

**Diastereoselective Methylation of Bis(N-confused Porphyrinato)nickel(II). An Access to Configurationally Stable Chiral Bis(Porphyrinoid) and Non-Symmetric Dimers**

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**Electronic Supplementary Information**

**Instrumentation:** NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker 600 MHz Avance III spectrometer equipped with variable temperature unit. 2D experiments were performed by means of standard Bruker software. The low-temperature NOESY spectra were recorded with 2048×512 data blocks and with 400 ms mixing time. Optical spectra were recorded on a Varian Cary 50 Bio spectrophotometer in dichloromethane. ESI mass spectra were obtained by means of Bruker Apex ultra spectrometer. Resolution of stereoisomers was performed at room temperature using a Merck-Hitachi LaChrom series chromatographic system equipped with a Chirex 3010 analytical column (25 cm length, 4.6 mm i.d.) packed with 5 μm silica gel coated with covalently bound (*S*)-valine and dinitroaniline. The applied dichloromethane was freshly distilled over calcium hydride. Circular dichroism spectra were obtained in dichloromethane at room temperature using a Jasco J-715 spectrometer. X-ray structures were obtained by means of Oxford Diffraction Xcalibur PX diffractometer with Onyx CCD detector. The structures were solved by direct method using SHELXS program<sup>[1]</sup> and refined anisotropically by full matrix least-square with SHELXL-97 program.<sup>[1]</sup>

**Syntheses:** Precursors **1** and **2** were obtained by the methods reported previously.<sup>[2]</sup>  
*Methylation of the bis(nickel(II)) complex 2:* A sample of **2** (30 mg, 0.02 mmole) was dissolved in deoxygenated dichloromethane (20 mL) and to the solution an excess of methyl iodide (200 μL, 3 mmole), solid potassium carbonate (10 mg), and dibenzo[18]crown-6 (1 mg) were added. The reaction mixture was heated under reflux in the inert atmosphere for two hours. After that time the solution was filtered and passed down a silica-gel column. The first fraction that was eluted with 1% solution of ethanol in dichloromethane contained dimethylated products **3** and **4**. The second fraction (eluent 2% EtOH in DCM) consisted of trimethylated product **5**. Separation of products **3** and **4** was accomplished by the flash-chromatography with 0.5 % MeOH in DCM. The faster moving band consisted of **3** and the second band contained **4**. Yields: **3**, 12 mg (39%); **4**, 9 mg (29%); **5**, 6 mg (18%).

Selected data for **3**: UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>) λ/nm (ε10<sup>-3</sup>/M<sup>-1</sup>cm<sup>-1</sup>) = 247 (sh), 292 (61.8), 361 (71.1), 440 (119.4), 479 (sh), 492 (sh), 569 (sh), 610 (18.6), 784 (sh). HRMS (ESI+): 1479.4793; Calc. for C<sub>98</sub>H<sub>75</sub>N<sub>8</sub>Ni<sub>2</sub> [M+H]<sup>+</sup> 1479.4822. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 213 K, TMS): δ<sub>H</sub> = 8.85 (dd, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz, 1H, tolyl 20-*o*), 8.71 (d, <sup>3</sup>J<sub>HH</sub> = 4.6 Hz, 1H, pyrrole 18), 8.61 (d, <sup>3</sup>J<sub>HH</sub> = 4.4 Hz, 1H, pyrrole 12), 8.53 (d, <sup>3</sup>J<sub>HH</sub> = 4.7 Hz, 1H, pyrrole 13), 8.41 (d, <sup>3</sup>J<sub>HH</sub> = 4.6 Hz, 1H, pyrrole 17), 8.28 (dd, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz, 1H, tolyl 10-*o*), 8.24 (dd, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, <sup>4</sup>J<sub>HH</sub> = 1.6 Hz, 1H, tolyl 20-*o*), 8.16 (dd, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, <sup>4</sup>J<sub>HH</sub> =

1.4 Hz, 1H, tolyl 15-*o*<sub>1</sub>), 8.08 (d, <sup>3</sup>*J*<sub>HH</sub> = 4.4 Hz, 1H, pyrrole 8), 7.98 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.5 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.4 Hz, 1H, tolyl 10-*o*<sub>1</sub>), 7.96 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.4 Hz, 1H, tolyl 15-*o*), 7.76 (m, 2H, tolyl 20-*m*, 20-*m*<sub>1</sub>), 7.69 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.1 Hz, 1H, tolyl 10-*m*), 7.63 (d, <sup>3</sup>*J*<sub>HH</sub> = 4.3 Hz, 1H, pyrrole 7), 7.60 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.3 Hz, 1H, tolyl 15-*m*<sub>1</sub>), 7.53 (m, 2H, tolyl 10-*m*<sub>1</sub>, 15-*m*), 6.46 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.4 Hz, 1H, tolyl 5-*o*), 5.45 (dd, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.4 Hz, 1H, tolyl 5-*o*<sub>1</sub>), 4.99 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.3 Hz, 1H, tolyl 5-*m*), 3.79 (dd, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.4 Hz, 1H, tolyl 5-*m*<sub>1</sub>), 2.77 (s, 3H, tolyl 20-Me), 2.69 (s, 3H, tolyl 10-Me), 2.66 (s, 3H, tolyl 15-Me), -0.60 (s, 3H, tolyl 5-Me), -3.28 (s, 3H, confused pyrrole 21-Me). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 300 K, TMS): δ<sub>C</sub> = 179.0, 158.5, 156.0, 153.8, 152.9, 151.3, 150.0, 147.9, 147.3, 138.7, 138.6, 137.9, 137.6, 137.2, 135.2, 134.7, 134.3, 134.1, 133.7, 133.6, 133.2, 132.6, 132.5, 132.2, 132.1, 131.7, 131.5, 130.8, 129.0, 128.8, 127.7, 127.6, 125.6, 122.7, 122.1, 33.0 (C21), 21.8, 21.5, 18.4, 16.2.

Selected data for **4**: UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>) λ/nm (ε·10<sup>-3</sup>/M<sup>-1</sup>cm<sup>-1</sup>) = 290 (38.3), 369 (56.3), 439 (59.5), 488 (sh), 569 (sh), 614, (16.7). HRMS (ESI<sup>+</sup>): 1479.4884; Calc. for C<sub>98</sub>H<sub>75</sub>N<sub>8</sub>Ni<sub>2</sub> [M+H]<sup>+</sup> 1479.4822. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 213 K, TMS): δ = 8.59 (d, <sup>3</sup>*J*<sub>HH</sub> = 4.9 Hz, 1H, pyrrole 18'), 8.57 (d, <sup>3</sup>*J*<sub>HH</sub> = 4.6 Hz, 1H, pyrrole 12'), 8.52 (d, <sup>3</sup>*J*<sub>HH</sub> = 4.6 Hz, 1H, pyrrole 13'), 8.40 (d, <sup>3</sup>*J*<sub>HH</sub> = 4.8 Hz, 1H, pyrrole 17'), 8.24 (d, <sup>3</sup>*J*<sub>HH</sub> = 4.8 Hz, 1H, pyrrole 8'), 8.18 (dd, <sup>3</sup>*J*<sub>HH</sub> = 4.9 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.1 Hz, 1H, tolyl 10'-*o*), 8.07 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.1 Hz, 1H, tolyl 20'-*o*<sub>1</sub>), 8.00 (d, <sup>3</sup>*J*<sub>HH</sub> = 4.7 Hz, 1H, pyrrole 7'), 7.97 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.1 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.4 Hz, 1H, tolyl 15'-*o*), 7.92 (m, 3H, tolyl 20'-*o*, 20-*o*), 7.89 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.3 Hz, 1H, tolyl 10'-*o*<sub>1</sub>), 7.67 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.2 Hz, 1H, tolyl 10-*o*<sub>1</sub>), 7.62 (m, 2H, tolyl 15'-*m*<sub>1</sub>, 15-*m*<sub>1</sub>), 7.60 (m, 2H, tolyl 20'-*m*<sub>1</sub>, 10'-*m*<sub>1</sub>), 7.59 (d, <sup>3</sup>*J*<sub>HH</sub> = 5.0 Hz, 1H, pyrrole 18), 7.54 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.5 Hz, 1H, tolyl 20'-*m*), 7.52 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.9 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.1 Hz, 1H, tolyl 15'-*o*<sub>1</sub>), 7.48 (m, 3H, tolyl 20-*m*<sub>1</sub>, 10'-*m*, 10-*o*), 7.46 (m, 2H, tolyl 5'-*o*, 15-*o*<sub>1</sub>), 7.45 (d, <sup>3</sup>*J*<sub>HH</sub> = 5.0 Hz, 1H, pyrrole 13), 7.42 (d, <sup>3</sup>*J*<sub>HH</sub> = 4.8 Hz, 1H, pyrrole 12), 7.41 (m, 2H, tolyl 15-*m*, 20-*m*), 7.40 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.4 Hz, 1H, 10-*m*<sub>1</sub>), 7.34 (m, 2H, tolyl 15-*o*, 15'-*m*), 7.27 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.4 Hz, 1H, tolyl 10-*m*), 7.18 (d, <sup>3</sup>*J*<sub>HH</sub> = 4.9 Hz, 1H, pyrrole 17), 6.89 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.3 Hz, 1H, tolyl 5'-*m*), 6.81 (d, <sup>3</sup>*J*<sub>HH</sub> = 4.9 Hz, 1H, pyrrole 8), 6.66 (d, <sup>3</sup>*J*<sub>HH</sub> = 5.0 Hz, 1H, pyrrole 7), 6.25 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.2 Hz, 1H, tolyl 5'-*o*<sub>1</sub>), 6.05 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.3 Hz, 1H, tolyl 5-*o*), 5.27 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.5 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.1 Hz, 1H, tolyl 5'-*m*<sub>1</sub>), 5.00 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.5 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.1 Hz, 1H, tolyl 5-*m*), 3.98 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.1 Hz, 1H, tolyl 5-*o*<sub>1</sub>), 3.65 (s, 3H, confused pyrrole 2-Me), 3.05 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.0 Hz, 1H, tolyl 5-*m*<sub>1</sub>), 2.65 (s, 6H, tolyl 20'-Me, 20-Me),

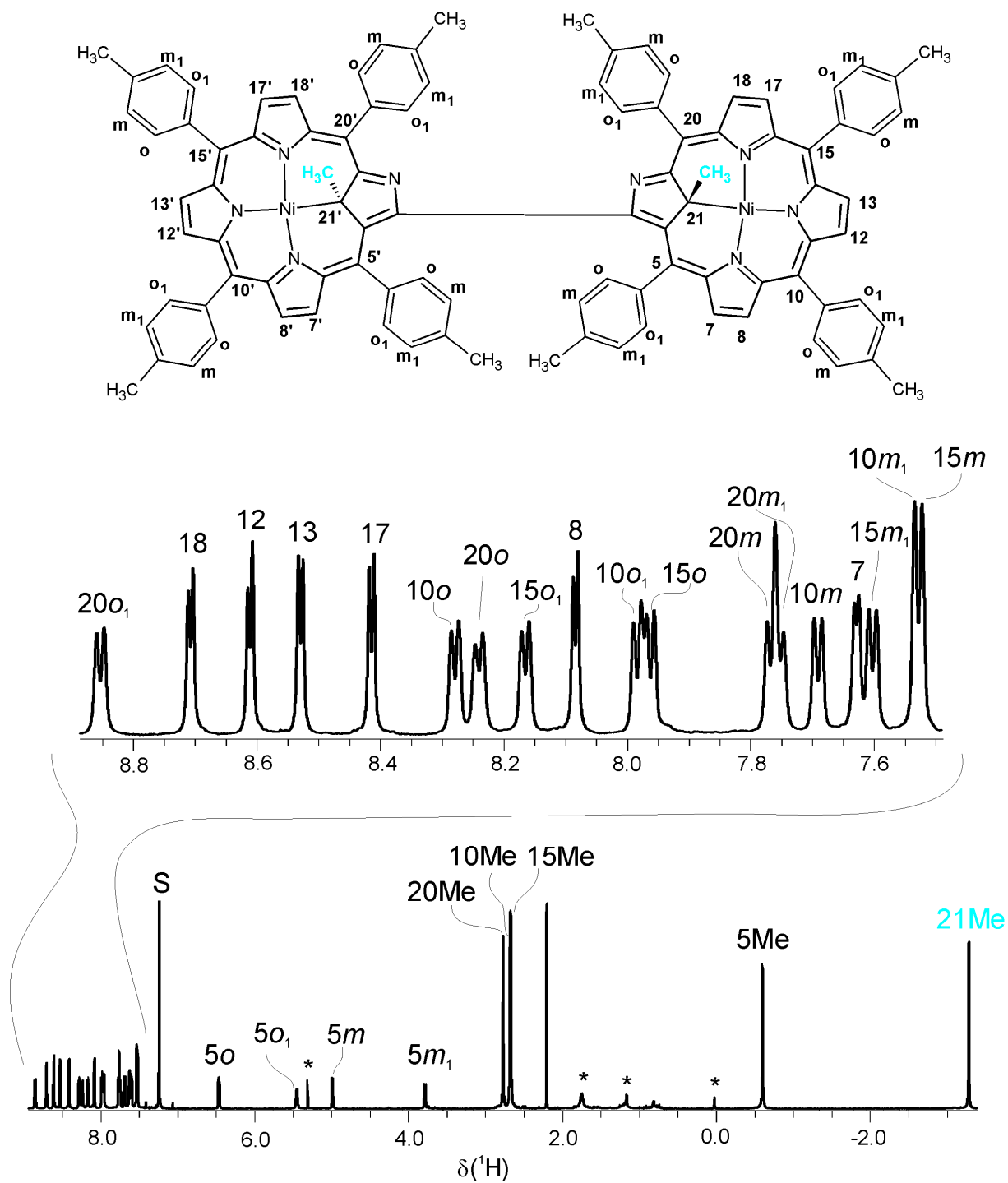
2.63 (s, 3H, tolyl 10'-Me), 2.60 (s, 3H, tolyl 15-Me), 2.52 (s, 3H, tolyl 15'-Me), 2.49 (s, 3H, tolyl 10-Me), 0.78 (s, 3H, tolyl 5'-Me), -0.68 (s, 3H, tolyl 5-Me), -3.40 (s, 3H, confused pyrrole 21'-Me). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 300 K, TMS): δ<sub>C</sub> = 179.2, 157.5, 155.4, 154.9, 153.7, 153.6, 153.3, 152.8, 152.6, 152.4, 152.3, 151.5, 150.8, 149.9, 149.2, 148.2, 147.9, 138.5, 138.4, 138.3, 138.1, 137.8, 137.6, 137.5, 137.2, 136.6, 136.5, 136.4, 135.8, 135.3, 134.4, 134.3, 134.1, 134.0, 133.9, 133.6, 133.3, 133.1, 132.9, 132.7, 132.6, 132.3, 132.0, 130.7, 130.43, 130.36, 128.9, 128.3, 128.1, 127.94, 127.87, 127.7, 127.4, 124.9, 124.4, 124.0, 123.3, 122.6, 118.9, 118.3, 117.4, 115.8, 112.0, 36.1 (2N-CH<sub>3</sub>), 30.1 (C21), 21.62, 21.56, 21.5, 21.4, 21.3, 19.7, 18.2, 17.9.

Selected data for **5**: UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>) λ/nm (ε·10<sup>-3</sup>/M<sup>-1</sup>cm<sup>-1</sup>) = 244 (70.6), 295 (63.6), 361 (67.1), 441 (89.1), 514 (sh), 630 (27.3), 786 (sh). HRMS (ESI+): 1493.5037; Calc. for C<sub>99</sub>H<sub>77</sub>N<sub>8</sub>Ni<sub>2</sub>[M-I]<sup>+</sup> 1493.4978. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 213 K, TMS): δ<sub>H</sub> = 8.72 (d, <sup>3</sup>J<sub>HH</sub> = 4.9 Hz, 1H, pyrrole 18'), 8.63 (d, <sup>3</sup>J<sub>HH</sub> = 4.7 Hz, 1H, pyrrole 12'), 8.57 (d, <sup>3</sup>J<sub>HH</sub> = 5.0 Hz, 1H, pyrrole 12), 8.55 (d, <sup>3</sup>J<sub>HH</sub> = 4.5 Hz, 1H, pyrrole 13'), 8.49 (d, <sup>3</sup>J<sub>HH</sub> = 4.7 Hz, 1H, pyrrole 13), 8.47 (d, <sup>3</sup>J<sub>HH</sub> = 4.9 Hz, 1H, pyrrole 18), 8.43 (d, <sup>3</sup>J<sub>HH</sub> = 4.7 Hz, 1H, pyrrole 17'), 8.27 (m, 3H, tolyl 20-o<sub>1</sub>, 20'-o, 20'-m<sub>1</sub>), 8.25 (d, <sup>3</sup>J<sub>HH</sub> = 5.2 Hz, 1H, pyrrole 17), 8.20 (d, <sup>3</sup>J = 6.7 Hz, 1H, tolyl 10-m<sub>1</sub>), 8.18 (d, <sup>3</sup>J<sub>HH</sub> = 4.9 Hz, 1H, pyrrole 8'), 8.17 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 1H, tolyl 10'-m<sub>1</sub>), 8.11 (m, 2H, tolyl 20'-o<sub>1</sub>, 15'-o<sub>1</sub>), 7.98 (m, 2H, tolyl 10'-m, pyrrole 8), 7.95 (m, 2H, tolyl 15-o<sub>1</sub>, 10-o), 7.91 (dd, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 1H, tolyl 15'-o), 7.88 (m, 2H, tolyl 20-m, 15-o), 7.85 (dd, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, <sup>4</sup>J<sub>HH</sub> = 1.4 Hz, 1H, tolyl 10'-o<sub>1</sub>), 7.78 (m, 2H, pyrrole 7', tolyl 20'-m), 7.69 (m, 3H, tolyl 10'-o, 20-o, 10-o<sub>1</sub>), 7.65 (dd, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, <sup>4</sup>J<sub>HH</sub> = 1.4 Hz, 1H, tolyl 20-m<sub>1</sub>), 7.61 (dd, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 1H, tolyl 15'-m<sub>1</sub>), 7.58 (d, <sup>3</sup>J<sub>HH</sub> = 5.0 Hz, 1H, pyrrole 7), 7.55 (m, 4H, tolyl 10-m, 15-m<sub>1</sub>, 15-m, 15'-m), 6.38 (dd, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, 1H, tolyl 5'-o), 6.32 (dd, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz, 1H, tolyl 5-o), 5.68 (m, 2H, tolyl 5'-m, 5'-o<sub>1</sub>), 5.42 (dd, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz, 1H, tolyl 5-o<sub>1</sub>), 4.92 (dd, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz, 1H, tolyl 5-m), 4.47 (s, 3H, confused pyrrole 2-Me), 4.22 (dd, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 1H, tolyl 5'-m<sub>1</sub>), 3.83 (dd, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.0 Hz, 1H, tolyl 5-m<sub>1</sub>), 2.79 (s, 3H, tolyl 20-Me), 2.76 (s, 3H, tolyl 10'-Me), 2.69 (s, 3H, tolyl 10-Me), 2.67 (s, 3H, tolyl 20'-Me), 2.66 (s, 3H, tolyl 15-Me), 2.64 (s, 3H, tolyl 15'-Me), -0.06 (s, 3H, tolyl 5'-Me), -0.61 (s, 3H, tolyl 5-Me), -1.78 (s, 3H, confused pyrrole 21-Me), -3.11 (s, 3H, confused pyrrole 21'-Me). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 300 K, TMS): δ<sub>C</sub> = 178.7, 160.1 (C1), 159.3, 156.9, 155.8, 155.0, 154.3, 154.1, 153.1, 152.8, 152.4, 151.8, 150.7, 148.9, 148.6, 144.2, 143.0, 142.5 (C3), 140.8, 139.1, 139.0, 138.9, 138.2, 138.1, 138.0, 137.8, 137.8, 137.3, 137.1,

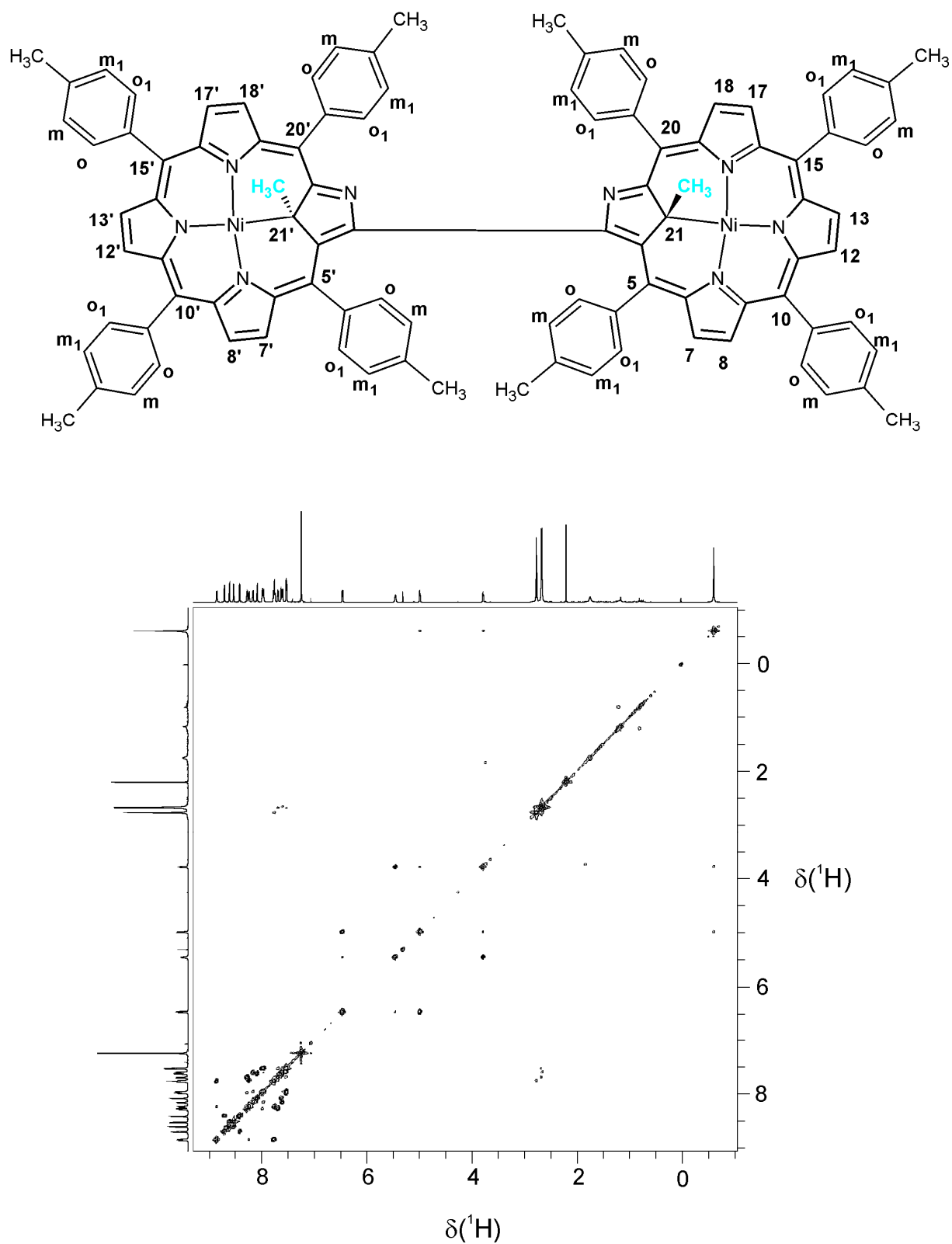
136.84, 136.75, 136.73, 136.66, 136.4, 136.1, 135.7, 135.2, 135.1, 134.8, 134.5, 134.22, 134.18, 133.9, 133.8, 133.6, 133.4, 133.3, 132.8, 132.4, 130.22, 130.19, 129.1, 129.0, 128.7, 128.4, 128.1, 128.0, 127.8, 124.3, 123.2, 122.7, 122.6, 120.0, 41.0 (2N-CH<sub>3</sub>), 34.1 (C21), 32.3 (C21'), 21.9, 21.7, 21.58, 21.56, 21.54, 19.1, 18.5, 17.1 (21'-CH<sub>3</sub>), 16.4 (21-CH<sub>3</sub>).

*Demetallation of 3.* A sample of **3** (5mg, 0.003 mmole) was dissolved in dichloromethane (3 mL) and to the solution a drop of the concentrated hydrochloric acid was added. The mixture was vigorously shaken for five minutes and then the solution was washed by several portions of water, neutralized with sodium carbonate, and washed again two times with water. The organic phase was separated and solvent was evaporated. The resulted compound was crystallized from dichloromethane by addition of hexane. Yield: 4 mg (87%).

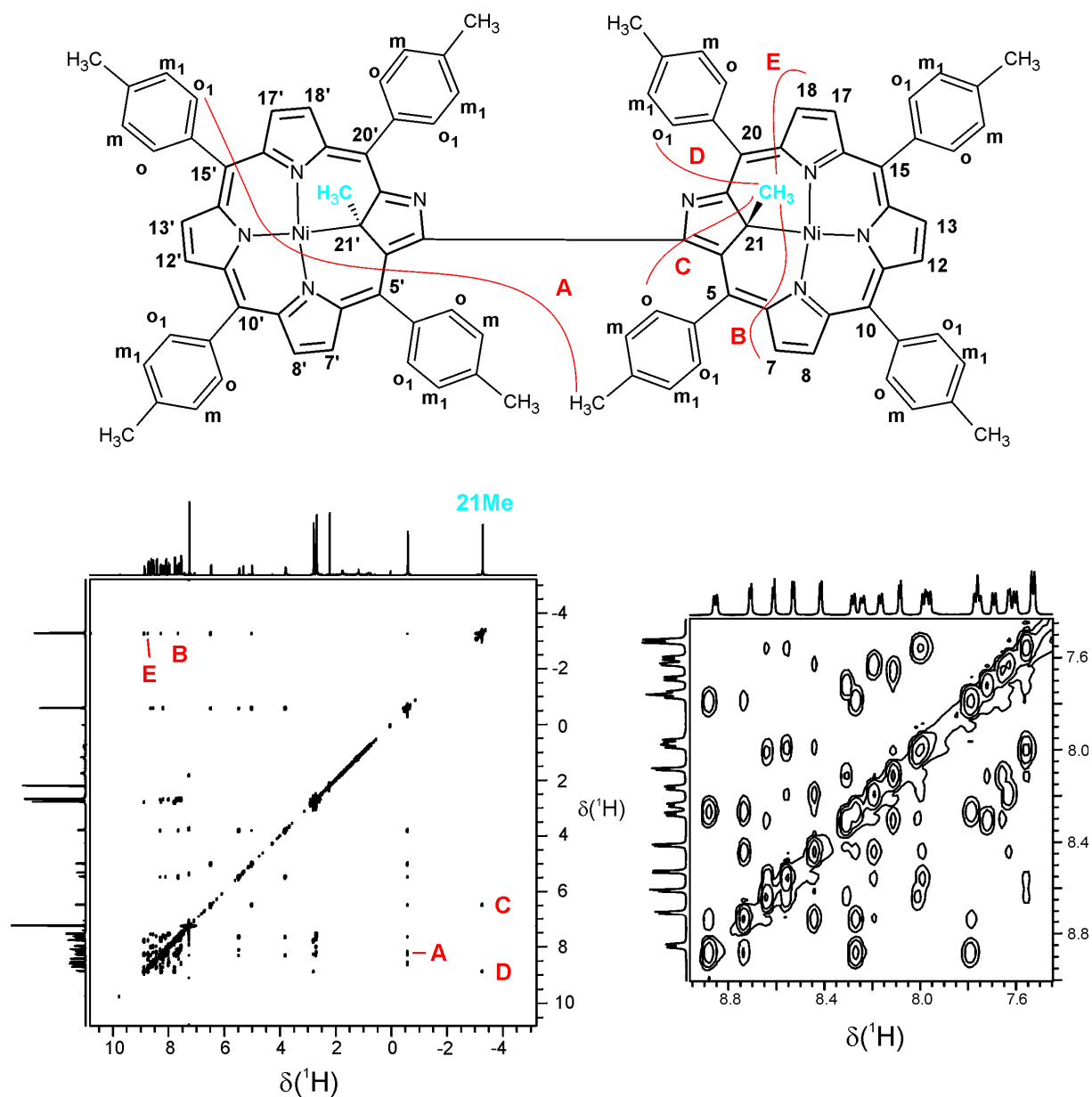
Selected data for **6**: UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda$ /nm ( $\epsilon$ 10<sup>-3</sup>/M<sup>-1</sup>cm<sup>-1</sup>) = 254 (36.0), 294 (38.7), 352 (sh), 444 (137.6), 459 (134.9), 574 (21.3), 602 (22.1), 722 (sh), 770 (11.1). HRMS (ESI+): 1367.64266; Calc. for C<sub>98</sub>H<sub>79</sub>N<sub>8</sub> [M+H]<sup>+</sup> 1367.64270. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 213 K, TMS):  $\delta$ <sub>H</sub> = 8.84 (dd, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 1H, tolyl 20-*o*<sub>1</sub>), 8.67 (dd, <sup>3</sup>J<sub>HH</sub> = 4.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 1H, pyrrole 18), 8.58 (d, <sup>3</sup>J<sub>HH</sub> = 4.3 Hz, 1H, pyrrole 13), 8.53 (d, <sup>3</sup>J<sub>HH</sub> = 4.3 Hz, 1H, pyrrole 12), 8.47 (dd, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 1H, tolyl 10-*o*), 8.30 (dd, <sup>3</sup>J<sub>HH</sub> = 4.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 1H, pyrrole 17), 8.27 (dd, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 1H, tolyl 15-*o*), 8.18 (dd, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 1H, tolyl 20-*o*), 8.02 (dd, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.4 Hz, 1H, tolyl 15-*o*<sub>1</sub>), 7.94 (dd, <sup>3</sup>J<sub>HH</sub> = 4.5 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 1H, pyrrole 8), 7.84 (dd, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 1H, tolyl 10-*o*<sub>1</sub>), 7.78 (dd, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 1H, tolyl 20-*m*<sub>1</sub>), 7.72 (dd, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz, 1H, tolyl 20-*m*), 7.68 (dd, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 1H, tolyl 10-*m*), 7.64 (dd, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 1H, tolyl 15-*m*), 7.56 (dd, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.4 Hz, 1H, tolyl 15-*m*<sub>1</sub>), 7.49 (dd, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz, 1H, tolyl 10-*m*<sub>1</sub>), 7.32 (d, <sup>3</sup>J<sub>HH</sub> = 4.5 Hz, 1H, pyrrole 7), 7.19 (dd, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.0 Hz, 1H, tolyl 5-*o*<sub>1</sub>), 5.47 (dd, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, <sup>4</sup>J<sub>HH</sub> = 1.0 Hz, 1H, tolyl 5-*m*<sub>1</sub>), 4.25 (dd, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz, tolyl 5-*o*), 2.77 (s, 3H, tolyl 20-Me), 2.70 (s, 3H, tolyl 15-Me), 2.66 (s, 3H, tolyl 10-Me), 2.57 (dd, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz, 1H, tolyl 5-*m*), -0.36 (s, 3H, tolyl 5-Me), -2.73 (s, 1H, pyrrole 24-NH), -2.93 (s, 1H, pyrrole 22-NH), -4.98 (s, 3H, confused pyrrole 21-Me). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 300 K, TMS):  $\delta$ <sub>C</sub> = 158.7, 152.7, 143.8, 138.4, 137.3, 136.7, 135.0, 134.7, 143.5, 133.8, 129.3, 128.9, 127.9, 127.6, 127.0, 125.4, 125.2, 123.5, 103.3 (C21), 21.7, 21.3, 18.2, 8.9.



**Figure S1.** <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>, 213 K) of 3,3'-bis(meso-tetratolyl-2-aza-21-methylcarbaporphyrinatonicel(II)) **3** with complete assignment of signals.

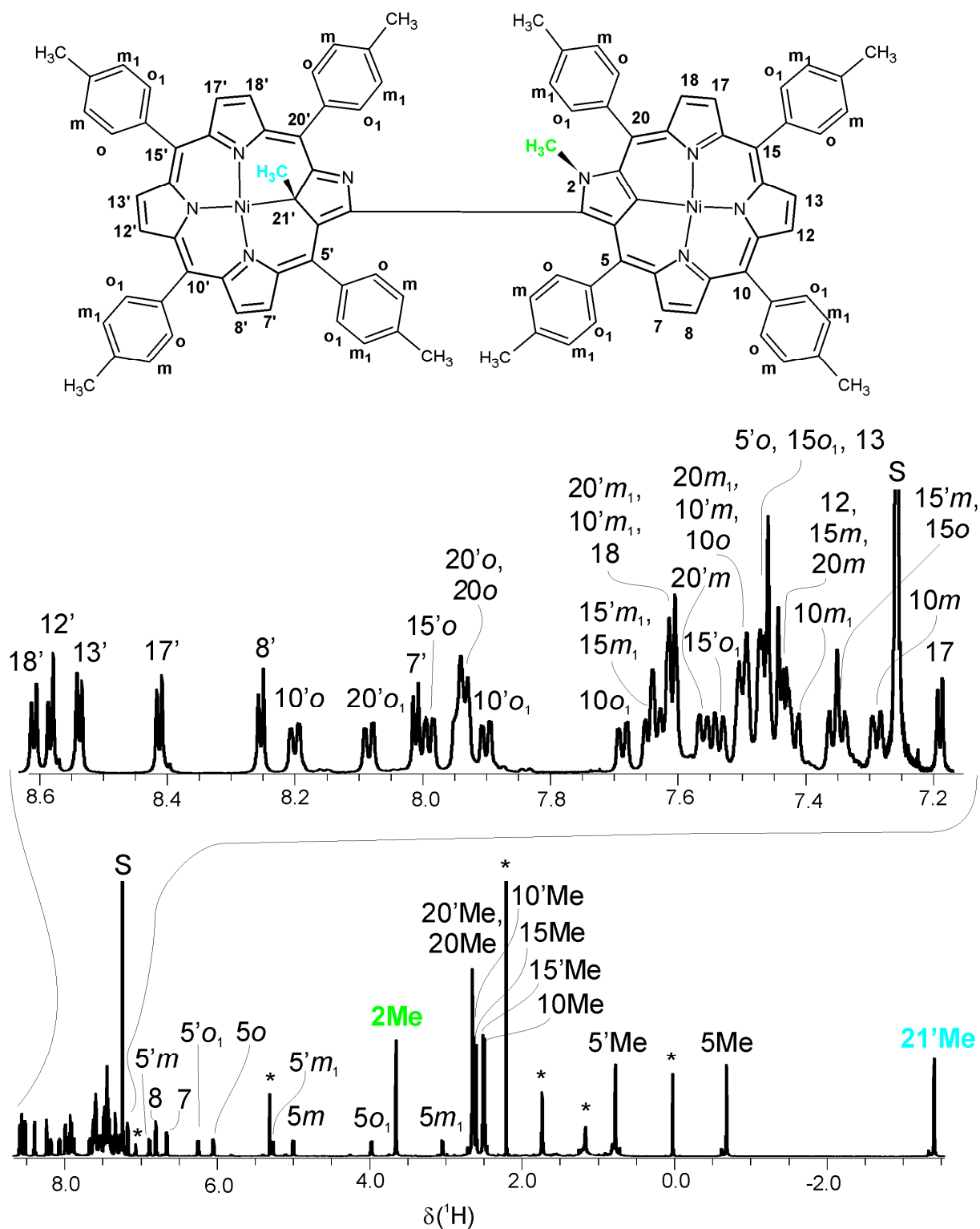


**Figure S2.** A fragment of  $^1\text{H}$ - $^1\text{H}$  COSY spectrum (600 MHz,  $\text{CDCl}_3$ , 213 K) of **3**.



**Figure S3.**  $^1\text{H}$ - $^1\text{H}$  NOESY spectrum of **3**, 600 MHz,  $\text{CDCl}_3$ , 213 K. The full correlation map is given on the left side. The map on the right presents the extension of the selected region (low-field part) of the spectrum. The red letters denote through-space interprotonic interactions represented on the schematic structure by curved lines.





**Figure S4.** <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>, 213 K) of 2,21'-dimethylo-3,3'-bis(meso-tetratolyl)-2-aza-21-carbaporphyrinatonickel(II) **4** with complete assignment of signals.

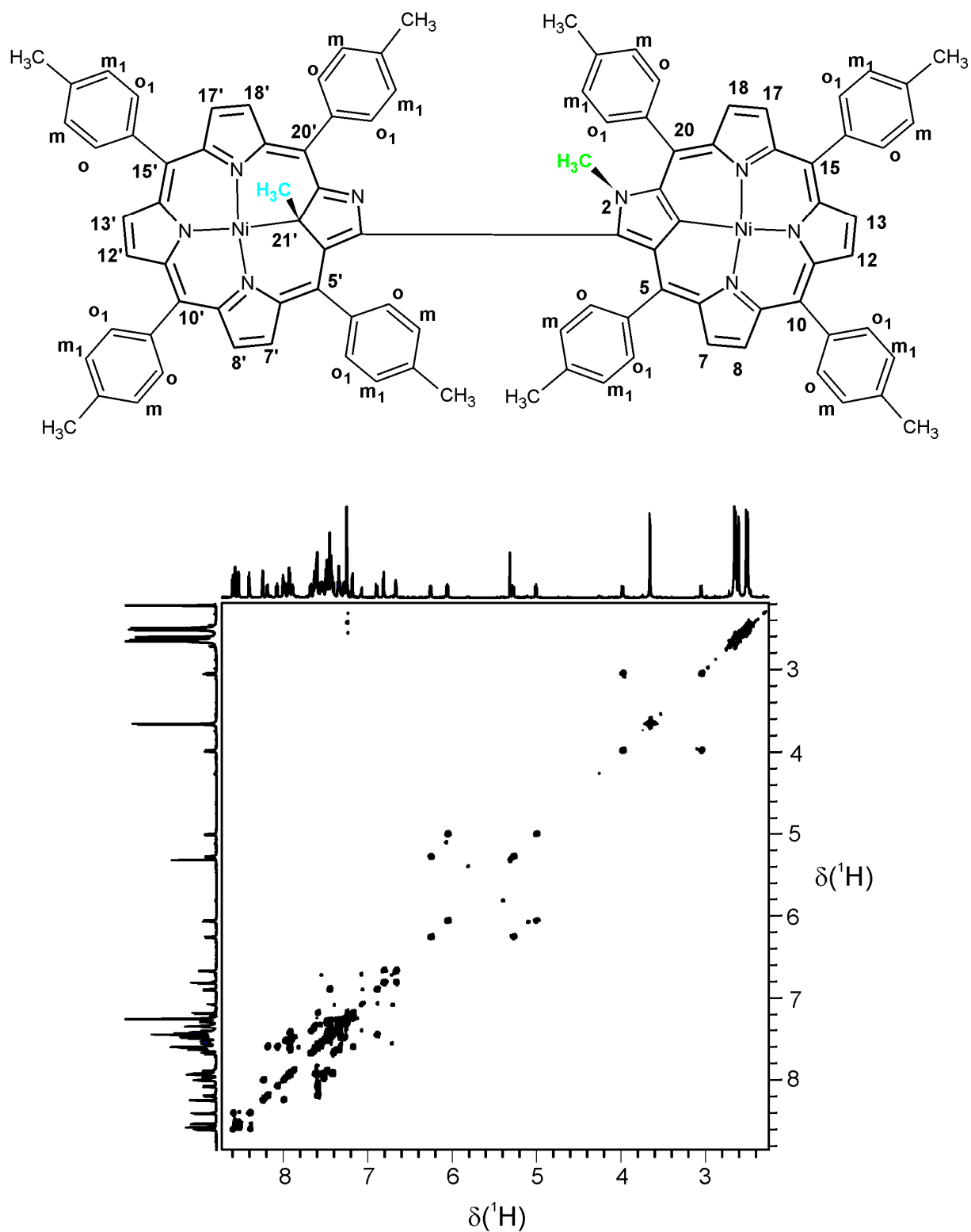
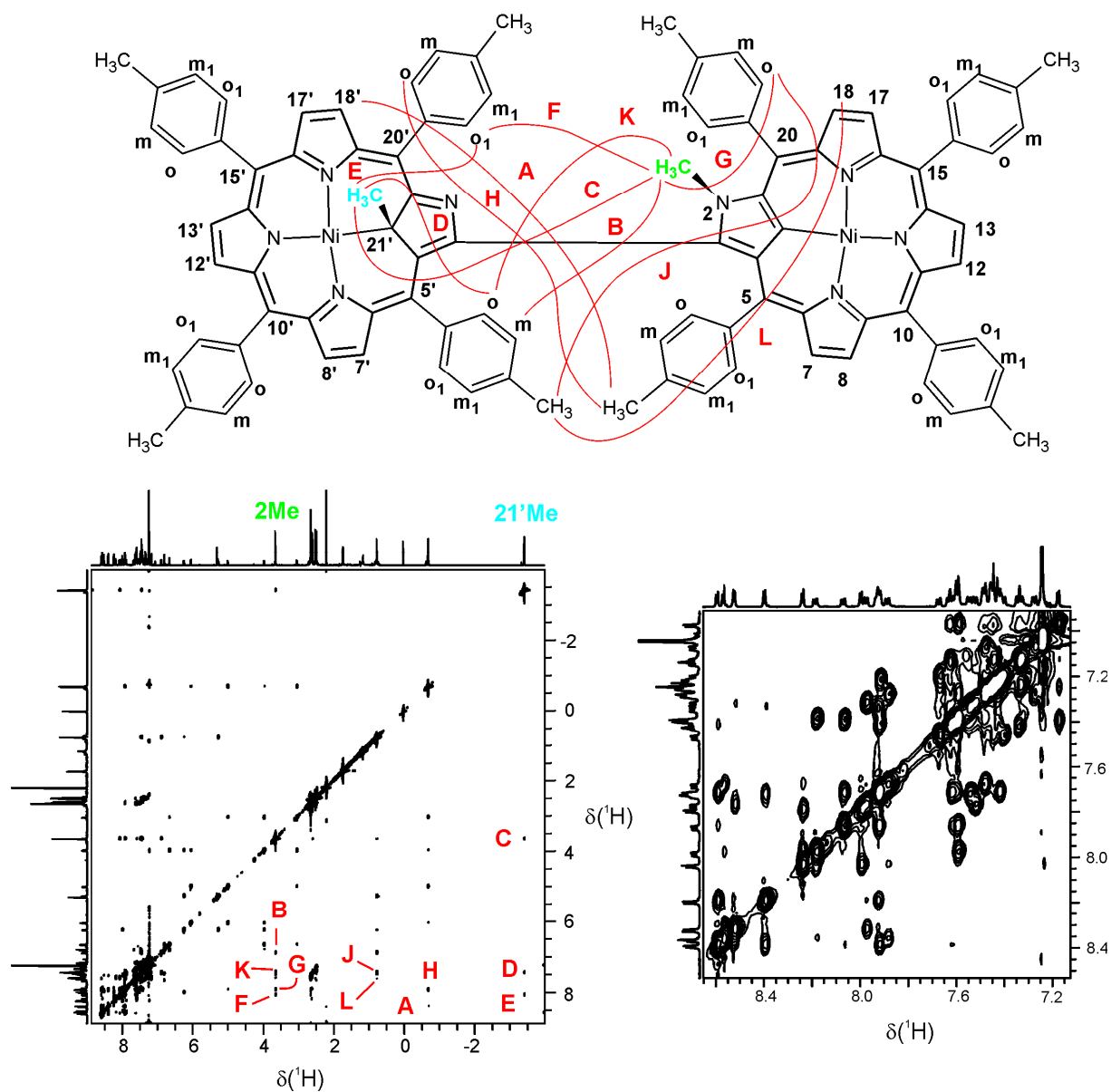
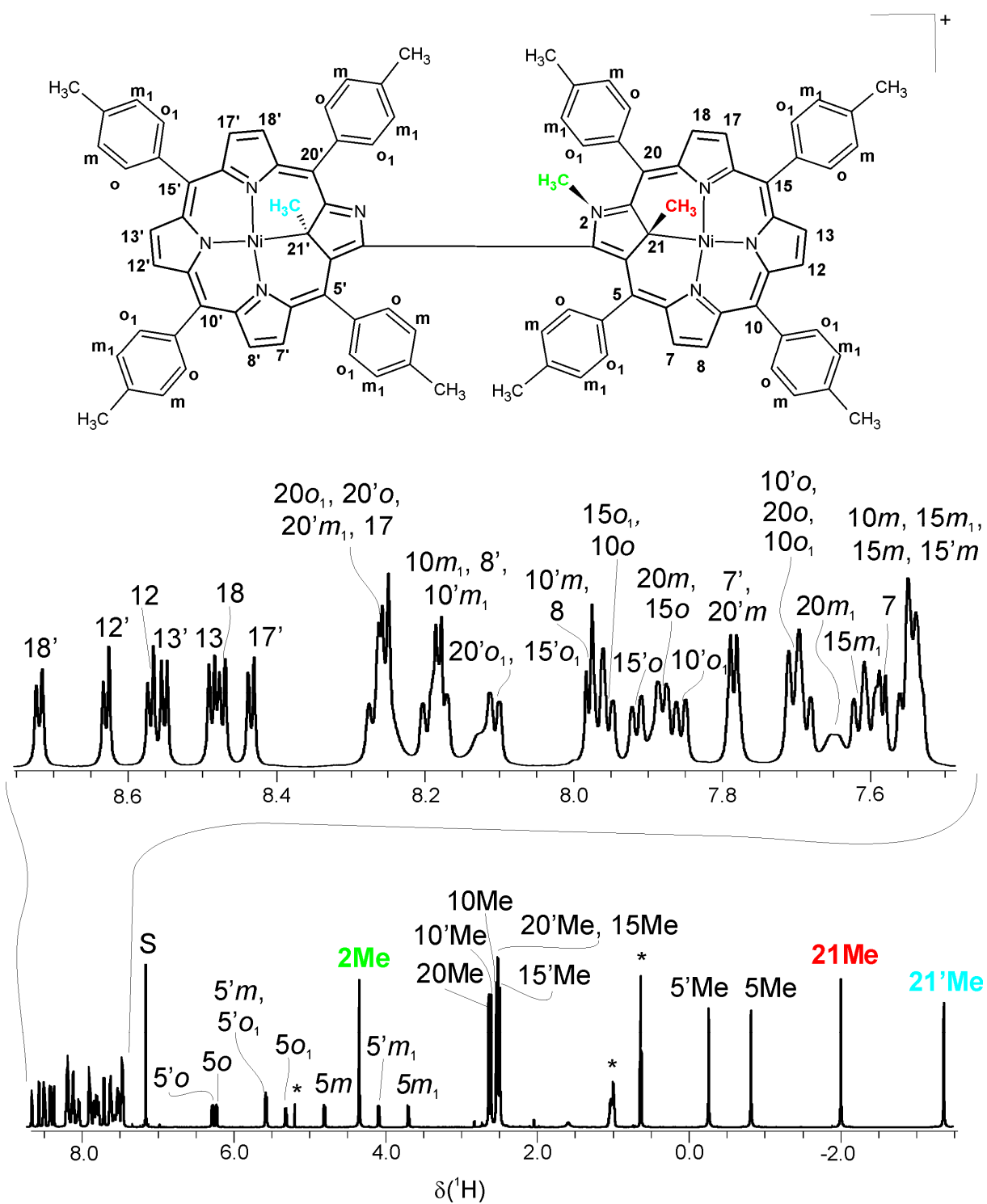


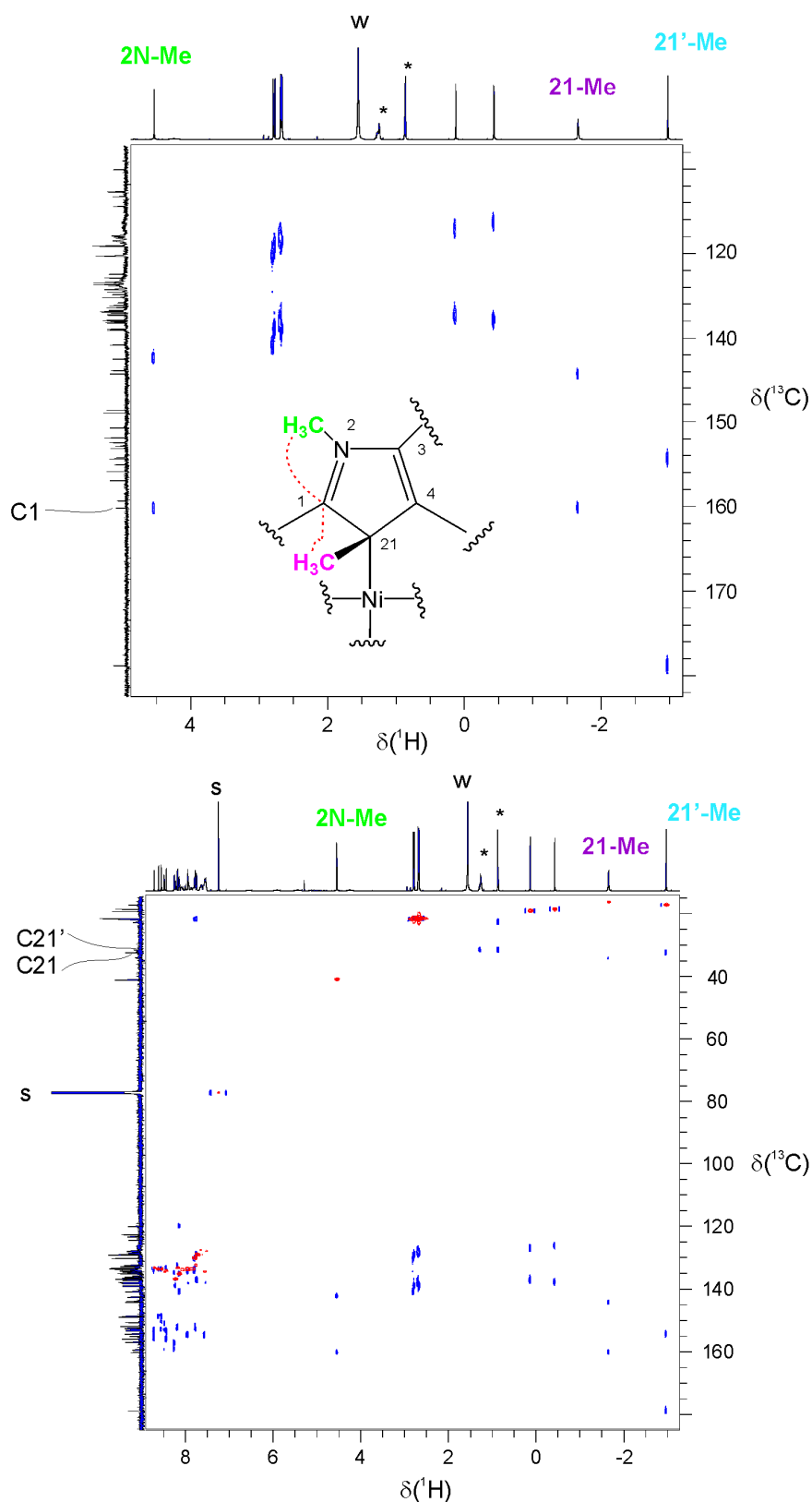
Figure S5. A fragment of  $^1\text{H}$ - $^1\text{H}$  COSY spectrum (600 MHz, CDCl<sub>3</sub>, 213 K) of 4.



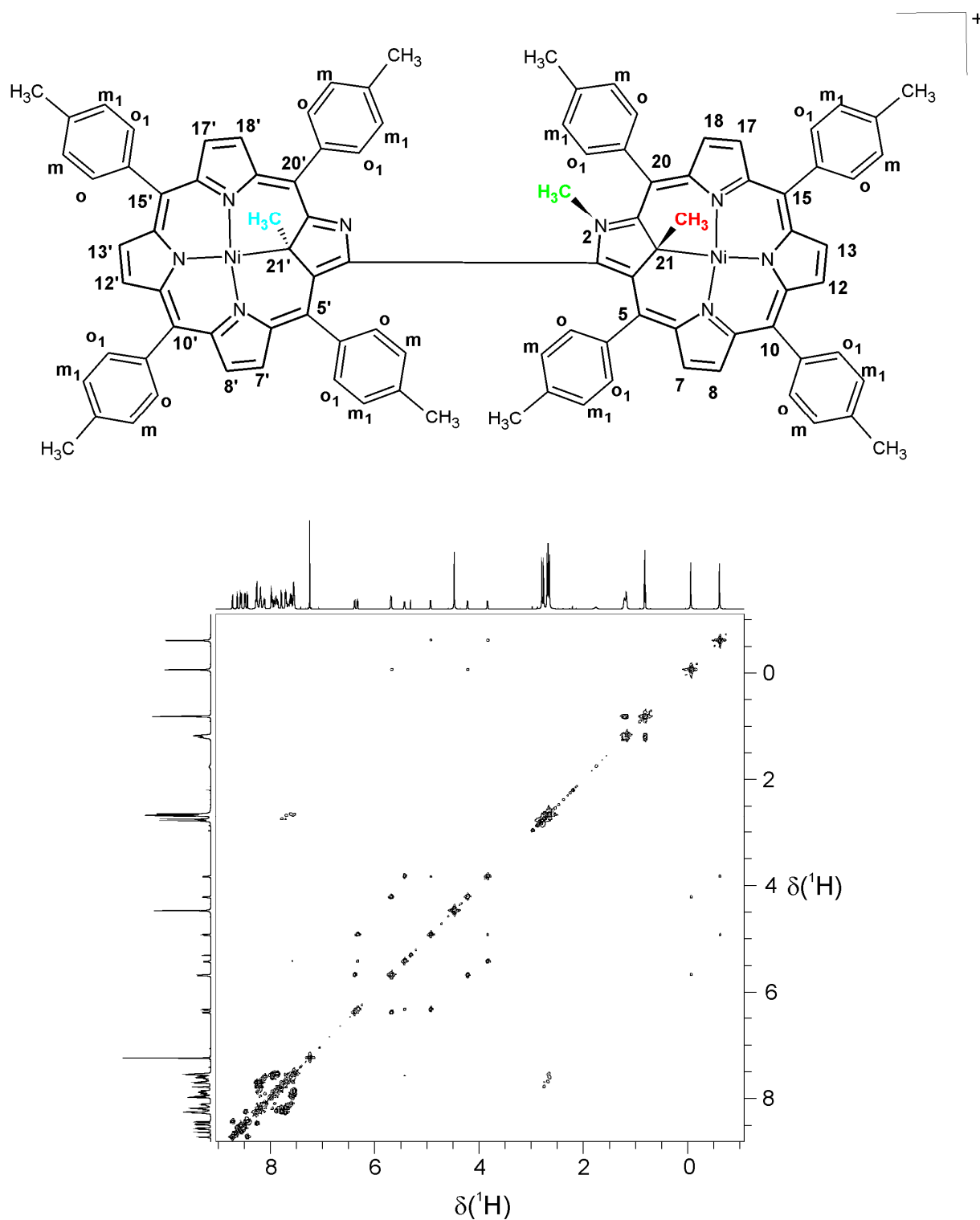
**Figure S6.**  $^1\text{H}$ - $^1\text{H}$  NOESY spectrum of **4**, 600 MHz,  $\text{CDCl}_3$ , 213 K. The full correlation map is given on the left side. The map on the right presents the extension of the selected region (low-field part) of the spectrum. The red letters denote through-space interprotonic interactions represented on the schematic structure by curved lines.



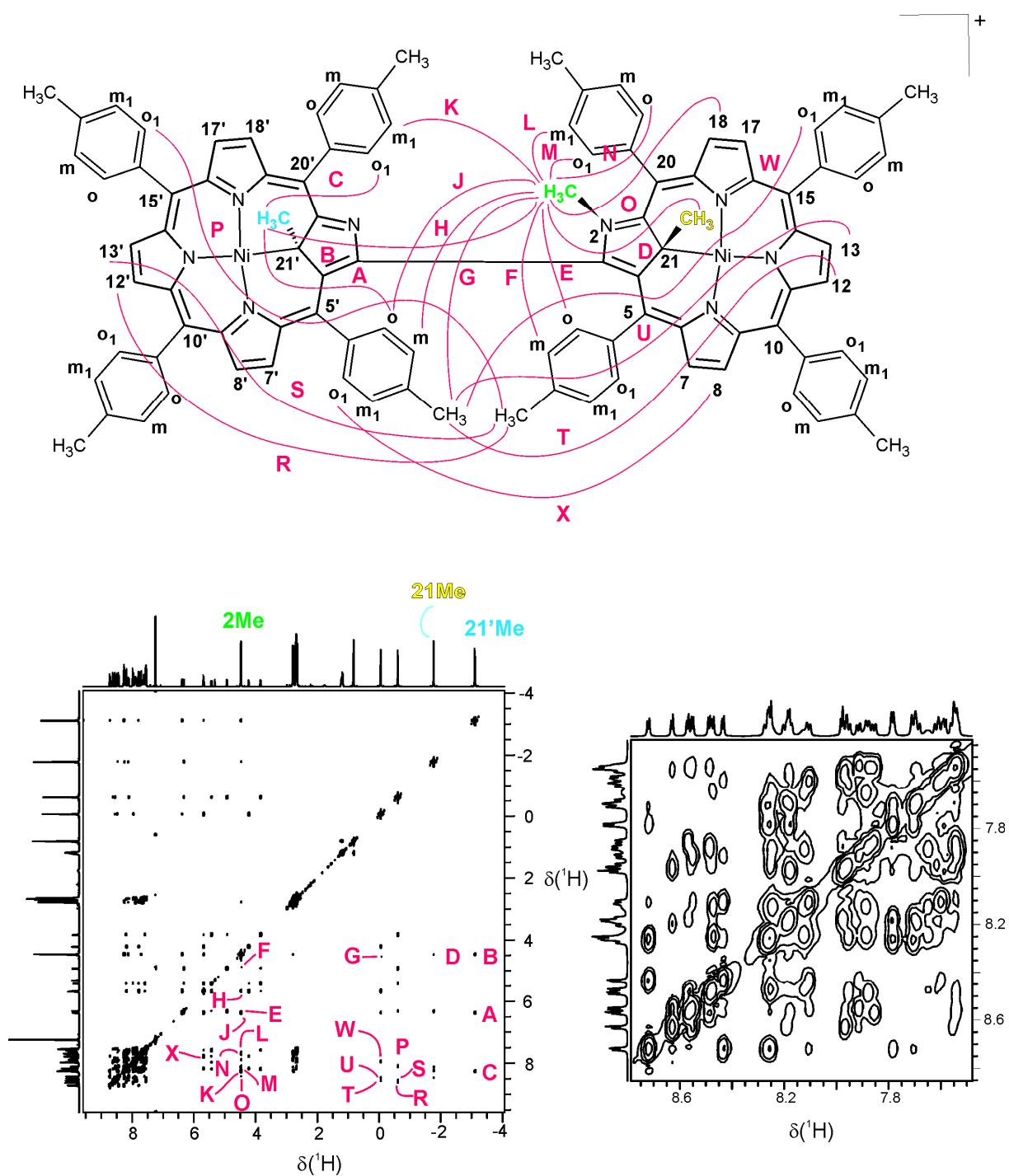
**Figure S7.**  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ , 213 K) of 2,21,21'-trimethylo-3,3'-bis(meso-tetratolyl-2-aza-21-methylcarbaporphyrinatonicel(II)) **5** with complete assignment of signals.



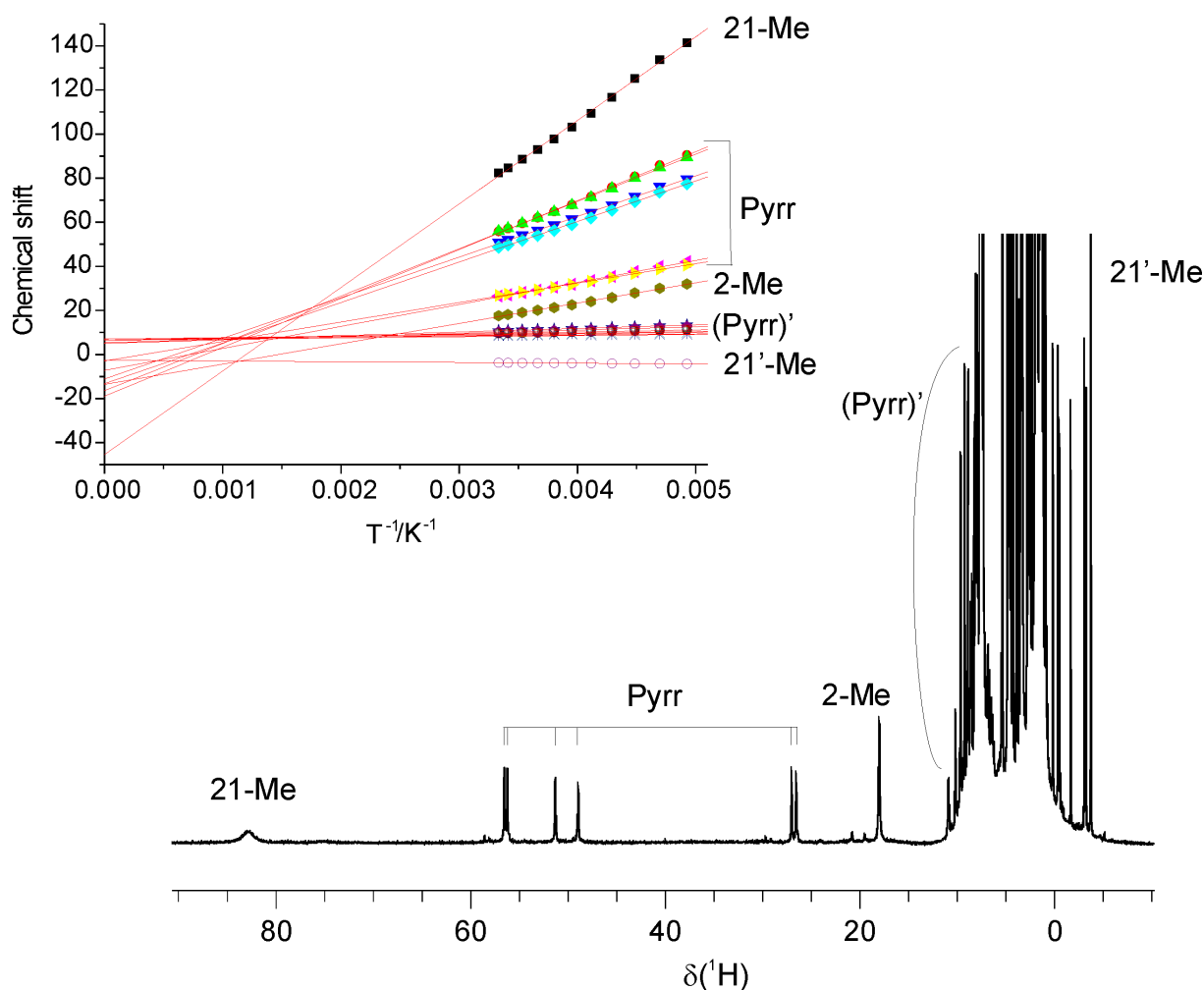
**Figure S8.** Bottom: Superimposed  $^1\text{H}$ - $^{13}\text{C}$  HMQC (red signals) and HMBC (blue signals) spectra of **5** ( $\text{CDCl}_3$ , 300 K). Top: Extension of a fragment of the HMBC map showing correlation of protons of internal (at C21) and external (at N2) methyl substituents with the same carbon (C1).



**Figure S9.** A fragment of  $^1\text{H}$ - $^1\text{H}$  COSY spectrum (600 MHz,  $\text{CDCl}_3$ , 213 K) of **5**.

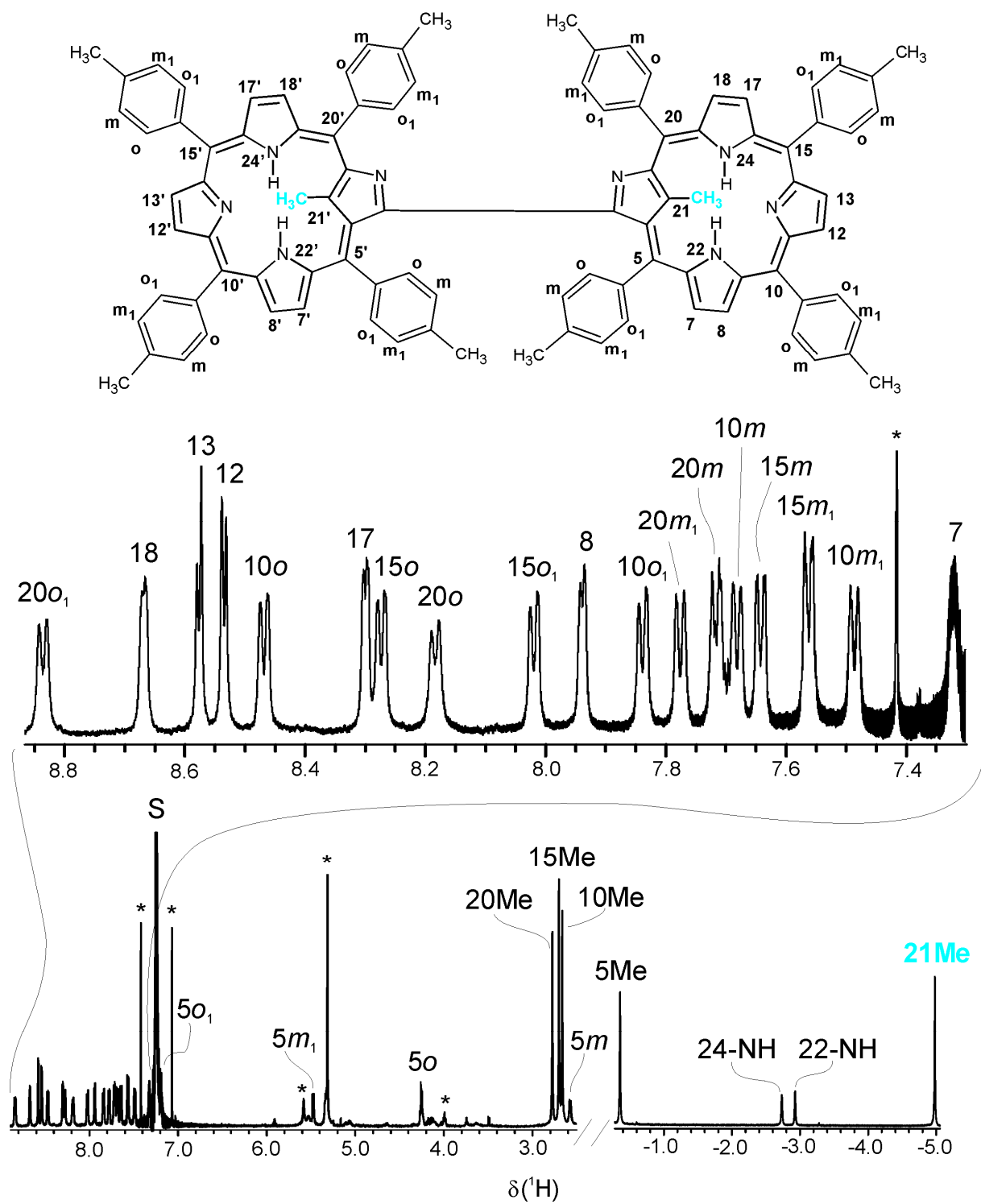


**Figure S10.**  $^1\text{H}$ - $^1\text{H}$  NOESY spectrum of **5**, 600 MHz,  $\text{CDCl}_3$ , 213 K. The full correlation map is given on the left side. The map on the right presents the extension of the selected region (low-field part) of the spectrum. The red letters denote through-space interprotonic interactions represented on the schematic structure by curved lines.

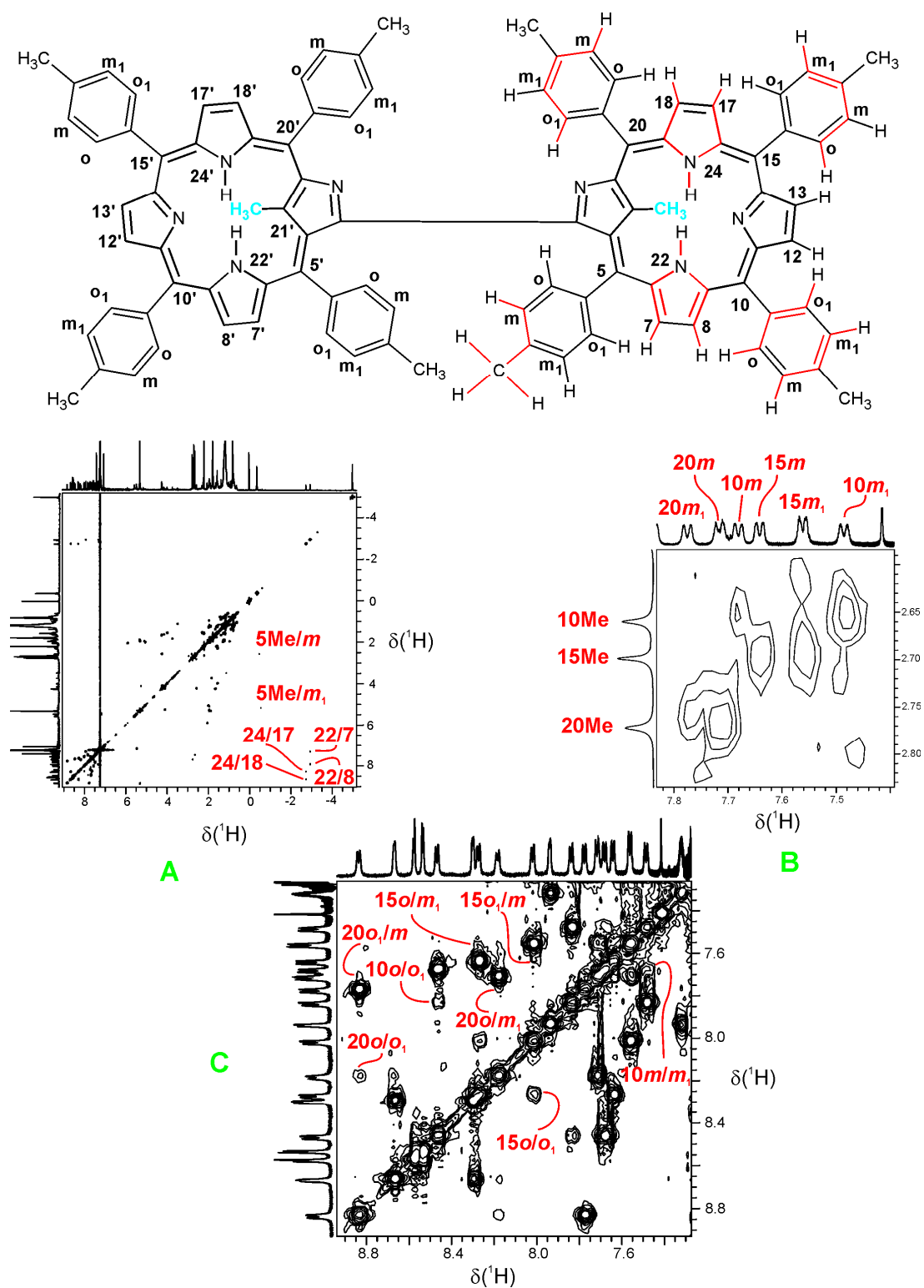


**Figure S10a.** <sup>1</sup>H NMR spectrum (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K) of **5** upon addition of 5 equiv of benzyltriethylammonium chloride. The assignments – Pyrr, 2-Me, 21-Me: β-pyrrole and methyl protons at the positions 2 or 21 of the bis(methylated) subunit of the complex, respectively; (Pyrr)' and 21'-Me: β-pyrrole and methyl at C21 of monomethylated subunit of the complex, respectively. The inset presents Curie plot for this solution based on the spectra recorded in the temperature range of 203-300K. Note strong temperature dependence of the chemical shifts for the protons of bis(methylated) fragment and very weak variation for those of monomethylated subunit.

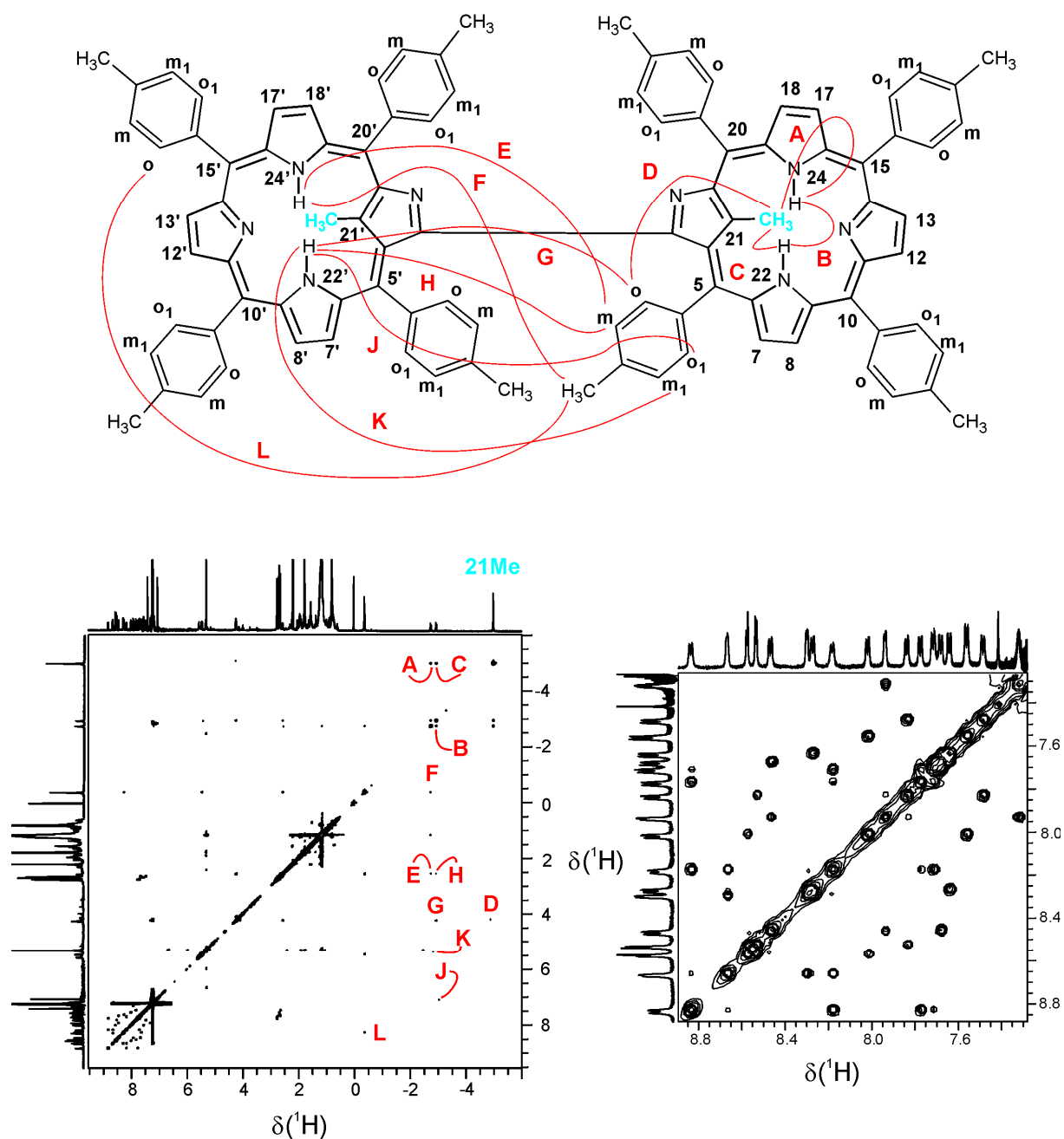




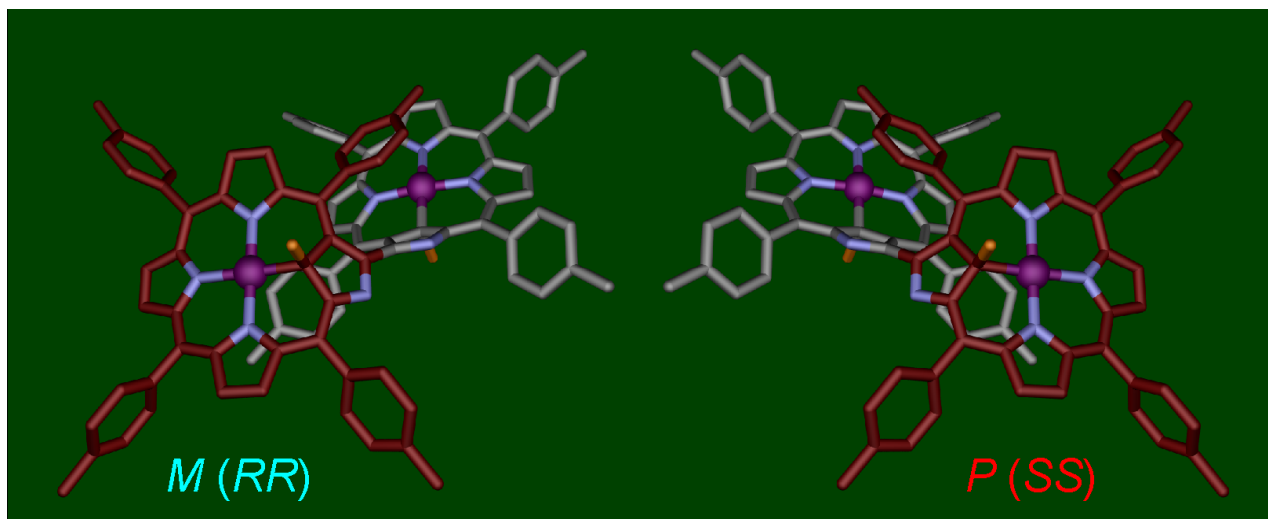
**Figure S11.**  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ , 213 K) of 3,3'-bis(meso-tetratolyl-2-aza-21-methylcarbaporphyrin) **6** with complete assignment of signals.



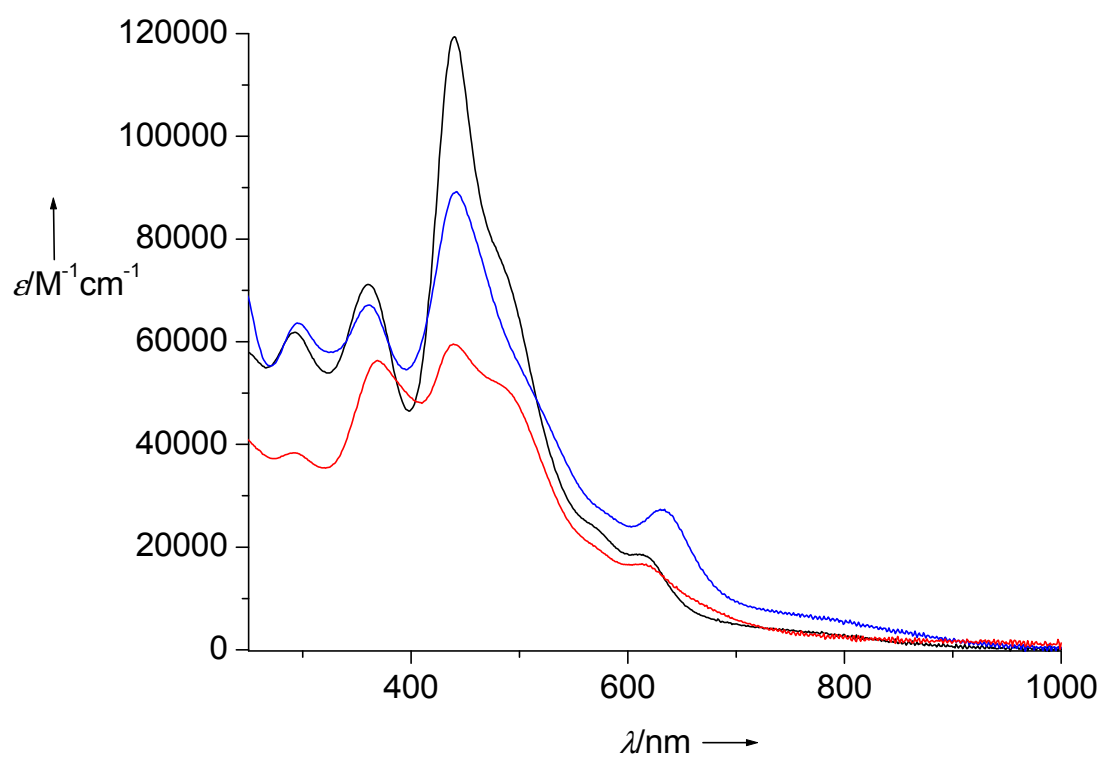
**Figure S12.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum (600 MHz,  $\text{CDCl}_3$ , 213 K) of **6**: A) full correlation map; B) and C) extensions of the selected regions of the spectrum. The scalar couplings between protons have been marked in the maps with red letters; some of the long-range interactions (through four or more bonds) are also shown on the schematic structure by means of red lines.



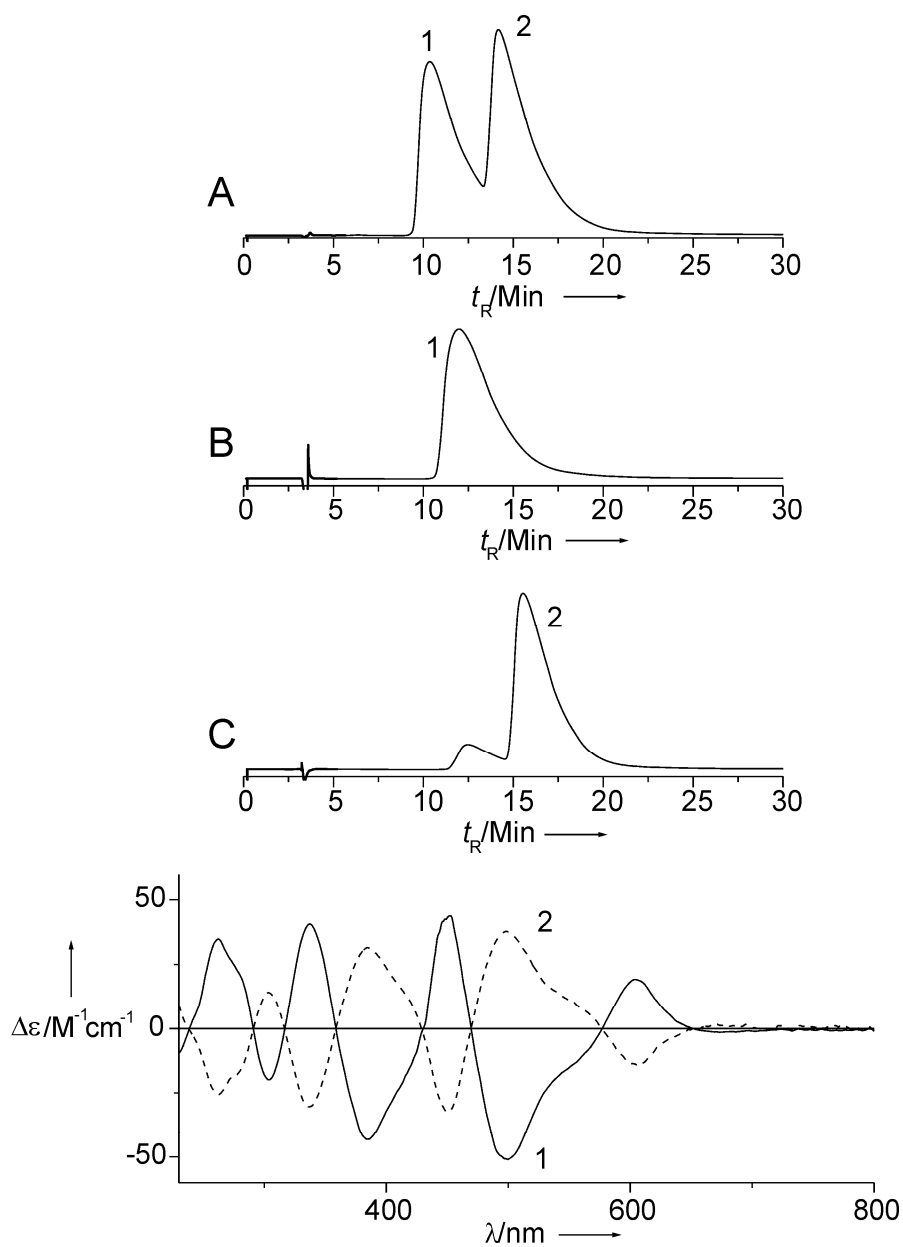
**Figure S13.**  $^1\text{H}$ - $^1\text{H}$  NOESY spectrum of **6**, 600 MHz,  $\text{CDCl}_3$ , 213 K. The full correlation map is given on the left side. The map on the right presents the extension of the selected region (low-field part) of the spectrum. The red letters denote through-space interprotonic interactions represented on the schematic structure by curved lines.



**Figure S14.** A pair of symmetry-dependent enantiomers present in the unit cell of racemic **3**. All hydrogen atoms are omitted.



**Figure S15.** Optical spectra (CH<sub>2</sub>Cl<sub>2</sub>) of **3** (black trace), **4** (red trace), and **5** (blue trace).



**Figure S16.** Chiral phase HPLC profile for the racemic **3** (A) and analytical chromatograms for fraction 1 (B) and 2 (C) collected for five runs of separation (Chirex 3010 column, dichloromethane as a mobile phase, flow rate 1 ml/min, RT). Bottom traces show CD spectra of the fraction 1 (solid line) and 2 (dashed line).

**Table S1.** Selected Bond Lengths [Å] for *rac-3*

Bond	Length	Bond	Length
Ni1– C21	2.033(1)	C3– C27	1.472(2)
Ni1– N22	1.943(1)	Ni2– C45	2.016(2)
Ni1– N23	1.958(1)	Ni2– N46	1.949(1)
Ni1– N24	1.944(1)	Ni2– N47	1.952(1)
C21– C1	1.471(2)	Ni2– N48	1.945(1)
C21– C4	1.477(2)	C45– C25	1.470(2)
C21– C61	1.547(2)	C45– C28	1.461(2)
N22– C6	1.389(2)	C45– C62	1.554(2)
N22– C9	1.386(2)	N46– C30	1.390(2)
N23– C11	1.376(2)	N46– C33	1.377(2)
N23– C14	1.372(2)	N47– C35	1.379(2)
N24– C16	1.386(2)	N47– C38	1.380(2)
N24– C19	1.384(2)	N48– C40	1.385(2)
C1– N2	1.365(2)	N48– C43	1.393(2)
C1– C20	1.388(2)	C25– N26	1.369(2)
N2– C3	1.337(2)	C25– C44	1.396(2)
C3– C4	1.426(2)	N26– C27	1.348(2)
C4– C5	1.389(2)	C27– C28	1.412(2)
C5– C6	1.410(2)	C28– C29	1.395(2)
C6– C7	1.440(2)	C29– C30	1.394(2)
C7– C8	1.349(2)	C30– C31	1.440(2)
C8– C9	1.434(2)	C31– C32	1.343(2)
C9– C10	1.396(2)	C32– C33	1.438(3)
C10– C11	1.387(2)	C33– C34	1.388(2)
C11– C12	1.435(2)	C34– C35	1.397(2)
C12– C13	1.353(2)	C35– C36	1.437(2)
C13– C14	1.437(2)	C36– C37	1.350(2)
C14– C15	1.395(2)	C37– C38	1.430(2)
C15– C16	1.392(2)	C38– C39	1.392(2)
C16– C17	1.442(2)	C39– C40	1.391(2)
C17– C18	1.350(2)	C40– C41	1.441(2)
C18– C19	1.439(2)	C41– C42	1.345(2)
C19– C20	1.402(2)	C42– C43	1.438(2)
		C43– C44	1.398(2)

**Table S2.** Selected Bond Angles [°] for *rac-3*.

Atoms	Angle	Atoms	Angle
C21–Ni1–N22	88.44(6)	C45–Ni2–N46	88.37(6)
C21–Ni1–N23	176.47(6)	C45–Ni2–N47	175.59(7)
C21–Ni1–N24	89.29(6)	C45–Ni2–N48	88.47(6)
N22–Ni1–N23	90.98(5)	N46–Ni2–N47	91.47(6)
N22–Ni1–N24	174.53(6)	N46–Ni2–N48	174.13(6)
N23–Ni1–N24	90.98(5)	N47–Ni2–N48	91.47(6)
Ni1–C21–C1	118.6(1)	Ni2–C45–C25	118.5(1)
Ni1–C21–C4	118.4(1)	Ni2–C45–C28	117.7(1)
Ni1–C21–C61	93.9(1)	Ni2–C45–C62	94.4(1)
C1–C21–C4	100.6(1)	C25–C45–C28	100.8(1)
C1–C21–C61	112.2(1)	C25–C45–C62	113.2(1)
C4–C21–C61	113.8(1)	C28–C45–C62	113.0(1)

Sum of the bond angles for C21:

$$\sum_{i \neq j} (X_i - C21 - X_j) = 657.6^\circ$$

Sum of the bond angles for C45:

$$\sum_{i \neq j} (X_i - C45 - X_j) = 657.7^\circ$$

For an idealized tetrahedral environment:

$$6 \cdot 109.5^\circ = 657.0^\circ$$

For a side-on coordination of  $sp^2$  carbon:

$$3 \cdot 120^\circ + 3 \cdot 90^\circ = 630^\circ$$

**Table S3.** Selected Bond Lengths [Å] for  
*P-3*

Bond	Length
Ni1–C21	2.003(3)
Ni1–N22	1.954(2)
Ni1–N24	1.955(2)
Ni1–N23	1.965(2)
C21–C1	1.471(4)
C21–C4	1.479(4)
C21–C31	1.560(4)
N22–C6	1.389(3)
N22–C9	1.380(3)
N24–C16	1.381(3)
N24–C19	1.395(3)
N23–C11	1.370(4)
N23–C14	1.363(4)
C1–N2	1.365(3)
C1–C20	1.379(3)
N2–C3	1.337(3)
C3–C4	1.409(4)
C3–C3'	1.474(4)
C4–C5	1.386(4)
C5–C6	1.391(4)
C6–C23	1.426(4)
C7–C8	1.341(4)
C8–C9	1.443(4)
C9–C10	1.379(4)
C10–C11	1.374(4)
C11–C12	1.443(4)
C12–C13	1.348(4)
C13–C14	1.436(4)
C14–C15	1.392(4)
C15–C16	1.371(4)
C16–C17	1.435(4)
C17–C18	1.324(4)
C18–C19	1.438(4)
C19–C20	1.398(4)

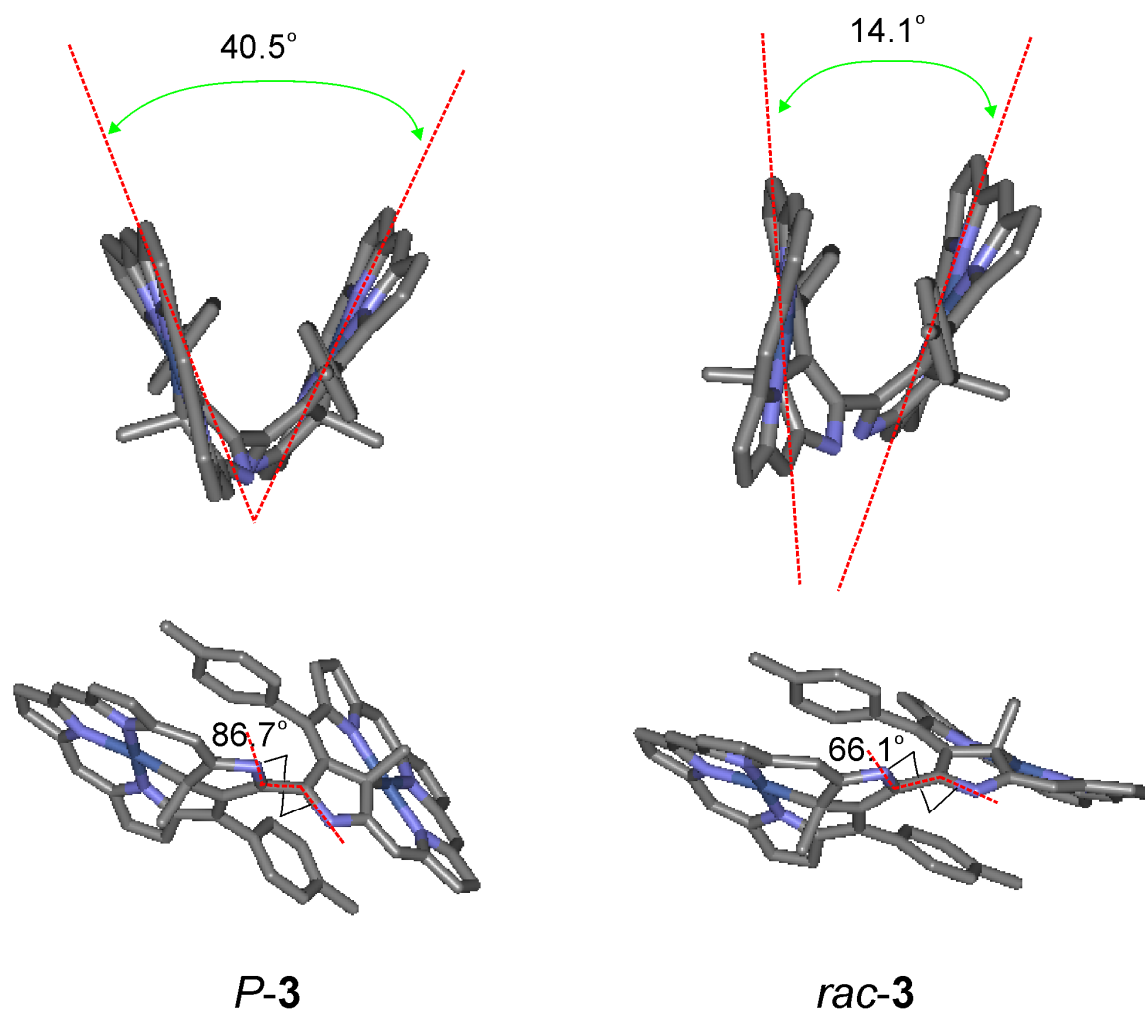


**Table S4.** Selected Bond Angles [°] for *P-3*.

Atoms	Angle
C21–Ni1–N22	88.8(1)
C21–Ni1–N24	88.8(1)
C21–Ni1–N23	173.7(1)
N22–Ni1–N24	176.94(9)
N22–Ni1–N23	90.51(9)
N24–Ni1–N23	91.66(9)
Ni1–C21–C1	120.7(2)
Ni1–C21–C4	119.5(2)
Ni1–C21–C31	94.9(2)
C1–C21–C4	100.5(2)
C1–C21–C31	110.3(2)
C4–C21–C31	110.9(2)

Sum of bond angles for C21:

$$\sum_{i \neq j} (X_i - C21 - X_j) = 656.8^\circ$$



**Figure S17.** Differences between some structural features of **3** in the crystal lattices of *P-3* enantiomorph and *rac-3* (enantiomer *P* is shown): upper row, dihedral angle between mean planes defined by nickel(II) and coordinated atoms (C21, N22, N23, N24); bottom row, torsion angle N2–C3–C3'–N2'.

**Table S5.** Selected Bond Lengths [Å] for **5**

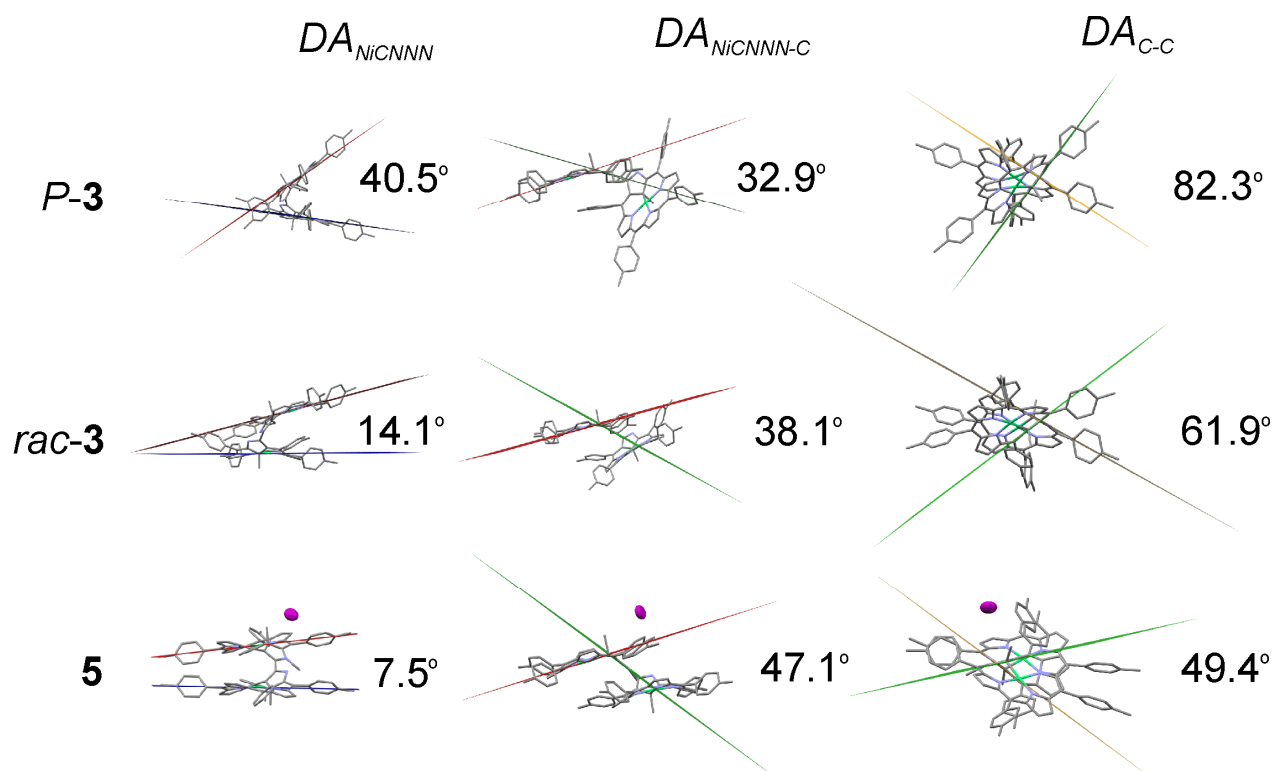
Bond	Length
Ni1–N24	1.935(6)
Ni1–N23	1.943(6)
Ni1–N22	1.972(6)
Ni1–C21	2.047(7)
C21–C1	1.426(11)
C21–C4	1.447(9)
C21–C26	1.547(11)
N22–C9	1.349(10)
N22–C6	1.429(9)
N23–C14	1.368(9)
N23–C11	1.369(10)
N24–C16	1.396(9)
N24–C19	1.416(10)
C1–N2	1.352(9)
C1–C20	1.417(10)
N2–C3	1.370(9)
N2–C25	1.681(16)
C3–C4	1.385(10)
C4–C5	1.398(10)
C5–C6	1.400(10)
C6–C7	1.437(10)
C7–C8	1.358(10)
C8–C9	1.427(11)
C9–C10	1.405(11)
C10–C11	1.397(11)
C11–C12	1.434(10)
C12–C13	1.326(11)
C13–C14	1.452(11)
C14–C15	1.409(11)
C15–C16	1.355(10)
C16–C17	1.428(11)
C17–C18	1.354(11)
C18–C19	1.466(10)
C19–C20	1.368(10)
C3–C3'	1.488(14)

**Table S6.** Selected Bond Angles [°] for **5**.

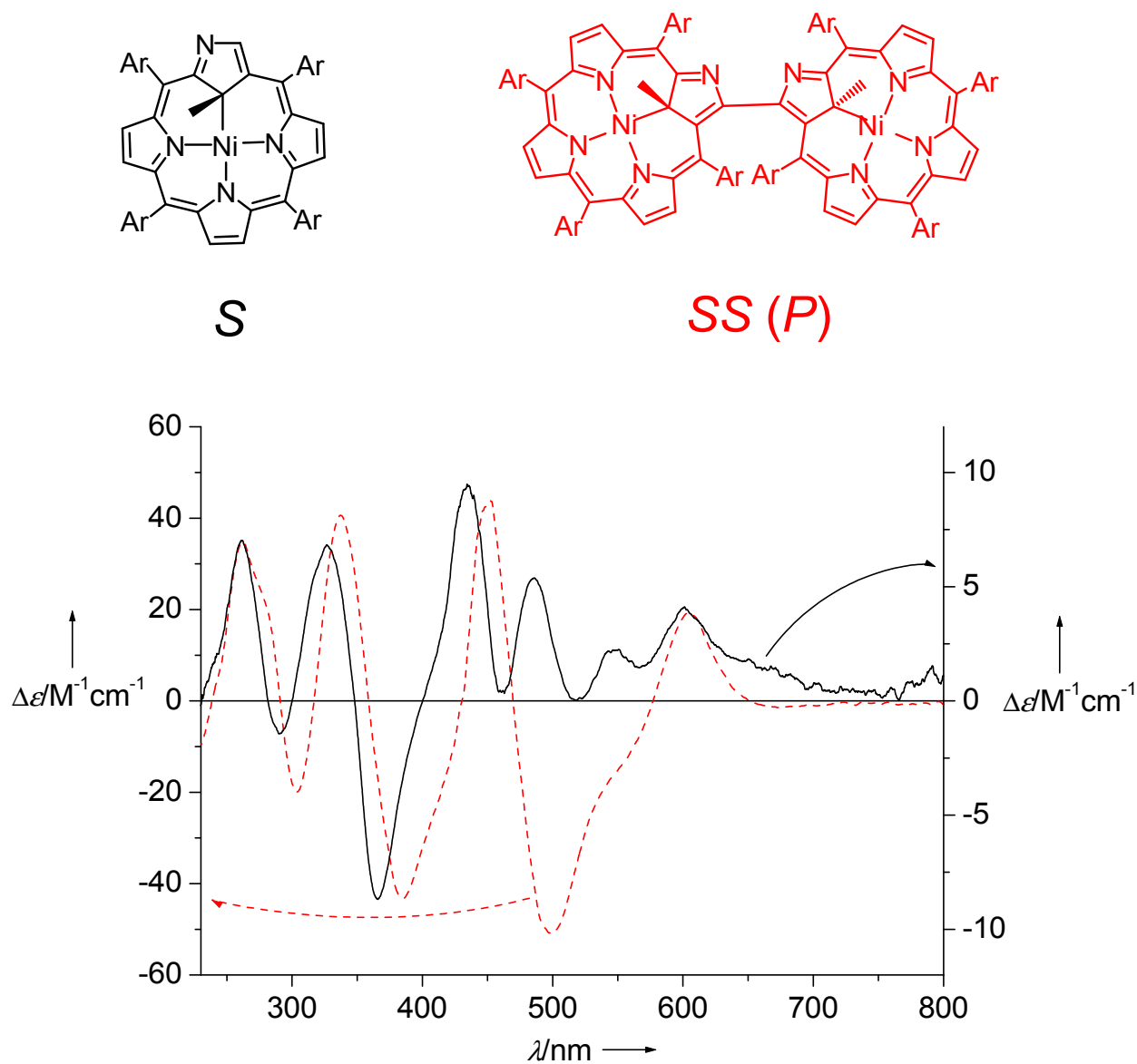
Atoms	Angle
N24–Ni1–N23	91.5(3)
N24–Ni1–N22	174.6(3)
N23–Ni1–N22	90.7(3)
N24–Ni1–C21	89.2(3)
N23–Ni1–C21	175.7(3)
N22–Ni1–C21	88.3(3)
C1–C21–C4	103.0(7)
C1–C21–C26	115.4(7)
C4–C21–C26	115.2(7)
C1–C21–Ni1	114.8(5)
C4–C21–Ni1	116.1(5)
C26–C21–Ni1	93.0(5)

Sum of bond angles for C21:

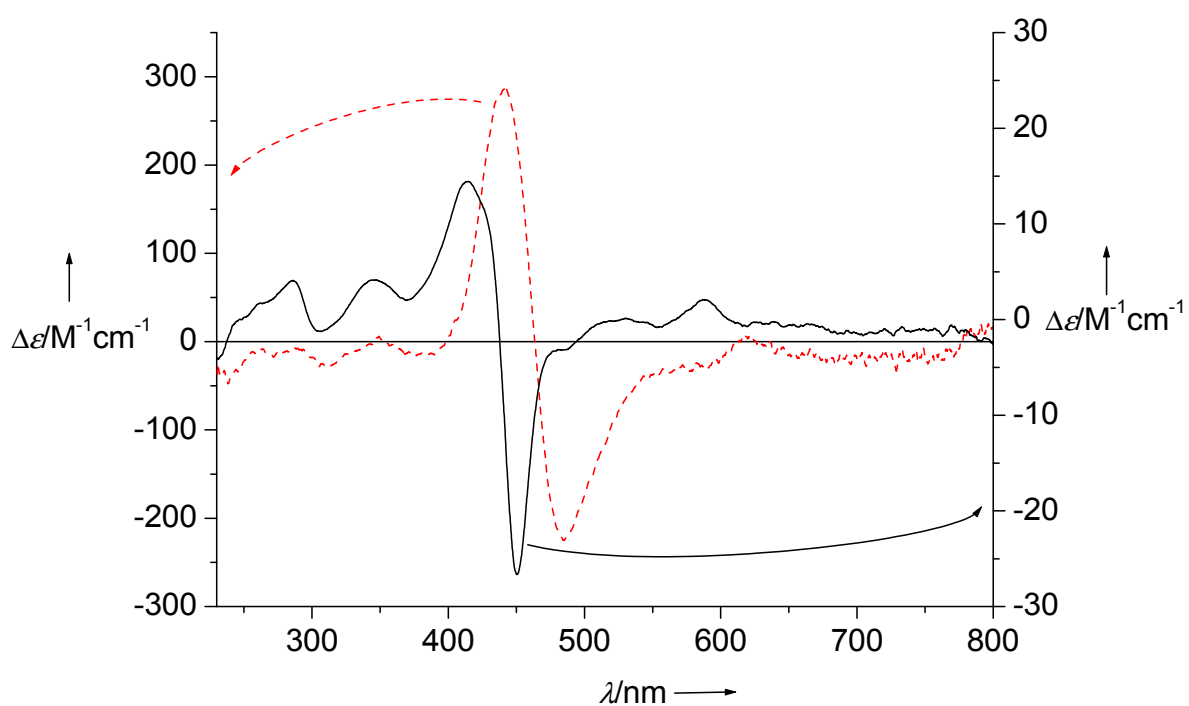
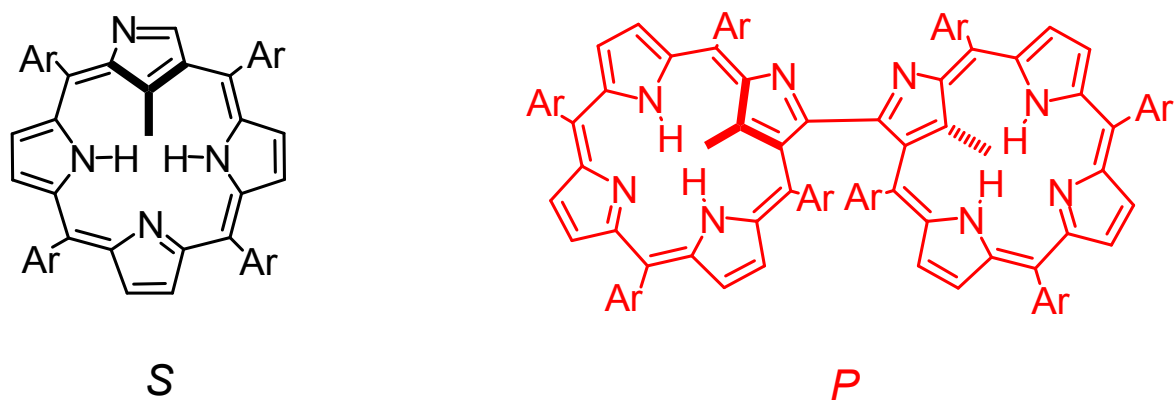
$$\sum_{i \neq j} (X_i - C21 - X_j) = 657.5^\circ$$



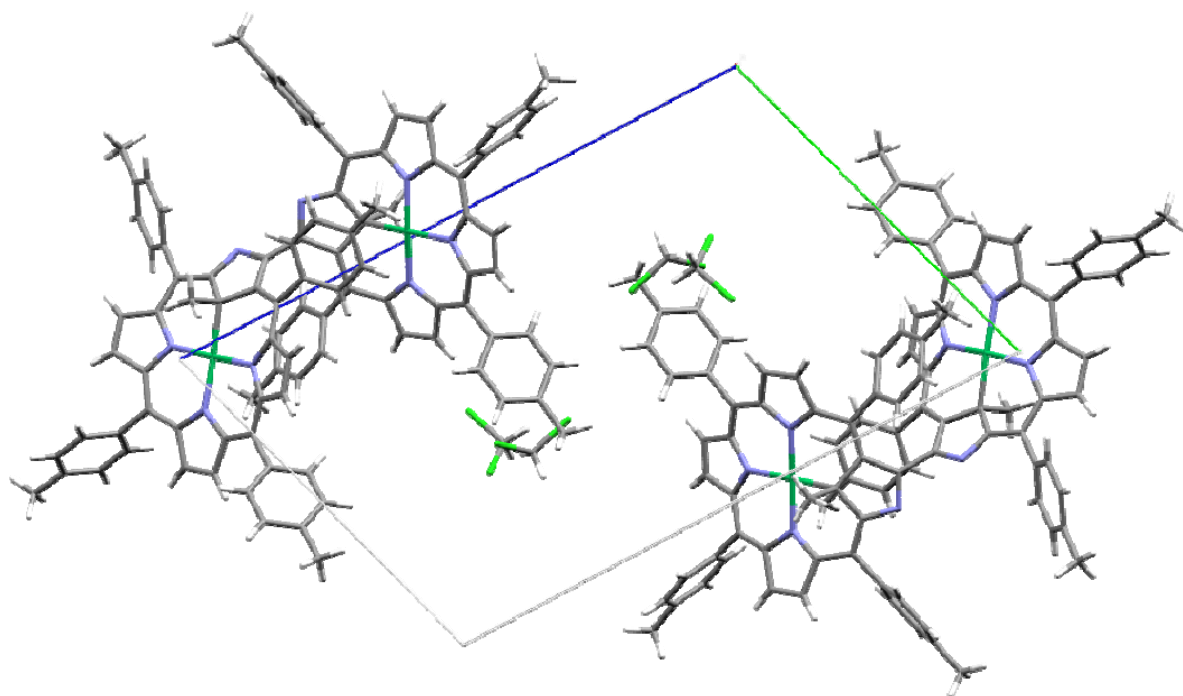
**Figure S18.** Dihedral angles between mean planes  $P_{NiCNNN}$  defined by coordination environment of nickel atoms (Ni, C21, N22, N23, and N24) in both subunits ( $DA_{NiCNNN}$ ), between  $P_{NiCNNN}$  and mean plane of the *confused* pyrrole ( $DA_{NiCNNN-C}$ ) in a subunit, and between mean planes of *confused* pyrroles of the subunits ( $DA_{C-C}$ ) calculated on the basis of the X-ray data for *P*-3, *rac*-3, and 5.



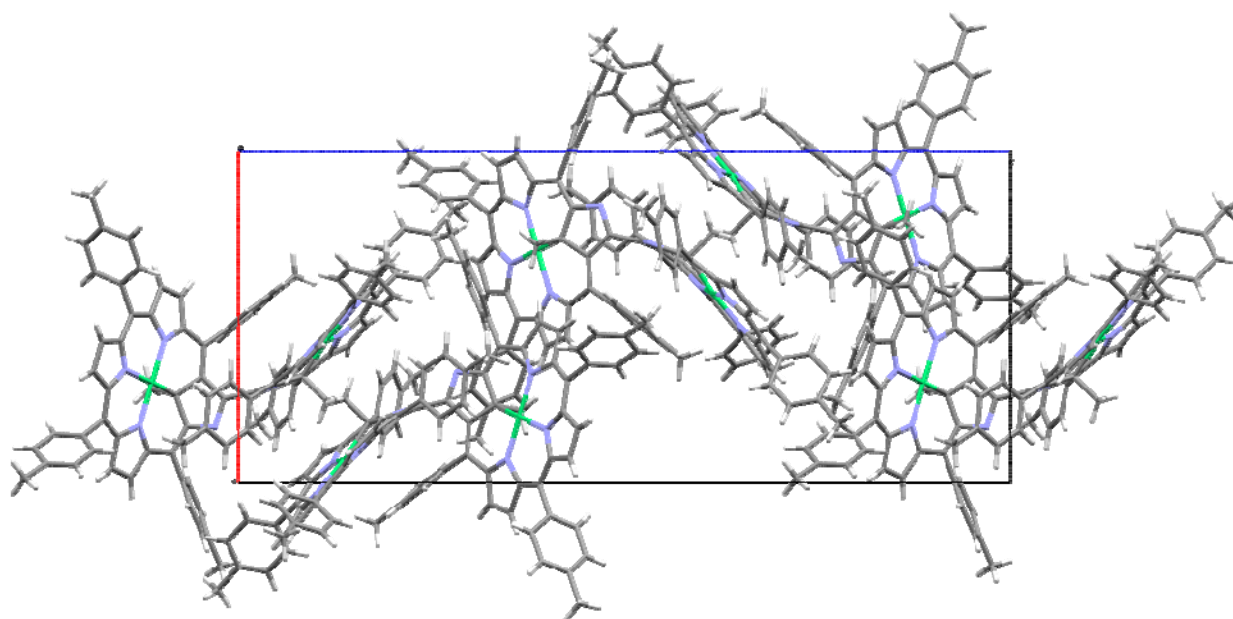
**Figure S19.** CD spectra ( $\text{CH}_2\text{Cl}_2$ ) of faster migrating enantiomers of 21-methyl-*meso*-tolyl-2-aza-21-carbaporphyrinatonicel(II) (solid black trace) and 3,3'-bis(21-methyl-*meso*-tolyl-2-aza-21-carbaporphyrinatonicel(II)) (dashed red trace). Note different intensity scales for both spectra.



**Figure S20.** CD spectra ( $\text{CH}_2\text{Cl}_2$ ) of one of the enantiomers of 21-methyl-*meso*-tolyl-2-aza-21-carbaporphyrin (solid black trace) and 3,3'-bis(21-methyl-*meso*-tolyl-2-aza-21-carbaporphyrin) (dashed red trace) obtained by demetalation of faster migrating enantiomers of their nickel(II) complexes. Note different intensity scales for the spectra.

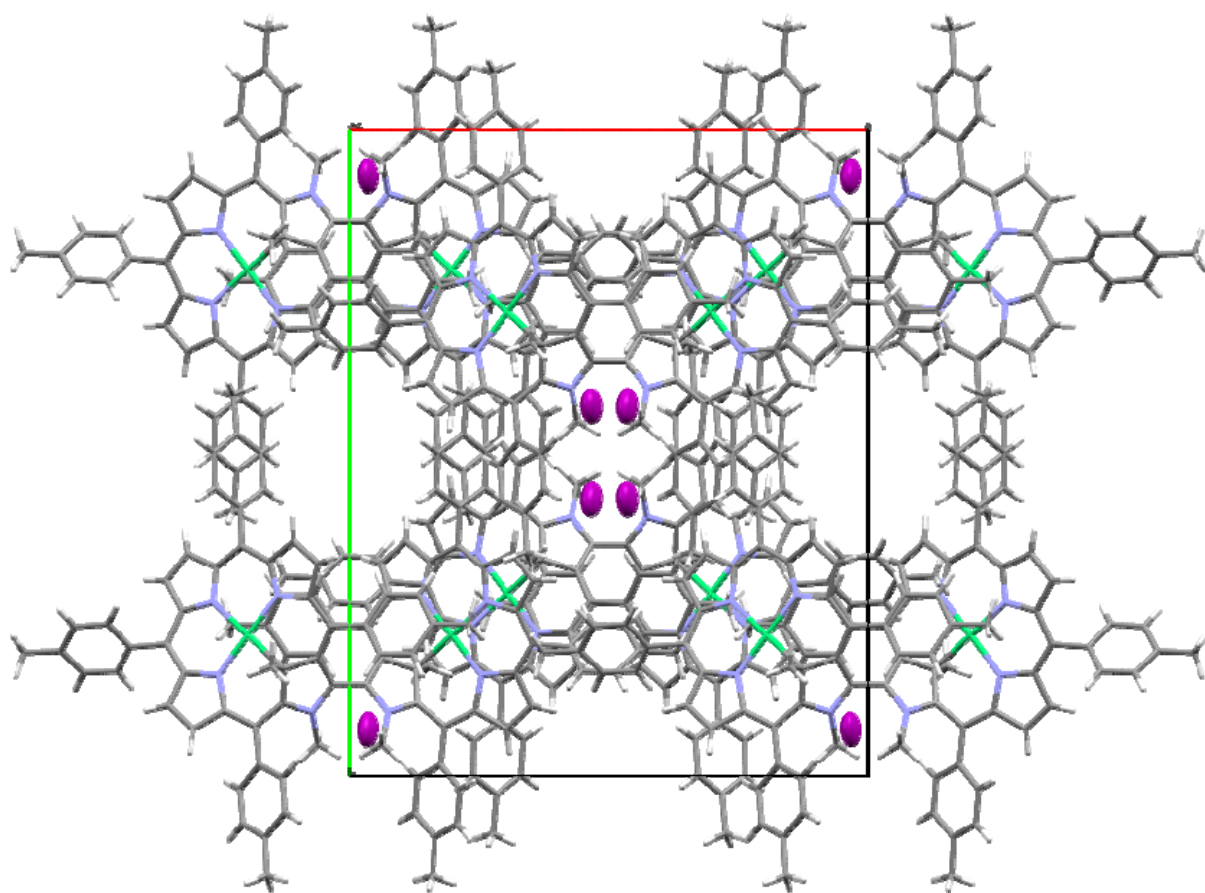


**Figure S21.** A packing diagram for *rac-3*.

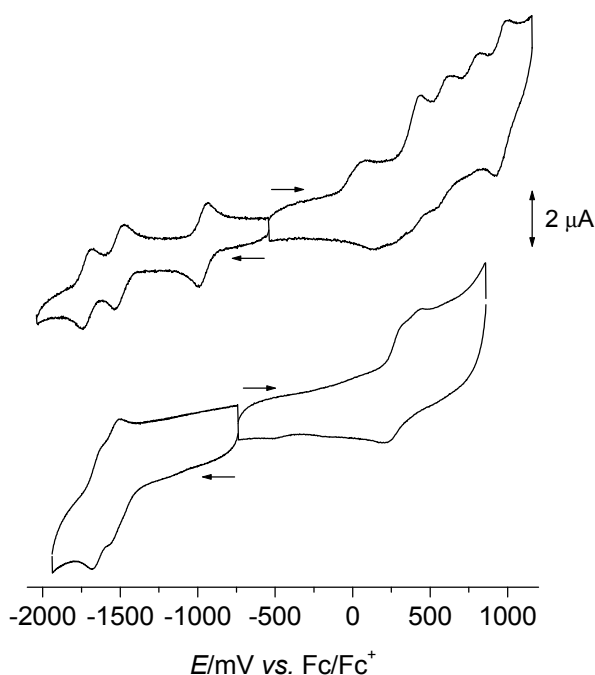


**Figure S22.** A packing diagram for *P-3*.





**Figure S23.** A packing diagram for **5**.



**Figure S24.** Cyclic voltammograms for **3** (bottom traces) and **5** (top traces). Conditions: solvent, dichloromethane; supporting electrolyte, tetrabutylammonium perchlorate, working electrode, glassy carbon; reference electrode, Ag/AgCl (oxidation potential for Fc/Fc<sup>+</sup> internal standard  $E_{st} = 525$  mV); auxiliary electrode, platinum wire; scan rate, 50 mV/s.

**Table S7.** Cyclovoltammetric Data (referenced against ferrocene/ferrocenium internal standard) for **3** and **5** in CH<sub>2</sub>Cl<sub>2</sub> Solutions.

Compound	$E_1^{OX}$ ( $\Delta E_{ac}$ ) [mV]	$E_2^{OX}$ ( $\Delta E_{ac}$ ) [mV]	$E_3^{OX}$ ( $\Delta E_{ac}$ ) [mV]	$E_4^{OX}$ ( $\Delta E_{ac}$ ) [mV]	$E_5^{OX}$ ( $\Delta E_{ac}$ ) [mV]	$E_1^{RED}$ ( $\Delta E_{ac}$ ) [mV]	$E_2^{RED}$ ( $\Delta E_{ac}$ ) [mV]	$E_3^{RED}$ ( $\Delta E_{ac}$ ) [mV]	HLG [mV]
<b>3</b>	260 (90)	410 <sup>a</sup>	-	-	-	-1555 (58)	-1674 (58)	-	1815
<b>5</b>	55 <sup>b</sup>	370 (63)	570 (66)	770 (80)	940 (63)	-990 (58)	-1524 (59)	-1730 (58)	1360

<sup>a</sup> Anodic peak potential of an irreversible wave. <sup>b</sup> Anodic peak potential of an irreversible wave due to oxidation of iodide identified by an independent experiment performed for [Bu<sub>4</sub>N]I under the same conditions.

#### Reference List

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 [2] P. J. Chmielewski, *Angew.Chem.Int.Ed.* 2004, **43**, 5655-5658.

