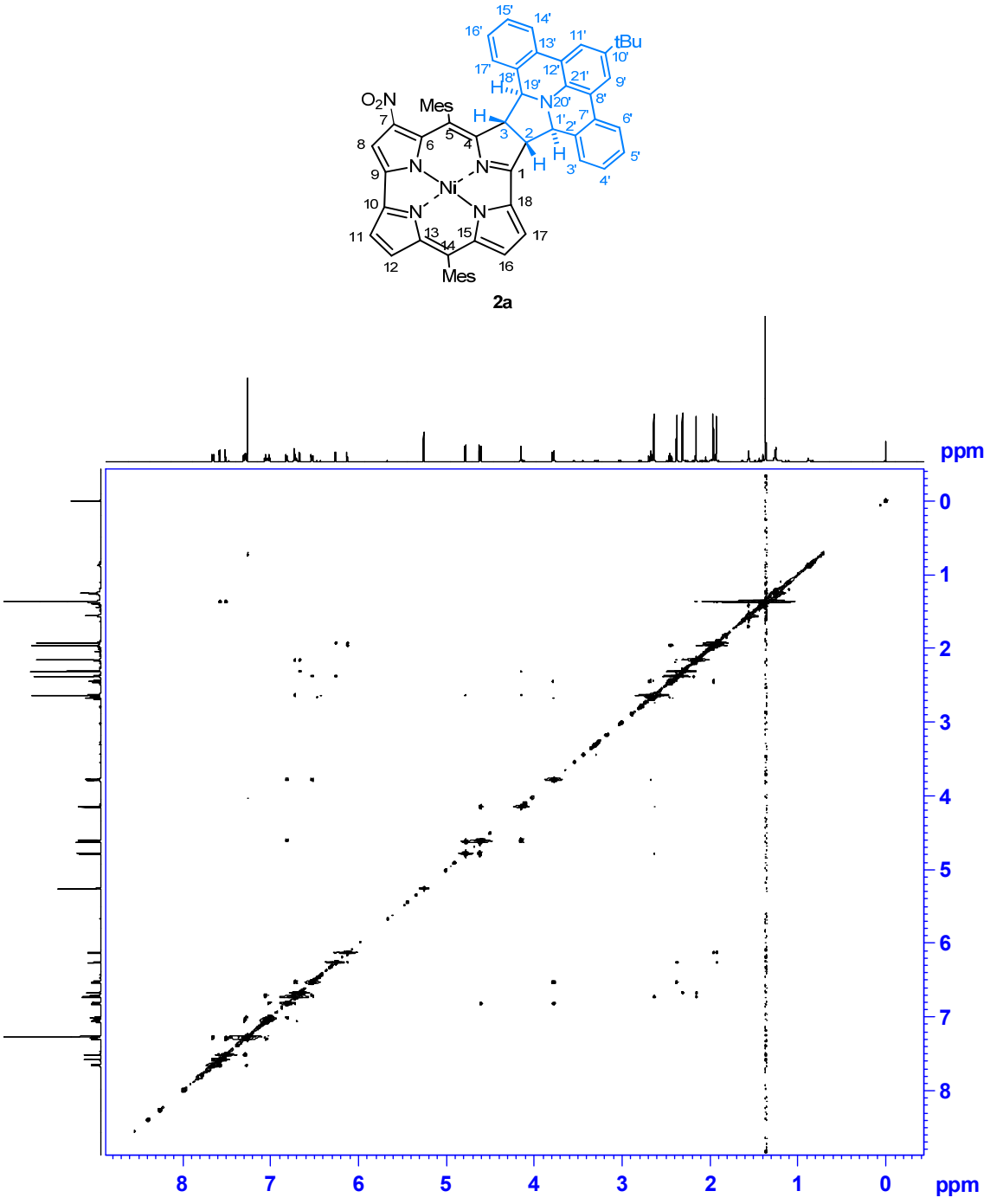


Figure S4. ^{1}H, ^{1}H NOESY spectrum of **2a** (500 MHz, 298 K, $CDCl_3$).

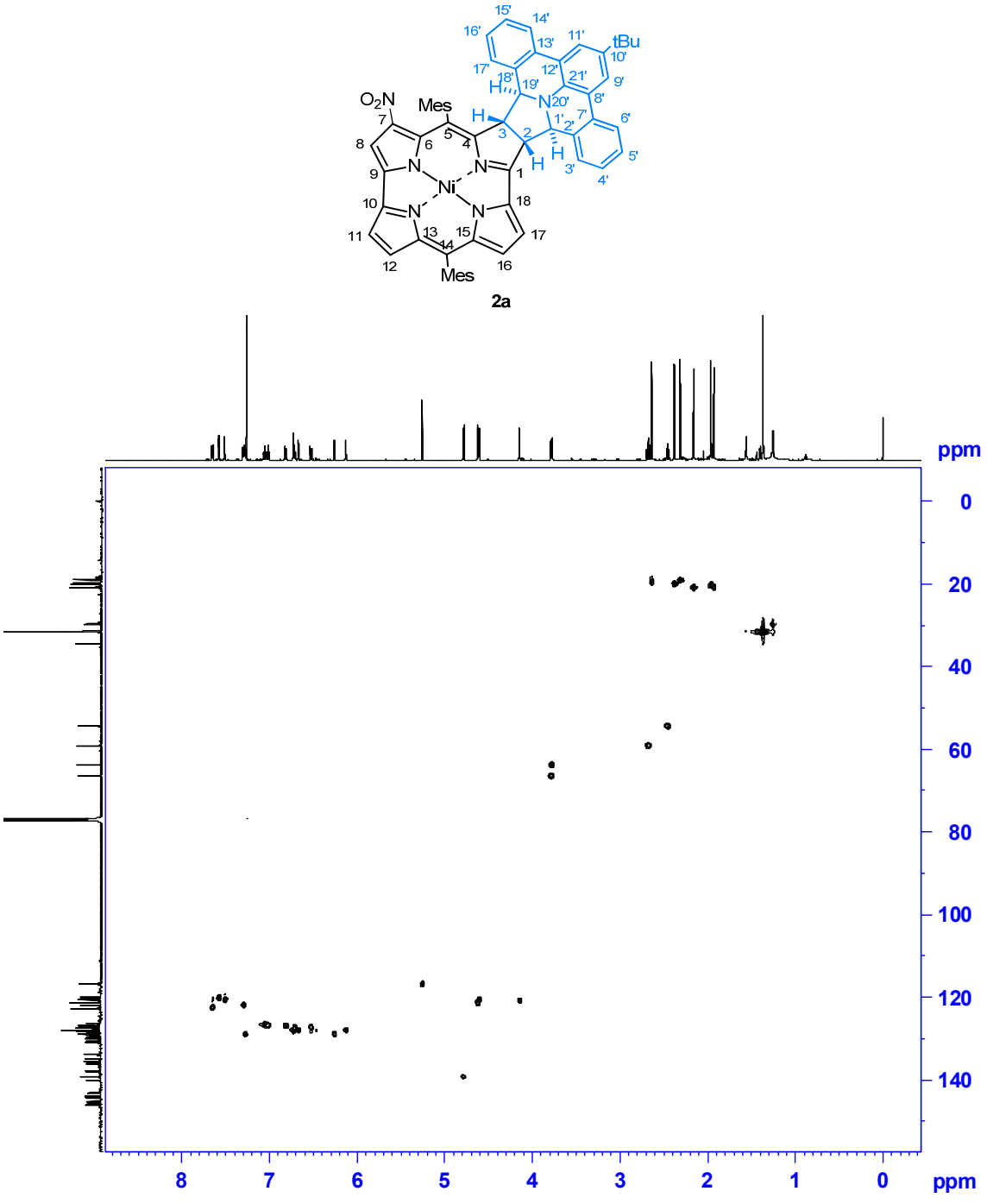


Figure S5. ^{1}H, ^{13}C HSQC spectrum of **2a** (500/125 MHz, 298 K, $CDCl_3$).

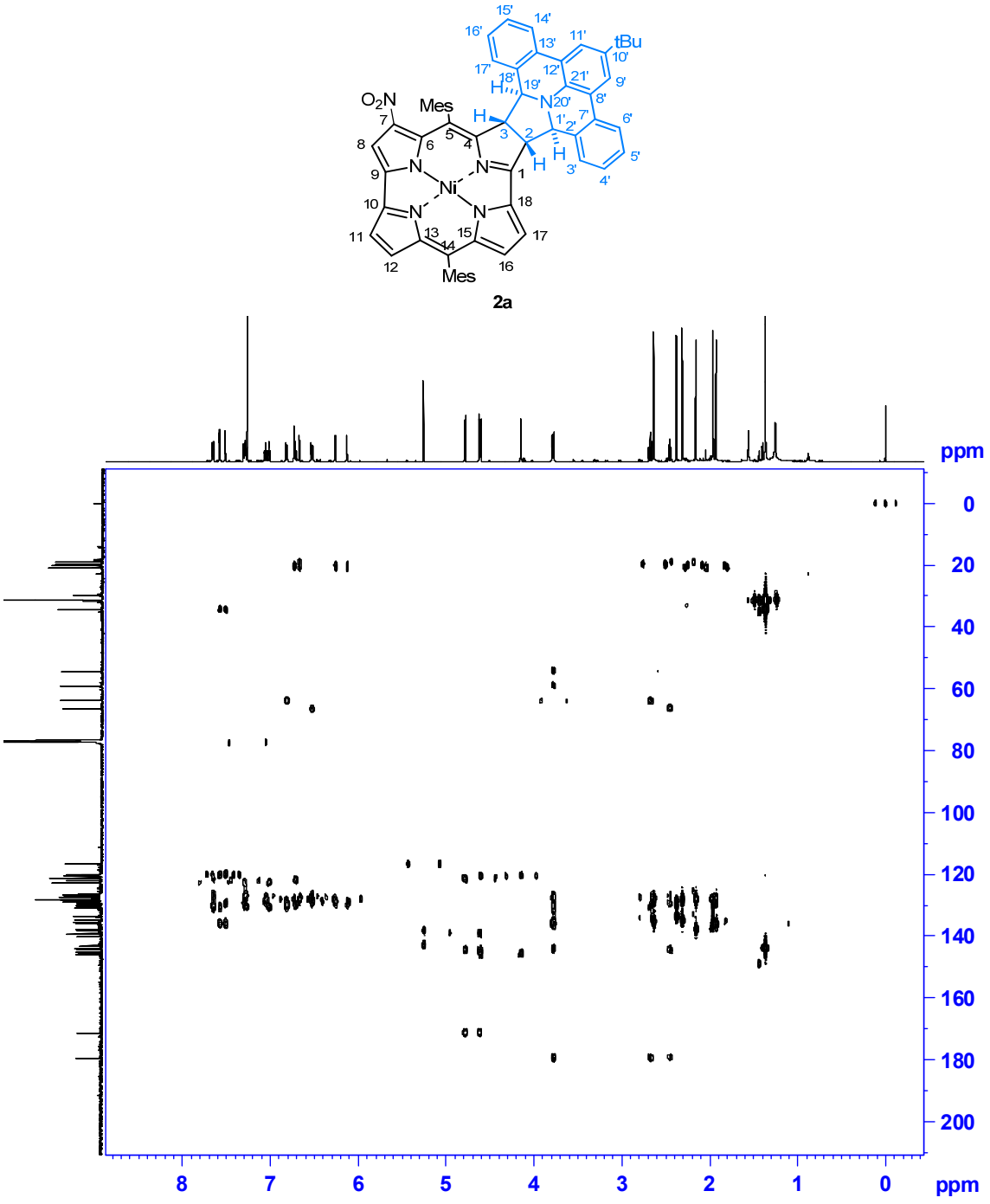


Figure S6. ^{1}H, ^{13}C HMBC spectrum of **2a** (500/125 MHz, 298 K, $CDCl_3$).

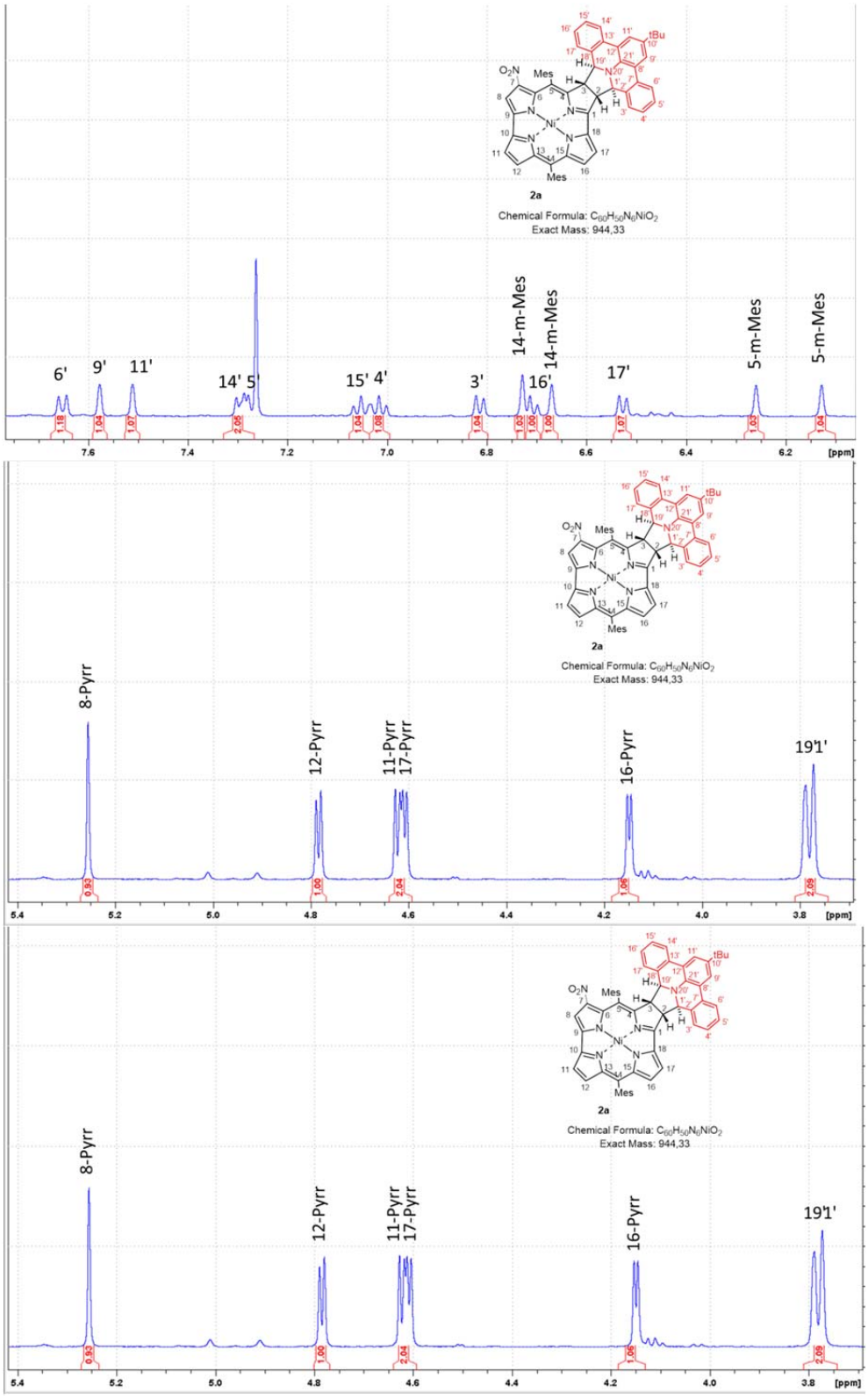


Figure S7. ^{1}H NMR signal assignments for **2a** (500 MHz, 298 K, $CDCl_3$).

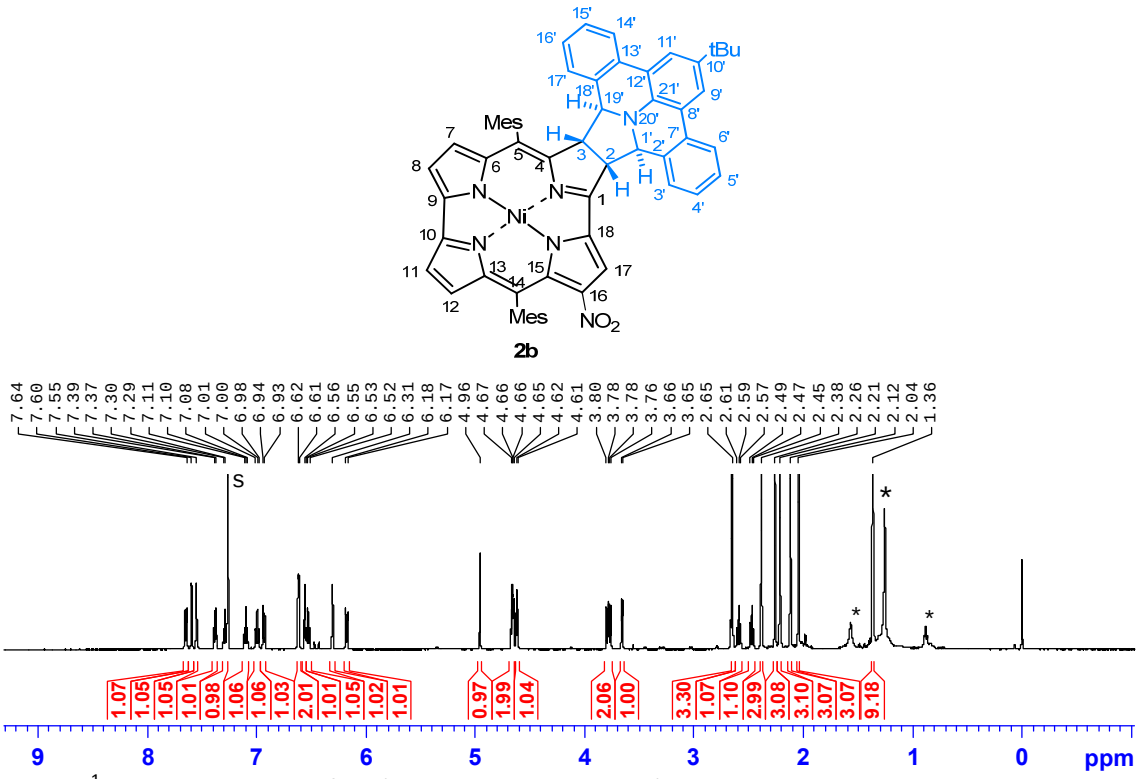


Figure S8. ^{1}H NMR spectrum of **2b** (500 MHz, 298 K, $CDCl_3$).

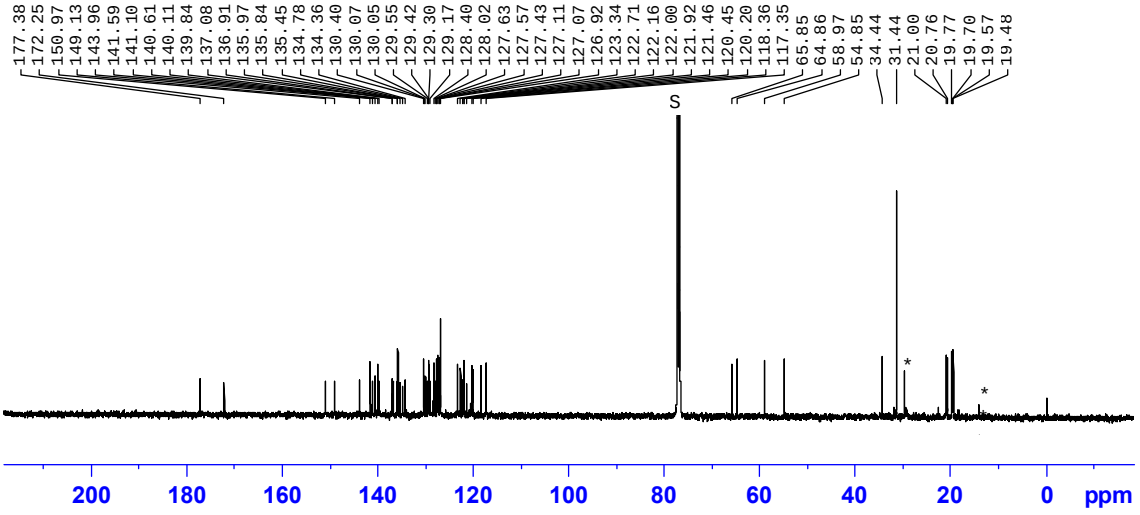


Figure S9. ^{13}C NMR spectrum of **2b** (125 MHz, 298 K, $CDCl_3$).

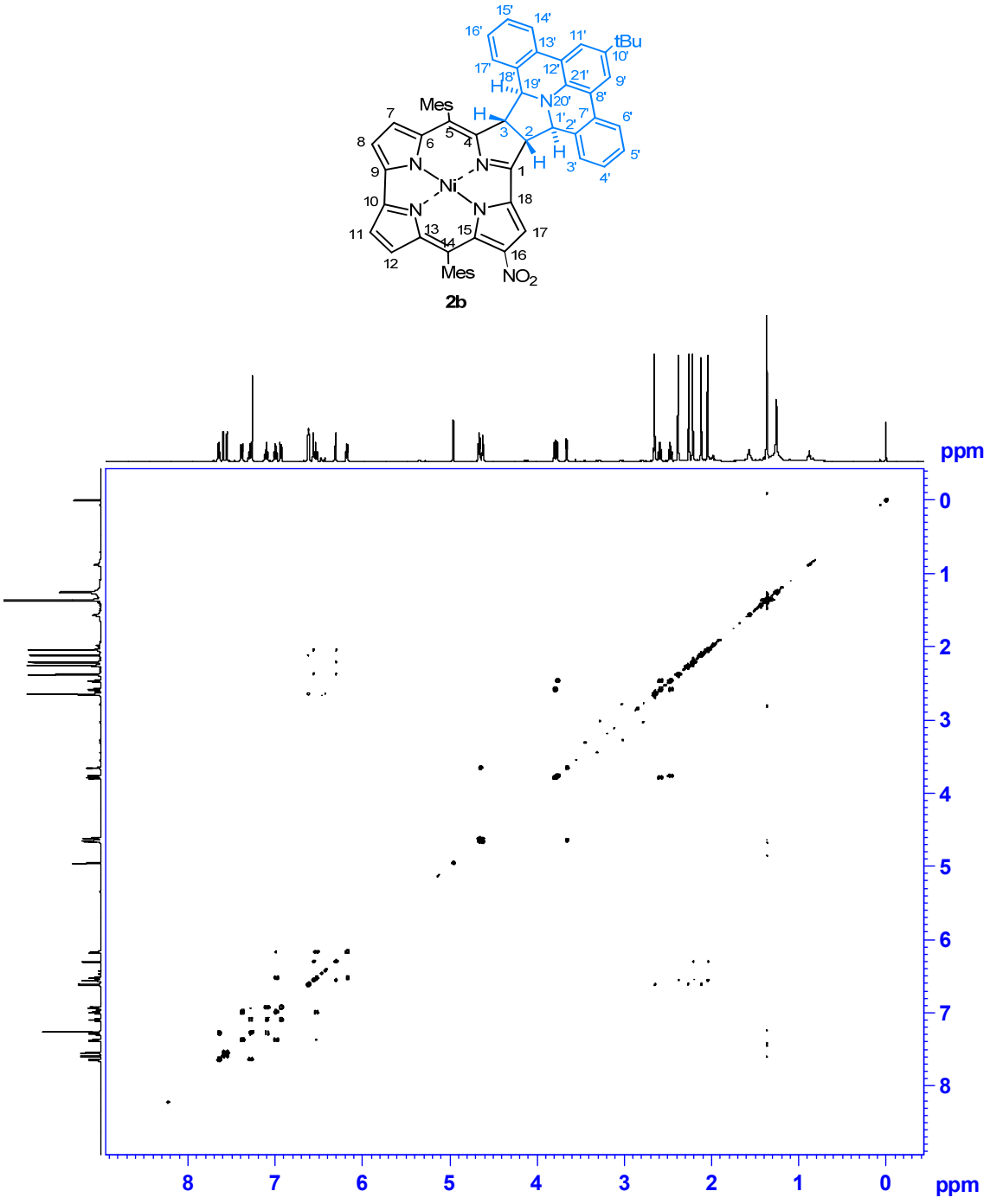


Figure S10. ^{1}H, ^{1}H COSY spectrum of **2b** (500 MHz, 298 K, $CDCl_3$).

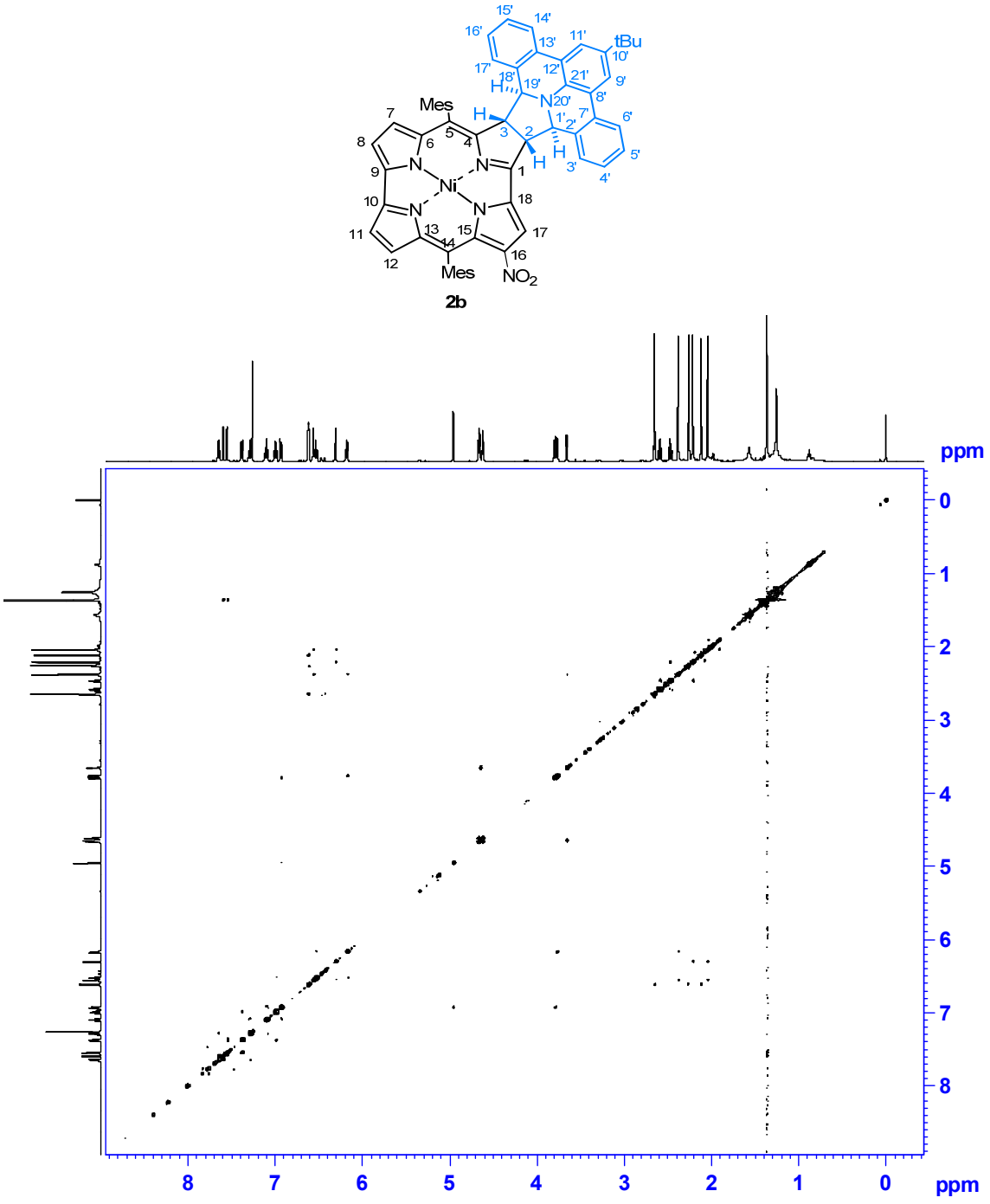


Figure S11. ^{1}H, ^{1}H NOESY spectrum of **2b** (500 MHz, 298 K, $CDCl_3$).

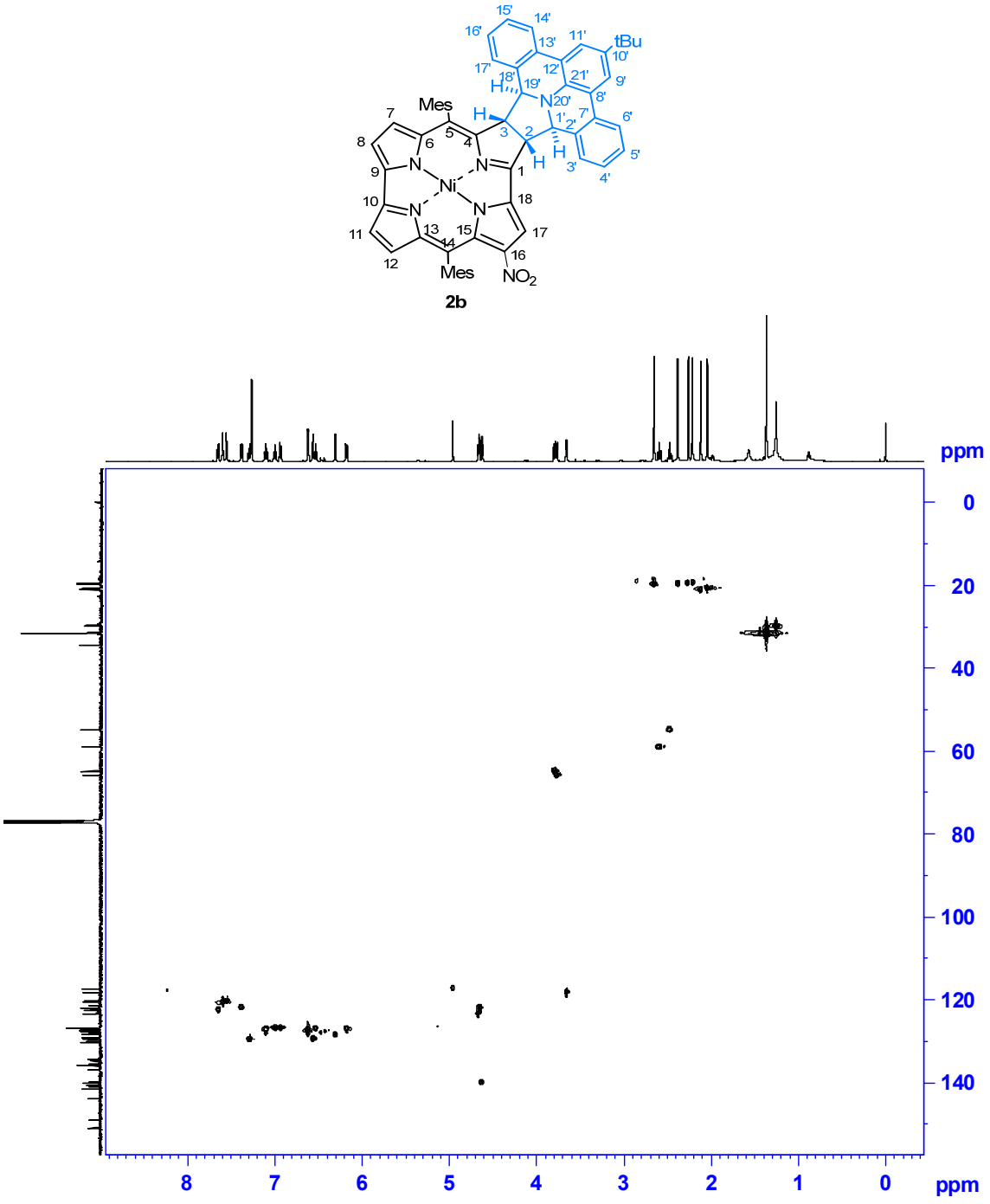


Figure S12. ^{1}H, ^{13}C HSQC spectrum of **2b** (500/125 MHz, 298 K, $CDCl_3$).

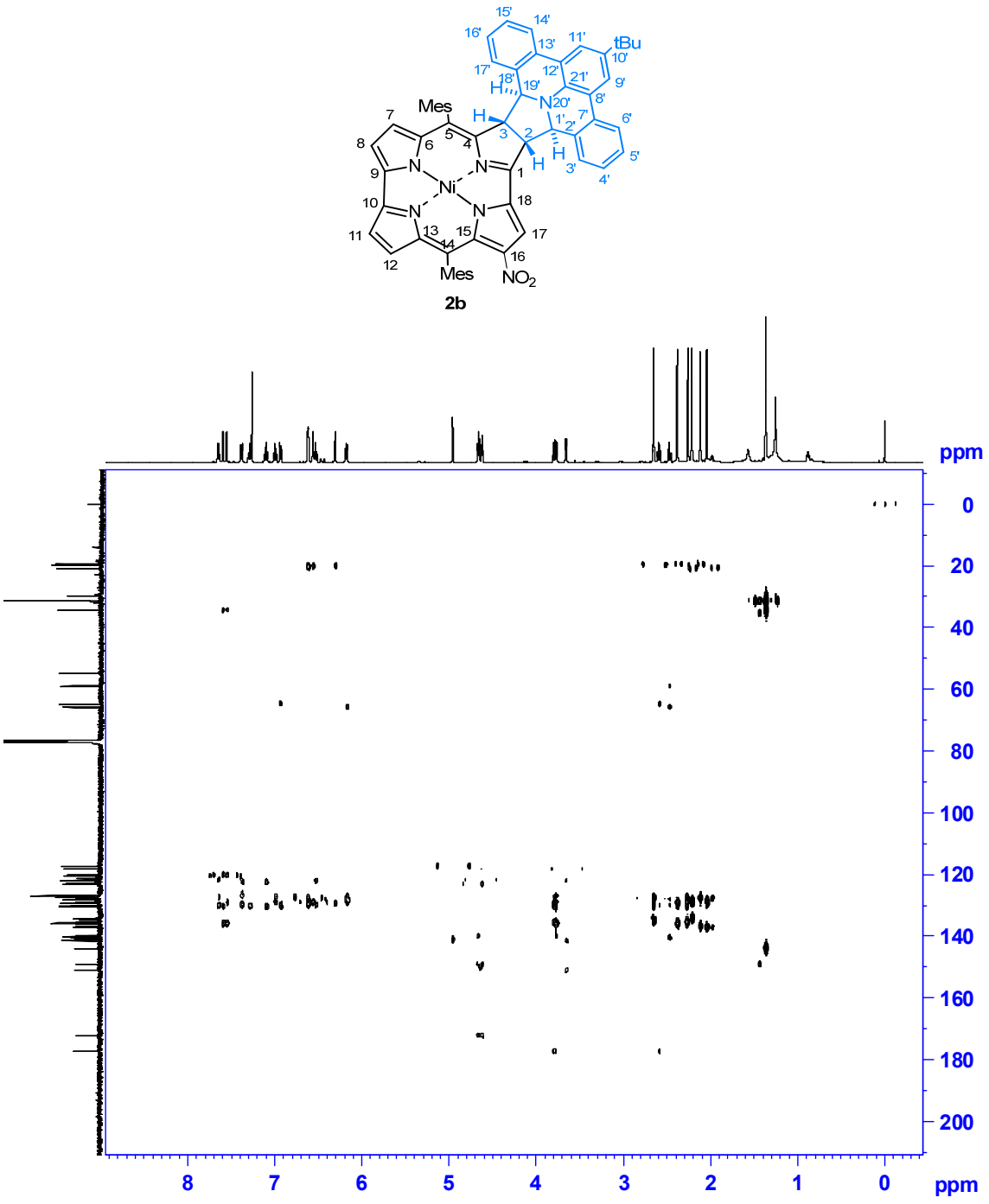


Figure S13. ^{1}H, ^{13}C HMBC spectrum of **2b** (500/125 MHz, 298 K, $CDCl_3$).

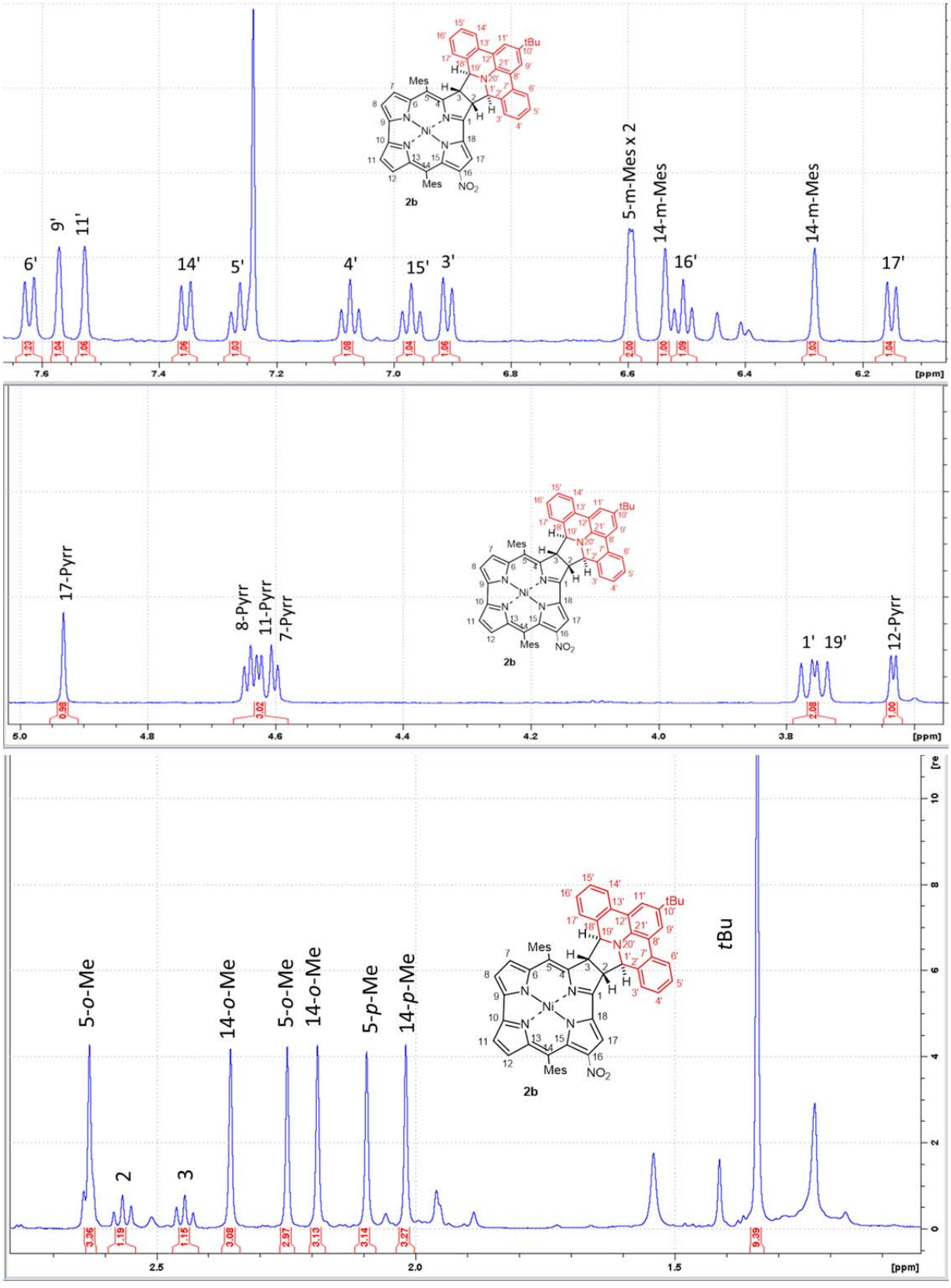


Figure S14. ^{1}H NMR signal assignments for **2b** (500 MHz, 298 K, $CDCl_3$).

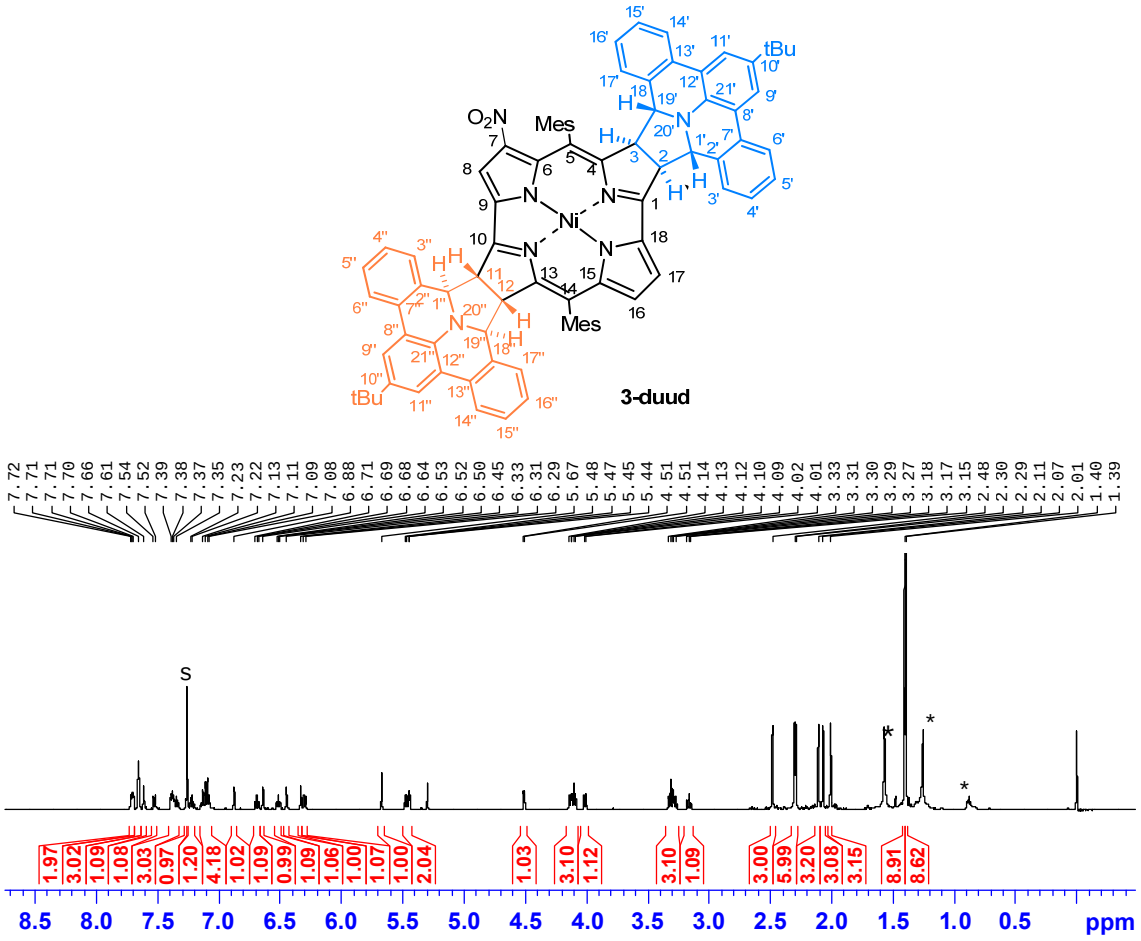


Figure S15. ^{1}H NMR spectrum of **3-duud** (500 MHz, 298 K, $CDCl_3$).

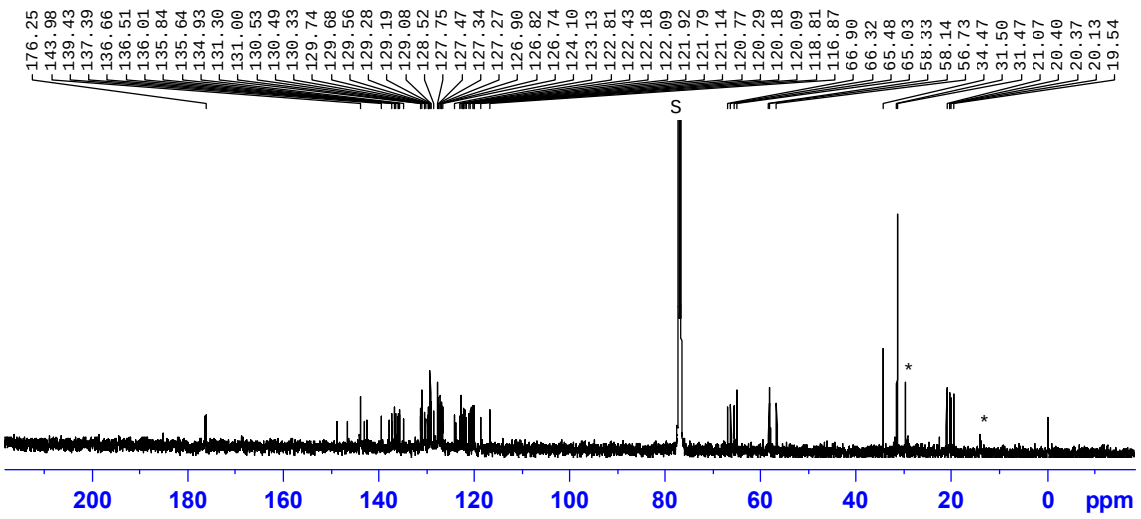


Figure S16. ^{13}C NMR spectrum of **3-duud** (125 MHz, 298 K, $CDCl_3$).

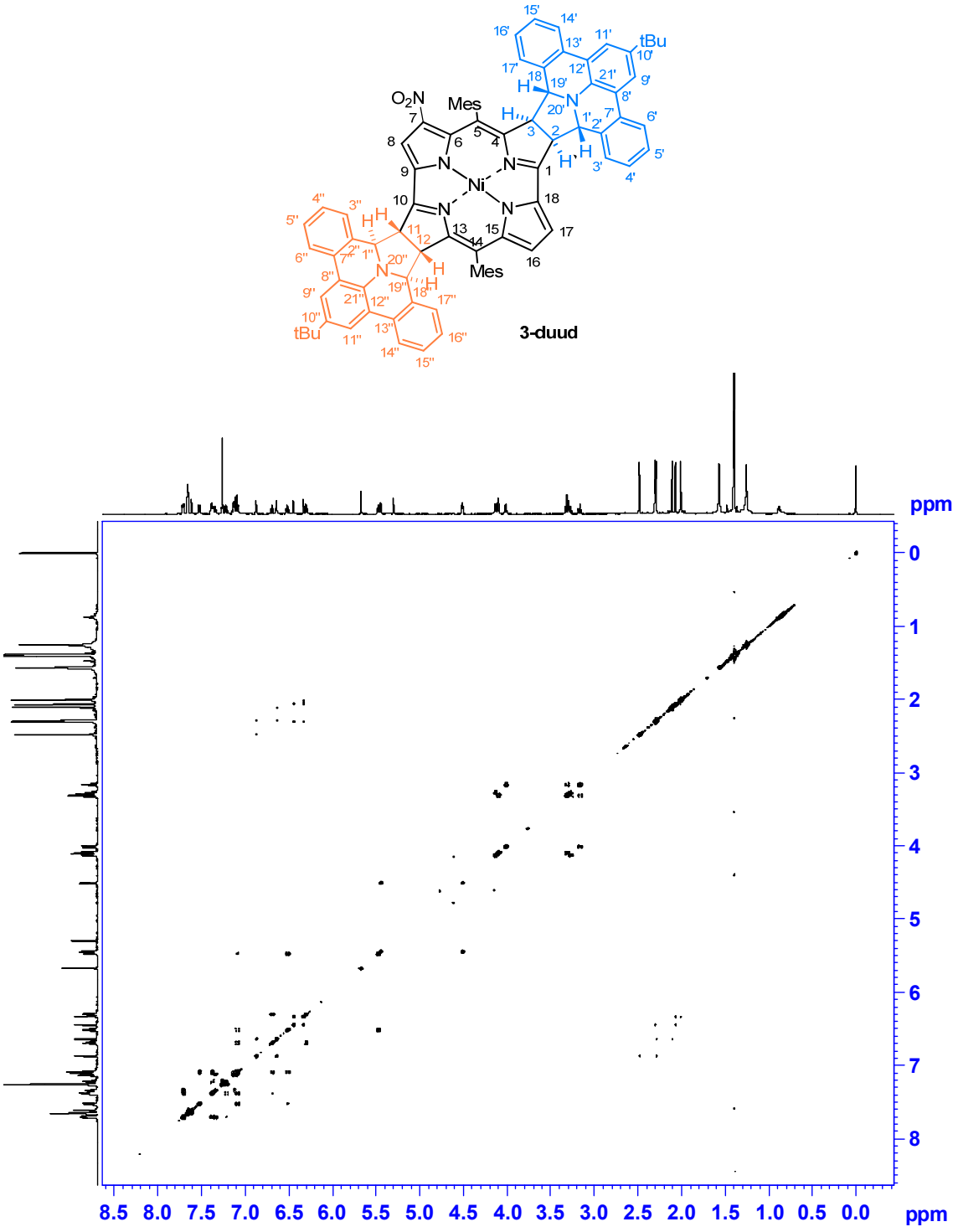


Figure S17. ^{1}H, ^{1}H COSY spectrum of **3-duud** (500 MHz, 298 K, $CDCl_3$).

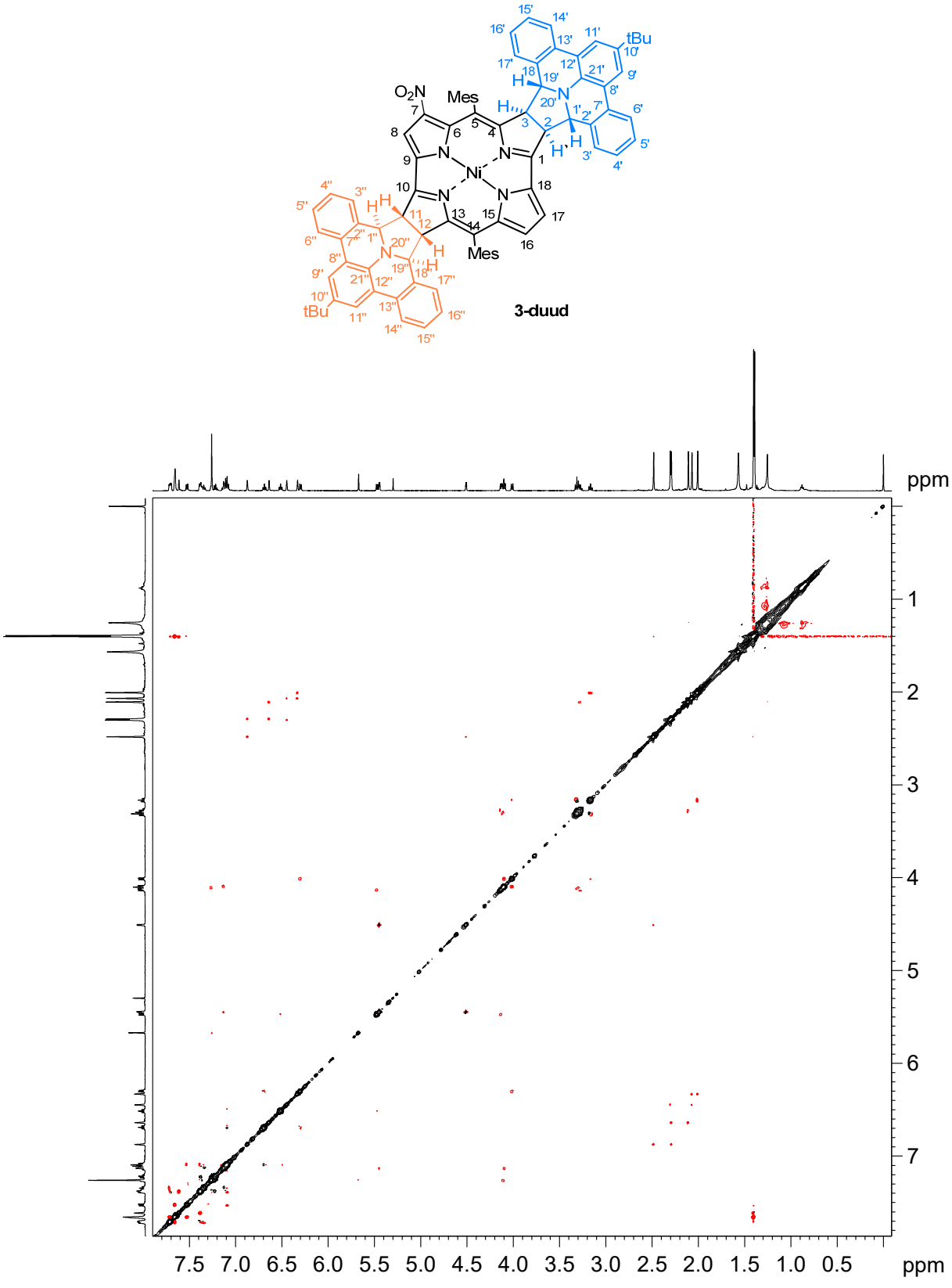


Figure S18. ^{1}H, ^{1}H NOESY spectrum of **3-duud** (500 MHz, 298 K, $CDCl_3$).

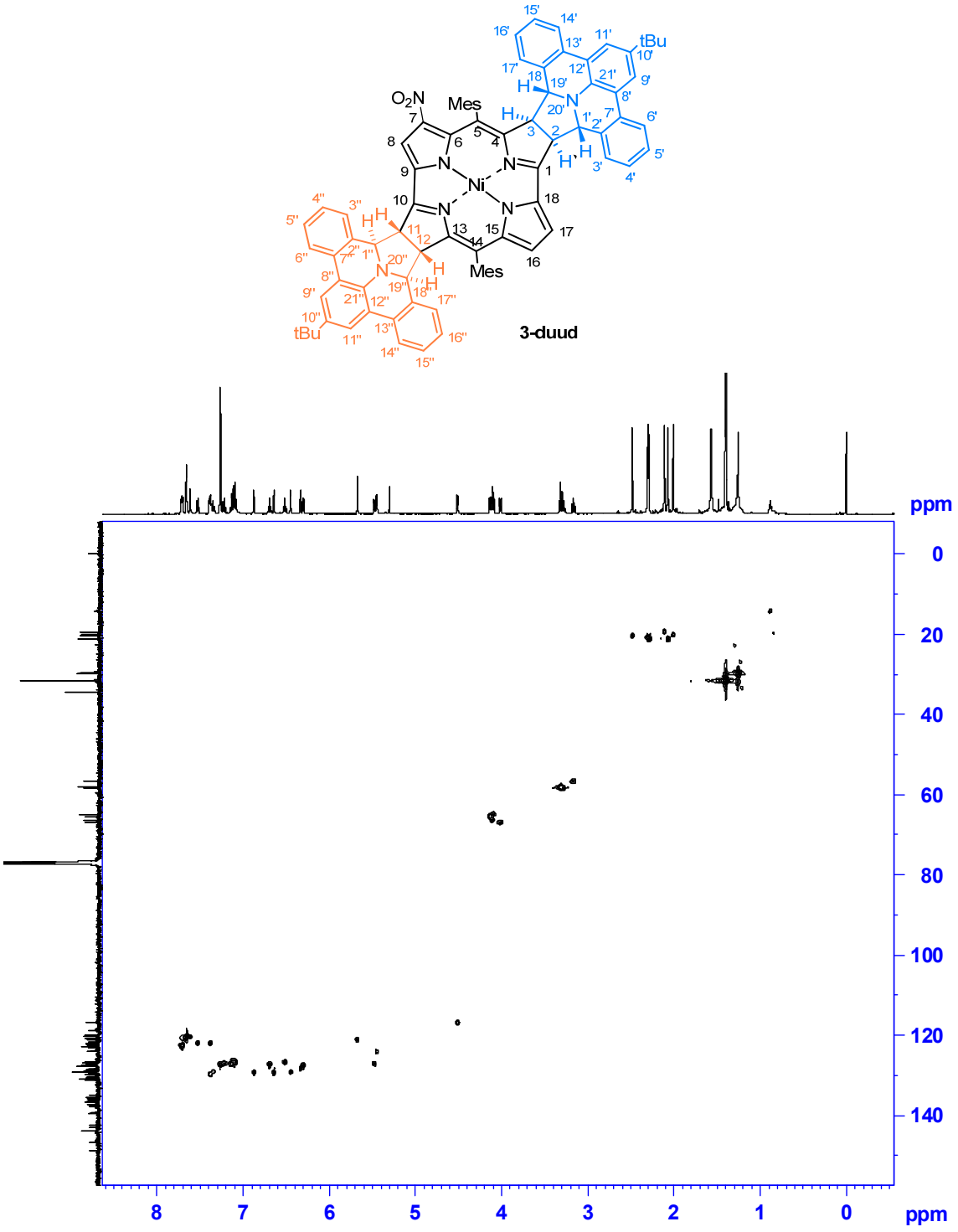


Figure S19. ^{1}H, ^{13}C HSQC spectrum of **3-duud** (500/125 MHz, 298 K, $CDCl_3$).

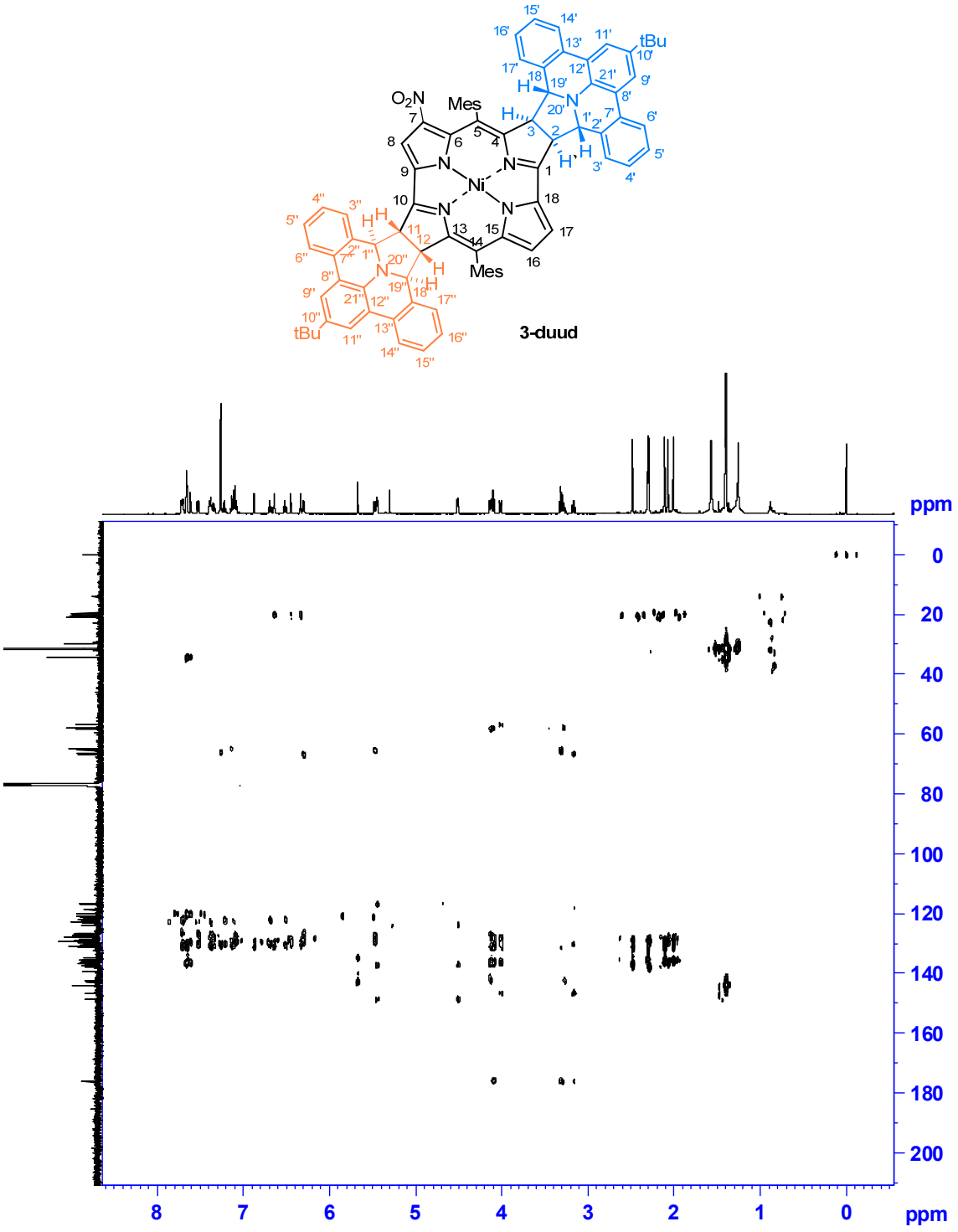


Figure S20. ^{1}H, ^{13}C HMBC spectrum of **3-duud** (500/125 MHz, 298 K, $CDCl_3$).

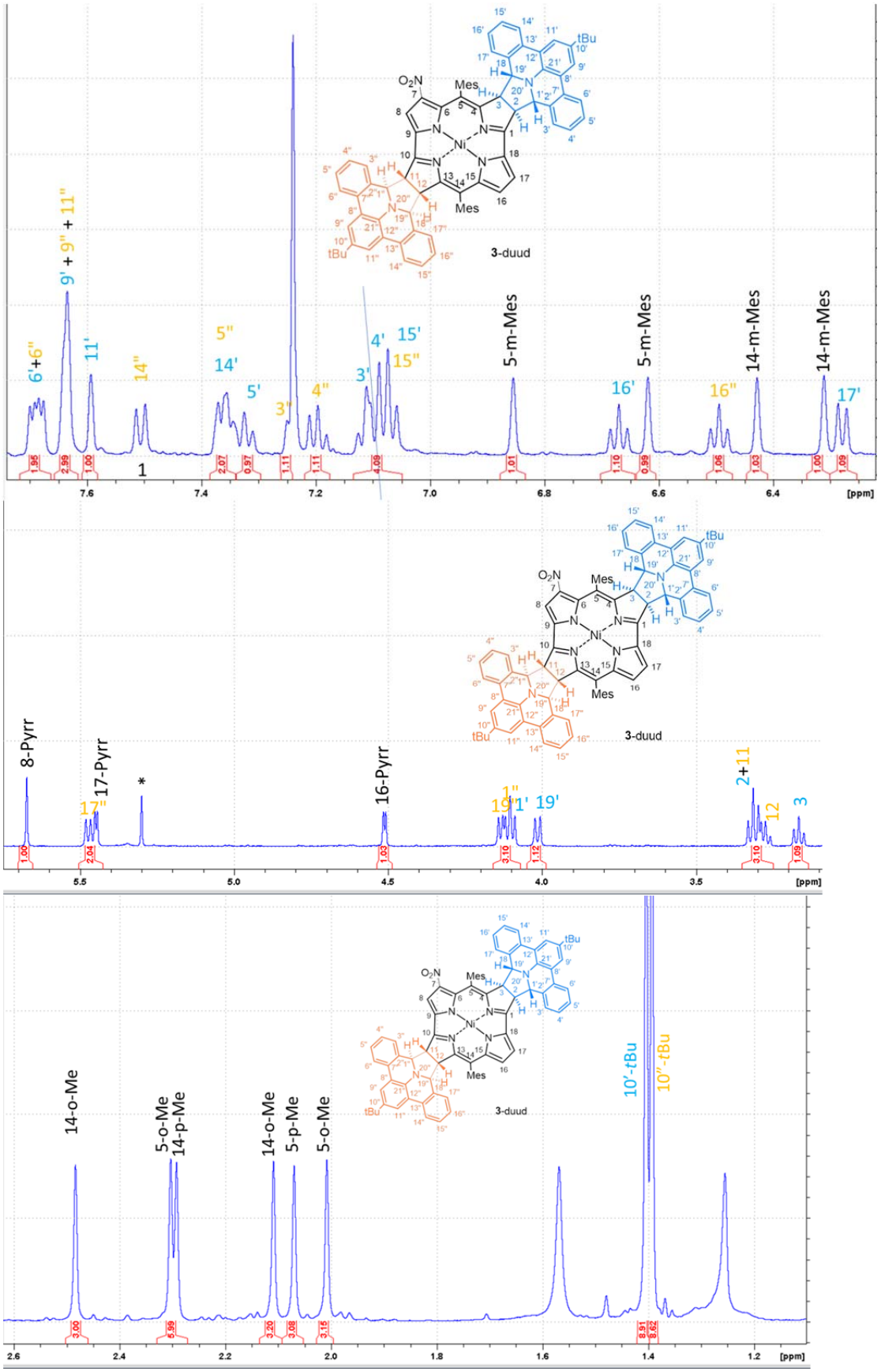


Figure S21. ^{1}H NMR signal assignments for **3-duud** (500 MHz, 298 K, $CDCl_3$).

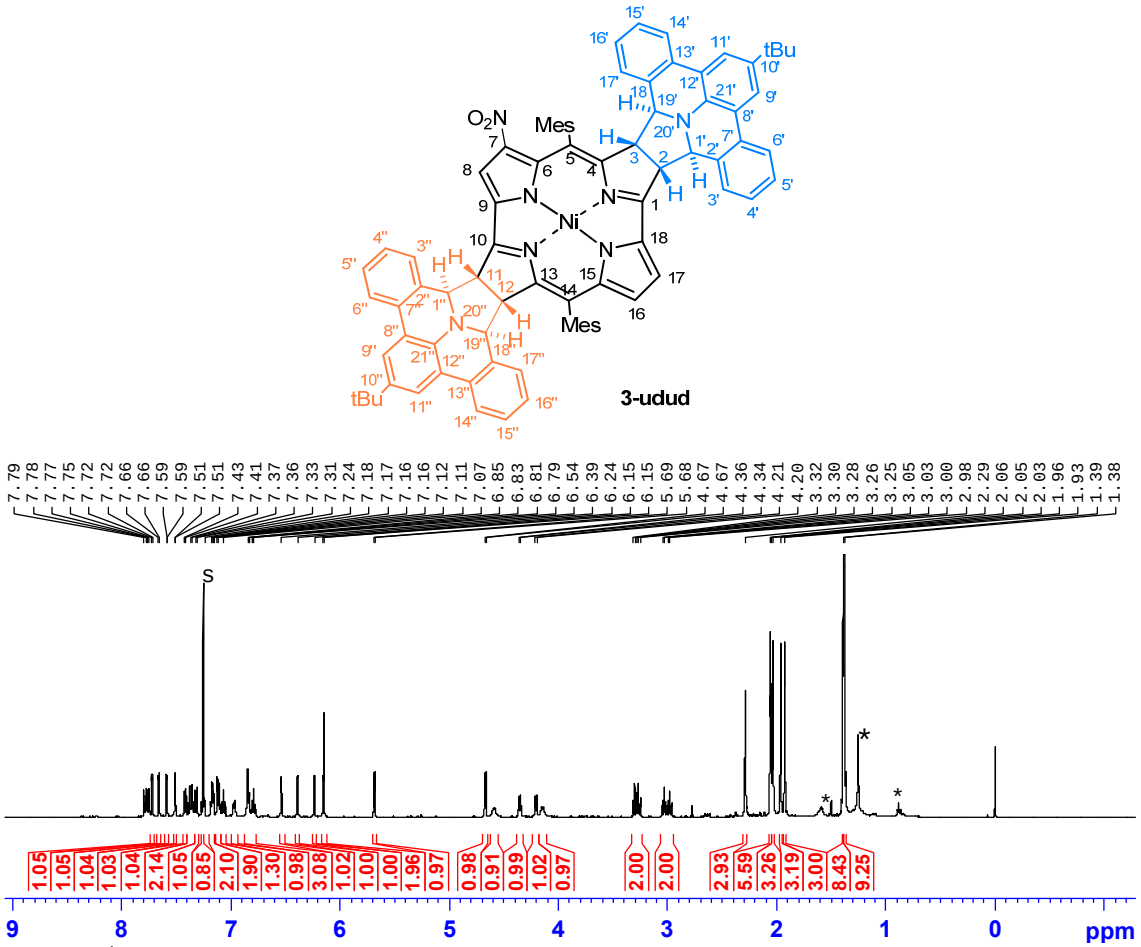


Figure S22. ^{1}H NMR spectrum of **3-udud** (500 MHz, 298 K, $CDCl_3$).

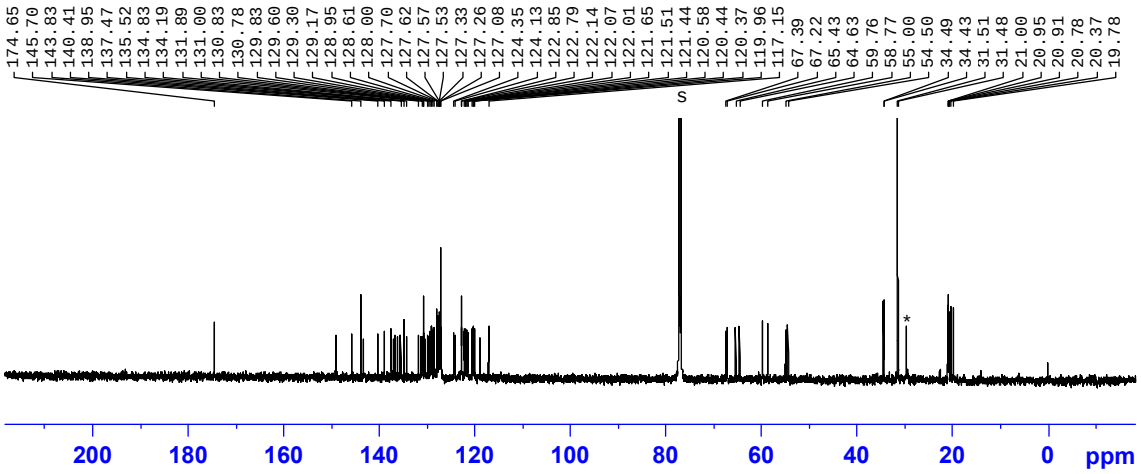


Figure S23. ^{13}C NMR spectrum of **3-udud** (125 MHz, 298 K, $CDCl_3$).

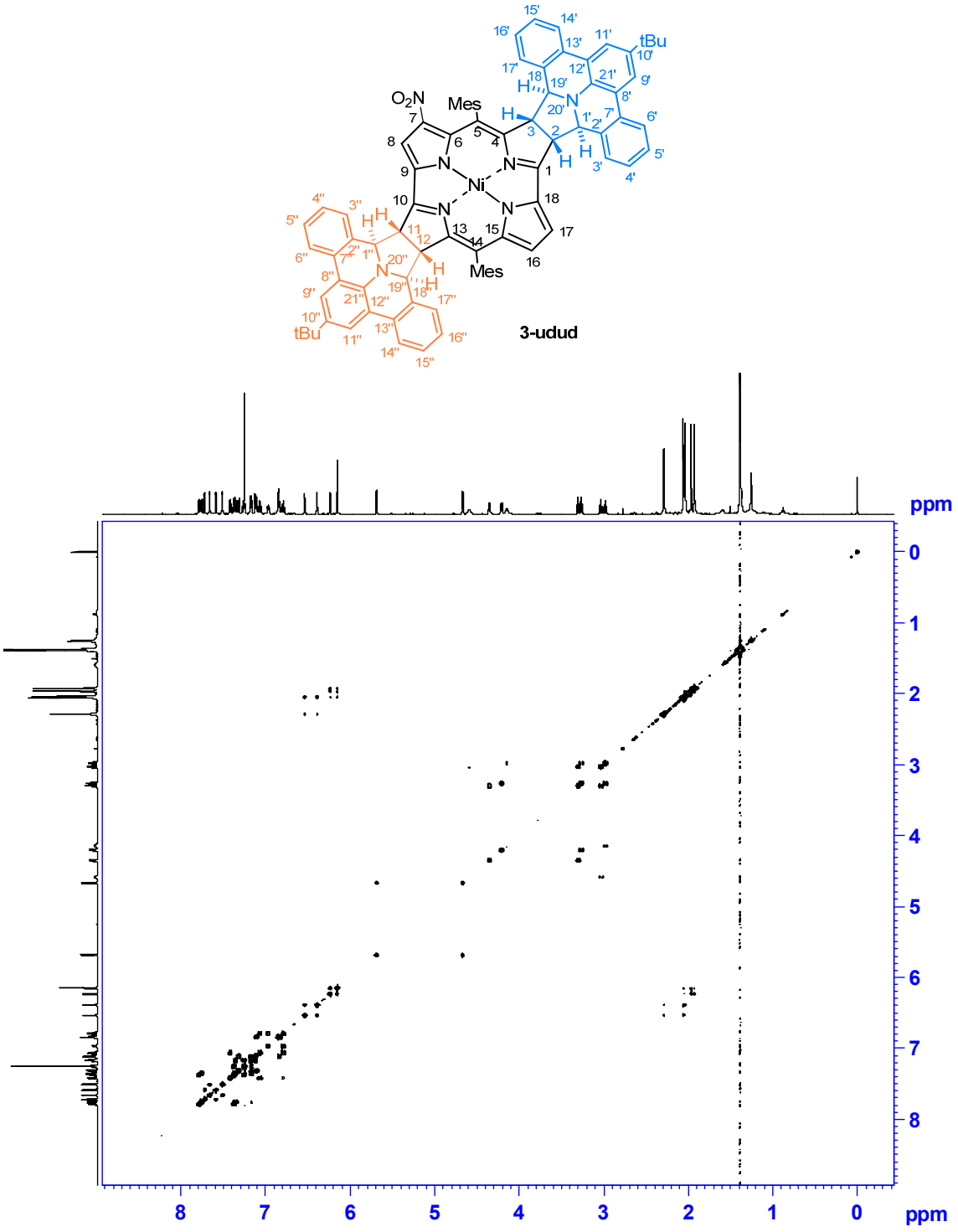


Figure S24. ^{1}H, ^{1}H COSY spectrum of **3-udud** (500 MHz, 298 K, $CDCl_3$).

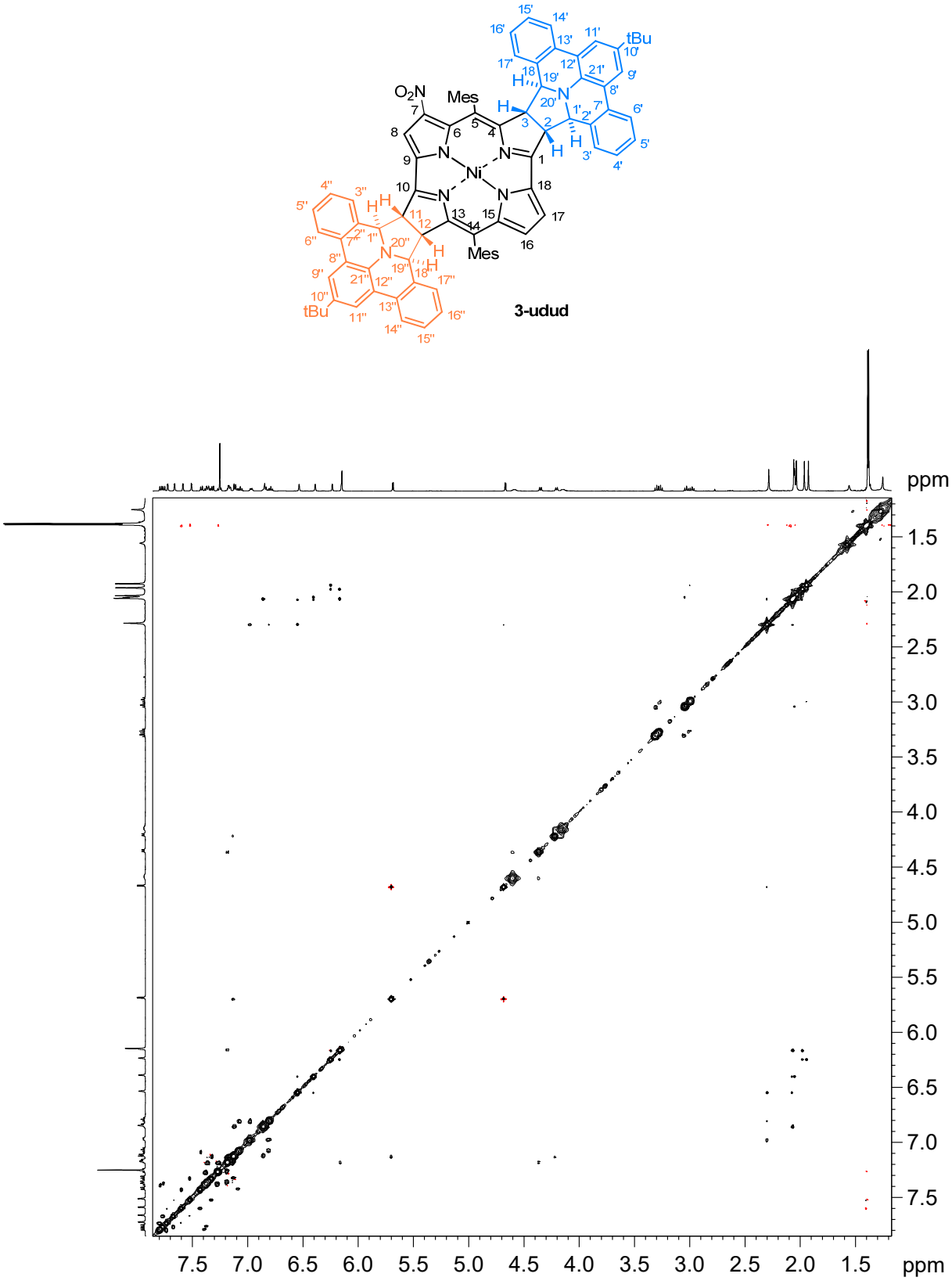


Figure S25. ^{1}H, ^{1}H NOESY spectrum of **3-udud** (500 MHz, 298 K, $CDCl_3$).

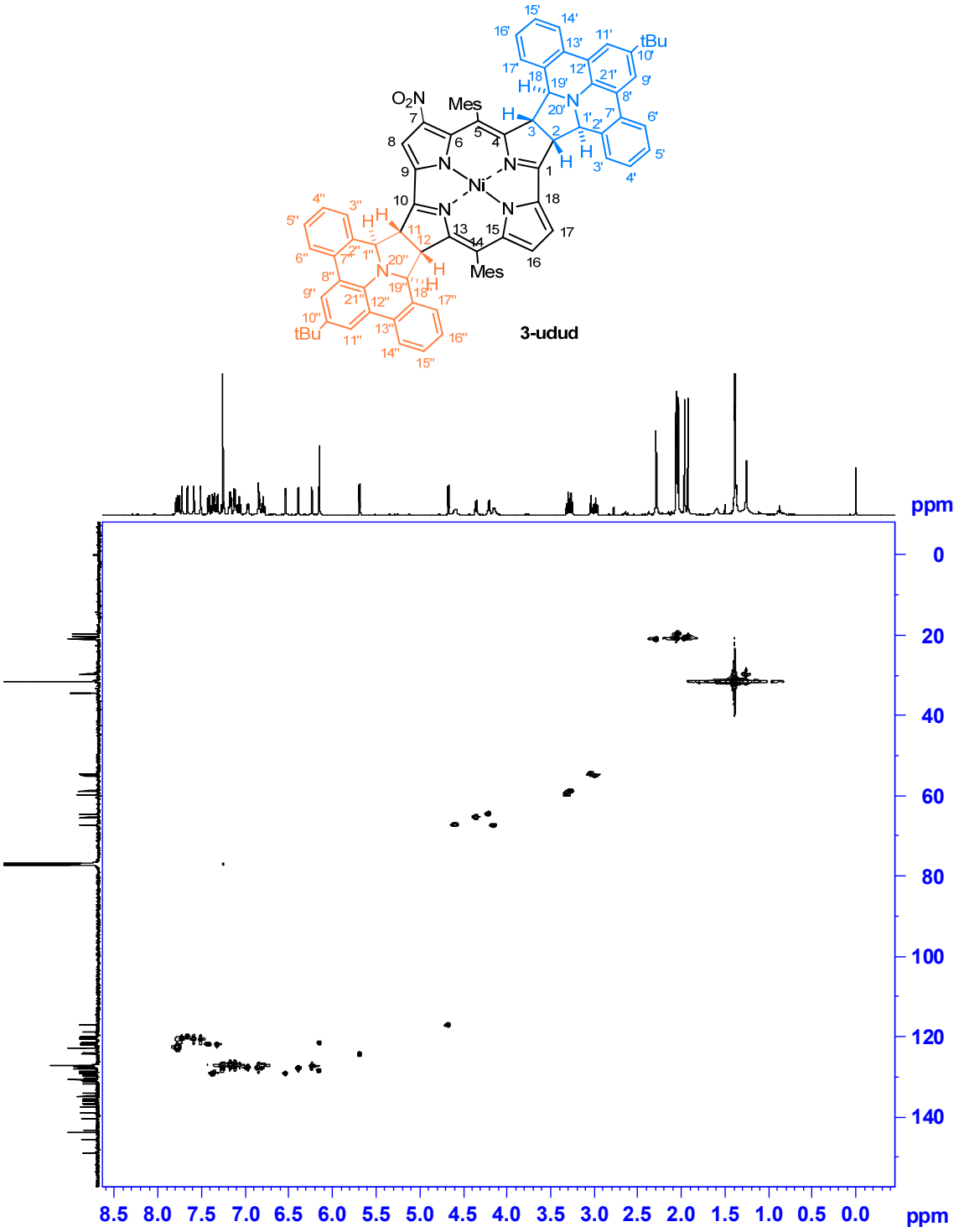


Figure S26. ^{1}H, ^{13}C HSQC spectrum of **3-udud** (500/125 MHz, 298 K, $CDCl_3$).

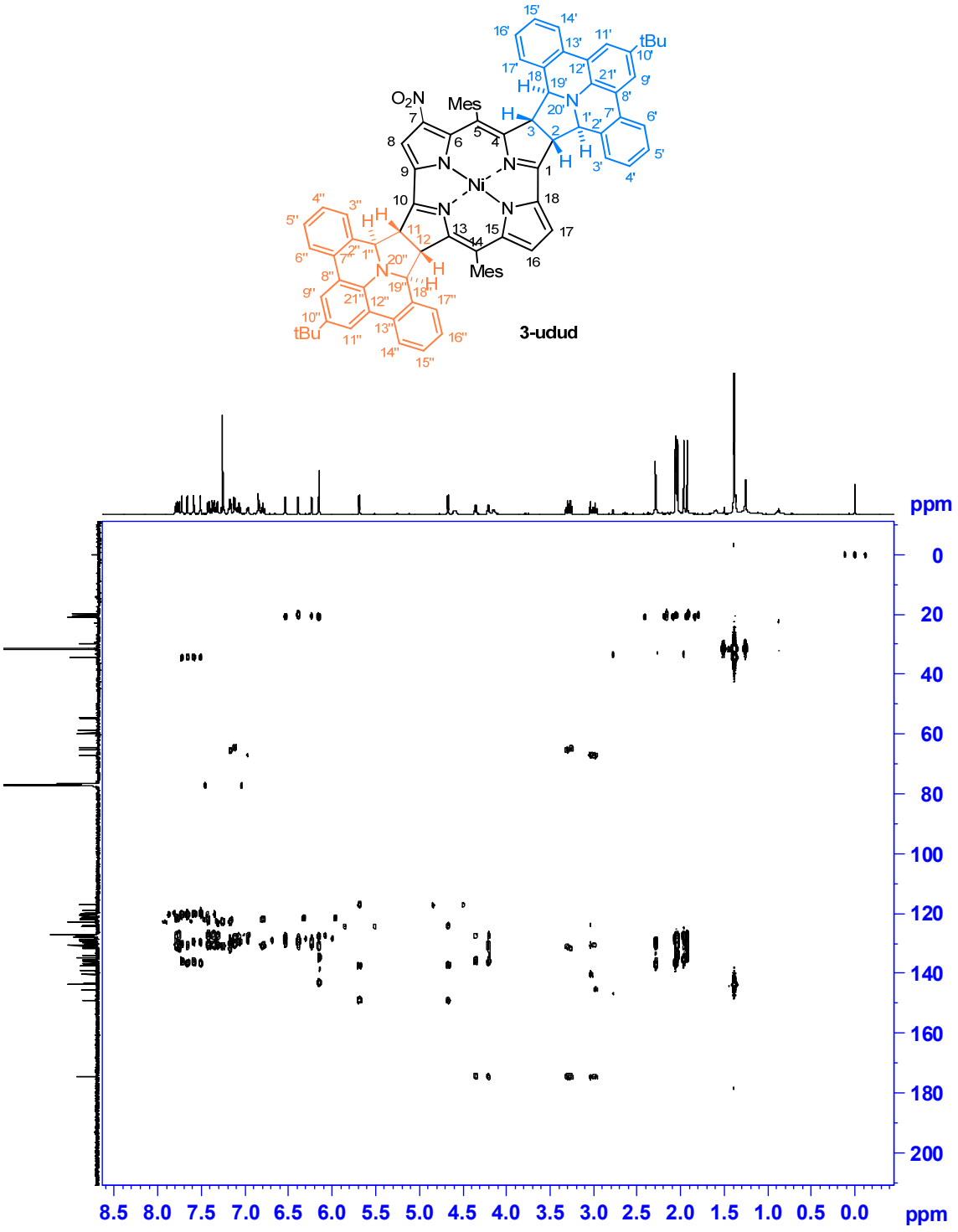


Figure S27. ^{1}H, ^{13}C HMBC spectrum of **3-udud** (500/125 MHz, 298 K, $CDCl_3$).

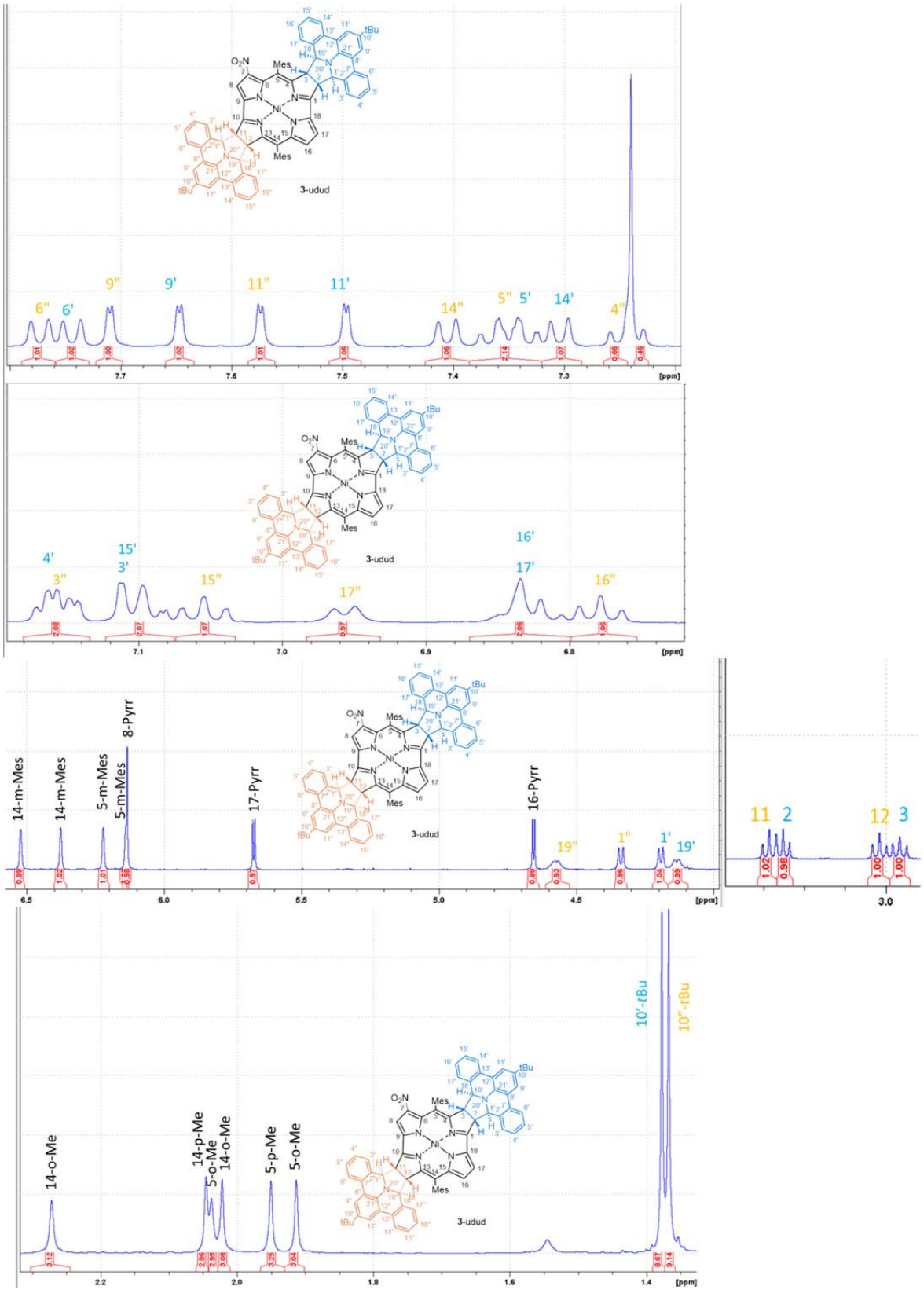


Figure S28. ^{1}H NMR signal assignments for **3**-ududd (500 MHz, 298 K, $CDCl_3$).

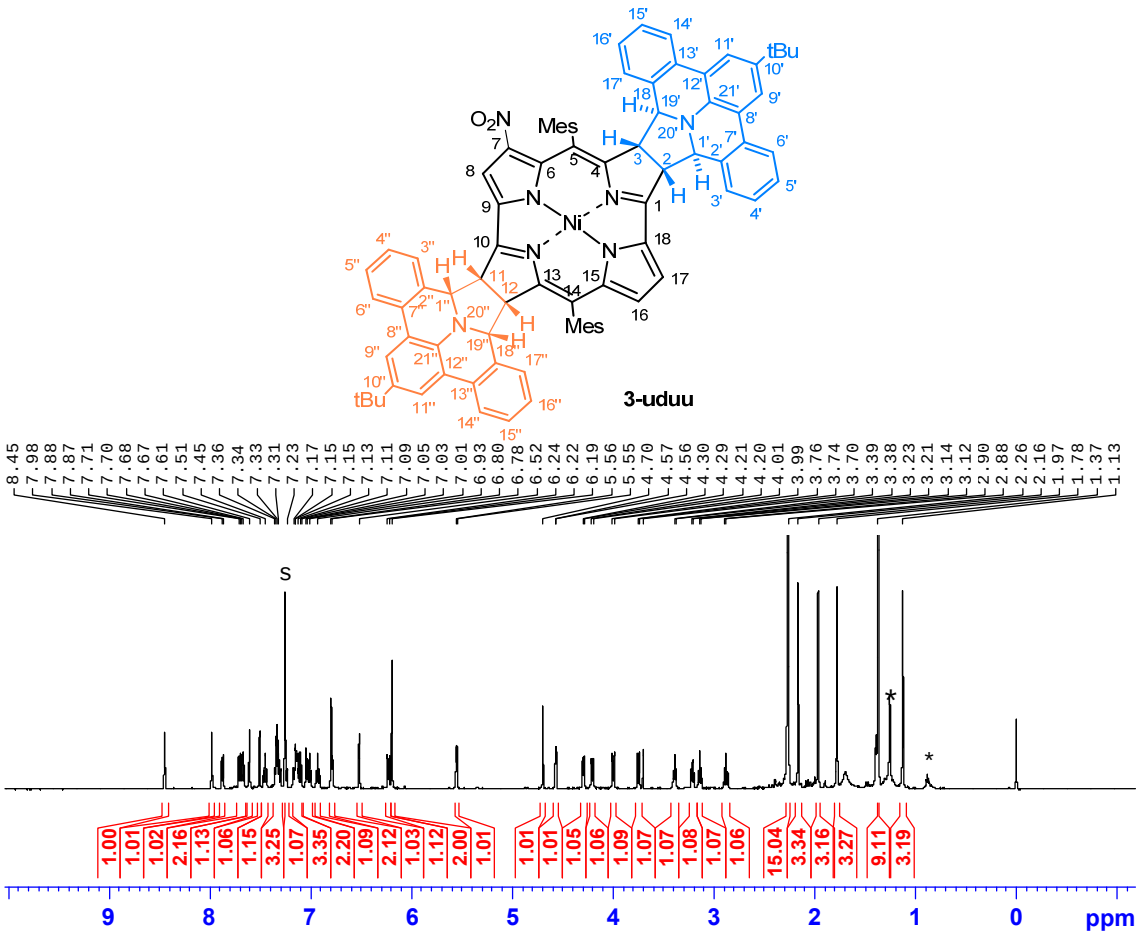


Figure S29. ^{1}H NMR spectrum of **3**-uduu (500 MHz, 298 K, $CDCl_3$).

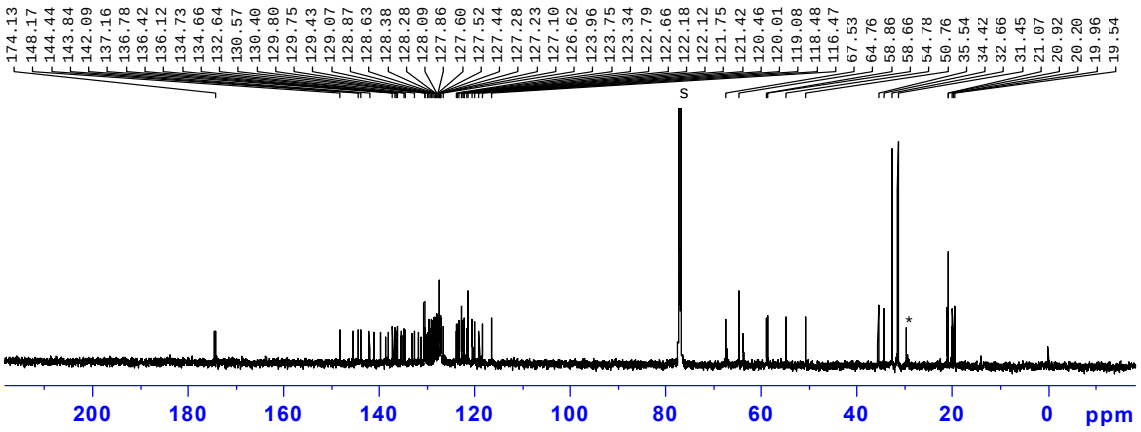


Figure S30. ^{13}C NMR spectrum of **3**-uduu (125 MHz, 298 K, $CDCl_3$).

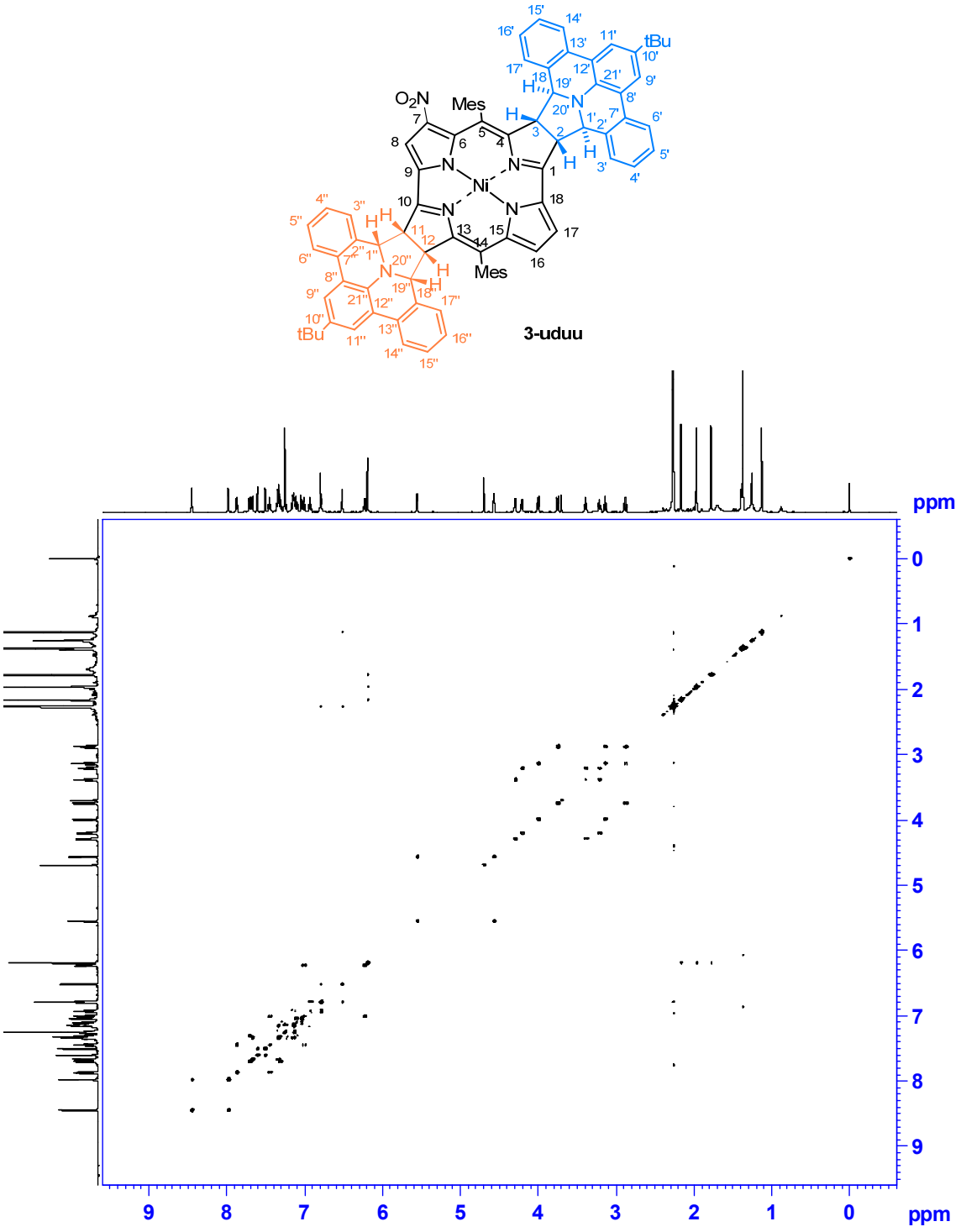


Figure S31. ^{1}H, ^{1}H COSY spectrum of **3**-uduu (500 MHz, 298 K, $CDCl_3$).

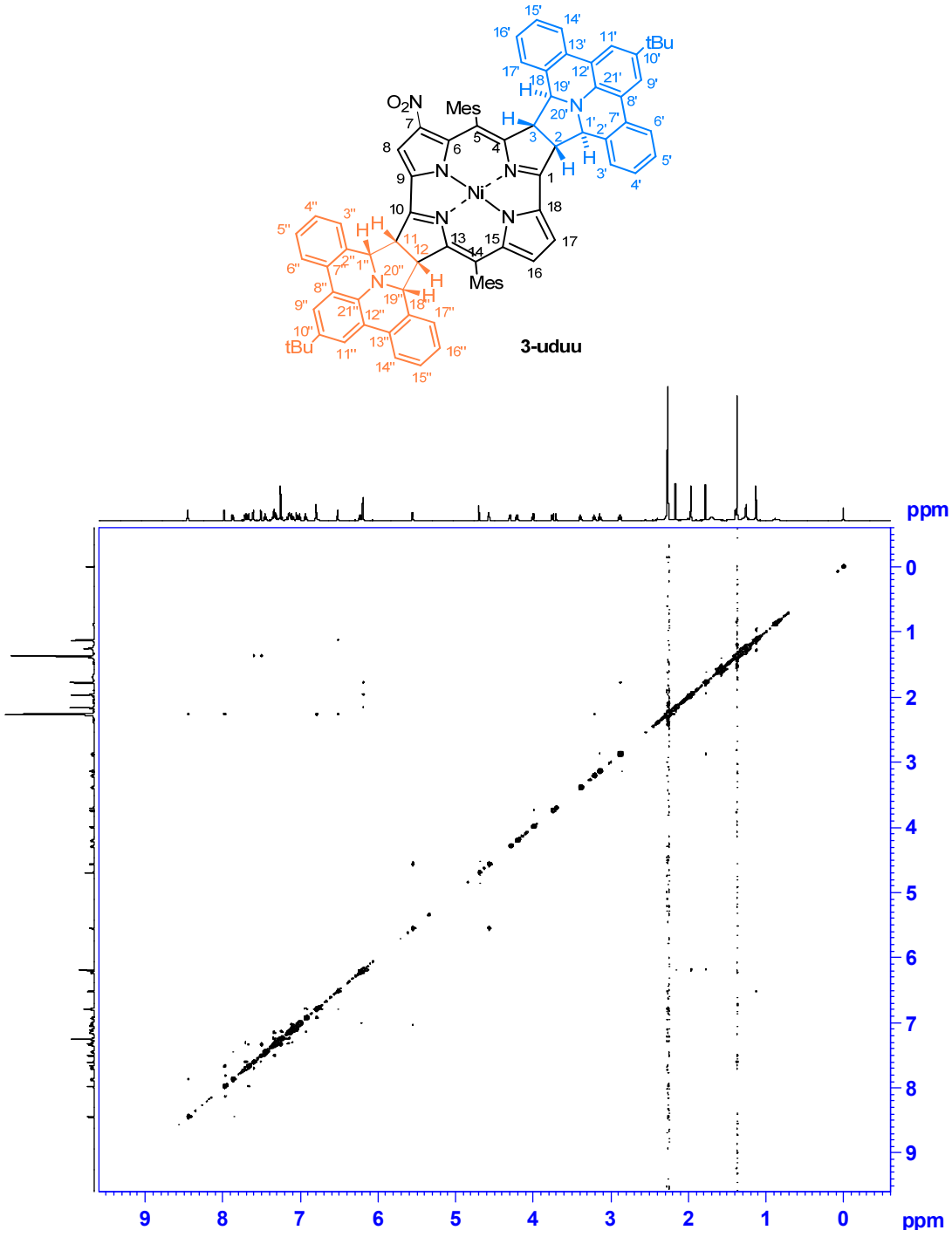


Figure S32. ^{1}H, ^{1}H NOESY spectrum of **3**-uduu (500 MHz, 298 K, $CDCl_3$).

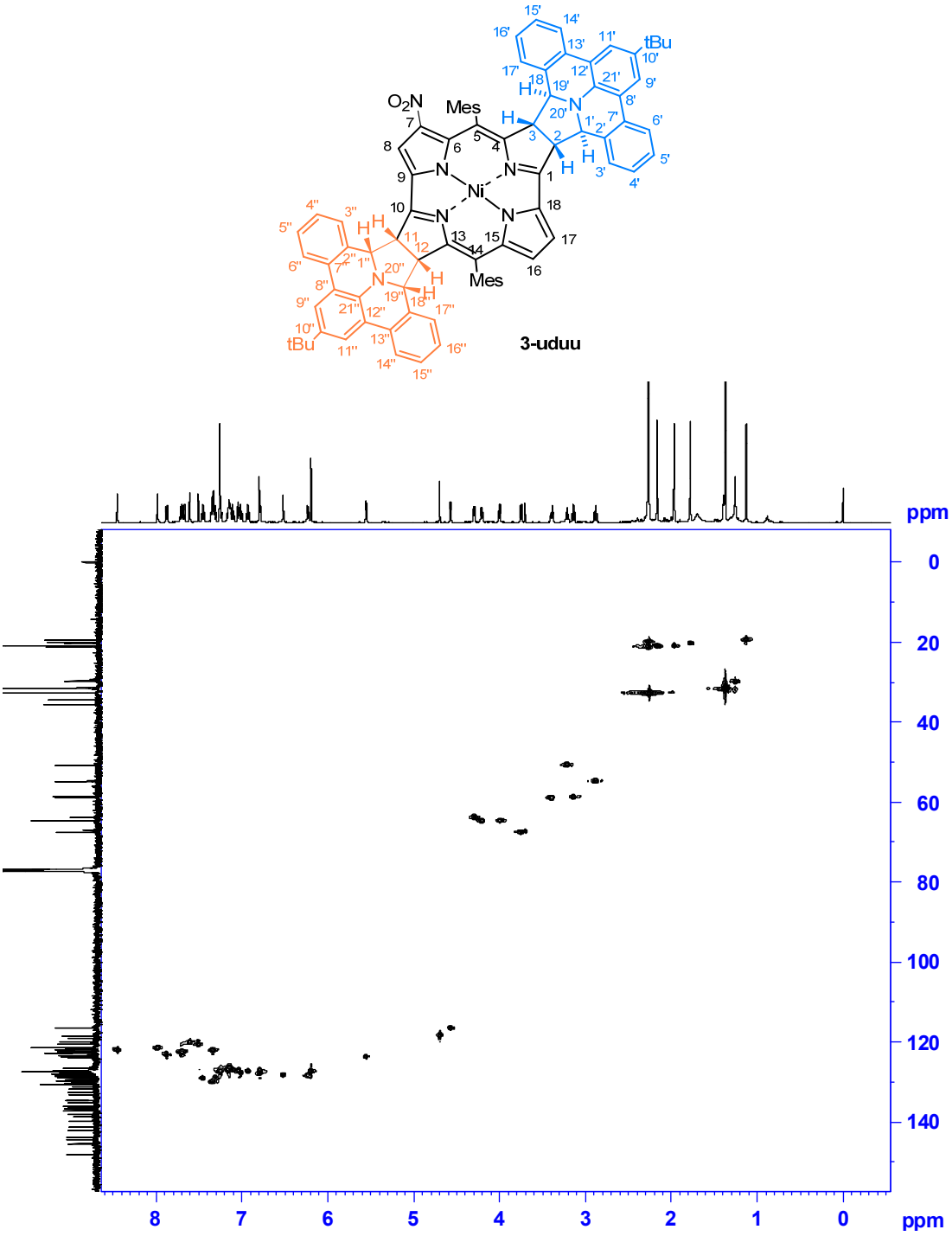


Figure S33. ^{1}H, ^{13}C HSQC spectrum of **3**-uduu (500/125 MHz, 298 K, $CDCl_3$).

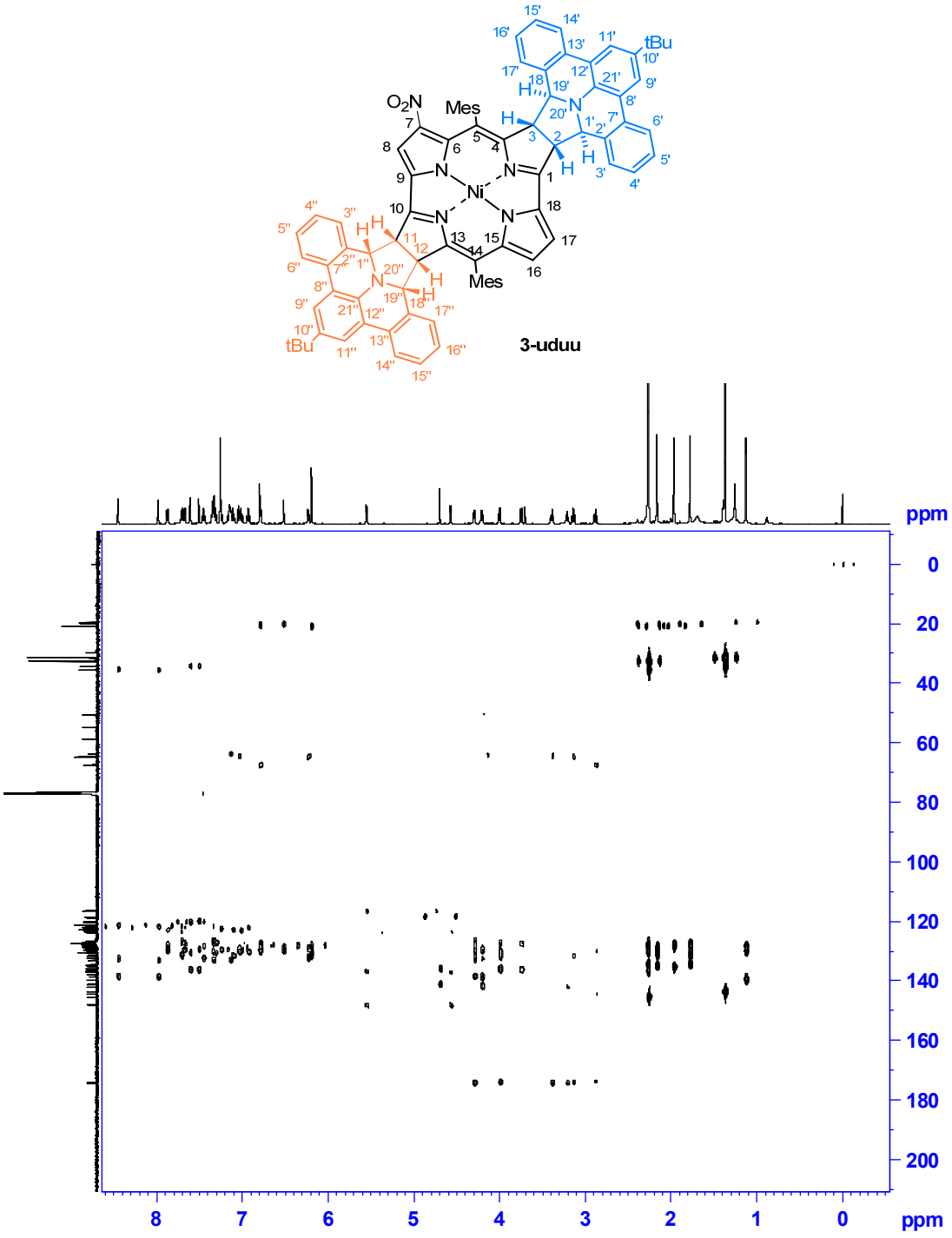


Figure S34. ^{1}H, ^{13}C HMBC spectrum of **3**-uduu (500/125 MHz, 298 K, $CDCl_3$).

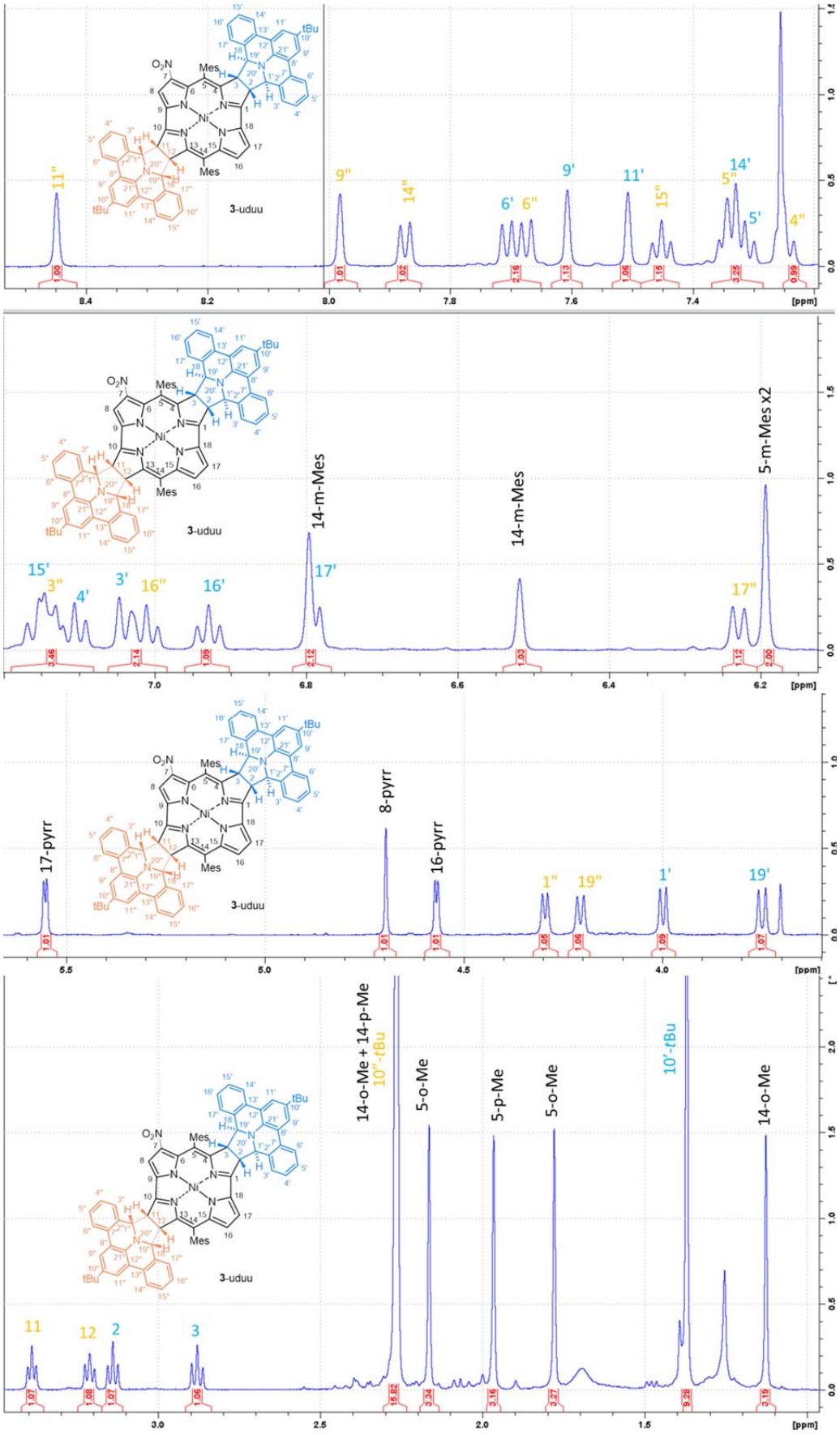


Figure S35. ^{1}H NMR signal assignments for **3**-uduu (500 MHz, 298 K, $CDCl_3$).

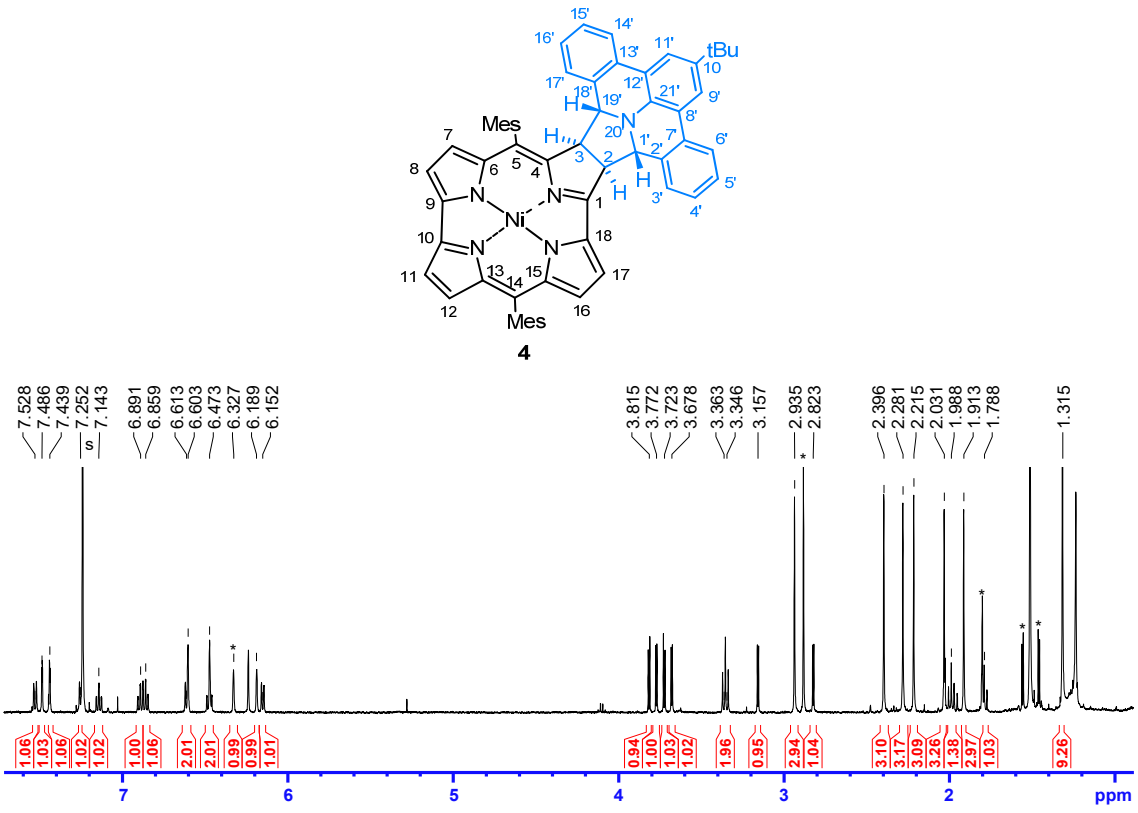


Figure S36. ^{1}H NMR spectrum of **4** (500 MHz, 298 K, $CDCl_3$). The signals of starting **1**-H were indicated with asterisks. The signals of contaminating **1**-H (retro-cycloaddition product)were indicated with asterisks.

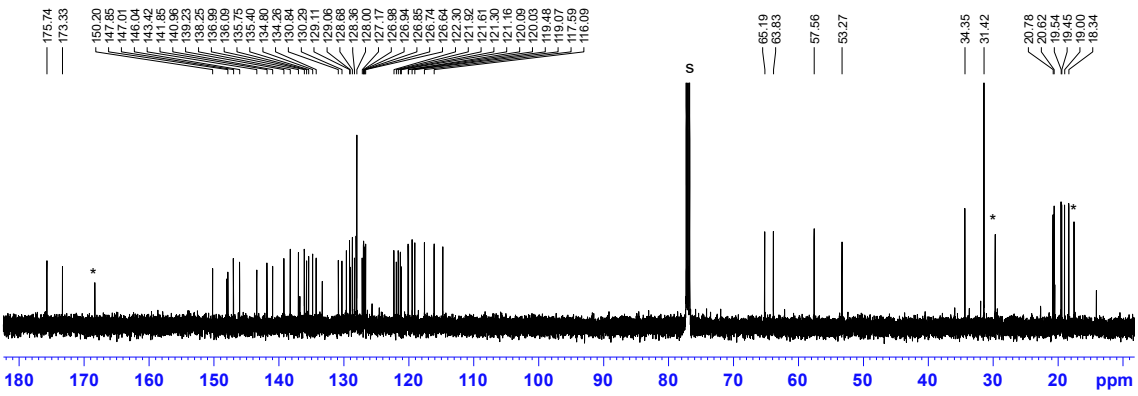


Figure S37. ^{13}C NMR spectrum of **4** (125 MHz, 298 K, $CDCl_3$). The signals of contaminating **1**-H (retro-cycloaddition product) were indicated with asterisks.

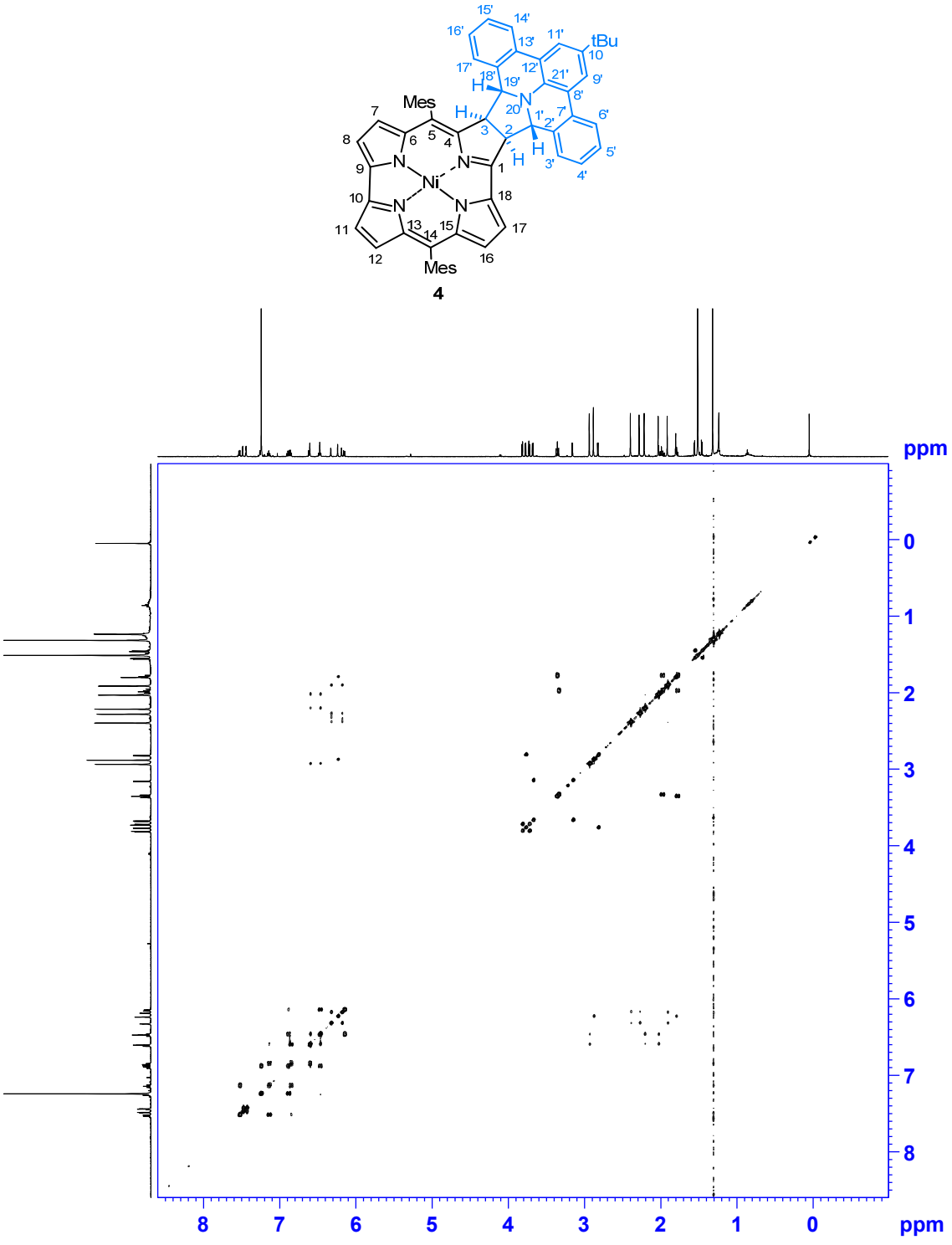


Figure S38. ^{1}H, ^{1}H COSY spectrum of **4** (500 MHz, 298 K, $CDCl_3$).

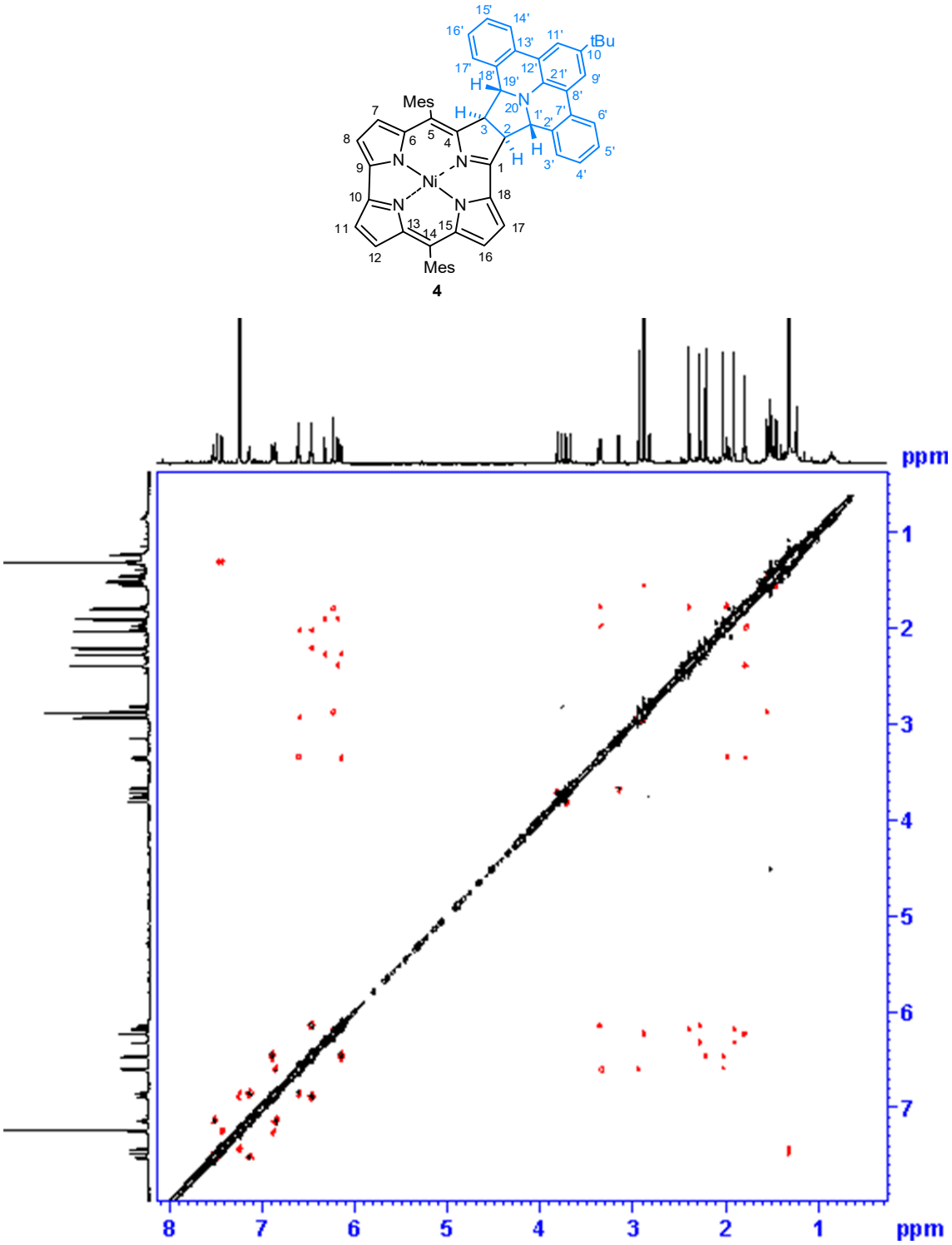


Figure S39. ^{1}H, ^{1}H NOESY spectrum of **4** (600 MHz, 298 K, $CDCl_3$).

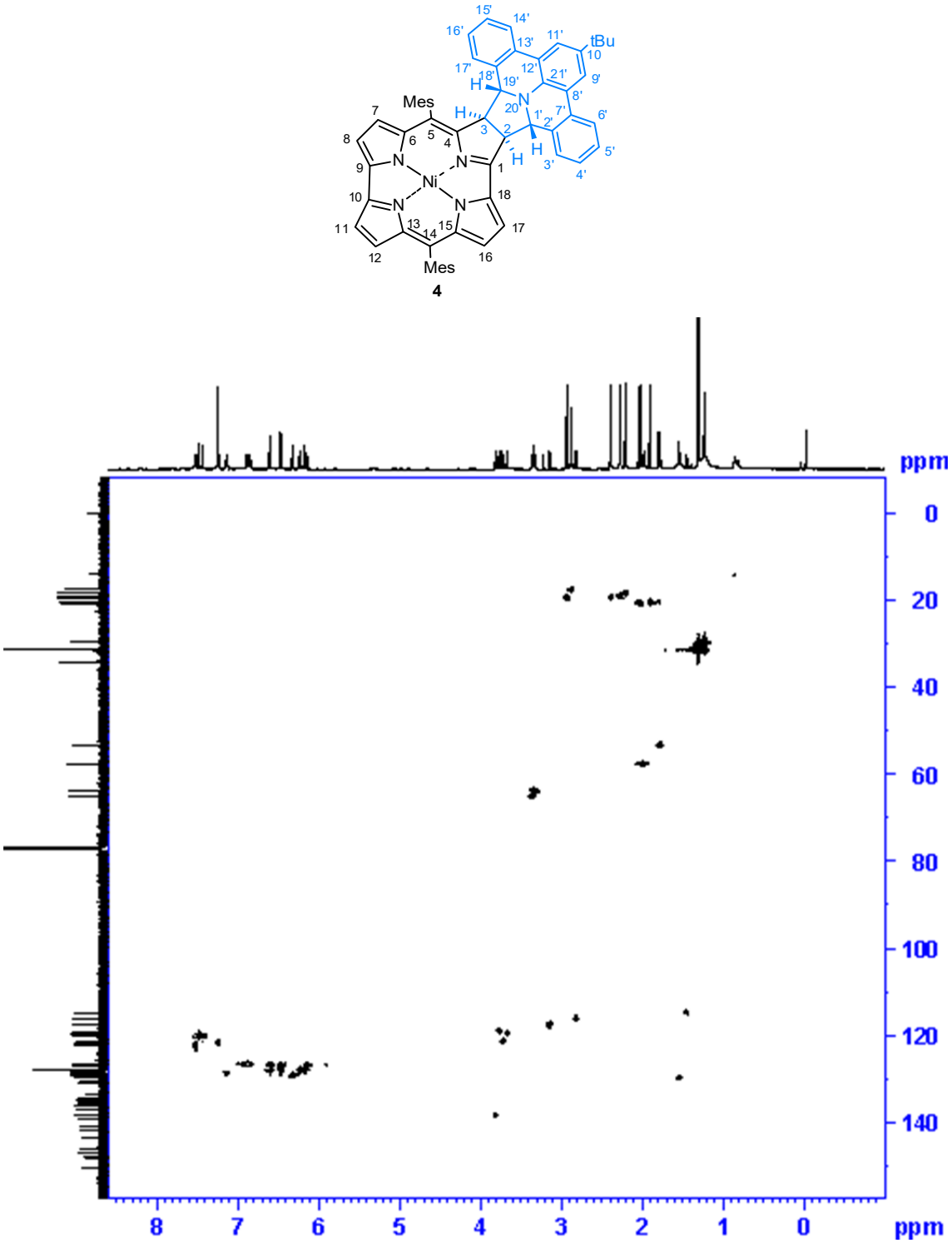


Figure S40. ^{1}H, ^{13}C HSQC spectrum of **4** (500/125 MHz, 298 K, $CDCl_3$).

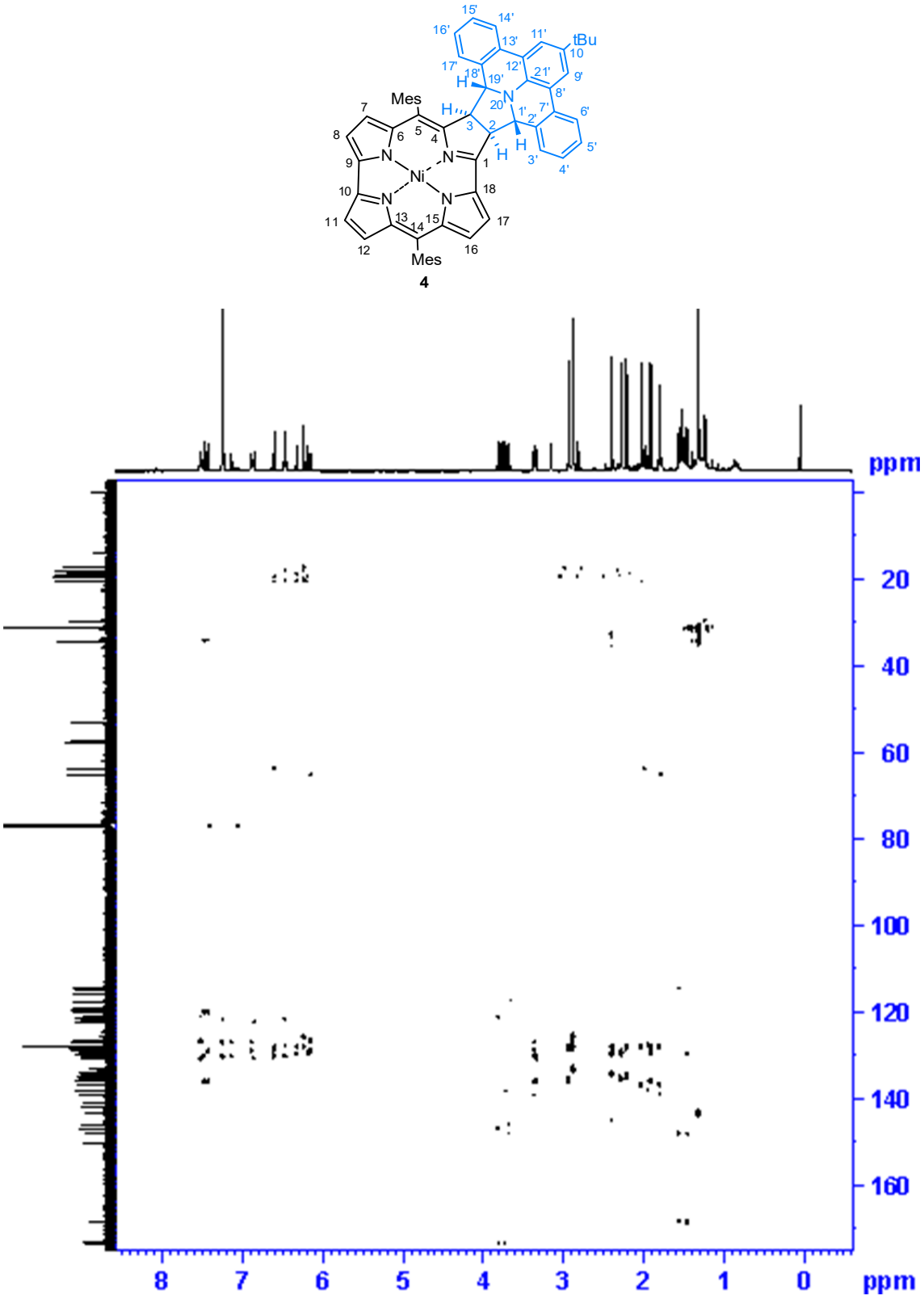


Figure S41. ^{1}H, ^{13}C HMBC spectrum of **4** (600/150 MHz, 298 K, $CDCl_3$).

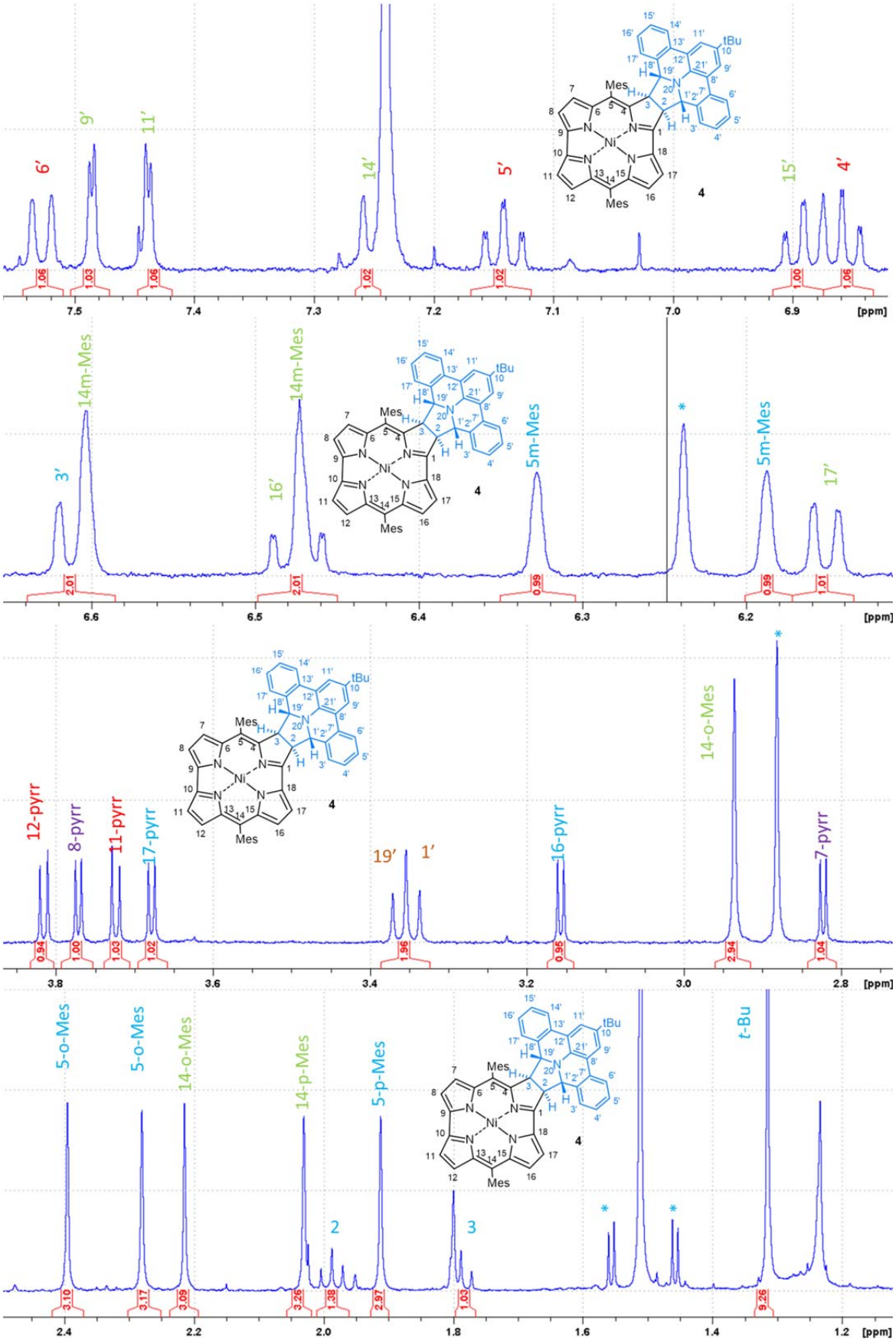


Figure S42. ^{1}H NMR signal assignments for **4** (500 MHz, 298 K, $CDCl_3$). The signals of contaminating **1**-H (retro-cycloaddition product) were indicated with asterisks.

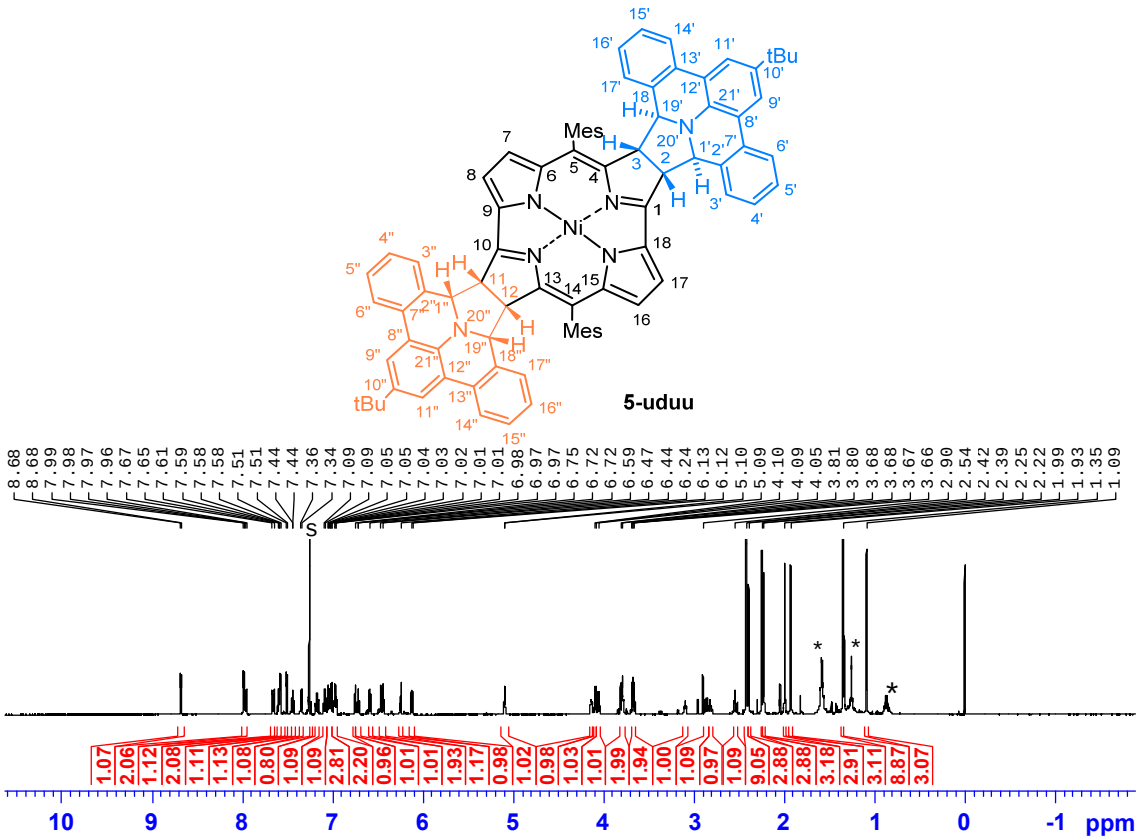


Figure S43. ^{1}H NMR spectrum of **5-uduu** (500 MHz, 298 K, $CDCl_3$).

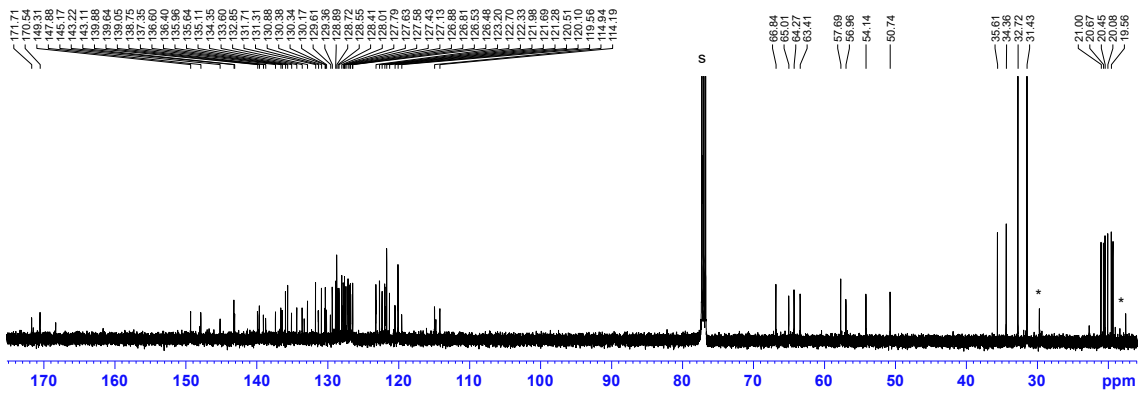


Figure S44. ^{13}C NMR spectrum of **5**-uduu (125 MHz, 298 K, $CDCl_3$).

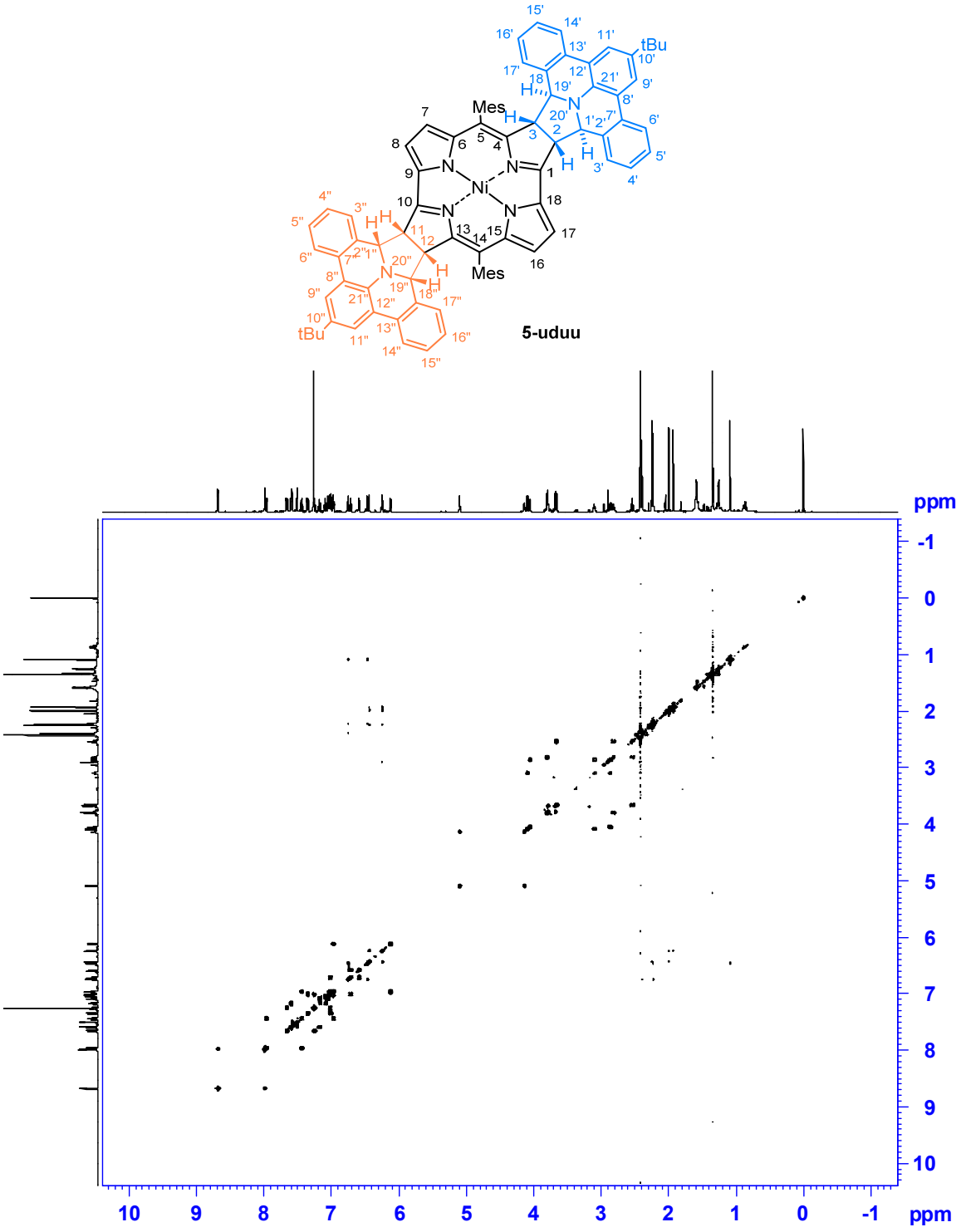


Figure S45. ^{1}H, ^{1}H COSY spectrum of **5**-uduu (500 MHz, 298 K, $CDCl_3$).

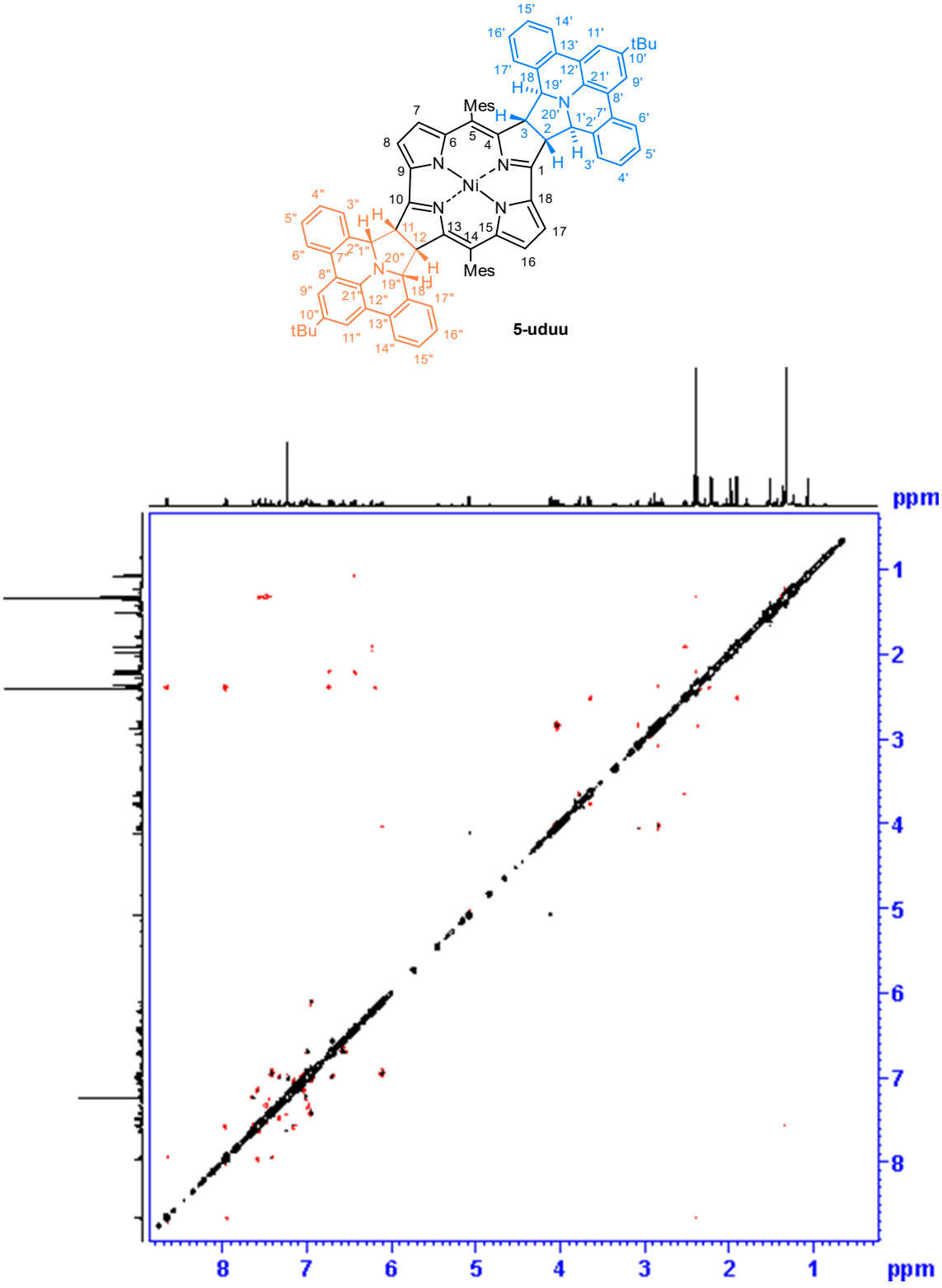


Figure S46. ^{1}H, ^{1}H NOESY spectrum of **5**-uduu (600 MHz, 298 K, $CDCl_3$).

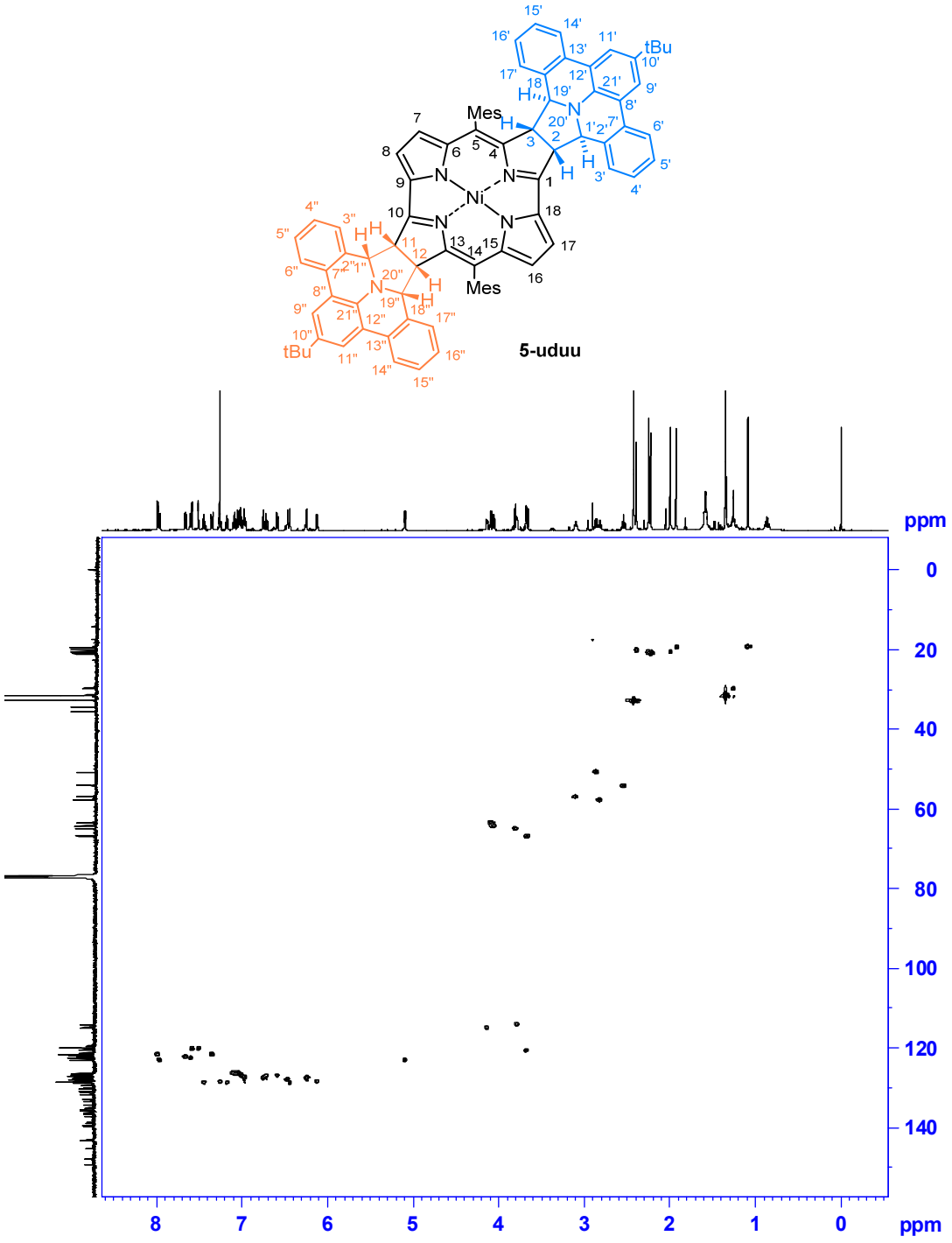


Figure S47. ^{1}H, ^{13}C HSQC spectrum of **5**-uduu (500/125 MHz, 298 K, $CDCl_3$).

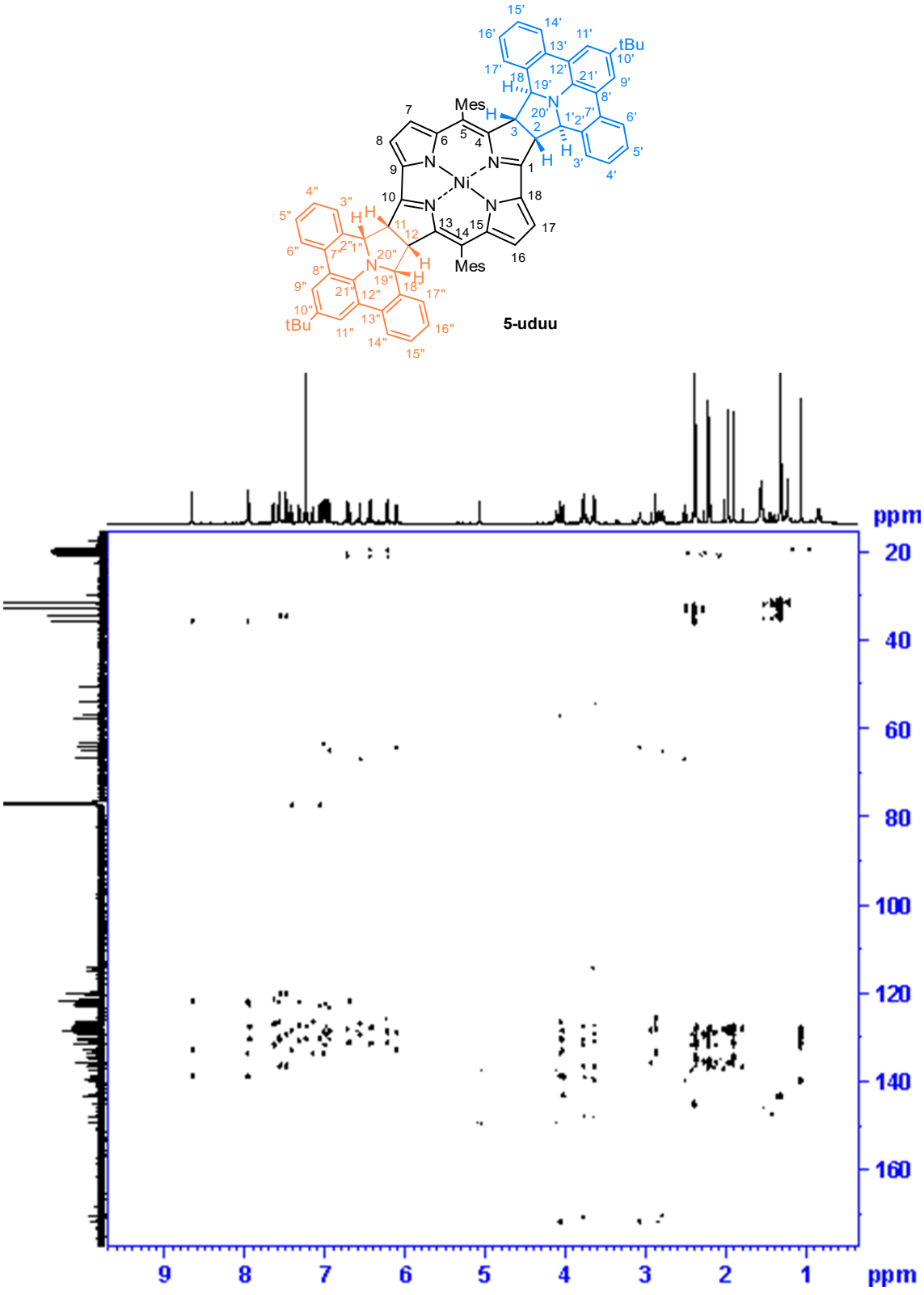
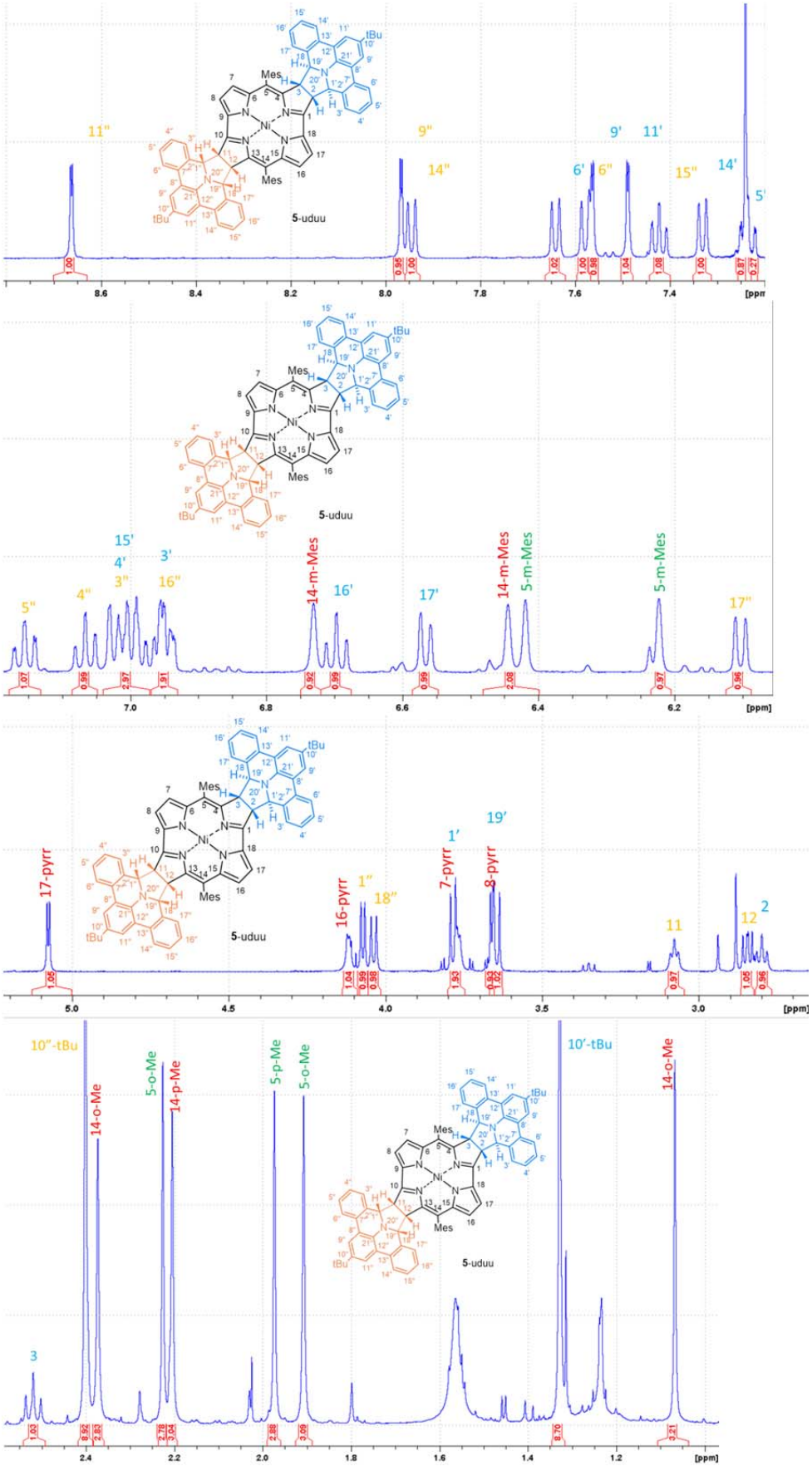


Figure S48. ^{1}H, ^{13}C HMBC spectrum of **5**-uduu (600/150 MHz, 298 K, $CDCl_3$).



Fgure S49. ^{1}H NMR signal assignments for **5**-uduu (500 MHz, 298 K, $CDCl_3$).

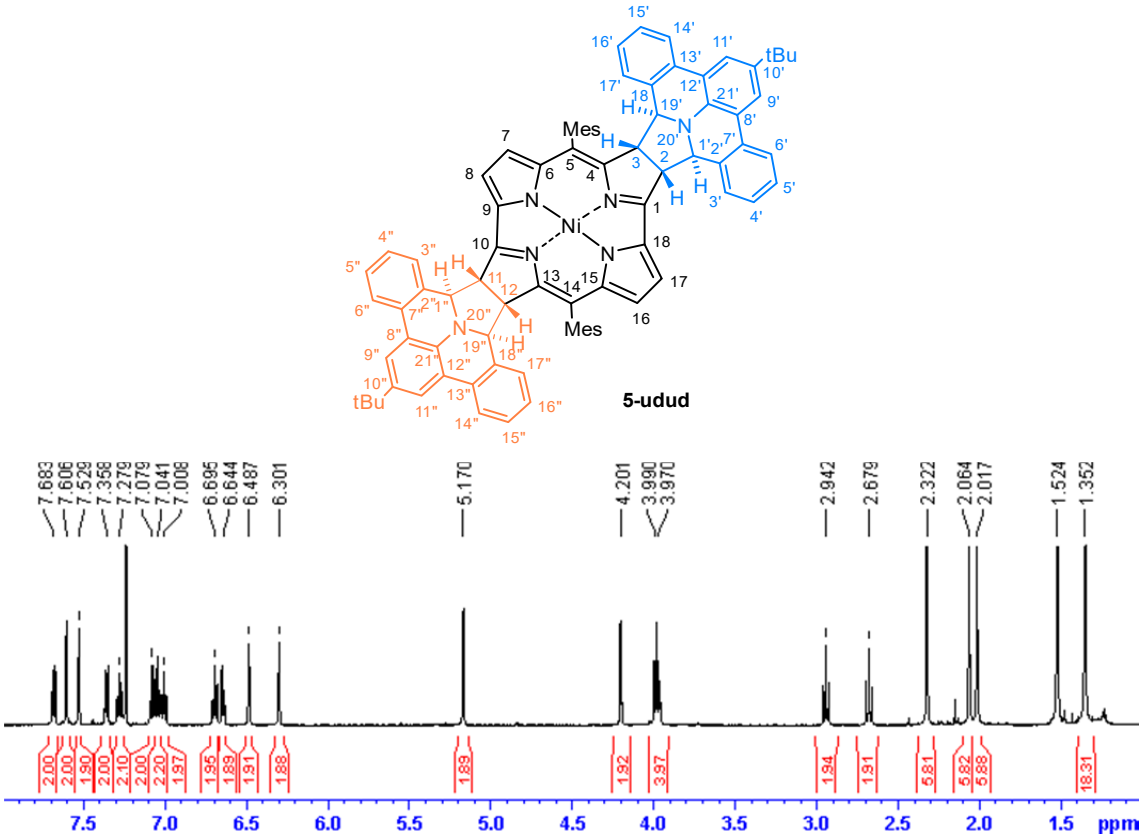


Figure S50. ^{1}H NMR spectrum of **5-udud** (600 MHz, 298 K, $CDCl_3$).

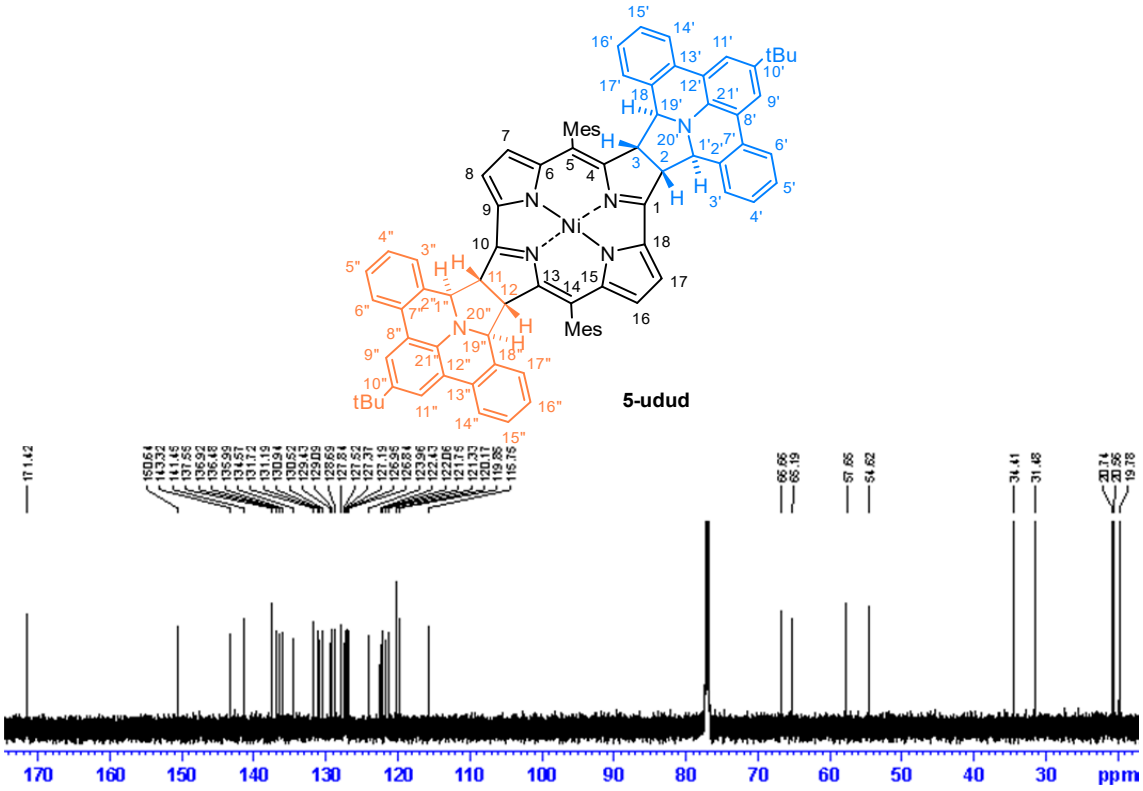


Figure S51. ^{13}C NMR spectrum of **5**-udud (150 MHz, 298 K, $CDCl_3$).

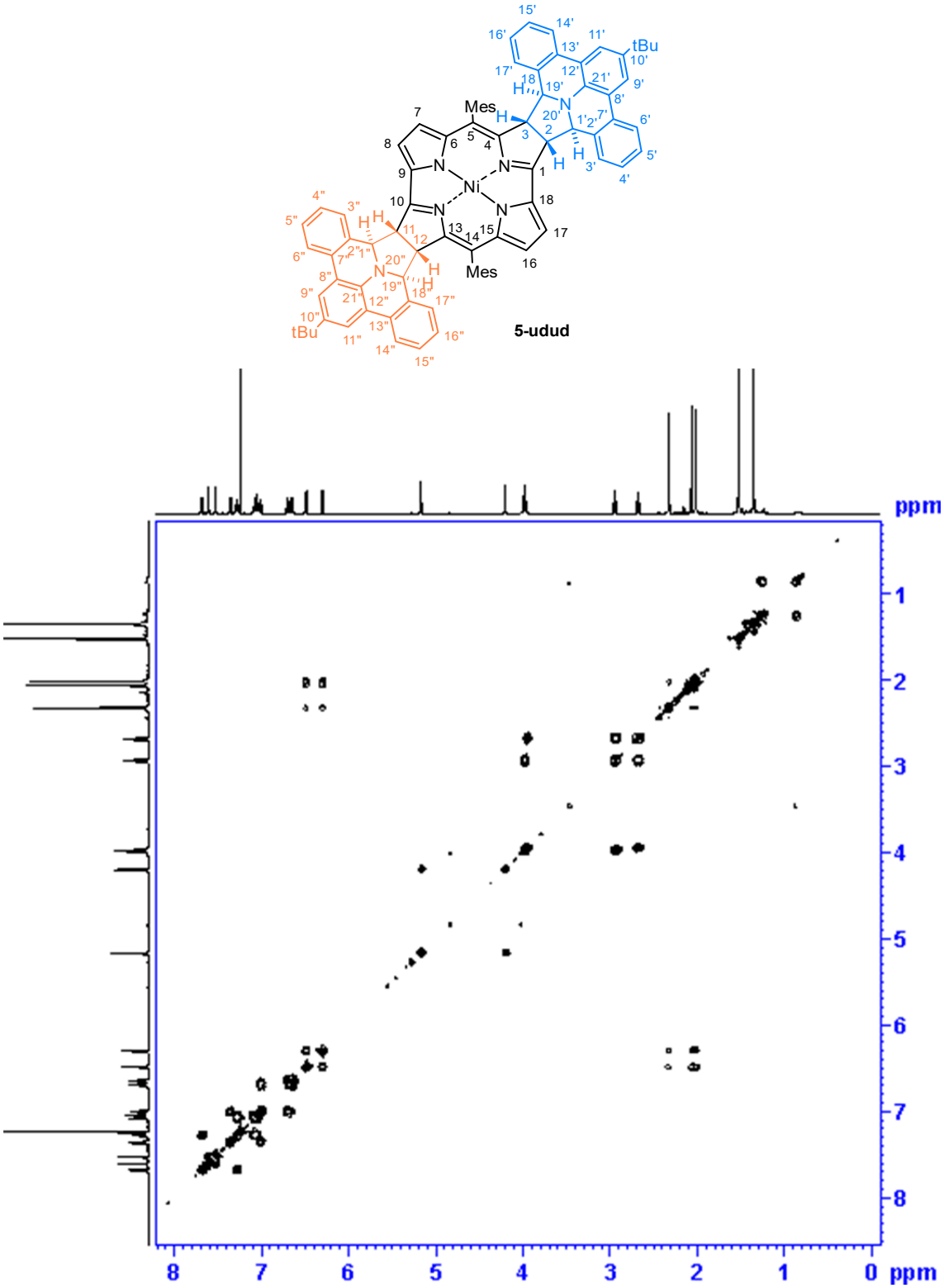


Figure S52. ^{1}H, ^{1}H COSY spectrum of **5**-udud (500 MHz, 298 K, $CDCl_3$).

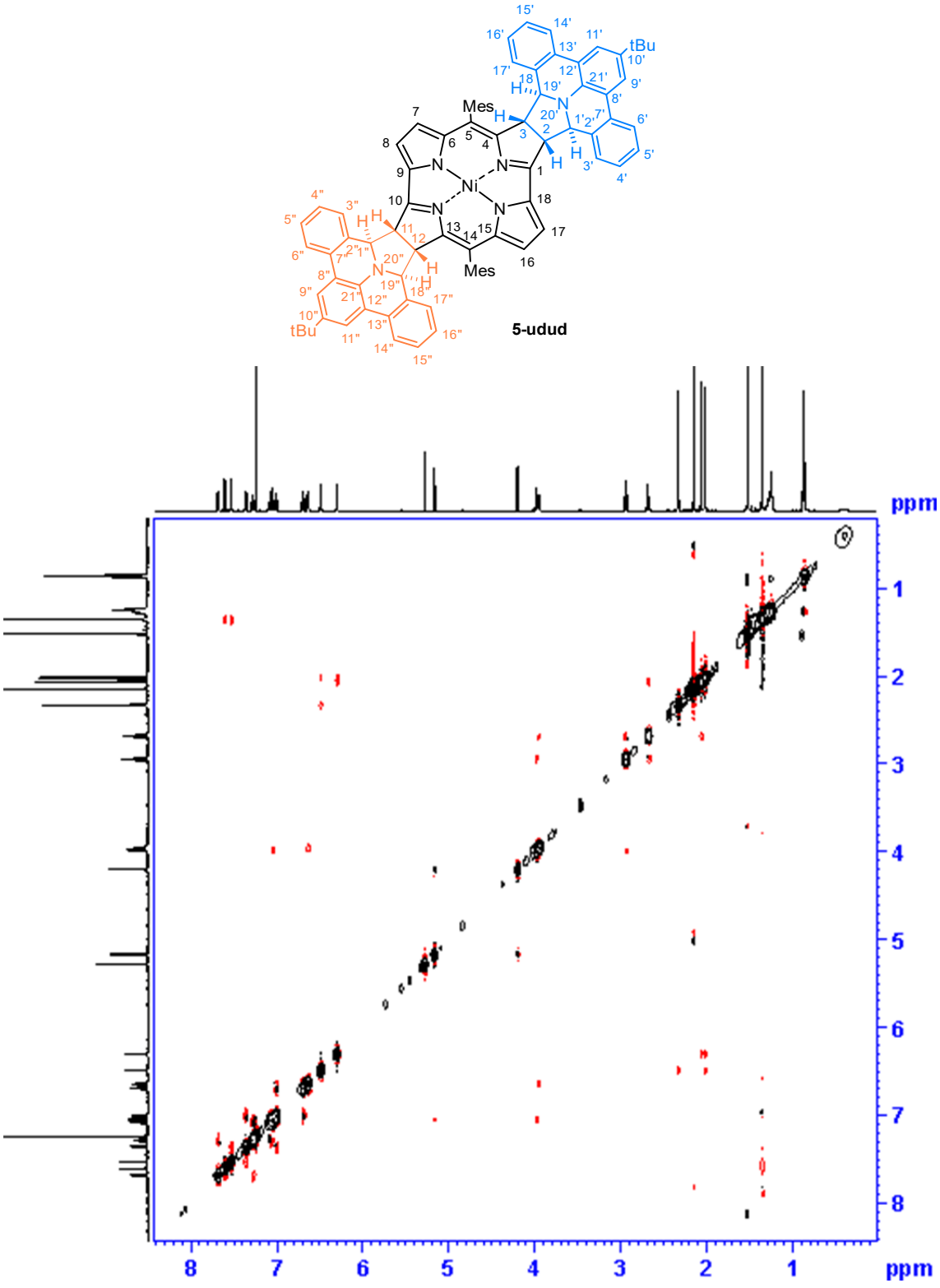


Figure S53. ^{1}H, ^{1}H NOESY spectrum of **5**-udud (500 MHz, 298 K, $CDCl_3$).

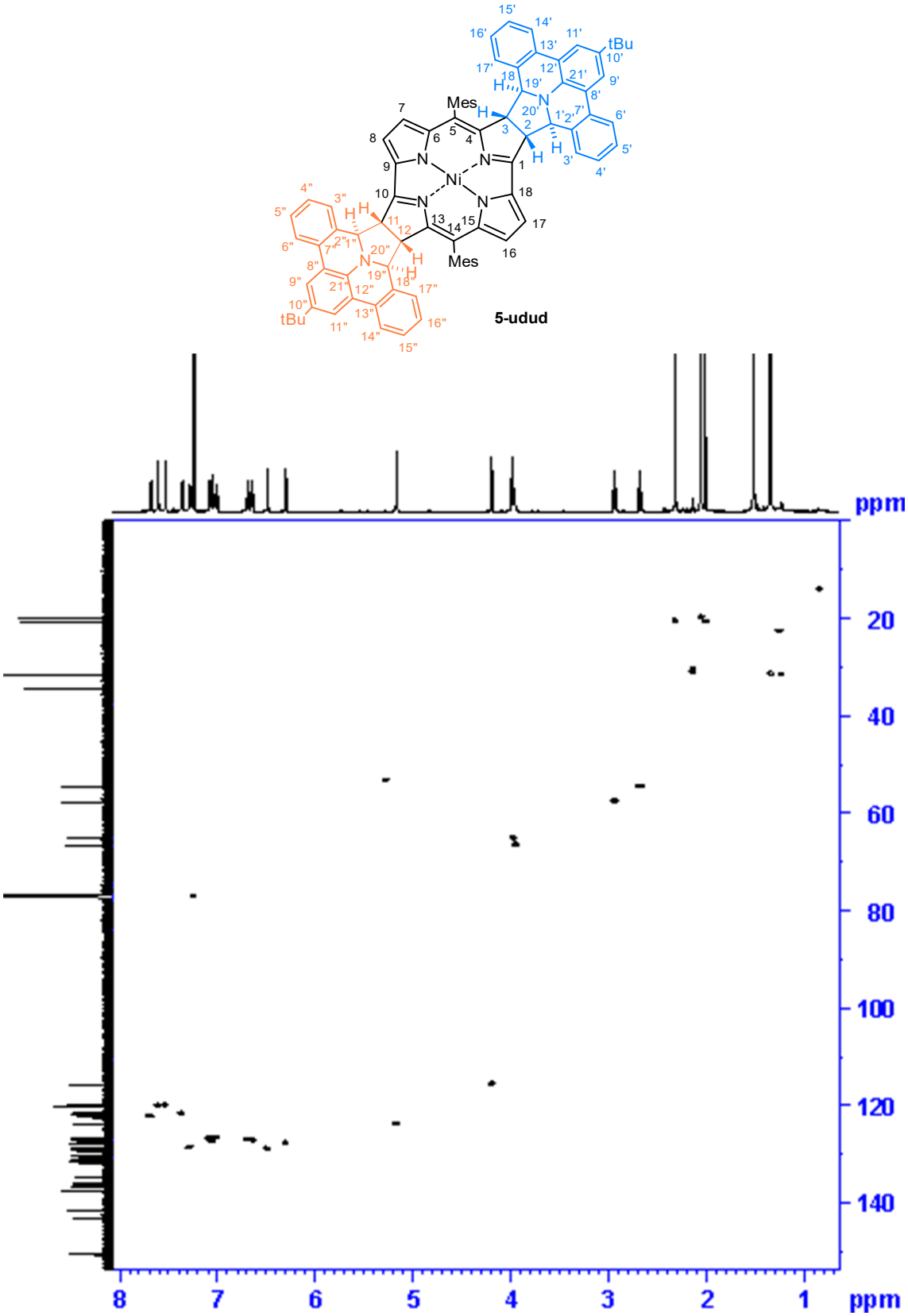


Figure S54. ^{1}H, ^{13}C HSQC spectrum of **5**-udud (500/125 MHz, 298 K, $CDCl_3$).

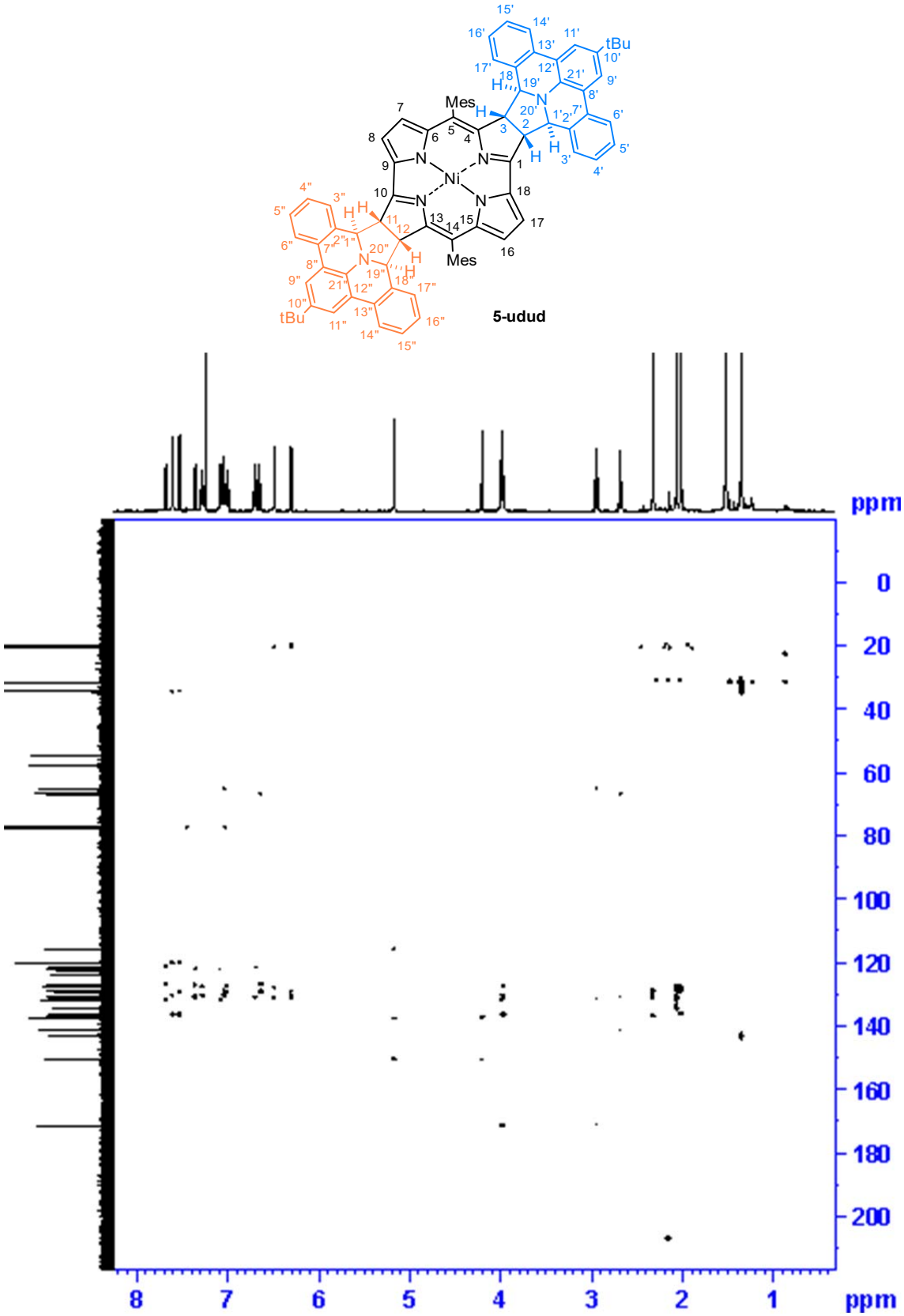
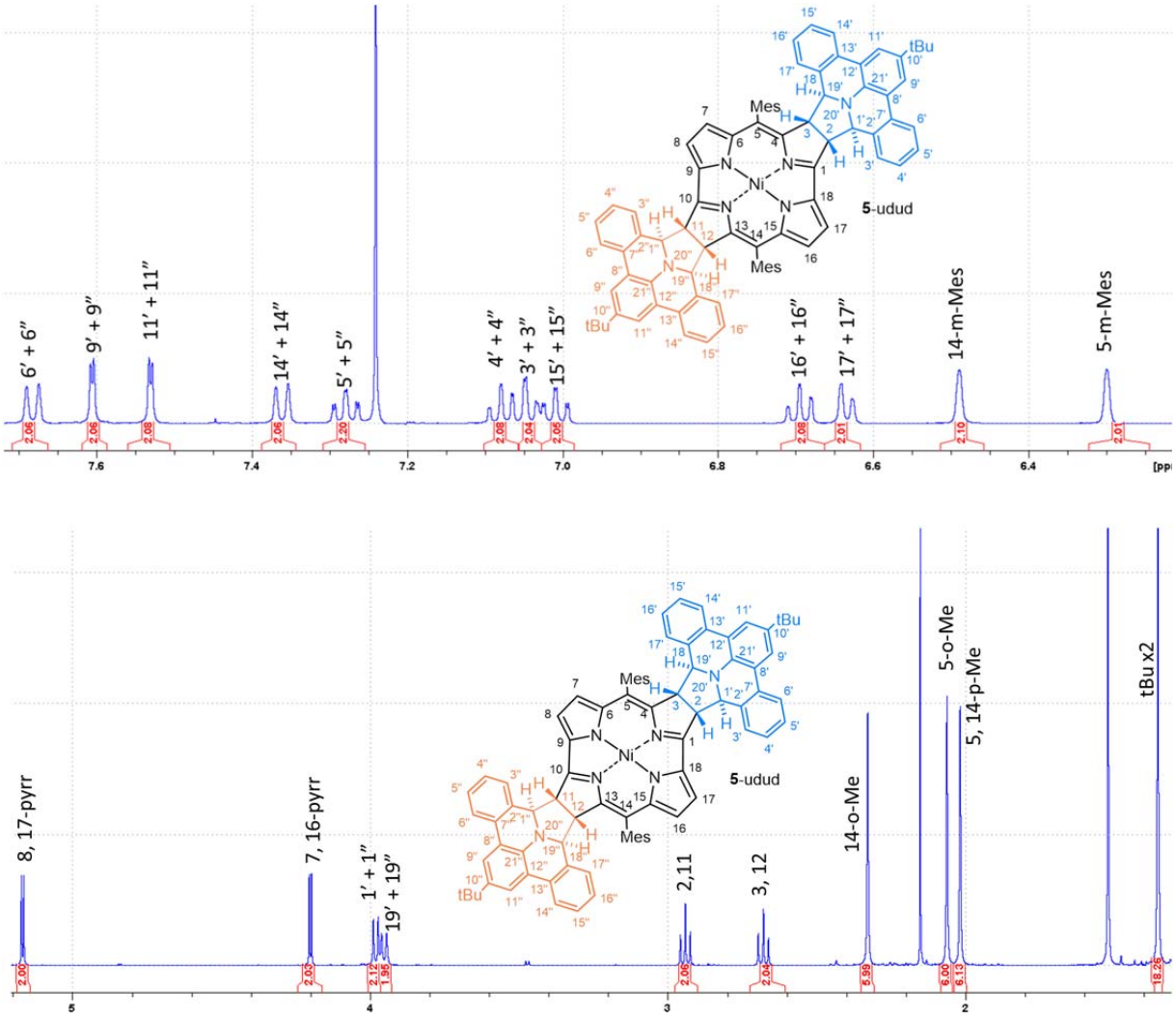


Figure S55. ^{1}H, ^{13}C HMBC spectrum of **5**-udud (500/125 MHz, 298 K, $CDCl_3$).



Fgure S56. ^{1}H NMR signal assignments for **5**-udud (500 MHz, 298 K, $CDCl_3$).

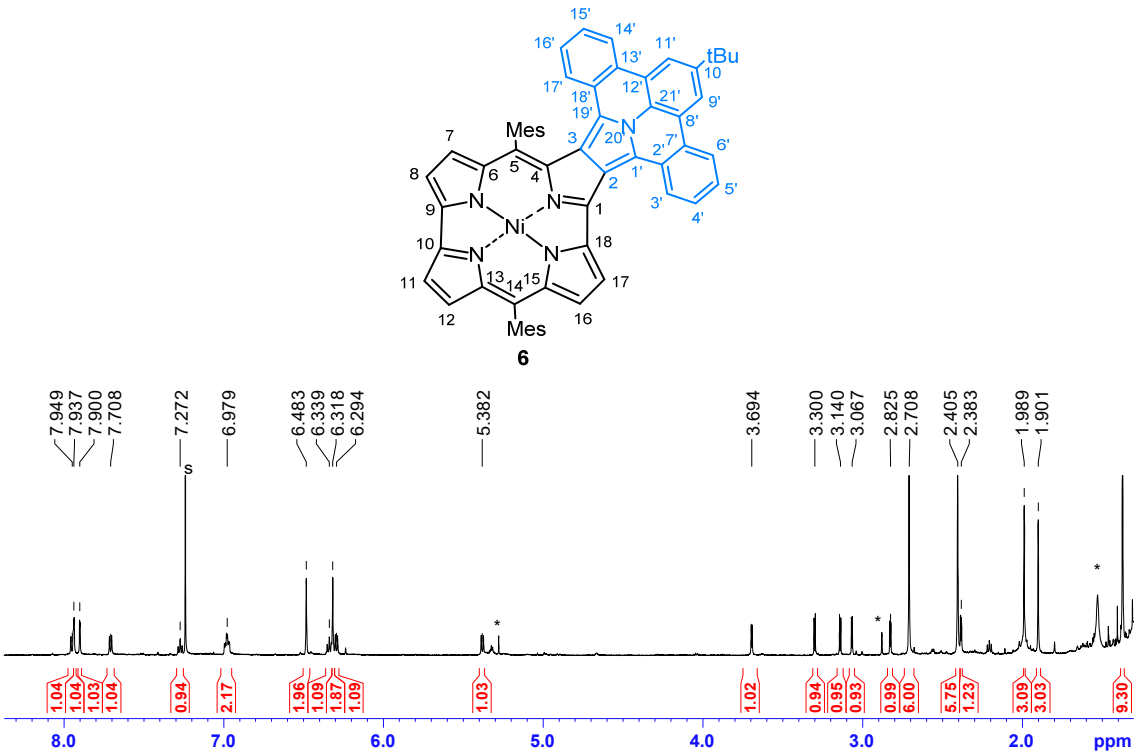


Figure S57. ^{1}H NMR spectrum of **6** (600 MHz, 298 K, $CDCl_3$).

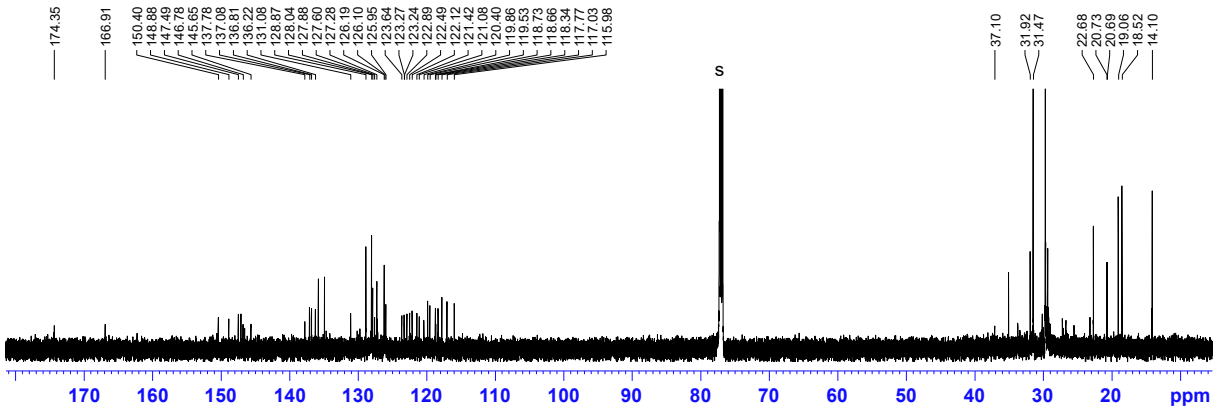


Figure S58. ^{13}C NMR spectrum of **6** (150 MHz, 298 K, $CDCl_3$).

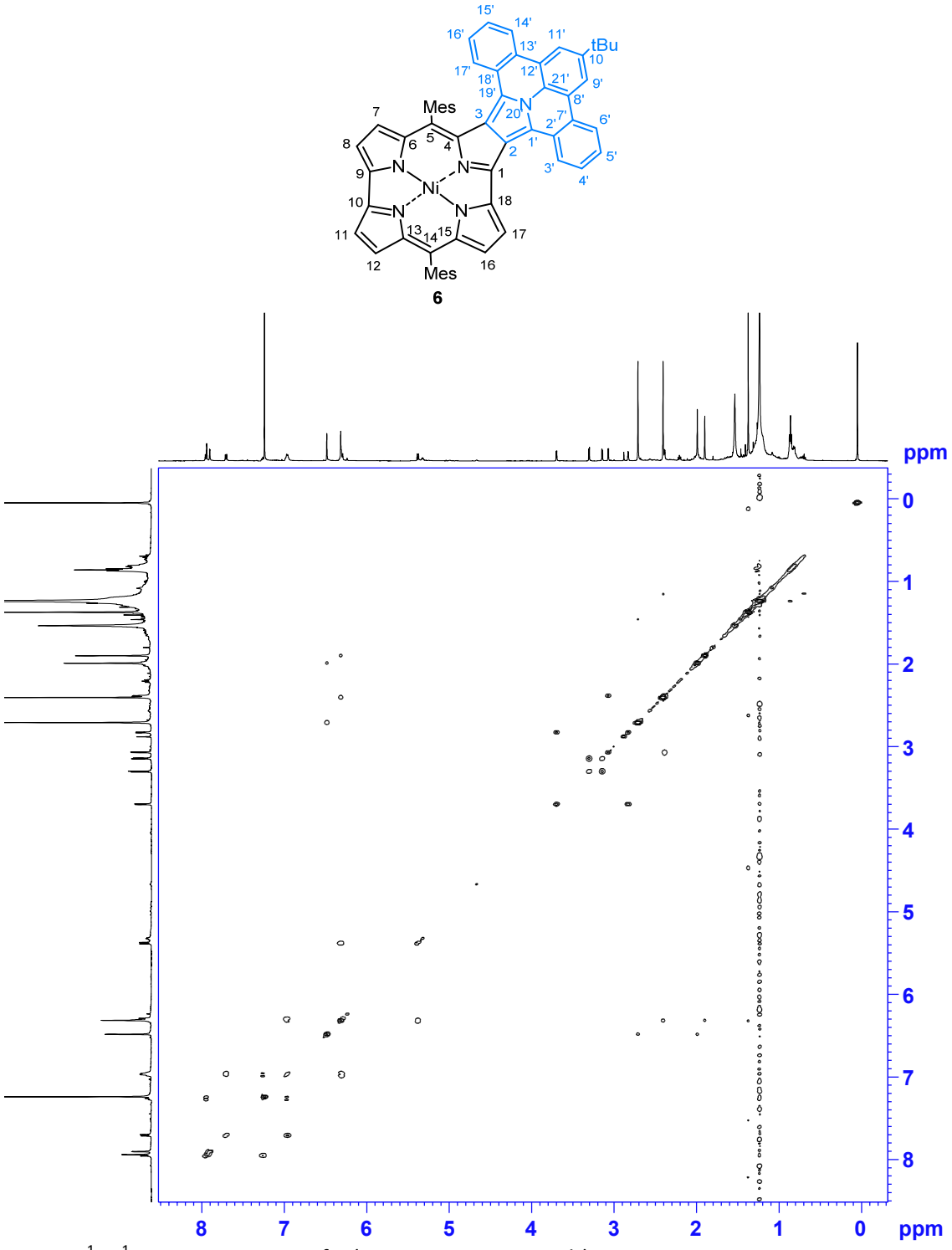


Figure S59. ^{1}H, ^{1}H COSY spectrum of **6** (500 MHz, 298 K, $CDCl_3$).

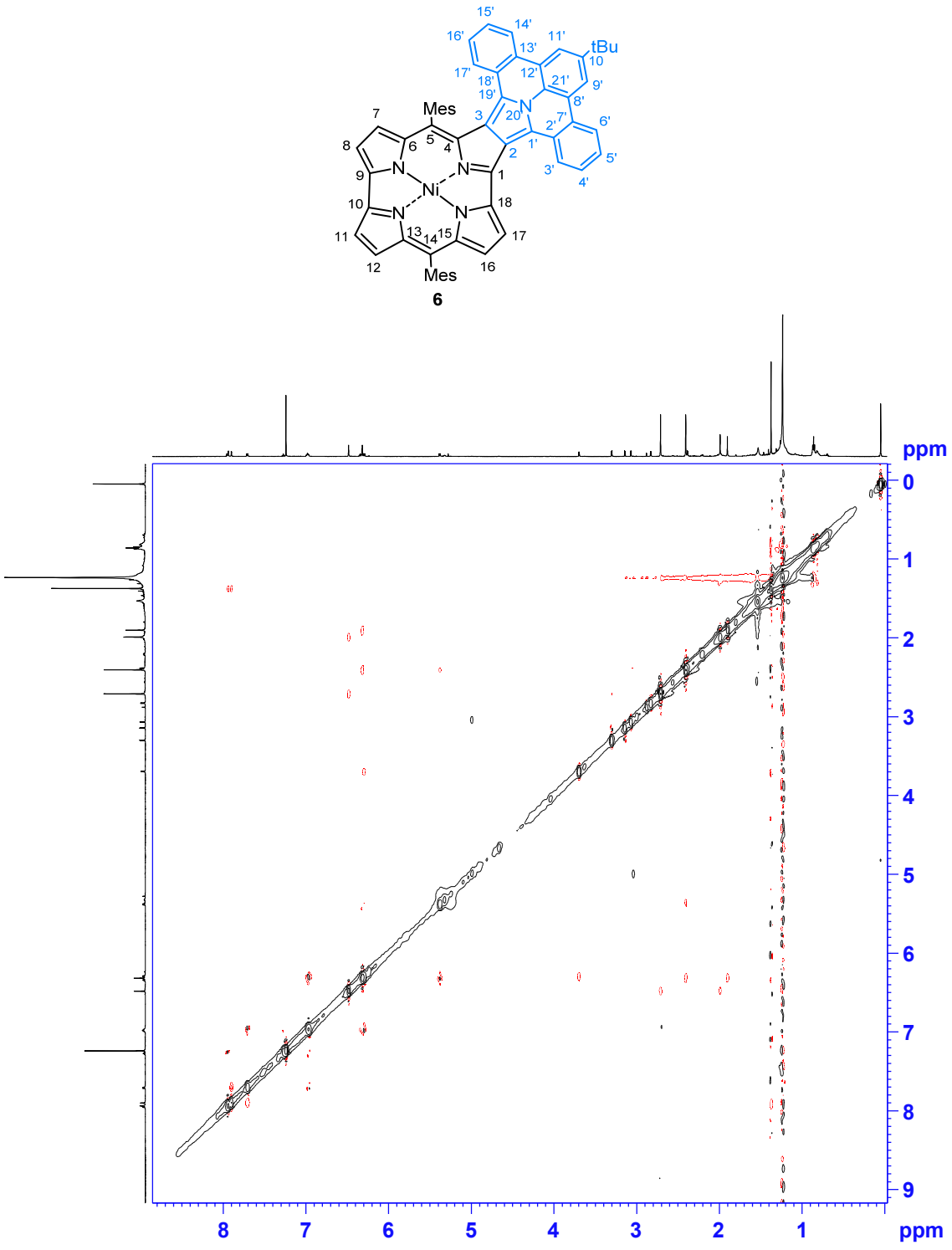


Figure S60. ^{1}H, ^{1}H NOESY spectrum of **6** (500 MHz, 298 K, $CDCl_3$).

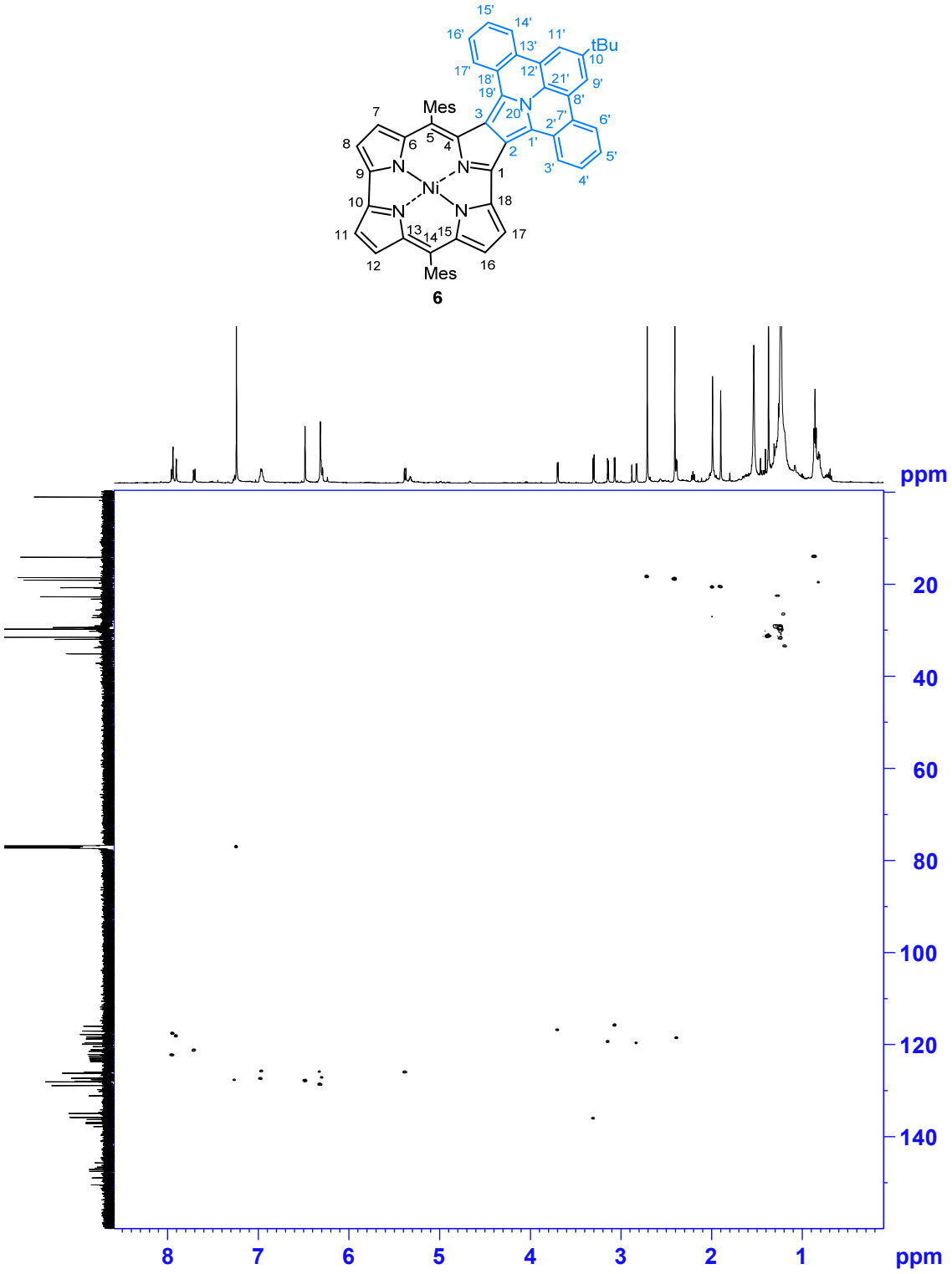


Figure S61. ^{1}H, ^{13}C HSQC spectrum of **6** (500/125 MHz, 298 K, $CDCl_3$).

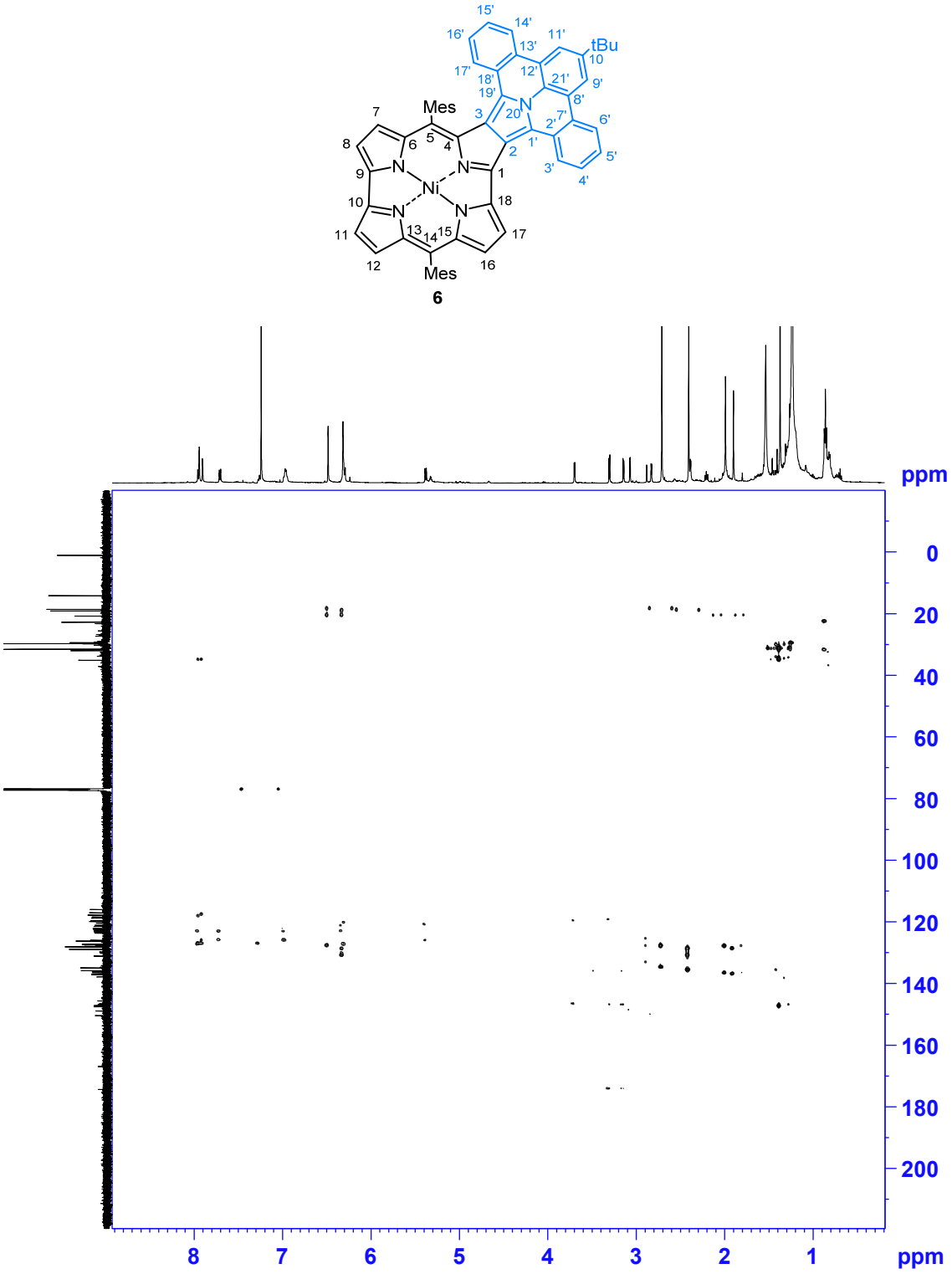


Figure S62. ^{1}H, ^{13}C HMBC spectrum of **6** (500/125 MHz, 298 K, $CDCl_3$).

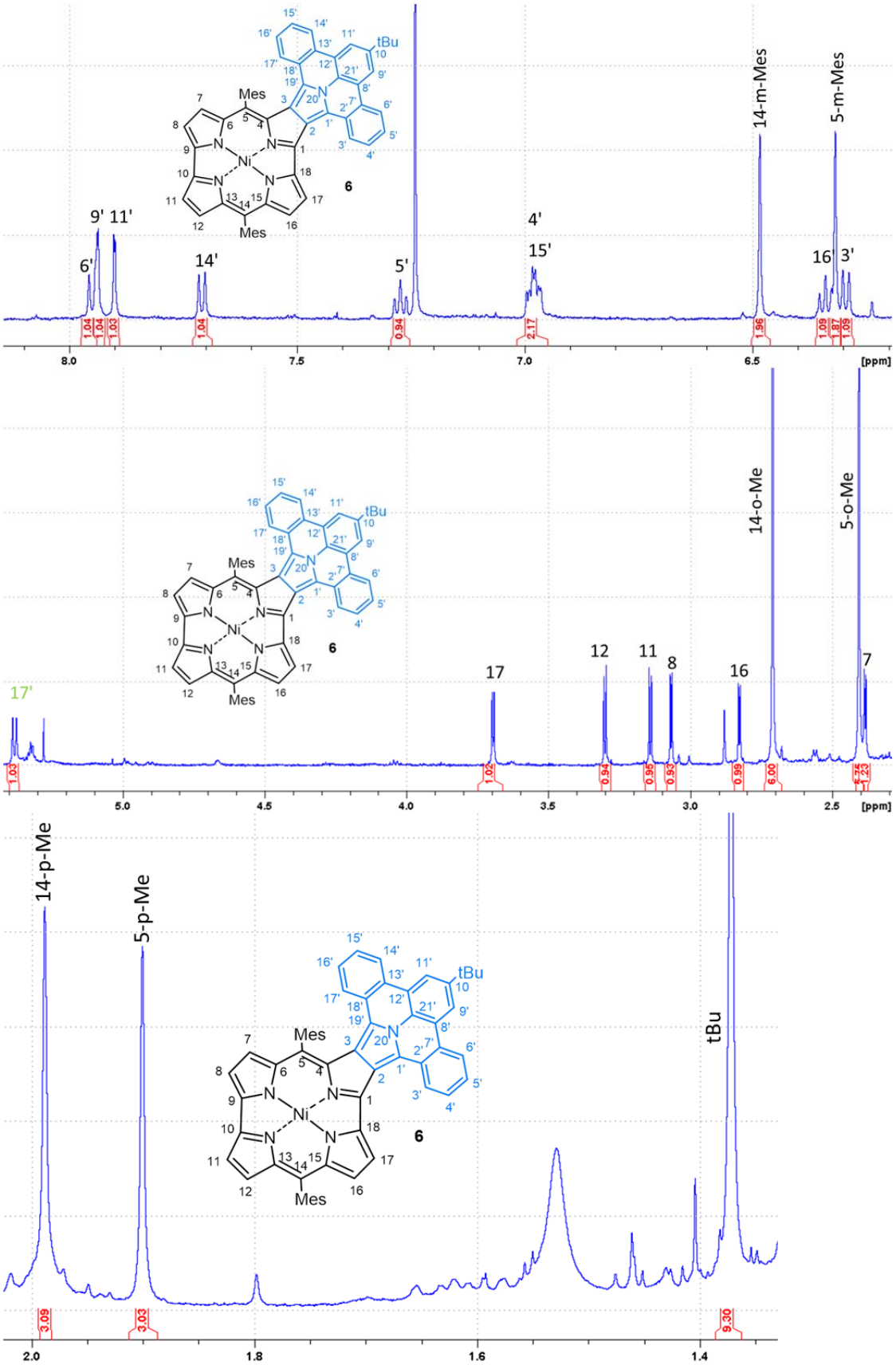


Figure S63. ^{1}H NMR signal assignments for **6** (500 MHz, 298 K, $CDCl_3$).

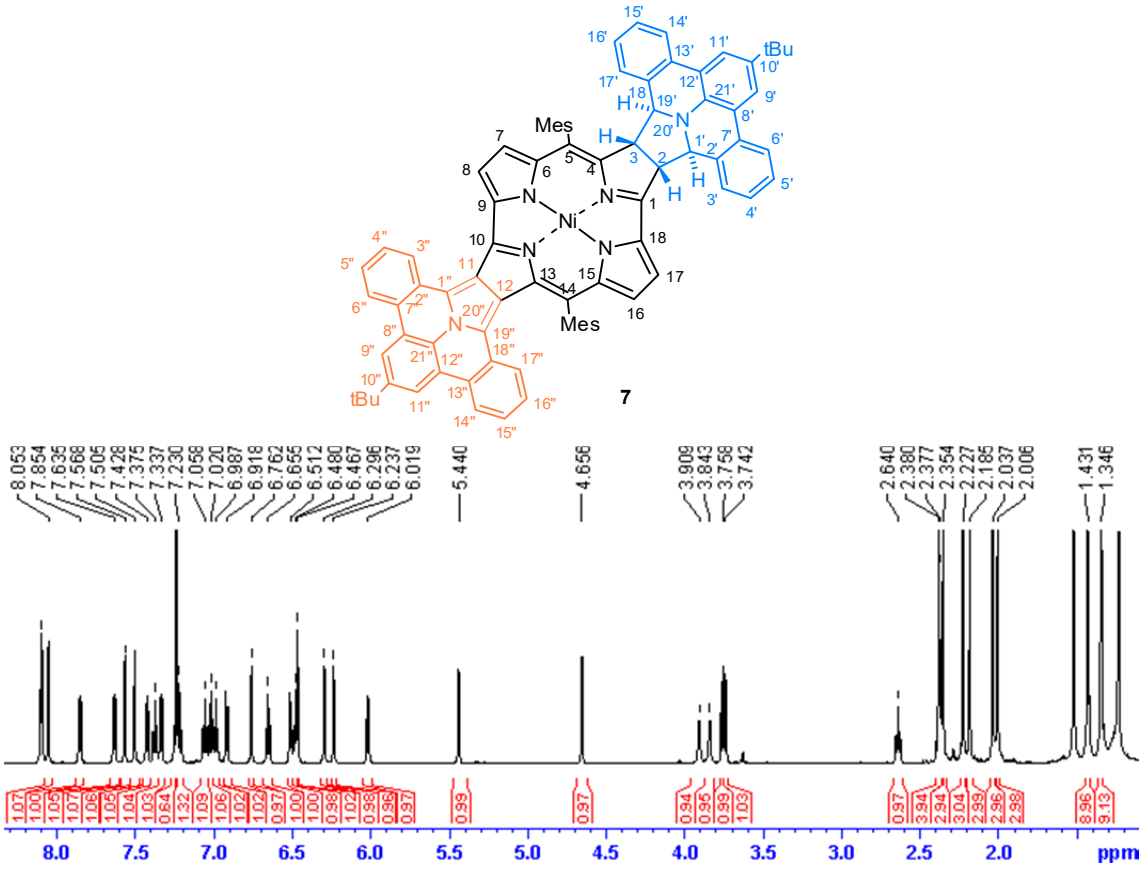


Figure S64. ^{1}H NMR spectrum of **7** (600 MHz, 298 K, $CDCl_3$).

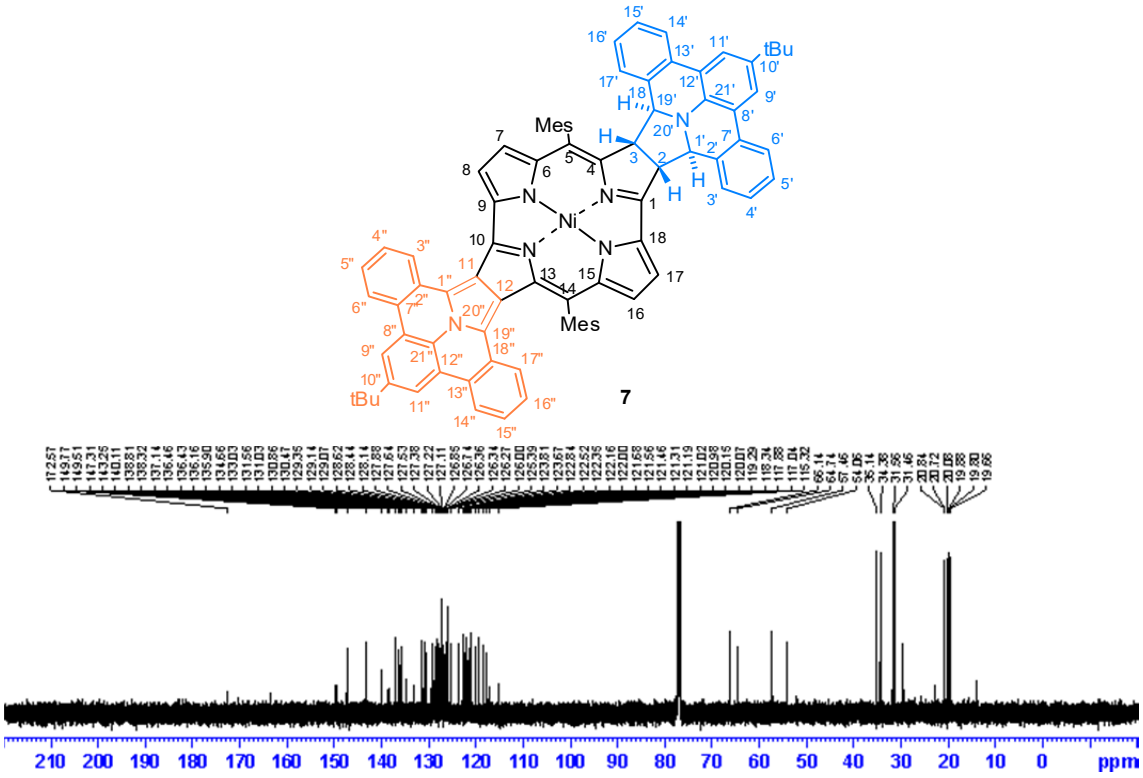


Figure S65. ^{13}C NMR spectrum of **7** (150 MHz, 298 K, $CDCl_3$).

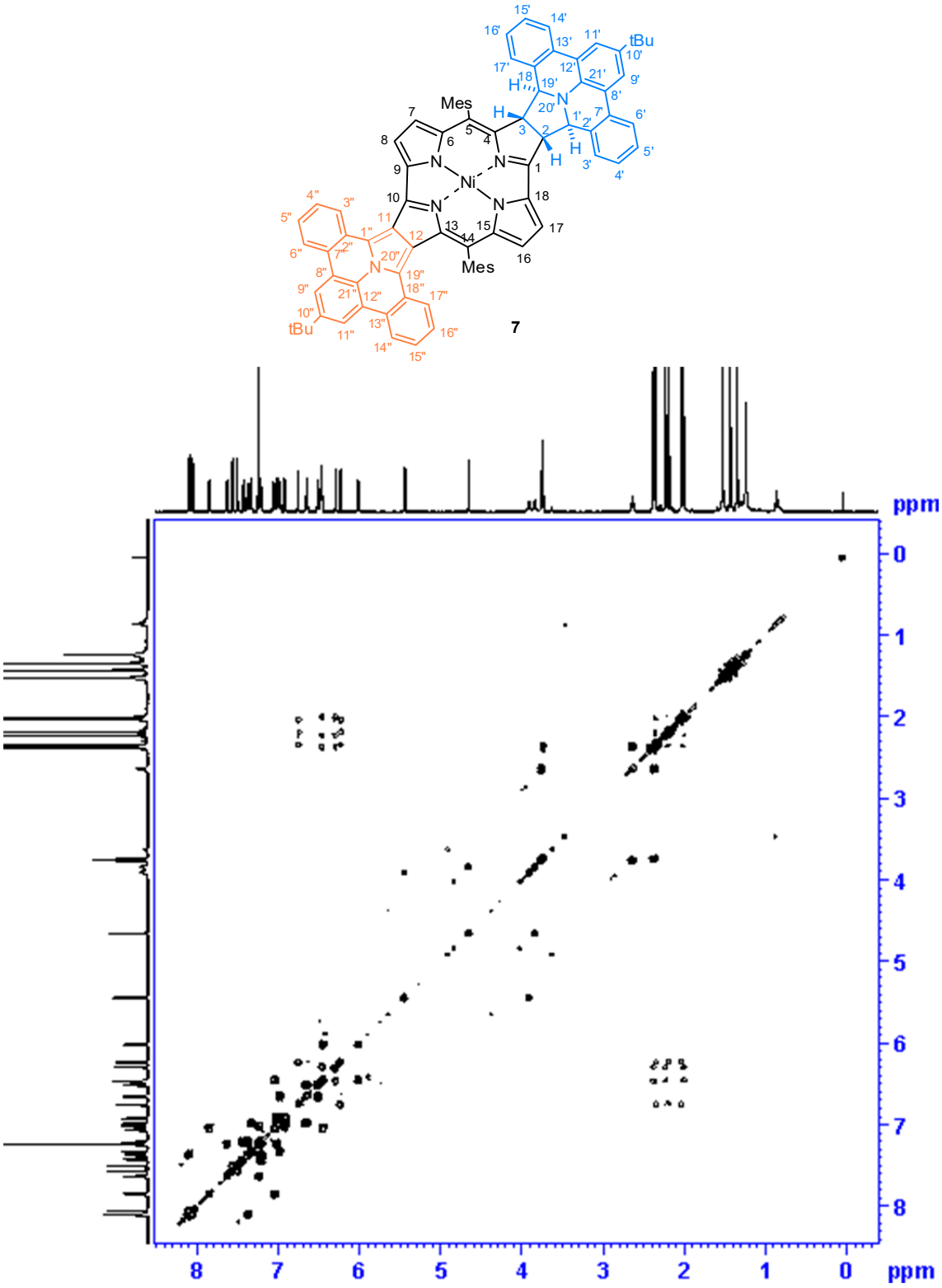


Figure S66. ^{1}H, ^{1}H COSY spectrum of **7** (500 MHz, 298 K, $CDCl_3$).

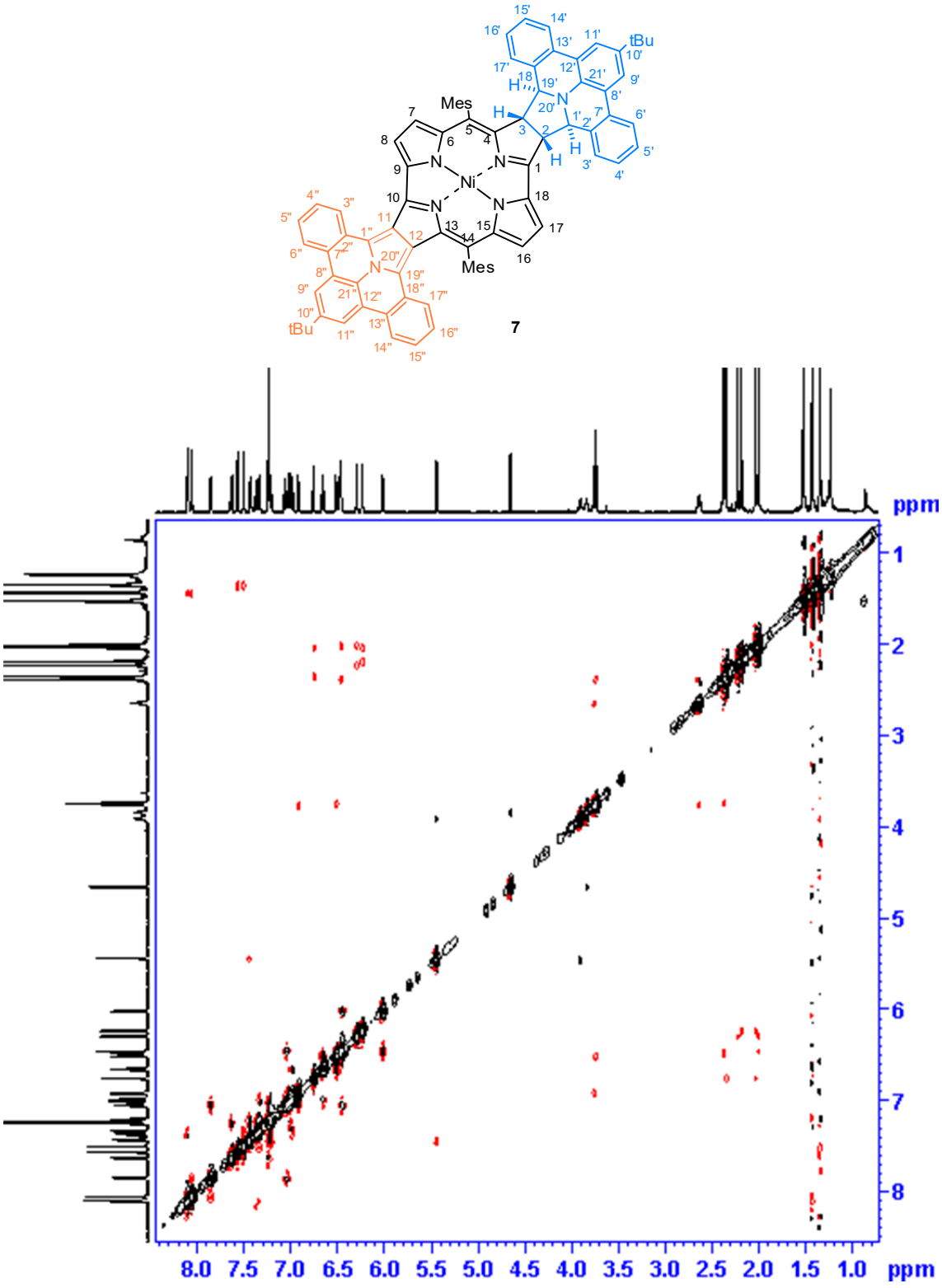


Figure S67. ^{1}H, ^{1}H NOESY spectrum of **7** (500 MHz, 298 K, $CDCl_3$).

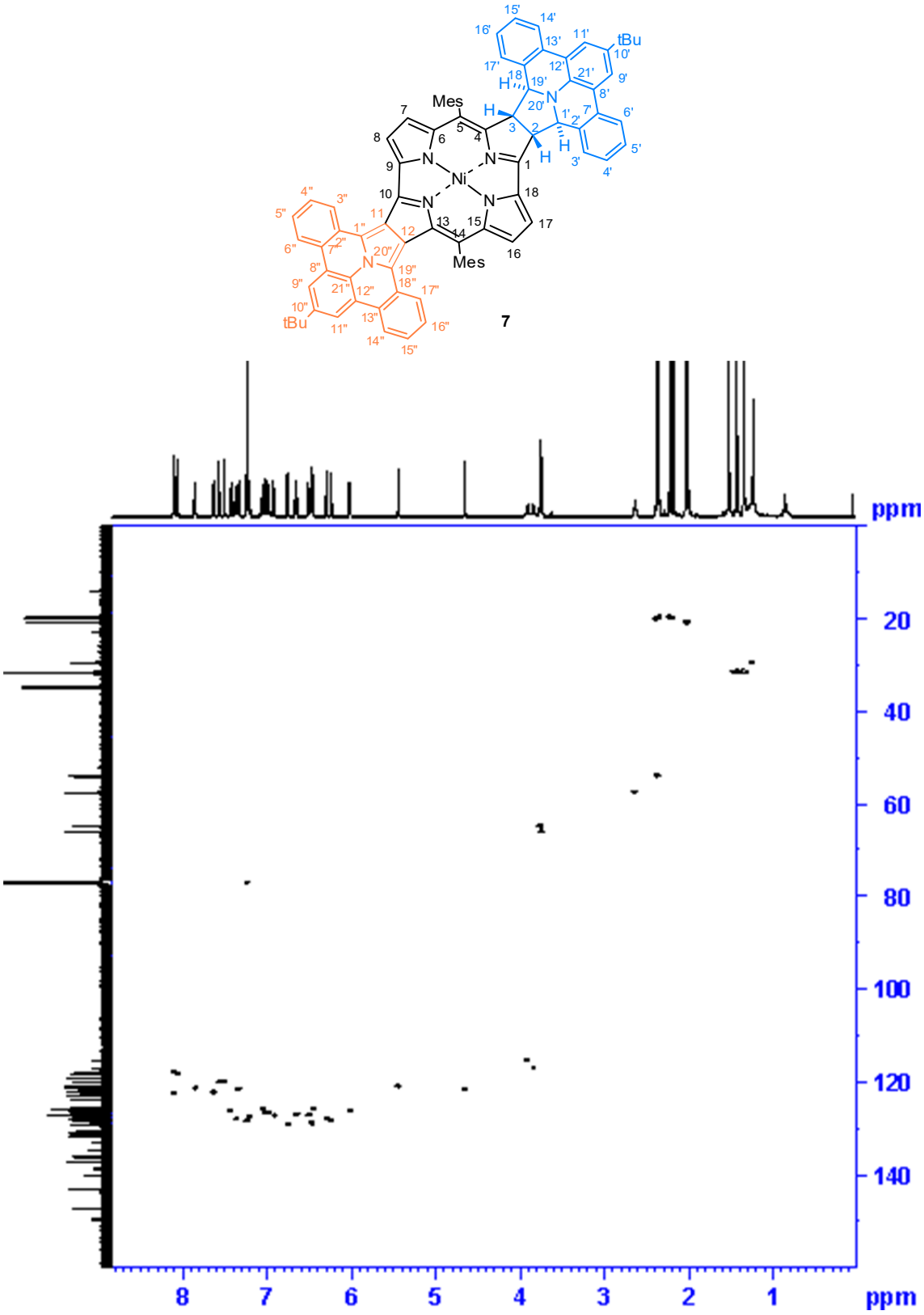


Figure S68. ^{1}H, ^{13}C HSQC spectrum of **7** (500/125 MHz, 298 K, $CDCl_3$).

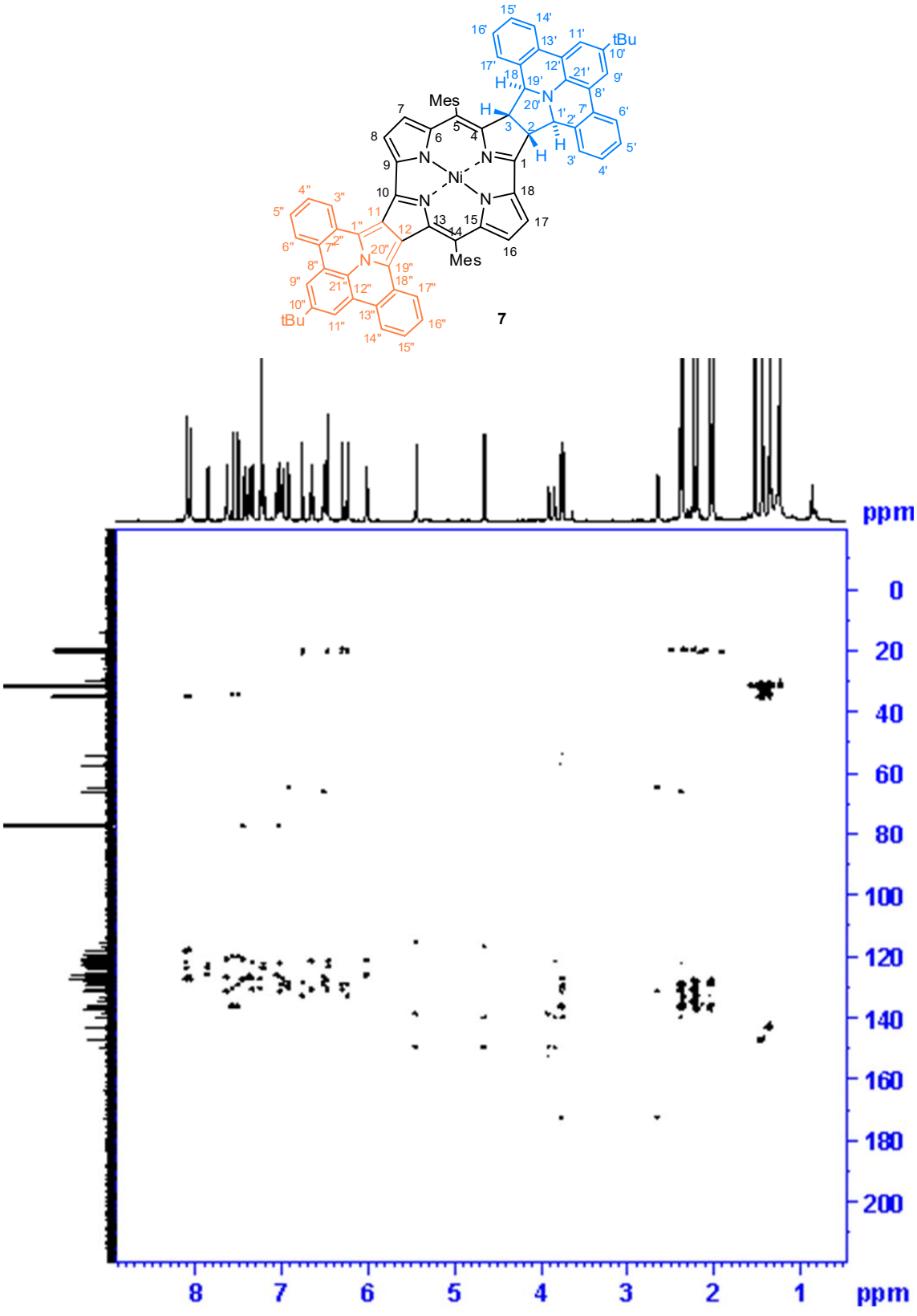


Figure S69. ^{1}H, ^{13}C HMBC spectrum of **7** (500/125 MHz, 298 K, $CDCl_3$).

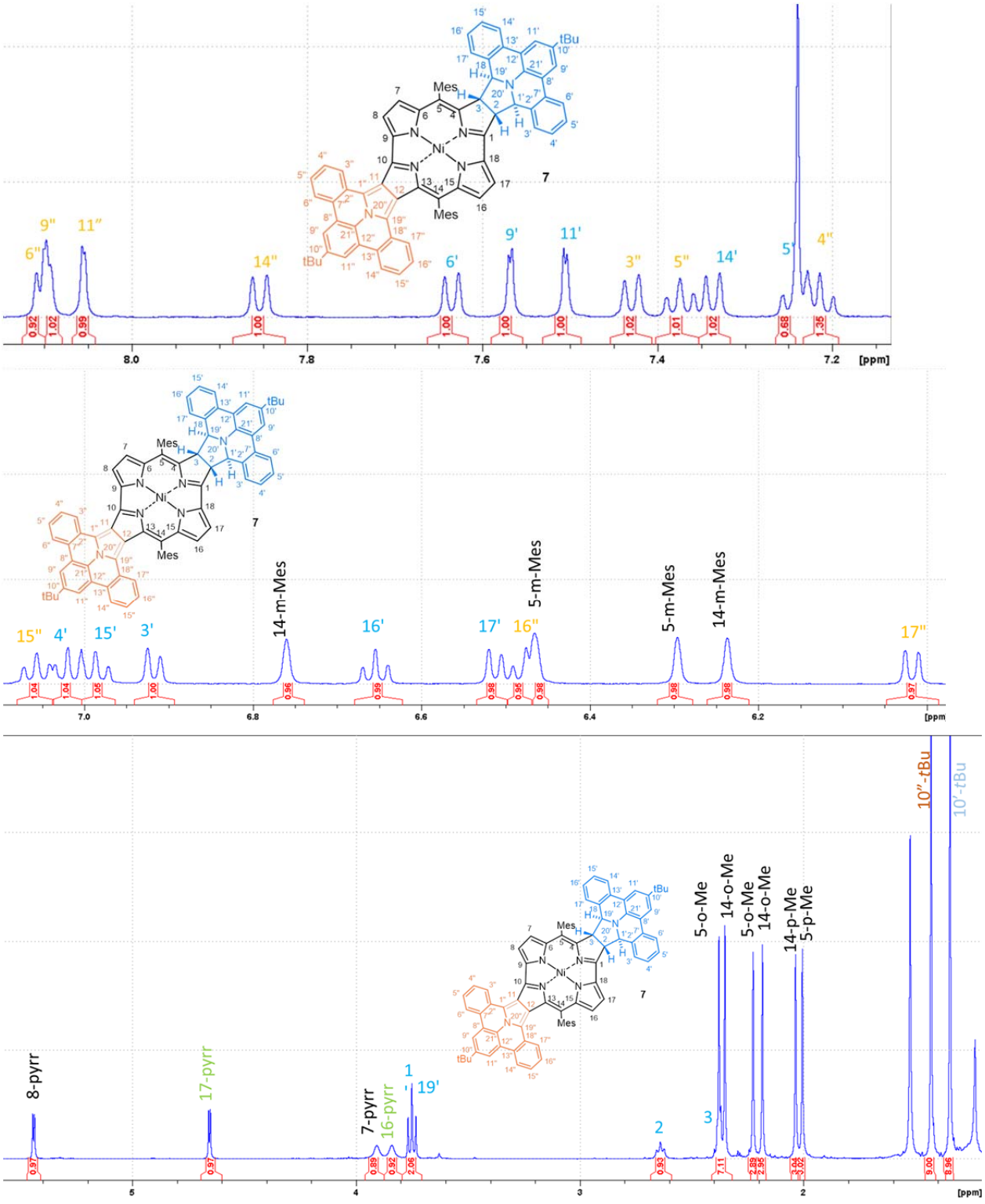


Figure S70. ^{1}H NMR signal assignments for **7** (500 MHz, 298 K, $CDCl_3$).

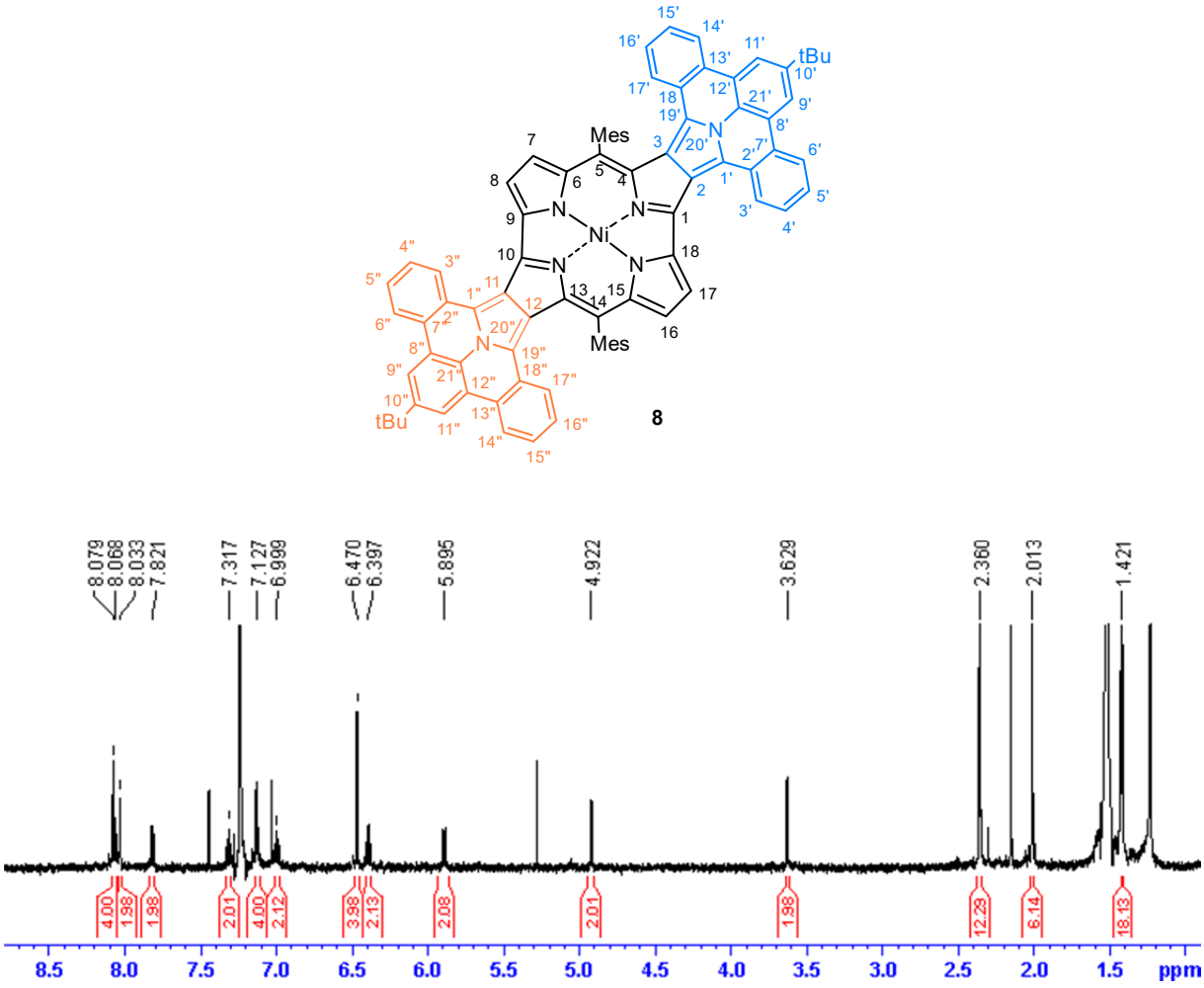


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Figure S71. ^{1}H NMR spectrum of **8** (500 MHz, 298 K, $CDCl_3$).

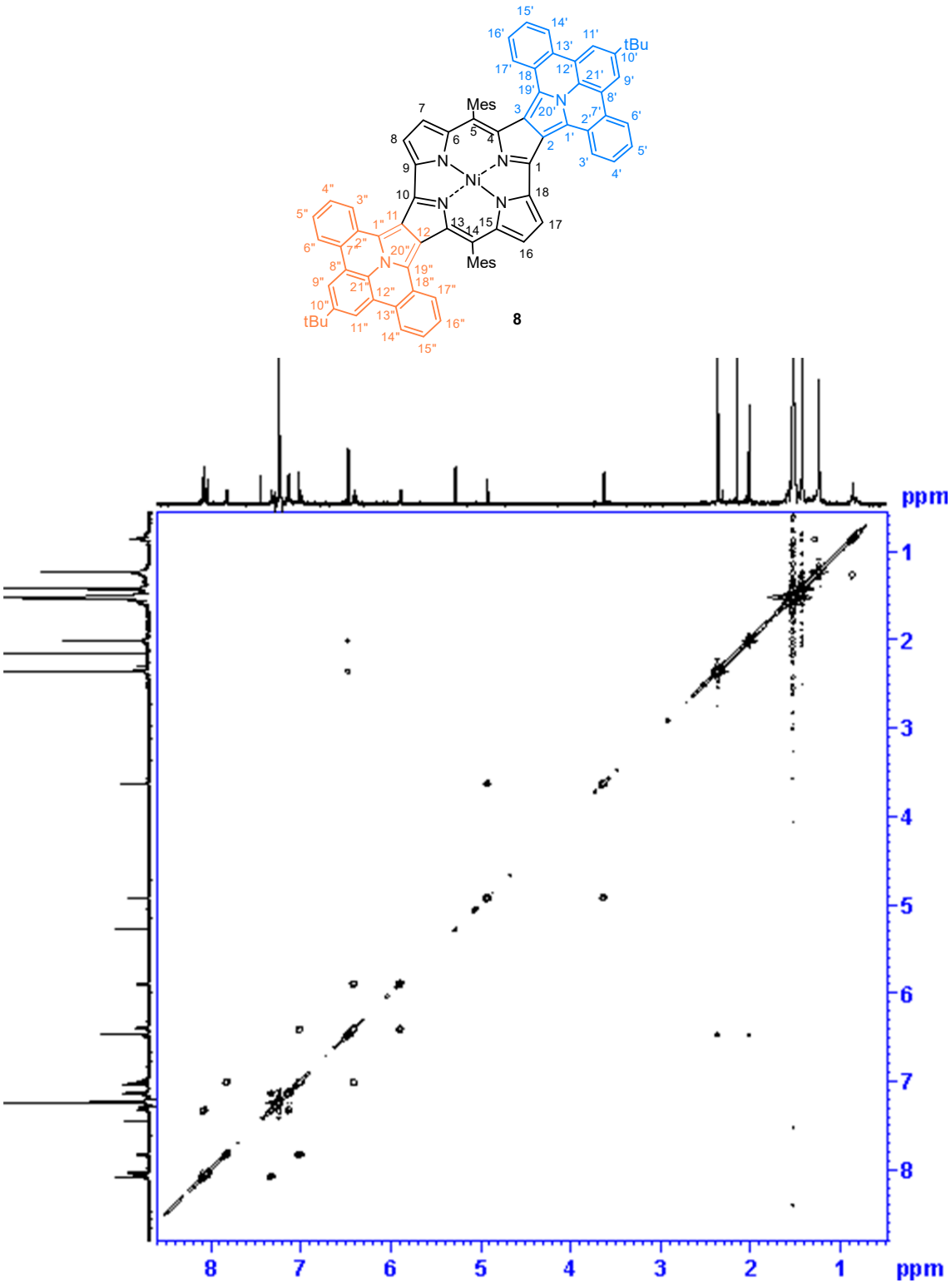


Figure S72. ^{1}H, ^{1}H COSY spectrum of **8** (600 MHz, 298 K, $CDCl_3$).

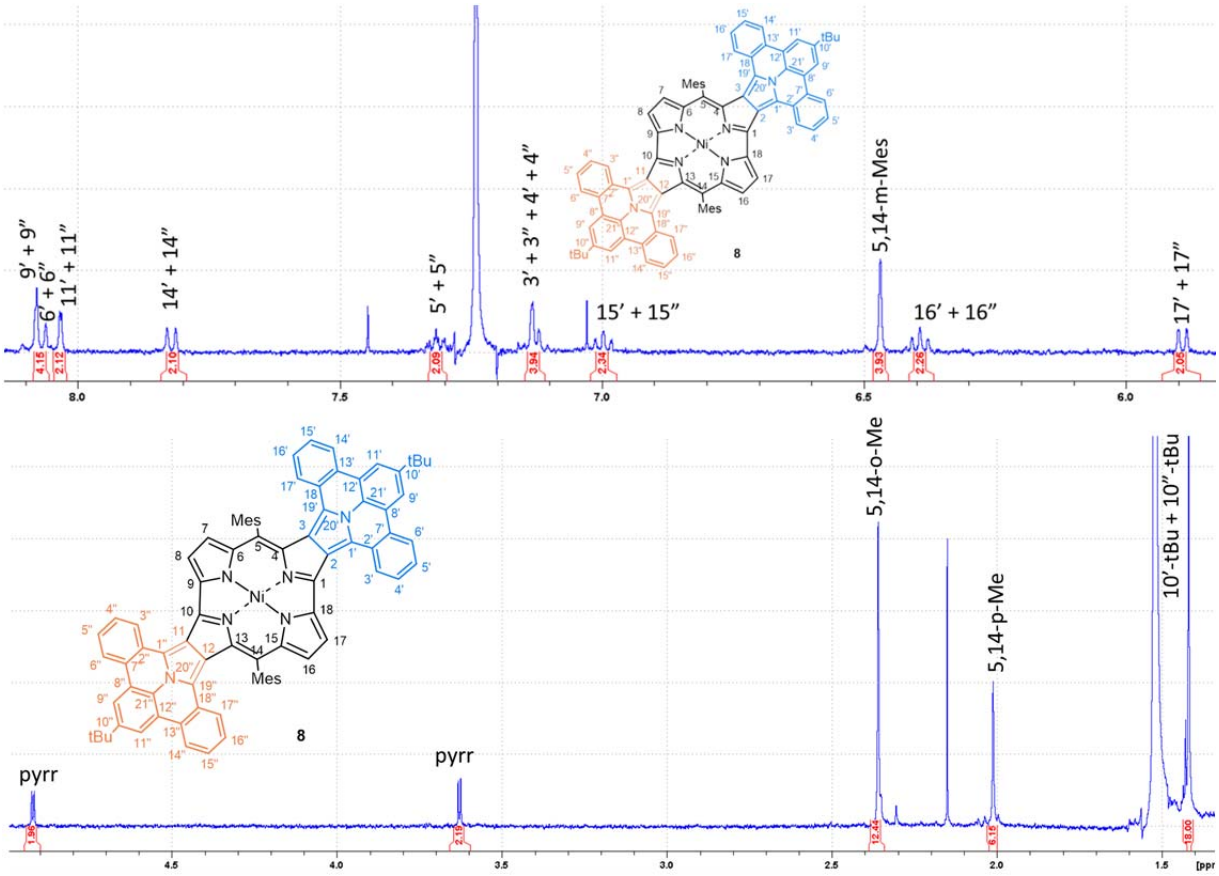


Figure S73. ^{1}H NMR signal assignments for **8** (500 MHz, 298 K, $CDCl_3$).

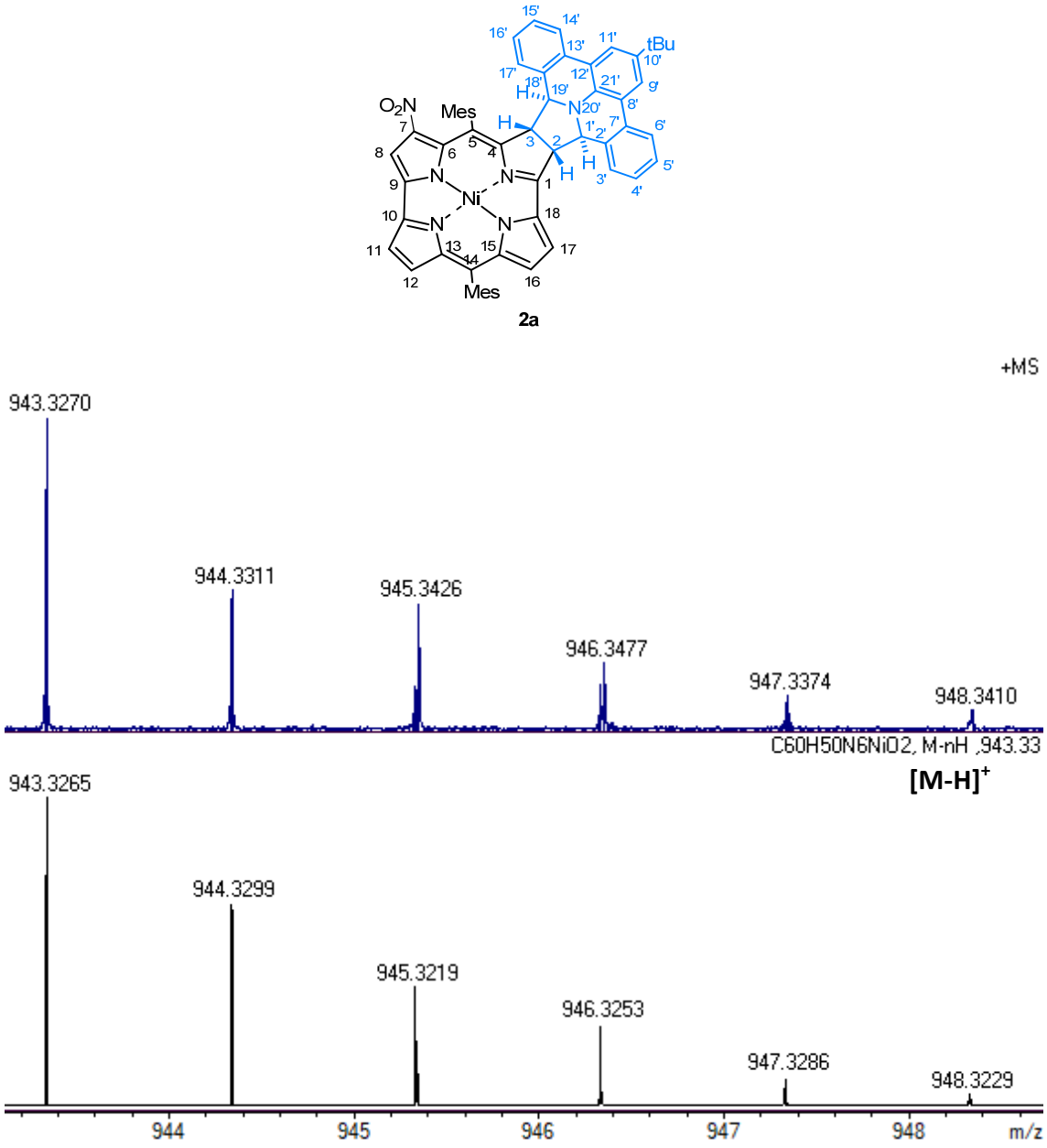


Figure S74. ESI(+) HRMS spectrum of **2a** (experimental: upper trace; simulated: black, bottom trace).

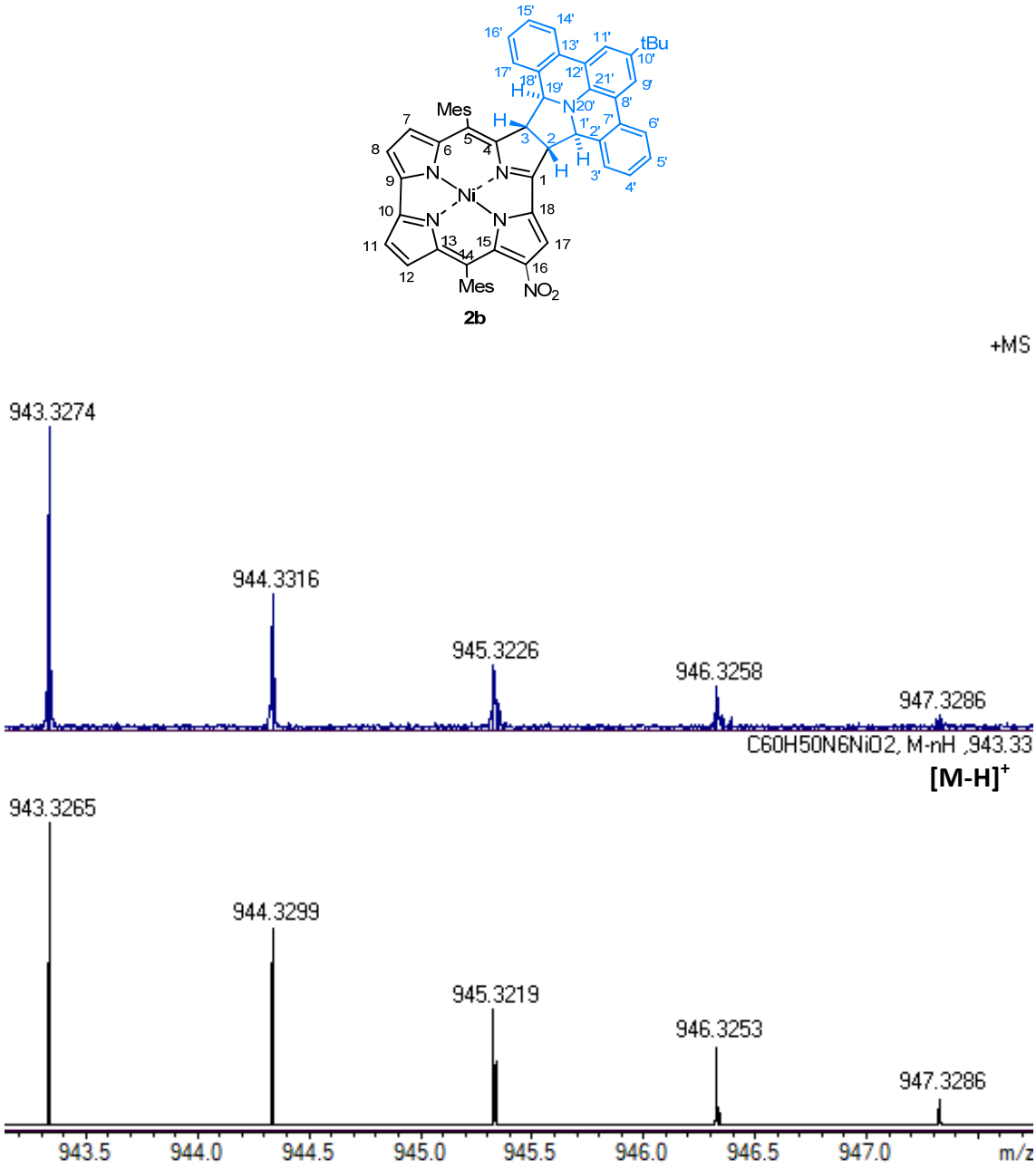
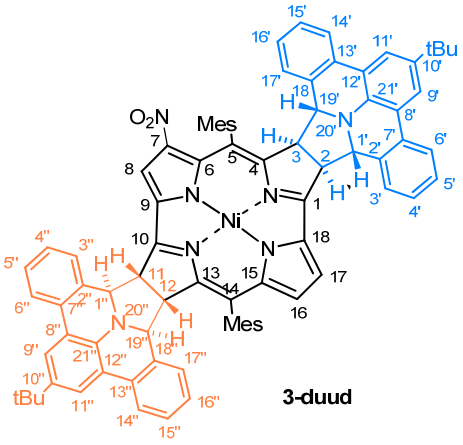


Figure S75 ESI(+) HRMS spectrum of **2b** (experimental: upper trace; simulated: black, bottom trace).



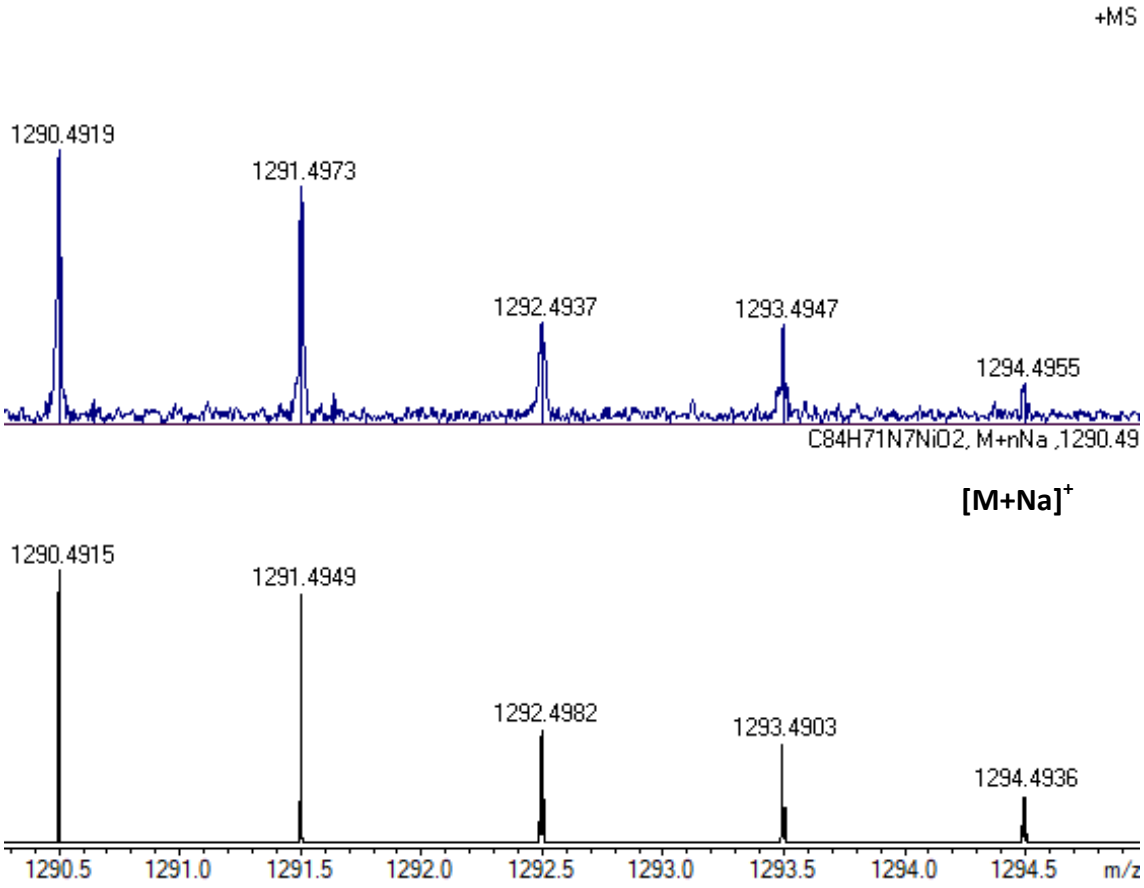


Figure S76. ESI(+) HRMS spectrum of **3**-duud (experimental: upper trace; simulated: black, bottom trace).

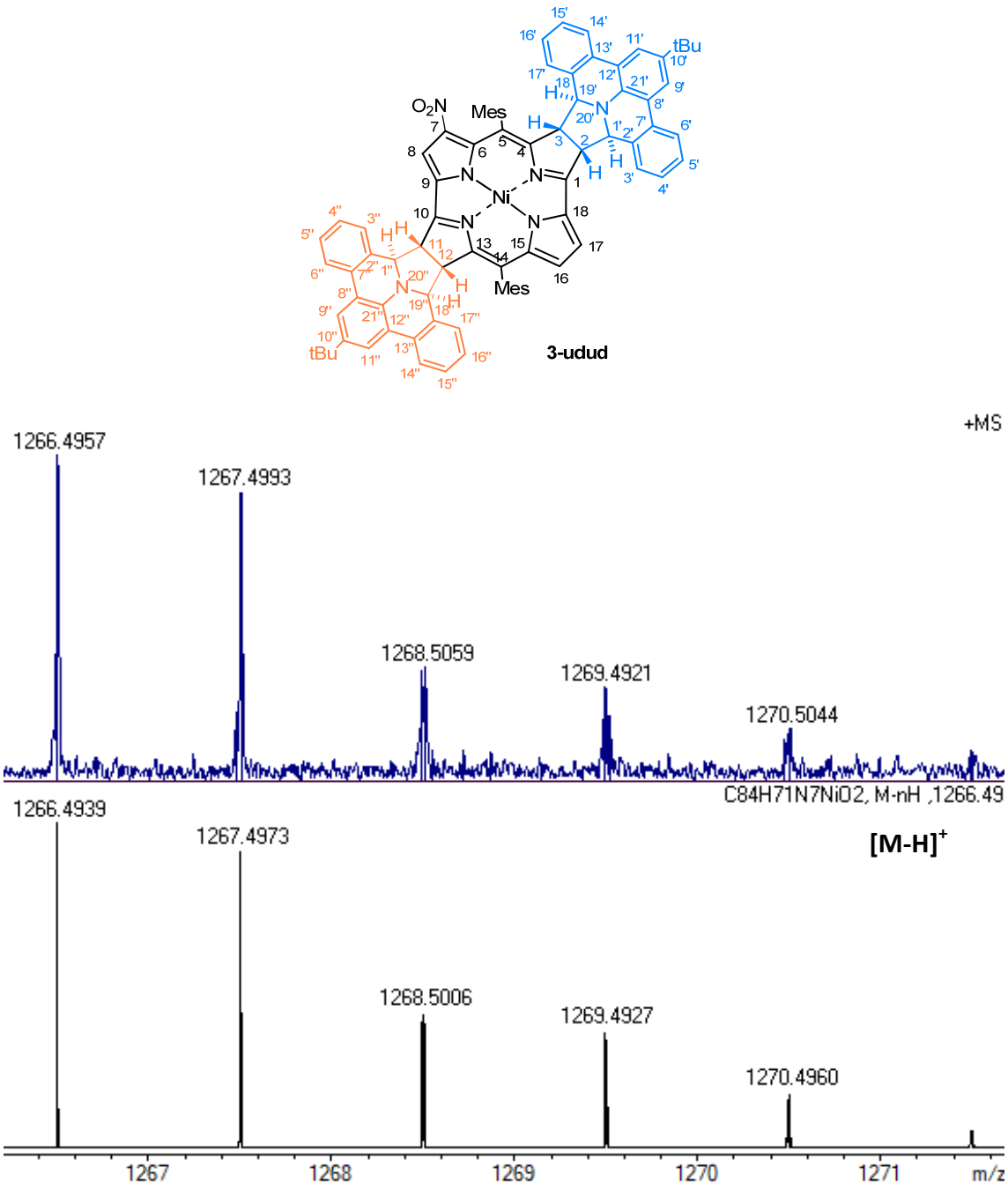


Figure S77. ESI(+) HRMS spectrum of **3**-udud (experimental: upper trace; simulated: black, bottom trace).

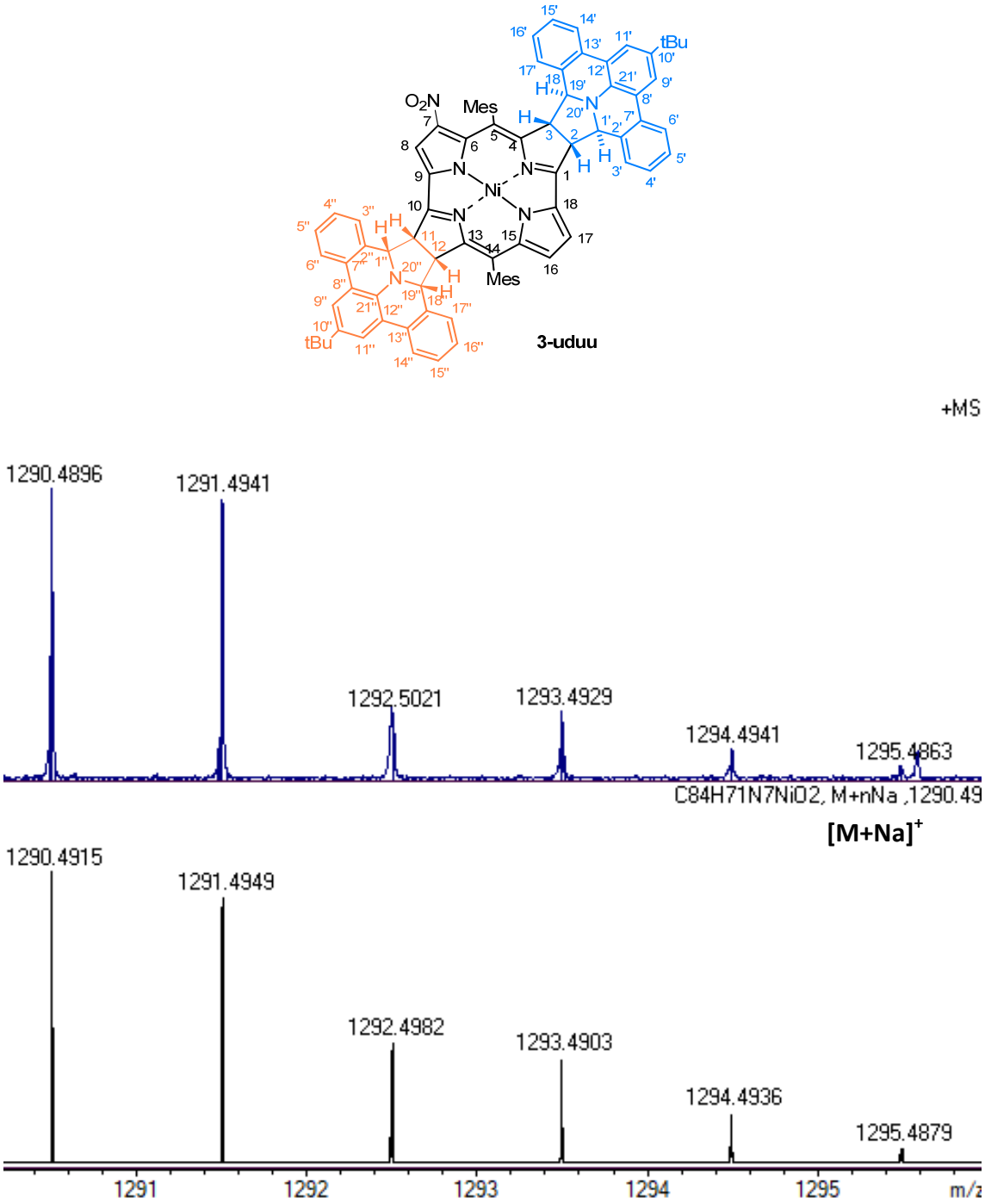


Figure S78. ESI(+) HRMS spectrum of **3**-uduu (experimental: upper trace; simulated: black, bottom trace).

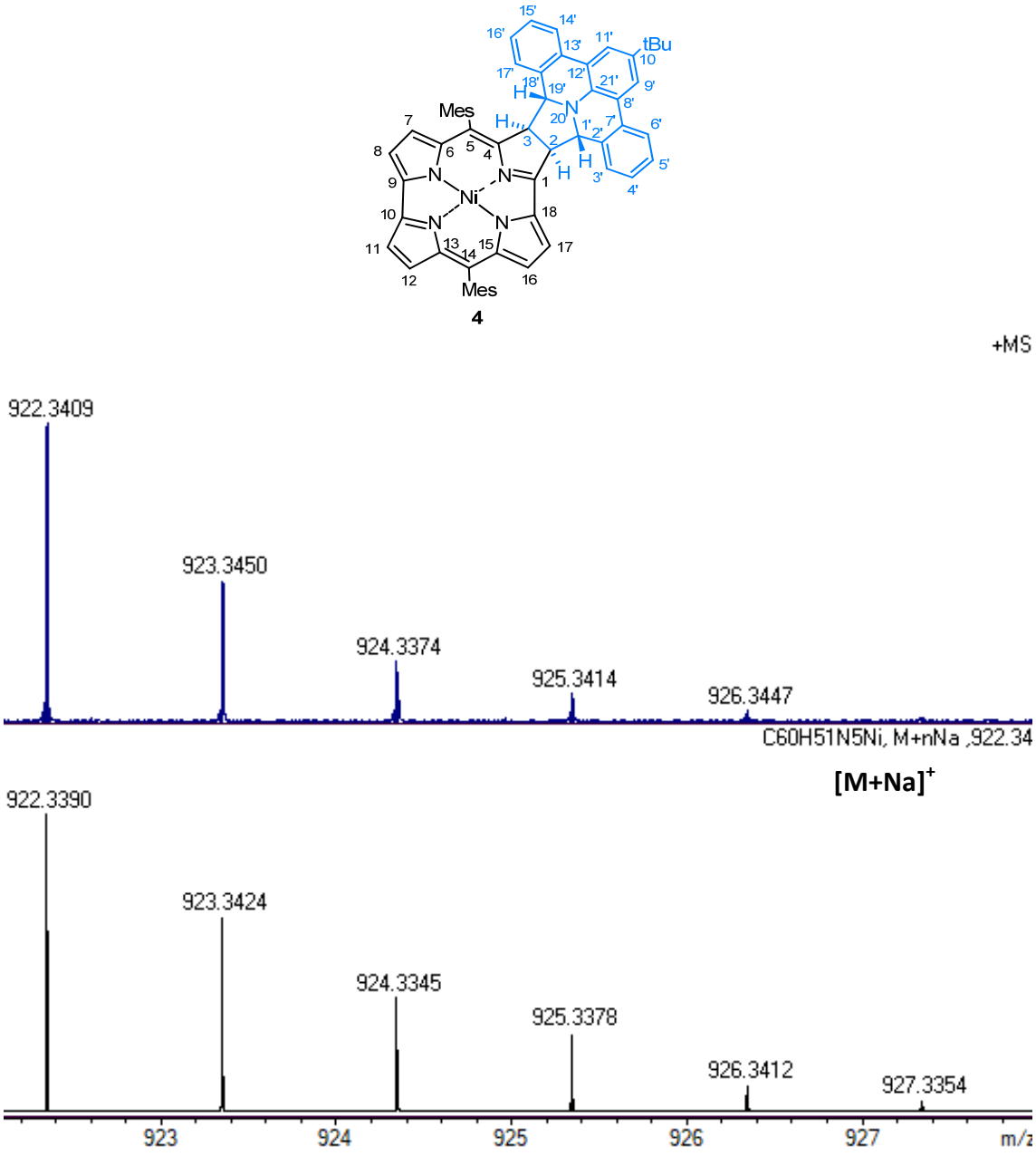


Figure S79. ESI(+) HRMS spectrum of **4** (experimental: upper trace; simulated: black, bottom trace).

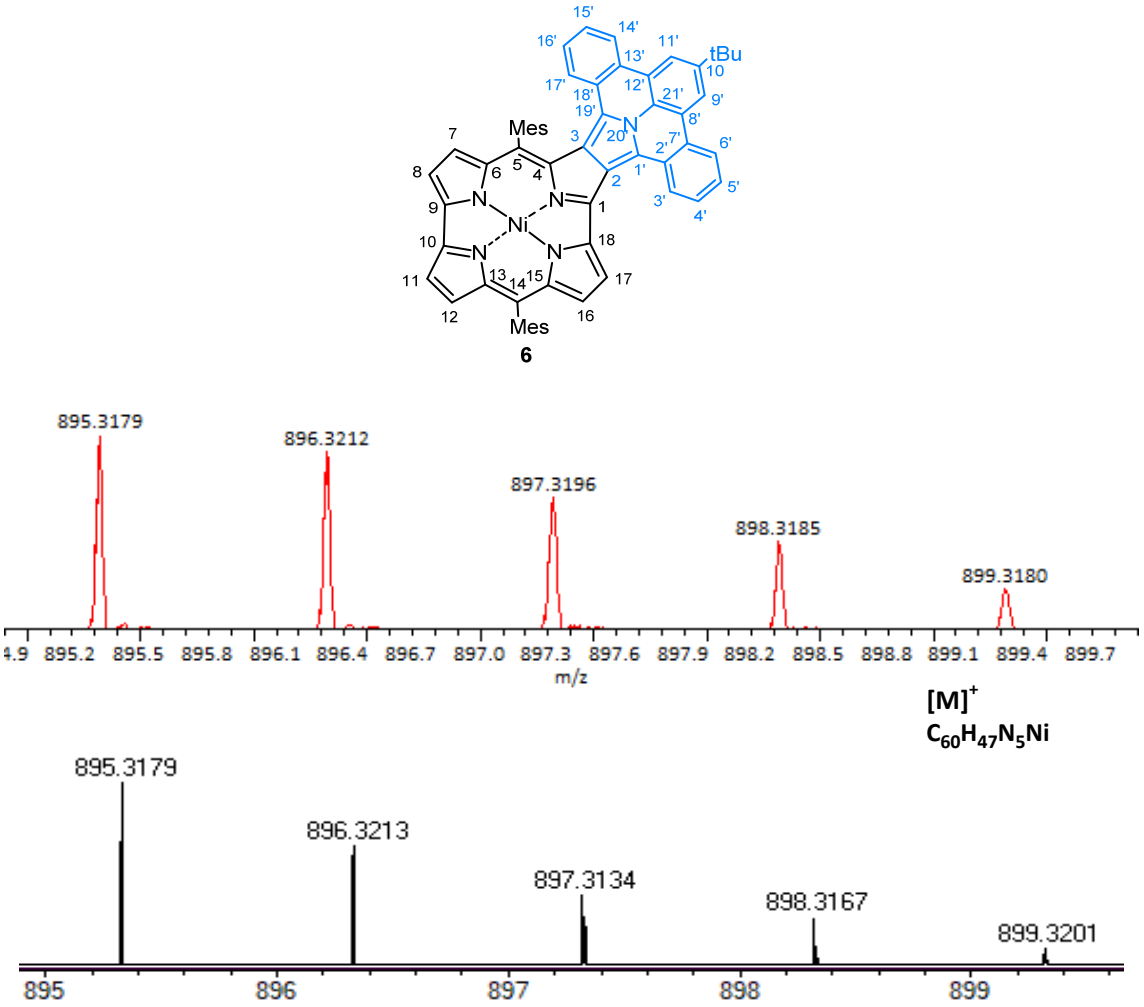


Figure S80. ESI(+) HRMS spectrum of **6** (experimental: upper trace; simulated: black, bottom trace).

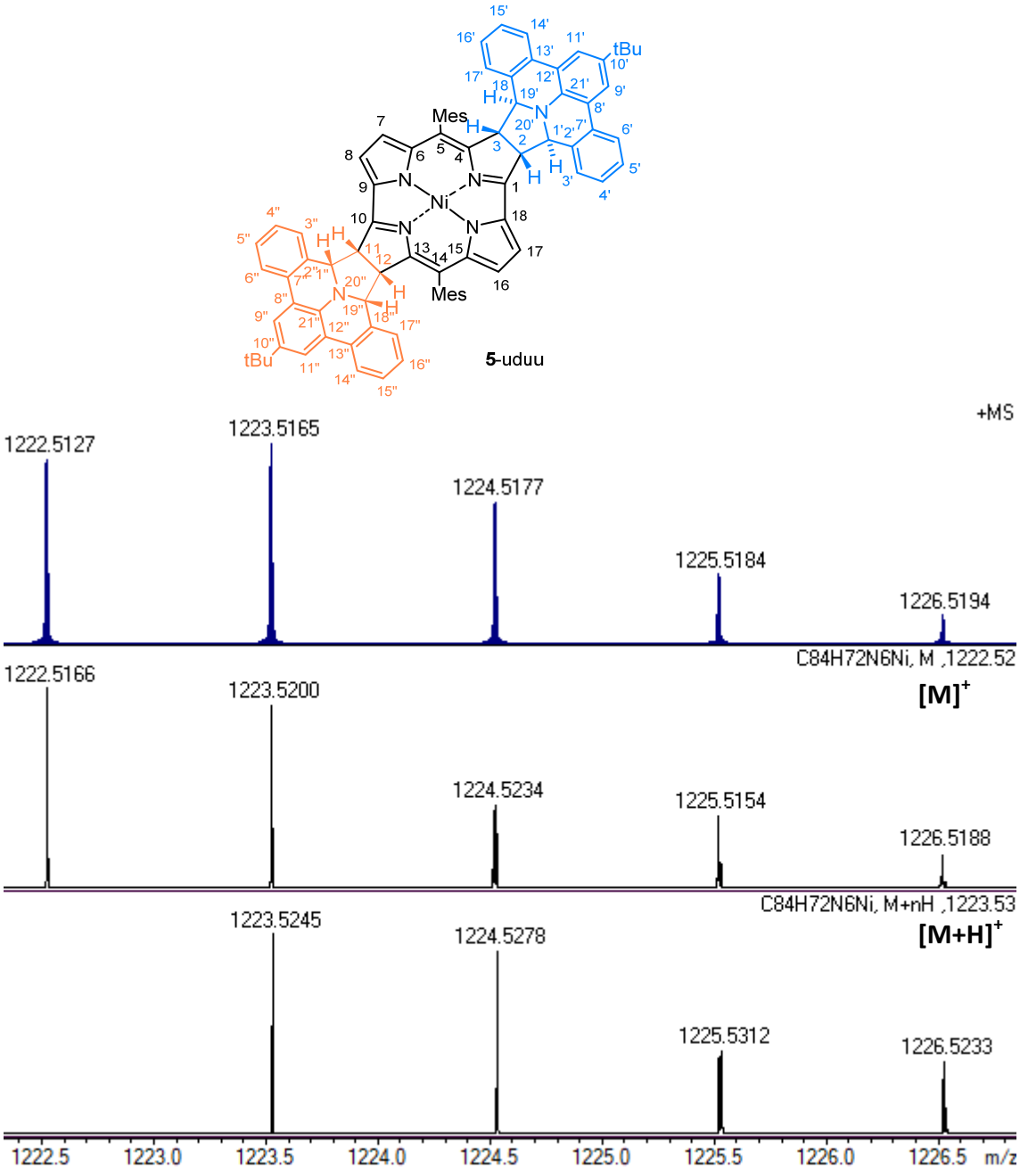


Figure S81. ESI(+) HRMS spectrum of **5**-uduu (experimental: upper trace; simulated: black, bottom trace).

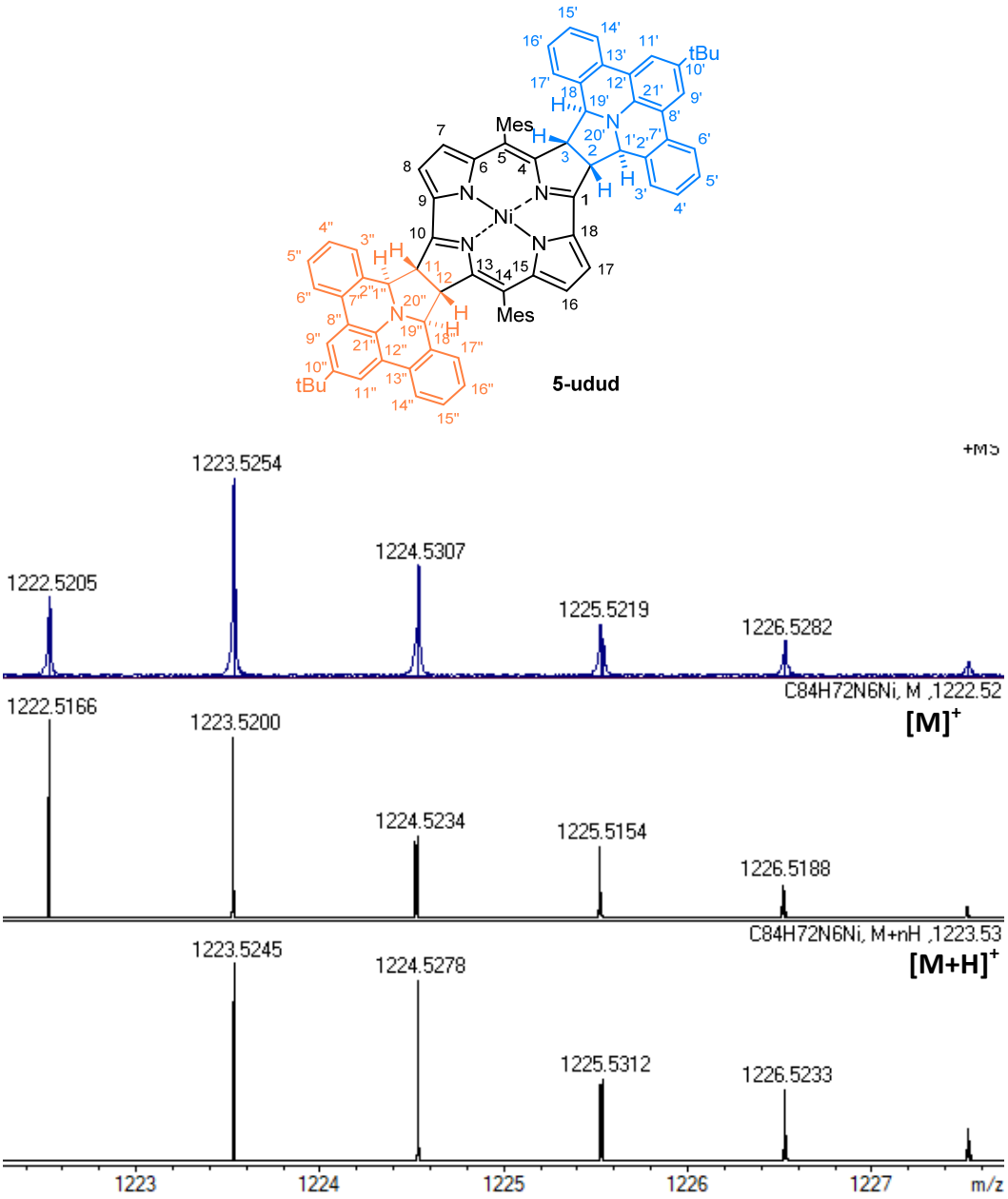


Figure S82. ESI(+) HRMS spectrum of **5**-ududd (experimental: upper trace; simulated: black, bottom trace).

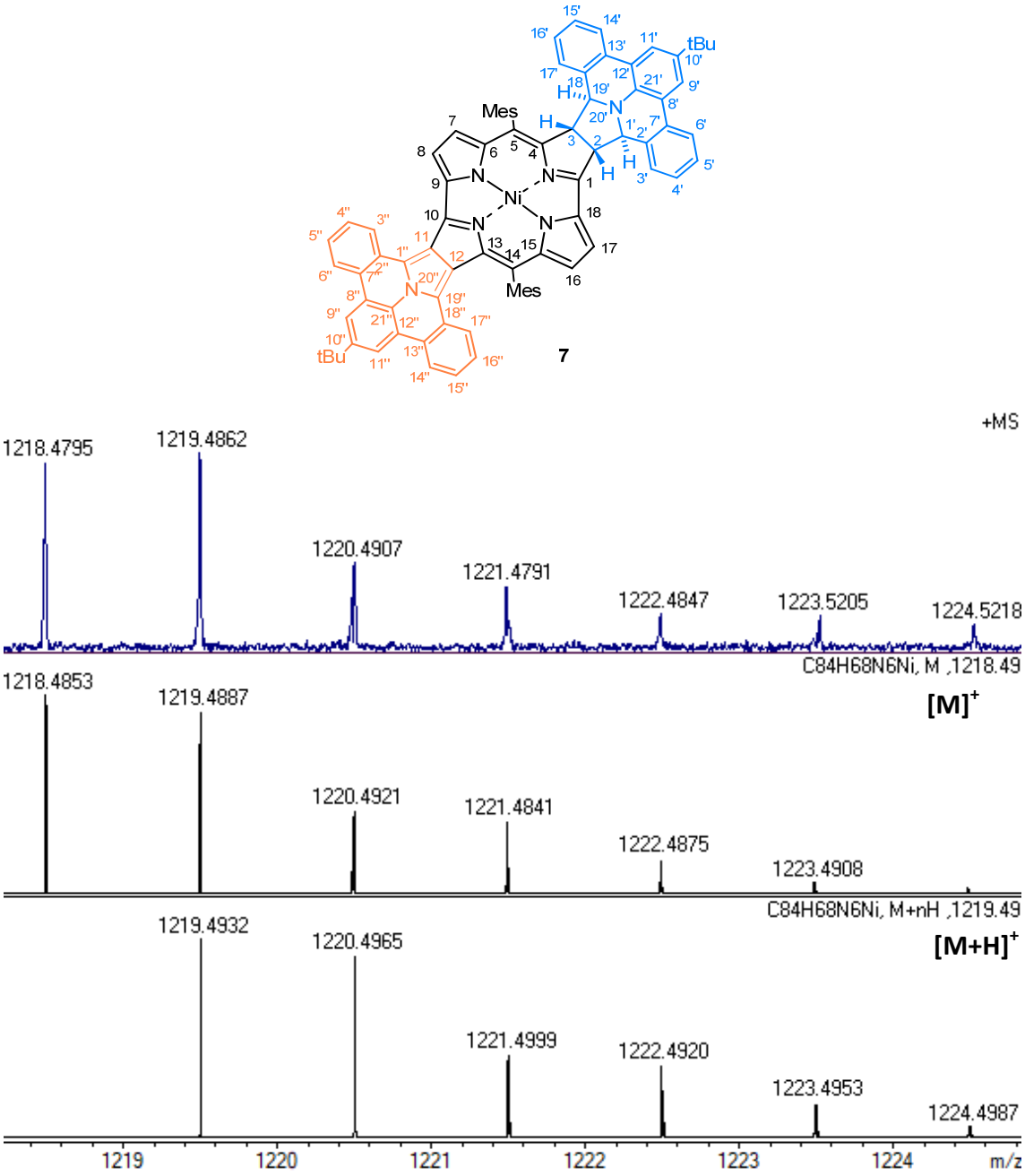


Figure S83. ESI(+) HRMS spectrum of **7** (experimental: upper trace; simulated: black, bottom trace).

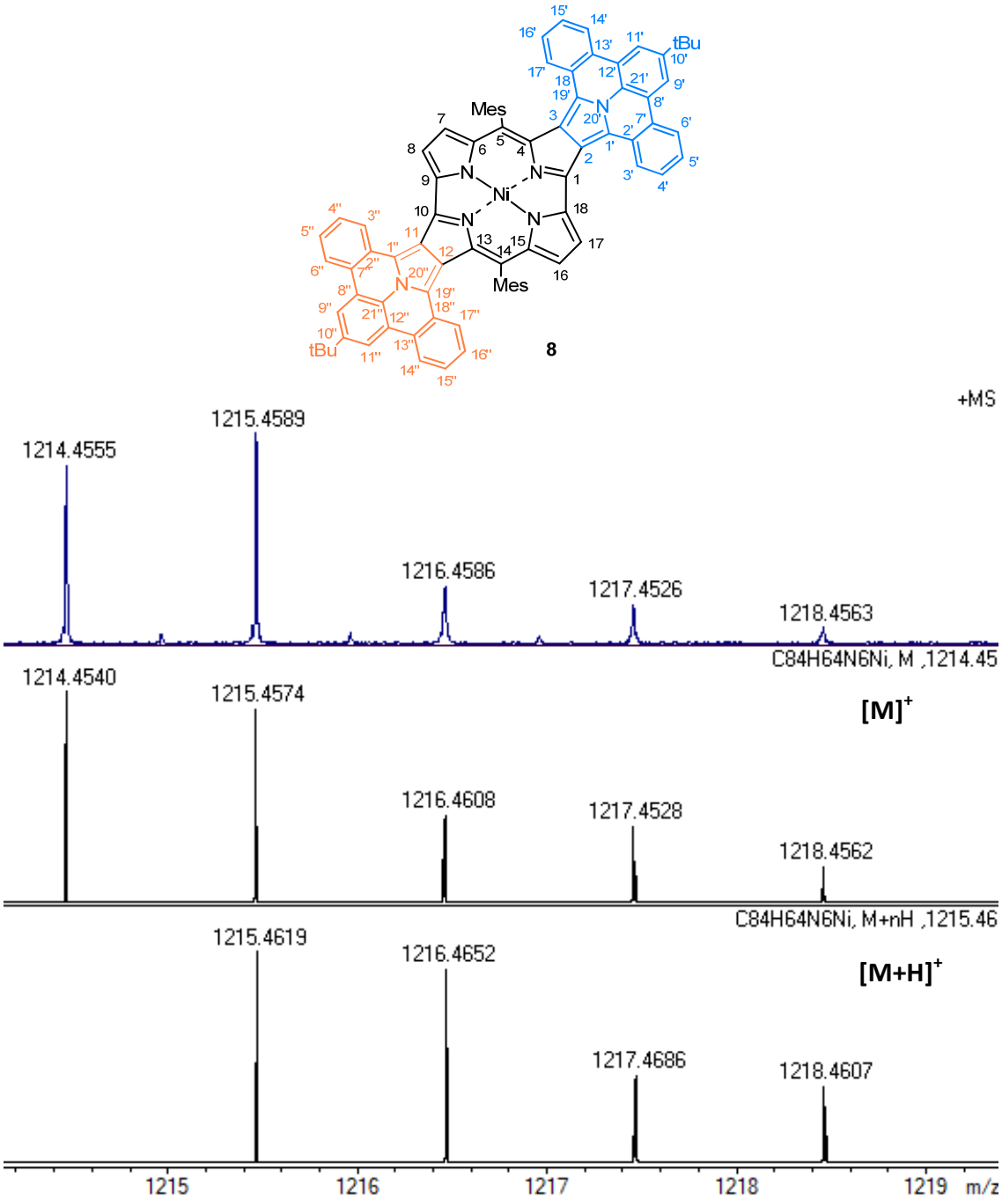


Figure S84. ESI(+) HRMS spectrum of **8** (experimental: upper trace; simulated: black, bottom trace).

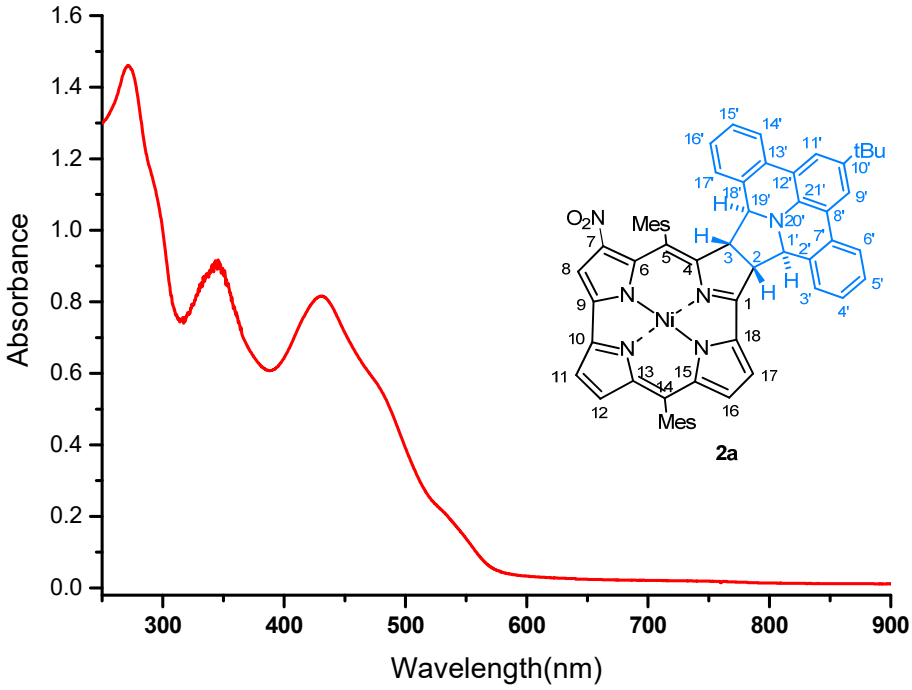


Figure S85. UV-vis spectrum of **2a** (CH_2Cl_2).

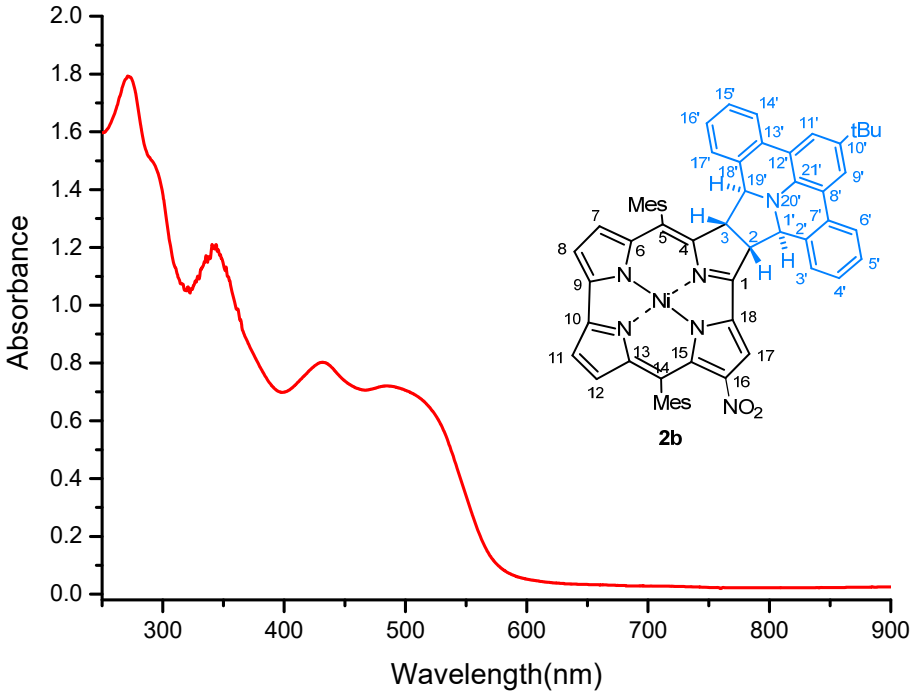


Figure S86. UV-vis spectrum of **2b** (CH_2Cl_2).

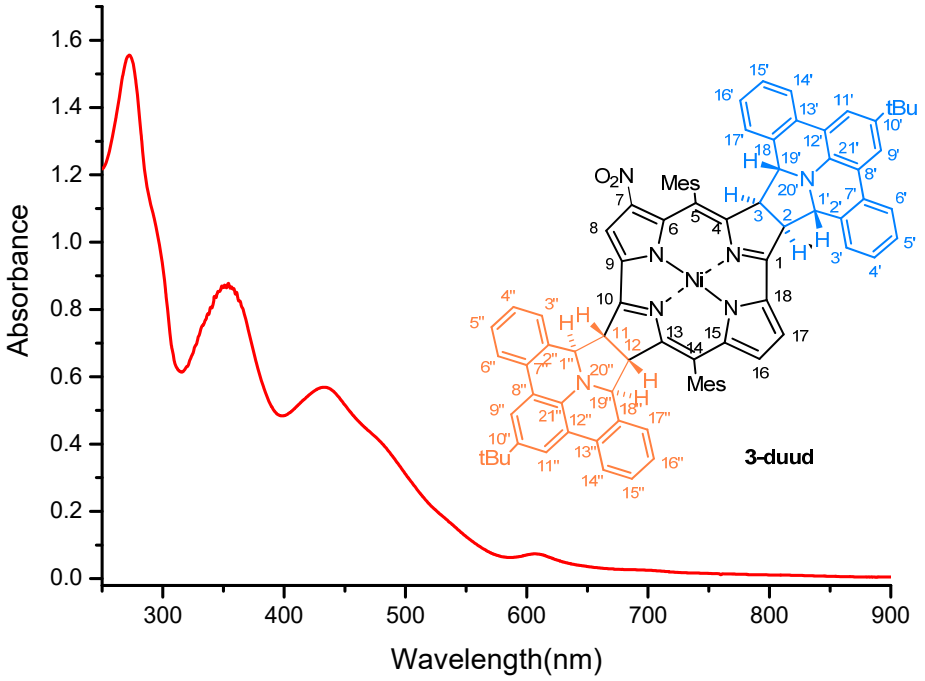


Figure S87. UV-vis spectrum of **3**-duud (CH_2Cl_2).

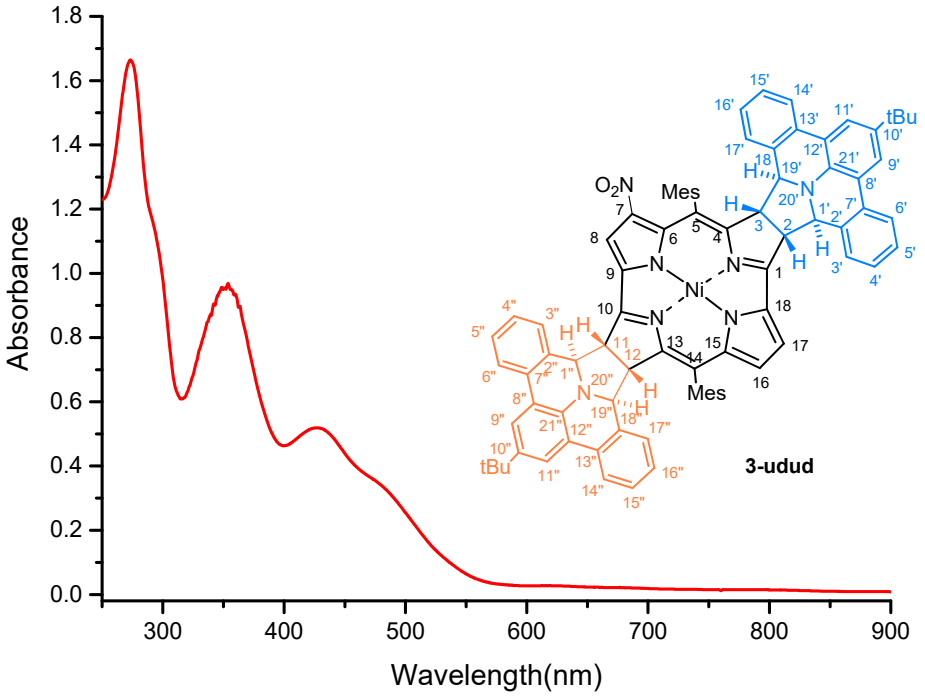


Figure S88. UV-vis spectrum of **3**-udud (CH_2Cl_2).

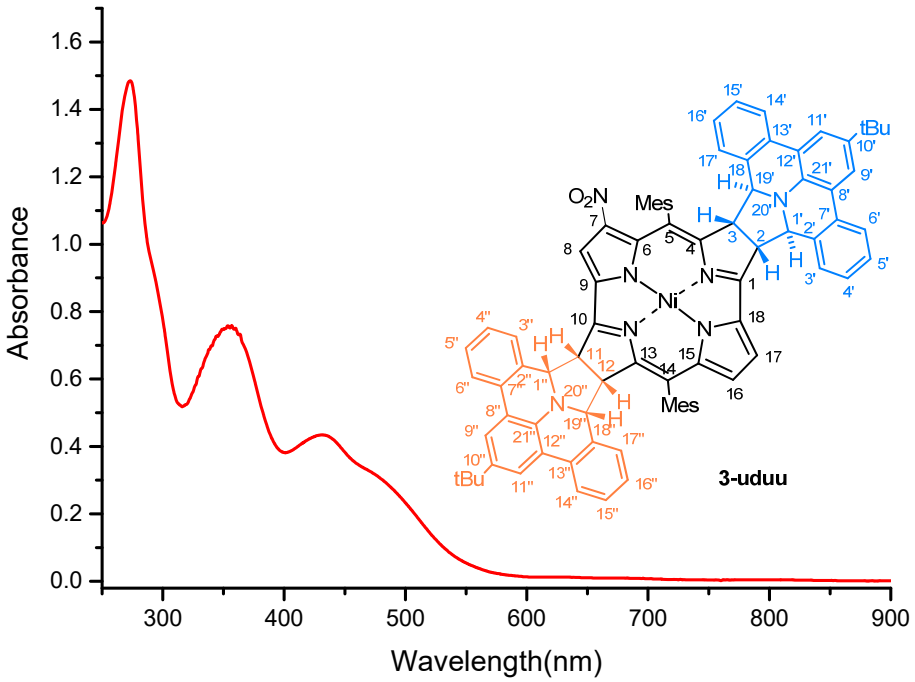


Figure S89. UV-vis spectrum of **3**-uduu (CH_2Cl_2).

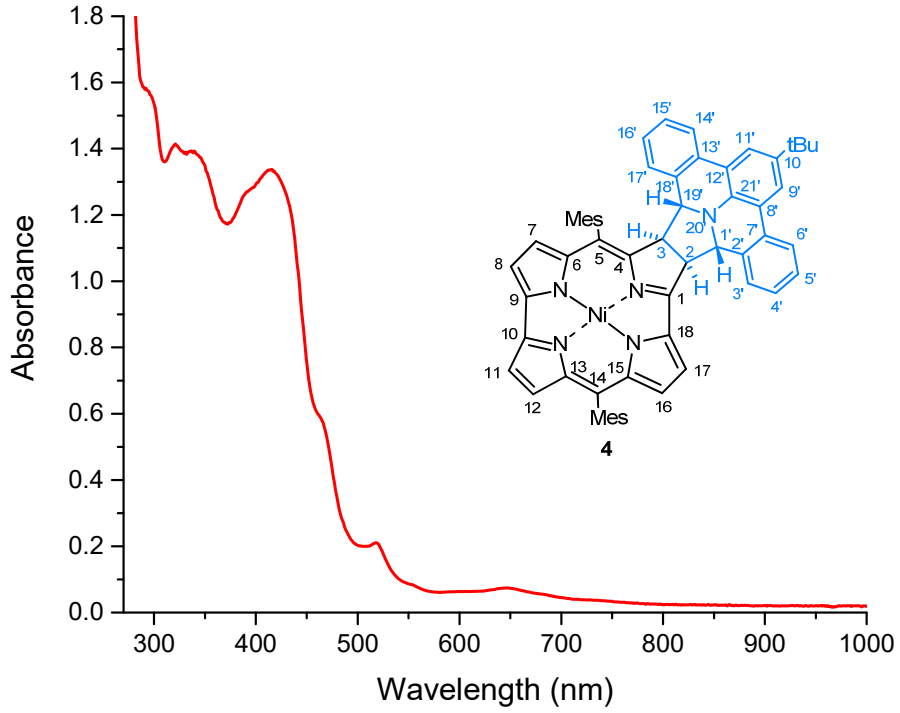


Figure S90. UV-vis spectrum of **4** (CH_2Cl_2).

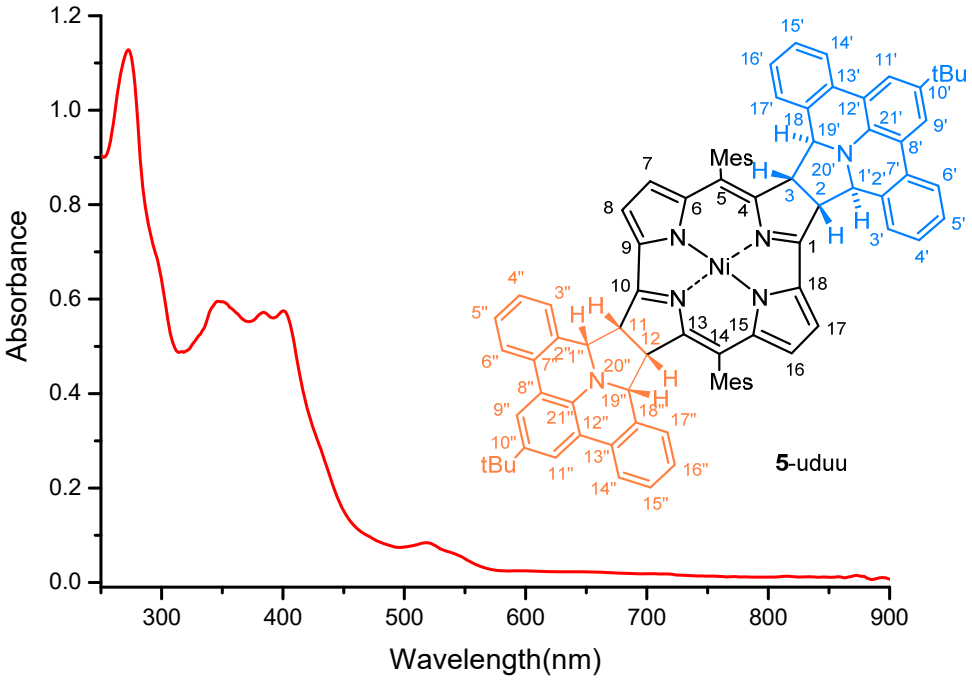


Figure S91. UV-vis spectrum of **5**-uduu (CH_2Cl_2).

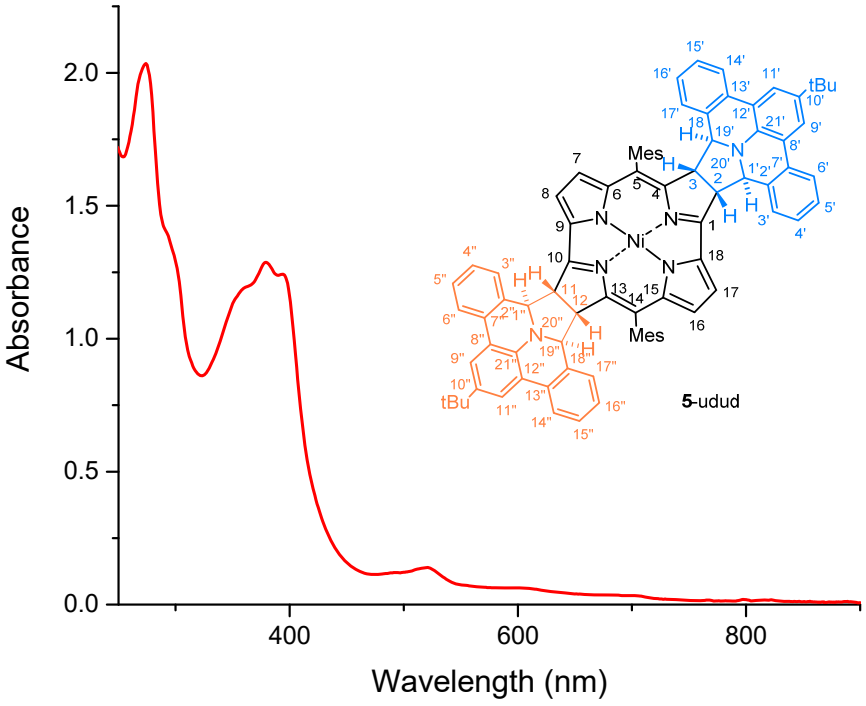


Figure S92. UV-vis spectrum of **5**-udud (CH_2Cl_2).

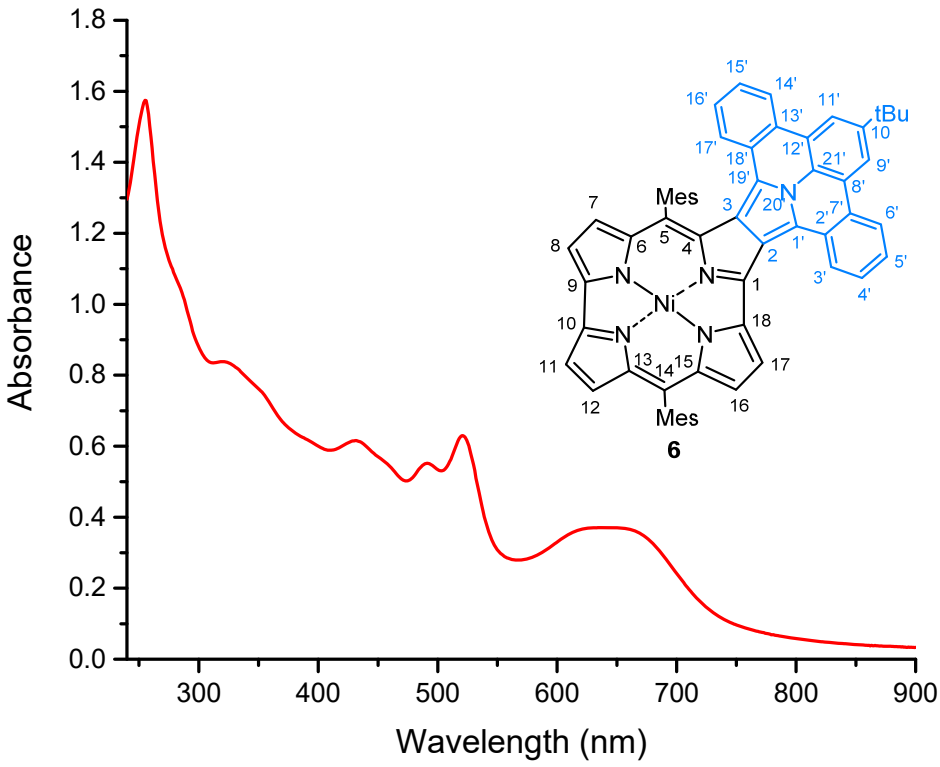


Figure S93. UV-vis spectrum of **6** (CH_2Cl_2).

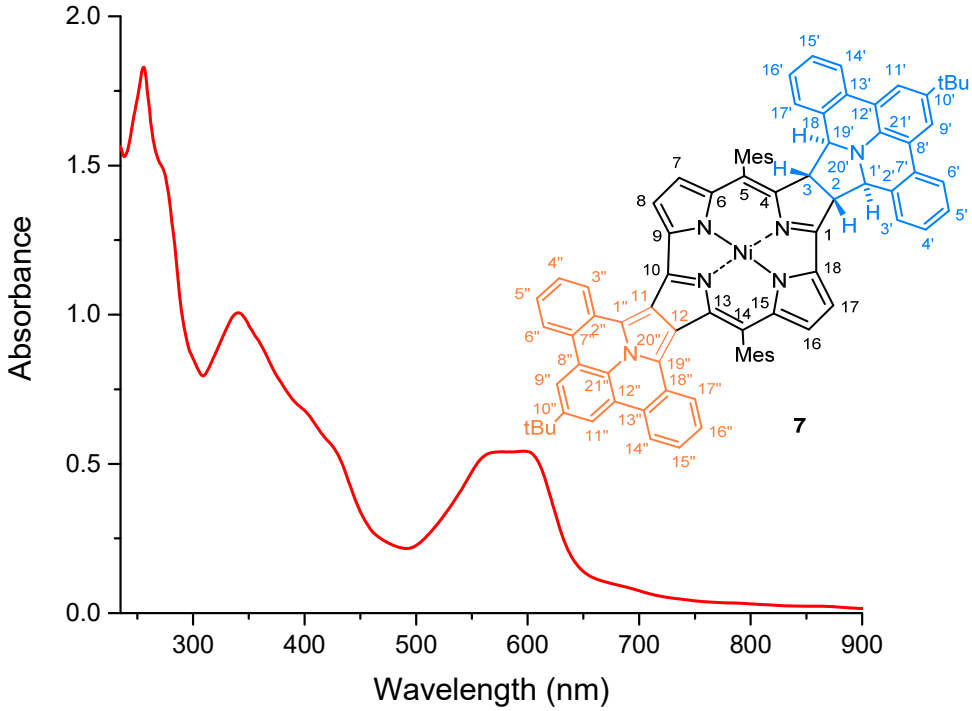


Figure S94. UV-vis spectrum of **7** (CH_2Cl_2).

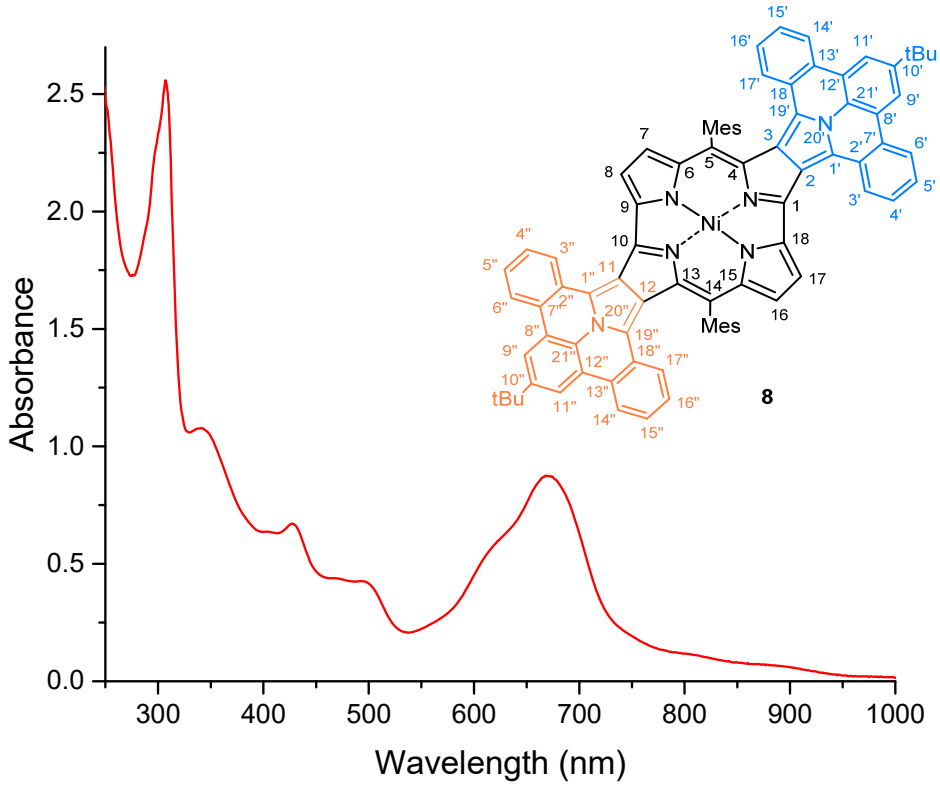


Figure S95. UV-vis spectrum of **8** (CH_2Cl_2).

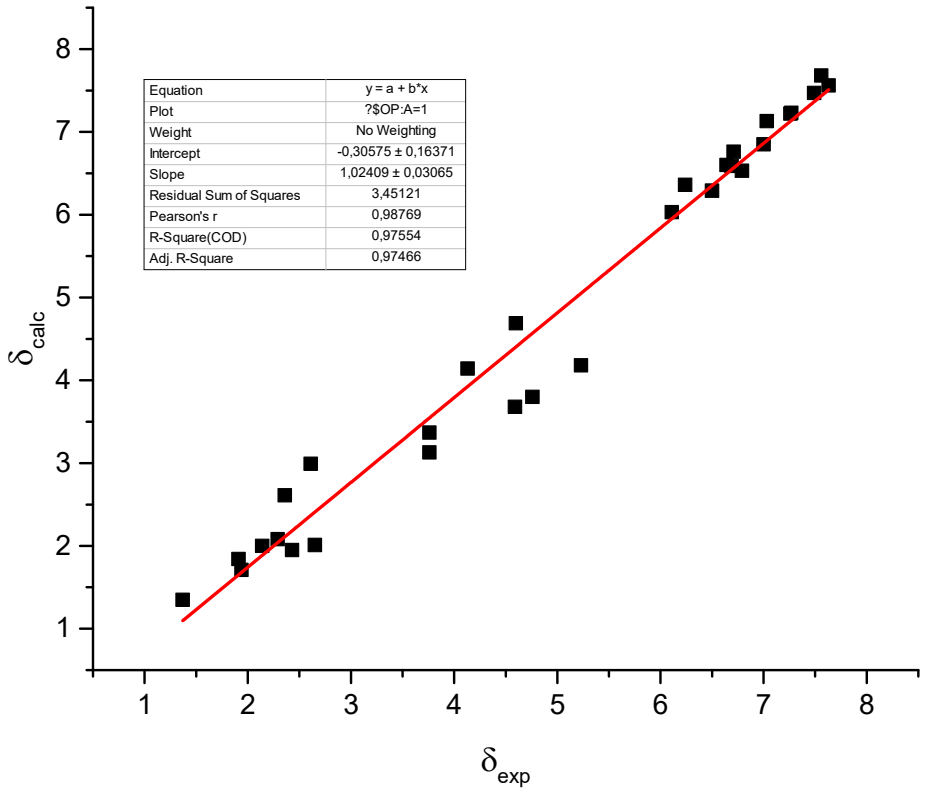


Figure S96. Correlations of the ^{1}H NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **2a**.

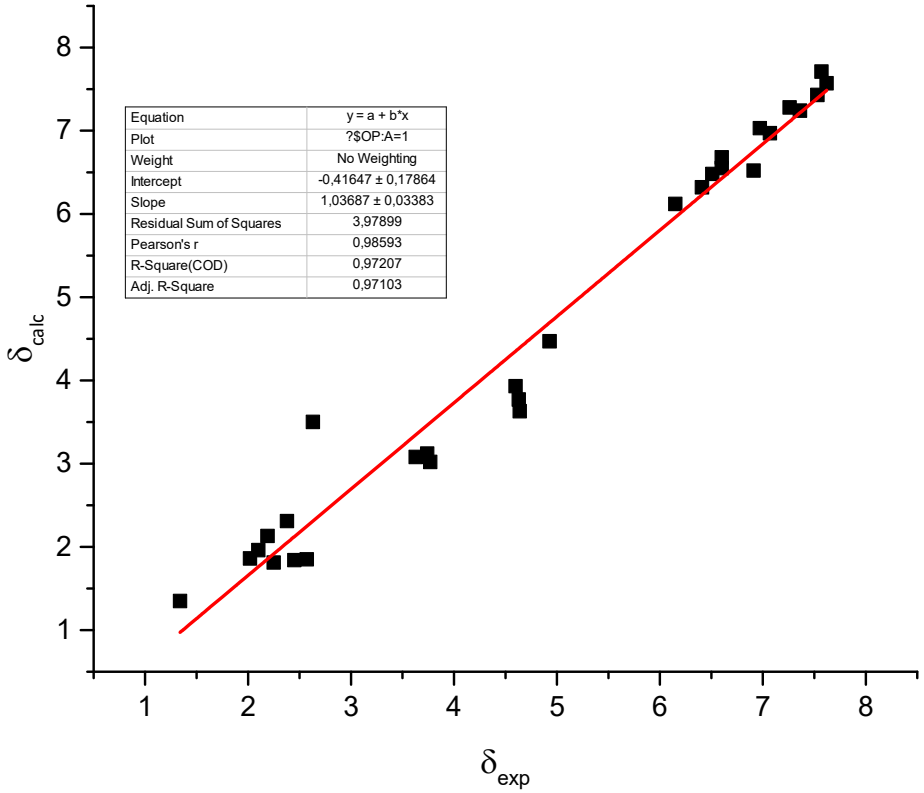


Figure S97. Correlations of the ^{1}H NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **2b**.

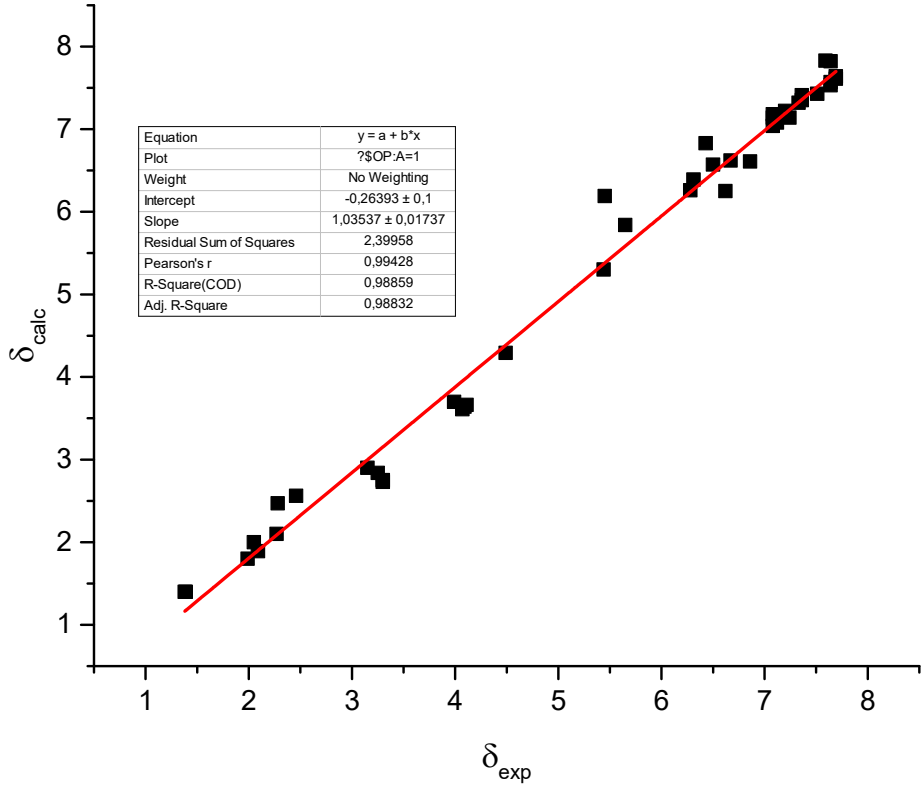


Figure S98. Correlations of the ^{1}H NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **3**-duud.

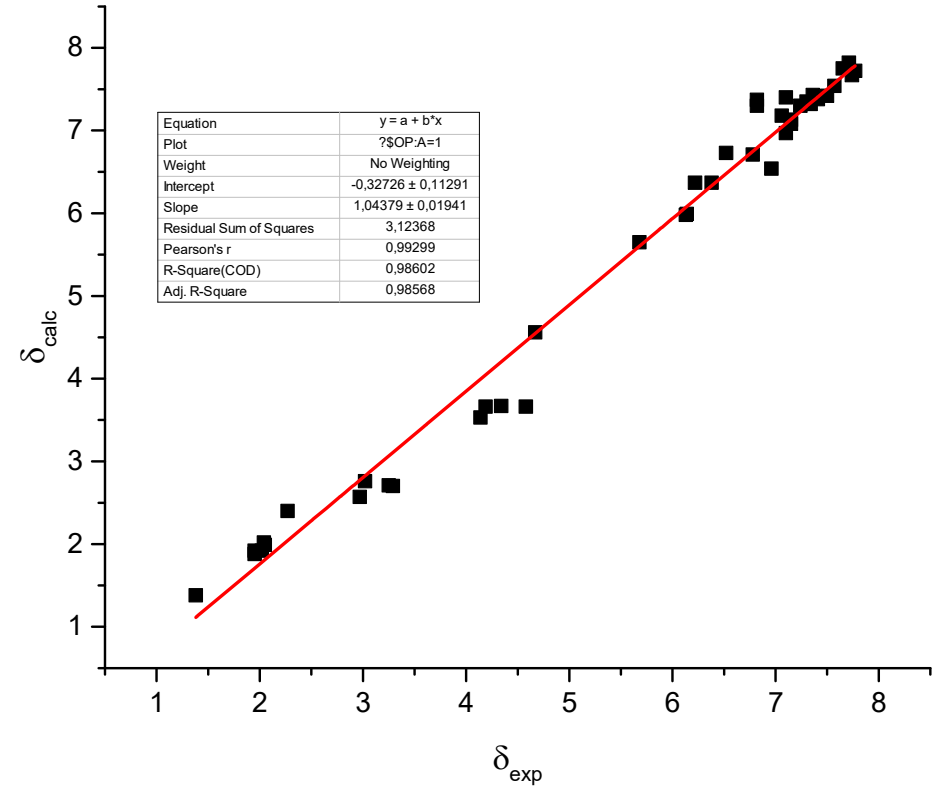


Figure S99. Correlations of the ^{1}H NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **3**-ududd.

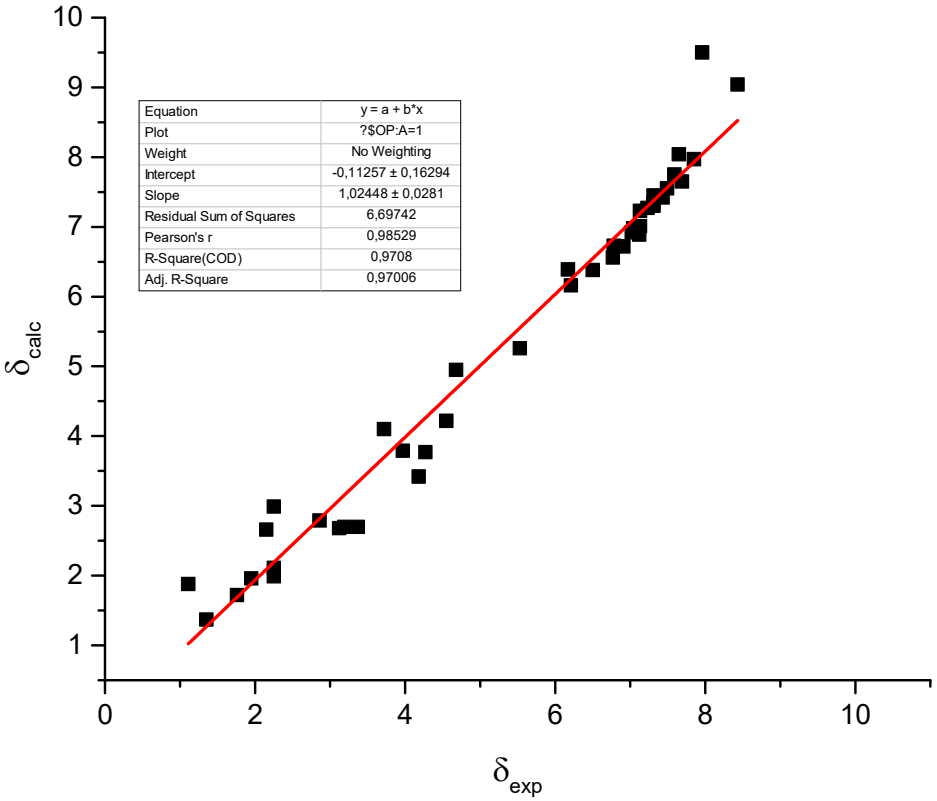


Figure S100. Correlations of the ^{1}H NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **3**-uduu.

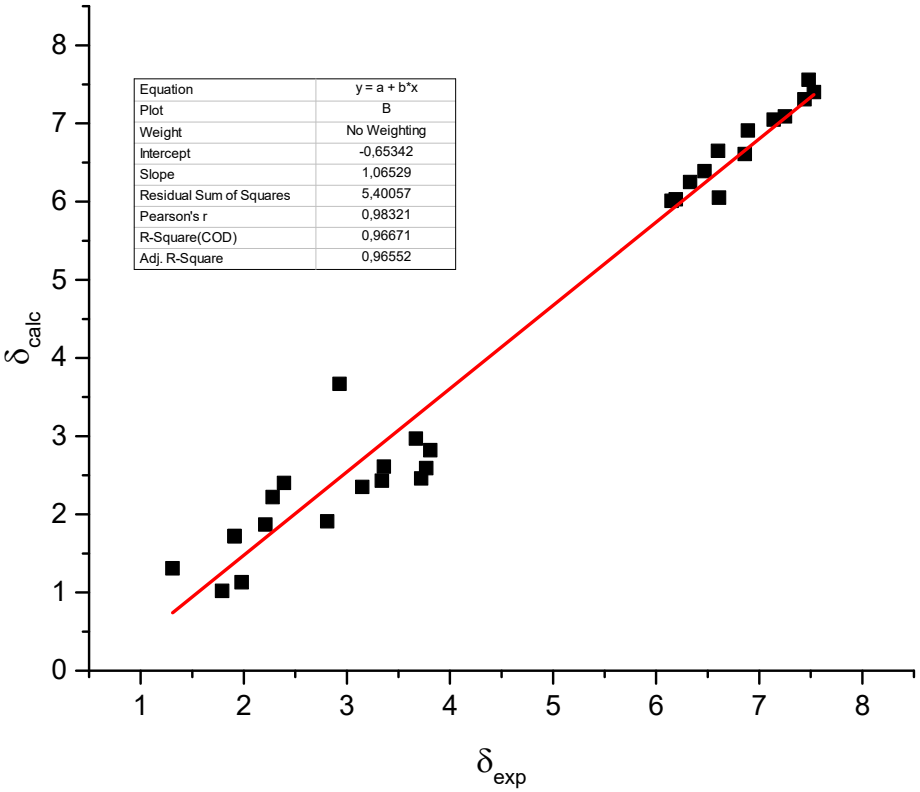


Figure S101. Correlations of the ^{1}H NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **4**.

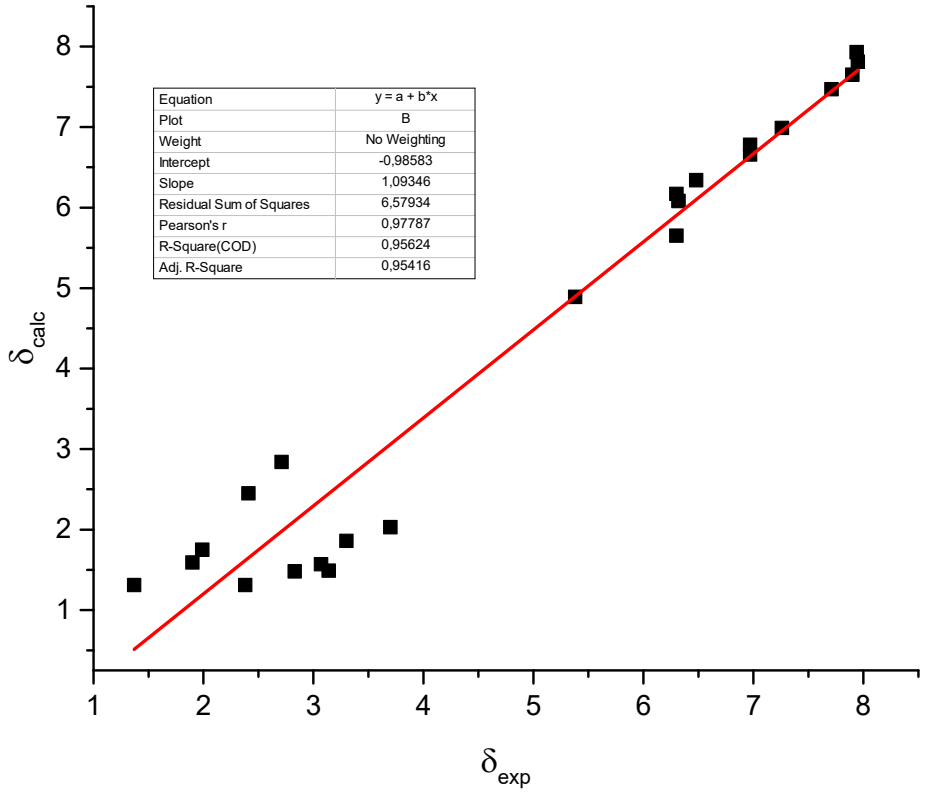


Figure S102. Correlations of the ^{1}H NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **6**.

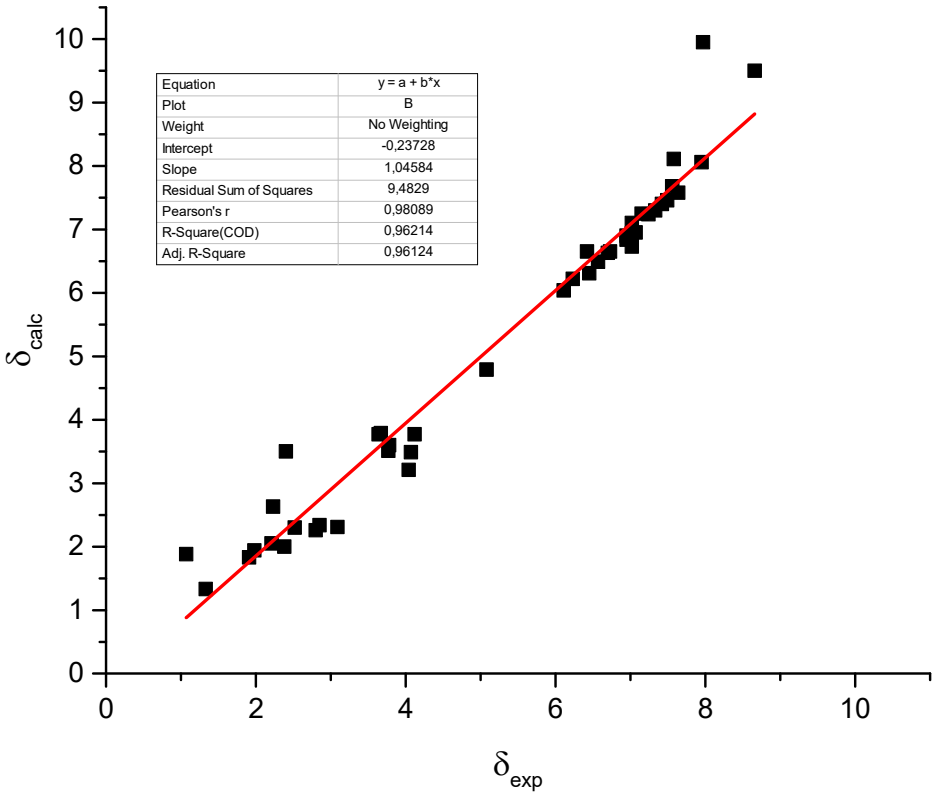


Figure S103. Correlations of the ^{1}H NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **5**-uduu.

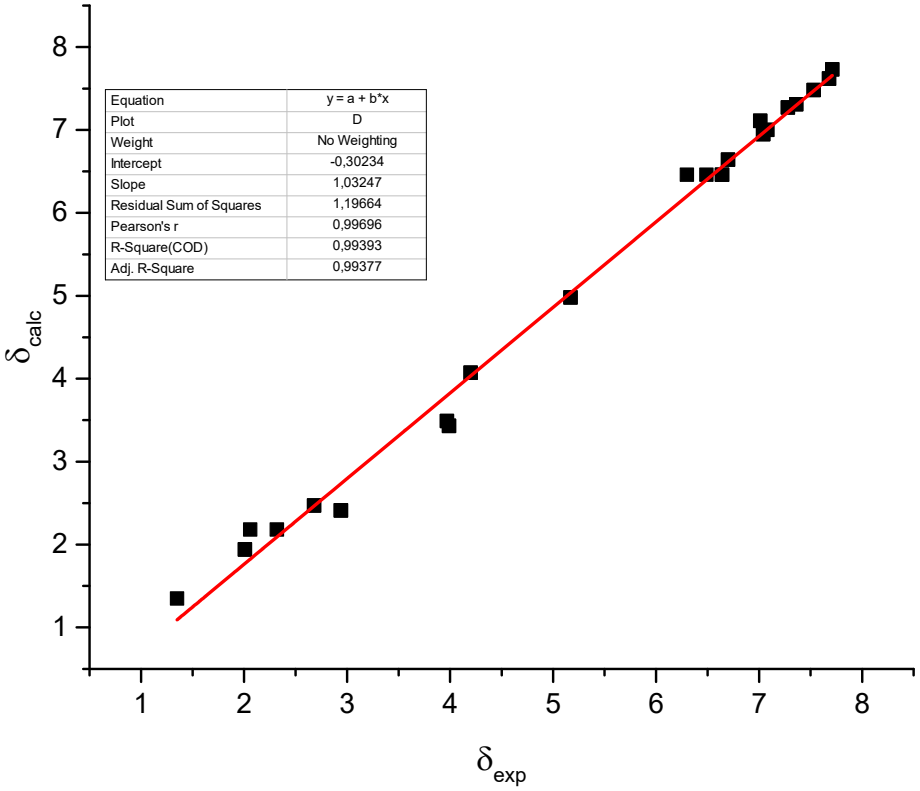


Figure S104. Correlations of the ^{1}H NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **5**-udud.

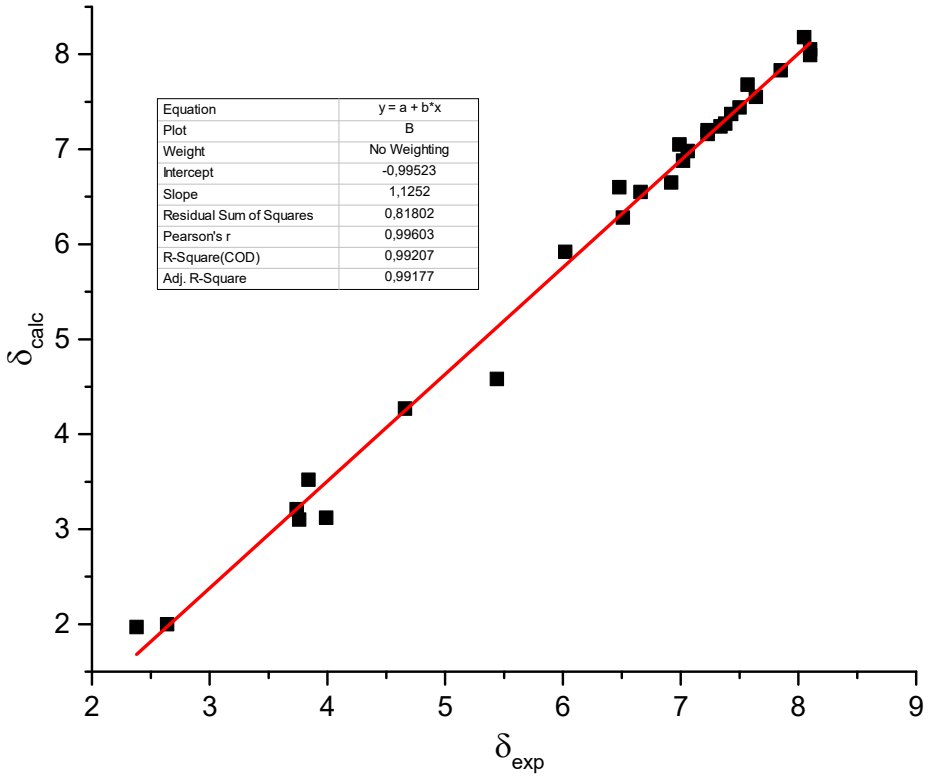


Figure S105. Correlations of the ^{1}H NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **7**.

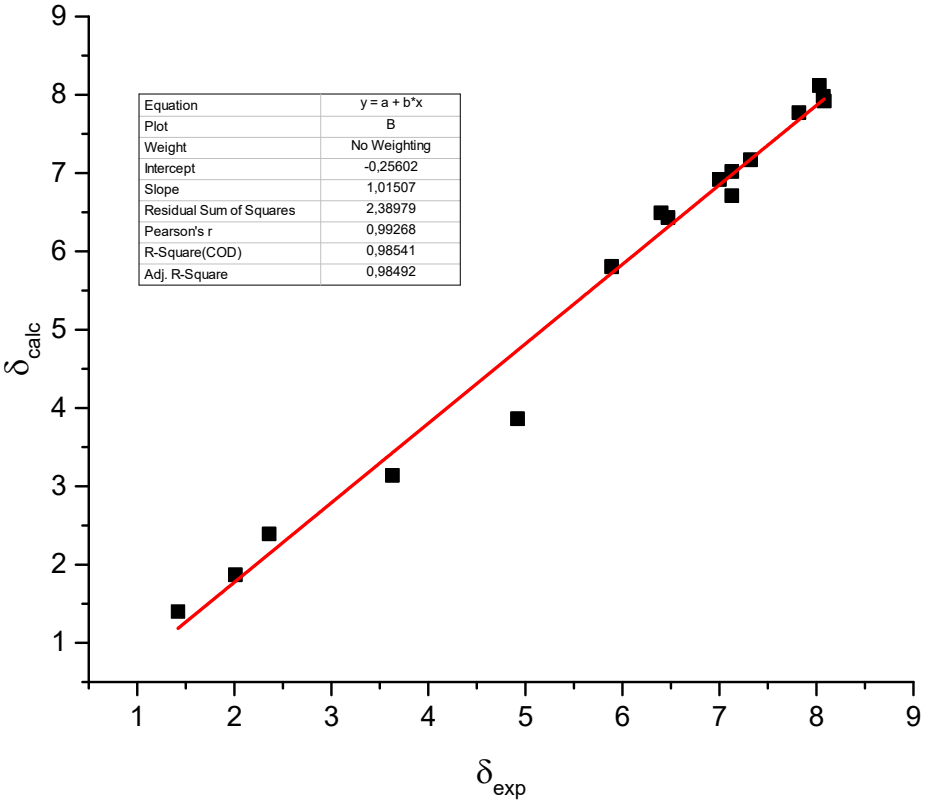


Figure S106. Correlations of the ^{1}H NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **8a**.

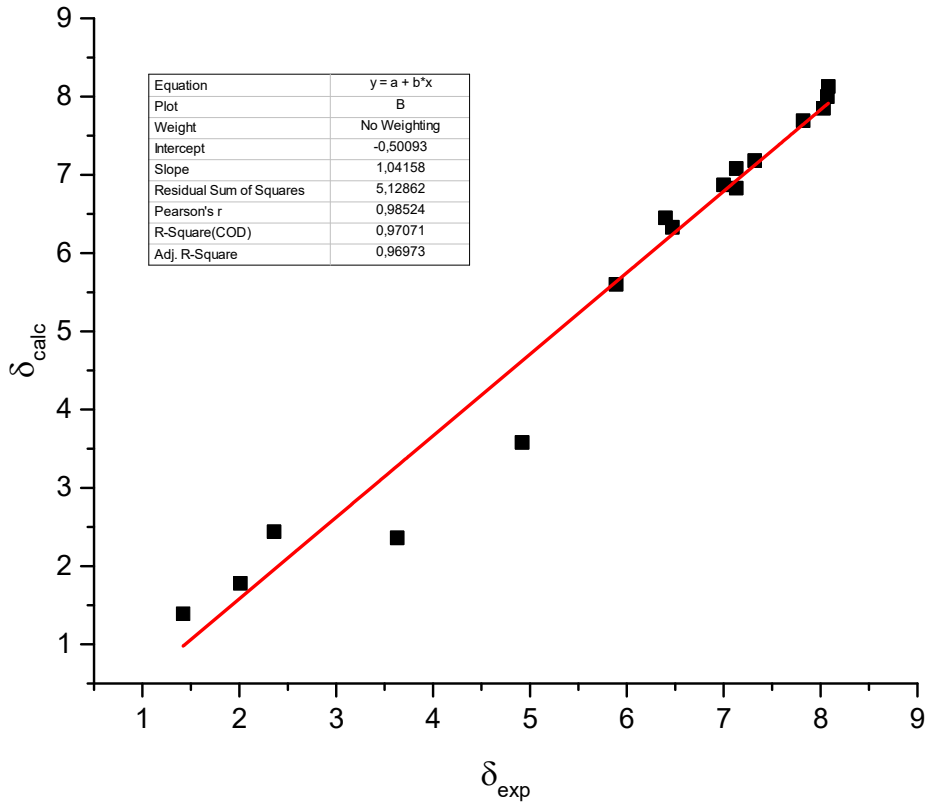


Figure S107. Correlations of the ^{1}H NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **8b**.

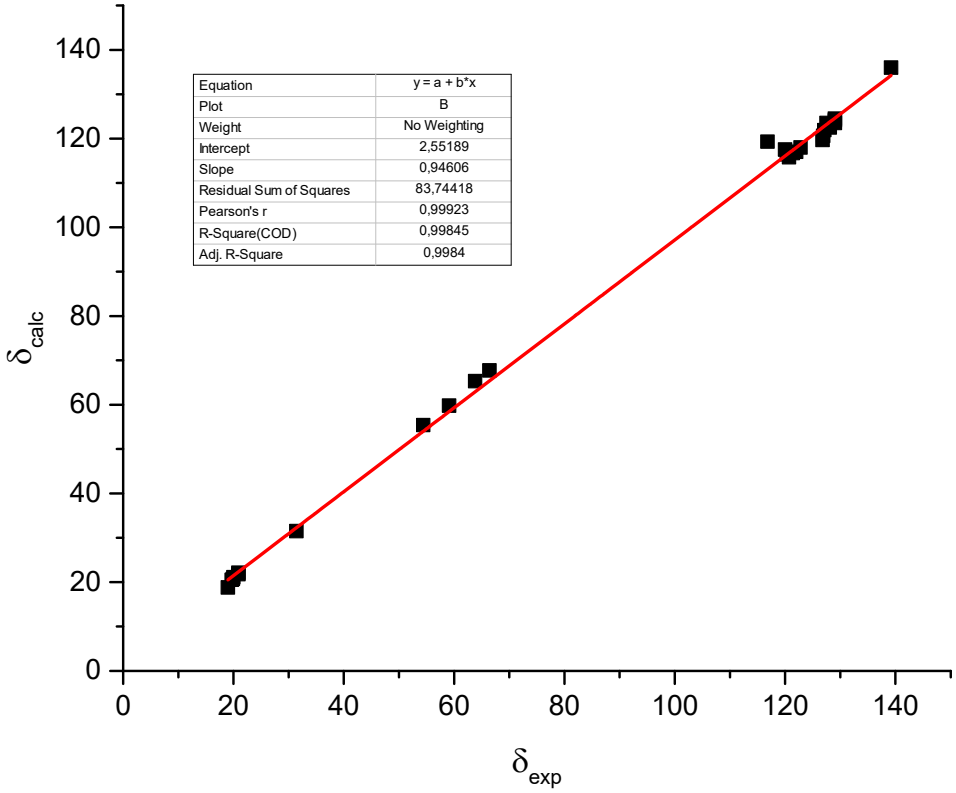


Figure S108. Correlations of the ^{13}C NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **2a**.

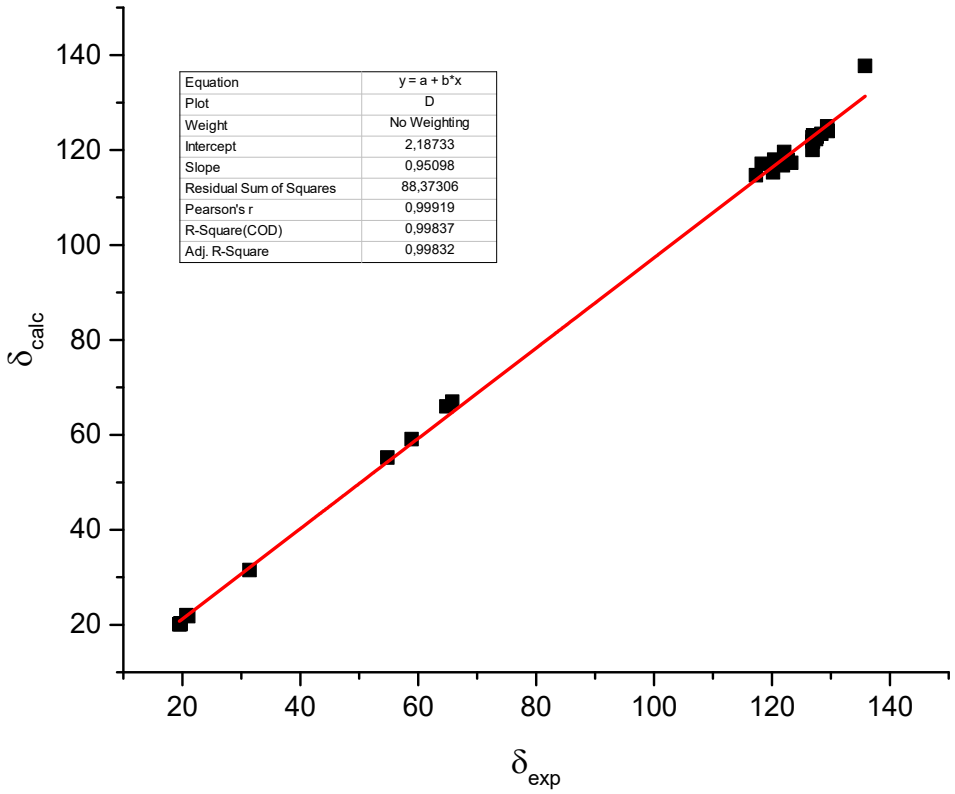


Figure S109. Correlations of the ^{13}C NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **2b**.

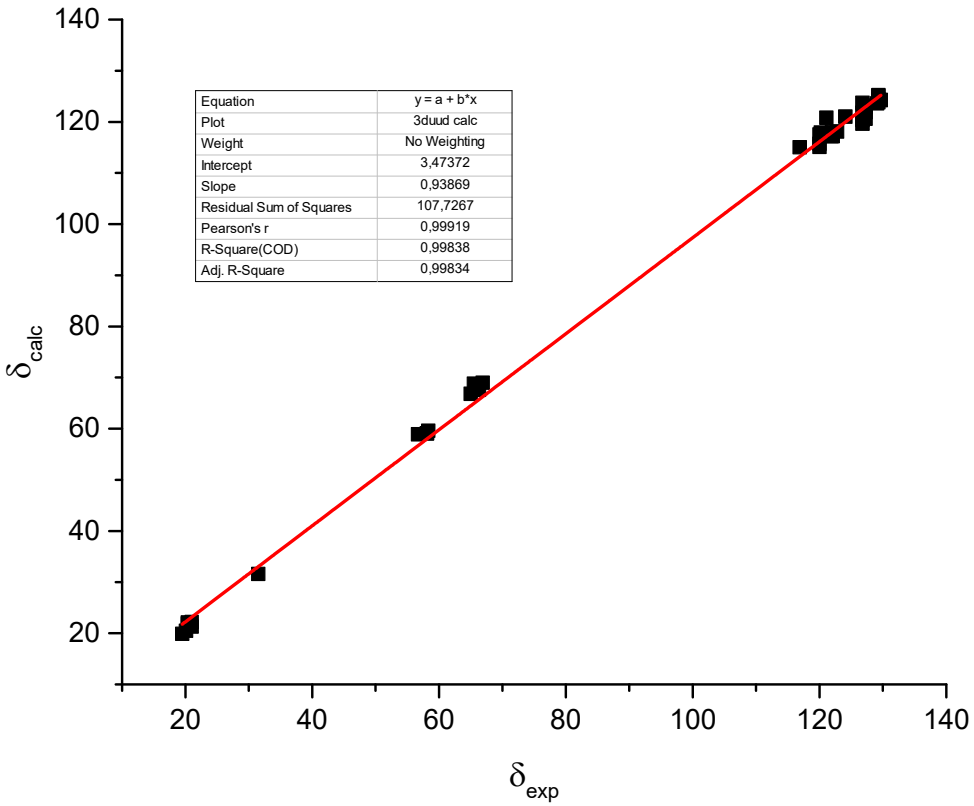


Figure S110. Correlations of the ^{13}C NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **3**-duud.

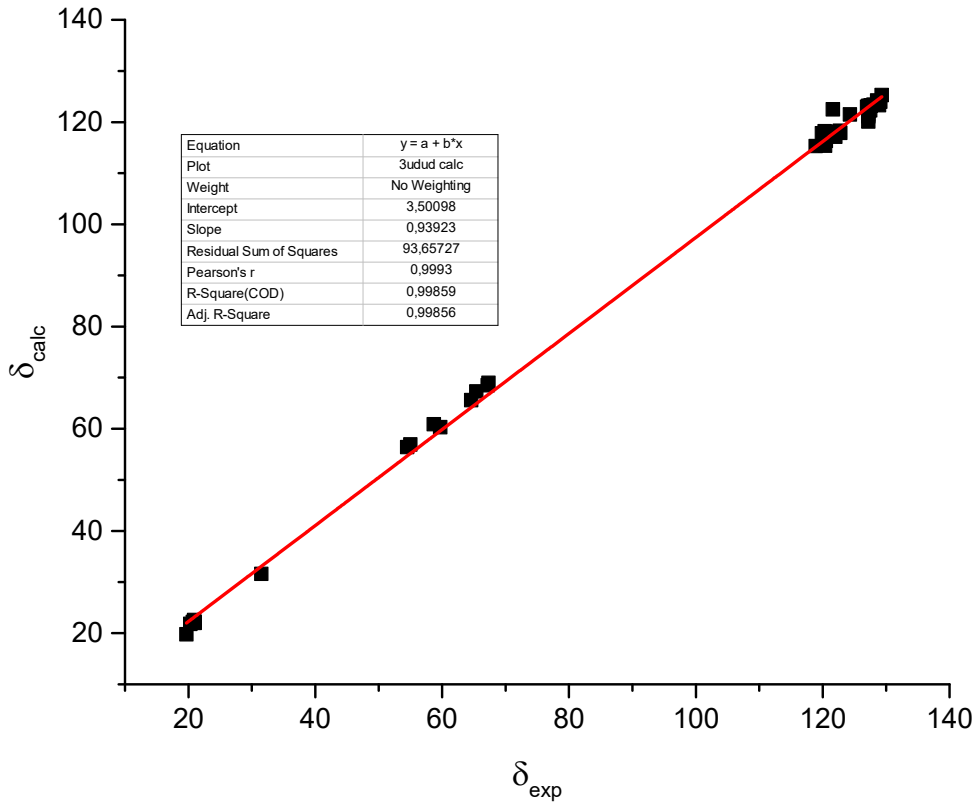


Figure S111. Correlations of the ^{13}C NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **3**-udud.

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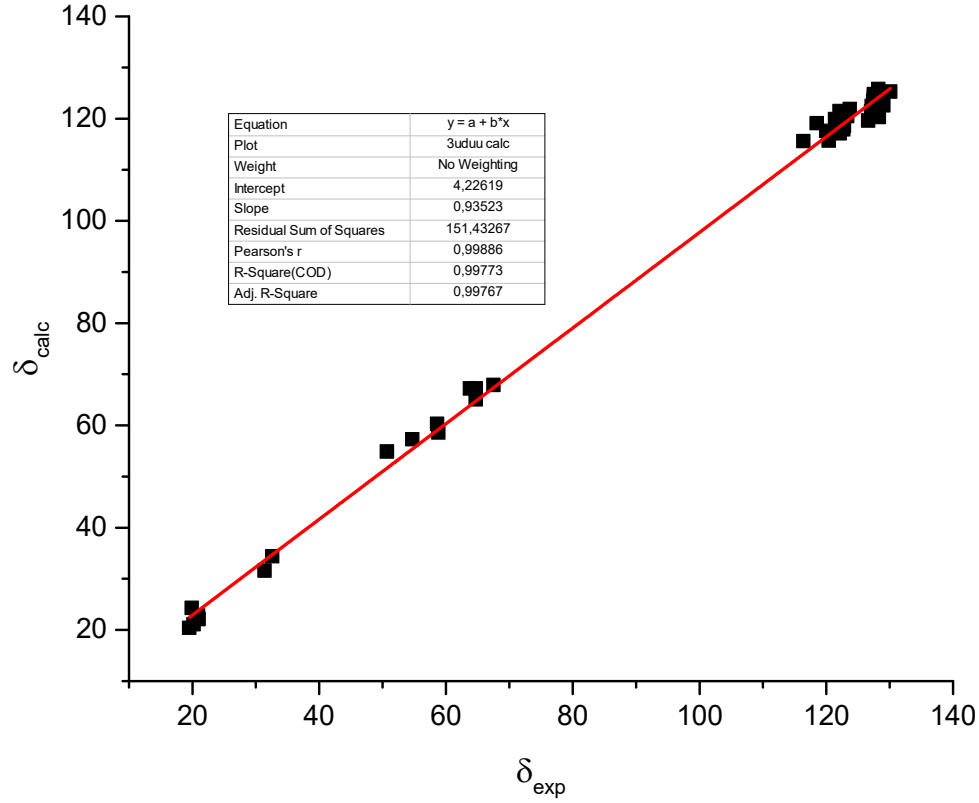


Figure S112. Correlations of the ^{13}C NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **3**-uduu.

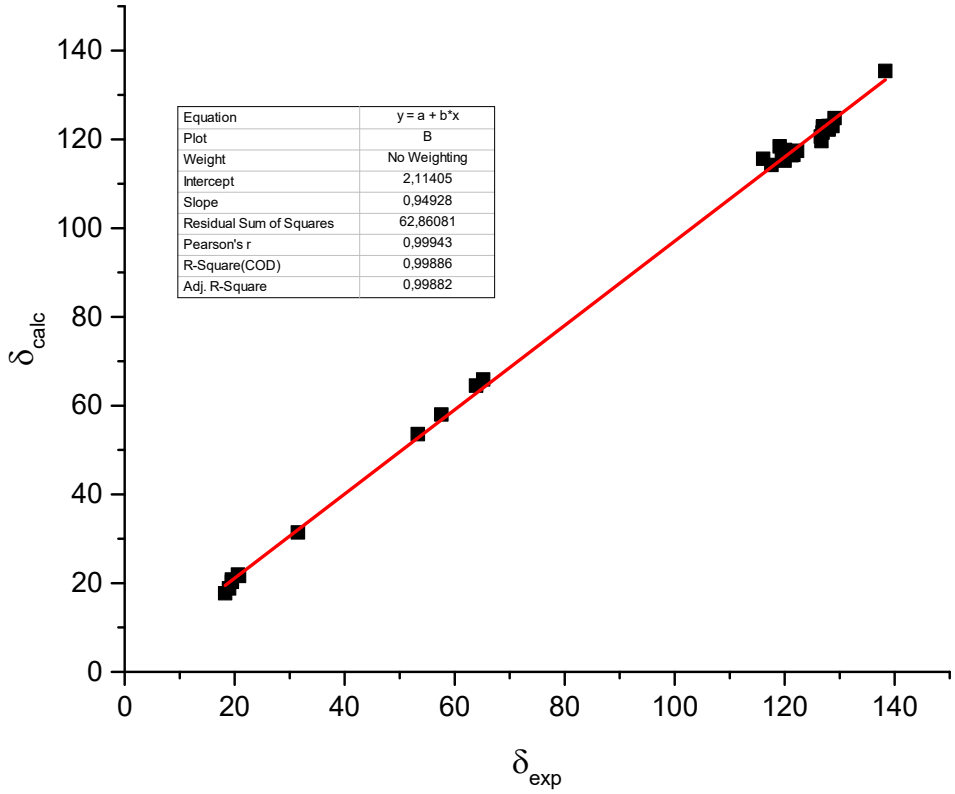


Figure S113. Correlations of the ^{13}C NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **4**.

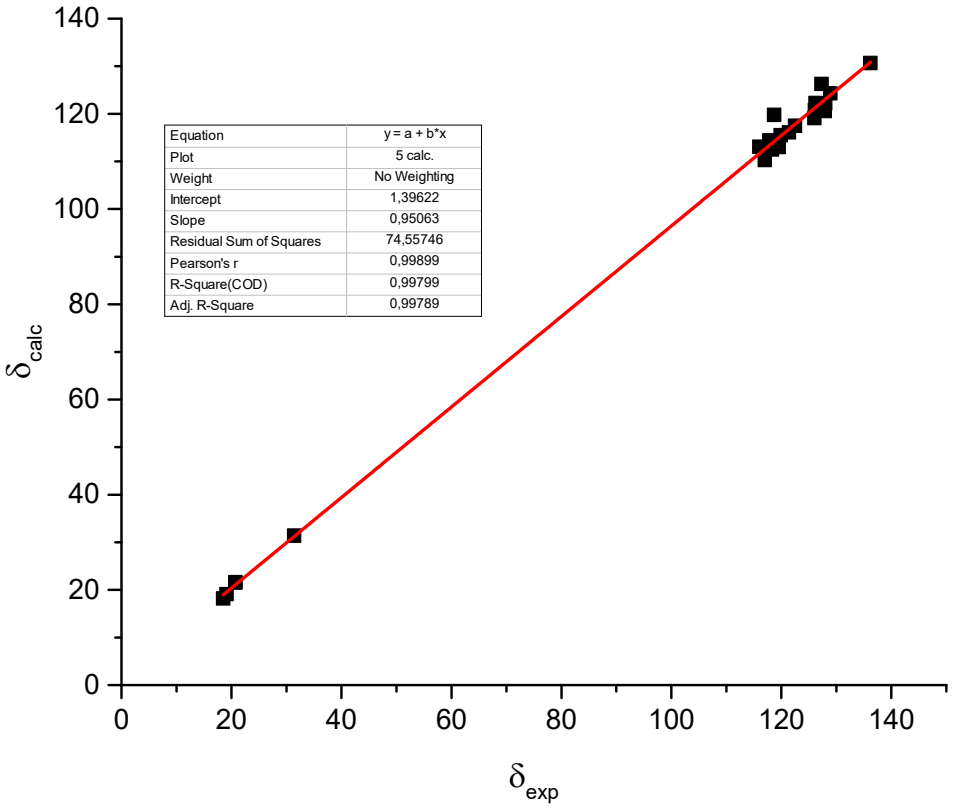


Figure S114. Correlations of the ^{13}C NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **6**.

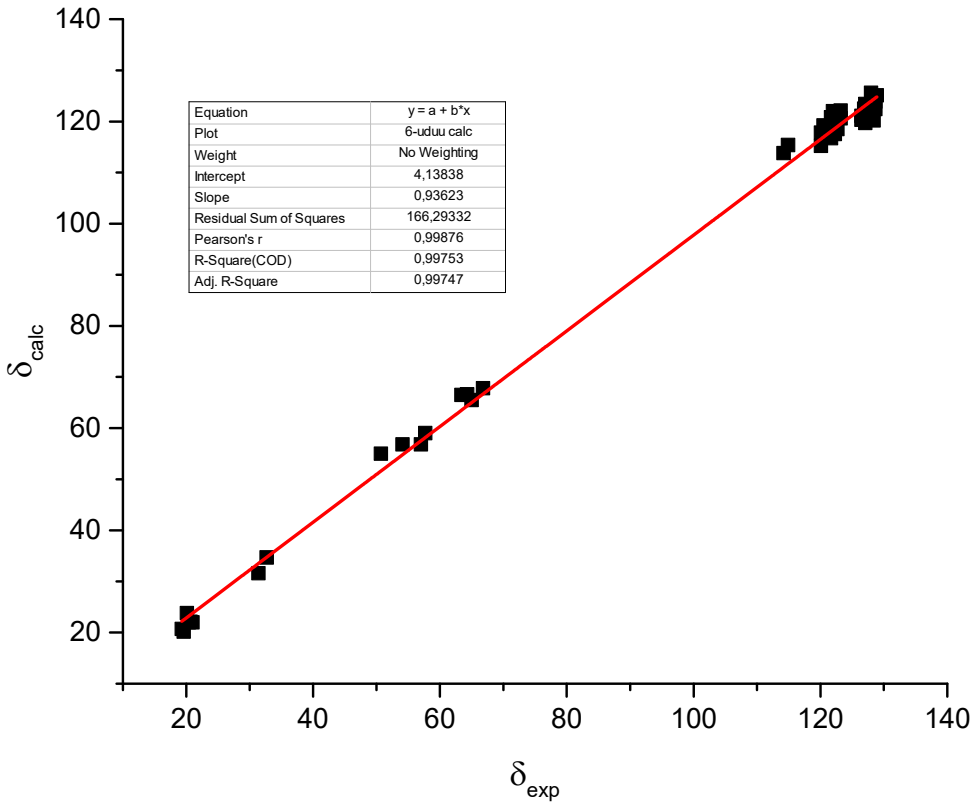


Figure S115. Correlations of the ^{13}C NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **5**-uduu.

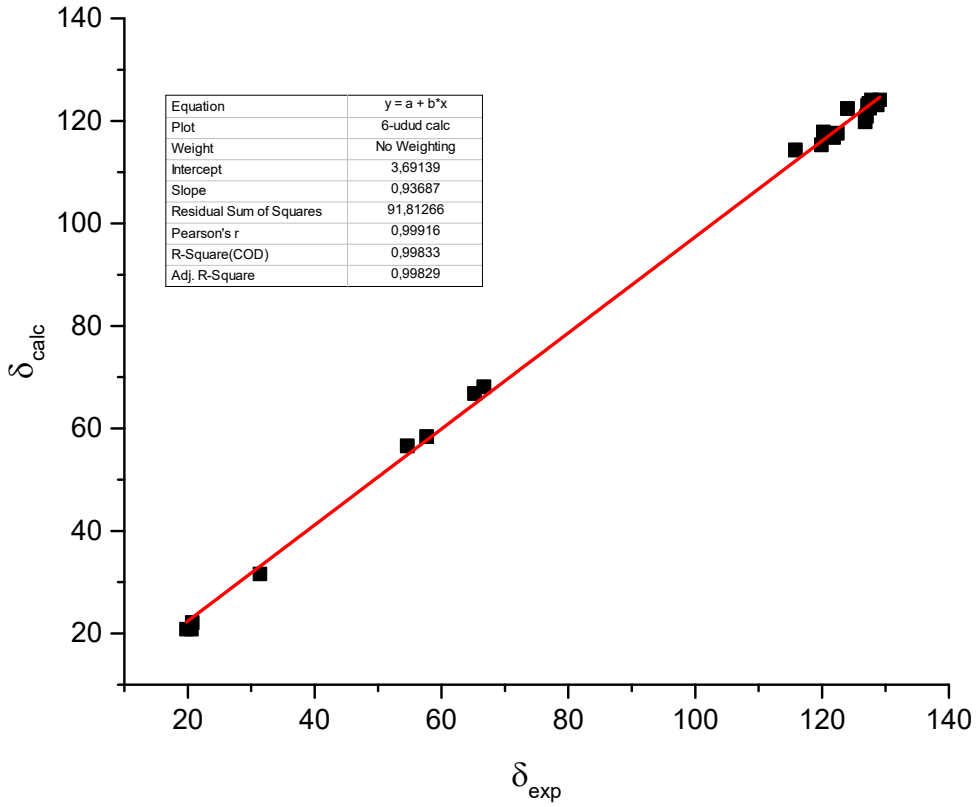


Figure S116. Correlations of the ^{13}C NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **5**-udud.

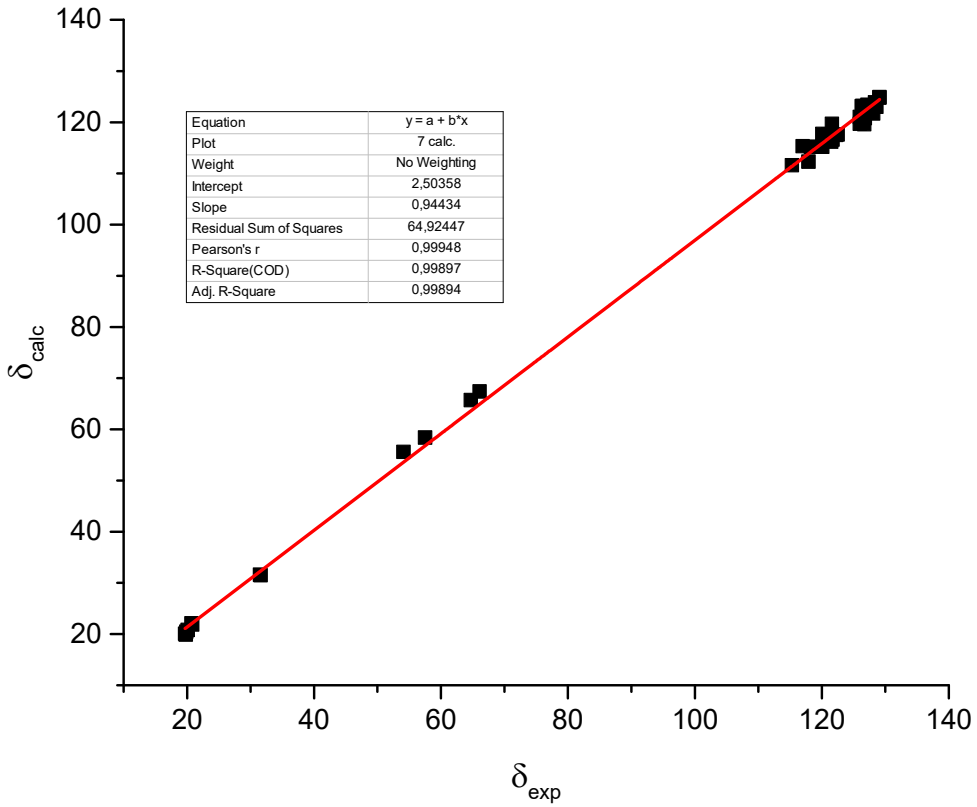
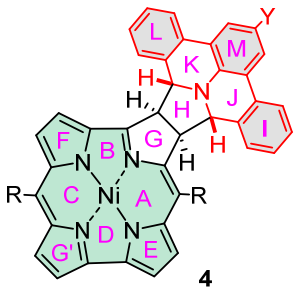


Figure S117. Correlations of the ^{13}C NMR experimental chemical shifts with those calculated by GIAO approach for the DFT-optimized structures of **7**.

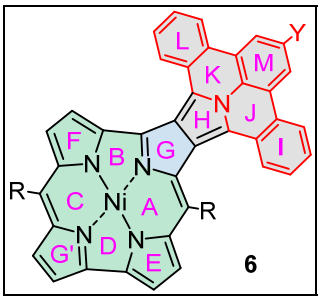
Table S1. NICS(*z*) (in ppm, *z* = 1, 0, –1) for the systems **3**-**8**.

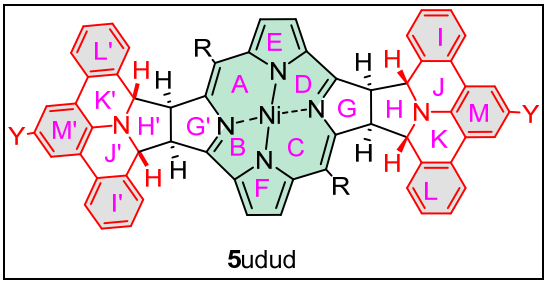
System	Ring	NICS(1)	NICS(0)	NICS(-1)
4	D	24.47	32.61	32.50
4	B	26.05	35.57	34.71
4	E	3.60	8.96	11.40
4	G	-10.65	-9.55	-5.84
4	F	-1.70	1.63	5.25
4	G'	3.90	9.36	9.53
4	H	-5.39	-5.34	-3.80
4	A	23.53	31.65	28.96
4	C	24.89	33.91	30.43
4	J	-2.15	0.66	-1.86
4	K	-1.77	0.85	-1.75
4	Aryl	-13.08	-11.06	-12.05
4	I	-11.29	-9.86	-12.09
4	M	-8.78	-7.52	-9.37
4	L	-10.83	-9.10	-10.84
4	Aryl	-12.08	-10.68	-11.94
6	D	40.67	42.93	32.60



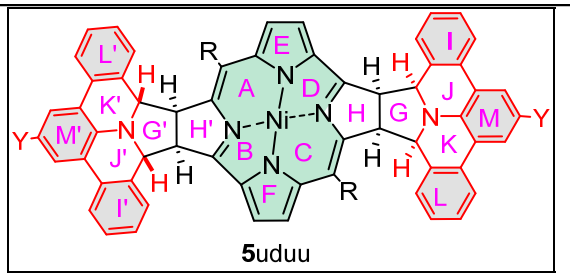
4

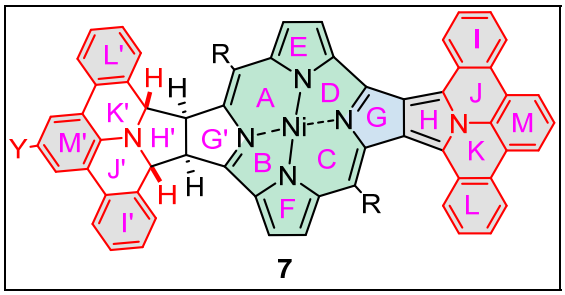
6	B	39.80	42.31	33.75
6	E	13.35	9.52	3.13
6	G'	8.25	7.94	3.55
6	F	3.20	2.99	2.60
6	G	2.97	0.89	-1.30
6	H	-5.43	-7.33	-6.92
6	A	37.79	41.89	32.42
6	C	35.74	41.55	32.74
6	K	-3.61	-1.33	-3.99
6	J	-2.60	-0.23	-3.22
6	Aryl	-12.42	-11.04	-12.30
6	L	-10.33	-8.57	-10.39
6	M	-10.15	-8.71	-10.35
6	I	-11.23	-9.42	-11.14
6	Aryl	-11.94	-10.89	-12.42
5udud	D	11.41	14.36	15.07
5udud	B	11.41	14.36	15.07
5udud	F	-2.08	0.45	0.63
5udud	G	-5.38	-4.28	-4.33
5udud	E	-2.08	0.45	0.63
5udud	G'	-5.38	-4.28	-4.33
5udud	H	-3.60	-4.76	-3.08
5udud	H'	-3.60	-4.76	-3.08
5udud	A	10.48	13.84	12.00
5udud	C	10.48	13.84	12.01
5udud	K	-1.67	1.34	-1.07
5udud	J	-1.13	1.63	-0.96
5udud	J'	-1.13	1.63	-0.96
5udud	K'	-1.67	1.34	-1.07
5udud	aryl	-12.24	-10.10	-11.14
5udud	L	-10.97	-9.44	-11.57
5udud	M	-8.51	-7.25	-9.12
5udud	I	-10.45	-8.61	-10.27
5udud	aryl	-12.24	-10.10	-11.14
5udud	L'	-10.97	-9.44	-11.57
5udud	M'	-8.51	-7.25	-9.12
5udud	I'	-10.45	-8.61	-10.27
5uduu	D	11.96	14.98	15.13
5uduu	B	12.48	15.48	15.68
5uduu	E	-2.24	0.13	0.54
5uduu	H	-6.31	-5.69	-5.80
5uduu	F	-2.23	0.32	0.82
5uduu	H'	-5.70	-4.73	-4.82
5uduu	G'	-3.65	-4.86	-3.15



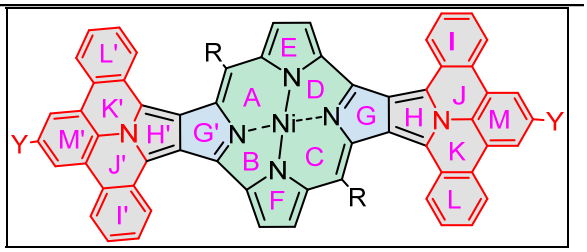


5duuu	G	-4.21	-6.29	-3.61
5duuu	A	11.45	14.56	12.24
5duuu	C	10.56	14.32	11.96
5duuu	J'	-1.20	1.53	-1.08
5duuu	K'	-1.66	1.32	-1.12
5duuu	K	-1.14	1.96	-1.18
5duuu	J	-0.49	2.26	-1.57
5duuu	L	-10.70	-9.21	-11.22
5duuu	M	-6.67	-4.75	-4.34
5duuu	I	-10.10	-8.65	-10.74
5duuu	Aryl	-11.96	-10.29	-11.31
5duuu	L'	-10.95	-9.45	-11.57
5duuu	M'	-8.53	-7.29	-9.18
5duuu	I'	-10.48	-8.68	-10.38
5duuu	Aryl	-12.26	-10.19	-11.22
7	D	17.59	21.00	21.77
7	B	17.88	24.06	23.74
7	E	0.80	2.53	2.70
7	G	1.73	4.30	3.36
7	F	-2.12	1.38	3.23
7	G'	-7.28	-6.29	-5.02
7	H'	-4.20	-4.98	-3.34
7	H	-8.11	-9.08	-7.19
7	A	16.36	20.92	18.12
7	C	17.54	22.58	19.98
7	J'	-1.34	1.37	-1.24
7	K'	-1.89	1.10	-1.33
7	K	-2.90	0.16	-2.30
7	J	-3.45	-0.97	-3.54
7	L	-11.06	-9.31	-11.06
7	M	-10.41	-8.89	-10.36
7	I	-10.17	-8.44	-10.40
7	Aryl	-11.58	-9.90	-11.02
7	L'	-11.10	-9.61	-11.73
7	M'	-8.59	-7.33	-9.18
7	I'	-10.57	-8.77	-10.46
7	Aryl	-12.56	-10.45	-11.44
8	D	24.44	27.82	24.80
8	B	24.81	27.83	24.43
8	E	-1.01	2.73	4.45
8	G	1.45	2.20	0.36
8	F	4.45	2.73	-1.01
8	G'	0.36	2.20	1.44
8	H'	-7.88	-8.98	-7.37

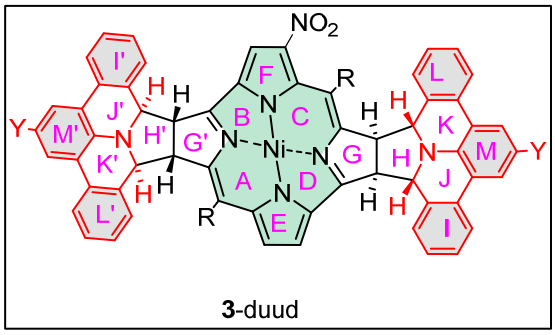




8	H	-7.37	-8.98	-7.88
8	A	22.58	27.96	24.35
8	C	24.36	27.96	22.58
8	J'	-3.58	-1.16	-3.71
8	K'	-2.96	0.09	-2.38
8	K	-2.38	0.09	-2.96
8	J	-3.71	-1.16	-3.58
8	L	-10.89	-9.25	-11.10
8	M	-10.36	-8.85	-10.33
8	I	-10.29	-8.44	-10.23
8	Aryl	-11.03	-9.83	-11.34
8	L'	-11.10	-9.25	-10.89
8	M'	-10.33	-8.85	-10.36
8	I'	-10.23	-8.44	-10.29
8	Aryl	-11.34	-9.83	-11.03

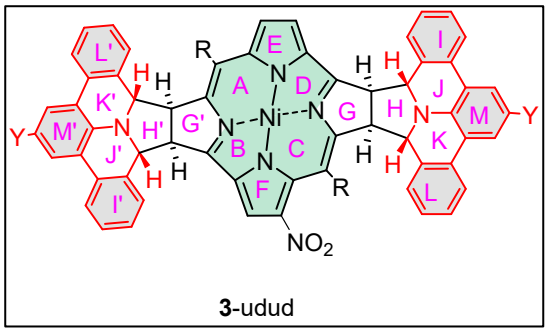


3duud	B	10.38	11.01	10.60
3duud	D	12.42	13.22	12.15
3duud	E	-1.30	-0.65	-1.87
3duud	G	-4.44	-3.42	-4.31
3duud	H	-3.08	-4.27	-3.33
3duud	F	-2.93	-2.88	-1.42
3duud	G'	-4.49	-3.38	-4.47
3duud	H'	-3.14	-4.03	-3.04
3duud	C	9.24	11.48	9.55
3duud	A	9.62	11.74	9.29
3duud	K	-2.19	1.13	-1.10
3duud	J	-1.44	1.44	-1.14
3duud	I	-10.53	-8.60	-10.21
3duud	M	-8.67	-7.35	-9.16
3duud	L	-11.22	-9.65	-11.57
3duud	aryl	-12.30	-10.22	-11.12
3duud	K'	-0.92	1.30	-1.95
3duud	J'	-1.21	1.42	-1.39
3duud	I'	-10.20	-8.55	-10.46
3duud	M'	-9.17	-7.33	-8.61
3duud	L'	-11.36	-9.52	-11.13
3duud	aryl	-10.88	-9.92	-11.99



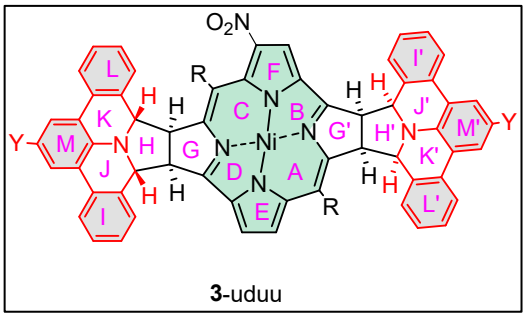
3-duud

3udud	D	9.24	11.53	12.28
3udud	B	8.40	9.92	10.54
3udud	F	-3.24	-2.76	-1.13
3udud	G	-4.63	-3.32	-4.16
3udud	E	-2.72	-0.63	-0.70
3udud	G'	-4.55	-3.18	-4.06
3udud	H	-3.57	-5.01	-3.44



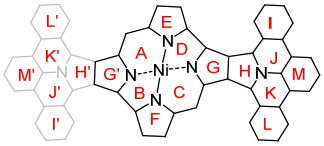
3-udud

3udud	H'	-3.26	-4.53	-2.97
3udud	A	8.19	10.78	9.07
3udud	C	8.12	10.54	9.09
3udud	K	-2.11	0.90	-1.80
3udud	J	-1.07	1.81	-0.70
3udud	J'	-1.04	1.70	-0.86
3udud	K'	-1.58	1.43	-0.97
3udud	aryl	-12.16	-10.12	-10.99
3udud	L	-10.90	-9.25	-11.47
3udud	M	-8.64	-7.44	-9.32
3udud	I	-10.44	-8.53	-10.12
3udud	aryl	-12.10	-9.94	-10.96
3udud	L'	-10.91	-9.35	-11.48
3udud	M'	-8.51	-7.24	-9.12
3udud	I'	-10.36	-8.48	-10.16
3uduu	B	7.99	9.83	10.26
3uduu	D	10.08	11.97	12.18
3uduu	F	-4.26	-3.55	-1.45
3uduu	G'	-5.49	-4.38	-5.15
3uduu	E	-2.75	-1.01	-0.92
3uduu	G	-4.60	-3.44	-4.30
3uduu	H	-3.28	-4.82	-3.18
3uduu	H'	-3.78	-5.97	-3.41
3uduu	C	8.73	10.80	8.85
3uduu	A	7.66	10.60	8.51
3uduu	J	-1.18	1.64	-0.89
3uduu	K	-1.79	1.30	-1.07
3uduu	K'	-1.10	1.96	-1.06
3uduu	J'	-0.29	2.40	-1.27
3uduu	L'	-10.71	-9.22	-11.26
3uduu	M'	-7.00	-5.27	-5.39
3uduu	I'	-9.95	-8.48	-10.69
3uduu	aryl	-11.89	-10.17	-11.14
3uduu	L	-10.98	-9.46	-11.55
3uduu	M	-8.56	-7.30	-9.16
3uduu	I	-10.47	-8.60	-10.25
3uduu	aryl	-12.18	-10.18	-11.16



3-uduu

Table S1A. Selected NICS(1) indices (in ppm) calculated for the systems **3-8**



	NICS(1)								
Ring	**4**	**6**	**3**-duud	**3**-udud	**3**-uduu	**5**-udud	**5**-uduu	**7**	**8**
A	23.53	37.79	9.62	8.19	7.66	10.48	11.45	16.36	22.58
B	26.05	39.80	10.38	8.40	7.99	11.41	12.48	17.88	24.81
C	24.89	35.74	9.24	8.12	8.73	10.48	10.56	17.54	24.36
D	24.47	40.67	12.42	9.24	10.08	11.41	11.96	17.59	24.44
E	3.60	13.35	−1.30	−2.72	−2.75	−2.08	−2.24	0.80	−1.01
F	−1.70	3.20	−2.93	−3.24	−4.26	−2.08	−2.23	−2.12	4.45
G	−10.65	2.97	−4.44	−4.63	−4.60	−5.38	−4.21	1.73	1.45
H	−5.39	−5.43	−3.08	−3.57	−3.28	−3.60	−6.31	−8.11	−7.37
I	−11.29	−11.23	−10.53	−10.44	−10.47	−10.45	−10.10	−10.17	−10.29
J	−2.15	−2.60	−1.44	−1.07	−1.18	−1.13	−0.49	−3.45	−3.71
K	−1.77	−3.61	−2.19	−2.11	−1.79	−1.67	−1.14	−2.90	−2.38
L	−10.83	−10.33	−11.22	−10.90	−10.98	−10.97	−10.70	−11.06	−10.89
M	−8.78	−10.15	−8.67	−8.64	−8.56	−8.51	−6.67	−10.41	−10.36
G'	3.90	8.25	−4.49	−4.55	−5.49	−5.38	−3.65	−7.28	0.36
H'			−3.14	−3.26	−3.78	−3.60	−5.70	−4.20	−7.88
I'			−10.20	−10.36	−9.95	−10.45	−10.48	−10.57	−10.23
J'			−1.21	−1.04	−0.29	−1.13	−1.20	−1.34	−3.58
K'			−0.92	−1.58	−1.10	−1.67	−1.66	−1.89	−2.96
L'			−11.36	−10.91	−10.71	−10.97	−10.95	−11.10	−11.10
M'			−9.17	−8.51	−7.00	−8.51	−8.53	−8.59	−10.33

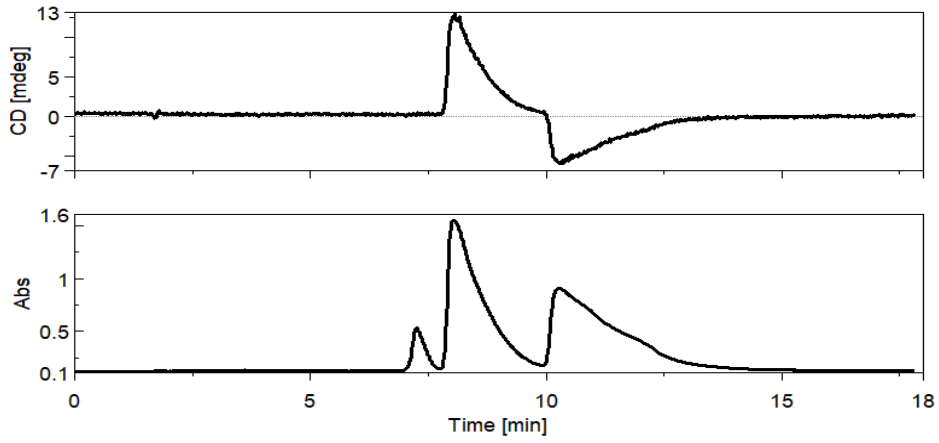


Figure S118. Chiral stationary phase HPLC profiles (bottom, absorbance detection; top ECD detection at 305 nm) for **2a** with DCM/hexane (60/40) mobile phase and 2 mL/min flow rate.

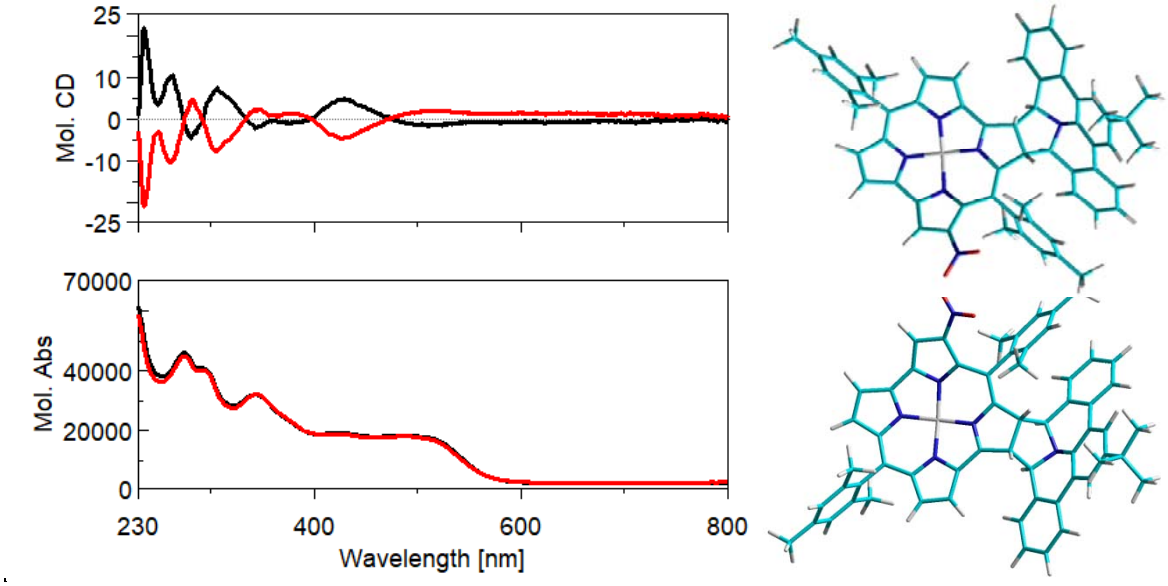
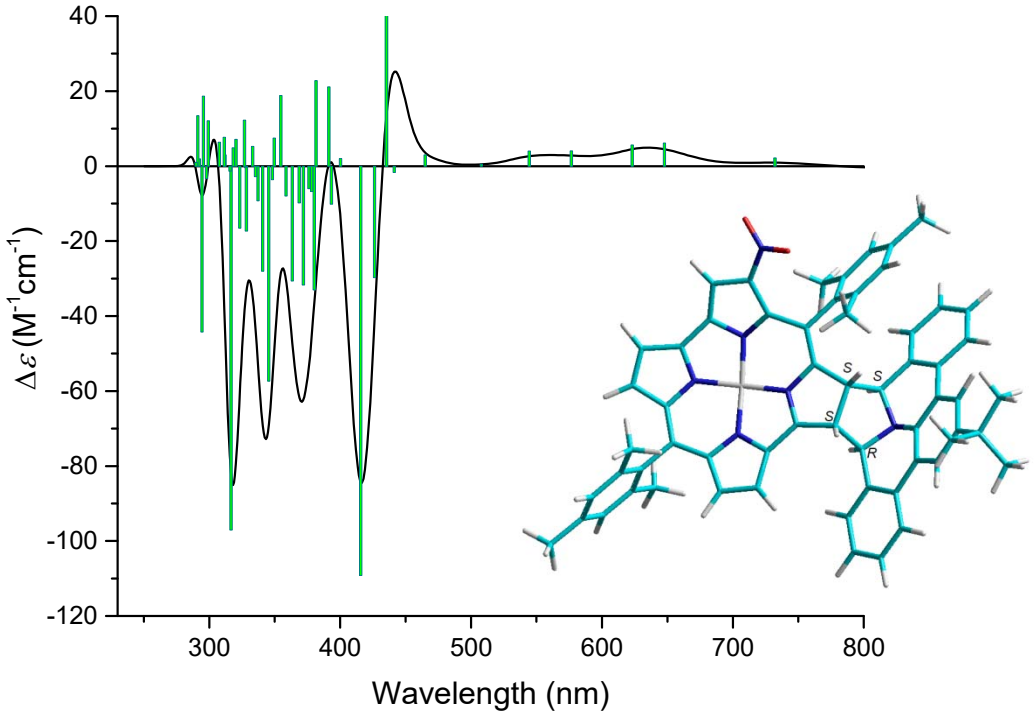


Figure S119. Absorbance (bottom) and ECD (top) spectra of *R,R,R,S*-**2a** (black traces) and *S,S,S,R*-**2a** (red traces) recorded in dichloromethane (298 K).



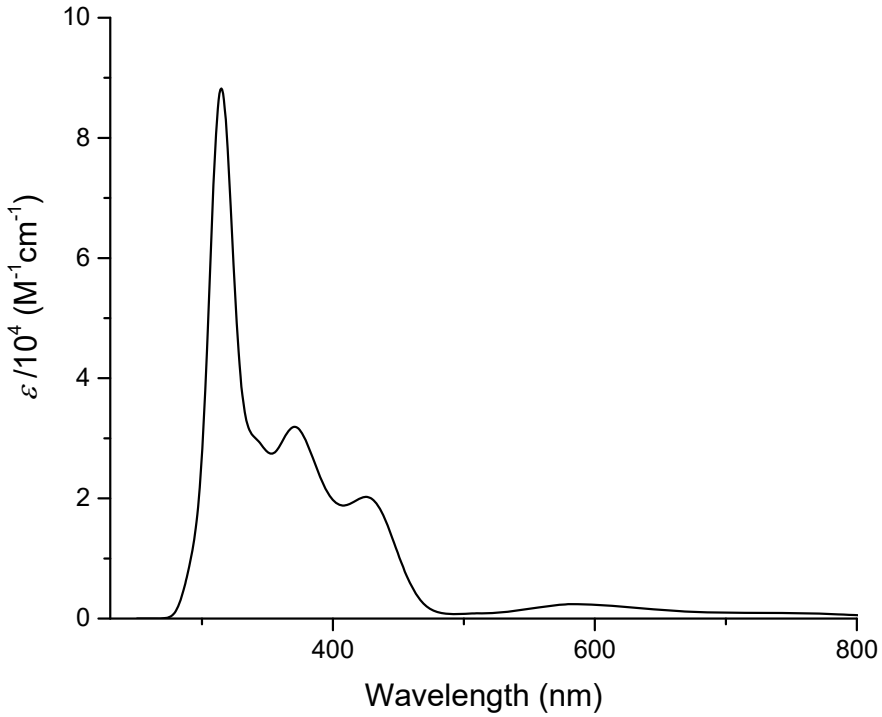


Figure S120. TD DFT calculated absorbance (bottom) and ECD (top) spectra of *S,S,S,R*-**2a.**

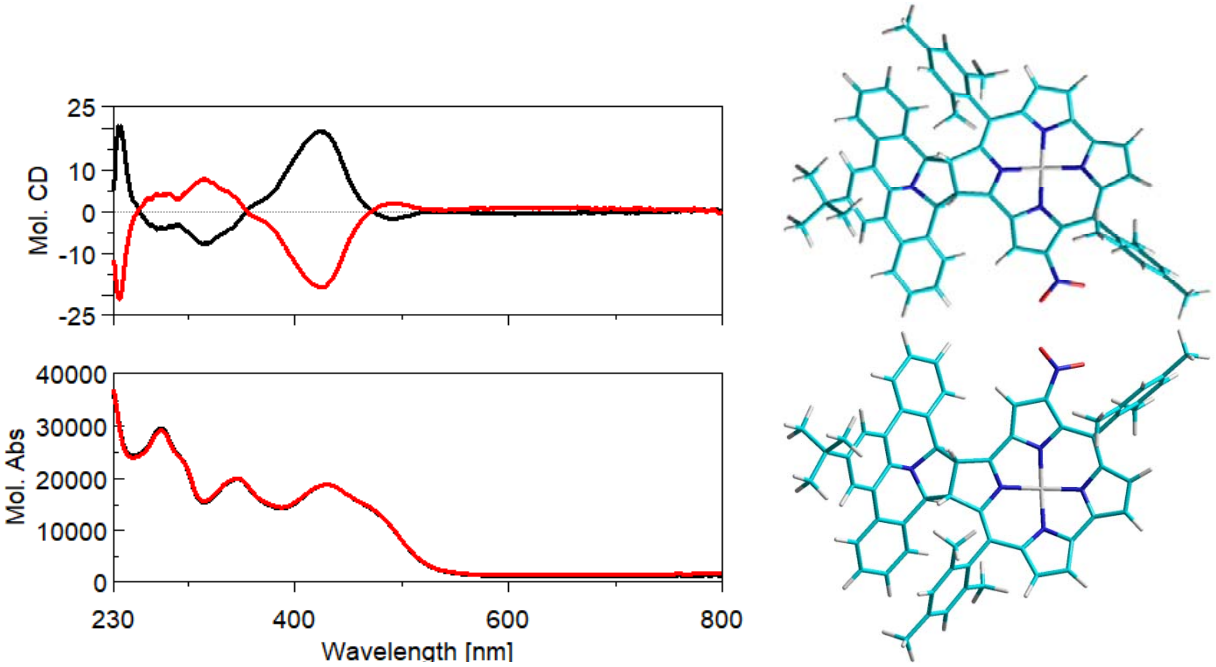


Figure S121. Absorbance (bottom) and ECD (top) spectra of *S,R,R,S*-**2b** (red traces) and *R,S,S,R*-**2b** (red traces) recorded in dichloromethane (298 K).

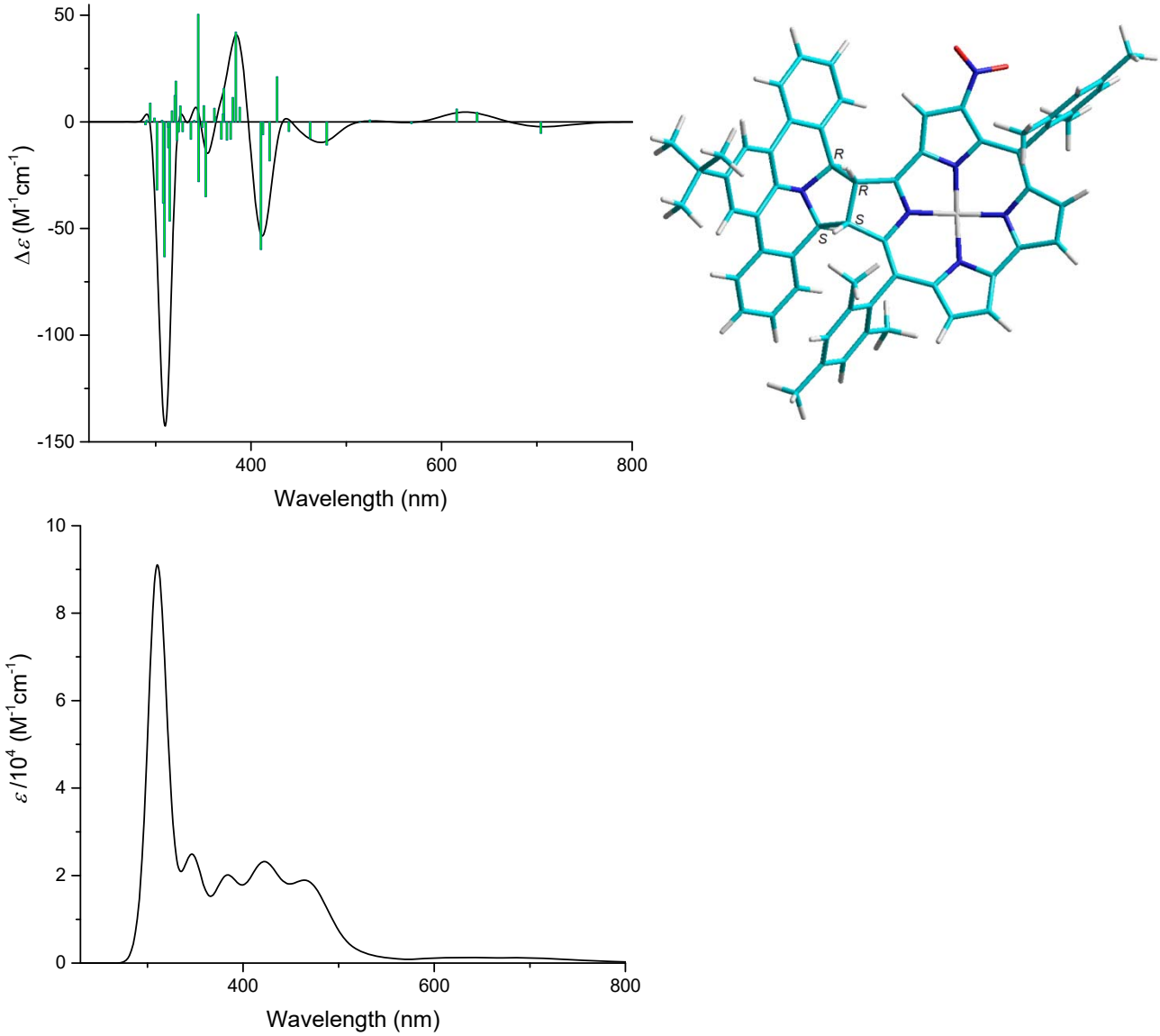


Figure S122. TD DFT calculated absorbance (bottom) and ECD (top) spectra of *R,S,S,R*-**2b**.

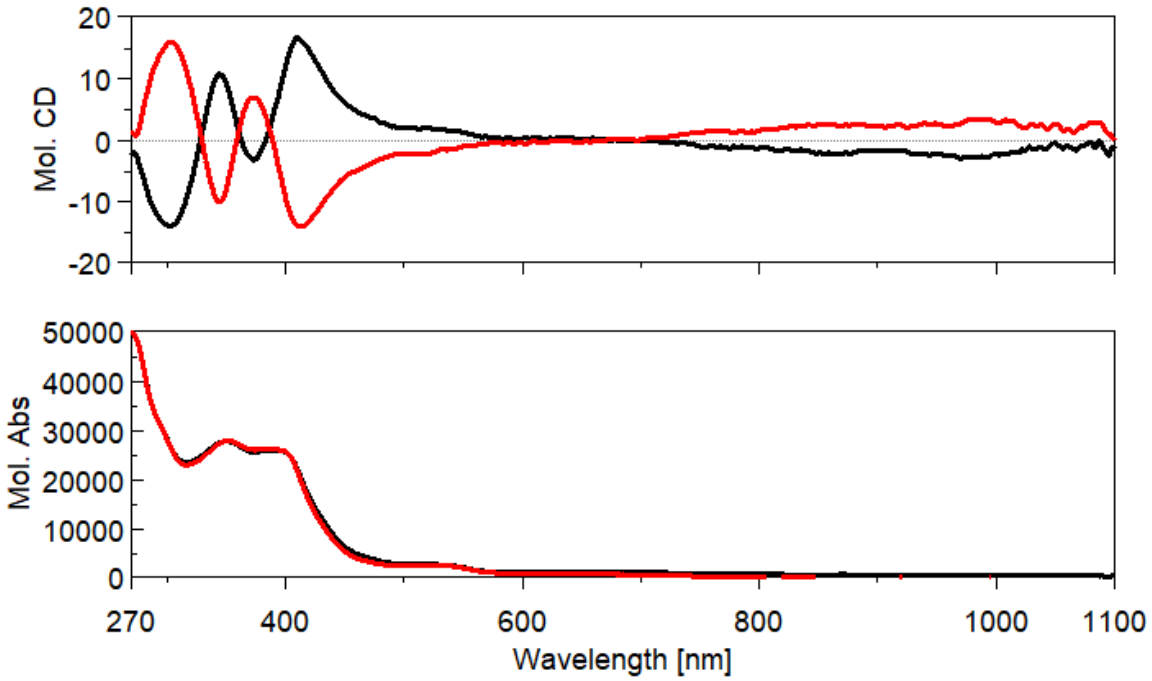
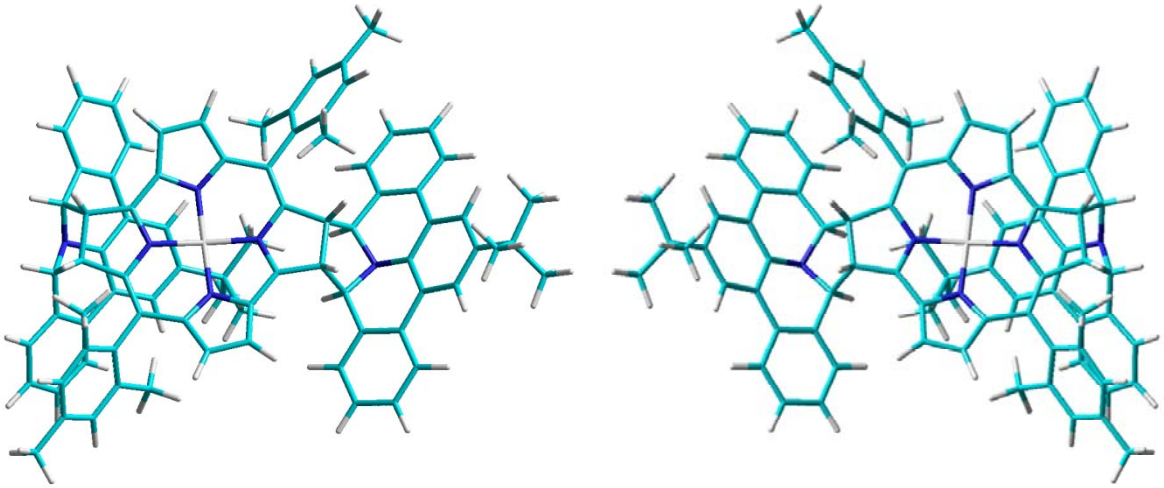


Figure S123. Absorbance (bottom) and ECD (top) spectra of *R,S,S,R,R,S,R,S*-**5** = **5**-uduu (black traces) and *S,R,R,S,S,R,S,R*-**5** = **5**-dudd (red traces) recorded in dichloromethane (298 K).



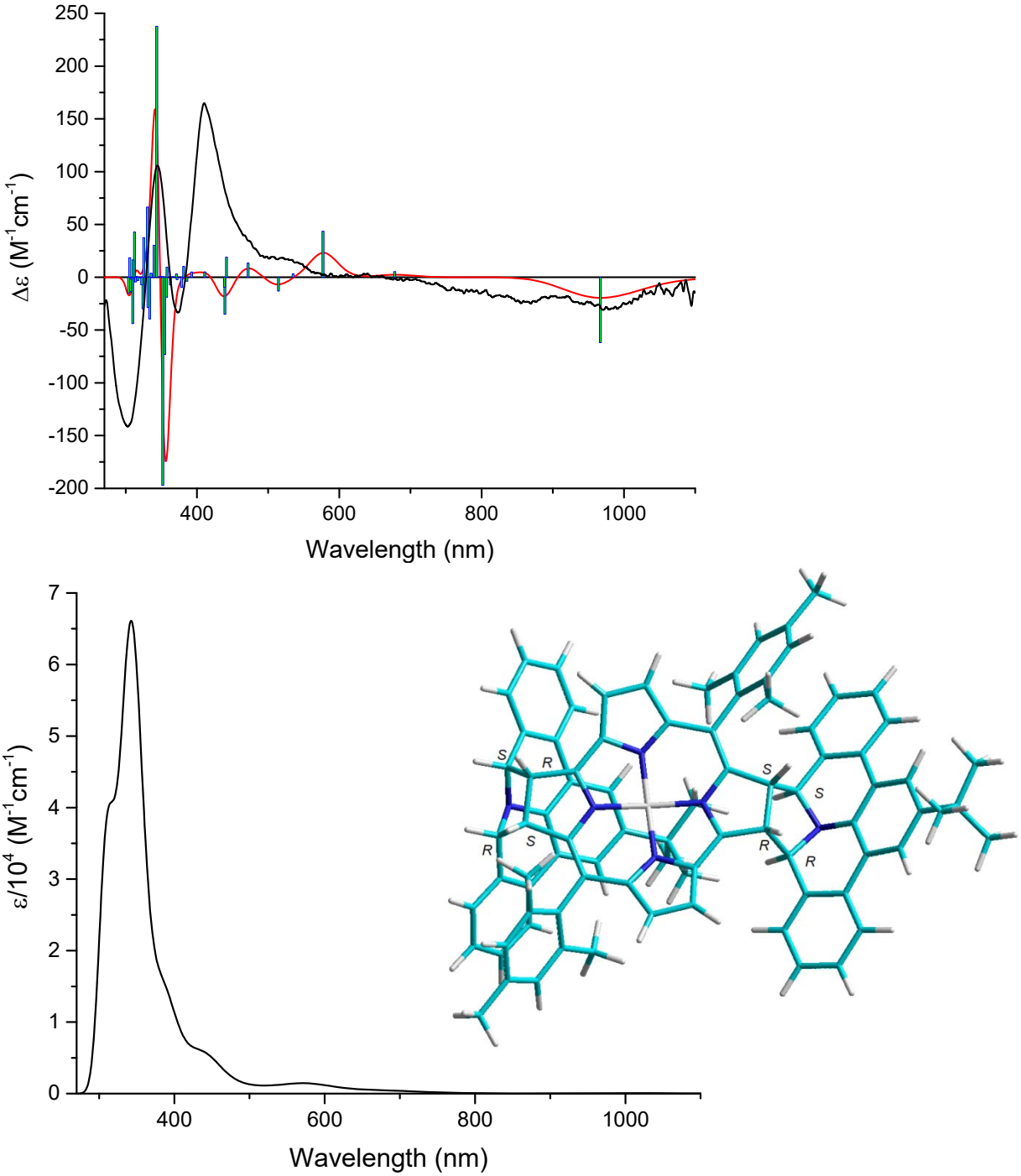


Figure S124. TD DFT calculated absorbance (bottom) and ECD (top) spectra of *R,S,S,R,R,S,R,S*-**5** = **5**-uduu with superimposed experimental ECD spectrum of the faster migrating enantiomer (red trace).

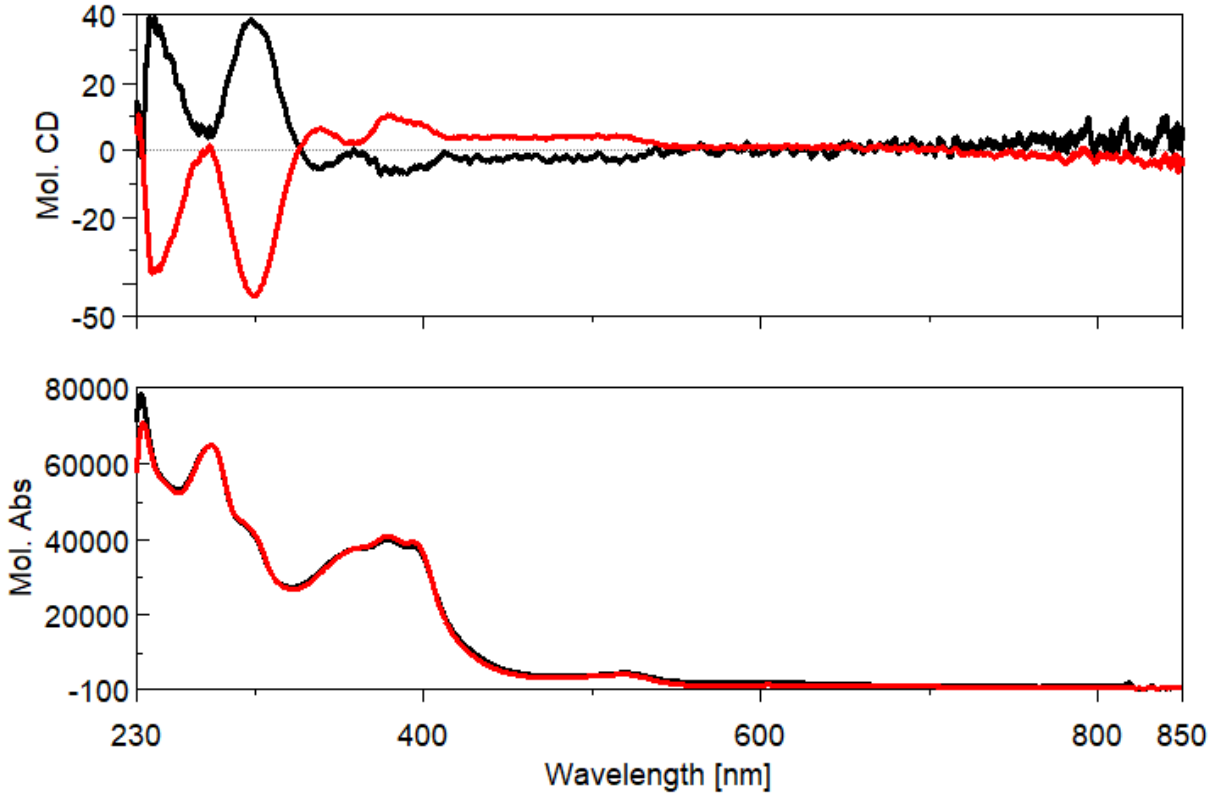
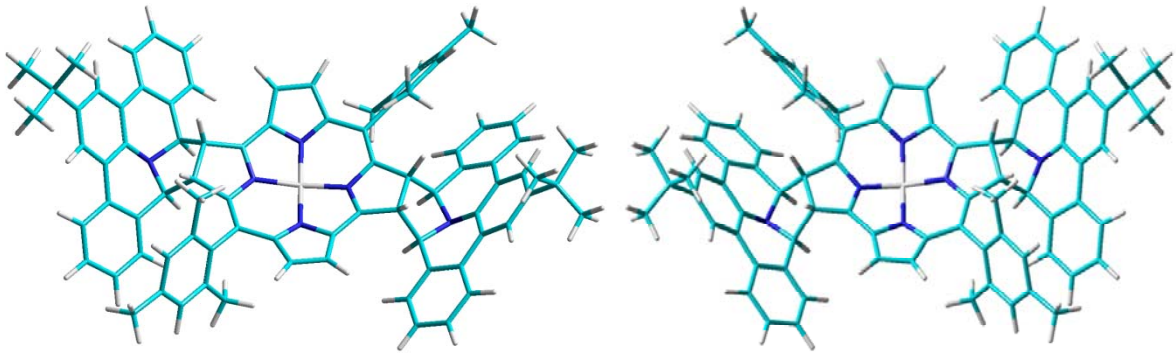


Figure S125. Absorbance (bottom) and ECD (top) spectra of *S,R,R,S,S,R,R,S*-**5** = **5**-dudu (black traces) and *R,S,S,R,R,S,S,R*-**5** = **5**-udud (red traces) recorded in dichloromethane (298 K).



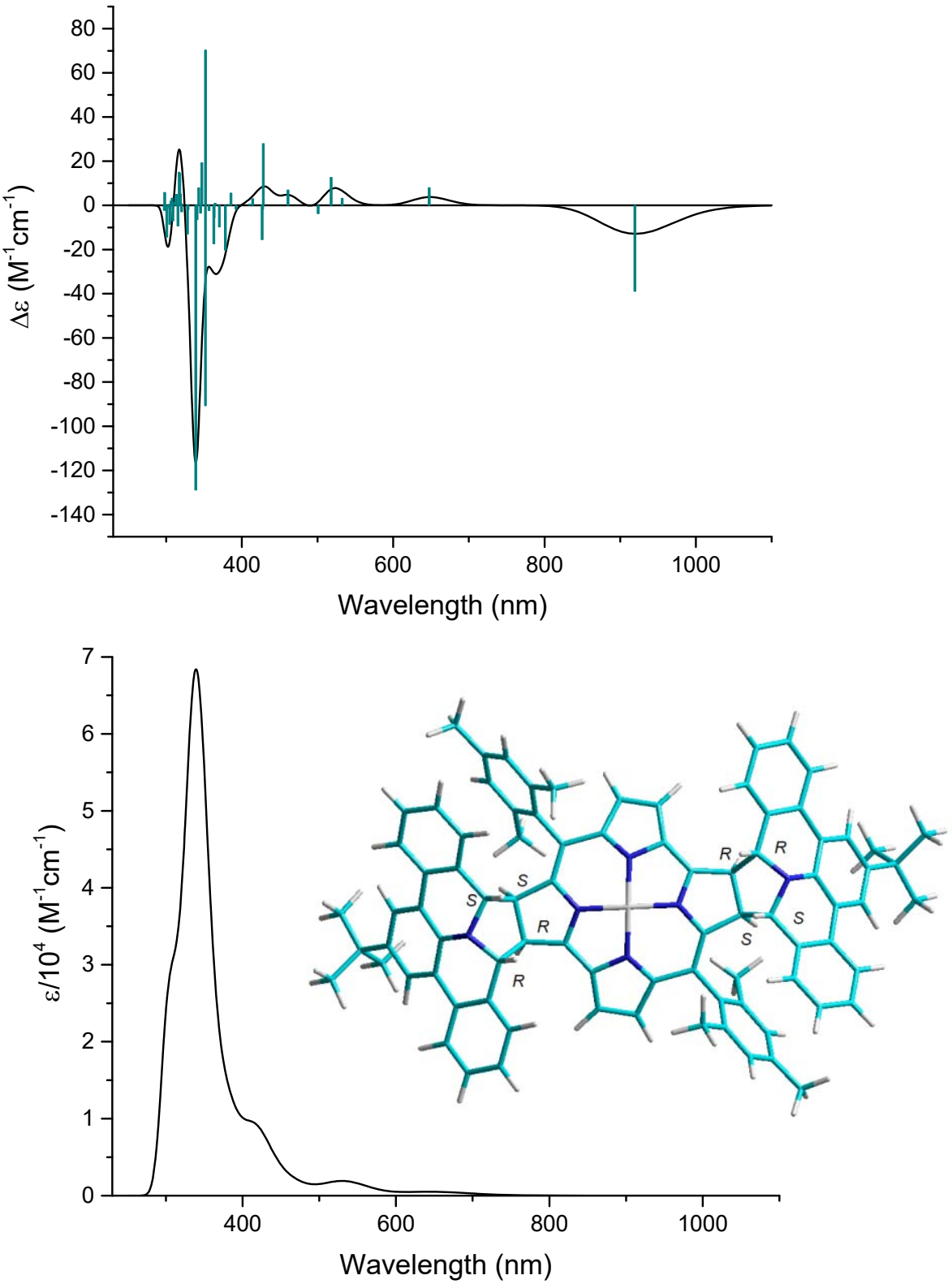


Figure S126. TD DFT calculated absorbance (bottom) and ECD (top) spectra of *R,S,S,R,R,S,S,R*-**5** = **5**-udud.

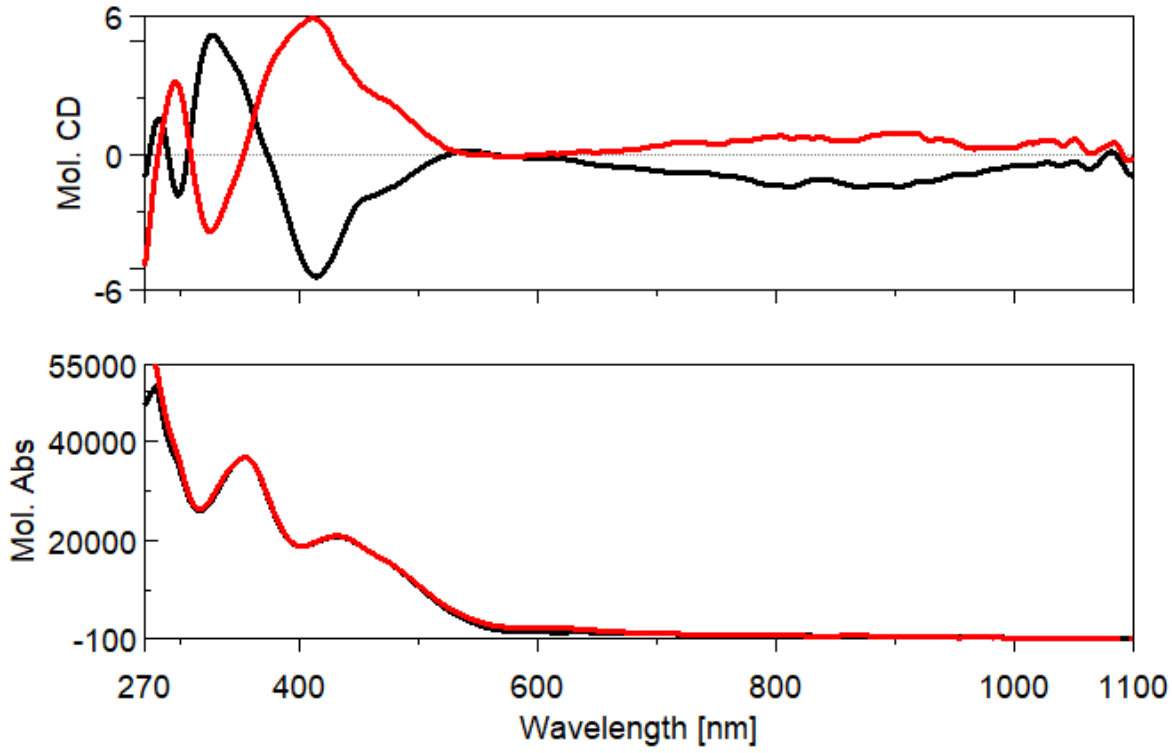
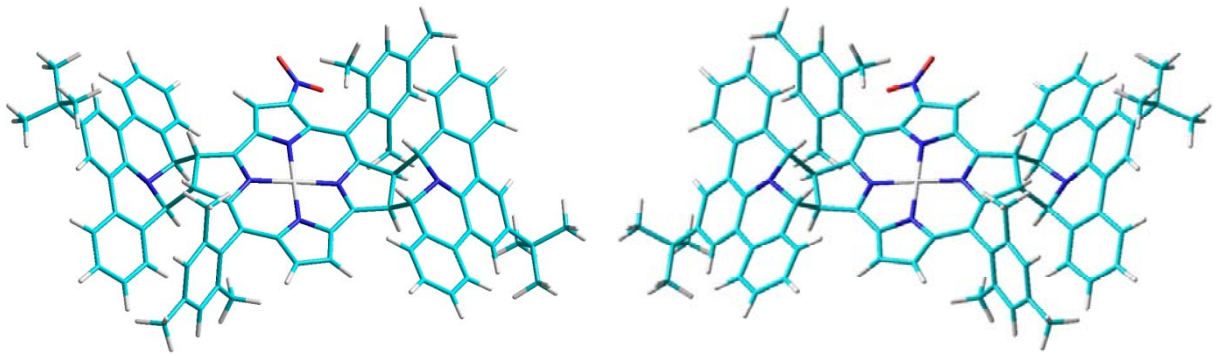


Figure S127. Absorbance (bottom) and ECD (top) spectra of *R,R,S,S,S,R,R,S*-**3** = **3**-uddu (black traces) and *S,S,R,R,R,S,S,R*-**3** = **3**-duud (red traces) recorded in dichloromethane (298 K).



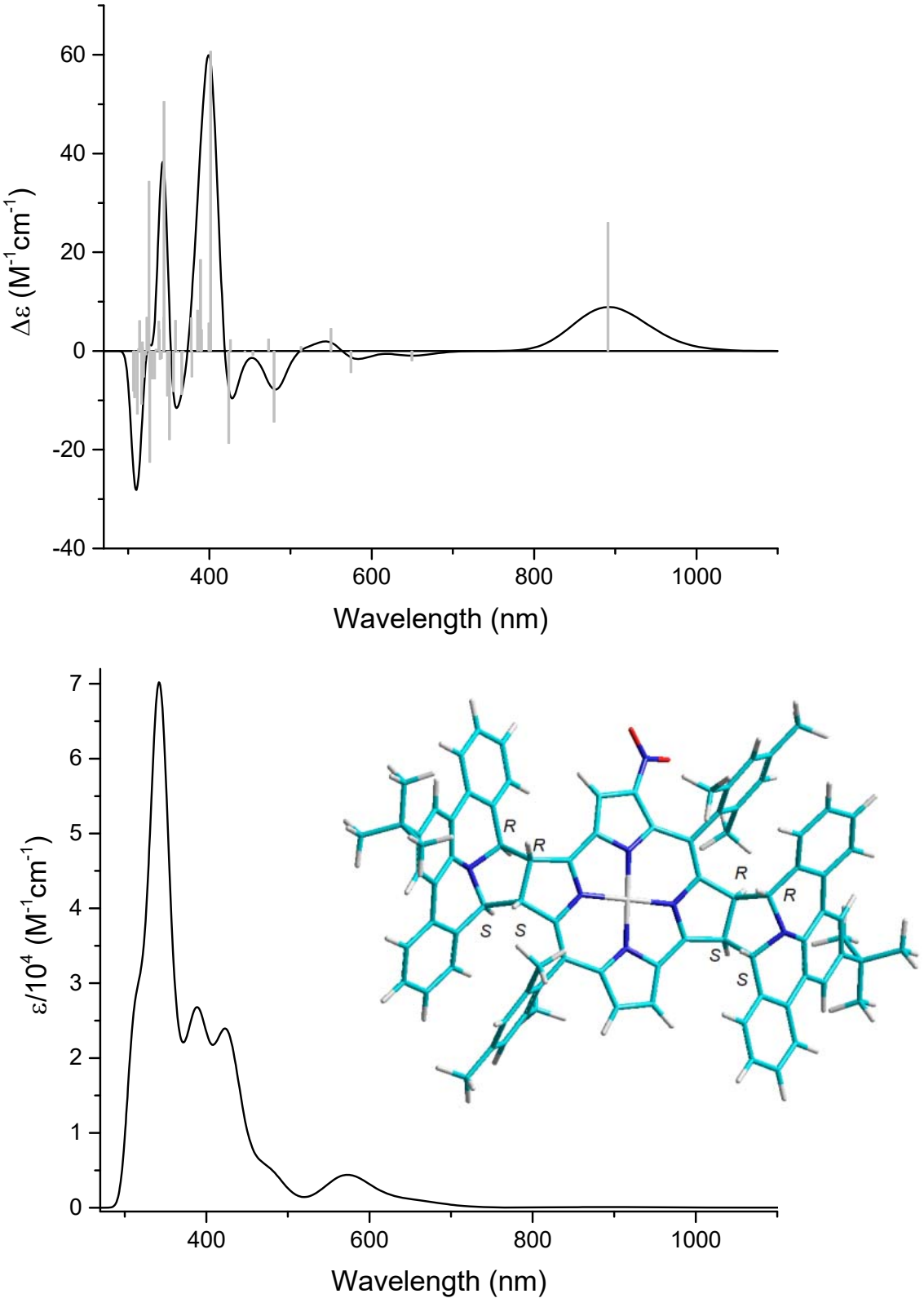


Figure S128. TD DFT calculated absorbance (bottom) and ECD (top) spectra of *S,S,R,R,R,S,S,R*-**3** = **3**-duud.

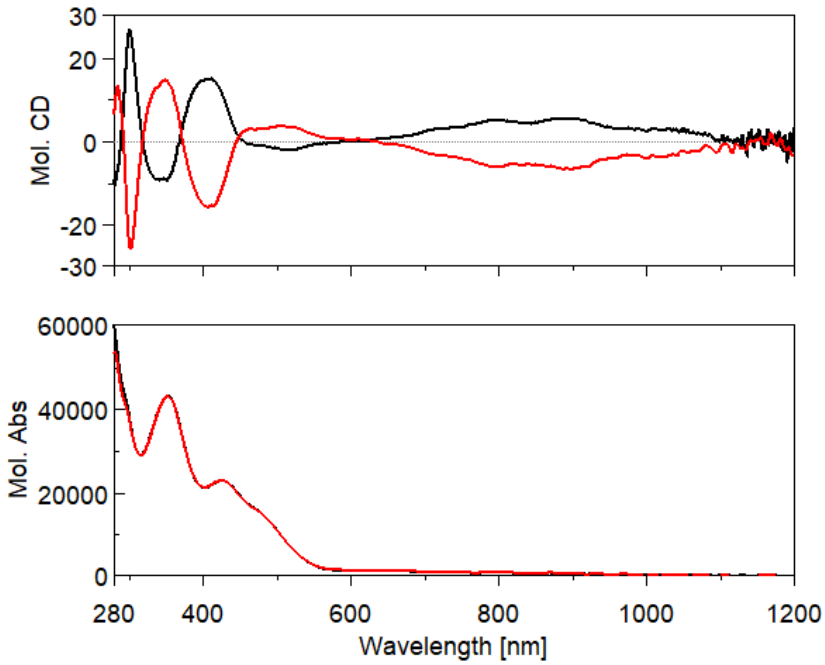
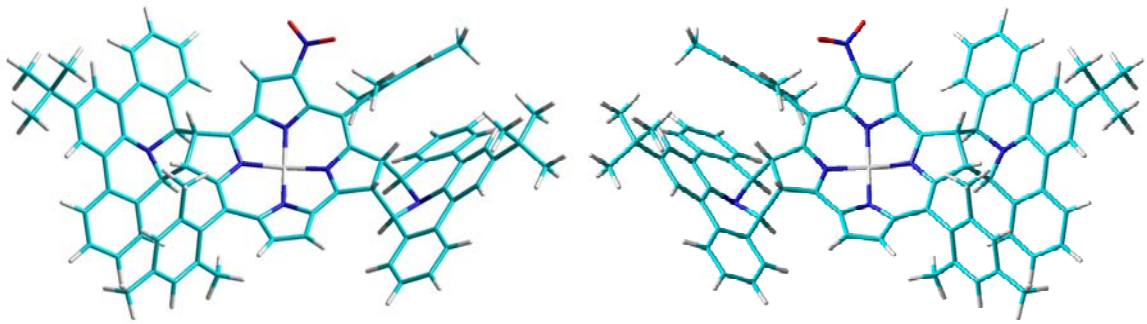


Figure S129. Absorbance (bottom) and ECD (top) spectra of *S,R,R,S,S,R,R,S*-**3** = **3**-dudu (black traces) and *R,S,S,R,R,S,S,R*-**3** = **3**-udud (red traces) recorded in dichloromethane (298 K).



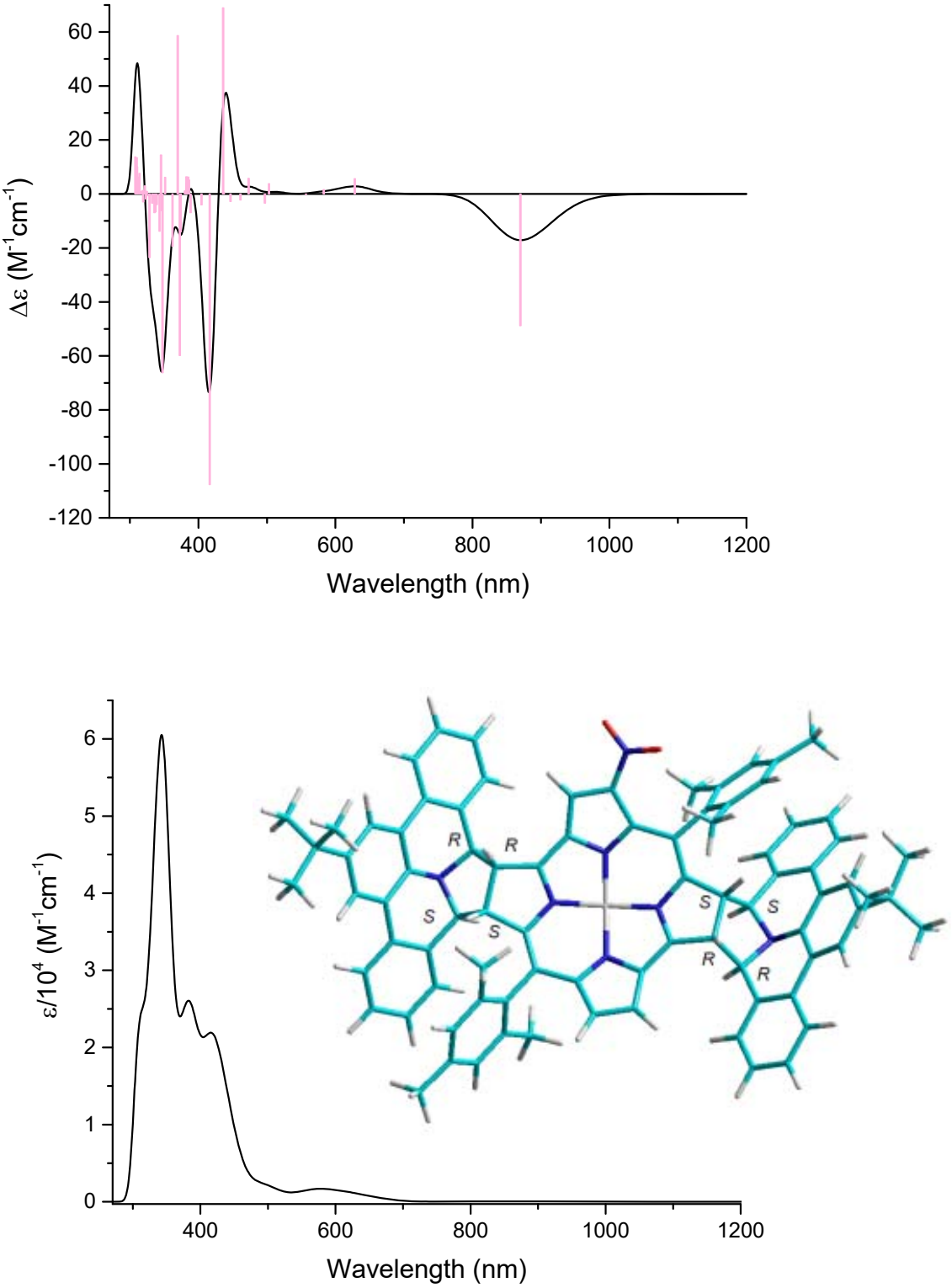


Figure S130. TD DFT calculated absorbance (bottom) and ECD (top) spectra of *R,S,S,R,R,S,S,R*-**3** = **3**-udud.

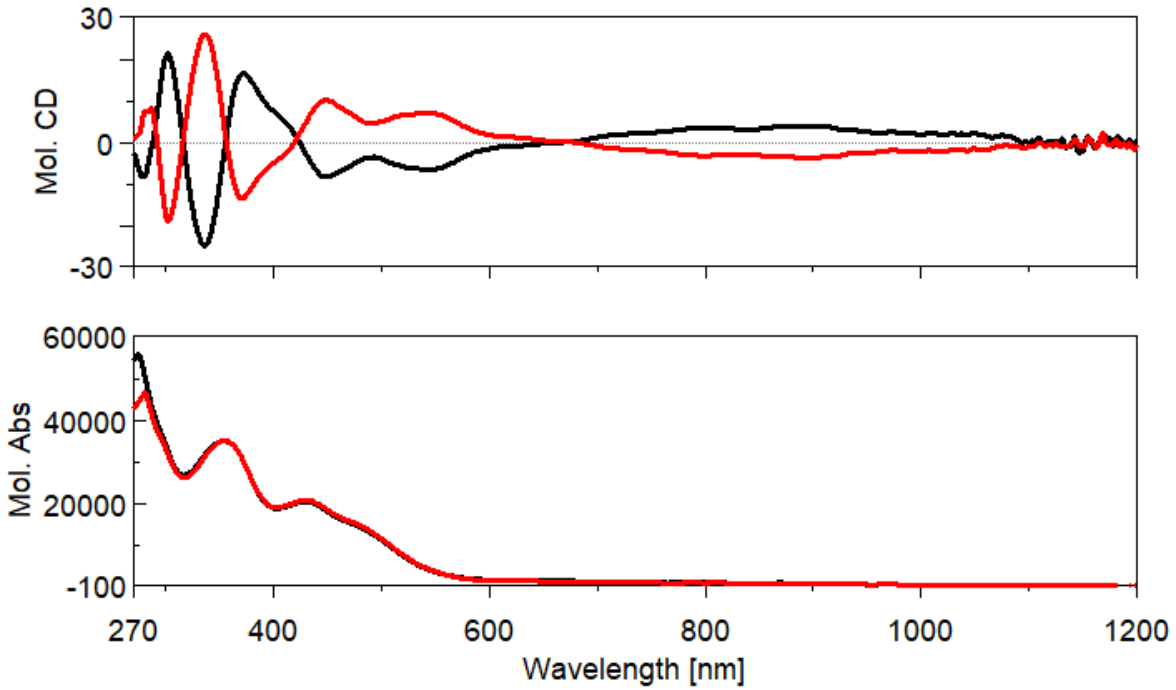
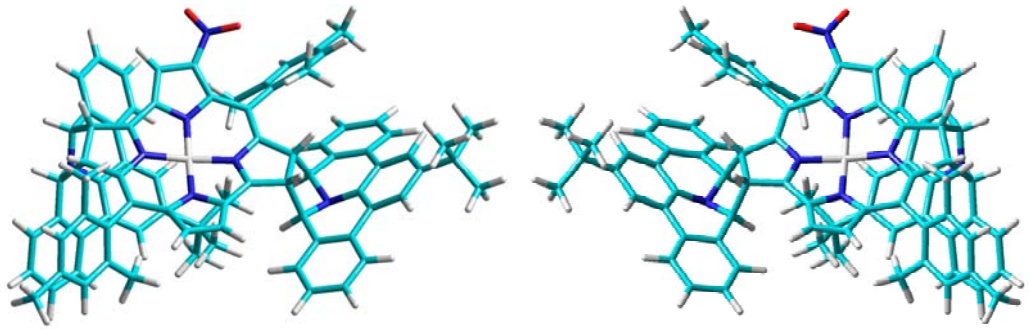


Figure S131. Absorbance (bottom) and ECD (top) spectra of *S,R,R,S,S,R,S,R*-**3** = **3**-dudd (black traces) and *R,S,S,R,R,S,R,S*-**3** = **3**-uduu (red traces) recorded in dichloromethane (298 K).



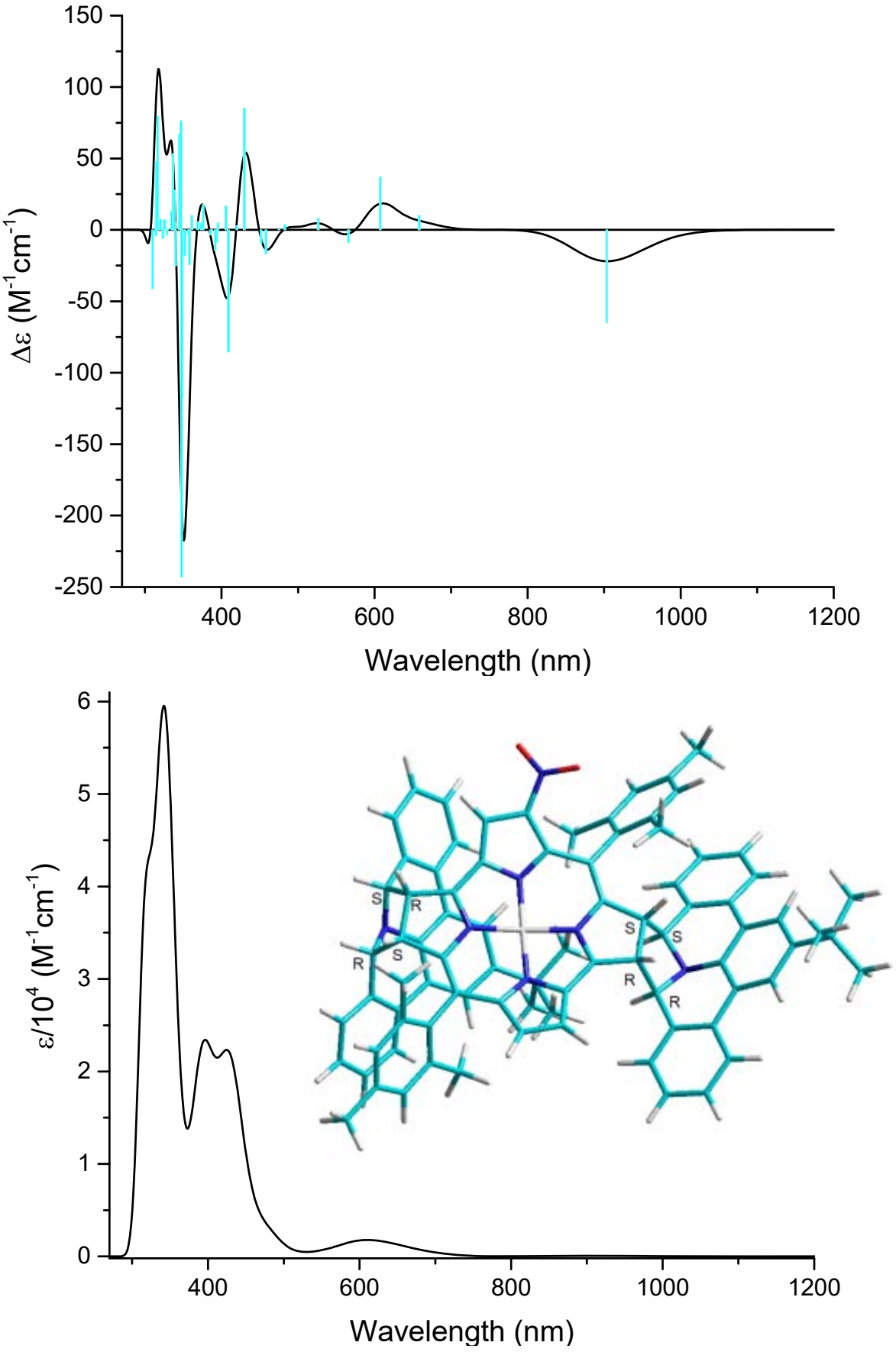


Figure S132. TD DFT calculated absorbance (bottom) and ECD (top) spectra of *R,S,S,R,R,S,R,S*-**3** = **3**-uduu.

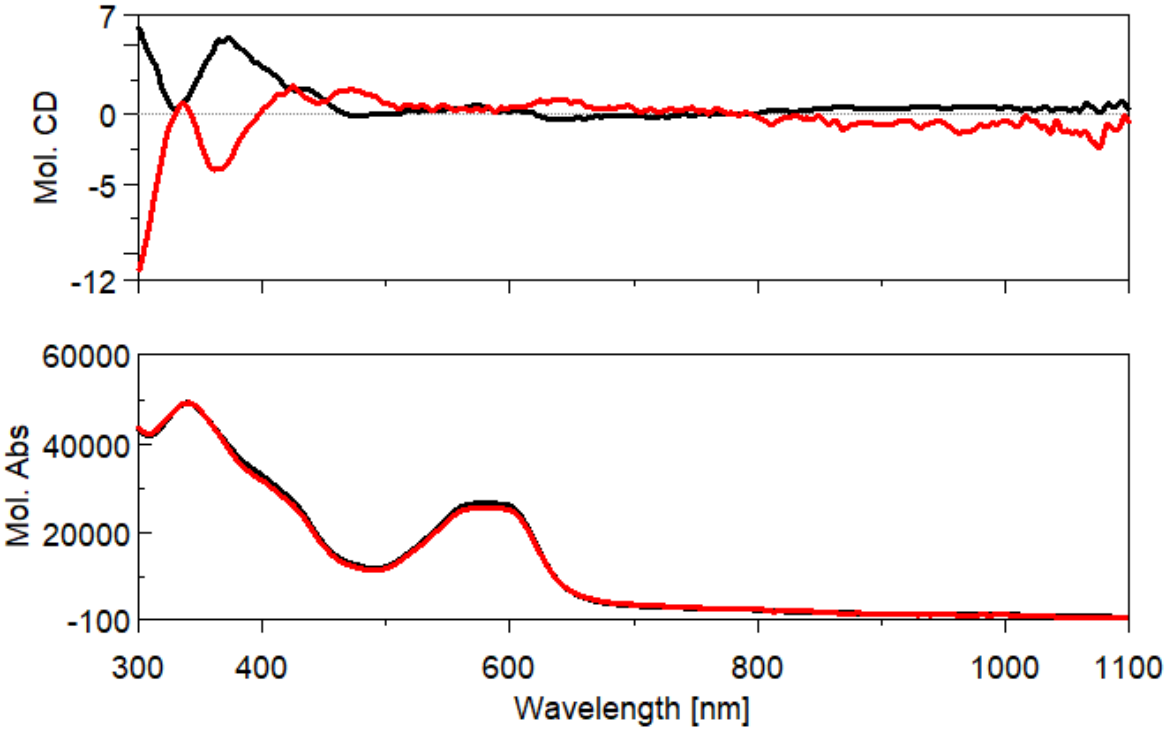
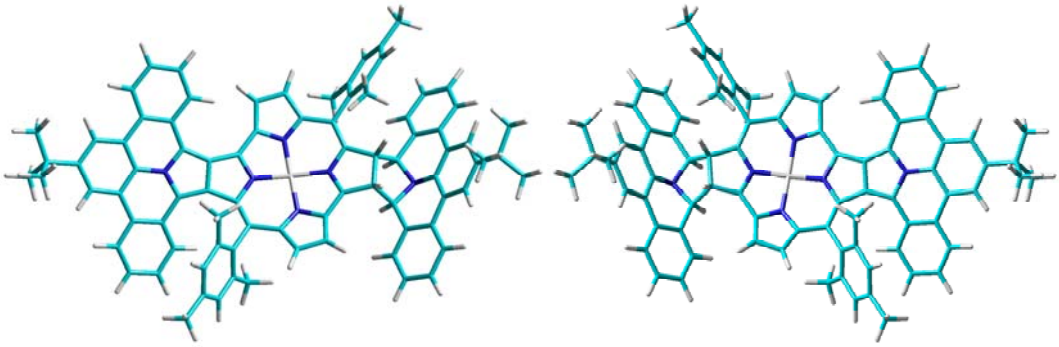


Figure S133. Absorbance (bottom) and ECD (top) spectra of *S,R,R,S*-**7** (black traces) and *R,S,S,R*-**7** (red traces) recorded in dichloromethane (298 K).



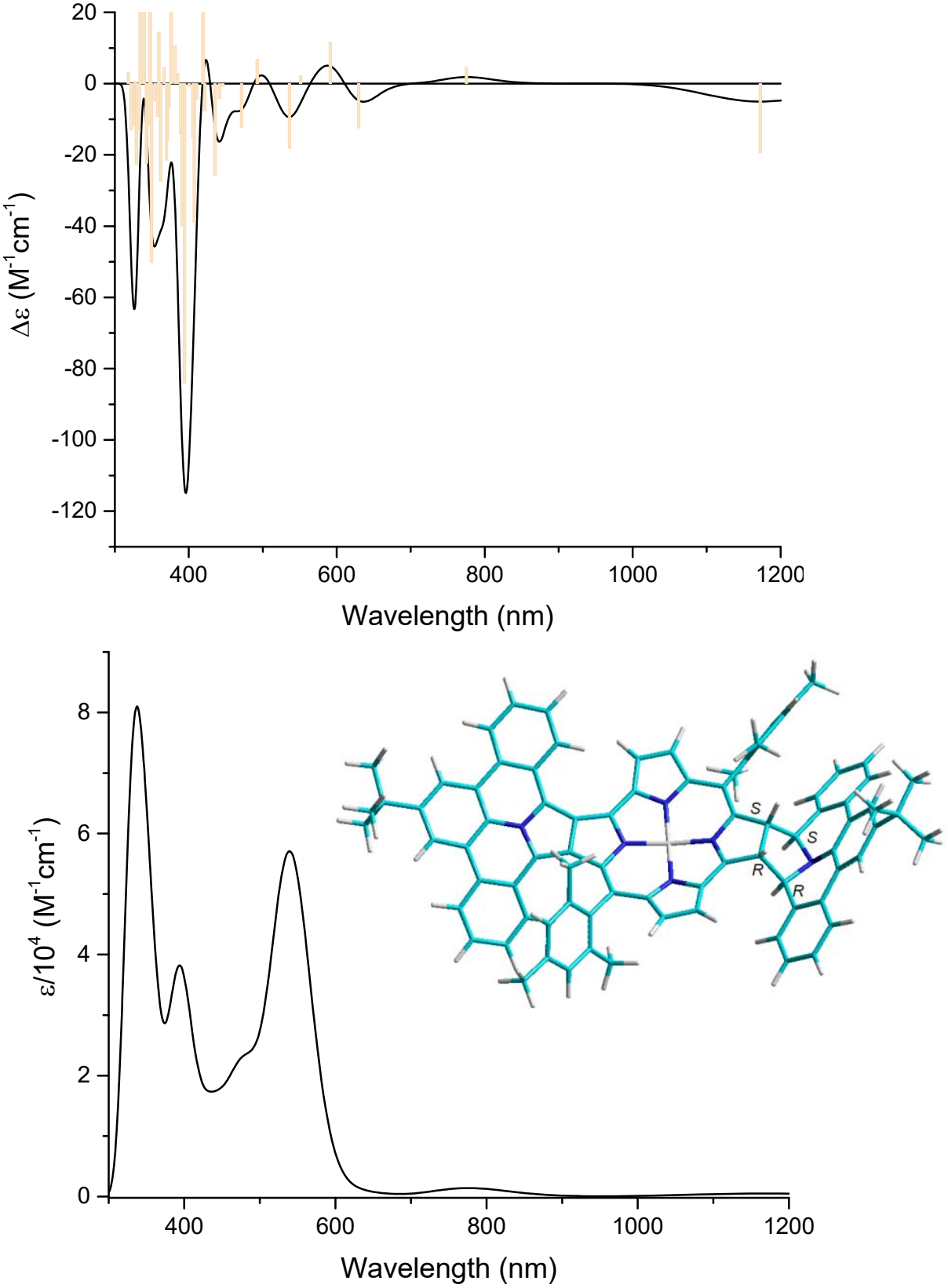


Figure S134. TD DFT calculated absorbance (bottom) and ECD (top) spectra of *R,S,S,R*-**7**.

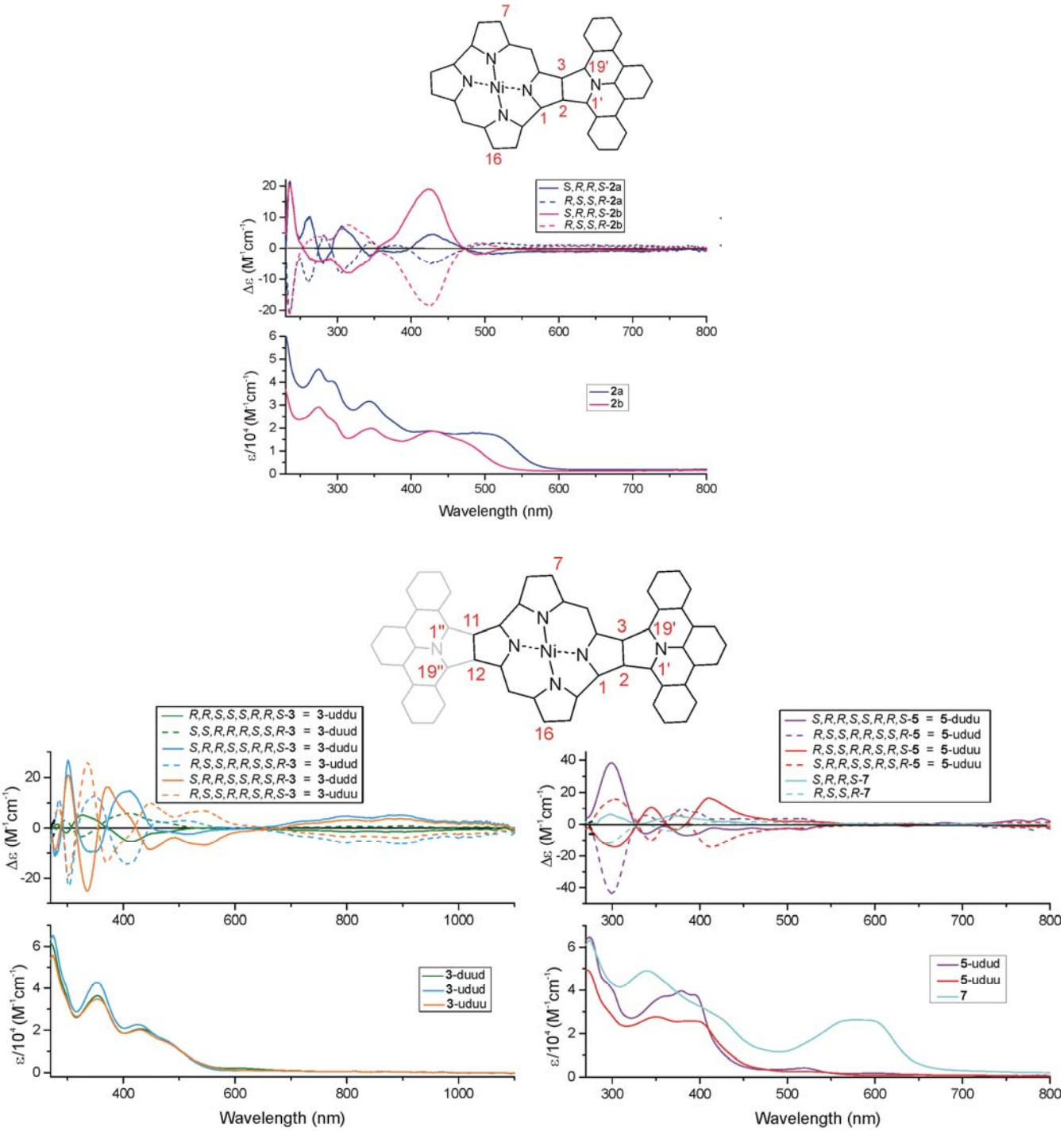


Figure S135. Absorption (lower rows) and ECD (upper rows) spectra of the enantiomers of **2**-**7** in dichloromethane. Configuration assignments is based on the TD DFT simulations of the ECD spectra. The order of the configuration labeling in the legends follows the atom numbering pattern: C2,C3,C19',C1' for monoadducts and **7,** and C2,C3,C19',C1',C11,C12,C19",C1" for the diadducts, as shown in the schematic structures.

Table S2. TD DFT Calculated Electronic Transitions for **2a**

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	8557	1168	0.008	HOMO->LUMO (96%)	
2	122577	815	0.0022	H-2->LUMO (92%)	H-3->LUMO (3%)
3	136577	732	0.0076	H-1->LUMO (85%)	H-5->LUMO (8%), H-4->LUMO (3%)
4	154387	648	0.0052	H-7->LUMO (43%), H-5->LUMO (41%)	H-4->LUMO (8%), H-1->LUMO (5%)
5	16048	623	0.008	H-7->LUMO (51%), H-5->LUMO (21%), H-4->LUMO (15%)	H-6->LUMO (3%), H-1->LUMO (7%)
6	17342	577	0.0173	H-3->LUMO (86%)	H-4->LUMO (6%), H-2->LUMO (3%)
7	18366	544	0.0027	H-5->LUMO (23%), H-4->LUMO (66%)	H-6->LUMO (2%), H-3->LUMO (8%)
8	19693	508	0.0064	H-6->LUMO (93%)	H-7->LUMO (3%)
9	21507	465	0.0021	H-8->LUMO (98%)	
10	22659	441	0.001	H-9->LUMO (98%)	
11	22973	435	0.1159	H-2->L+1 (15%), H-2->L+7 (11%), HOMO->L+1 (48%)	H-16->LUMO (3%), H-11->LUMO (2%), H-2->L+8 (2%)
12	23457	426	0.0185	H-11->LUMO (61%)	H-12->LUMO (5%), H-2->L+1 (4%), H-2->L+7 (9%), H-2->L+8 (2%), HOMO->L+1 (5%)
13	24056	415	0.0707	H-11->LUMO (18%), H-10->LUMO (11%), H-2->L+7 (18%), HOMO->L+1 (16%)	H-16->LUMO (5%), H-12->LUMO (2%), H-2->L+8 (5%)
14	24985	400	0.0468	H-12->LUMO (14%), H-10->LUMO (74%)	H-1->L+1 (3%), HOMO->L+1 (3%)
15	25424	393	0.0294	H-2->L+1 (62%)	H-12->LUMO (3%), H-2->L+3 (4%), H-2->L+7 (5%), H-2->L+8 (2%), HOMO->L+1 (3%)
16	25548	391	0.023	H-1->L+1 (70%)	H-10->LUMO (2%), H-7->L+7 (6%), H-5->L+1 (2%)
17	26206	381	0.0079	H-5->L+7 (24%)	H-20->L+7 (3%), H-12->LUMO (3%), H-7->L+1 (6%), H-7->L+7 (7%), H-5->L+1 (3%), H-5->L+3 (2%), H-5->L+5 (2%), H-5->L+8 (7%), H-4->L+7 (3%), H-2->L+1 (5%), H-2->L+7 (3%), HOMO->L+3 (2%)
18	26296	380	0.0808	H-14->LUMO (21%), H-12->LUMO (30%)	H-16->LUMO (3%), H-15->LUMO (9%), H-11->LUMO (6%), H-10->LUMO (2%), H-5->L+1 (7%), H-5->L+7 (2%), H-1->L+1 (2%)
19	26438	378	0.0162	H-12->LUMO (10%), H-7->L+7 (29%), H-1->L+1 (17%)	H-7->L+1 (5%), H-7->L+5 (3%), H-7->L+8 (8%), H-7->L+10 (2%), H-2->L+3 (2%)
20	26585	376	0.0116	HOMO->L+2 (95%)	
21	26890	371	0.0381	H-13->LUMO (87%)	HOMO->L+3 (4%)
22	27117	368	0.0404	H-16->LUMO (17%), H-14->LUMO (32%), H-12->LUMO (10%), HOMO->L+3 (19%)	H-5->L+1 (5%)
23	27518	363	0.12	H-14->LUMO (15%), HOMO->L+3 (37%)	H-15->LUMO (4%), H-13->LUMO (3%), H-12->LUMO (7%), H-11->LUMO (2%), H-4->L+1 (4%), H-3->L+1 (5%)
24	27878	358	0.0032	H-15->LUMO (62%), H-14->LUMO (21%)	H-16->LUMO (9%)
25	28198	354	0.012	H-3->L+1 (44%), HOMO->L+3 (17%)	H-15->LUMO (2%), H-6->L+1 (5%), H-5->L+1 (2%), H-4->L+1 (9%)
26	28597	349	0.018	H-21->LUMO (44%), H-19->LUMO (16%)	H-20->LUMO (7%), H-18->LUMO (3%), H-16->LUMO (5%), H-14->LUMO (4%), H-5->L+1 (3%)
27	28718	348	0.0092	H-7->L+1 (52%), H-5->L+1 (12%)	H-21->LUMO (5%), H-16->LUMO (5%), H-7->L+3 (3%), H-5->L+7 (2%), H-4->L+1 (6%)
28	28945	345	0.0529	H-1->L+2 (83%)	H-16->LUMO (2%)
29	29343	340	0.0797	H-7->L+1 (16%), H-4->L+1 (32%), H-3->L+1 (10%)	H-21->LUMO (3%), H-18->LUMO (4%), H-17->LUMO (2%), H-16->LUMO (8%), H-7->L+7 (3%)

30	29648	337	0.0592	H-18->LUMO (14%), H-17->LUMO (19%), H-4->L+1 (28%)	H-16->LUMO (6%), H-6->L+1 (4%), H-5->L+1 (7%), H-3->L+1 (7%)
31	29819	335	0.0212	H-17->LUMO (40%), H-5->L+1 (28%)	H-19->LUMO (2%), H-7->L+1 (4%), H-6->L+1 (7%), H-4->L+1 (2%)
32	30012	333	0.0078	H-18->LUMO (50%), H-17->LUMO (30%)	H-5->L+1 (8%)
33	30449	328	0.0079	H-20->LUMO (16%), H-19->LUMO (25%), HOMO->L+4 (15%)	H-21->LUMO (2%), H-11->L+1 (4%), H-6->L+1 (7%), H-3->L+1 (7%), H-2->L+3 (4%)
34	30515	327	0.0114	HOMO->L+4 (70%)	H-11->L+1 (2%), H-6->L+1 (9%), H-3->L+1 (5%)
35	30581	326	0.0132	H-19->LUMO (33%)	H-21->LUMO (5%), H-20->LUMO (9%), H-18->LUMO (3%), H-17->LUMO (3%), H-11->L+1 (3%), H-6->L+1 (8%), H-5->L+1 (3%), H-3->L+1 (6%), H-3->L+3 (2%), H-2->L+3 (3%), HOMO->L+4 (7%)
36	30926	323	0.0095	H-21->L+7 (11%), HOMO->L+7 (28%)	H-21->L+8 (3%), H-20->LUMO (6%), H-19->LUMO (4%), H-19->L+7 (2%), H-2->L+3 (3%), HOMO->L+4 (4%), HOMO->L+5 (7%), HOMO->L+8 (5%)
37	31204	320	0.0208	H-21->LUMO (28%), H-20->LUMO (44%)	H-19->LUMO (6%), H-2->L+3 (5%), HOMO->L+7 (2%)
38	31413	318	0.0115	H-6->L+1 (30%), H-2->L+3 (21%), H-1->L+3 (14%)	H-18->LUMO (4%), H-5->L+1 (4%), HOMO->L+3 (2%)
39	31573	316	0.3428	H-6->L+1 (10%), H-1->L+3 (27%)	H-18->LUMO (6%), H-16->LUMO (8%), H-15->LUMO (3%), H-11->L+1 (5%), H-4->L+1 (4%), H-2->L+2 (4%), H-2->L+3 (5%), HOMO->L+1 (3%), HOMO->L+3 (2%)
40	31655	315	0.0071	H-2->L+2 (90%)	H-1->L+3 (6%)
41	32046	312	0.1569	H-21->L+7 (14%), H-1->L+3 (18%)	H-21->L+8 (4%), H-20->L+7 (3%), H-19->L+7 (3%), H-18->LUMO (3%), H-16->LUMO (3%), H-5->L+1 (4%), H-2->L+3 (4%), HOMO->L+5 (3%), HOMO->L+7 (7%)
42	32099	311	0.2751	H-1->L+3 (19%), HOMO->L+7 (11%)	H-21->L+7 (9%), H-21->L+8 (2%), H-20->L+7 (2%), H-18->LUMO (5%), H-16->LUMO (7%), H-2->L+2 (2%), HOMO->L+1 (3%), HOMO->L+5 (6%), HOMO->L+8 (2%)
43	32496	307	0.0147	H-11->L+1 (14%), H-2->L+3 (35%), H-1->L+3 (10%)	H-11->L+3 (3%), H-6->L+1 (8%), H-4->L+1 (2%), HOMO->L+3 (3%), HOMO->L+5 (2%)
44	33409	299	0.0177	HOMO->L+5 (65%)	H-4->L+2 (2%), H-3->L+2 (3%), H-1->L+5 (3%), HOMO->L+6 (4%), HOMO->L+7 (9%), HOMO->L+8 (4%)
45	33566	297	0.0025	HOMO->L+6 (90%)	HOMO->L+7 (5%)
46	33834	295	0.0117	H-22->LUMO (42%), H-1->L+4 (42%)	
47	33955	294	0.0299	H-4->L+2 (16%), H-3->L+2 (57%)	H-6->L+2 (3%), H-5->L+2 (2%), HOMO->L+5 (5%)
48	34187	292	0.013	H-22->LUMO (47%), H-1->L+4 (32%)	H-4->L+2 (4%), H-1->L+5 (3%)
49	34332	291	0.0046	H-4->L+3 (11%), H-3->L+3 (32%)	H-18->L+1 (6%), H-18->L+3 (4%), H-16->L+1 (4%), H-11->L+1 (7%), H-8->L+1 (3%), H-3->L+2 (4%), H-1->L+4 (6%)
50	34473	290	0.0115	H-6->L+2 (17%), H-4->L+2 (48%), H-3->L+2 (11%)	H-4->L+3 (6%), H-3->L+3 (5%)

Table S3. TD DFT Calculated Electronic Transitions for **2b**

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	8427	1186	0.0142	HOMO->LUMO (96%)	
2	12171	821	0.0012	H-2->LUMO (95%)	
3	14199	704	0.0094	H-4->LUMO (11%), H-1->LUMO (82%)	H-3->LUMO (3%)
4	15689	637	0.0023	H-6->LUMO (85%), H-4->LUMO (10%)	H-3->LUMO (2%)
5	16235	615	0.0085	H-6->LUMO (14%), H-4->LUMO (48%), H-3->LUMO (12%), H-1->LUMO (15%)	H-5->LUMO (4%), HOMO->L+1 (4%)
6	17593	568	0.0022	H-5->LUMO (92%)	H-4->LUMO (3%), H-3->LUMO (2%)
7	19052	524	0.0134	H-4->LUMO (21%), H-3->LUMO (76%)	
8	19445	514	0.0001	H-7->LUMO (99%)	
9	20851	479	0.0697	H-8->LUMO (45%), HOMO->L+1 (42%)	H-2->L+1 (3%)
10	21647	461	0.1101	H-8->LUMO (49%), H-2->L+1 (11%), HOMO->L+1 (26%)	H-11->LUMO (4%)
11	22739	439	0.0062	H-9->LUMO (91%)	H-2->L+1 (6%)
12	23394	427	0.1272	H-2->L+1 (69%)	H-16->LUMO (3%), H-9->LUMO (4%), H-4->L+1 (2%), H-1->L+1 (5%), HOMO->L+1 (8%)
13	23839	419	0.0035	H-2->L+6 (10%), H-2->L+7 (44%)	H-20->L+7 (3%), H-16->L+7 (2%), H-11->LUMO (4%), H-2->L+8 (8%), H-2->L+9 (3%), H-2->L+10 (5%)
14	24236	412	0.0633	H-1->L+1 (74%)	H-16->LUMO (4%), H-11->LUMO (2%), H-10->LUMO (7%), HOMO->L+1 (3%)
15	24365	410	0.035	H-11->LUMO (21%), H-10->LUMO (47%), H-1->L+1 (15%)	HOMO->L+3 (4%)
16	25760	388	0.012	HOMO->L+2 (98%)	
17	26029	384	0.1196	H-11->LUMO (53%), H-10->LUMO (17%)	H-16->LUMO (2%), H-12->LUMO (6%), H-4->L+1 (5%)
18	26250	380	0.0062	H-6->L+1 (26%), H-6->L+7 (23%), H-4->L+1 (16%)	H-10->LUMO (3%), H-6->L+6 (6%), H-6->L+8 (4%), H-6->L+10 (2%), H-3->L+1 (4%)
19	26407	378	0.0028	H-12->LUMO (14%), H-6->L+1 (25%), H-4->L+7 (12%)	H-10->LUMO (2%), H-6->L+7 (8%), H-4->L+1 (3%), H-4->L+6 (3%), H-4->L+8 (2%), H-3->L+7 (3%)
20	26684	374	0.0249	H-12->LUMO (60%)	H-16->LUMO (2%), H-15->LUMO (9%), H-6->L+1 (6%), H-6->L+7 (3%), H-5->L+1 (3%), HOMO->L+3 (2%)
21	26914	371	0.006	H-6->L+1 (22%), H-4->L+7 (16%)	H-13->LUMO (6%), H-12->LUMO (3%), H-5->L+1 (8%), H-4->L+6 (4%), H-4->L+8 (3%), H-3->L+7 (4%), H-1->L+7 (2%), HOMO->L+3 (5%)
22	26980	370	0.011	H-13->LUMO (39%), H-6->L+1 (14%), H-5->L+1 (16%)	H-15->LUMO (7%), H-15->L+1 (2%), HOMO->L+3 (4%)
23	27101	368	0.0033	H-13->LUMO (46%), H-5->L+1 (34%)	H-15->LUMO (4%), H-15->L+1 (3%), H-12->LUMO (4%)
24	27601	362	0.0019	H-16->LUMO (11%), H-6->L+7 (12%), H-4->L+1 (22%), H-3->L+1 (10%), HOMO->L+3 (19%)	H-14->LUMO (2%), H-13->LUMO (2%), H-6->L+6 (3%), H-6->L+8 (2%), H-5->L+1 (6%)
25	27652	361	0.0066	H-15->LUMO (45%), H-5->L+1 (14%), HOMO->L+3 (14%)	H-6->L+7 (4%), H-4->L+1 (8%), H-3->L+1 (4%)
26	28367	352	0.0518	H-21->LUMO (10%), H-15->LUMO (10%), H-3->L+1 (23%), HOMO->L+3 (16%)	H-19->LUMO (5%), H-16->LUMO (5%), H-14->LUMO (5%), H-12->LUMO (4%), H-10->LUMO (4%), H-5-

					>L+1 (3%), H-1->L+2 (3%)
27	28529	350	0.0106	H-4->L+1 (27%), H-3->L+1 (40%)	H-21->LUMO (7%), H-19->LUMO (4%), H-1->L+2 (5%), HOMO->L+3 (6%)
28	28652	349	0.0007	H-14->LUMO (76%)	H-21->LUMO (3%), H-19->LUMO (2%), H-16->LUMO (2%), H-4->L+1 (3%), H-3->L+1 (5%), H-1->L+2 (3%)
29	28970	345	0.0787	H-1->L+2 (61%)	H-21->LUMO (7%), H-19->LUMO (3%), H-16->LUMO (5%), H-14->LUMO (9%), H-4->L+1 (2%), H-3->L+1 (4%)
30	29021	344	0.0736	H-21->LUMO (34%), H-19->LUMO (14%), H-1->L+2 (19%)	H-16->LUMO (3%), H-15->LUMO (5%), H-12->LUMO (3%), H-10->LUMO (2%), HOMO->L+3 (2%)
31	29375	340	0.0001	H-7->L+1 (98%)	
32	29677	336	0.0193	HOMO->L+4 (94%)	
33	30466	328	0.0024	HOMO->L+6 (14%), HOMO->L+7 (46%)	H-21->L+7 (4%), HOMO->L+8 (8%), HOMO->L+9 (3%), HOMO->L+10 (4%)
34	30682	325	0.0105	H-20->LUMO (23%), H-17->LUMO (10%), H-15->L+1 (11%), H-2->L+3 (13%)	H-18->LUMO (3%), H-15->L+3 (3%), H-10->L+1 (8%), H-5->L+1 (5%), H-2->L+2 (6%)
35	30861	324	0.0179	H-21->LUMO (29%), H-19->LUMO (39%), H-18->LUMO (12%)	H-2->L+2 (3%)
36	31015	322	0.0074	H-2->L+2 (82%)	H-19->LUMO (4%), H-8->L+1 (4%)
37	31128	321	0.0603	H-18->LUMO (13%), H-8->L+1 (50%)	H-20->LUMO (2%), H-19->LUMO (7%), H-17->LUMO (3%), H-16->LUMO (3%), H-2->L+2 (7%), H-2->L+3 (5%)
38	31229	320	0.0254	H-18->LUMO (31%), H-8->L+1 (33%)	H-19->LUMO (8%), H-17->LUMO (8%), H-16->LUMO (3%), H-15->L+1 (4%)
39	31535	317	0.0007	H-20->LUMO (11%), H-18->LUMO (16%), H-17->LUMO (37%), H-15->L+1 (13%)	H-15->LUMO (3%), H-15->L+3 (3%), H-10->L+1 (6%), H-5->L+1 (2%)
40	31778	314	0.071	H-20->LUMO (21%), H-18->LUMO (11%), H-17->LUMO (18%)	H-21->L+7 (8%), H-19->L+7 (2%), H-16->LUMO (4%), H-15->LUMO (2%), H-15->L+1 (3%), HOMO->L+3 (3%), HOMO->L+5 (2%)
41	31918	313	0.1178	H-2->L+3 (34%)	H-21->L+7 (5%), H-20->LUMO (5%), H-17->LUMO (4%), H-16->LUMO (8%), H-10->L+1 (6%), H-8->L+1 (3%), HOMO->L+3 (7%), HOMO->L+7 (3%)
42	31936	313	0.0663	H-21->L+7 (18%), H-20->LUMO (17%), H-17->LUMO (13%)	H-21->L+6 (4%), H-21->L+8 (4%), H-21->L+10 (2%), H-19->L+7 (6%), H-16->LUMO (3%), H-10->L+1 (3%), H-2->L+3 (5%), HOMO->L+7 (3%)
43	32337	309	0.3149	H-16->LUMO (11%), H-2->L+3 (20%), H-1->L+3 (11%), HOMO->L+5 (11%)	H-21->L+7 (2%), H-20->LUMO (9%), H-18->LUMO (2%), H-17->LUMO (2%), H-8->L+1 (3%), HOMO->L+3 (3%)
44	32476	307	0.1375	H-9->L+1 (16%), HOMO->L+5 (61%)	H-16->LUMO (4%), H-2->L+3 (2%), HOMO->L+6 (2%), HOMO->L+10 (3%)
45	32613	306	0.0284	H-9->L+1 (78%)	H-1->L+3 (3%), HOMO->L+5 (9%)
46	33178	301	0.1515	H-1->L+3 (78%)	H-16->LUMO (4%), H-2->L+3 (3%)
47	33480	298	0.0013	HOMO->L+6 (69%), HOMO->L+7 (16%)	HOMO->L+5 (4%), HOMO-

					>L+8 (5%)
48	33984	294	0.0104	H-1->L+4 (81%)	H-22->LUMO (3%)
49	34419	290	0.025	HOMO->L+8 (71%), HOMO->L+9 (12%)	H-1->L+4 (3%), HOMO->L+7 (7%)
50	34562	289	0.0054	H-11->L+1 (21%), H-10->L+1 (25%), H-5->L+3 (11%), HOMO->L+10 (10%)	H-15->L+1 (8%), HOMO->L+9 (2%)

Table S4. TD DFT Calculated Electronic Transitions for **3**-duud

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	11223	891	0.0009	HOMO->LUMO (99%)	
2	15395	649	0.0085	H-2->LUMO (73%), H-1->LUMO (19%)	H-4->LUMO (3%)
3	17411	574	0.0363	H-2->LUMO (15%), H-1->LUMO (73%)	H-3->LUMO (7%)
4	18190	549	0.0052	H-3->LUMO (88%)	H-2->LUMO (5%), H-1->LUMO (4%)
5	19493	512	0.0027	H-9->LUMO (39%), H-8->LUMO (53%)	H-7->LUMO (6%)
6	20844	479	0.0115	H-4->LUMO (69%), HOMO->L+1 (10%)	H-9->LUMO (4%), H-7->LUMO (5%), H-5->LUMO (5%), H-2->LUMO (3%)
7	21144	472	0.0314	H-9->LUMO (25%), H-7->LUMO (19%), H-4->LUMO (15%), HOMO->L+1 (22%)	H-8->LUMO (8%), H-5->LUMO (2%), H-1->LUMO (2%)
8	22042	453	0.0031	H-6->LUMO (17%), H-5->LUMO (69%), H-4->LUMO (11%)	
9	22529	443	0.0169	H-6->LUMO (79%), H-5->LUMO (19%)	
10	23475	425	0.0433	H-9->LUMO (21%), H-8->LUMO (31%), H-7->LUMO (24%), HOMO->L+1 (11%)	H-2->L+1 (5%)
11	23588	423	0.1525	H-7->LUMO (37%), H-2->L+1 (14%), HOMO->L+1 (29%)	H-21->LUMO (2%), H-5->LUMO (2%), H-1->L+1 (2%), HOMO->L+4 (3%)
12	24896	401	0.0162	H-2->L+13 (32%)	H-4->L+13 (2%), H-2->L+4 (4%), H-2->L+8 (2%), H-2->L+9 (4%), H-2->L+10 (3%), H-2->L+14 (6%), H-2->L+15 (3%), H-1->L+13 (8%)
13	25029	399	0.0048	H-10->LUMO (87%)	H-12->LUMO (5%)
14	25625	390	0.0193	H-2->L+1 (10%), HOMO->L+2 (74%)	H-1->L+1 (7%), HOMO->L+1 (2%)
15	25696	389	0.169	H-2->L+1 (25%), H-1->L+1 (18%), HOMO->L+1 (10%), HOMO->L+2 (24%)	H-3->L+1 (2%), HOMO->L+3 (3%)
16	25937	385	0.0051	HOMO->L+3 (95%)	H-2->L+1 (2%)
17	26424	378	0.0014	H-12->LUMO (19%), H-11->LUMO (55%), H-1->L+1 (15%)	H-2->L+1 (5%)
18	26479	377	0.0232	H-11->LUMO (23%), H-2->L+1 (21%), H-1->L+1 (46%)	
19	27192	367	0.015	H-3->L+1 (75%)	H-14->LUMO (3%), H-9->L+13 (2%), H-8->L+13 (2%), H-2->L+1 (4%), H-1->L+1 (2%), HOMO->L+4 (3%)
20	27315	366	0.0589	H-12->LUMO (27%), H-11->LUMO (10%), HOMO->L+4 (22%)	H-21->LUMO (3%), H-14->LUMO (5%), H-13->LUMO (5%), H-10->LUMO (2%), H-3->L+1 (9%)
21	27693	361	0.0119	H-13->LUMO (11%), H-8->L+13 (13%)	H-14->LUMO (7%), H-12->LUMO (9%), H-11->LUMO (3%), H-9->L+13 (9%), H-9->L+14 (2%), H-8->L+4 (3%), H-8->L+14 (2%), H-7->L+1 (3%), H-4->L+1 (4%), H-3->L+1 (7%), HOMO->L+4 (2%)
22	27914	358	0.0166	H-13->LUMO (20%), H-4->L+1 (21%)	H-20->L+1 (3%), H-14->LUMO (9%), H-12->LUMO (8%), H-9->L+13 (3%), H-8->L+13 (3%), H-5->L+1 (6%)
23	28099	355	0.0086	H-14->LUMO (12%), H-13->LUMO (14%), H-4->L+1 (23%)	H-9->L+13 (3%), H-8->L+13 (7%), H-7->L+1 (3%), H-5->L+1 (6%), HOMO->L+4

					(4%)
24	28495	350	0.0104	H-9->L+13 (15%)	H-21->L+13 (3%), H-12->L+13 (5%), H-9->L+4 (3%), H-9->L+14 (2%), H-8->L+1 (8%), H-8->L+13 (4%), H-7->L+1 (2%), H-7->L+13 (9%), H-1->L+13 (2%), HOMO->L+4 (3%)
25	28695	348	0.099	H-14->LUMO (37%), H-13->LUMO (11%), HOMO->L+4 (18%)	H-21->LUMO (2%), H-12->LUMO (9%), H-1->L+3 (7%)
26	29056	344	0.0228	H-3->L+2 (58%), H-1->L+2 (13%), H-1->L+3 (15%)	
27	29089	343	0.1764	H-3->L+2 (13%), H-1->L+3 (50%)	H-14->LUMO (9%), H-13->LUMO (6%), H-3->L+3 (3%), H-2->L+3 (5%), H-1->L+2 (2%)
28	29340	340	0.2399	H-15->LUMO (21%), H-13->LUMO (21%), HOMO->L+4 (14%)	H-21->LUMO (4%), H-17->LUMO (6%), H-14->LUMO (9%), H-12->LUMO (6%), H-1->L+3 (4%)
29	29465	339	0.0058	H-9->L+1 (37%), H-8->L+1 (41%)	H-8->L+4 (3%), H-7->L+1 (3%), HOMO->L+5 (3%)
30	29543	338	0.0177	HOMO->L+5 (91%)	
31	29610	337	0.006	H-7->L+1 (13%), H-6->L+1 (19%), H-5->L+1 (46%), H-4->L+1 (10%)	H-15->LUMO (2%), H-8->L+1 (4%)
32	29898	334	0.0036	HOMO->L+6 (96%)	
33	30069	332	0.0703	H-15->LUMO (68%)	H-21->LUMO (2%), H-17->LUMO (3%), H-16->LUMO (3%), H-13->LUMO (3%), H-12->LUMO (3%), HOMO->L+4 (5%)
34	30372	329	0.0208	H-17->LUMO (14%), H-16->LUMO (75%)	H-15->LUMO (3%), H-2->L+2 (3%)
35	30474	328	0.0035	H-2->L+2 (68%), H-1->L+2 (16%)	H-16->LUMO (4%), H-3->L+2 (7%)
36	30608	326	0.0452	H-17->LUMO (54%)	H-20->L+1 (3%), H-16->LUMO (8%), H-14->L+1 (2%), H-4->L+1 (5%), HOMO->L+4 (3%)
37	30691	325	0.0306	H-20->LUMO (15%), H-17->LUMO (15%), H-4->L+1 (15%)	H-20->L+1 (8%), H-18->LUMO (5%), H-16->LUMO (6%), H-14->L+1 (4%), H-13->L+1 (2%), H-9->L+1 (4%), H-8->L+1 (6%), H-2->L+2 (2%), H-2->L+4 (2%)
38	30956	323	0.0116	H-20->LUMO (28%), H-18->LUMO (15%), H-9->L+1 (13%)	H-8->L+1 (5%), H-7->L+1 (8%), H-2->L+4 (8%), HOMO->L+9 (2%), HOMO->L+13 (3%)
39	31066	321	0.0054	H-2->L+3 (87%)	H-1->L+3 (7%)
40	31284	319	0.0023	H-6->L+1 (57%), H-5->L+1 (25%)	H-20->LUMO (2%), H-19->LUMO (3%)
41	31354	318	0.0181	H-18->LUMO (12%), H-7->L+1 (25%), H-6->L+1 (11%), HOMO->L+13 (11%)	H-20->LUMO (6%), H-4->L+1 (8%), HOMO->L+8 (5%), HOMO->L+9 (3%), HOMO->L+14 (3%)
42	31474	317	0.0056	H-18->LUMO (14%), H-2->L+2 (12%), H-1->L+2 (35%)	H-20->LUMO (8%), H-7->L+1 (5%), H-3->L+2 (5%), H-2->L+4 (3%), HOMO->L+13 (5%)
43	31491	317	0.0202	H-20->LUMO (16%), H-18->LUMO (19%), H-2->L+2 (11%), H-1->L+2 (27%)	H-7->L+1 (7%), H-3->L+2 (5%)
44	31590	316	0.0115	H-18->LUMO (26%), H-7->L+1 (10%), HOMO->L+13 (14%)	H-21->LUMO (4%), H-20->LUMO (6%), H-9->L+1 (5%), HOMO->L+7 (3%), HOMO->L+8 (5%), HOMO->L+9 (5%)
45	31829	314	0.0017	H-2->L+4 (17%)	H-25->LUMO (3%), H-24->LUMO (3%), H-21->LUMO (3%), H-19->LUMO (2%), H-9->L+1 (8%), H-8->L+1

					(8%), H-7->L+1 (4%), H-4->L+1 (3%), H-1->L+4 (9%), HOMO->L+7 (3%), HOMO->L+8 (5%), HOMO->L+13 (3%)
46	31937	313	0.0526	H-19->LUMO (84%)	H-21->LUMO (2%), H-20->LUMO (3%)
47	32115	311	0.051	H-25->LUMO (34%), H-24->LUMO (29%)	H-21->LUMO (8%), H-9->L+1 (3%), H-8->L+1 (2%), H-2->L+4 (5%)
48	32476	307	0.0085	H-1->L+4 (11%)	H-20->LUMO (2%), H-20->L+1 (9%), H-14->L+1 (9%), H-13->L+1 (7%), H-12->L+1 (2%), H-10->L+1 (6%), H-9->L+1 (6%), H-8->L+1 (8%), H-7->L+1 (5%), H-5->L+1 (5%), H-2->L+4 (4%), HOMO->L+7 (2%)
49	32543	307	0.0006	H-3->L+3 (93%)	H-1->L+3 (6%)
50	32613	306	0.0719	HOMO->L+7 (66%), HOMO->L+8 (11%)	HOMO->L+11 (3%)

Table S5. TD DFT Calculated Electronic Transitions for **3**-ududd

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	11494	870	0.0005	HOMO->LUMO (98%)	
2	15917	628	0.0072	H-3->LUMO (85%)	H-4->LUMO (5%), H-2->LUMO (3%)
3	17158	582	0.0078	H-1->LUMO (92%)	H-2->LUMO (3%)
4	17955	556	0.0077	H-2->LUMO (91%)	H-3->LUMO (4%), H-1->LUMO (2%)
5	19879	503	0.0029	H-9->LUMO (89%)	H-8->LUMO (5%), H-4->LUMO (2%)
6	20123	496	0.0125	H-4->LUMO (88%)	H-9->LUMO (2%), H-5->LUMO (3%), H-3->LUMO (5%)
7	21127	473	0.0058	H-8->LUMO (52%), HOMO->L+1 (35%)	H-9->LUMO (4%), H-1->LUMO (2%)
8	21676	461	0.0056	H-5->LUMO (89%)	H-7->LUMO (7%), H-4->LUMO (3%)
9	22385	446	0.0209	H-6->LUMO (97%)	
10	22881	437	0.0078	H-7->LUMO (92%)	H-5->LUMO (6%)
11	22937	435	0.0548	H-8->LUMO (12%), H-3->L+1 (15%), H-3->L+10 (21%), HOMO->L+1 (15%)	H-4->L+10 (3%), H-3->L+8 (5%)
12	24015	416	0.1332	H-3->L+10 (19%), HOMO->L+1 (26%)	H-21->LUMO (3%), H-10->LUMO (6%), H-8->LUMO (9%), H-4->L+10 (2%), H-3->L+1 (4%), H-3->L+8 (5%)
13	24725	404	0.0355	H-10->LUMO (85%)	H-12->LUMO (4%), H-8->LUMO (3%)
14	25749	388	0.0051	H-9->L+10 (14%), H-1->L+1 (63%)	H-9->L+8 (4%), H-4->L+1 (2%)
15	25903	386	0.0466	HOMO->L+2 (86%)	H-3->L+1 (5%), H-2->L+1 (3%)
16	25975	384	0.0714	H-3->L+1 (36%), H-2->L+1 (18%), HOMO->L+2 (11%)	H-12->LUMO (2%), H-3->L+4 (2%), H-1->L+1 (7%), HOMO->L+1 (7%)
17	26129	382	0.0114	H-11->LUMO (13%), HOMO->L+3 (79%)	H-12->LUMO (2%)
18	26145	382	0.0367	H-11->LUMO (76%), HOMO->L+3 (12%)	H-12->LUMO (4%), H-3->L+1 (2%)
19	26296	380	0.0042	H-9->L+10 (30%), H-1->L+1 (21%)	H-9->L+1 (4%), H-9->L+8 (8%), H-9->L+9 (2%), H-9->L+11 (2%), H-8->L+10 (3%), H-3->L+1 (4%), H-2->L+1 (4%), HOMO->L+3 (4%)
20	26743	373	0.0088	H-4->L+1 (58%), H-2->L+1 (13%)	H-20->L+1 (3%), H-5->L+1 (5%), H-3->L+1 (5%)
21	26834	372	0.0263	H-8->L+10 (15%), H-3->L+1 (12%), H-2->L+1 (29%)	H-12->L+10 (3%), H-8->L+8 (4%), H-4->L+1 (6%), H-1->L+10 (2%)
22	27042	369	0.025	H-8->L+10 (17%), H-2->L+1 (27%)	H-12->LUMO (7%), H-12->L+10

					(3%), H-8->L+8 (4%), H-4->L+1 (9%), H-3->L+1 (3%), H-1->L+1 (4%), H-1->L+10 (2%)
23	27616	362	0.0501	H-12->LUMO (46%), HOMO->L+4 (29%)	H-11->LUMO (4%), H-3->L+1 (3%)
24	28467	351	0.024	H-14->LUMO (38%), H-13->LUMO (32%)	H-15->LUMO (4%), H-12->LUMO (5%), HOMO->L+4 (9%)
25	28771	347	0.0908	H-1->L+3 (74%)	H-14->LUMO (5%), H-2->L+3 (8%)
26	28892	346	0.0911	H-5->L+1 (12%), H-2->L+2 (51%), H-1->L+2 (15%)	H-14->LUMO (4%), H-7->L+1 (4%)
27	28960	345	0.0412	H-7->L+1 (19%), H-5->L+1 (53%), H-2->L+2 (14%)	H-4->L+1 (4%), H-1->L+2 (4%)
28	29140	343	0.1661	H-14->LUMO (35%), H-13->LUMO (11%), HOMO->L+4 (17%)	H-21->LUMO (4%), H-12->LUMO (6%), H-8->L+1 (4%), H-5->L+1 (3%), H-1->L+3 (8%)
29	29498	339	0.0195	H-13->LUMO (26%), H-9->L+1 (33%)	H-15->LUMO (7%), H-14->LUMO (3%), H-8->L+1 (2%), HOMO->L+5 (3%), HOMO->L+8 (3%), HOMO->L+10 (8%)
30	29648	337	0.0614	H-15->LUMO (23%), H-13->LUMO (13%), H-9->L+1 (39%)	H-17->LUMO (3%), H-9->L+4 (3%), H-8->L+1 (2%), HOMO->L+4 (3%)
31	29770	335	0.0256	H-15->LUMO (10%), HOMO->L+5 (45%), HOMO->L+10 (13%)	H-13->LUMO (2%), H-9->L+1 (3%), HOMO->L+4 (4%), HOMO->L+8 (6%)
32	29998	333	0.0064	H-15->LUMO (18%), HOMO->L+5 (28%), HOMO->L+6 (23%)	H-17->LUMO (3%), HOMO->L+4 (4%), HOMO->L+8 (4%), HOMO->L+10 (8%)
33	30082	332	0.0019	HOMO->L+5 (14%), HOMO->L+6 (63%)	HOMO->L+8 (3%), HOMO->L+10 (9%)
34	30387	329	0.0133	H-17->LUMO (84%), H-15->LUMO (11%)	H-16->LUMO (3%)
35	30424	328	0.1317	H-16->LUMO (18%), H-15->LUMO (19%)	H-21->LUMO (6%), H-14->LUMO (3%), H-13->LUMO (7%), H-12->LUMO (4%), H-8->L+1 (4%), HOMO->L+4 (6%), HOMO->L+5 (4%), HOMO->L+6 (5%), HOMO->L+7 (3%), HOMO->L+10 (3%)
36	30550	327	0.0248	H-16->LUMO (77%)	H-17->LUMO (5%), H-15->LUMO (3%)
37	30829	324	0.0027	H-6->L+1 (87%)	
38	30903	323	0.002	H-20->LUMO (20%), H-7->L+1 (33%), H-4->L+1 (10%)	H-20->L+1 (8%), H-14->L+1 (6%), H-5->L+1 (7%)
39	31057	321	0.0006	H-20->LUMO (13%), H-3->L+2 (60%)	H-8->L+1 (7%), H-7->L+1 (2%), H-6->L+1 (4%), H-2->L+2 (3%)
40	31092	321	0.0037	H-20->LUMO (24%), H-8->L+1 (18%), H-7->L+1 (10%), H-3->L+2 (29%)	H-6->L+1 (3%), H-5->L+1 (4%)
41	31269	319	0.0085	H-2->L+2 (11%), H-1->L+2 (51%)	H-20->L+1 (2%), H-8->L+1 (9%), H-7->L+1 (8%), H-5->L+1 (2%), H-3->L+2 (4%)
42	31311	319	0.0188	H-8->L+1 (15%), H-7->L+1 (16%), H-1->L+2 (25%)	H-20->LUMO (3%), H-20->L+1 (5%), H-14->L+1 (3%), H-5->L+1 (6%), H-3->L+3 (4%), H-2->L+2 (7%)
43	31379	318	0.0004	H-3->L+3 (71%)	H-8->L+1 (7%), H-3->L+4 (2%), H-2->L+3 (8%)
44	31616	316	0.0005	H-24->L+10 (10%), H-3->L+4 (11%)	H-26->L+10 (6%), H-25->L+10 (5%), H-24->LUMO (2%), H-24->L+8 (2%), H-20->LUMO (7%), H-8->L+1 (5%), H-3->L+3 (5%), HOMO->L+8 (7%), HOMO->L+10 (4%)
45	31750	314	0.0098	H-18->LUMO (84%)	
46	31858	313	0.007	H-20->LUMO (10%), H-18->LUMO (10%)	H-26->L+10 (4%), H-25->L+10 (3%), H-24->L+10 (5%), H-20->L+1 (7%), H-19->LUMO (6%), H-14->L+1 (6%), H-8->L+1 (5%), H-3->L+4 (2%), HOMO->L+7 (2%), HOMO->L+10 (3%)
47	32094	311	0.0325	H-19->LUMO (84%)	H-20->LUMO (6%)
48	32205	310	0.0025	H-2->L+3 (50%)	H-20->LUMO (2%), H-14->L+1

					(2%), H-4->L+3 (2%), H-3->L+3 (5%), H-3->L+4 (9%), H-1->L+3 (6%), H-1->L+4 (5%)
49	32290	309	0.0036	H-3->L+4 (25%), H-2->L+3 (24%)	H-20->LUMO (3%), H-14->L+1 (2%), H-10->L+1 (3%), H-3->L+3 (9%), H-2->L+4 (4%), H-1->L+3 (3%), H-1->L+4 (5%)
50	32494	307	0.1347	HOMO->L+7 (79%)	

Table S6. TD DFT Calculated Electronic Transitions for **3**-uduu

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	11068	903	0.0006	HOMO->LUMO (99%)	
2	15191	658	0.006	H-3->LUMO (26%), H-2->LUMO (45%), H-1->LUMO (22%)	H-4->LUMO (3%)
3	16461	607	0.0129	H-3->LUMO (39%), H-1->LUMO (58%)	
4	17670	565	0.0042	H-3->LUMO (30%), H-2->LUMO (50%), H-1->LUMO (16%)	
5	18998	526	0.0018	H-8->LUMO (53%), H-6->LUMO (18%), H-5->LUMO (16%)	H-7->LUMO (7%)
6	20708	482	0.0007	H-7->LUMO (44%), HOMO->L+1 (29%)	H-9->LUMO (8%), H-6->LUMO (2%), H-4->LUMO (9%)
7	21047	475	0.0212	H-4->LUMO (66%)	H-9->LUMO (4%), H-8->LUMO (5%), H-7->LUMO (4%), H-6->LUMO (7%), H-5->LUMO (8%)
8	21835	457	0.0061	H-8->LUMO (31%), H-6->LUMO (14%), H-5->LUMO (46%)	H-4->LUMO (8%)
9	22140	451	0.0061	H-6->LUMO (57%), H-5->LUMO (22%)	H-8->LUMO (5%), H-4->LUMO (9%), HOMO->L+1 (3%)
10	23264	429	0.1638	H-7->LUMO (10%), HOMO->L+1 (40%)	H-9->LUMO (8%), H-5->LUMO (3%), H-3->L+1 (5%), H-2->L+1 (9%), HOMO->L+4 (3%)
11	23808	420	0.0095	H-9->LUMO (75%), H-7->LUMO (18%)	H-8->LUMO (2%)
12	24442	409	0.0391	H-3->L+13 (17%), H-2->L+13 (18%)	H-24->L+13 (3%), H-4->L+13 (3%), H-1->L+13 (6%), HOMO->L+1 (4%), HOMO->L+3 (6%)
13	24632	405	0.0048	HOMO->L+3 (83%)	H-3->L+1 (2%), H-2->L+1 (3%), HOMO->L+2 (3%)
14	25282	395	0.034	H-10->LUMO (25%), H-2->L+1 (16%), H-1->L+1 (23%)	H-12->LUMO (7%), H-3->L+1 (7%), HOMO->L+1 (4%), HOMO->L+3 (4%)
15	25393	393	0.0826	H-10->LUMO (59%), H-1->L+1 (17%)	H-12->LUMO (3%), H-2->L+1 (6%), HOMO->L+1 (4%), HOMO->L+3 (2%)
16	25519	391	0.0054	HOMO->L+2 (93%)	HOMO->L+3 (2%)
17	25795	387	0.0576	H-3->L+1 (44%), H-1->L+1 (35%)	H-10->LUMO (2%), H-2->L+1 (7%), HOMO->L+1 (2%)
18	25939	385	0.0035	H-11->LUMO (92%)	H-12->LUMO (3%), H-1->L+1 (2%)
19	26588	376	0.0042	H-3->L+1 (32%), H-2->L+1 (45%)	H-12->LUMO (4%), H-8->L+13 (3%), H-1->L+1 (4%)
20	26775	373	0.002	H-8->L+13 (23%), H-1->L+1 (12%)	H-13->LUMO (3%), H-8->L+9 (2%), H-8->L+10 (2%), H-7->L+13 (8%), H-6->L+13 (3%), H-5->L+13 (3%), H-3->L+1 (3%), H-2->L+1 (4%), HOMO->L+4 (2%), HOMO->L+13 (2%)
21	27113	368	0.0206	H-12->LUMO (29%), HOMO->L+4 (33%)	H-10->LUMO (4%), H-8->L+13 (5%), H-2->L+1 (3%)
22	27688	361	0.0253	H-7->L+13 (14%)	H-13->LUMO (7%), H-12->L+13 (5%), H-9->L+13 (5%),

					H-8->L+1 (7%), H-5->L+1 (5%), H-4->L+1 (5%), H-1->L+13 (3%), HOMO->L+4 (6%)
23	27917	358	0.0085	H-14->LUMO (15%), H-13->LUMO (55%)	H-12->LUMO (7%), H-8->L+13 (3%)
24	28036	356	0.0003	H-5->L+1 (13%), H-4->L+1 (41%)	H-20->L+1 (3%), H-13->LUMO (2%), H-13->L+1 (3%), H-9->L+1 (3%), H-8->L+1 (2%), H-6->L+1 (4%), HOMO->L+4 (6%)
25	28391	352	0.0075	HOMO->L+5 (76%)	H-12->LUMO (3%), H-1->L+3 (4%), HOMO->L+4 (5%)
26	28653	348	0.0828	H-2->L+2 (16%), H-1->L+2 (48%)	H-14->LUMO (5%), H-12->LUMO (6%), H-3->L+2 (5%), H-2->L+3 (3%), HOMO->L+4 (2%), HOMO->L+5 (3%)
27	28751	347	0.0527	H-2->L+3 (14%), H-1->L+3 (30%), HOMO->L+5 (14%)	H-14->LUMO (4%), H-12->LUMO (4%), H-8->L+1 (4%), H-6->L+1 (3%), H-3->L+3 (6%), H-1->L+2 (7%), HOMO->L+4 (3%)
28	28818	346	0.0862	H-8->L+1 (16%), H-6->L+1 (16%), H-1->L+3 (18%)	H-14->LUMO (3%), H-12->LUMO (2%), H-7->L+1 (5%), H-5->L+1 (5%), H-2->L+2 (4%), H-2->L+3 (6%), H-1->L+2 (3%), HOMO->L+4 (3%)
29	29008	344	0.1119	H-14->LUMO (35%), H-8->L+1 (13%)	H-19->LUMO (2%), H-13->LUMO (5%), H-12->LUMO (5%), H-7->L+1 (6%), H-6->L+1 (5%), H-5->L+1 (3%), H-2->L+2 (2%), H-2->L+3 (2%), H-1->L+2 (4%), H-1->L+3 (3%), HOMO->L+4 (3%)
30	29406	340	0.0036	H-3->L+3 (61%), H-2->L+3 (23%)	H-15->LUMO (3%), H-14->LUMO (4%)
31	29498	339	0.0006	H-17->LUMO (13%), H-15->LUMO (79%)	H-3->L+3 (2%)
32	29556	338	0.0315	HOMO->L+6 (76%)	H-14->LUMO (6%), H-13->LUMO (3%), HOMO->L+4 (4%)
33	29723	336	0.1444	H-14->LUMO (14%), HOMO->L+6 (17%)	H-13->LUMO (7%), H-12->LUMO (5%), H-7->L+1 (5%), H-6->L+1 (8%), H-5->L+1 (9%), H-4->L+1 (5%), H-3->L+3 (3%), HOMO->L+4 (7%)
34	29880	334	0.078	H-6->L+1 (22%), H-5->L+1 (25%), H-4->L+1 (11%)	H-14->LUMO (4%), H-13->LUMO (4%), H-12->LUMO (3%), H-9->L+1 (8%), H-8->L+1 (3%), HOMO->L+4 (4%)
35	30310	329	0.0008	H-17->LUMO (11%), HOMO->L+7 (10%), HOMO->L+13 (21%)	H-25->LUMO (2%), H-25->L+13 (6%), H-24->L+13 (2%), H-9->L+1 (3%), H-7->L+1 (4%), HOMO->L+9 (7%), HOMO->L+10 (5%), HOMO->L+11 (4%)
36	30415	328	0.008	H-17->LUMO (64%), H-15->LUMO (11%)	H-16->LUMO (5%), HOMO->L+7 (3%), HOMO->L+13 (4%)
37	30631	326	0.004	H-3->L+2 (10%), H-2->L+2 (42%), H-1->L+2 (10%)	H-16->LUMO (3%), H-9->L+1 (3%), H-7->L+1 (2%), H-5->L+1 (2%), H-2->L+3 (3%), H-2->L+4 (2%)
38	30654	326	0.0424	H-16->LUMO (59%)	H-17->LUMO (6%), H-9->L+1 (3%), H-8->L+1 (3%), H-7->L+1 (9%), H-6->L+1 (3%), H-5->L+1 (4%)
39	30737	325	0.0052	H-16->LUMO (22%), H-2->L+2 (22%)	H-20->L+1 (2%), H-19->LUMO (3%), H-9->L+1 (7%), H-7->L+1 (6%), H-4->L+1 (3%), H-3->L+2 (4%), H-2->L+4 (2%), H-1->L+2 (2%), H-

					1->L+4 (3%)
40	30891	323	0.0043	H-20->LUMO (14%), H-6->L+1 (10%), H-2->L+3 (14%), H-1->L+3 (16%)	H-18->LUMO (7%), H-16->LUMO (3%), H-8->L+1 (8%), H-5->L+1 (6%), H-4->L+1 (4%), H-3->L+3 (5%)
41	30933	323	0.0066	H-20->LUMO (31%), H-19->LUMO (15%)	H-18->LUMO (7%), H-8->L+1 (6%), H-7->L+1 (7%), H-4->L+1 (4%), H-3->L+3 (3%), H-2->L+3 (9%), H-1->L+3 (7%)
42	31010	322	0.0169	H-8->L+1 (16%), H-6->L+1 (11%), H-2->L+3 (17%), H-1->L+3 (12%)	H-20->L+1 (3%), H-19->LUMO (3%), H-13->L+1 (2%), H-9->L+1 (6%), H-5->L+1 (6%), H-3->L+3 (7%)
43	31244	320	0.0036	H-7->L+1 (13%), H-2->L+4 (11%)	H-25->LUMO (5%), H-25->L+13 (3%), H-24->LUMO (6%), H-20->LUMO (3%), H-19->LUMO (8%), H-8->L+1 (2%), H-3->L+4 (5%), H-1->L+4 (6%), HOMO->L+7 (7%), HOMO->L+8 (3%)
44	31433	318	0.0022	H-3->L+2 (71%), H-1->L+2 (18%)	H-3->L+3 (2%), H-2->L+2 (6%)
45	31565	316	0.1831	H-19->LUMO (19%), H-18->LUMO (30%)	H-21->LUMO (6%), H-20->LUMO (7%), H-7->L+1 (9%), H-6->L+1 (3%), H-5->L+1 (3%), HOMO->L+4 (3%), HOMO->L+8 (2%)
46	31638	316	0.0319	H-25->LUMO (16%), H-19->LUMO (12%), H-7->L+1 (14%), HOMO->L+7 (16%)	H-25->L+13 (4%), H-24->LUMO (4%), H-8->L+1 (5%), H-4->L+1 (3%)
47	31805	314	0.0413	H-9->L+1 (20%), H-2->L+4 (15%), H-1->L+4 (15%)	H-25->LUMO (3%), H-24->LUMO (4%), H-20->LUMO (4%), H-18->LUMO (3%), H-8->L+1 (2%), H-4->L+1 (8%), H-3->L+4 (5%)
48	31821	314	0.0034	HOMO->L+7 (42%), HOMO->L+9 (25%)	H-20->LUMO (8%), H-19->LUMO (4%), H-18->LUMO (8%), HOMO->L+13 (3%)
49	31874	313	0.0036	H-20->LUMO (23%), H-19->LUMO (10%), H-18->LUMO (33%)	H-25->LUMO (6%), HOMO->L+7 (4%), HOMO->L+9 (8%), HOMO->L+13 (2%)
50	32267	309	0.0297	H-1->L+4 (16%), HOMO->L+8 (43%)	H-19->LUMO (2%), H-13->L+1 (2%), H-9->L+1 (7%), H-5->L+1 (2%), H-3->L+4 (7%)

Table S7. TD DFT Calculated Electronic Transitions for **4**

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	7334	1363	0.0076	HOMO->LUMO (97%)	
2	11400	877	0.0007	H-1->LUMO (97%)	
3	14430	692	0.0075	H-3->LUMO (44%), H-2->LUMO (51%)	
4	15117	661	0.0022	H-4->LUMO (93%)	H-3->LUMO (3%), H-2->LUMO (3%)
5	16667	599	0.0173	H-3->LUMO (46%), H-2->LUMO (44%)	H-4->LUMO (7%)
6	20608	485	0.0156	H-5->LUMO (97%)	
7	21895	456	0.0002	H-6->LUMO (88%)	HOMO->L+1 (5%)
8	22598	442	0.003	H-8->LUMO (91%)	H-7->LUMO (4%)
9	23088	433	0.0371	HOMO->L+1 (65%), HOMO->L+2 (16%)	H-10->LUMO (6%), H-9->LUMO (4%), H-7->LUMO (3%)
10	23431	426	0.0025	H-10->LUMO (18%), H-9->LUMO (18%), H-7->LUMO (18%), HOMO->L+2 (38%)	
11	23587	423	0.0015	H-10->LUMO (11%), H-1->L+10 (38%), H-1->L+11 (10%)	H-16->L+10 (4%), H-9->LUMO (3%), H-1->L+7 (6%), H-1->L+8 (3%), H-1->L+9 (9%)
12	23670	422	0.002	H-10->LUMO (11%), H-7->LUMO (64%)	H-9->LUMO (7%), H-8->LUMO (6%), H-1->L+10 (4%)
13	23832	419	0.002	H-11->LUMO (66%), H-10->LUMO (22%), H-9->LUMO (11%)	
14	24721	404	0.1592	H-14->LUMO (13%), HOMO->L+1 (14%), HOMO->L+2 (29%)	H-15->LUMO (3%), H-13->LUMO (5%), H-10->LUMO (5%), H-9->LUMO (4%), H-

					7->LUMO (7%), H-6->LUMO (4%)
15	25296	395	0.0015	H-1->L+1 (54%), H-1->L+2 (34%)	H-4->L+10 (2%)
16	26085	383	0.195	H-11->LUMO (19%), H-10->LUMO (12%), H-9->LUMO (29%)	H-3->L+10 (8%), H-3->L+11 (2%), HOMO->L+11 (4%)
17	26577	376	0.0048	H-4->L+9 (10%), H-4->L+10 (44%), H-4->L+11 (12%)	H-4->L+7 (7%), H-4->L+8 (4%), H-3->L+1 (3%), H-3->L+2 (2%), H-2->L+1 (2%), H-1->L+1 (3%)
18	26660	375	0.0686	H-3->L+10 (26%)	H-11->LUMO (5%), H-10->LUMO (3%), H-9->LUMO (9%), H-3->L+7 (3%), H-3->L+8 (2%), H-3->L+9 (6%), H-3->L+11 (7%), H-2->L+10 (6%), HOMO->L+3 (2%)
19	27236	367	0.0213	HOMO->L+3 (96%)	
20	27894	358	0.0097	H-17->LUMO (25%), H-12->LUMO (64%)	H-18->LUMO (4%)
21	28174	354	0.0199	H-18->LUMO (15%), H-17->LUMO (42%), H-12->LUMO (27%)	H-13->LUMO (2%), H-2->L+1 (7%)
22	28273	353	0.059	H-2->L+1 (68%), H-2->L+2 (10%)	H-17->LUMO (4%), H-12->LUMO (4%)
23	28608	349	0.0008	H-1->L+1 (37%), H-1->L+2 (58%)	H-2->L+1 (3%)
24	28834	346	0.0366	H-13->LUMO (80%)	H-14->LUMO (6%), H-2->L+1 (4%)
25	29044	344	0.0253	H-4->L+1 (24%), H-4->L+2 (17%), H-2->L+2 (46%)	H-14->LUMO (3%), H-2->L+1 (3%)
26	29180	342	0.0123	H-14->LUMO (10%), H-4->L+1 (27%), H-4->L+2 (19%), H-2->L+2 (21%)	H-13->LUMO (2%), H-3->L+1 (7%), H-3->L+2 (3%), H-2->L+1 (3%)
27	29761	336	0.0104	H-16->LUMO (85%)	H-17->LUMO (4%), H-15->LUMO (4%)
28	29861	334	0.0038	HOMO->L+4 (39%), HOMO->L+10 (31%)	H-17->L+10 (2%), HOMO->L+7 (4%), HOMO->L+8 (3%), HOMO->L+9 (6%), HOMO->L+11 (5%)
29	30292	330	0.0405	H-15->LUMO (32%), H-14->LUMO (17%), HOMO->L+4 (12%)	H-18->LUMO (9%), H-3->L+1 (4%), H-3->L+2 (2%), H-2->L+2 (7%), HOMO->L+10 (2%)
30	30424	328	0.0164	H-15->LUMO (36%), HOMO->L+4 (30%)	H-16->LUMO (2%), H-14->LUMO (5%), HOMO->L+9 (3%), HOMO->L+10 (7%), HOMO->L+11 (4%)
31	30524	327	0.0236	H-15->LUMO (10%), H-3->L+1 (27%), H-3->L+2 (13%), HOMO->L+4 (12%)	H-4->L+1 (3%), H-2->L+1 (2%), H-2->L+2 (5%), HOMO->L+6 (2%), HOMO->L+9 (2%), HOMO->L+10 (5%)
32	30999	322	0.0111	H-18->LUMO (41%), H-17->LUMO (12%), HOMO->L+5 (29%)	H-3->L+1 (5%), HOMO->L+4 (3%)
33	31186	320	0.0291	H-18->LUMO (20%), HOMO->L+5 (48%), HOMO->L+6 (18%)	H-17->LUMO (6%)
34	31291	319	0.0103	HOMO->L+5 (15%), HOMO->L+6 (74%)	
35	31779	314	0.003	H-18->L+10 (12%), H-17->L+10 (32%)	H-18->L+9 (3%), H-18->L+11 (4%), H-17->L+7 (4%), H-17->L+8 (3%), H-17->L+9 (7%), H-17->L+11 (9%), HOMO->L+10 (6%)
36	32335	309	0.2537	H-3->L+1 (42%), H-3->L+2 (30%)	H-15->LUMO (3%), H-14->LUMO (9%)
37	32574	306	0.3944	H-14->LUMO (15%), H-3->L+2 (25%), HOMO->L+7 (19%)	H-15->LUMO (4%), HOMO->L+1 (3%), HOMO->L+2 (3%), HOMO->L+8 (8%), HOMO->L+9 (3%), HOMO->L+11 (4%)
38	32608	306	0.0004	H-1->L+3 (94%)	
39	32710	305	0.096	H-3->L+2 (13%), HOMO->L+7 (41%), HOMO->L+8 (10%)	H-15->LUMO (3%), H-14->LUMO (6%), H-1->L+3 (4%), HOMO->L+9 (9%)
40	33264	300	0.0107	HOMO->L+7 (12%), HOMO->L+8 (67%), HOMO->L+10 (16%)	
41	33286	300	0.005	HOMO->L+9 (67%), HOMO->L+10 (20%)	HOMO->L+7 (4%), HOMO->L+8 (4%)
42	33613	297	0.0008	H-4->L+1 (40%), H-4->L+2 (58%)	
43	33630	297	0.0119	H-2->L+3 (85%)	H-5->L+2 (2%), H-2->L+4 (3%)
44	34000	294	0.0105	H-5->L+1 (61%), H-5->L+2 (32%)	
45	34906	286	0.0738	H-1->L+4 (55%), H-1->L+5 (14%)	H-6->L+1 (3%), H-1->L+7 (8%), H-1->L+11 (4%), HOMO->L+11 (4%)
46	35002	285	0.0035	H-6->L+1 (50%), H-2->L+4 (16%)	H-5->L+1 (4%), H-5->L+2 (8%), H-2->L+5 (3%), H-1->L+4 (5%)
47	35325	283	0.0037	H-6->L+1 (27%), H-6->L+2 (12%), H-2->L+4 (45%)	H-5->L+1 (3%)
48	35620	280	0.1606	H-6->L+2 (12%), H-5->L+1 (12%), H-5->L+2 (27%), H-2->L+4 (18%)	H-19->LUMO (2%), H-7->L+1 (3%), H-7->L+2 (2%), H-2->L+5 (5%), HOMO->L+11 (3%)
49	35814	279	0.1674	HOMO->L+11 (30%)	H-21->LUMO (2%), H-9->L+1 (2%), H-7->L+1 (4%), H-6->L+1 (7%), H-6->L+2 (9%), H-5->L+1 (3%), H-5->L+2 (7%), H-1->L+4 (8%), HOMO->L+7 (3%)
50	35875	278	0.0007	H-19->LUMO (82%)	H-22->LUMO (7%)

Table S8. TD DFT Calculated Electronic Transitions for **5**-ududd

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	10877	919	0.0001	HOMO->LUMO (99%)	
2	15439	647	0.0056	H-1->LUMO (96%)	
3	18776	532	0.0196	H-2->LUMO (90%)	H-4->LUMO (6%)
4	19308	517	0.0016	H-5->LUMO (66%), H-3->LUMO (33%)	
5	19965	500	0.0007	H-5->LUMO (33%), H-3->LUMO (66%)	
6	21693	460	0.0184	H-4->LUMO (72%), HOMO->L+3 (10%)	H-6->LUMO (3%), H-2->LUMO (8%), HOMO->L+1 (2%)
7	23346	428	0.0122	H-1->L+10 (11%), H-1->L+12 (22%), HOMO->L+1 (46%)	H-21->L+12 (2%), H-1->L+14 (7%)
8	23387	427	0.0001	HOMO->L+2 (99%)	
9	23422	426	0.0147	H-1->L+10 (10%), H-1->L+12 (19%), HOMO->L+1 (50%)	H-1->L+14 (6%), HOMO->L+3 (2%)
10	24143	414	0.0703	H-6->LUMO (91%)	H-4->LUMO (4%)
11	24382	410	0.0	H-7->LUMO (98%)	
12	25485	392	0.0138	H-8->LUMO (83%)	H-12->LUMO (8%), H-10->LUMO (4%)
13	25929	385	0.0001	H-9->LUMO (57%), H-5->L+12 (16%)	H-5->L+10 (8%), H-5->L+14 (5%), H-1->L+3 (6%)
14	26127	382	0.0	H-9->LUMO (41%), H-5->L+10 (11%), H-5->L+12 (22%)	H-5->L+14 (7%), H-1->L+3 (8%)
15	26432	378	0.1009	H-12->LUMO (21%), HOMO->L+3 (49%)	H-20->LUMO (3%), H-18->LUMO (5%), H-10->LUMO (3%), H-8->LUMO (6%), H-4->LUMO (2%), HOMO->L+5 (3%)
16	27010	370	0.0051	H-4->L+10 (15%), H-4->L+12 (30%)	H-21->L+12 (2%), H-12->L+10 (3%), H-12->L+12 (5%), H-4->L+14 (9%), H-4->L+16 (2%), H-2->L+10 (3%), H-2->L+12 (7%)
17	27399	364	0.0054	H-12->LUMO (22%), H-10->LUMO (75%)	
18	27432	364	0.0	HOMO->L+4 (94%)	H-11->LUMO (4%)
19	27533	363	0.0005	H-11->LUMO (94%)	HOMO->L+4 (4%)
20	27553	362	0.0155	HOMO->L+5 (89%)	H-10->LUMO (4%)
21	28039	356	0.0002	H-1->L+1 (36%), H-1->L+3 (41%)	H-5->L+10 (3%), H-5->L+12 (6%), H-3->L+2 (2%)
22	28412	351	0.1784	H-3->L+1 (33%), H-2->L+2 (41%), H-1->L+2 (15%)	
23	28425	351	0.0037	H-3->L+2 (34%), H-2->L+1 (51%)	H-1->L+3 (7%)
24	28806	347	0.0245	H-1->L+2 (83%)	H-3->L+1 (4%), H-2->L+2 (9%)
25	28956	345	0.0001	H-13->LUMO (16%), H-1->L+1 (54%), H-1->L+3 (21%)	H-2->L+1 (3%)
26	29158	342	0.0006	H-13->LUMO (41%), HOMO->L+10 (10%), HOMO->L+12 (19%)	H-1->L+1 (6%), H-1->L+3 (8%), HOMO->L+7 (5%), HOMO->L+14 (5%)
27	29342	340	0.0014	H-13->LUMO (36%), HOMO->L+10 (11%), HOMO->L+12 (22%)	H-22->L+12 (4%), HOMO->L+7 (5%), HOMO->L+14 (6%)
28	29493	339	0.5078	H-12->LUMO (26%), HOMO->L+3 (14%), HOMO->L+6 (15%)	H-20->LUMO (4%), H-18->LUMO (6%), H-15->LUMO (3%), H-10->LUMO (6%), H-4->LUMO (2%), H-3->L+1 (2%), HOMO->L+5 (2%), HOMO->L+9 (6%), HOMO->L+11 (4%)
29	30414	328	0.0	HOMO->L+7 (81%)	HOMO->L+8 (5%), HOMO->L+10 (5%), HOMO->L+12 (4%)
30	30470	328	0.1895	HOMO->L+6 (79%)	H-15->LUMO (2%), H-12->LUMO (5%), HOMO->L+9 (3%)
31	31171	320	0.0	H-3->L+2 (18%), H-2->L+1 (14%), HOMO->L+8 (48%)	H-2->L+3 (8%), HOMO->L+7 (5%)
32	31210	320	0.0041	H-5->L+3 (19%), H-3->L+1 (40%), H-2->L+2 (29%)	H-5->L+1 (2%), H-3->L+3 (6%)
33	31270	319	0.0005	H-3->L+2 (33%), H-2->L+1 (23%), HOMO->L+8 (38%)	H-2->L+3 (2%)

34	31370	318	0.0288	H-15->LUMO (12%), H-5->L+3 (21%), HOMO->L+9 (51%)	H-3->L+1 (4%), H-2->L+2 (3%)
35	31437	318	0.0273	H-15->LUMO (10%), H-5->L+3 (36%), H-3->L+1 (11%), HOMO->L+9 (19%)	H-5->L+1 (3%), H-3->L+3 (3%), H-2->L+2 (9%)
36	31537	317	0.0002	H-22->LUMO (15%), H-22->L+10 (13%), H-22->L+12 (28%), H-14->LUMO (10%)	H-22->L+14 (8%), H-22->L+16 (2%), HOMO->L+8 (2%), HOMO->L+10 (3%), HOMO->L+12 (5%)
37	31685	315	0.0003	H-14->LUMO (86%)	H-22->L+10 (2%), H-22->L+12 (5%)
38	31910	313	0.0469	H-15->LUMO (66%), HOMO->L+9 (13%)	H-3->L+3 (5%), HOMO->L+11 (6%)
39	31956	312	0.0001	H-2->L+3 (75%)	H-3->L+2 (7%), H-2->L+1 (3%), HOMO->L+8 (3%), HOMO->L+12 (3%)
40	32381	308	0.0003	H-22->LUMO (36%), H-17->LUMO (48%)	H-22->L+10 (2%), H-22->L+12 (4%), H-14->LUMO (3%)
41	32383	308	0.0729	H-16->LUMO (88%)	H-3->L+3 (4%), HOMO->L+11 (2%)
42	32489	307	0.0168	H-3->L+3 (63%), HOMO->L+11 (14%)	H-18->LUMO (4%), H-5->L+3 (4%), H-2->L+4 (3%)
43	32630	306	0.0001	H-22->LUMO (42%), H-17->LUMO (47%)	H-22->L+12 (2%)
44	32827	304	0.0012	H-1->L+5 (46%), HOMO->L+10 (28%), HOMO->L+12 (18%)	
45	32842	304	0.0012	H-1->L+4 (97%)	
46	32854	304	0.0012	H-1->L+5 (49%), HOMO->L+10 (27%), HOMO->L+12 (16%)	H-2->L+3 (4%)
47	33255	300	0.1709	H-20->LUMO (10%), H-18->LUMO (26%), HOMO->L+11 (25%), HOMO->L+15 (19%)	H-16->LUMO (3%), HOMO->L+13 (7%)
48	33518	298	0.0101	HOMO->L+13 (86%)	HOMO->L+11 (6%)
49	33563	297	0.0009	HOMO->L+14 (73%)	H-4->L+1 (3%), H-3->L+4 (2%), H-2->L+5 (5%), HOMO->L+10 (5%), HOMO->L+12 (7%)
50	33612	297	0.0015	H-4->L+1 (79%)	H-4->L+3 (3%), H-2->L+5 (3%), HOMO->L+14 (6%)

Table S9. TD DFT Calculated Electronic Transitions for **5**-uduu

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	10344	966	0.0005	HOMO->LUMO (99%)	
2	14751	677	0.0046	H-1->LUMO (93%)	H-2->LUMO (3%)
3	17330	577	0.0149	H-2->LUMO (90%)	H-5->LUMO (4%), H-1->LUMO (3%)
4	18685	535	0.0009	H-5->LUMO (21%), H-4->LUMO (62%)	H-6->LUMO (9%), H-3->LUMO (4%), H-2->LUMO (2%)
5	19434	514	0.0073	H-3->LUMO (89%)	H-4->LUMO (5%)
6	21193	471	0.0104	H-5->LUMO (55%), H-4->LUMO (10%), HOMO->L+2 (12%)	H-6->LUMO (4%), H-3->LUMO (5%), H-2->LUMO (3%), HOMO->L+1 (3%), HOMO->L+3 (4%)
7	22652	441	0.0241	HOMO->L+2 (66%), HOMO->L+3 (15%)	H-6->LUMO (4%), H-5->LUMO (5%), HOMO->L+1 (6%)
8	22771	439	0.0091	H-6->LUMO (63%), H-4->LUMO (15%)	H-7->LUMO (7%), HOMO->L+1 (6%), HOMO->L+2 (5%)
9	22798	438	0.0179	HOMO->L+1 (83%)	H-6->LUMO (5%), H-4->LUMO (2%), HOMO->L+2 (7%)
10	24272	411	0.0009	H-1->L+14 (60%)	H-21->L+14 (6%), H-2->L+14 (3%), H-1->L+10 (4%), H-1->L+12 (2%)
11	24332	410	0.0314	H-7->LUMO (85%)	H-6->LUMO (8%)
12	25483	392	0.0098	H-12->LUMO (15%), H-8->LUMO (59%)	H-11->LUMO (3%), H-10->LUMO (5%), H-9->LUMO

					(4%), HOMO->L+3 (9%)
13	25916	385	0.0743	H-8->LUMO (13%), H-1->L+2 (12%), HOMO->L+3 (27%)	H-12->LUMO (7%), H-10->LUMO (3%), H-5->L+14 (2%), H-4->L+14 (4%), H-1->L+1 (2%), H-1->L+3 (3%), H-1->L+14 (3%)
14	26055	383	0.0446	H-9->LUMO (18%), H-8->LUMO (13%), H-1->L+2 (17%)	H-5->L+14 (5%), H-4->L+14 (5%), H-1->L+1 (4%), H-1->L+3 (9%), HOMO->L+3 (9%)
15	26228	381	0.0042	H-9->LUMO (72%), H-1->L+2 (10%)	H-12->LUMO (3%), H-1->L+3 (3%)
16	26433	378	0.0064	HOMO->L+5 (94%)	HOMO->L+4 (4%)
17	26883	371	0.0035	H-10->LUMO (71%), HOMO->L+4 (14%)	H-12->LUMO (7%), H-11->LUMO (5%)
18	26942	371	0.0072	HOMO->L+4 (77%)	H-12->LUMO (6%), H-10->LUMO (8%), HOMO->L+5 (4%)
19	27287	366	0.003	H-5->L+14 (16%), H-4->L+14 (17%), H-1->L+2 (32%)	H-13->LUMO (2%), H-6->L+14 (4%), H-2->L+14 (2%), H-1->L+1 (6%)
20	27564	362	0.0052	H-12->LUMO (18%), H-11->LUMO (78%)	
21	27938	357	0.0108	H-5->L+14 (11%), H-1->L+1 (24%)	H-13->LUMO (2%), H-12->L+14 (5%), H-4->L+14 (9%), H-3->L+1 (7%), H-2->L+1 (2%), H-2->L+14 (8%), H-1->L+2 (7%)
22	27973	357	0.0499	H-1->L+1 (42%), H-1->L+2 (14%)	H-13->LUMO (4%), H-12->L+14 (2%), H-5->L+14 (4%), H-4->L+14 (7%), H-2->L+14 (4%), H-1->L+3 (4%)
23	28192	354	0.0067	H-2->L+1 (17%), H-2->L+2 (37%), H-1->L+3 (12%)	H-13->LUMO (3%), H-5->L+14 (3%), H-3->L+1 (7%), H-3->L+2 (4%), H-1->L+1 (3%), H-1->L+2 (2%)
24	28370	352	0.0181	H-13->LUMO (54%), H-3->L+1 (14%), H-2->L+1 (12%)	H-1->L+1 (7%), H-1->L+3 (5%)
25	28406	352	0.0695	H-13->LUMO (12%), H-3->L+1 (25%), H-2->L+2 (29%)	H-12->LUMO (4%), H-2->L+1 (6%)
26	28677	348	0.0006	H-13->LUMO (15%), H-1->L+3 (51%)	H-4->L+14 (5%), H-2->L+1 (2%), H-2->L+2 (7%), H-1->L+1 (6%)
27	29109	343	0.432	H-12->LUMO (17%), HOMO->L+3 (10%), HOMO->L+6 (19%)	H-18->LUMO (3%), H-16->LUMO (2%), H-11->LUMO (3%), H-10->LUMO (2%), H-3->L+1 (6%), H-2->L+2 (6%), HOMO->L+7 (3%), HOMO->L+8 (4%)
28	29423	339	0.1023	HOMO->L+6 (21%), HOMO->L+7 (54%)	H-12->LUMO (4%), HOMO->L+3 (2%), HOMO->L+10 (4%)
29	29801	335	0.0241	HOMO->L+6 (29%), HOMO->L+7 (34%), HOMO->L+14 (11%)	HOMO->L+9 (6%), HOMO->L+10 (4%)
30	29973	333	0.0209	H-3->L+1 (14%), H-2->L+1 (26%), H-2->L+3 (19%)	H-4->L+2 (3%), H-4->L+3 (3%), H-3->L+2 (3%), H-2->L+2 (3%), HOMO->L+9 (5%), HOMO->L+10 (4%), HOMO->L+14 (2%)
31	30193	331	0.0169	H-3->L+1 (16%), H-2->L+1 (28%)	H-5->L+2 (4%), H-5->L+3 (3%), H-4->L+2 (7%), H-4->L+3 (6%), H-2->L+2 (3%), H-2->L+3 (4%), HOMO->L+6 (2%), HOMO->L+9 (4%), HOMO->L+14 (5%)
32	30262	330	0.0788	HOMO->L+6 (20%), HOMO->L+14 (24%)	H-22->L+14 (3%), H-12->LUMO (2%), H-5->L+2 (3%), H-4->L+2 (5%), H-4->L+3 (4%), H-3->L+2 (4%), HOMO->L+7 (5%), HOMO->L+9 (6%)
33	30669	326	0.0012	HOMO->L+9 (64%), HOMO->L+14 (10%)	H-22->L+14 (3%), H-4->L+2 (2%), H-2->L+3 (3%), HOMO->L+10 (6%), HOMO->L+12

					(2%)
34	30740	325	0.0378	H-3->L+2 (13%), H-2->L+3 (10%), HOMO->L+8 (54%)	H-4->L+2 (4%), HOMO->L+9 (2%), HOMO->L+10 (5%)
35	30848	324	0.0141	H-2->L+3 (39%), HOMO->L+8 (16%)	H-5->L+2 (3%), H-4->L+2 (6%), H-3->L+2 (5%), H-3->L+3 (5%), H-2->L+1 (3%), H-1->L+3 (2%), HOMO->L+9 (6%)
36	31026	322	0.0061	H-3->L+2 (56%), HOMO->L+8 (14%)	H-4->L+2 (4%), H-3->L+3 (2%), H-2->L+2 (3%), HOMO->L+10 (3%)
37	31133	321	0.002	H-14->LUMO (84%)	H-17->LUMO (7%), H-15->LUMO (6%)
38	31466	317	0.0073	H-22->LUMO (49%), H-15->LUMO (11%), HOMO->L+10 (10%)	H-22->L+14 (8%), H-21->LUMO (6%), H-1->L+5 (3%)
39	31545	317	0.0015	H-1->L+5 (92%)	H-22->LUMO (2%), H-1->L+4 (3%)
40	31724	315	0.0206	H-15->LUMO (63%)	H-22->LUMO (7%), H-17->LUMO (6%), H-14->LUMO (7%), HOMO->L+11 (4%), HOMO->L+14 (3%)
41	31887	313	0.0281	H-17->LUMO (76%)	H-15->LUMO (8%), H-14->LUMO (3%), HOMO->L+11 (4%)
42	32025	312	0.0507	HOMO->L+10 (25%), HOMO->L+11 (17%), HOMO->L+12 (11%)	H-22->LUMO (6%), H-17->LUMO (6%), H-2->L+3 (3%), HOMO->L+13 (7%), HOMO->L+14 (7%)
43	32156	310	0.0004	H-1->L+4 (92%)	H-1->L+5 (3%)
44	32223	310	0.1512	H-16->LUMO (59%), HOMO->L+11 (13%)	HOMO->L+12 (8%)
45	32279	309	0.0306	H-16->LUMO (15%), HOMO->L+11 (36%), HOMO->L+12 (15%)	H-18->LUMO (2%), H-15->LUMO (4%), H-5->L+2 (3%), H-4->L+2 (3%), H-3->L+3 (5%), HOMO->L+10 (4%)
46	32491	307	0.0145	H-5->L+2 (11%), H-4->L+2 (33%), H-4->L+3 (11%)	H-18->LUMO (8%), H-16->LUMO (7%), H-6->L+2 (3%), H-5->L+1 (5%), H-5->L+3 (6%), H-3->L+2 (3%), H-2->L+5 (3%)
47	32597	306	0.008	H-5->L+2 (19%), H-3->L+3 (45%)	H-5->L+3 (6%), H-4->L+3 (2%), HOMO->L+12 (9%), HOMO->L+13 (2%)
48	32717	305	0.0792	H-18->LUMO (62%)	H-4->L+2 (5%), H-4->L+3 (5%), HOMO->L+11 (2%), HOMO->L+13 (3%), HOMO->L+15 (6%)
49	32776	305	0.0025	HOMO->L+12 (29%), HOMO->L+13 (58%)	HOMO->L+11 (4%)
50	32879	304	0.0197	H-5->L+2 (16%), HOMO->L+13 (15%)	H-22->L+14 (5%), H-20->LUMO (3%), H-4->L+1 (6%), H-4->L+3 (3%), H-3->L+2 (3%), H-2->L+5 (6%), HOMO->L+10 (6%), HOMO->L+11 (3%), HOMO->L+12 (8%), HOMO->L+14 (3%)

Table S10. TD DFT Calculated Electronic Transitions for **6**

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	6024	1659	0.0108	HOMO->LUMO (97%)	
2	10067	993	0.0054	H-1->LUMO (91%)	H-3->LUMO (7%)
3	11941	837	0.0009	H-2->LUMO (96%)	
4	13554	737	0.0016	H-4->LUMO (99%)	
5	15994	625	0.1935	H-3->LUMO (80%), HOMO->L+1 (10%)	H-1->LUMO (6%)
6	19921	501	0.025	H-5->LUMO (65%), HOMO->L+1 (13%), HOMO->L+2 (12%)	H-7->LUMO (4%)
7	20187	495	0.2751	H-5->LUMO (22%), HOMO->L+1 (42%), HOMO->L+2 (15%), HOMO->L+3 (11%)	H-3->LUMO (4%)
8	20919	478	0.0664	HOMO->L+2 (63%)	H-8->LUMO (2%), H-6-

					>LUMO (9%), HOMO->L+1 (9%), HOMO->L+3 (8%)
9	21643	462	0.009	H-1->L+1 (82%)	H-6->LUMO (3%), H-3->L+1 (2%), H-2->L+1 (2%), H-1->L+2 (4%)
10	21904	456	0.1376	H-6->LUMO (64%), HOMO->L+3 (16%)	H-10->LUMO (7%), H-7->LUMO (3%), H-1->L+1 (3%)
11	22064	453	0.0382	H-8->LUMO (59%), H-7->LUMO (17%)	H-9->LUMO (5%), H-6->LUMO (6%), HOMO->L+3 (9%)
12	22402	446	0.1434	H-10->LUMO (12%), H-7->LUMO (11%), HOMO->L+3 (44%)	H-14->LUMO (3%), H-9->LUMO (4%), H-6->LUMO (5%), HOMO->L+1 (8%), HOMO->L+2 (2%)
13	22778	439	0.082	H-10->LUMO (25%), H-7->LUMO (44%)	H-8->LUMO (9%), H-6->LUMO (5%), H-5->LUMO (6%), H-2->L+1 (3%)
14	23240	430	0.0113	H-9->LUMO (88%)	H-10->LUMO (4%), H-8->LUMO (3%), H-7->LUMO (3%)
15	23261	429	0.0017	H-11->LUMO (97%)	
16	23928	417	0.006	H-10->LUMO (28%), H-2->L+1 (31%)	H-8->LUMO (9%), H-7->LUMO (3%), H-6->LUMO (2%), H-1->L+11 (7%), HOMO->L+4 (2%)
17	24103	414	0.0355	H-2->L+1 (41%), HOMO->L+4 (15%)	H-10->LUMO (8%), H-8->LUMO (7%), H-7->LUMO (7%), H-3->L+1 (5%), H-2->L+3 (2%)
18	24246	412	0.0036	H-1->L+11 (45%)	H-15->L+11 (3%), H-3->L+11 (4%), H-2->L+1 (4%), H-2->L+11 (2%), H-1->L+5 (2%), H-1->L+12 (8%), HOMO->L+4 (8%)
19	24450	408	0.0684	H-12->LUMO (11%), HOMO->L+4 (65%)	H-10->LUMO (4%), H-8->LUMO (3%), H-1->L+11 (2%), HOMO->L+3 (2%)
20	25169	397	0.0026	H-4->L+1 (86%)	H-4->L+2 (7%)
21	25304	395	0.1984	H-12->LUMO (45%), H-3->L+1 (28%)	H-16->LUMO (2%), H-15->LUMO (3%), H-1->L+2 (6%), HOMO->L+4 (4%)
22	25603	390	0.0431	H-1->L+2 (75%)	H-15->LUMO (2%), H-12->LUMO (5%), H-1->L+1 (4%), H-1->L+3 (2%)
23	26196	381	0.0129	H-1->L+3 (84%)	H-4->L+11 (3%), H-1->L+2 (4%)
24	26453	378	0.0214	H-16->LUMO (19%), H-15->LUMO (21%), H-3->L+1 (10%), H-2->L+11 (20%)	H-18->LUMO (7%), H-2->L+12 (4%)
25	26788	373	0.0087	H-15->LUMO (12%), H-2->L+11 (32%)	H-18->LUMO (2%), H-16->LUMO (8%), H-4->L+1 (2%), H-4->L+11 (5%), H-3->L+1 (7%), H-2->L+2 (2%), H-2->L+12 (6%)
26	27242	367	0.0632	H-4->L+11 (35%), H-2->L+2 (15%)	H-18->LUMO (3%), H-16->LUMO (4%), H-15->LUMO (2%), H-12->LUMO (3%), H-4->L+12 (6%), H-3->L+1 (3%), H-2->L+1 (3%), H-2->L+11 (4%), H-1->L+2 (2%)
27	27450	364	0.0813	H-12->LUMO (13%), H-3->L+1 (27%)	H-15->LUMO (3%), H-14->LUMO (8%), H-4->L+11 (8%), H-3->L+2 (6%), H-2->L+1 (5%), H-2->L+3 (3%), HOMO->L+11 (2%)
28	27851	359	0.0026	H-14->LUMO (12%), H-3->L+2 (15%), H-2->L+2 (27%), H-2->L+3 (14%)	H-16->LUMO (5%), H-15->LUMO (4%), H-4->L+11 (8%), H-3->L+3 (5%)
29	28064	356	0.0369	H-14->LUMO (15%), H-13->LUMO (16%), H-3->L+2 (12%), H-2->L+2 (30%)	H-16->LUMO (4%), H-15->LUMO (7%), H-4->L+11 (5%), H-3->L+3 (2%)
30	28335	352	0.0118	H-16->LUMO (24%), H-15->LUMO (14%), H-3->L+2	H-18->LUMO (5%), H-14-

				(22%)	>LUMO (7%), H-13->LUMO (8%), H-12->LUMO (2%), H-3->L+1 (3%)
31	28716	348	0.0904	H-13->LUMO (37%), H-3->L+2 (32%)	H-18->LUMO (5%), H-3->L+3 (9%), H-2->L+3 (7%)
32	29184	342	0.14	H-13->LUMO (14%), H-2->L+2 (11%), H-2->L+3 (45%)	H-3->L+1 (2%), H-3->L+3 (5%), H-1->L+4 (8%)
33	29294	341	0.0799	H-3->L+3 (35%), H-2->L+3 (18%), H-1->L+4 (23%)	H-5->L+1 (3%), H-3->L+4 (7%)
34	29646	337	0.1224	HOMO->L+5 (84%)	H-16->LUMO (2%), H-15->LUMO (3%), HOMO->L+11 (2%)
35	29708	336	0.0316	H-3->L+3 (21%), H-1->L+4 (54%)	H-18->LUMO (4%), H-5->L+1 (6%), H-2->L+2 (3%)
36	30149	331	0.0322	H-18->LUMO (55%), H-16->LUMO (19%)	H-14->LUMO (5%), H-13->LUMO (4%), H-5->L+1 (6%)
37	30320	329	0.0006	H-4->L+2 (68%), H-4->L+3 (25%)	H-4->L+1 (3%)
38	30817	324	0.0721	HOMO->L+7 (59%), HOMO->L+8 (13%)	H-15->LUMO (2%), H-14->LUMO (3%), H-5->L+1 (5%), HOMO->L+11 (6%)
39	30914	323	0.0128	H-4->L+3 (13%), HOMO->L+6 (60%)	H-14->LUMO (2%), H-4->L+2 (5%), H-3->L+4 (2%), HOMO->L+7 (6%)
40	30941	323	0.0037	H-4->L+2 (18%), H-4->L+3 (56%), HOMO->L+6 (19%)	H-4->L+1 (4%)
41	31071	321	0.0047	H-5->L+1 (38%), H-3->L+4 (26%)	H-17->LUMO (4%), H-1->L+4 (7%), HOMO->L+6 (8%), HOMO->L+11 (3%)
42	31408	318	0.0295	H-3->L+4 (14%), HOMO->L+9 (19%), HOMO->L+11 (22%)	H-16->L+11 (4%), H-15->L+11 (3%), H-5->L+1 (2%), H-5->L+2 (2%), HOMO->L+7 (7%), HOMO->L+8 (8%), HOMO->L+12 (4%)
43	31541	317	0.0211	H-17->LUMO (21%), H-3->L+4 (11%)	H-16->LUMO (3%), H-15->LUMO (4%), H-14->LUMO (8%), H-5->L+1 (6%), H-5->L+2 (3%), HOMO->L+6 (3%), HOMO->L+7 (8%), HOMO->L+8 (9%), HOMO->L+9 (9%)
44	31674	315	0.0085	H-17->LUMO (54%), H-3->L+4 (15%), HOMO->L+9 (21%)	H-18->LUMO (2%)
45	31748	314	0.0049	H-3->L+4 (10%), HOMO->L+9 (17%), HOMO->L+11 (19%)	H-18->L+11 (2%), H-17->LUMO (2%), H-16->L+11 (5%), H-15->L+11 (4%), H-6->L+1 (2%), H-5->L+1 (3%), H-2->L+4 (4%), HOMO->L+7 (3%), HOMO->L+8 (9%), HOMO->L+12 (3%)
46	32139	311	0.1013	H-2->L+4 (70%)	H-6->L+1 (9%), HOMO->L+8 (7%)
47	32215	310	0.0883	HOMO->L+8 (20%), HOMO->L+9 (21%)	H-17->LUMO (8%), H-15->LUMO (3%), H-14->LUMO (4%), H-7->L+1 (2%), H-6->L+1 (3%), H-5->L+1 (5%), H-5->L+2 (3%), H-2->L+4 (8%), HOMO->L+6 (2%), HOMO->L+7 (6%)
48	32474	307	0.0014	H-16->L+11 (19%), H-15->L+11 (14%), HOMO->L+11 (24%)	H-18->L+11 (9%), H-16->L+12 (4%), H-15->L+12 (3%), H-6->L+1 (7%), HOMO->L+12 (3%)
49	32667	306	0.0409	H-6->L+1 (61%), HOMO->L+10 (10%)	H-5->L+3 (2%), H-2->L+4 (8%), HOMO->L+7 (2%), HOMO->L+9 (2%), HOMO->L+11 (3%)
50	32773	305	0.0013	HOMO->L+10 (85%)	H-6->L+1 (8%)

Table S11. TD DFT Calculated Electronic Transitions for **7**

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	8527	1172	0.0047	HOMO->LUMO (97%)	
2	12896	775	0.013	H-1->LUMO (83%)	H-3->LUMO (8%), H-2->LUMO (6%)
3	15881	629	0.0066	H-4->LUMO (36%), H-2->LUMO (50%)	H-3->LUMO (9%)
4	16910	591	0.0022	H-5->LUMO (94%)	H-4->LUMO (3%)
5	18142	551	0.145	H-4->LUMO (27%), H-3->LUMO (62%)	H-5->LUMO (3%), H-2->LUMO (2%), H-1->LUMO (2%)
6	18652	536	0.3866	H-4->LUMO (25%), H-3->LUMO (16%), H-2->LUMO (37%), H-1->LUMO (10%)	HOMO->L+1 (4%), HOMO->L+2 (2%)
7	20300	492	0.0905	HOMO->L+1 (94%)	
8	21214	471	0.1301	HOMO->L+2 (89%)	H-7->LUMO (5%)
9	22416	446	0.0027	H-6->LUMO (86%)	H-7->LUMO (4%), HOMO->L+3 (8%)
10	22652	441	0.0552	H-7->LUMO (11%), H-6->LUMO (11%), HOMO->L+3 (73%)	H-8->LUMO (2%)
11	22971	435	0.0582	H-7->LUMO (38%), HOMO->L+3 (13%), HOMO->L+4 (37%)	H-8->LUMO (6%), HOMO->L+2 (2%)
12	23710	421	0.0068	H-8->LUMO (72%), H-7->LUMO (12%)	H-11->LUMO (2%), H-1->L+1 (2%)
13	23851	419	0.008	H-1->L+15 (57%)	H-20->L+15 (6%), H-3->L+15 (6%), H-2->L+15 (6%), H-1->L+2 (2%)
14	24365	410	0.0053	H-9->LUMO (22%), H-1->L+1 (40%), H-1->L+2 (10%)	H-8->LUMO (6%), H-1->L+4 (7%), HOMO->L+5 (5%)
15	24547	407	0.077	H-9->LUMO (32%), H-1->L+1 (13%), HOMO->L+5 (10%)	H-11->LUMO (9%), H-10->LUMO (8%), H-7->LUMO (3%), H-1->L+2 (8%), H-1->L+4 (4%), HOMO->L+4 (5%)
16	24650	405	0.024	H-11->LUMO (10%), H-9->LUMO (12%), HOMO->L+5 (50%)	H-7->LUMO (4%), H-1->L+1 (3%), H-1->L+2 (3%), HOMO->L+4 (7%)
17	24990	400	0.0127	H-1->L+1 (26%), H-1->L+2 (32%), HOMO->L+5 (12%)	H-11->LUMO (3%), H-5->L+15 (4%), H-2->L+2 (2%), H-1->L+4 (6%)
18	25358	394	0.1113	H-10->LUMO (24%), H-7->LUMO (10%), HOMO->L+4 (18%), HOMO->L+5 (12%)	H-17->LUMO (3%), H-14->LUMO (8%), H-12->LUMO (4%), H-9->LUMO (6%)
19	25583	390	0.0617	H-10->LUMO (61%)	H-11->LUMO (8%), H-9->LUMO (3%), H-7->LUMO (5%), HOMO->L+4 (8%), HOMO->L+5 (4%)
20	25690	389	0.0376	H-12->LUMO (47%), H-11->LUMO (31%)	H-9->LUMO (3%), HOMO->L+4 (3%), HOMO->L+5 (2%)
21	25976	384	0.055	H-12->LUMO (35%), H-11->LUMO (13%), H-2->L+1 (13%)	H-13->LUMO (3%), H-9->LUMO (9%), H-3->L+1 (9%), H-1->L+1 (5%), H-1->L+2 (6%)
22	26225	381	0.0097	H-13->LUMO (70%)	H-5->L+15 (8%), H-3->L+1 (2%), H-2->L+1 (3%), H-2->L+2 (4%)
23	26592	376	0.0145	H-1->L+2 (16%), H-1->L+3 (21%), H-1->L+4 (41%)	H-4->L+1 (4%), H-2->L+1 (3%), H-1->L+1 (3%)
24	26800	373	0.009	HOMO->L+6 (97%)	
25	26953	371	0.0096	H-5->L+15 (50%)	H-13->LUMO (9%), H-4->L+15 (3%), H-2->L+1 (4%), H-1->L+2 (8%)
26	27034	369	0.0068	H-4->L+15 (36%)	H-20->L+15 (4%), H-14->L+15 (3%), H-13->LUMO (2%), H-11->L+15 (3%), H-5->L+15 (4%), H-3->L+15 (7%), H-2->L+1 (6%), H-2->L+15 (9%)
27	27279	366	0.0029	H-11->LUMO (15%), H-2->L+1 (37%)	H-13->LUMO (3%), H-12->LUMO (6%), H-9->LUMO (5%), H-4->L+2 (2%), H-4->L+15 (5%), H-3->L+1 (8%)

28	27626	361	0.0776	H-4->L+1 (13%), H-3->L+1 (26%), H-1->L+3 (29%)	H-14->LUMO (5%), H-3->L+2 (4%), H-2->L+1 (3%), H-2->L+2 (4%), H-2->L+3 (4%)
29	27815	359	0.0121	H-3->L+1 (11%), H-1->L+3 (41%), H-1->L+4 (28%)	H-4->L+1 (5%), H-2->L+2 (3%)
30	27924	358	0.0604	H-14->LUMO (53%)	H-3->L+1 (2%), H-3->L+2 (6%), H-2->L+2 (5%), HOMO->L+4 (3%), HOMO->L+7 (2%), HOMO->L+8 (7%)
31	28228	354	0.0307	H-3->L+3 (25%), H-2->L+2 (18%), H-2->L+3 (33%)	H-4->L+1 (3%), H-3->L+1 (4%), H-1->L+3 (2%)
32	28604	349	0.1865	H-3->L+1 (15%), H-2->L+3 (13%), H-1->L+5 (17%)	H-14->LUMO (3%), H-3->L+2 (5%), H-3->L+3 (5%), H-3->L+4 (4%), H-3->L+5 (3%), H-2->L+1 (5%), H-2->L+2 (9%), H-2->L+5 (4%)
33	28766	347	0.0035	H-5->L+2 (15%), H-5->L+4 (11%), H-1->L+5 (30%)	H-5->L+1 (4%), H-4->L+1 (5%), H-3->L+3 (3%), H-3->L+5 (4%), H-2->L+2 (3%), H-2->L+4 (8%), H-2->L+5 (3%)
34	28877	346	0.0323	H-5->L+2 (25%), H-5->L+4 (17%), H-1->L+5 (12%)	H-5->L+1 (5%), H-5->L+3 (2%), H-4->L+1 (2%), H-3->L+1 (5%), H-3->L+2 (4%), H-2->L+1 (3%), H-2->L+2 (4%), H-2->L+4 (3%)
35	29172	342	0.0604	H-3->L+2 (28%), H-2->L+2 (24%)	H-5->L+15 (3%), H-4->L+1 (7%), H-4->L+2 (7%), H-3->L+1 (2%), H-2->L+1 (8%), H-2->L+4 (4%)
36	29437	339	0.078	H-4->L+1 (42%), H-3->L+2 (26%)	H-3->L+1 (3%), H-3->L+4 (4%), H-1->L+5 (3%), HOMO->L+7 (3%)
37	29570	338	0.101	H-15->LUMO (41%), HOMO->L+7 (21%), HOMO->L+8 (10%)	H-14->LUMO (3%), HOMO->L+15 (8%)
38	29772	335	0.073	H-15->LUMO (17%), HOMO->L+7 (40%), HOMO->L+8 (11%)	H-4->L+1 (5%), H-2->L+2 (6%), H-2->L+3 (2%), H-2->L+4 (7%), H-1->L+5 (2%)
39	29899	334	0.0661	H-2->L+4 (38%)	H-4->L+2 (2%), H-4->L+3 (2%), H-4->L+4 (3%), H-2->L+2 (2%), H-2->L+3 (7%), H-1->L+5 (6%), HOMO->L+7 (8%), HOMO->L+8 (6%), HOMO->L+11 (3%), HOMO->L+15 (6%)
40	30032	332	0.0114	H-21->LUMO (44%), H-15->LUMO (22%), HOMO->L+8 (11%)	H-16->LUMO (4%), HOMO->L+15 (4%)
41	30049	332	0.097	H-21->LUMO (38%), H-4->L+2 (12%), HOMO->L+15 (10%)	H-18->LUMO (2%), H-15->LUMO (8%), H-3->L+2 (2%), HOMO->L+8 (7%), HOMO->L+9 (2%)
42	30082	332	0.0625	H-4->L+2 (14%), H-3->L+3 (14%), H-3->L+4 (35%)	H-21->LUMO (7%), H-4->L+3 (2%), H-4->L+4 (4%), H-2->L+3 (4%), H-1->L+5 (6%)
43	30370	329	0.0289	H-4->L+2 (13%), HOMO->L+7 (11%), HOMO->L+15 (30%)	H-21->L+15 (6%), H-16->LUMO (7%), H-5->L+1 (4%), H-4->L+4 (2%), H-2->L+4 (2%), HOMO->L+9 (3%), HOMO->L+10 (5%)
44	30501	327	0.0057	H-5->L+1 (62%), H-5->L+2 (17%)	H-16->LUMO (3%), HOMO->L+9 (4%)
45	30624	326	0.018	H-16->LUMO (71%), HOMO->L+9 (10%)	H-4->L+2 (3%), HOMO->L+8 (2%)
46	30661	326	0.0091	H-4->L+2 (18%), H-2->L+5 (16%), HOMO->L+9 (15%)	H-5->L+1 (6%), H-5->L+2 (3%), H-3->L+4 (3%), H-3->L+5 (8%), H-1->L+5 (7%), HOMO->L+8 (5%)
47	30720	325	0.0084	H-3->L+3 (27%), H-2->L+3 (17%)	H-4->L+2 (5%), H-3->L+4 (5%), H-3->L+5 (5%), H-2->L+4 (6%), H-2->L+5 (6%), H-1->L+5 (4%), HOMO->L+8 (3%), HOMO->L+9 (6%),

					HOMO->L+10 (2%)
48	30890	323	0.0583	H-3->L+5 (11%), H-2->L+5 (14%), HOMO->L+9 (25%)	H-16->LUMO (5%), H-4->L+3 (3%), H-3->L+3 (7%), H-3->L+4 (5%), H-2->L+3 (4%), H-2->L+4 (5%), H-1->L+5 (3%), HOMO->L+10 (4%)
49	31044	322	0.1284	HOMO->L+8 (13%), HOMO->L+9 (22%), HOMO->L+10 (24%)	H-21->L+15 (3%), H-3->L+4 (7%), H-2->L+4 (2%), HOMO->L+14 (2%), HOMO->L+15 (7%)
50	31414	318	0.0276	H-4->L+3 (39%), H-4->L+4 (15%)	H-20->LUMO (9%), H-3->L+2 (2%), H-3->L+4 (9%), H-2->L+4 (6%)

Table S12. TD DFT Calculated Electronic Transitions for **8a**

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	7131	1402	0.0	HOMO->LUMO (98%)	
2	11451	873	0.0383	H-2->LUMO (31%), H-1->LUMO (64%)	H-3->LUMO (3%)
3	13442	743	0.0053	H-3->LUMO (82%), H-2->LUMO (13%)	
4	15108	661	0.0044	H-5->LUMO (99%)	
5	15838	631	0.872	H-2->LUMO (52%), H-1->LUMO (31%)	H-3->LUMO (9%), HOMO->L+1 (5%)
6	18747	533	0.0	H-4->LUMO (88%)	H-1->L+1 (3%), HOMO->L+2 (2%)
7	19601	510	0.3794	HOMO->L+1 (75%)	H-7->LUMO (5%), H-3->LUMO (2%), HOMO->L+3 (7%), HOMO->L+5 (6%)
8	20126	496	0.0	HOMO->L+2 (87%)	H-6->LUMO (9%)
9	20513	487	0.0624	HOMO->L+3 (83%)	H-7->LUMO (8%), HOMO->L+5 (5%)
10	20671	483	0.0	H-6->LUMO (80%)	HOMO->L+2 (9%), HOMO->L+4 (5%)
11	21327	468	0.0	H-1->L+1 (13%), HOMO->L+4 (80%)	H-6->LUMO (4%)
12	21791	458	0.0	H-2->L+1 (11%), H-1->L+1 (57%), HOMO->L+4 (12%)	H-4->LUMO (3%), H-3->L+1 (3%), H-3->L+3 (2%), H-1->L+3 (4%)
13	22108	452	0.3667	H-7->LUMO (24%), HOMO->L+5 (67%)	H-9->LUMO (3%)
14	23444	426	0.0	H-8->LUMO (92%)	H-13->LUMO (3%)
15	23528	425	0.0	H-2->L+16 (14%), H-1->L+3 (15%), H-1->L+16 (18%)	H-2->L+1 (4%), H-2->L+3 (3%), H-2->L+9 (5%), H-2->L+17 (3%), H-1->L+1 (5%), H-1->L+9 (6%), H-1->L+17 (4%)
16	23546	424	0.198	H-11->LUMO (22%), H-9->LUMO (24%), H-7->LUMO (26%), HOMO->L+5 (10%)	HOMO->L+1 (4%), HOMO->L+3 (3%), HOMO->L+6 (4%)
17	23906	418	0.126	H-9->LUMO (46%), H-7->LUMO (27%)	H-15->LUMO (3%), H-11->LUMO (3%), H-1->L+4 (2%), HOMO->L+1 (4%), HOMO->L+3 (3%), HOMO->L+5 (2%)
18	24207	413	0.0	H-10->LUMO (12%), H-3->L+1 (33%), H-2->L+1 (15%), HOMO->L+7 (12%)	H-13->LUMO (9%), H-6->LUMO (2%), H-5->L+16 (3%)
19	24232	412	0.0	H-3->L+1 (25%), H-1->L+3 (11%), HOMO->L+7 (26%)	H-13->LUMO (4%), H-2->L+1 (7%), H-2->L+16 (2%), H-1->L+1 (6%), H-1->L+16 (3%)
20	24237	412	0.0055	H-11->LUMO (20%), H-1->L+2 (62%), HOMO->L+6 (11%)	
21	24512	407	0.1242	H-1->L+2 (14%), HOMO->L+6 (76%)	
22	24533	407	0.0	H-13->LUMO (25%), H-10->LUMO (32%), H-3->L+1 (12%), HOMO->L+7 (16%)	H-1->L+1 (3%), H-1->L+3 (2%)
23	24611	406	0.0	H-13->LUMO (15%), H-1->L+3 (19%), HOMO->L+7 (34%)	H-3->L+1 (5%), H-2->L+1 (4%), H-2->L+16 (2%), H-1->L+16 (3%)
24	24797	403	0.0076	H-12->LUMO (96%)	
25	24838	402	0.0	H-14->LUMO (48%), H-13->LUMO (18%), H-10->LUMO (28%)	
26	25288	395	0.0	H-2->L+1 (42%), H-1->L+3 (23%)	H-14->LUMO (7%), H-10->LUMO (6%), H-3->L+1 (4%), H-1->L+1 (3%), HOMO->L+7 (5%)

27	25341	394	0.0624	H-11->LUMO (40%), H-9->LUMO (20%), H-1->L+2 (15%)	H-18->LUMO (3%), H-4->L+1 (2%), H-2->L+2 (7%), HOMO->L+6 (3%)
28	25383	393	0.0	H-14->LUMO (24%), H-5->L+1 (12%), H-1->L+5 (16%)	H-13->LUMO (8%), H-10->LUMO (7%), H-5->L+3 (3%), H-2->L+1 (4%), H-2->L+3 (5%), H-1->L+3 (9%)
29	25529	391	0.0	H-5->L+1 (60%), H-5->L+3 (11%)	H-14->LUMO (8%), H-13->LUMO (2%), H-10->LUMO (4%)
30	25660	389	0.0788	H-1->L+4 (84%)	H-3->L+2 (3%), H-2->L+4 (6%)
31	25877	386	0.0	H-1->L+5 (58%)	H-14->LUMO (8%), H-13->LUMO (7%), H-10->LUMO (6%), H-5->L+16 (2%), H-2->L+5 (5%), H-1->L+3 (3%)
32	26457	377	0.0	H-5->L+16 (15%), H-3->L+16 (22%)	H-5->L+9 (5%), H-5->L+17 (4%), H-3->L+3 (5%), H-3->L+9 (6%), H-3->L+15 (2%), H-3->L+17 (8%), H-2->L+3 (3%), H-1->L+5 (8%)
33	26593	376	0.0676	H-15->LUMO (69%)	H-20->LUMO (3%), H-18->LUMO (6%), H-11->LUMO (3%), H-2->L+2 (2%), HOMO->L+9 (4%)
34	26692	374	0.0	H-3->L+16 (14%), H-2->L+3 (27%)	H-5->L+1 (5%), H-5->L+9 (2%), H-5->L+16 (9%), H-5->L+17 (2%), H-3->L+1 (2%), H-3->L+9 (3%), H-3->L+17 (5%), H-2->L+1 (4%), H-1->L+3 (3%)
35	26759	373	0.0736	H-2->L+2 (79%)	H-11->LUMO (7%), H-3->L+2 (4%)
36	27276	366	0.0	H-5->L+16 (13%), H-2->L+3 (45%)	H-5->L+9 (4%), H-5->L+17 (3%), H-3->L+1 (3%), H-3->L+3 (4%), H-3->L+5 (2%), H-3->L+16 (3%), H-3->L+17 (2%), H-2->L+5 (2%)
37	27332	365	0.0872	H-4->L+1 (10%), H-3->L+2 (56%), H-2->L+4 (20%)	H-2->L+2 (3%)
38	27997	357	0.0096	H-4->L+1 (57%), H-3->L+2 (13%), H-3->L+4 (16%)	H-18->LUMO (3%), H-2->L+2 (2%)
39	28082	356	0.0	H-3->L+3 (48%), H-3->L+5 (21%), H-2->L+5 (10%)	H-5->L+16 (4%)
40	28139	355	0.1397	H-3->L+2 (11%), H-2->L+4 (30%), H-1->L+7 (40%)	H-4->L+6 (4%), H-3->L+4 (2%), H-2->L+7 (2%), H-1->L+4 (2%)
41	28155	355	0.0	H-3->L+3 (12%), H-2->L+5 (22%), H-1->L+6 (50%)	H-4->L+7 (5%), H-2->L+6 (2%)
42	28352	352	0.0344	H-20->LUMO (20%), H-18->LUMO (33%), H-17->LUMO (19%)	H-15->LUMO (4%), H-3->L+2 (3%), H-2->L+4 (4%), H-1->L+7 (4%), HOMO->L+9 (6%)
43	28601	349	0.4403	H-3->L+4 (61%), H-1->L+7 (13%)	H-4->L+1 (8%), H-3->L+2 (2%), H-2->L+4 (3%)
44	28650	349	0.1944	H-3->L+4 (12%), H-2->L+4 (28%), H-1->L+7 (27%)	H-20->LUMO (2%), H-18->LUMO (2%), H-17->LUMO (3%), H-15->LUMO (2%), H-4->L+1 (7%), H-3->L+2 (2%)
45	28673	348	0.0	H-2->L+5 (42%), H-1->L+6 (33%)	H-3->L+3 (7%), H-1->L+5 (3%)
46	29078	343	0.0	H-3->L+5 (57%)	H-4->L+2 (4%), H-3->L+1 (2%), H-3->L+3 (8%), H-2->L+3 (5%), H-2->L+5 (4%), HOMO->L+8 (3%), HOMO->L+10 (3%)
47	29461	339	0.0072	H-20->LUMO (29%), H-19->LUMO (21%), H-17->LUMO (41%)	
48	29507	338	0.0	HOMO->L+8 (85%)	H-4->L+2 (4%)
49	29700	336	0.0	H-5->L+3 (70%)	H-5->L+1 (9%), H-5->L+5 (9%), H-5->L+16 (3%), H-5->L+17 (4%)
50	29794	335	0.2712	H-4->L+3 (17%), HOMO->L+9 (46%)	H-18->LUMO (2%), H-15->LUMO (4%), H-6->L+1 (4%), H-4->L+1 (3%), HOMO->L+11 (4%), HOMO->L+16 (7%), HOMO->L+17 (2%)

Table S13. TD DFT Calculated Electronic Transitions for **8b**

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	6819	1466	0.0001	HOMO->LUMO (98%)	
2	11087	901	0.0295	H-2->LUMO (24%), H-1->LUMO (71%)	H-3->LUMO (3%)
3	13291	752	0.0132	H-3->LUMO (69%), H-2->LUMO (25%)	
4	15109	661	0.0017	H-5->LUMO (96%)	H-4->LUMO (3%)
5	16017	624	0.9421	H-3->LUMO (22%), H-2->LUMO (48%), H-1->LUMO (24%)	HOMO->L+1 (3%)
6	18606	537	0.0039	H-4->LUMO (85%)	H-6->LUMO (3%), H-5->LUMO (3%), H-1->L+1 (2%)
7	19329	517	0.2225	HOMO->L+1 (80%)	H-7->LUMO (5%), H-3->LUMO (2%), HOMO->L+3 (2%), HOMO->L+5 (7%)
8	19971	500	0.0009	HOMO->L+2 (93%)	H-6->LUMO (5%)
9	20421	489	0.0893	HOMO->L+3 (89%)	H-7->LUMO (6%), HOMO->L+5 (3%)
10	20556	486	0.0014	H-6->LUMO (76%), HOMO->L+4 (14%)	HOMO->L+2 (5%)
11	21130	473	0.0022	H-6->LUMO (10%), HOMO->L+4 (76%)	H-1->L+1 (9%)
12	21775	459	0.0015	H-1->L+1 (66%)	H-4->LUMO (3%), H-3->L+1 (3%), H-3->L+3 (2%), H-2->L+1 (7%), H-1->L+3 (5%), H-1->L+5 (2%), HOMO->L+4 (6%)
13	21958	455	0.3582	H-7->LUMO (36%), HOMO->L+5 (57%)	H-9->LUMO (3%)
14	23240	430	0.0001	H-8->LUMO (96%)	
15	23346	428	0.1173	H-13->LUMO (14%), H-9->LUMO (44%), H-7->LUMO (13%), HOMO->L+5 (13%)	HOMO->L+6 (5%)
16	23806	420	0.1366	H-9->LUMO (35%), H-7->LUMO (29%)	H-18->LUMO (2%), H-15->LUMO (5%), H-1->L+2 (4%), H-1->L+4 (2%), HOMO->L+1 (4%), HOMO->L+3 (3%), HOMO->L+5 (7%), HOMO->L+6 (3%)
17	23949	417	0.0001	H-2->L+1 (26%), H-1->L+3 (19%), HOMO->L+7 (35%)	H-10->LUMO (4%), H-1->L+1 (6%)
18	24161	413	0.0142	H-13->LUMO (12%), H-1->L+2 (55%), HOMO->L+6 (19%)	H-1->L+16 (4%)
19	24278	411	0.0562	H-2->L+16 (11%), H-1->L+16 (22%), HOMO->L+6 (49%)	H-18->L+16 (2%), H-1->L+2 (4%)
20	24365	410	0.0001	H-1->L+3 (19%), HOMO->L+7 (56%)	H-10->LUMO (7%), H-2->L+1 (3%), H-1->L+1 (4%)
21	24416	409	0.0004	H-14->LUMO (24%), H-10->LUMO (21%), H-3->L+1 (22%), H-1->L+3 (21%)	H-2->L+1 (2%), H-1->L+1 (2%)
22	24488	408	0.0729	H-2->L+16 (12%), H-1->L+2 (23%), H-1->L+16 (22%), HOMO->L+6 (15%)	H-18->L+16 (2%), H-11->LUMO (8%), HOMO->L+5 (2%)
23	24642	405	0.0245	H-11->LUMO (84%)	H-13->LUMO (3%), HOMO->L+6 (3%)
24	24645	405	0.0011	H-12->LUMO (64%), H-10->LUMO (28%)	H-3->L+1 (5%)
25	24767	403	0.0	H-14->LUMO (14%), H-12->LUMO (21%), H-10->LUMO (10%), H-3->L+1 (31%), H-2->L+1 (11%)	H-3->L+5 (2%), H-1->L+5 (3%)
26	25279	395	0.0049	H-14->LUMO (25%), H-2->L+1 (10%), H-1->L+3 (11%), H-1->L+5 (30%)	H-12->LUMO (4%), H-10->LUMO (5%), H-2->L+3 (5%)
27	25303	395	0.0027	H-13->LUMO (22%), H-1->L+4 (45%)	H-9->LUMO (7%), H-4->L+1 (2%), H-2->L+2 (9%), H-1->L+2 (6%)
28	25443	393	0.01	H-14->LUMO (12%), H-10->LUMO (12%), H-3->L+1 (16%), H-2->L+1 (30%), H-1->L+3 (11%)	H-12->LUMO (3%), H-2->L+3 (4%), H-1->L+1 (2%), HOMO->L+7 (2%)
29	25519	391	0.1137	H-13->LUMO (28%), H-1->L+4 (41%)	H-9->LUMO (3%), H-2->L+2 (4%), H-2->L+4 (5%), H-1->L+2 (4%), HOMO->L+5 (2%)
30	25746	388	0.0015	H-14->LUMO (13%), H-1->L+5 (54%)	H-12->LUMO (3%), H-10->LUMO (9%), H-3->L+1 (5%), H-2->L+5 (5%), H-1->L+3 (4%)
31	25864	386	0.0031	H-5->L+1 (71%), H-5->L+3 (14%)	H-5->L+5 (4%), H-3->L+16 (3%)
32	26615	375	0.0381	H-13->LUMO (11%), H-2->L+2 (75%)	H-3->L+2 (3%)
33	26767	373	0.0001	H-5->L+16 (13%), H-2->L+3 (56%)	H-14->LUMO (7%), H-3->L+5 (2%), H-2->L+1 (3%), H-1->L+3 (4%)
34	27113	368	0.1026	H-3->L+2 (26%), H-3->L+16 (32%), H-2->L+4	H-19->L+16 (3%), H-15->LUMO

				(10%)	(3%), H-15->L+16 (2%), H-4->L+1 (3%), H-3->L+4 (2%), H-2->L+16 (2%)
35	27285	366	0.0935	H-15->LUMO (48%), H-3->L+16 (20%)	H-3->L+2 (7%), H-2->L+4 (2%), HOMO->L+9 (4%)
36	27410	364	0.0018	H-15->LUMO (21%), H-3->L+2 (19%), H-3->L+16 (14%), H-2->L+4 (16%)	H-4->L+1 (6%), H-1->L+7 (3%), HOMO->L+9 (2%)
37	27604	362	0.0002	H-5->L+16 (37%), H-3->L+3 (14%), H-2->L+3 (14%)	H-3->L+1 (2%), H-2->L+5 (9%), H-1->L+6 (9%)
38	28014	356	0.1363	H-4->L+1 (30%), H-3->L+2 (26%), H-3->L+4 (23%)	H-2->L+2 (2%), H-2->L+4 (7%)
39	28046	356	0.1194	H-4->L+1 (19%), H-2->L+4 (17%), H-1->L+7 (39%)	H-4->L+6 (4%), H-3->L+2 (6%), H-3->L+4 (3%), H-2->L+7 (3%)
40	28070	356	0.0079	H-3->L+3 (15%), H-2->L+5 (13%), H-1->L+6 (50%)	H-5->L+16 (5%), H-4->L+7 (5%), H-2->L+6 (3%)
41	28201	354	0.0006	H-20->LUMO (41%), H-5->L+16 (12%), H-3->L+3 (21%)	H-16->LUMO (6%), H-3->L+5 (9%)
42	28348	352	0.0	H-20->LUMO (39%), H-3->L+3 (11%), H-3->L+5 (23%)	H-16->LUMO (3%), H-5->L+16 (7%), H-2->L+5 (7%)
43	28402	352	0.1653	H-4->L+1 (15%), H-2->L+4 (28%), H-1->L+7 (38%)	H-3->L+2 (3%), H-3->L+4 (4%)
44	28627	349	0.0103	H-2->L+5 (48%), H-1->L+6 (25%)	H-20->LUMO (4%), H-3->L+3 (5%), H-1->L+5 (3%), HOMO->L+8 (2%)
45	28723	348	0.3342	H-4->L+1 (11%), H-3->L+4 (60%)	H-3->L+2 (6%), H-2->L+4 (3%), H-1->L+7 (4%)
46	28949	345	0.0025	HOMO->L+8 (79%)	H-20->LUMO (3%), H-3->L+3 (3%), H-3->L+5 (6%)
47	29016	344	0.0028	H-3->L+3 (14%), H-3->L+5 (44%), HOMO->L+8 (11%)	H-20->LUMO (3%), H-5->L+16 (4%), H-4->L+2 (3%), H-3->L+1 (4%), H-2->L+3 (7%)
48	29415	339	0.0028	H-19->LUMO (31%), H-18->LUMO (14%), H-17->LUMO (45%)	
49	29761	336	0.0023	H-5->L+3 (57%), H-5->L+5 (10%), H-4->L+3 (17%)	H-5->L+1 (9%)
50	29790	335	0.0018	H-4->L+2 (80%)	H-3->L+3 (4%)

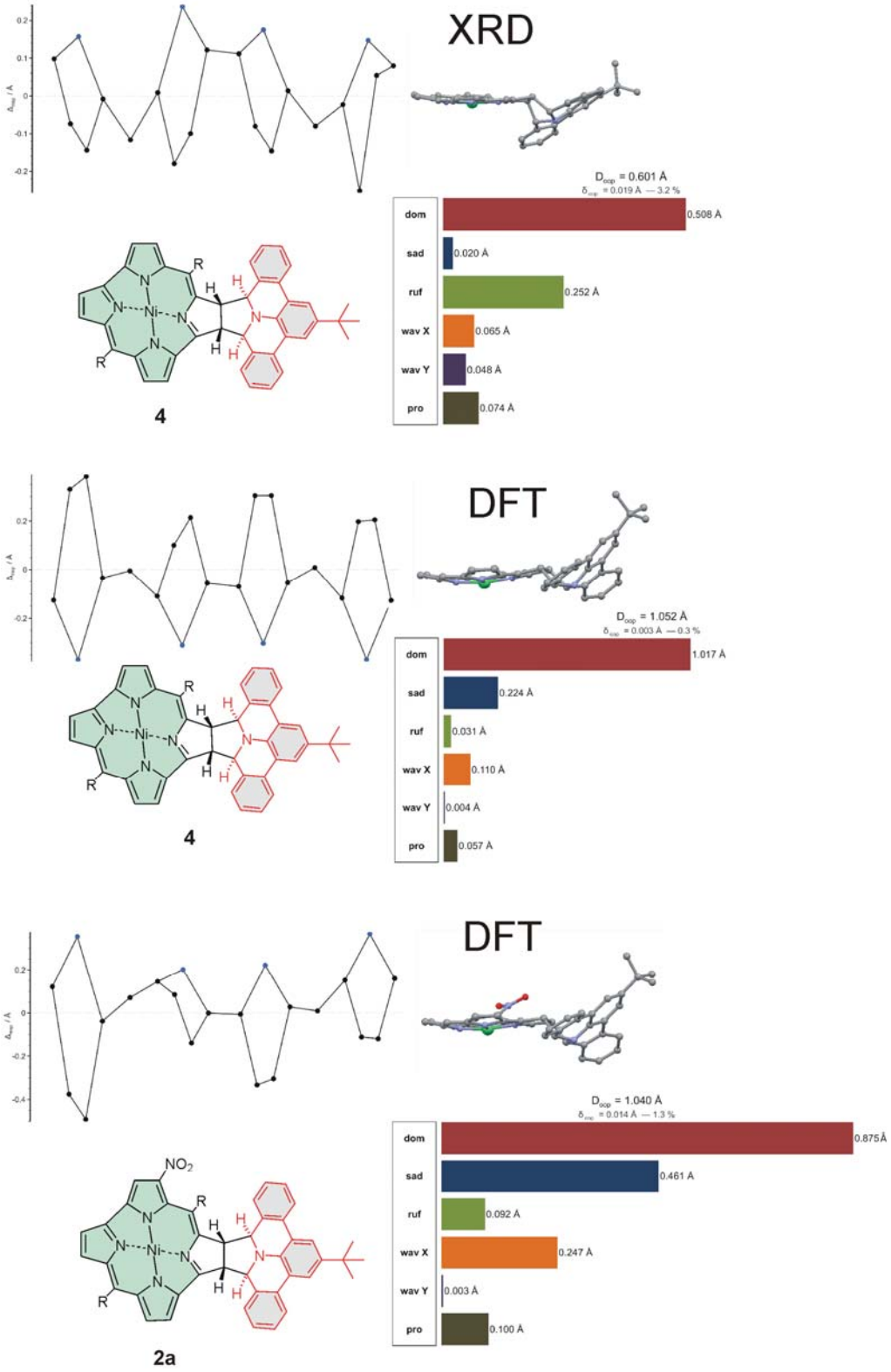


Figure S136. Out-of-plane displacement for norcorrolatonickel(II) moiety in **2a** and **4.** Color code: brown, doming (*dom*); dark blue, saddling (*sad*); green, ruffling (*ruf*); orange, waving *x* (wav X); purple, waving *y* (wav Y); olive, propellering (*pro*). D_{oop}, the total out-of-plane distortion; δ_{oop}, difference between D_{oop} calculated by *PorphyStruct*[11] and estimated by of the normal-coordinate structure decomposition (NSD) simulation.[12,13]

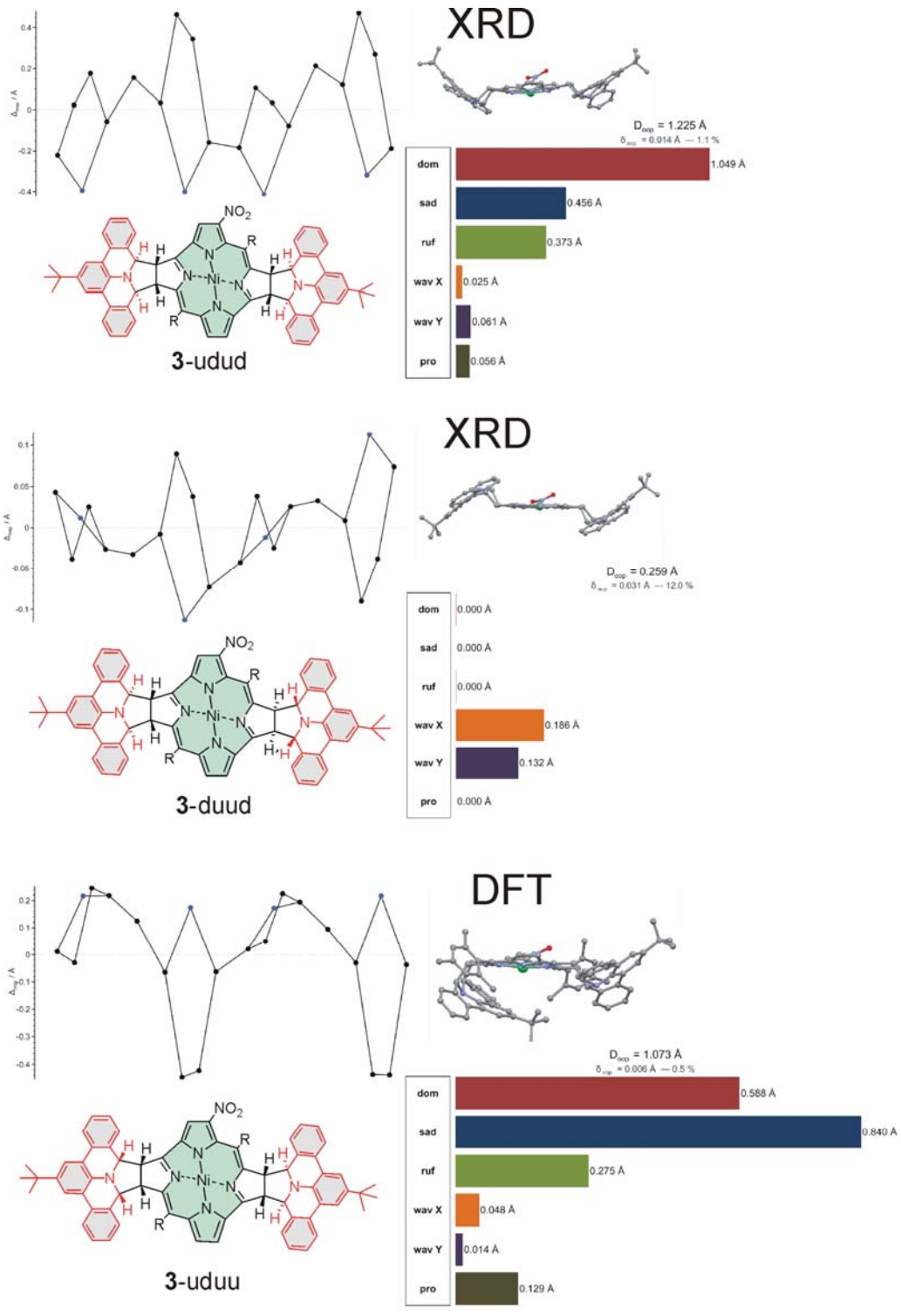


Figure S137. Out-of-plane displacement for norcorrolatonickel(II) moiety in the stereoisomers of **3**. Color code: brown, doming (*dom*); dark blue, saddling (*sad*); green, ruffling (*ruf*); orange, waving *x* (wav X); purple, waving *y* (wav Y); olive, propellering (*pro*). D_{oop}, the total out-of-plane distortion; δ_{oop}, difference between D_{oop} calculated by *PorphyStruct*[11] and estimated by of the normal-coordinate structure decomposition (NSD) simulation.[12,13]

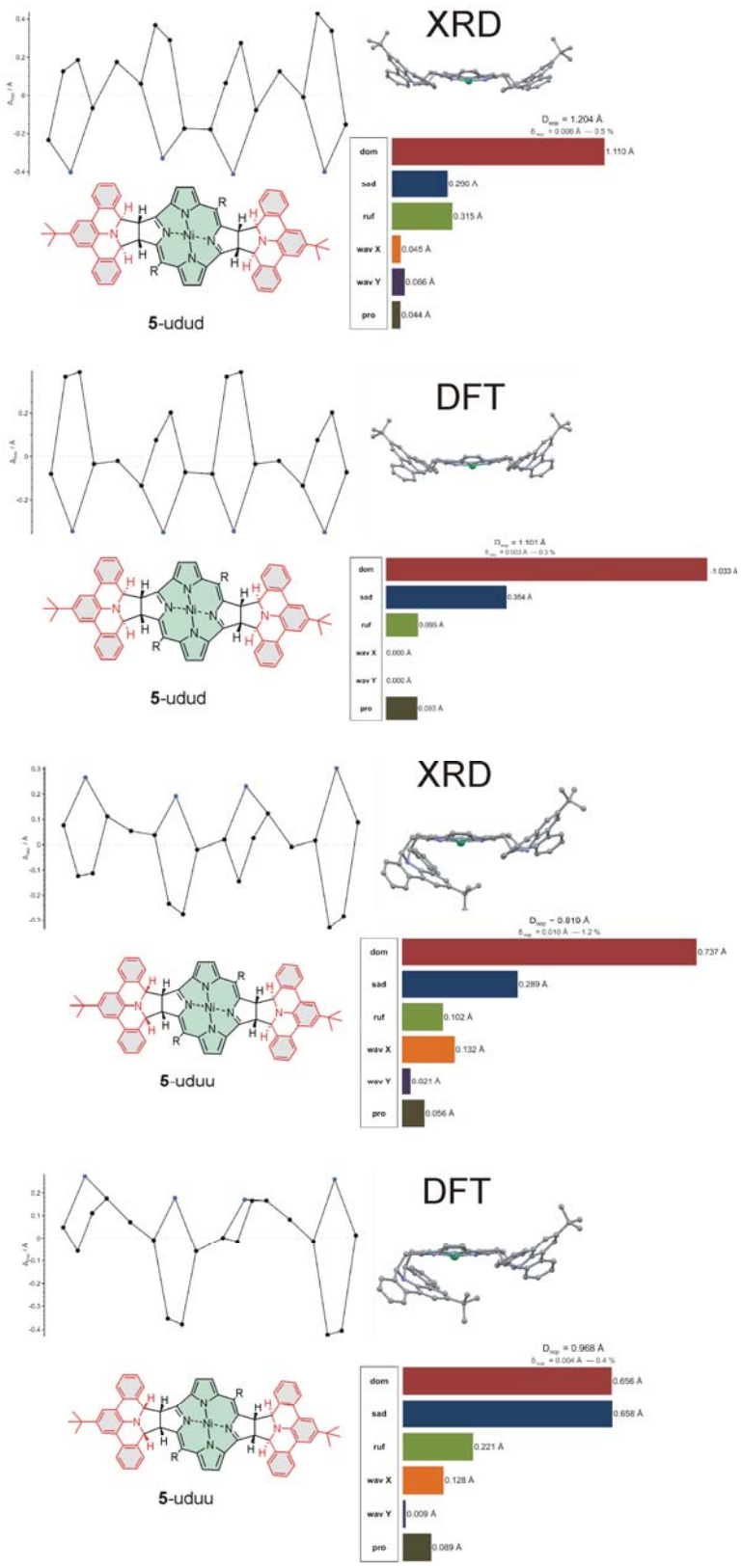


Figure S138. Out-of-plane displacement for norcorrolatonickel(II) moiety in the stereoisomers of **5**. Color code: brown, doming (*dom*); dark blue, saddling (*sad*); green, ruffling (*ruf*); orange, waving *x* (wav X); purple, waving *y* (wav Y); olive, propellering (*pro*). D_{oop}, the total out-of-plane distortion; δ_{oop}, difference between D_{oop} calculated by *PorphyStruct*[11] and estimated by of the normal-coordinate structure decomposition (NSD) simulation.[12,13]

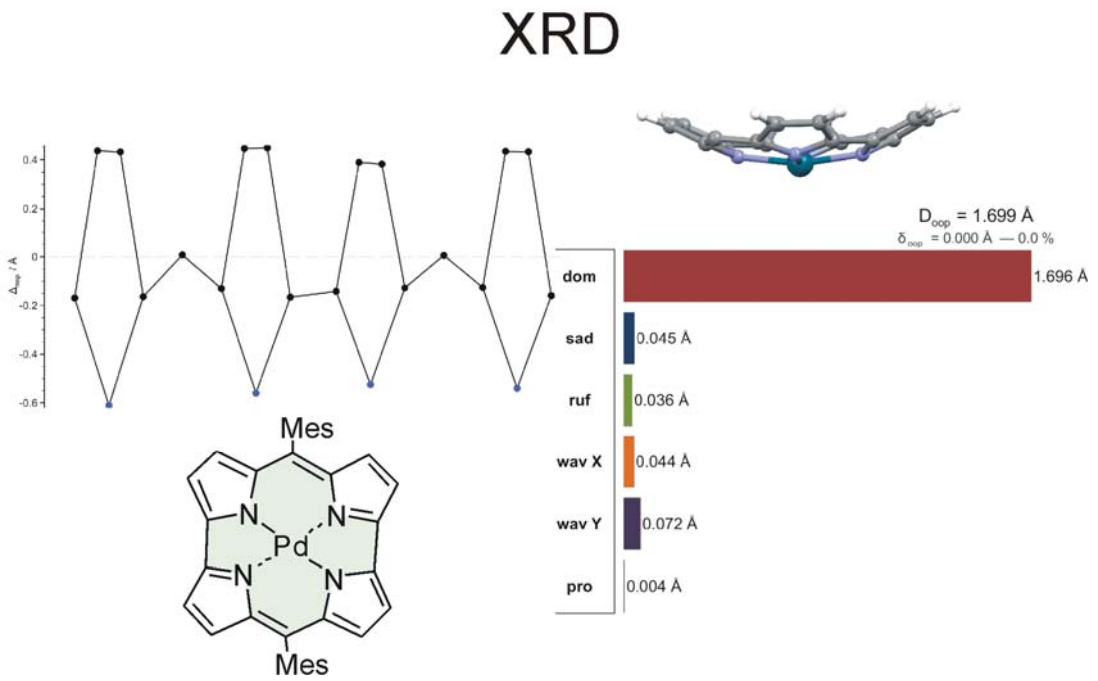


Figure S139. Out-of-plane displacement for norcorrolatopalladium(II).[14] Color code: brown, doming (*dom*); dark blue, saddling (*sad*); green, ruffling (*ruf*); orange, waving *x* (wav X); purple, waving *y* (wav Y); olive, propellering (*pro*). D_{oop}, the total out-of-plane distortion; δ_{oop}, difference between D_{oop} calculated by *PorphyStruct*[11] and estimated by the normal-coordinate structure decomposition (NSD) simulation.[12,13]

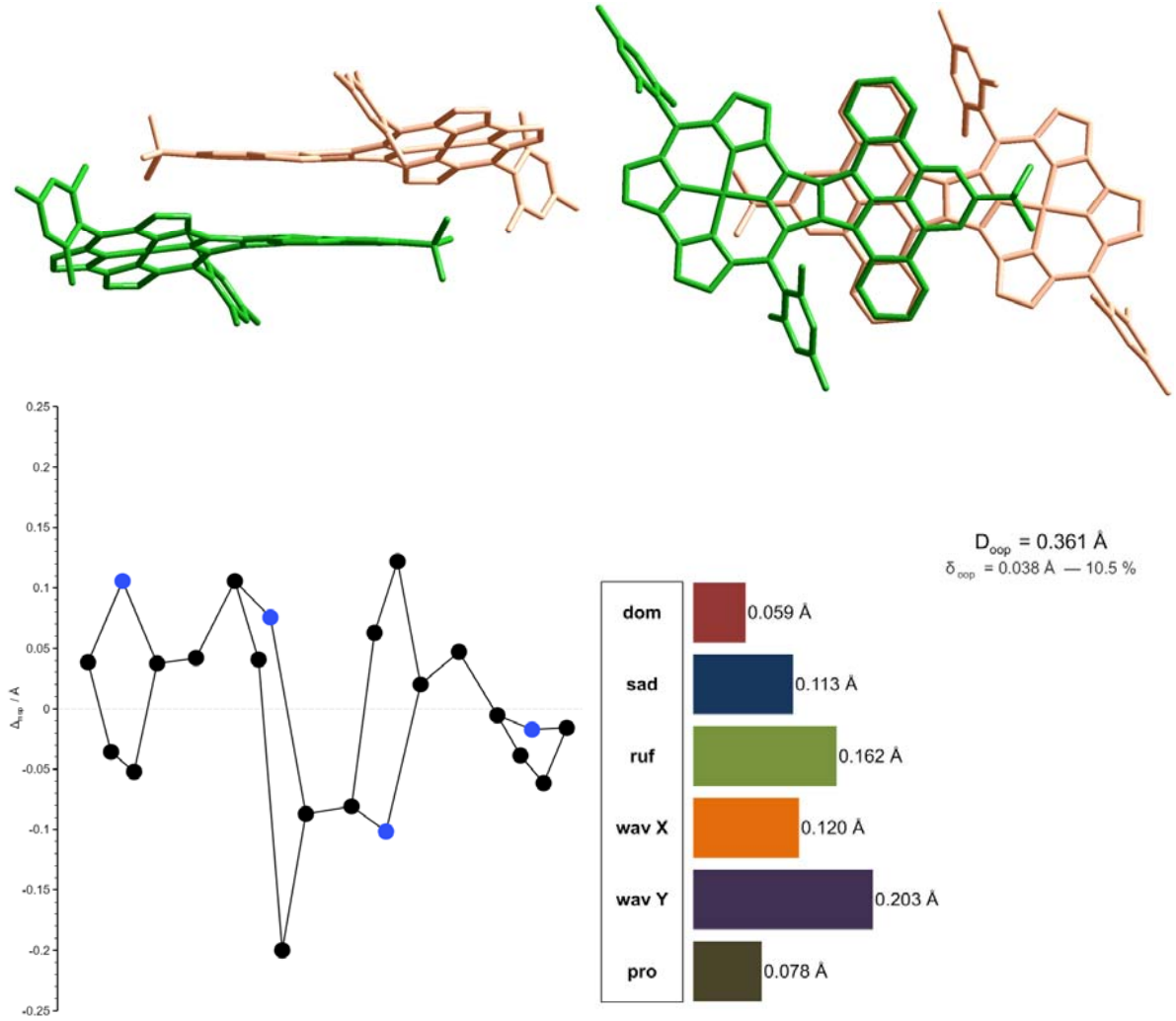


Figure S140. Two projections of a fragment of the packing diagram of **6** (top) and out-of-plane displacement for **6** in the solid state (bottom). Color code: brown, doming (*dom*); dark blue, saddling (*sad*); green, ruffling (*ruf*); orange, waving *x* (wav X); purple, waving *y* (wav Y); olive, propellering (*pro*). D_{oop}, the total out-of-plane distortion; δ_{oop}, difference between D_{oop} calculated by *PorphyStruct*[11] and estimated by the normal-coordinate structure decomposition (NSD) simulation.[12,13]

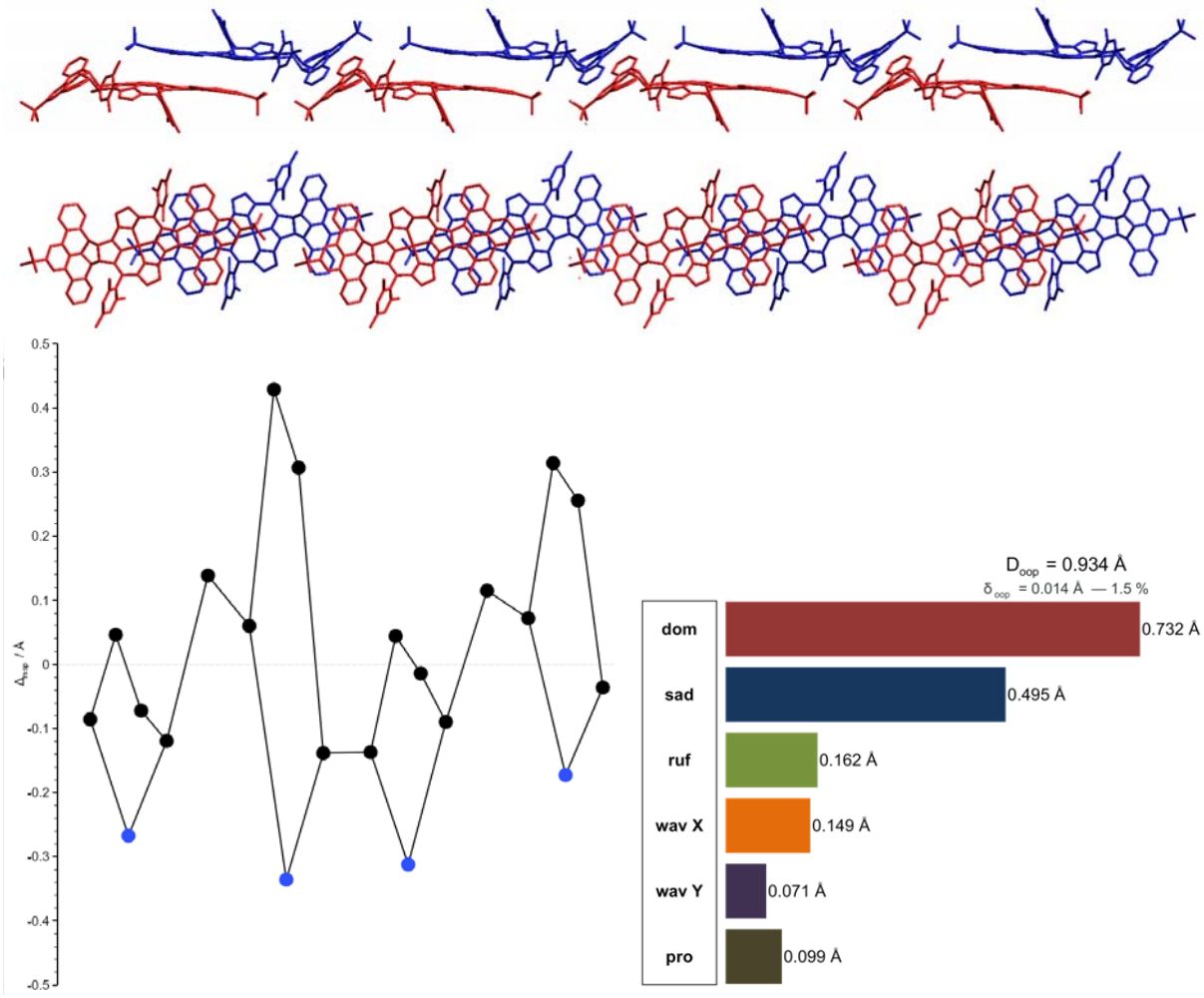


Figure S141. Two projections of a part of the packing diagram of **7** (top) and out-of-plane displacement for **7** in the solid state (bottom). Color code: brown, doming (*dom*); dark blue, saddling (*sad*); green, ruffling (*ruf*); orange, waving *x* (wav X); purple, waving *y* (wav Y); olive, propellering (*pro*). D_{oop}, the total out-of-plane distortion; δ_{oop}, difference between D_{oop} calculated by *PorphyStruct*[11] and estimated by the normal-coordinate structure decomposition (NSD) simulation.[12,13]

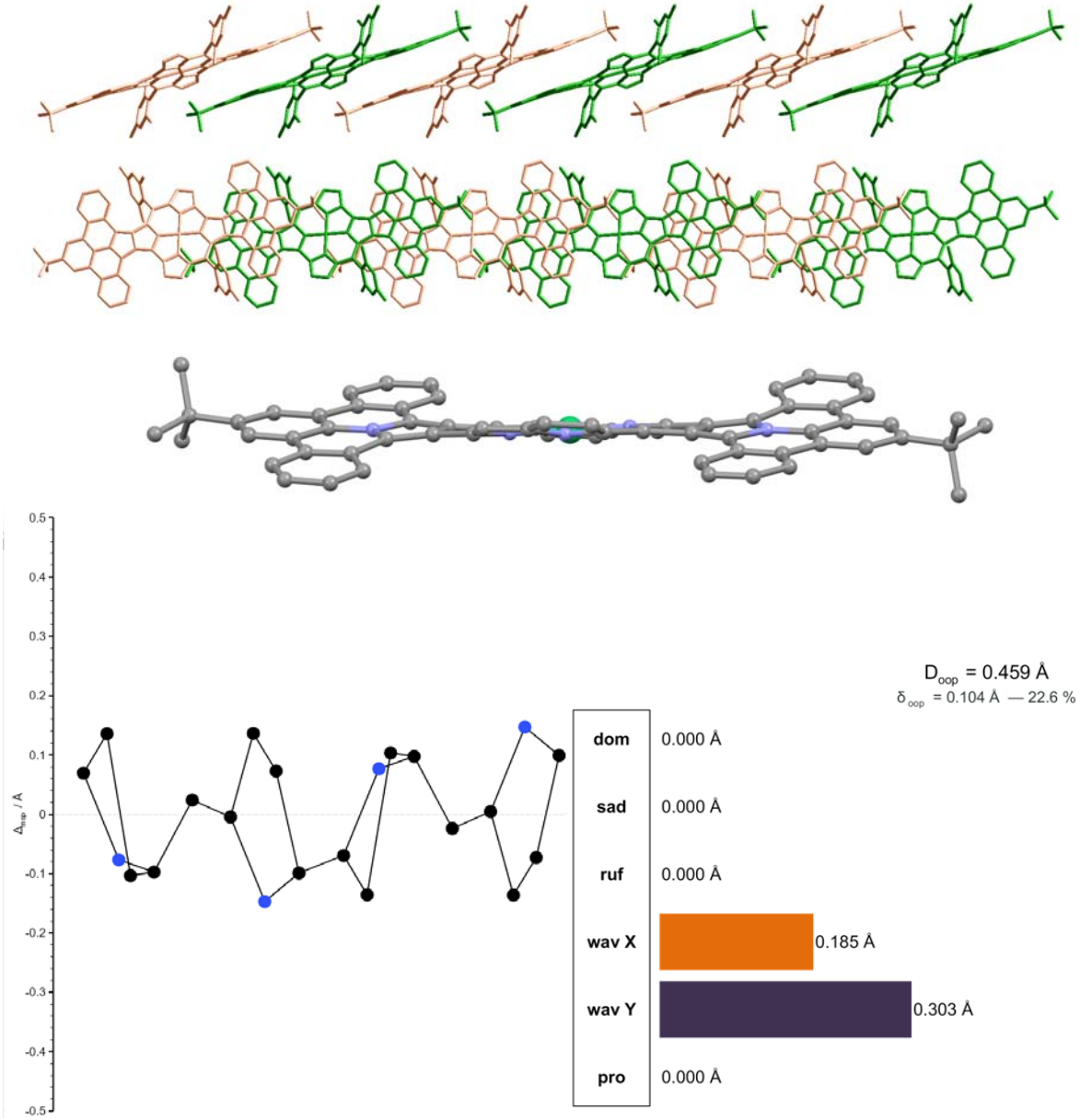


Figure S142. Two projections of a part of the packing diagram of **8** (top), side view of the molecular structure of **8** (balls and sticks representation), and out-of-plane displacement for **8** in the solid state (bottom). Color code: brown, doming (*dom*); dark blue, saddling (*sad*); green, ruffling (*ruf*); orange, waving *x* (wav X)purple, waving *y* (wav Y); olive propellering (*pro*). D_{oop}, the total out-of-plane distortion; δ_{oop}, difference between D_{oop} calculated by *PorphyStruct*[11] and estimated by the normal-coordinate structure decomposition (NSD) simulation.[12,13]

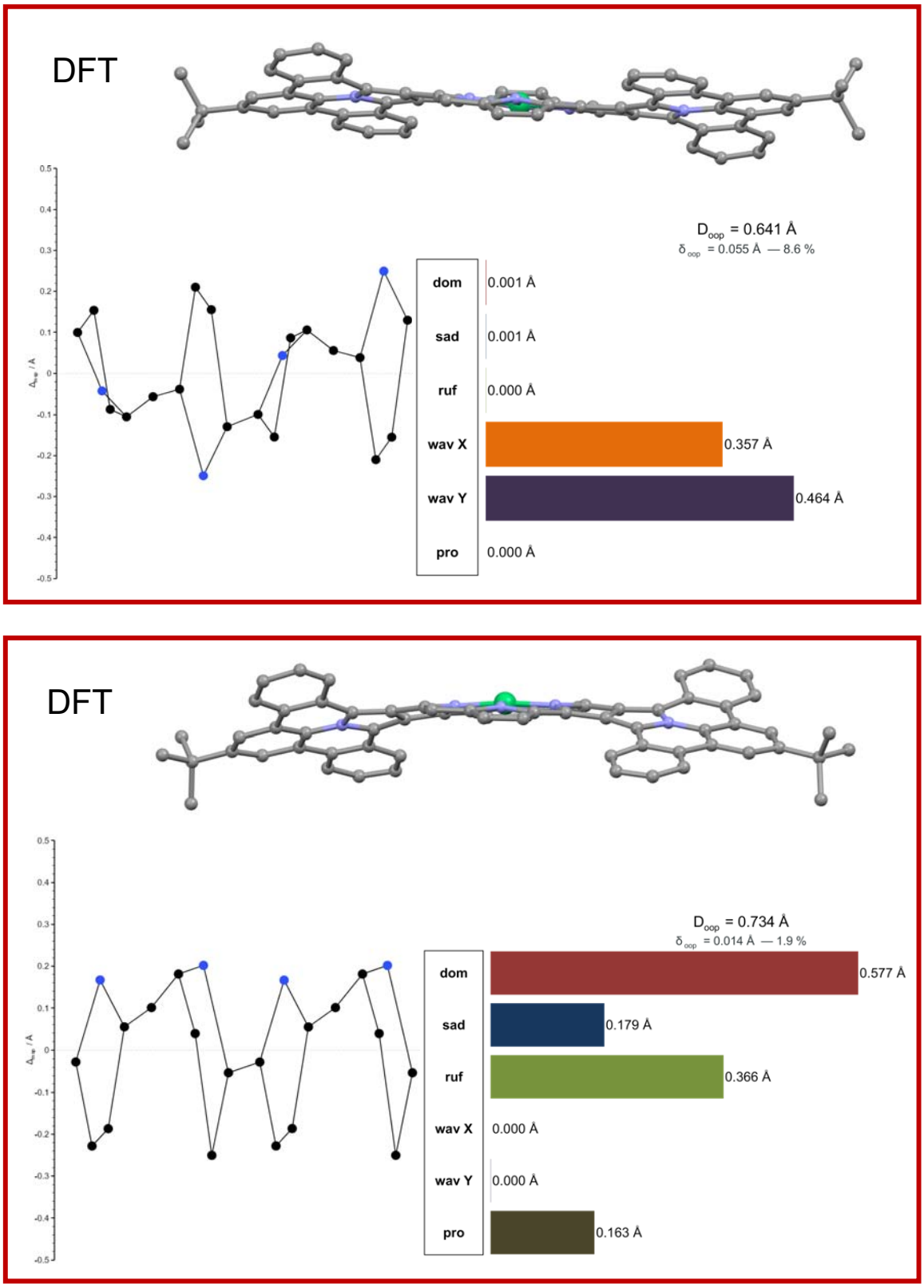


Figure S143. Side view of a projection of the DFT calculated structure for lowest-energy conformer of **8** and out-of-plane displacement (upper panel) and analogous presentations for the 1.11 kcal/mol less stable conformer **8b** (lower panel). Color code: brown, doming (*dom*); dark blue, saddling (*sad*); green, ruffling (*ruf*); orange, waving *x* (wav X)purple, waving *y* (wav Y); olive propellering (*pro*). D_{oop}, the total out-of-plane distortion; δ_{oop}, difference between D_{oop} calculated by *PorphyStruct*[11] and estimated by the normal-coordinate structure decomposition (NSD) simulation.[12,13]

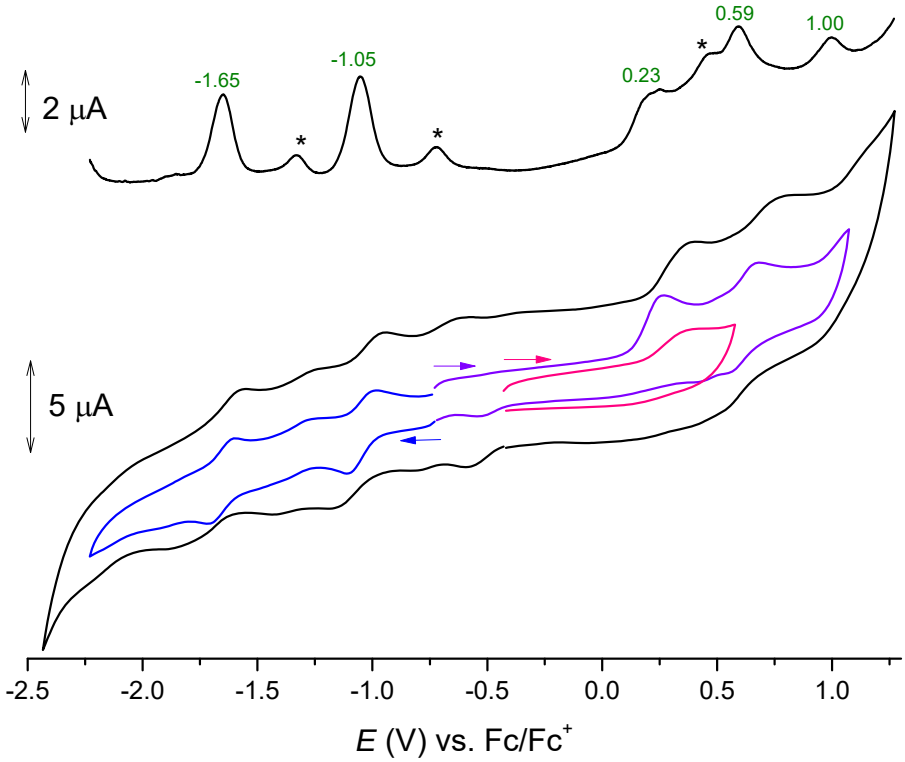


Figure S144. Cyclic (bottom) and differential pulse (top) voltammograms of **2a** in dichloromethane. The weaker peaks of retro-cycloaddition product **1**-NO_2 are marked with asterisks.

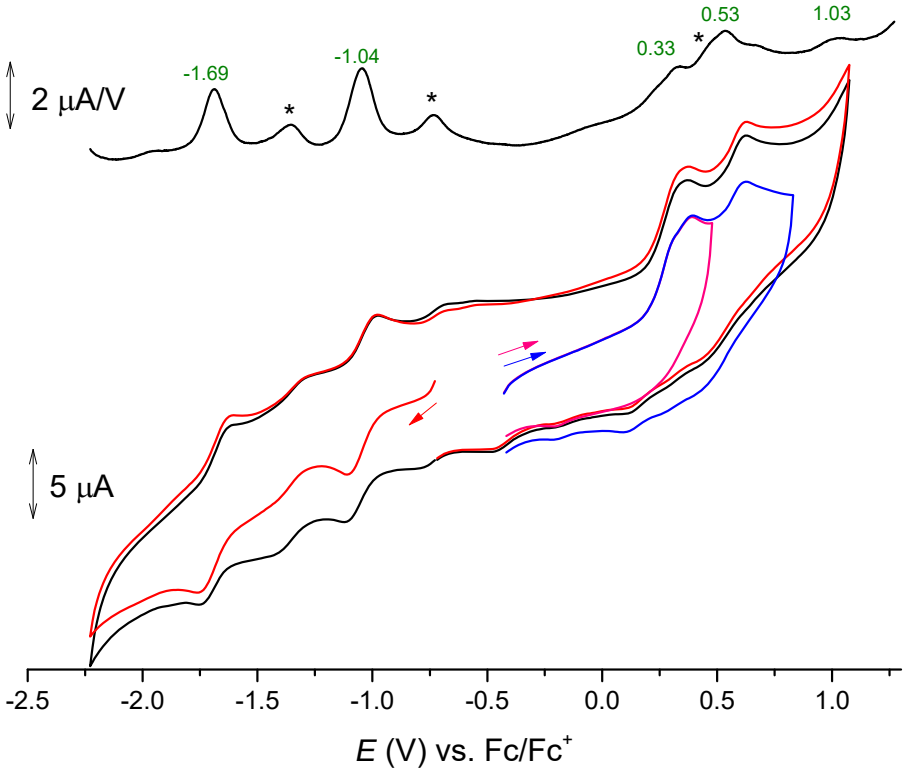


Figure S145. Cyclic (bottom) and differential pulse (top) voltammograms of **2b** in dichloromethane. The weaker peaks of retro-cycloaddition product **1**-NO_2 are marked with asterisks.

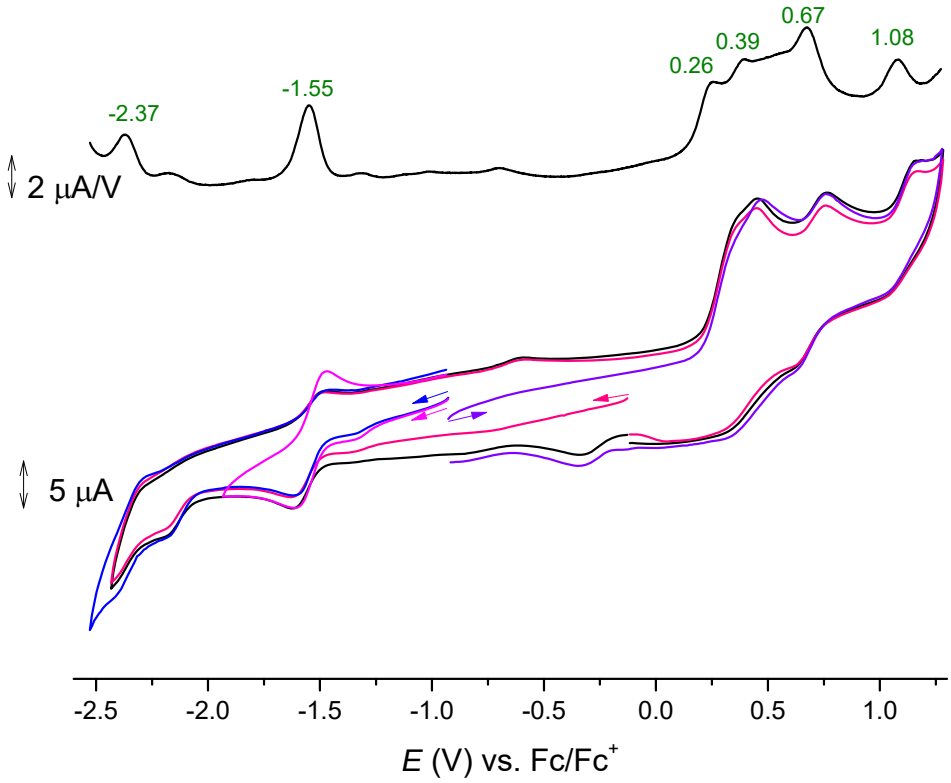


Figure S146. Cyclic (bottom) and differential pulse (top) voltammograms of **3**-ududd in dichloromethane.

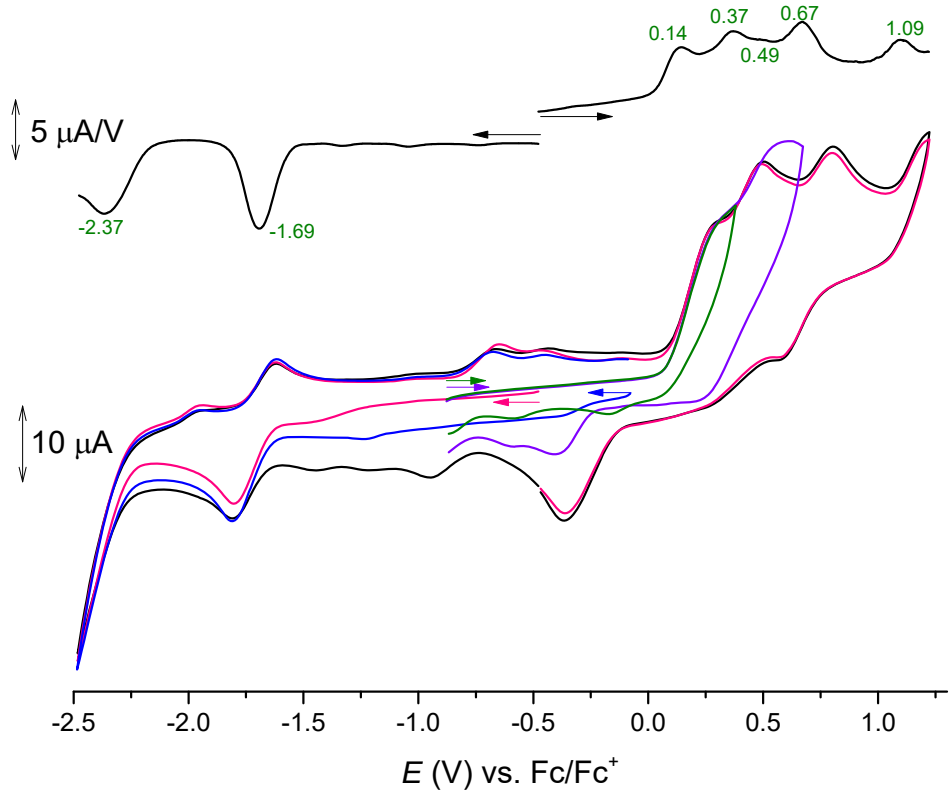


Figure S147. Cyclic (bottom) and differential pulse (top) voltammograms of **3**-uduu in dichloromethane.

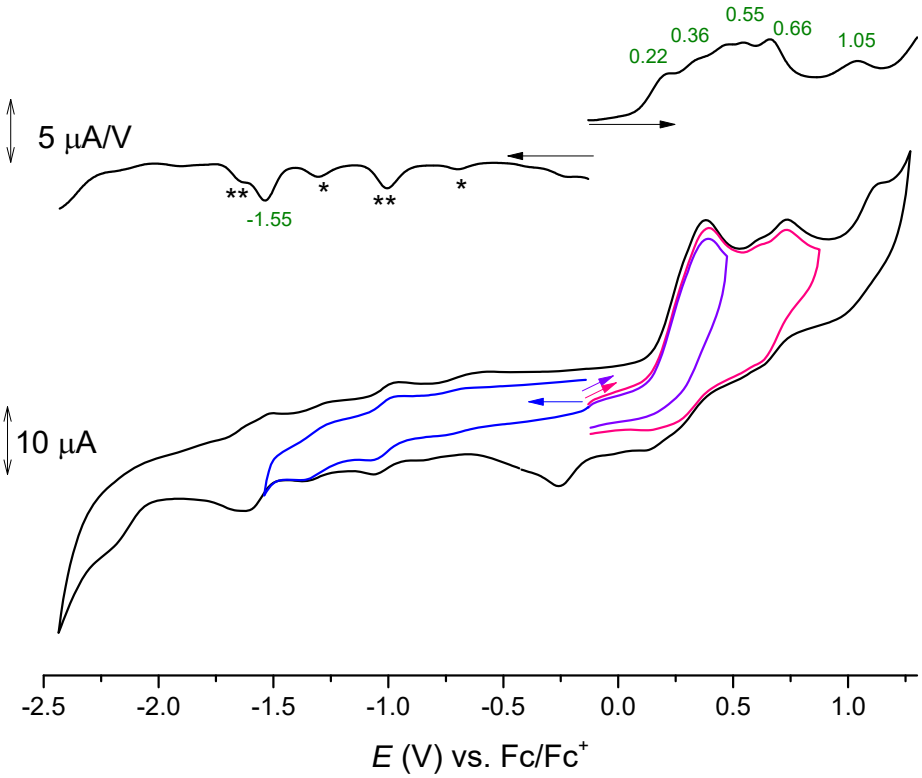


Figure S148. Cyclic (bottom) and differential pulse (top) voltammograms of **3**-duud in dichloromethane. The weaker peaks of retro-cycloaddition product **1**-NO_2 are marked with asterisks and those of **2** – with double asterisks.

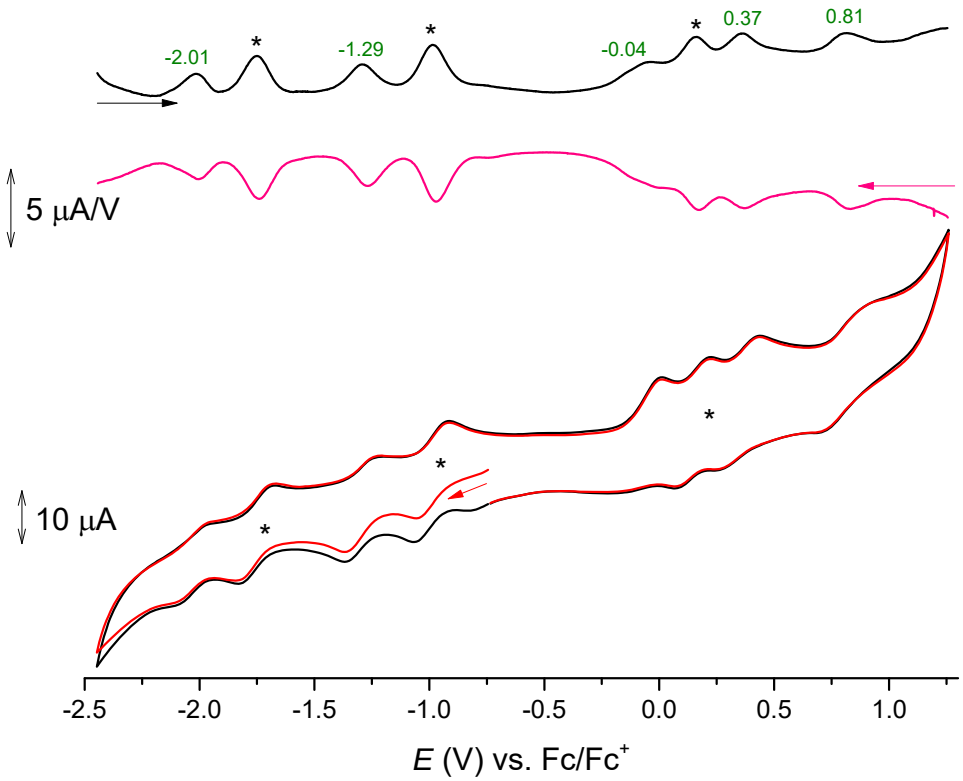


Figure S149. Cyclic (bottom) and differential pulse (top) voltammograms of **4** in dichloromethane. The peaks of retro-cycloaddition product **1**-H are marked with asterisks.

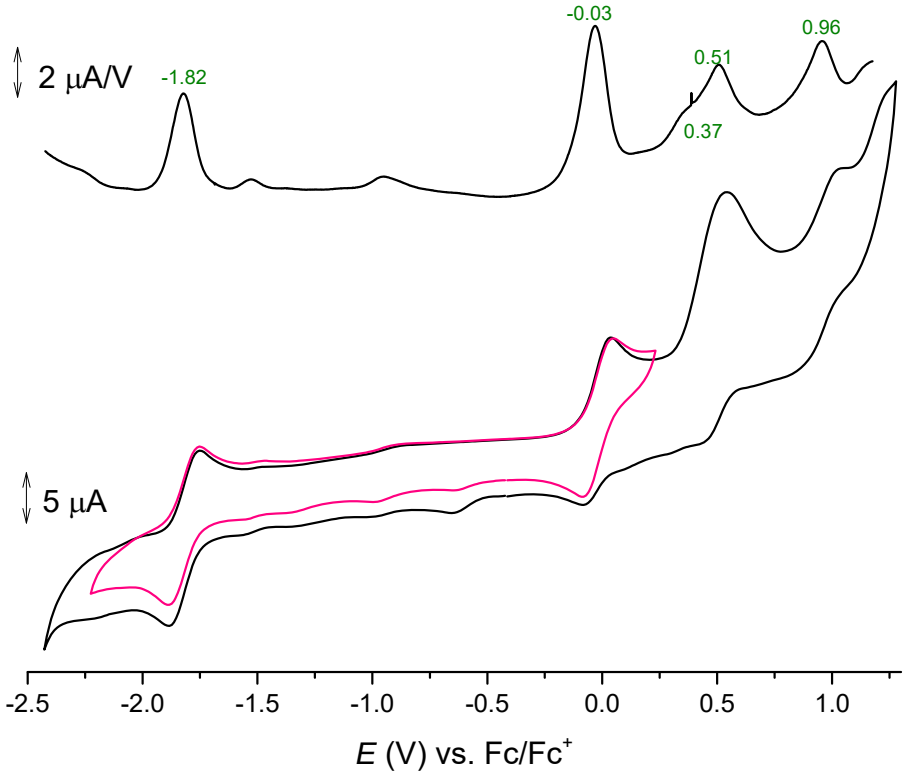


Figure S150. Cyclic (bottom) and differential pulse (top) voltammograms of **5**-ududd in dichloromethane.

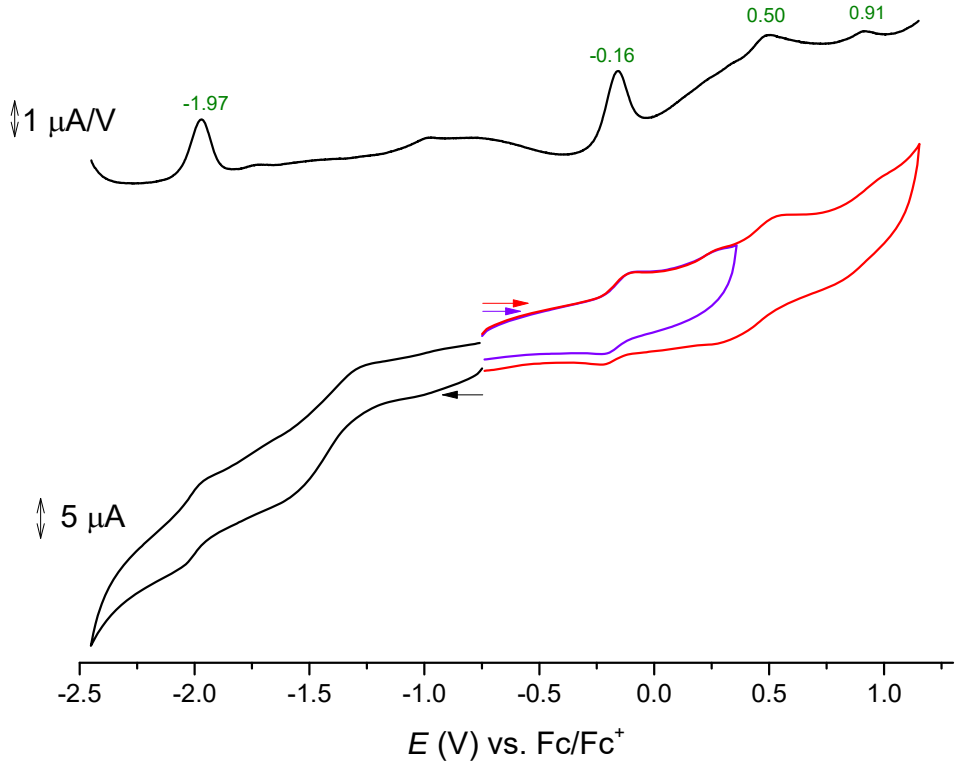


Figure S151. Cyclic (bottom) and differential pulse (top) voltammograms of **5**-uduu in dichloromethane.

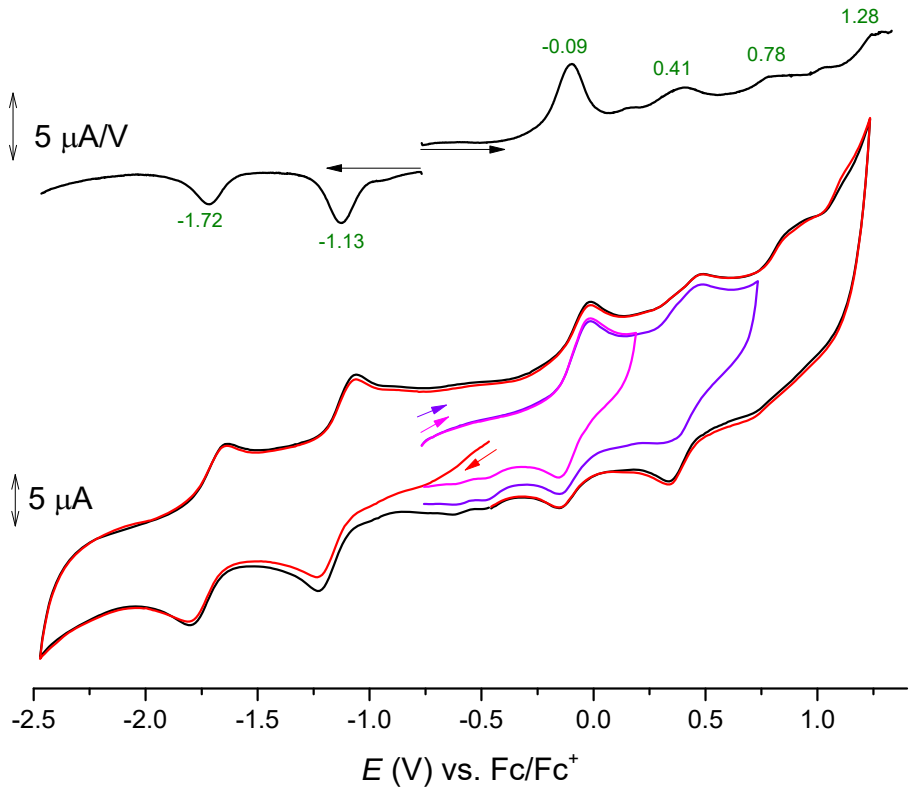


Figure S152. Cyclic (bottom) and differential pulse (top) voltammograms of **6** in dichloromethane.

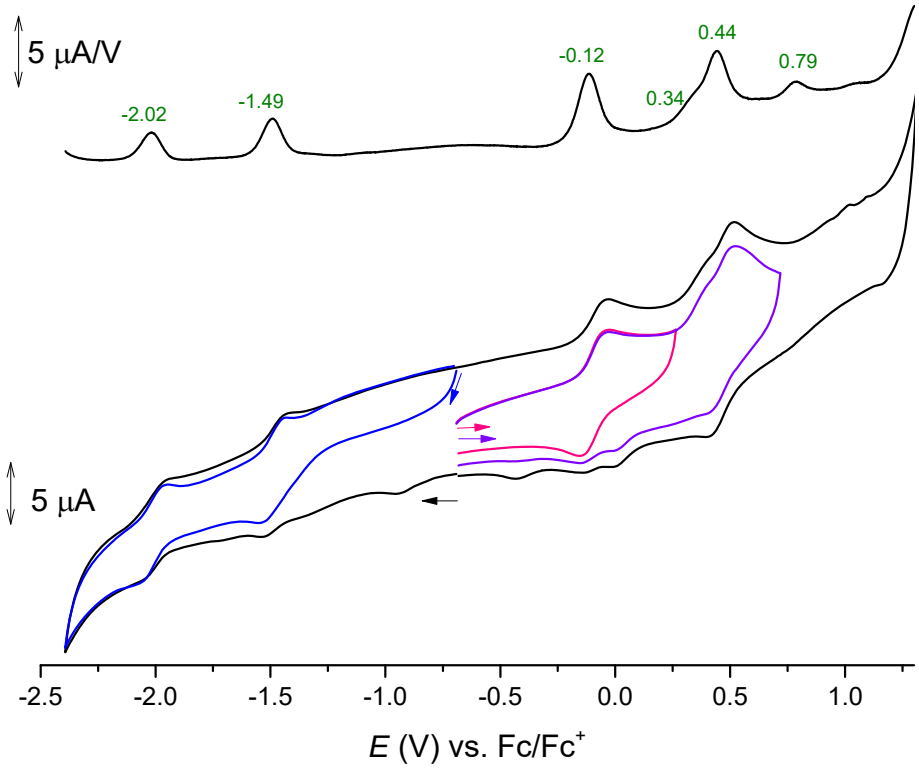


Figure S153. Cyclic (bottom) and differential pulse (top) voltammograms of **7** in dichloromethane.

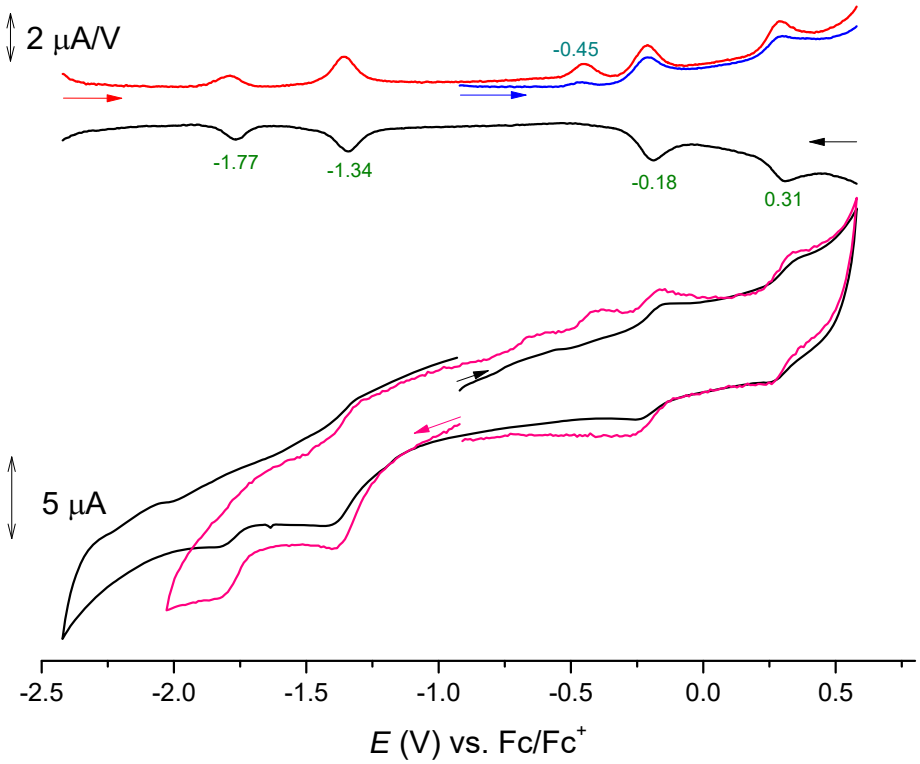


Figure S154. Cyclic (bottom) and differential pulse (top) voltammograms of **8** in dichloromethane.

Table S14. Crystallographic data for **3**-duud, **3**-udud, and **4**

Crystal data 1			
	3-DUUD	**3-UDUD**	**4**
Chemical formula	$C_{84}H_{71}N_7NiO_2 \cdot C_6H_{14}$	$2(C_{84}H_{71}N_7NiO_2) \cdot 3(C_6H_{14})$	$C_{60}H_{51}N_5Ni$
M_r	1355.35	2796.88	900.77
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$
Temperature (K)	170	170	100
a, b, c (Å)	12.3458 (2), 12.9810 (2), 16.1260 (3)	13.9400 (3), 22.0062 (3), 28.7167 (4)	10.9639 (3), 27.0997 (6), 16.6678 (5)
α, β, γ (°)	109.234 (2), 102.943 (2), 103.838 (2)	75.192 (1), 78.676 (1), 86.730 (1)	β =105.144 (3)
V (Å^3)	2236.35 (7)	8350.7 (2)	4780.4 (2)
Z	1	2	4
Radiation type	Cu Kα	Cu Kα	Cu Kα
μ (mm^{-1})	0.66	0.72	0.93
Crystal Size	0.32 × 0.18 × 0.15	0.12 × 0.11 × 0.02	0.28 × 0.24 × 0.12
Data collection			
Diffractometer	XtaLAB Synergy R, HyPix	XtaLAB Synergy R, HyPix	XtaLAB Synergy R, DW system, HyPix-Arc 150
Absorption correction	Multi-scan CrysAlis PRO 1.171.40.67a (Rigaku Oxford Diffraction, 2019) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan CrysAlis PRO 1.171.40.67a (Rigaku Oxford Diffraction, 2019) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Analytical CrysAlis PRO 1.171.41.75a (Rigaku Oxford Diffraction, 2020) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
Tmin, Tmax	0.767, 1.000	0.691, 1.000	0.831, 0.921
No. of measured, independent and observed [I > 2σ(I)] reflections	33345, 8863, 8055	123013, 33267, 22710	38217, 7595, 6373
Rint	0.044	0.063	0.092
(sin θ/λ)max (Å^{-1})	0.628	0.629	0.575
Refinement			
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.067, 0.197, 1.10	0.077, 0.242, 1.02	0.083, 0.203, 1.07
No. of reflections	8863	33267	7595
No. of parameters	504	1885	607
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.85, −0.50	1.15, −0.45	1.31, −0.64
CCDC number	2116817	2116818	2116823

Table S15. Crystallographic data for **5**-uduu, **5**-udud, and **6**

Crystal data 2			
	5-UDUU	**5-UDUD**	**6**
Chemical formula	$C_{84}H_{72}N_6Ni$	$C_{84}H_{72}N_6Ni$	$C_{60}H_{47}N_5Ni$
M_r	1224.18	1224.18	896.73
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1$	Triclinic, $P\bar{1}$
Temperature (K)	170	100	170
a, b, c (Å)	13.2040 (1), 14.0442 (1), 21.9436 (2)	14.0097 (6), 28.3409 (11), 19.4461 (6)	10.9575 (2), 13.4987 (3), 18.8848 (4)
α, β, γ (°)	82.844 (1), 73.132 (1), 85.129 (1)	β = 91.810 (3)	73.327 (2), 74.156 (2), 82.126 (2)
V (Å^3)	3858.71 (6)	7717.2 (5)	2568.97 (10)
Z	2	4	2
Radiation type	Cu Kα	Cu Kα	Cu Kα
μ (mm^{-1})	0.69	0.69	0.86
Crystal Size	0.25 × 0.25 × 0.05	0.14 × 0.10 × 0.09	0.27 × 0.18 × 0.04
Data collection			
Diffractometer	XtaLAB Synergy R, HyPix	XtaLAB Synergy R, HyPix	XtaLAB Synergy R, DW system, HyPix-Arc 150
Absorption correction	Multi-scan CrysAlis PRO 1.171.40.67a (Rigaku Oxford Diffraction, 2019) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan CrysAlis PRO 1.171.40.67a (Rigaku Oxford Diffraction, 2019) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan CrysAlis PRO 1.171.40.67a (Rigaku Oxford Diffraction, 2019) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
Tmin, Tmax	0.949, 1.000	0.651, 1.000	0.878, 1.000
No. of measured, independent and observed [I > 2σ(I)] reflections	59921, 14118, 13358	22671, 22671, 13816	37849, 10270, 9403
Rint	0.021	TWIN	0.023
(sin θ/λ)max (Å^{-1})	0.602	0.575	0.628
Refinement			
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.139, 1.09	0.102, 0.304, 1.02	0.041, 0.114, 1.05
No. of reflections	14118	22671	10270
No. of parameters	863	1604	604
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.45	1.90, −0.61	0.26, −0.29
CCDC number	2116821	2116820	2116819

Table S16. Crystallographic data for **7** and **8**.

Crystal data 3		
	7	**8**
Chemical formula	$C_{84}H_{68}N_6Ni$	$C_{84}H_{64}N_6Ni{\cdot}2(C_6H_6)$
M_r	1220.15	1372.33
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Temperature (K)	100	100
a, b, c (Å)	14.1056 (3), 16.2881 (4), 16.8703 (3)	11.8776 (7), 12.4674 (5), 13.0460 (7)
α, β, γ (°)	68.754 (2), 68.962 (2), 83.788 (2)	104.320 (4), 108.420 (5), 98.286 (4)
V (Å^3)	3370.7 (2)	1723.3 (2)
Z	2	1
Radiation type	Cu Kα	Cu Kα
μ (mm^{-1})	0.80	0.84
Crystal Size	0.09 × 0.09 × 0.04	0.14 × 0.07 × 0.04
Data collection		
Diffractometer	XtaLAB Synergy R, DW system, HyPix-Arc 150	XtaLAB Synergy R, DW system, HyPix-Arc 150
Absorption correction	Analytical CrysAlis PRO 1.171.41.75a (Rigaku Oxford Diffraction, 2020) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Analytical CrysAlis PRO 1.171.41.75a (Rigaku Oxford Diffraction, 2020) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
Tmin, Tmax	0.951, 0.980	0.926, 0.971
No. of measured, independent and observed [I > 2σ(I)] reflections	60317, 10751, 7938	19555, 5833, 4069
Rint	0.072	0.042
(sin θ/λ)max (Å^{-1})	0.575	0.588
Refinement		
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.066, 0.197, 1.03	0.071, 0.197, 1.07
No. of reflections	10751	5833
No. of parameters	869	472
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.01, −0.50	0.88, −0.74
CCDC number	2116822	2116824

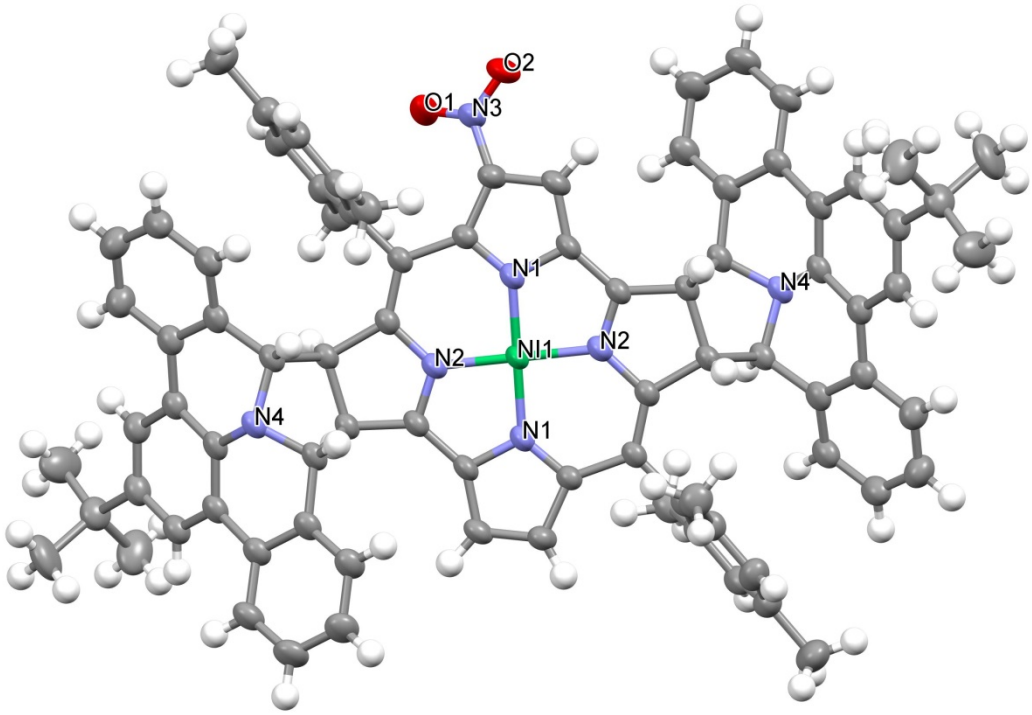


Figure S155. Perspective plot (thermal ellipsoids are set at a 50% probability level) of the molecular structure of **3**-duud.

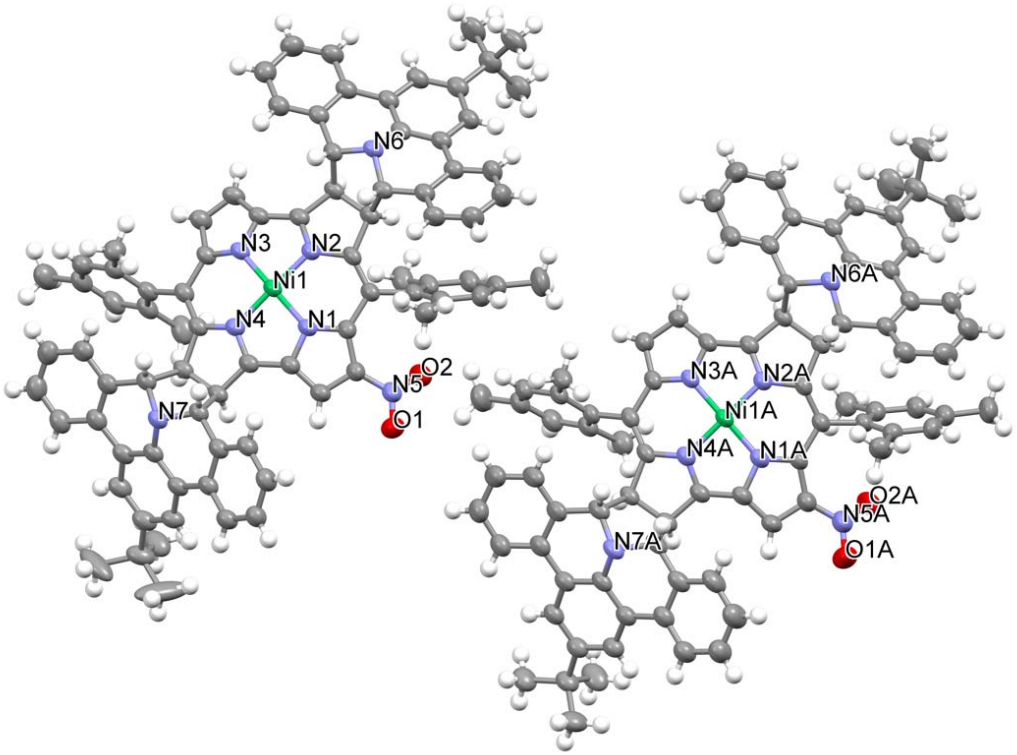


Figure S156. Perspective plot (thermal ellipsoids are set at a 50% probability level) of the asymmetric part of the crystal structure of **3**-udud. The solvent molecules (3 hexane molecules) are omitted for clarity.

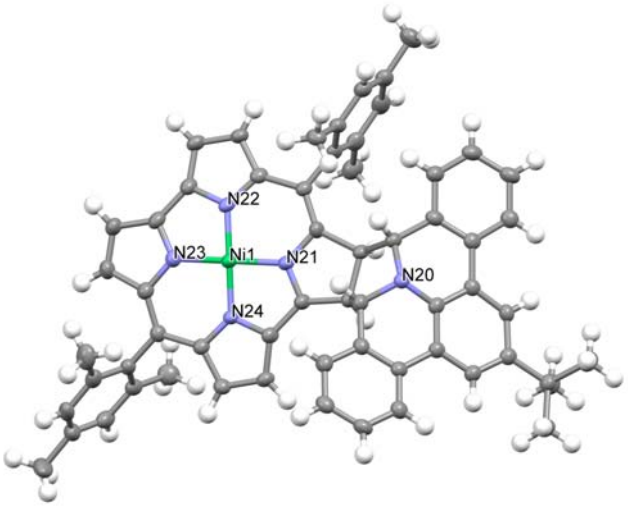


Figure S157. Perspective plot (thermal ellipsoids are set at a 50% probability level) of the molecular structure of **4**.

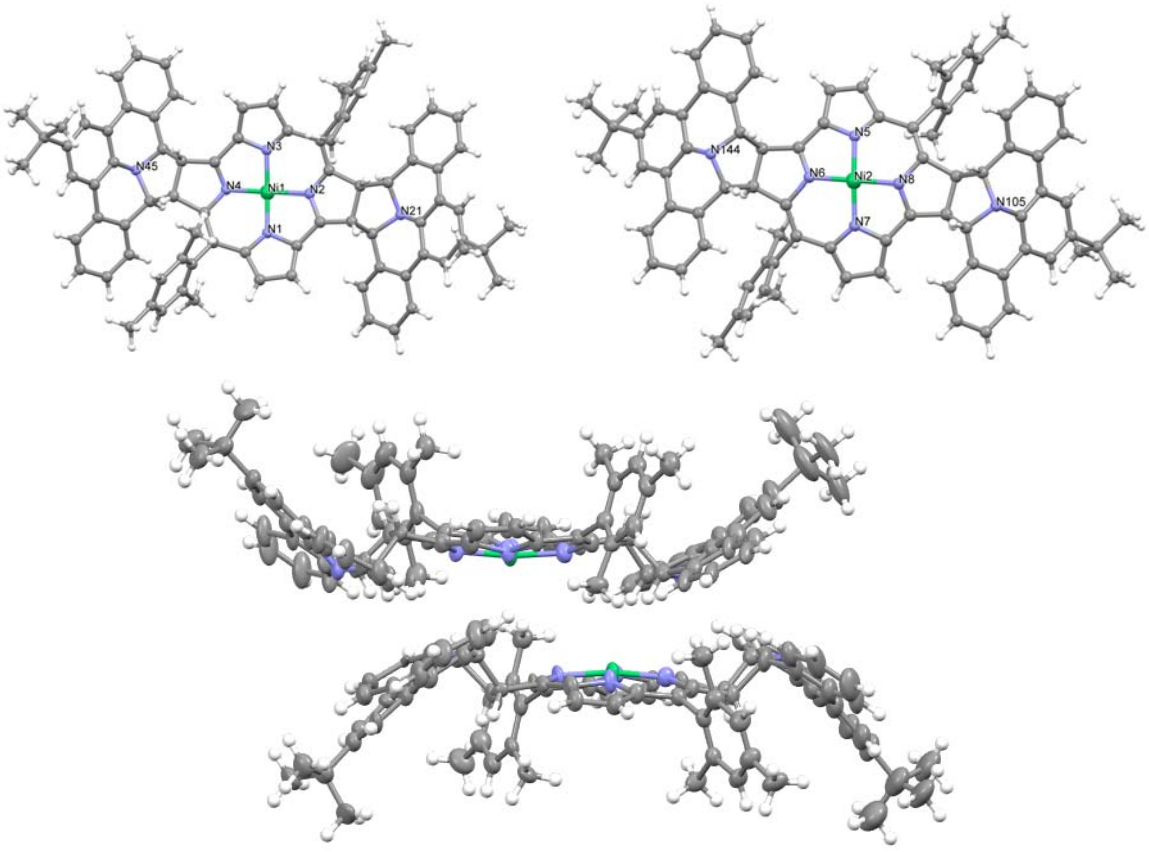


Figure S158. Perspective ball-and-sticks plot of the independent molecules from asymmetric part of the crystal structure of **5**-ududd (top) and a side view of these molecules with thermal ellipsoids set at a 50% probability level (bottom).

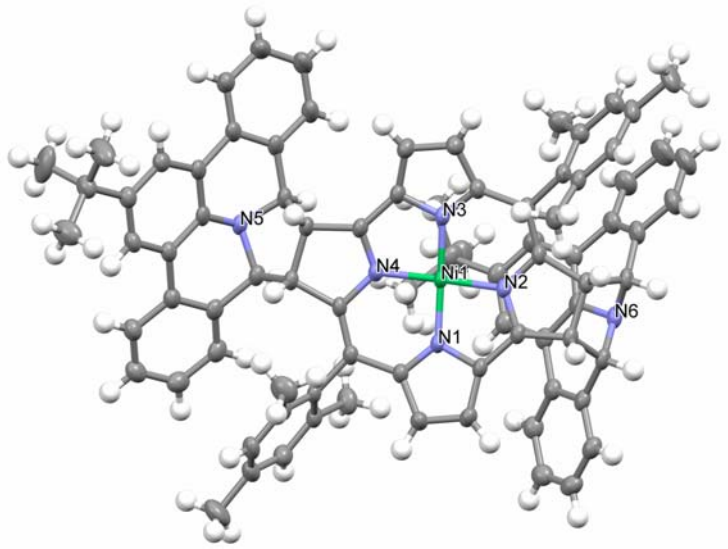


Figure S159. Perspective plot (thermal ellipsoids are set at a 50% probability level) of the molecular structure of **5**-uduu.

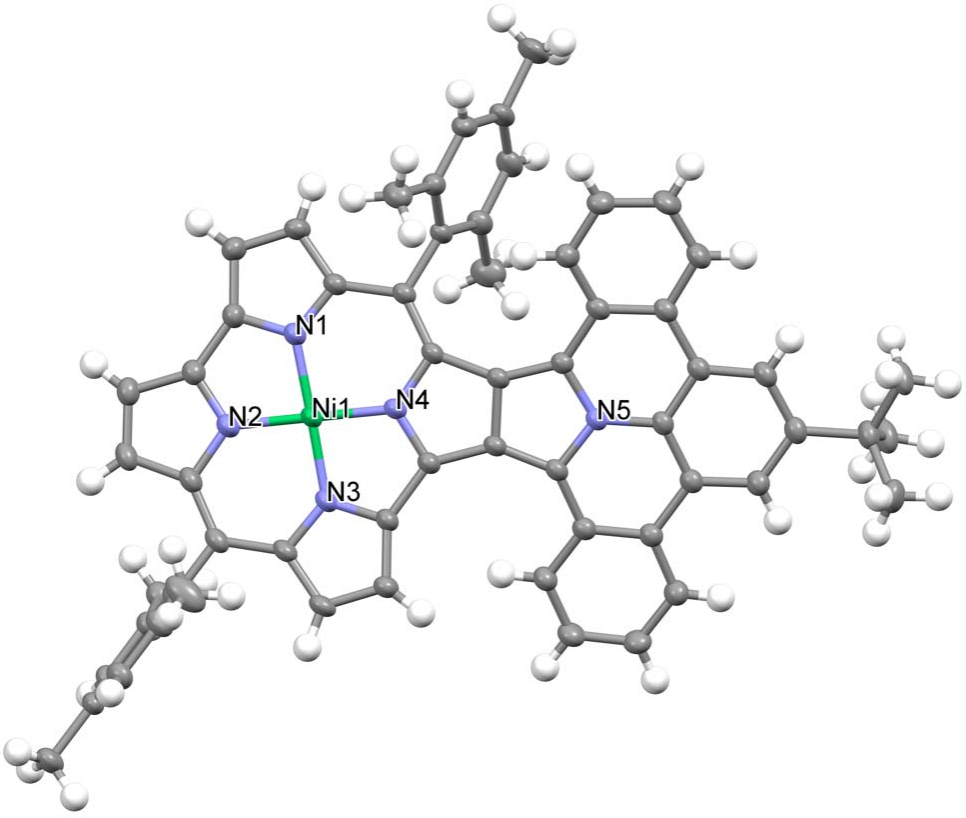


Figure S160. Perspective plot (thermal ellipsoids are set at a 50% probability level) of the molecular structure of **6**.

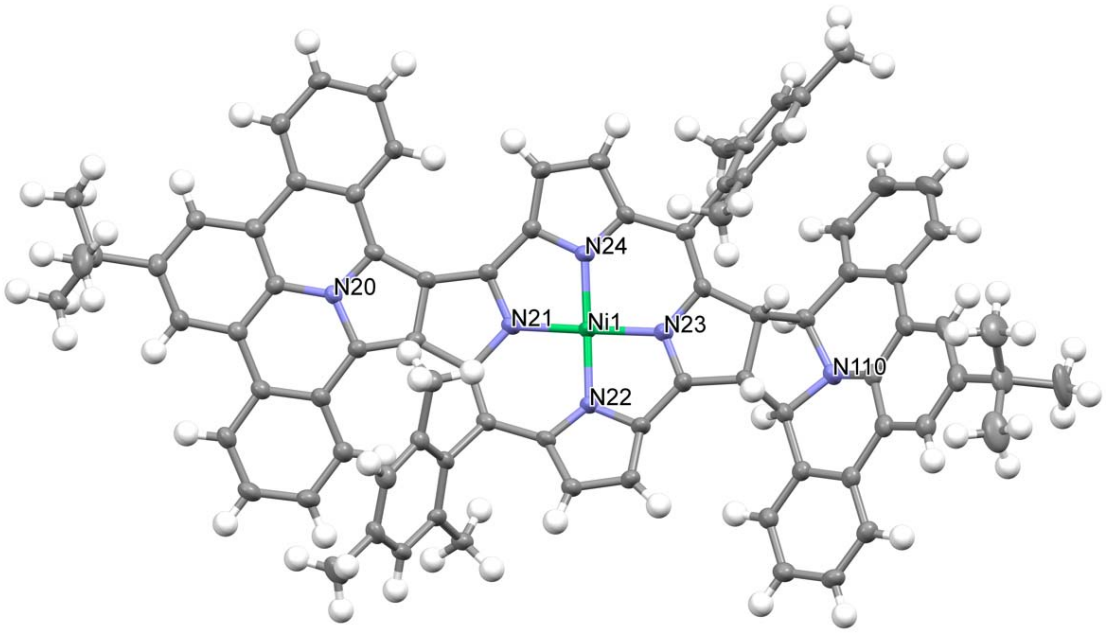


Figure S161. Perspective plot (thermal ellipsoids are set at a 50% probability level) of the molecular structure of **7**.

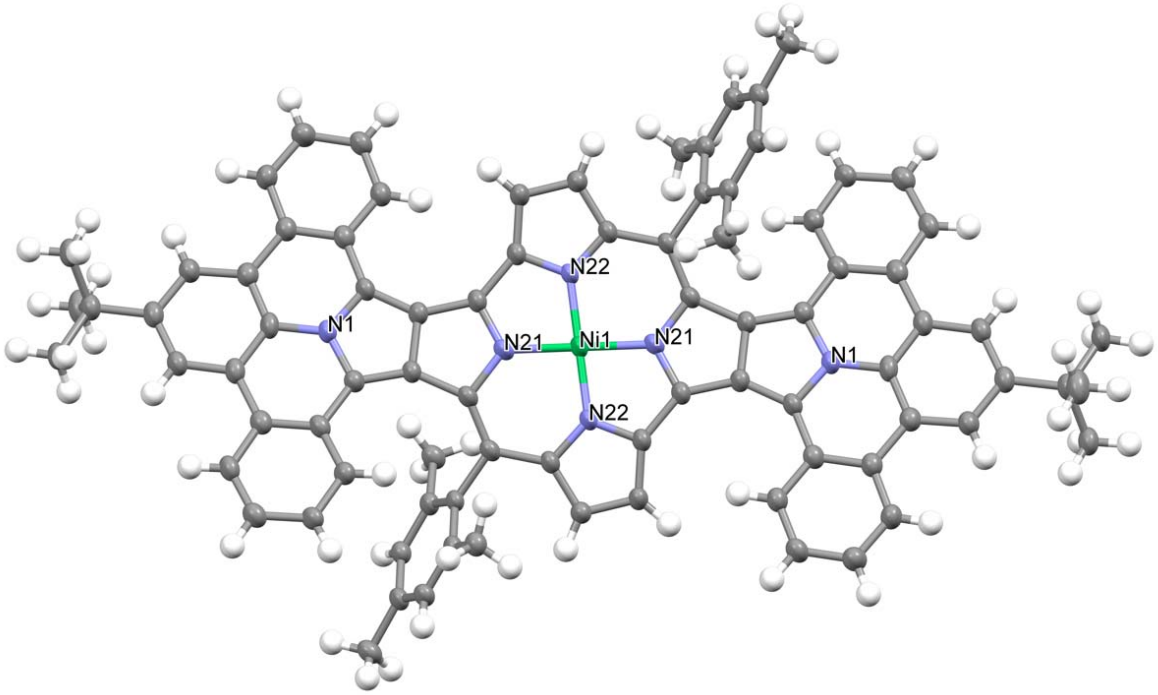


Figure S162. Perspective plot (thermal ellipsoids are set at a 50% probability level) of the molecular structure of **8**.

Table S17. Computational details for the optimized structures of compounds

Structure / Name[a]	SCF E	ZPV[b]	lowest freq.	E	ΔH	ΔG[c]	ΔG_{rel}	HOMO	LUMO	HLG
	a.u.	a.u.	cm^{-1}	a.u.	a.u.	a.u.	kcal/mol	eV	eV	eV
2a / oof_2a	-4304.083881	0.960343	11.78	-4303.065811	-4303.064866	-4303.217546	0.00	-4.92	-3.23	1.68
2b / oof_2b	-4304.083194	0.960356	11.32	-4303.065182	-4303.064238	-4303.216103	0.91	-4.85	-3.20	1.65
3-uduu/ oof_3cuduu	-5286.290626	1.352	9.43	-5284.862444	-5284.8615	-5285.048115	0.00	-4.67	-2.61	2.06
3-udud / oof_3buddu	-5286.270624	1.351038	8.733	-5284.842552	-5284.841608	-5285.033904	8.92	-4.81	-2.69	2.12
3-duud / oof_3auddu	-5286.265403	1.35102	7.153	-5284.837428	-5284.836484	-5285.028451	12.34	-4.76	-2.68	2.08
4 /oof_4	-4099.578405	0.95767	10.75	-4098.565695	-4098.564751	-4098.710939	0.00	-4.40	-2.85	1.55
6 /oof_5	-4097.177997	0.910181	12.05	-4096.212843	-4096.211898	-4096.358148	0.00	-4.26	-2.92	1.35
5-uduu/ oof_6uduu	-5081.784191	1.349354	9.05	-5080.361375	-5080.36043	-5080.540696	0.00	-4.26	-2.27	1.98
5-udud/ oof_6udud	-5081.766911	1.348664	9.07	-5080.344026	-5080.343082	-5080.528343	7.75	-4.37	-2.31	2.06
7 / oof_7	-5079.362409	1.30122	8.22	-5077.987075	-5077.986131	-5078.17103	0.00	-4.23	-2.53	1.70
8 / oof_8	-5076.960674	1.253867	7.09	-5075.632815	-5075.631871	-5075.816645	0.00	-4.13	-2.64	1.48
8b / oof_8b	-5076.958747	1.253825	7.44	-5075.630877	-5075.629932	-5075.814875	1.11	-4.11	-2.65	1.46

[a] Data set name (Cartesian coordinated available as *.pdb files). [b] Zero-point vibrational energy. [c] Gibbs free energy.

Table S18. Normal-coordinate structure decomposition analyses of deviations from planarity in selected norcorrole derivatives.[a]

Compound (structure)	*dom* [Å]	*sad* [Å]	*ruf* [Å]	*wav X* [Å]	*wav Y* [Å]	*pro* [Å]	D_{oop} [Å]
2a (DFT)	0.875	0.461	0.092	0.247	0.003	0.100	0.875
2b (DFT)	0.922	0.074	0.008	0.265	0.034	0.017	0.963
4 (XRD)	0.508	0.02	0.252	0.065	0.048	0.074	0.601
4 (DFT)	1.017	0.224	0.031	0.11	0.004	0.057	1.017
3-udud (XRD)	1.049	0.456	0.373	0.025	0.061	0.056	1.225
3-udud (DFT)	0.952	0.567	0.128	0.010	0.043	0.163	1.143
3-duud (XRD)	0.000	0.000	0.000	0.186	0.132	0.000	0.259
3-duud (DFT)	0.041	0.212	0.023	0.218	0.135	0.055	0.375
3-uduu (DFT)	0.588	0.840	0.275	0.048	0.014	0.129	1.073
5-udud (XRD)	1.204	0.290	0.315	0.045	0.066	0.044	1.204
5-udud (DFT)	1.033	0.354	0.095	0.000	0.000	0.093	1.101
5-uduu (XRD)	0.737	0.289	0.102	0.132	0.021	0.056	0.819
5-uduu (DFT)	0.656	0.658	0.221	0.128	0.009	0.089	0.968
6 (XRD)	0.059	0.113	0.162	0.120	0.203	0.078	0.361
6 (DFT)	0.617	0.086	0.123	0.259	0.218	0.082	0.739
7 (XRD)	0.732	0.495	0.162	0.149	0.071	0.099	0.934
7 (DFT)	0.799	0.267	0.231	0.155	0.118	0.129	0.910
8 (XRD)	0.000	0.000	0.000	0.185	0.303	0.000	0.459
8 (DFT)	0.001	0.001	0.000	0.357	0.464	0.000	0.641
8b (DFT)[b]	0.577	0.179	0.366	0.000	0.000	0.163	0.734
1-H (XRD)[c]	0.000	0.000	0.000	0.226	0.025	0.000	0.241
1-H (DFT)[d]	0.619	0.001	0.000	0.000	0.001	0.000	0.619
1-NO_2 (XRD)[d]	0.149	0.018	0.004	0.173	0.028	0.038	0.251
1-NO_2 (DFT)[d]	0.549	0.11	0.011	0.131	0.005	0.020	0.578
NCRPd (XRD)[e]	1.696	0.045	0.036	0.044	0.072	0.004	1.699

[a] absolute values of doming (*dom*), saddling (*sad*), ruffling (*ruf*), waving (*wav X* and *wav Y*), and propelling (*pro*) distortions. D_{oop} is the total out-of-plane displacement. [b] data calculated for 1.1 kcal/mol less stable non-centrosymmetric conformer of **8**. [c] Calculated for XRD data from T. Ito, Y. Hayashi, S. Shimizu, J.-Y. Shin, N. Kobayashi, and H. Shinokubo, *Angew.Chem.Int.Ed.*, 2012**, 51**, 8542. [d] Calculated for the data from Z. Deng, X. Li, M. Stępień, and P. J. Chmielewski, *Chem.Eur.J.*, 2016**, 22**, 4231. [e] Calculated for the data from T. Yonezawa, S. A. Shafie, S. Hiroto, and H. Shinokubo, *Angew.Chem.Int.Ed.*, 2017**, 56**, 11822.

Table S19. Electrochemical data for the compounds **1-8** (CH_2Cl_2, electrode potentials in volts *vs*, Fc/Fc^+)

Compd.	E_{Red2}	E_{Red1}	E_{Ox1}	E_{Ox2}	E_{Ox3}	E_{Ox4}	ΔE[c]
1-H[b]	–1.68	–0.91	0.16	0.74	-	-	1.07
1-NO_2[b]	–1.28	–0.69	0.47	0.87	-	-	1.16
2a	–1.65	–1.05	0.23[a]	0.59[a]		1.00[a]	1.28
2b	–1.69	–1.04	0.33[a]	0.53[a]		1.03[a]	1.37
3-udud	–2.37	–1.55	0.26[a]	0.39[a]	0.67[a]	1.08[a]	1.81
3-duud	-	–1.55	0.22[a]	0.36[a]	0.66 [a]	1.05[a]	1.77
3-uduu	–2.37[a]	–1.69	0.14[a]	0.37[a]	0.67[a]	1.09[a]	1.73
4	–2.01	–1.29	–0.04[a]	0.37[a]	0.81[a]	-	1.25
5-udud	-	–1.82	–0.03	0.51[a]	0.96[a]	-	1.79
5-uduu	-	–1.97	–0.16	0.50[a]	0.91[a]	-	1.81
6	–1.72	–1.13	–0.09	0.41	0.78[a]	1.28[a]	1.04
7	–2.02	–1.49	–0.12	0.44[a]	0.79[a]	-	1.37
8	–1.77	–1.34	–0.18	0.31	-	-	1.16

[a] Irreversible process. [b] Data from Z. Deng, X. Li, M. Stępień, and P. J. Chmielewski, *Chem.Eur.J.*, 2016**, 22**, 4231. [c] $\Delta E = E_{Ox1} - E_{Red1}$

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