

## Electronic Supplementary Information for Journal of Materials Chemistry:

# Mesogenic nickel (II) and copper (II) complexes of barbituric acid derivatives – toward one- dimensional magnets

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## Instrumental

The NMR spectra of the ligand semi-products and nickel(II) complexes were recorded using a Varian Unity Plus spectrometer operating at 500 MHz. For <sup>1</sup>H NMR spectra, the chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. Results from NMR analyses of the synthesized Ni(II) complexes are consistent with the assumed structures without any sign of additives or impurities. The 2D NMR spectra were taken on 2 M solutions in CDCl<sub>3</sub> in standard 5 mm tubes on a Bruker Avance DRX-500 system (11.7 T). The elemental C, H and N analyses for all compounds were satisfactory. The UV-VIS spectra were recorded in chloromethylene solution on a Shimadzu UV-3101PC scanning spectrometer. The mesophase identification was based on a routine microscopic examination of textures, using Zeiss Jenapol-U polarizing microscope, equipped with a Mettler FP82HT hot stage. Phase transition temperatures were determined by differential scanning calorimetry performed with a Perkin-Elmer DSC-7. The X-ray data for chosen compounds were collected with Bruker D8 Discover diffractometer (K $\alpha$  line, parallel beam obtained with Gobel mirror) working in reflection geometry. The sample was one surface free, and its temperature was controlled with DCS hot stage. The magnetic characterization of the samples was performed using Superconducting Quantum Interference Device (SQUID) magnetometer in magnetic field range -6.0 T < B < +6.0 T, at temperatures 10.0 K < T < 300.0 K.

## Synthesis

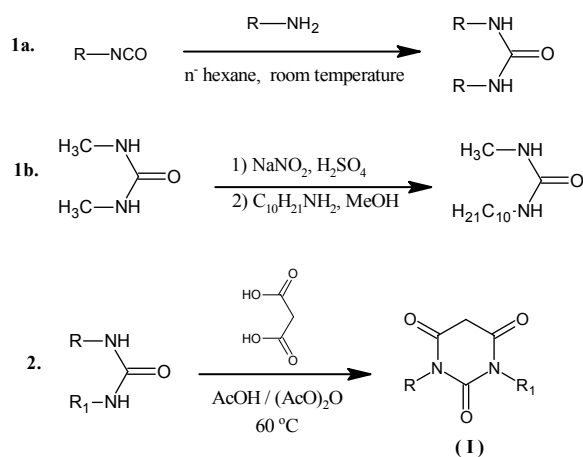
The synthetic procedure to obtain the series of Ni(II) and Cu(II) complexes with two identical or different barbituric acid moieties is shown below. The whole synthesis can be divided into a few following packages. The first step which is common for all obtained materials is the reaction that gives 1,3-dialkylbarbituric acid derivative (**I**) (Scheme 1). Disubstituted symmetrical ureas were obtained by the reaction between appropriate *n*-alkylisocyanate and amine<sup>1</sup> (1a). Unsymmetrical urea derivative was obtained by nitrosation of 1,3-dimethylurea and therefore by the reaction with decylamine<sup>2</sup> (1b). The series of symmetrical barbituric acids<sup>3</sup> containing up to twelve carbon atoms in *N,N'*-alkyl chains was synthesized (from **I-1** to **I-10** and **I-12**). An exception is 1,1-dimethylbarbituric acid compound, which is commercially available and was used without any purification in the next reaction step. In order to reduce a melting point of desired mesogenic molecule, unsymmetrical barbituric acid derivative was also obtained (**I-13**). The each compound (**I-n**) was further attached to 4,5-dioctyloxy-1,2-phenylenediamine, which resulted in free ligands (**II**). The symmetrical compounds (from **II-1** to **II-10** and **II-12**) were synthesized using as intermediate the appropriate *N,N'*-disubstituted derivatives of barbituric acid (Scheme 2a). The three isomeric ligands (**II-13.1**, **II-13.2**, and **II-13.3**) were obtained in the same manner using as intermediate **I-13** unsymmetrical compound (Scheme 2b). The condensation at room temperature between 1,3-dimethylbarbituric acid and 4,5-dioctyloxy-1,2-phenylene-diamine proceeds selectively at only one amino group to give a monosubstituted product (Scheme 2c). The compound with unsubstituted amino group reacts further with **I-10** at higher temperature, giving an unsymmetrical ligand **II-14**. To obtain designed structures of final complexes [series **III** for nickel(II) and series **IV** for copper(II)] appropriate metal acetates were used (Scheme 3).

<sup>1</sup> T. M. Laakso, D. D. Reynolds, *J. Am. Chem. Soc.* **1957**, *79*, 5717-5720.

<sup>2</sup> J. K. Snyder, L. M. Stock, *J. Org. Chem.* **1980**, *45*, 886-891.

<sup>3</sup> J. W. Clark-Lewis, M. J. Thompson, *J. Chem. Soc.* **1959**, *Notes*, 1628-1629.

**Scheme 1.** Syntheses of barbituric acid *N,N'*-alkyl derivatives

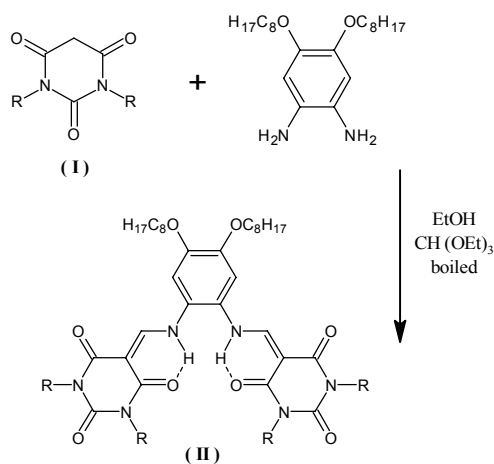


R = C<sub>n</sub>H<sub>2n+1</sub>; R<sub>1</sub> = C<sub>m</sub>H<sub>2m+1</sub>

R = R<sub>1</sub> for symmetrical derivatives (from I-1 to I-10 and I-12)

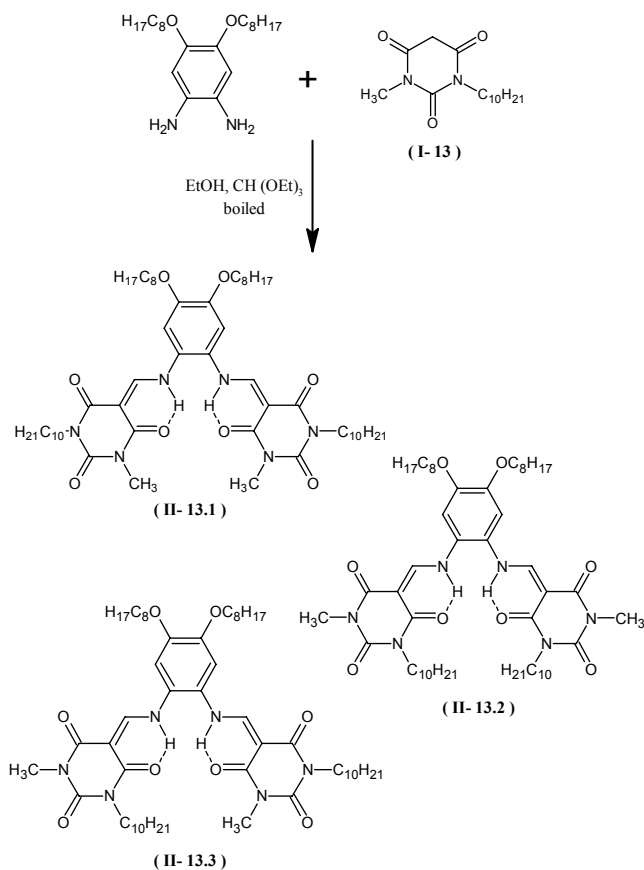
R = CH<sub>3</sub>; R<sub>1</sub> = C<sub>10</sub>H<sub>21</sub> for unsymmetrical compound I-11

**Scheme 2a.** Synthesis of symmetrical ligands

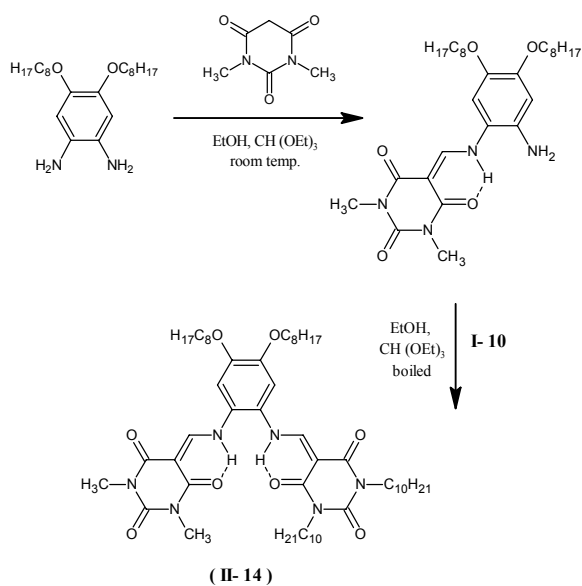


R = C<sub>n</sub>H<sub>2n+1</sub>; n = 1-10 and 12 (from II-1 to II-10 and II-12)

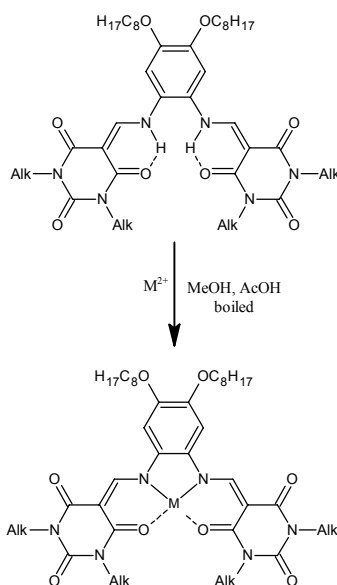
**Scheme 2b.** Synthesis of isomeric mixture of the ligand



**Scheme 2c.** Synthesis of the unsymmetrical ligand



**Scheme 3.** Synthesis of nickel(II) and copper(II) complexes



Alk = n-alkyl chain

M = Ni(II), Cu(II)

All compounds were named according to the series (**I-IV**) and the number of carbon atoms in  $N,N'$ -alkyl chains (from **1** to **10** and **12**), except from the unsymmetrical and isomeric molecules. The details of synthetic route to obtain the new series of Ni(II) and Cu(II) complexes are described below. As examples the compounds containing nine carbon atoms in  $N,N'$ -alkyl chains are chosen.

**1, 3-dinonylurea:** To the cooled mixture of n-nonylisocyanate [4 g, 23.6 mmol (1 equiv)] dissolved in n-hexane (100 ml), a solution of n-nonylamine [4.6 ml, 26 mmol (1.1 equiv)] in n-hexane (20 ml) was carefully added. The crude product was collected by filtration and repeatedly washed with cooled n-hexane. Yield ~ 90%. Each sym-disubstituted urea was previously described in the literature.

**1-decyl-3-methylurea:** A solution of 1,3-dimethylurea [5 g, 67.6 mmol (1.3 equiv)] was carefully added to the ice-cooled mixture of sodium nitrite [3.5 g, 52.2 mmol (1 equiv)], sulfuric acid (2 ml) and laboratory distilled water. The remaining yellowish precipitate was filtered off and dissolved in methanol (50 ml). To the stirred mixture at room temperature n-decylamine [5 ml, 25.5 mmol (0.4 equiv)] was added dropwise. The reaction mixture was left overnight in the fridge, resulting in a precipitate that was filtered off and recrystallized from methanol. Yield ~ 80%; Found: C, 67.26; H, 12.20; N, 13.05. Calc. for  $\text{C}_{12}\text{H}_{26}\text{N}_2\text{O}$  (214.35): C, 67.24; H, 12.22; N, 13.07%.  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.9 (3H, t,  $J$  6.2, Me), 1.27-1.32 (14H, m,  $\text{CH}_2$ ), 1.43-1.56 (2H, m), 2.74 (3H, d,  $J$  12.6, Me), 3.12-3.24 (2H, m, NMe) and 5.04 (2H, s,  $\text{NCH}_2$ ).

**1, 3-dinonylbarbituric acid (I-9):** 1,3-dinonylurea [5 g, 16 mmol (1 equiv)] and malonic acid [2 g, 0.02 mmol (1.1 equiv)] were dissolved in acetic acid (20 ml). To the stirred mixture at 65-70 °C acetic anhydride (30 ml) was added dropwise. Thereafter the addition, the temperature was raised and kept at 90 °C. The solution was evaporated under the pressure, and the residue was boiled for 15 minutes with ethanol (250 ml). The crude product was purified by repeated recrystallizations with methanol to give a white crystal needles. Yield ~ 65%; mp 36-37 °C. Found: C, 69.40; H, 10.47; N, 7.31. Calc. for  $\text{C}_{22}\text{H}_{40}\text{N}_2\text{O}_3$  (380.56): C, 69.43; H, 10.59; N, 7.36%.  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.88 (6H, t,  $J$  6.5,  $2 \times \text{Me}$ ), 1.20-1.68 (28H, m,  $(\text{CH}_2)_{14}$ ), 3.65 (2H, s,  $\text{CH}_2$ ) and 3.85 (4H, t,  $J$  7.6,  $2 \times \text{NCH}_2$ ).

For **I-5**. mp 58 °C. Found: C, 62.58; H, 9.07; N, 10.40. Calc. for  $\text{C}_{14}\text{H}_{24}\text{N}_2\text{O}_3$  (268.35): C, 62.66; H, 9.01; N, 10.44%.  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.90 (6H, t,  $J$  7.1), 1.25-1.64 (12H, m), 3.65 (2H, s) and 3.86 (4H, t,  $J$  7.6).

For **I-6**. mp 31 °C. Found: C, 64.80; H, 9.58; N, 9.32. Calc. for  $\text{C}_{16}\text{H}_{28}\text{N}_2\text{O}_3$  (296.40): C, 64.83; H, 9.52; N, 9.45%.  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.89 (6H, t,  $J$  7.0), 1.24-1.63 (16H, m), 3.65 (2H, s) and 3.85 (4H, t,  $J$  7.7).

For **I-7**. mp 46 °C. Found: C, 66.58; H, 9.97; N, 8.60. Calc. for  $\text{C}_{18}\text{H}_{32}\text{N}_2\text{O}_3$  (324.51): C, 66.63; H, 9.94; N, 8.63%.  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.88 (6H, t,  $J$  6.8), 1.20-1.64 (20H, m), 3.65 (2H, s) and 3.85 (4H, t,  $J$  7.6).

For **I-8**. mp 56 °C. Found: C, 68.20; H, 10.35; N, 7.74. Calc. for C<sub>20</sub>H<sub>36</sub>N<sub>2</sub>O<sub>3</sub> (352.51): C, 68.14; H, 10.29; N, 7.94%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.88 (6H, t, *J* 7.1), 1.20-1.64 (24H, m), 3.65 (2H, s) and 3.85 (4H, t, *J* 7.6).

For **I-10**. mp 40 °C. Found: C, 70.65; H, 10.78; N, 6.90. Calc. for C<sub>24</sub>H<sub>44</sub>N<sub>2</sub>O<sub>3</sub> (408.62): C, 70.54; H, 10.85; N, 6.85%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.88 (6H, t, *J* 6.8), 1.22-1.68 (32H, m), 3.65 (2H, s) and 3.85 (4H, t, *J* 7.6).

For **I-12**. mp 47 °C. Found: C, 72.45; H, 11.26; N, 6.11. Anal. Calc. for C<sub>28</sub>H<sub>52</sub>N<sub>2</sub>O<sub>3</sub> (464.72): C, 72.36; H, 11.28; N, 6.03%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.88 (6H, t, *J* 6.8), 1.25-1.54 (40H, m), 3.65 (2H, s) and 3.85 (4H, t, *J* 7.6).

For **I-13**. oil state (separated by column chromatography). Found: C, 63.82; H, 9.27; N, 9.87. Anal. Calc. for C<sub>15</sub>H<sub>26</sub>N<sub>2</sub>O<sub>3</sub> (282.38): C, 63.80; H, 9.28; N, 9.92%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.88 (6H, t, *J* 6.4), 1.25-1.68 (16H, m), 3.31 (3H, s), 3.67 (2H, s) and 3.86 (2H, t, *J* 7.6).

**Ligand II-9**: 4,5-dioctyloxy-1,2-phenylenediamine [1.9 g, 4 mmol (1 equiv)] was dissolved in ethanol and boiled under reflux. To the boiling mixture a solution of **I-9** [4 g, 10 mmol (2.2 equiv)] in ethanol, ethyl orthoformate and a few traces of acetic acid was added. After 15 minutes the mixture was cooled, resulting in precipitate that was filtered off and recrystallized from 2-propanol to give a yellow solid. Yield ~ 85%; mp 76.6 °C. Found: C, 71.45; H, 10.16; N, 7.38. Calc. for C<sub>68</sub>H<sub>116</sub>N<sub>6</sub>O<sub>8</sub> (1145.68): C, 71.29; H, 10.20; N, 7.33%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.86-0.90 (18H, m, 6 × Me), 1.26-1.38 (64H, m, CH<sub>2</sub>), 1.46-1.52 (4H, dt, *J* 6.8 and 14.1, 2 × OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.61-1.64 (8H, m, 2 × NCH<sub>2</sub>CH<sub>2</sub>), 1.82-1.88 (4H, dt, *J* 6.8 and 14.1, 2 × OCH<sub>2</sub>CH<sub>2</sub>), 3.88-3.95 (8H, dt, *J* 7.3 and 15.6, 4 × NCH<sub>2</sub>), 3.99-4.02 (4H, t, *J* 6.3, 2 × OCH<sub>2</sub>), 6.80 (2H, s, Ph), 8.45-8.50 (2H, d, *J* 13.1, 2 × CH=C) and 12.22-12.27 (2H, d, *J* 13.1, 2 × NH).  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.32; 22.87; 26.13; 27.16; 27.23; 28.42; 29.30; 29.45; 29.47; 29.49; 29.51; 29.55; 29.63; 29.73; 29.80; 32.00; 32.06; 41.18; 41.72; 70.15; 76.98; 77.23; 77.49; 94.72; 105.65; 123.96; 149.38; 151.47; 154.14; 162.62; 165.12.

For **II-1**. mp 134.5 °C. Found: C, 62.08; H, 7.46; N, 12.15. Calc. for C<sub>36</sub>H<sub>52</sub>N<sub>6</sub>O<sub>8</sub> (696.83): C, 62.05; H, 7.52; N, 12.06%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.87-0.90 (6H, t, *J* 6.8), 1.29-1.34 (16H, m), 1.44-1.50 (4H, dt, *J* 6.8 and 13.1), 1.79-1.81 (4H, dt, *J* 6.3 and 12.2), 3.37 (12H, s), 3.91-3.96 (4H, k, *J* 6.8), 6.77 (2H, s), 8.51-8.54 (2H, d, *J* 14.1) and 12.09-12.13 (2H, d, *J* 14.1).  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.07; 22.62; 25.88; 27.37; 27.99; 29.05; 29.20; 29.26; 31.75; 69.92; 76.74; 77.00; 77.25; 94.24; 105.57; 123.70; 149.24; 151.73; 153.98; 162.46; 165.00.

For **II-2**. mp 114.8 °C. Found: C, 63.72; H, 8.14; N, 11.09. Calc. for C<sub>40</sub>H<sub>60</sub>N<sub>6</sub>O<sub>8</sub> (752.94): C, 63.80; H, 8.03; N, 11.16%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.89-0.91 (6H, t, *J* 6.7), 1.23-1.40 (28H, m), 1.46-1.52 (4H, dt, *J* 2.1 and 5.5), 1.82-1.88 (4H, dt, *J* 6.7, *J*<sub>2</sub> 13.7), 3.99-4.03 (12H, m), 6.81 (2H, s), 8.47-8.49 (2H, d, *J* 13.1) and 12.25-12.31 (2H, d, *J* 13.1).  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 13.30; 13.38; 14.07; 22.63; 25.88; 29.05; 29.20; 29.26; 31.76; 35.98; 36.50; 69.91; 76.73; 76.98; 77.24; 94.50; 105.36; 123.65; 149.15; 150.87; 153.85; 162.18; 164.78.

For **II-3**. mp 89.4 °C. Found: C, 65.46; H, 8.36; N, 10.42. Calc. for C<sub>44</sub>H<sub>68</sub>N<sub>6</sub>O<sub>8</sub> (809.04): C, 65.32; H, 8.47; N, 10.39%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.88-0.90 (6H, t, *J* 6.7), 0.94-0.98 (12H, m), 1.30-1.38 (16H, m), 1.46-1.52 (4H, dt, *J*<sub>1</sub> 2.1, *J*<sub>2</sub> 5.5), 1.62-1.7 (8H, m), 1.82-1.88 (4H, dt, *J* 6.7 and 13.7), 3.87-3.93 (8H, dt, *J* 7.6 and 15.1), 3.98-4.03 (4H, t, *J* 6.7), 6.81 (2H, s), 8.46-8.49 (2H, d, *J* 13.1) and 12.25-12.31 (2H, d, *J* 13.1).  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 11.25; 11.27; 14.07; 21.33; 21.39; 22.63; 25.88; 29.05; 29.20; 29.25; 31.75; 42.31; 42.86; 69.89; 76.74; 76.99; 77.24; 94.38; 105.32; 123.64; 149.13; 151.27; 153.90; 162.38; 164.94.

For **II-4**. mp 72.4 °C. Found: C, 66.73; H, 8.91; N, 9.68. Calc. for C<sub>48</sub>H<sub>76</sub>N<sub>6</sub>O<sub>8</sub> (865.15): C, 66.64; H, 8.85; N, 9.71%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.88-0.91 (6H, t, *J* 6.7), 0.93-0.98 (12H, m), 1.30-1.41 (24H, m), 1.43-1.51 (4H, dt, *J* 6.7 and 14.3), 1.58-1.66 (8H, m), 1.82-1.88 (4H, dt, *J* 6.7 and 13.7), 3.90-3.96 (8H, dt, *J* 7.6 and 14.6), 4.00-4.03 (4H, t, *J* 6.5), 6.81 (2H, s), 8.46-8.50 (2H, d, *J* 13.1) and 12.20-12.25 (2H, d, *J* 13.1).  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 13.75; 14.05; 20.12; 20.14; 22.63; 25.88; 29.04; 29.19; 29.25; 30.16; 30.20; 30.75; 31.75; 40.64; 41.20; 69.84; 76.74; 76.99; 77.25; 94.42; 105.37; 123.66; 149.12; 151.25; 153.93; 162.39; 164.88.

For **II-5**. mp 118.1 °C. Found: C, 67.71; H, 9.24; N, 9.08. Calc. for C<sub>52</sub>H<sub>84</sub>N<sub>6</sub>O<sub>8</sub> (921.26): C, 67.80; H, 9.19; N, 9.12%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.87-0.91 (18H, m), 1.33-1.36 (32H, m), 1.46-1.51 (4H, dt, *J* 7.6 and 15.2), 1.60-1.66 (8H, m), 1.82-1.88 (4H, dt, *J*<sub>1</sub> 6.7 and 13.7), 3.88-3.95 (8H, dt, *J* 7.3 and 15.2), 4.00-4.03 (4H, t, *J* 6.7), 6.8 (2H, s), 8.45-8.50 (2H, d, *J* 13.1) and 12.20-12.26 (2H, d, *J* 12.8).  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.17; 22.61; 22.89; 26.14; 28.06; 29.26; 29.31; 29.46; 29.51; 32.05; 41.12; 41.67; 70.16; 76.98; 77.23; 77.48; 94.73; 105.69; 123.95; 149.39; 151.50; 154.17; 162.63; 165.14.

For **II-6**. mp 104.3 °C. Found: C, 68.87; H, 9.43; N, 8.67. Calc. for C<sub>56</sub>H<sub>92</sub>N<sub>6</sub>O<sub>8</sub> (977.36): C, 68.82; H, 9.49; N, 8.60%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.87-0.90 (18H, m), 1.31-1.33 (40H, m), 1.46-1.52 (4H, dt, *J* 6.7 and 13.7), 1.60-1.64 (8H, m), 1.82-1.88 (4H, dt, *J*<sub>1</sub> 6.7 and 13.7), 3.88-3.95 (8H, dt, *J* 7.6 and 15.5), 4.00-4.02 (4H, t, *J* 6.7), 6.8 (2H, s), 8.41-8.45 (2H, d, *J* 13.1) and 12.22-12.26 (2H, d, *J* 13.1).  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.25; 22.76; 22.81; 22.89; 26.14; 26.81; 26.85; 28.33; 29.31; 29.46; 29.51; 31.72; 31.75; 32.02; 41.17; 41.70; 70.16; 76.98; 77.24; 77.49; 94.73; 105.69; 123.95; 149.39; 151.49; 154.15; 162.61; 165.13.

For **II-7**. mp 87.6 °C. Found: C, 69.68; H, 9.82; N, 8.17. Calc. for C<sub>60</sub>H<sub>100</sub>N<sub>6</sub>O<sub>8</sub> (1033.47): C, 69.73; H, 9.75; N, 8.13%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.86-0.91 (18H, m), 1.27-1.38 (48H, m), 1.46-1.51 (4H, dt, *J* 6.3 and 14.1), 1.58-1.66 (8H, m), 1.81-1.88 (4H, dt, *J* 6.8 and 14.1), 3.88-3.95 (8H, dt, *J* 7.3 and 15.6), 3.99-4.03 (4H, t, *J* 6.3), 6.80 (2H, s), 8.45-8.50 (2H, d, *J* 13.2) and 12.21-12.28 (2H, d, *J* 13.2).  $\delta_{\text{C}}$

(125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.29; 14.32; 22.80; 22.85; 26.13; 27.15; 27.16; 28.34; 29.21; 29.26; 29.30; 29.45; 29.51; 31.98; 32.00; 32.03; 41.17; 41.72; 70.15; 76.95; 77.23; 77.48; 94.72; 105.67; 123.93; 149.39; 151.47; 154.14; 162.63; 165.12.

For **II-8**. mp 84.6 °C. Found: C, 70.23; H, 9.78; N, 7.82. Calc. for C<sub>64</sub>H<sub>108</sub>N<sub>6</sub>O<sub>8</sub> (1089.58): C, 70.55; H, 9.99; N, 7.71%. δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.86-0.90 (18H, m), 1.25-1.30 (56H, m), 1.42-1.50 (4H, dt, *J* 7.8 and 14.1), 1.60-1.62 (8H, m), 1.82-1.86 (4H, dt, *J* 6.8 and 13.1), 3.88-4.23 (12H, m), 6.80 (2H, s), 8.45-8.50 (2H, d, *J* 13.2) and 12.20-12.28 (2H, d, *J* 13.2). δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.10; 22.65; 22.69; 25.93; 25.99; 26.07; 26.13; 26.97; 27.03; 27.10; 28.10; 28.20; 29.11; 29.26; 29.31; 29.38; 29.53; 29.70; 31.82; 31.85; 31.94; 40.98; 41.52; 70.02; 76.78; 77.04; 77.29; 94.53; 105.46; 123.73; 149.19; 151.28; 153.93; 162.42; 164.93.

For **II-10**. mp 72 °C. Found: C, 71.91; H, 10.52; N, 6.92. Calc. for C<sub>36</sub>H<sub>52</sub>N<sub>6</sub>O<sub>8</sub> (1201.79): C, 71.95; H, 10.40; N, 6.99%. δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.86-0.90 (18H, m), 1.25-1.34 (72H, m), 1.42-1.48 (4H, dt, *J* 6.8 and 14.1), 1.62-1.66 (8H, m), 1.80-1.83 (4H, dt, *J* 6.8 and 14.1), 3.92-3.96 (12H, m), 6.77 (2H, s), 8.50-8.55 (2H, d, *J* 14.1) and 12.05-12.15 (2H, d, *J* 13.7). δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.14; 22.71; 25.95; 26.99; 27.06; 28.22; 28.24; 29.13; 29.27; 29.33; 29.36; 29.37; 29.45; 29.59; 29.60; 29.61; 29.68; 31.83; 31.92; 40.99; 41.53; 69.97; 76.80; 77.05; 77.30; 94.55; 105.47; 123.75; 149.20; 151.29; 153.94; 162.43; 164.94.

For **II-12**. mp 90 °C Found: C, 73.21; H, 10.68; N, 6.32. Calc. for C<sub>80</sub>H<sub>140</sub>N<sub>6</sub>O<sub>8</sub> (1314.00): C, 73.12; H, 10.74; N, 6.40%. δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.87-0.90 (18H, m), 1.24-1.32 (88H, m), 1.46-1.50 (4H, dt, *J* 6.4 and 14.0), 1.61-1.62 (8H, m), 1.82-1.88 (4H, dt, *J* 6.7 and 13.7), 3.88-4.02 (16H, m), 6.90 (2H, s), 8.45-8.50 (2H, d, *J* 13.1) and 12.02-12.05 (2H, d, *J* 13.4). δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.13; 22.68; 22.70; 25.94; 25.94; 26.98; 27.05; 28.21; 28.23; 29.11; 29.25; 29.31; 29.37; 29.38; 29.45; 29.59; 29.62; 29.65; 29.67; 29.70; 31.81; 31.93; 40.99; 41.54; 69.96; 76.78; 77.03; 77.28; 94.53; 105.46; 123.73; 149.20; 151.27; 153.94; 162.44; 164.92.

For **II-13**. Found: C, 68.28; H, 9.28; N, 8.90. Calc. for C<sub>54</sub>H<sub>88</sub>N<sub>6</sub>O<sub>8</sub> (949.31): C, 68.32; H, 9.34; N, 8.85%. δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.86-0.90 (12H, m), 1.25-1.35 (44H, m), 1.43-1.49 (4H, dt, *J* 7.1 and 13.7), 1.58-1.65 (8H, m), 1.77-1.90 (4H, m, *J* 6.3 and 13.2), 3.36 (6H, s), 3.92-3.96 (4H, m, *J* 6.3), 4.02-4.04 (4H, m, *J* 6.3), 6.76-6.79 (2H, s), 8.51-8.54 (2H, d, *J* 14.0) and 12.09-12.12 (2H, d, *J* 14.0)

For **II-14**. Found: C, 68.30; H, 9.36; N, 8.81. Calc. for C<sub>54</sub>H<sub>88</sub>N<sub>6</sub>O<sub>8</sub> (949.31): C, 68.32; H, 9.34; N, 8.85%. δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.86-0.90 (12H, m, 4 × CH<sub>3</sub>), 1.25-1.39 (44H, m, CH<sub>2</sub>), 1.47-1.52 (4H, dt, *J* 6.8 and 14.1, 2 × OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.62-1.64 (8H, m, 4 × NCH<sub>2</sub>CH<sub>2</sub>), 1.82-1.88 (4H, dt, *J* 6.3 and 13.2, 2 × OCH<sub>2</sub>CH<sub>2</sub>), 3.33-3.65 (6H, d, 2 × NMe), 3.89-3.94 (4H, k, *J* 6.3, 2 × NCH<sub>2</sub>), 4.02-4.04 (4H, k, *J* 6.3, 2 × OCH<sub>2</sub>), 6.81-6.83 (2H, s, Ph), 8.45-8.52 (2H, dd, 2 × CH=C) and 12.20-12.26 (2H, d, *J* 13.6, 2 × NH). δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.13; 22.69; 25.95; 26.97; 27.00; 27.35; 28.05; 28.20; 29.10; 29.12; 29.26; 29.32; 29.36; 29.43; 29.58; 29.61; 31.81; 31.89; 31.90; 41.02; 41.52; 69.95; 69.99; 94.22; 94.57; 104.99; 105.65; 105.99; 123.68; 123.77; 149.19; 149.30; 151.26; 151.79; 153.55; 154.06; 154.40; 162.39; 162.55; 164.96; 165.04.

**Complex III-9 or IV-9**: Pure ligand **II-9** was dissolved in 2-propanol and heated under reflux. To the boiling mixture an appropriate salt of the metal, 1mmol of Ni(OAc)<sub>2</sub> or 1mmol of Cu(OAc)<sub>2</sub>, was being added until the solid compound precipitated out. Complex was filtered off and purified by repeated recrystallizations from toluene. Yield ~ 85%; For **III-9**. mp 119.9 °C. Found: C, 67.94; H, 9.53; N, 6.97. Calc. for C<sub>68</sub>H<sub>114</sub>N<sub>6</sub>NiO<sub>8</sub> (1202.36): C, 67.93; H, 9.55; N, 6.99%. δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.86-0.90 (18H, m, 6 × Me), 1.26-1.32 (64H, m, CH<sub>2</sub>), 1.45-1.48 (4H, dt, *J* 6.8 and 14.1, 2 × OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.60-1.61 (8H, m, 4 × NCH<sub>2</sub>CH<sub>2</sub>), 1.81-1.85 (4H, dt, *J* 6.8 and 14.1, 2 × OCH<sub>2</sub>CH<sub>2</sub>), 3.87-3.95 (12H, m, 2 × OCH<sub>2</sub>, 4 × NCH<sub>2</sub>), 6.90 (2H, s, Ph) and 8.10 (2H, s, 2 × CH=C). δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.34; 14.36; 22.92; 22.93; 26.19; 26.97; 27.21; 27.30; 28.27; 28.60; 29.41; 29.51; 29.57; 29.60; 29.77; 29.92; 32.07; 32.10; 32.12; 41.93; 42.31; 69.88; 76.07; 77.27; 77.53; 94.03; 98.38; 135.54; 149.19; 150.18; 150.86; 161.47; 162.52; For **IV-9**. mp 74.6 °C. Found: C, 67.62; H, 9.48; N, 6.98. Calc. for C<sub>68</sub>H<sub>114</sub>CuN<sub>6</sub>O<sub>8</sub> (1207.21): C, 67.65; H, 9.52; N, 6.96%.

For **III-1**. mp 290.5 °C. Found: C, 57.35; H, 6.73; N, 11.15. Calc. for C<sub>36</sub>H<sub>50</sub>N<sub>6</sub>NiO<sub>8</sub> (752.51): C, 57.38; H, 6.69; N, 11.15%. δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.87-0.90 (6H, m), 1.29-1.34 (16H, m), 1.44-1.50 (4H, m), 1.79-1.81 (4H, dt, *J* 6.3 and 12.2), 3.37 (12H, s), 3.91-3.96 (4H, m), 6.77 (2H, s) and 8.51-8.54 (2H, d, *J* 14.1). δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.02; 23.10; 26.60; 28.62; 30.32; 30.60; 32.50; 72.64; 102.20; 108.30; 125.5; 135.30; 151.3; 159.2; 164.80.

For **III-2**. mp 221.3 °C. Found: C, 59.36; H, 7.16; N, 10.42. Calc. for C<sub>40</sub>H<sub>58</sub>N<sub>6</sub>NiO<sub>8</sub> (809.62): C, 59.34; H, 7.22; N, 10.38%. δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.88-0.90 (6H, m), 1.19-1.47 (28H, m), 1.44-1.48 (4H, m), 1.79-1.85 (4H, dt, *J* 6.8 and 13.7), 3.89-4.02 (12H, m), 6.87 (2H, s) and 8.07 (2H, s). δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 13.49; 13.65; 14.38; 22.56; 22.95; 24.70; 26.20; 29.42; 29.53; 29.63; 32.08; 37.02; 37.64; 69.84; 77.03; 77.28; 77.54; 94.10; 98.24; 135.50; 149.21; 149.78; 150.61; 161.36; 162.33.

For **III-3**. mp 143.6 °C. Found: C, 61.09; H, 7.73; N, 9.69. Calc. for C<sub>44</sub>H<sub>66</sub>N<sub>6</sub>NiO<sub>8</sub> (865.72): C, 61.04; H, 7.68; N, 9.70%. δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.88-0.96 (18H, m) 1.30-1.46 (16H, m), 1.44-1.49 (4H, m), 1.63-1.70 (8H, m), 1.80-1.82 (4H, dt, *J* 6.7 and 13.7), 3.88-3.92 (12H, m), 6.87 (2H, s) and 8.08 (2H, s). δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 11.53; 11.58; 14.37; 21.53; 21.70; 22.94; 26.19; 29.41; 29.52; 29.62; 32.07; 43.33; 43.65; 69.84; 77.02; 77.28; 77.53; 93.96; 98.24; 135.48; 149.17; 150.20; 150.78; 161.50; 162.49.

For **III-4**. mp 130.3 °C. Found: C, 62.53; H, 8.11; N, 9.08. Calc. for C<sub>48</sub>H<sub>74</sub>N<sub>6</sub>NiO<sub>8</sub> (921.83): C, 62.57; H, 8.09; N, 9.11%. δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.89-0.97 (18H, m), 1.30-1.40 (24H, m), 1.42-1.48 (4H, dt, *J* 7.6 and 14.6), 1.56-1.63 (8H, m), 1.80-1.84 (4H, dt, *J* 6.7 and 13.7), 3.83-3.92 (12H, m), 6.83 (2H, s) and 8.04 (2H, s). δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 13.74; 13.85; 14.07; 20.16; 22.64; 25.90;

29.13; 29.23; 29.35; 30.01; 30.36; 31.78; 41.36; 41.75; 60.46; 76.75; 77.00; 77.26; 93.70; 97.74; 135.10; 148.85; 149.81; 150.36; 161.12; 162.09.

For **III-5**. mp 126.6 °C. Found: C, 63.81; H, 8.51; N, 8.57. Calc. for C<sub>52</sub>H<sub>82</sub>N<sub>6</sub>NiO<sub>8</sub> (977.94): C, 63.86; H, 8.45; N, 8.59%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.89-0.93 (18H, m), 1.29-1.37 (32H, m), 1.45-1.48 (4H, dt, *J* 6.8 and 13.7), 1.60-1.65 (8H, m), 1.80-1.85 (4H, dt, *J* 6.8 and 13.7), 3.86-3.94 (12H, m), 6.8 (2H, s) and 8.45-8.50 (2H, d, *J* 13.1).  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.00; 14.07; 14.12; 22.40; 22.52; 22.69; 25.95; 27.68; 28.03; 29.07; 29.10; 29.17; 29.27; 29.37; 31.82; 41.64; 42.00; 69.64; 76.78; 77.03; 77.29; 93.79; 98.10; 135.29; 148.94; 149.95; 150.60; 161.23; 162.27.

For **III-6**. mp 77.5 °C. Found: C, 65.07; H, 8.73; N, 8.15. Calc. for C<sub>56</sub>H<sub>90</sub>N<sub>6</sub>NiO<sub>8</sub> (1034.04): C, 65.04; H, 8.77; N, 8.13%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.88-0.90 (18H, m), 1.29-1.32 (40H, m), 1.44-1.48 (4H, dt, *J* 7.8 and 15.1), 1.60-1.63 (8H, m), 1.80-1.85 (4H, dt, *J* 7.3 and 14.1), 3.85-3.93 (12H, m), 6.8 (2H, s) and 8.41-8.45 (2H, d, *J* 13.1).  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.06; 14.12; 22.56; 22.68; 25.96; 26.61; 26.71; 27.95; 28.32; 29.18; 29.28; 29.38; 31.51; 31.65; 31.83; 41.67; 42.04; 69.62; 76.79; 77.04; 77.29; 93.79; 98.06; 135.28; 148.94; 149.92; 150.56; 161.20; 162.23.

For **III-7**. mp 123.5 °C. Found: C, 66.12; H, 9.02; N, 7.73. Calc. for C<sub>60</sub>H<sub>98</sub>N<sub>6</sub>NiO<sub>8</sub> (1090.15): C, 66.10; H, 9.06; N, 7.71%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.86-0.90 (18H, m), 1.28-1.34 (48H, m), 1.42-1.48 (4H, dt, *J* 7.8 and 14.6), 1.60-1.62 (8H, m), 1.80-1.85 (4H, dt, *J* 7.3 and 14.1), 3.86-3.95 (12H, m), 6.92 (2H, s) and 8.11 (2H, d).  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.29; 14.32; 22.80; 22.84; 22.89; 26.15; 27.12; 27.23; 28.23; 28.58; 29.22; 29.36; 29.39; 29.47; 29.56; 31.97; 32.03; 32.10; 41.90; 42.29; 69.87; 76.98; 77.23; 77.48; 94.00; 98.40; 135.52; 149.16; 150.16; 150.86; 161.45; 162.52.

For **III-8**. mp 115 °C. Found: C, 67.09; H, 9.37; N, 7.30. Calc. for C<sub>64</sub>H<sub>106</sub>N<sub>6</sub>NiO<sub>8</sub> (1146.25): C, 67.06; H, 9.32; N, 7.33%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.86-0.90 (18H, m), 1.29-1.32 (56H, m), 1.44-1.48 (4H, dt, *J* 7.3 and 14.6), 1.60-1.62 (8H, m), 1.80-1.82 (4H, dt, *J* 6.8 and 13.1), 3.87-3.96 (12H, m), 6.93 (2H, s) and 8.13 (2H, s).  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.10; 22.65; 22.66; 22.70; 25.94; 26.00; 26.97; 27.07; 28.03; 28.36; 29.15; 29.23; 29.26; 29.31; 29.35; 29.37; 29.44; 29.47; 31.81; 31.85; 41.69; 42.11; 69.68; 76.77; 77.02; 77.28; 93.80; 98.24; 135.33; 148.94; 149.97; 150.70; 161.25; 162.35.

For **III-10**. mp 128.8 °C. Found: C, 68.67; H, 9.74; N, 6.69. Calc. for C<sub>72</sub>H<sub>122</sub>N<sub>6</sub>NiO<sub>8</sub> (1258.47): C, 68.71; H, 9.77; N, 6.67%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.86-0.90 (18H, m), 1.25-1.32 (72H, m), 1.44-1.49 (4H, dt, *J* 7.1 and 14.8), 1.60-1.62 (8H, m), 1.79-1.84 (4H, dt, *J* 6.7 and 13.7), 3.85-3.94 (12H, m), 6.89 (2H, s) and 8.09 (2H, s).  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.14; 22.71; 26.97; 27.00; 27.21; 27.07; 28.05; 28.38; 29.41; 29.19; 29.29; 29.33; 29.38; 29.54; 29.59; 29.60; 29.65; 29.75; 31.84; 31.92; 31.93; 41.70; 42.07; 69.64; 76.79; 77.05; 77.30; 93.80; 98.10; 135.30; 148.95; 149.93; 150.60; 161.23; 162.26.

For **III-12**. mp 115.1 °C. Found: C, 70.14; H, 10.12; N, 6.12. Calc. for C<sub>80</sub>H<sub>138</sub>N<sub>6</sub>NiO<sub>8</sub> (1370.68): C, 70.10; H, 10.15; N, 6.13%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.86-0.90 (18H, m), 1.25-1.31 (88H, m), 1.44-1.49 (4H, dt, *J* 7.8 and 15.1), 1.59-1.63 (8H, m), 1.79-1.85 (4H, dt, *J* 6.8 and 13.7), 3.87-3.96 (12H, m), 6.93 (2H, s) and 8.13 (2H, s).  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.32; 22.89; 26.15; 27.18; 27.26; 27.26; 28.23; 28.56; 29.37; 29.47; 29.57; 29.73; 29.78; 29.82; 29.86; 29.88; 29.91; 32.02; 32.02; 41.89; 42.27; 69.85; 76.97; 77.22; 77.48; 93.99; 98.34; 135.50; 149.15; 150.13; 150.81; 161.43; 162.47.

For **III-13**. mp 61.7 °C. Found: C, 64.43; H, 8.57; N, 8.37. Calc. for C<sub>54</sub>H<sub>86</sub>N<sub>6</sub>NiO<sub>8</sub> (1005.99): C, 64.47; H, 8.61; N, 8.35%. Isomeric composition of this mixture was determined from 2D correlation NMR spectra which are carefully described later in this paper.

For **III-14**. mp 62 °C. Found: C, 64.48; H, 8.60; N, 8.33. Calc. for C<sub>54</sub>H<sub>86</sub>N<sub>6</sub>NiO<sub>8</sub> (1005.99): C, 64.47; H, 8.61; N, 8.35%.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.88-0.90 (12H, m), 1.25-1.33 (44H, m), 1.44-1.50 (4H, dt, *J* 6.8 and 14.1), 1.54-1.62 (8H, m), 1.80-1.84 (4H, dt, *J* 7.3 and 13.7), 3.22 (3H, s), 3.30 (3H, s), 3.72-3.76 (4H, dd, *J* 6.3 and 12.1), 3.84-3.90 (4H, dd, *J* 6.3 and 12.1), 6.77-6.79 (2H, d) and 7.97-7.99 (2H, d).  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.14; 22.69; 22.72; 25.99; 26.00; 27.04; 27.19; 27.99; 28.06; 28.08; 28.20; 29.23; 29.33; 29.34; 29.37; 29.39; 29.46; 29.59; 29.62; 29.74; 31.87; 31.91; 31.92; 41.74; 42.29; 69.45; 69.56; 76.79; 77.05; 77.30; 93.60; 93.76; 97.51; 97.80; 135.06; 135.29; 148.90; 150.16; 150.20; 150.23; 161.06; 161.14; 161.98; 162.06.

For **IV-1**. mp 251.6 °C. Found: C, 57.04; H, 6.61; N, 11.05. Calc. for C<sub>36</sub>H<sub>50</sub>CuN<sub>6</sub>O<sub>8</sub> (758.36): C, 57.01; H, 6.64; N, 11.08%.

For **IV-2**. mp 192.5 °C. Found: C, 58.96; H, 7.21; N, 10.30. Calc. for C<sub>40</sub>H<sub>58</sub>CuN<sub>6</sub>O<sub>8</sub> (814.47): C, 58.98; H, 7.18; N, 10.32%.

For **IV-3**. mp 128 °C. Found: C, 60.68; H, 7.65; N, 9.66. Calc. for C<sub>44</sub>H<sub>66</sub>CuN<sub>6</sub>O<sub>8</sub> (870.57): C, 60.70; H, 7.64; N, 9.65%.

For **IV-4**. mp 120.2 °C. Found: C, 62.25; H, 8.09; N, 9.03. Calc. for C<sub>48</sub>H<sub>74</sub>CuN<sub>6</sub>O<sub>8</sub> (926.68): C, 62.21; H, 8.05; N, 9.07%.

For **IV-5**. mp 135.4 °C. Found: C, 63.58; H, 8.45; N, 8.57. Calc. for C<sub>52</sub>H<sub>82</sub>CuN<sub>6</sub>O<sub>8</sub> (982.79): C, 63.55; H, 8.41; N, 8.55%.

For **IV-6**. mp 120.5 °C. Found: C, 64.78; H, 8.78; N, 8.05. Calc. for C<sub>56</sub>H<sub>90</sub>CuN<sub>6</sub>O<sub>8</sub> (1038.89): C, 64.74; H, 8.73; N, 8.09%.

For **IV-7**. mp 124.3 °C. Found: C, 65.82; H, 9.05; N, 7.69. Calc. for C<sub>60</sub>H<sub>98</sub>CuN<sub>6</sub>O<sub>8</sub> (1095.00): C, 65.81; H, 9.02; N, 7.67%.

For **IV-8**. mp 114.7 °C. Found: C, 66.75; H, 9.31; N, 7.28. Calc. for C<sub>64</sub>H<sub>106</sub>CuN<sub>6</sub>O<sub>8</sub> (1151.11): C, 66.78; H, 9.28; N, 7.30%.

For **IV-10**. mp 63.9 °C. Found: C, 68.47; H, 9.76; N, 6.68. Calc. for C<sub>72</sub>H<sub>122</sub>CuN<sub>6</sub>O<sub>8</sub> (1263.32): C, 68.45; H, 9.73; N, 6.65%.

For **IV-12**. mp 80.1 °C. Found: C, 69.87; H, 10.16; N, 6.08. Calc. for C<sub>80</sub>H<sub>138</sub>CuN<sub>6</sub>O<sub>8</sub> (1375.53): C, 69.85; H, 10.11; N, 6.11%.

For **IV-13**. mp 69.5 °C. Found: C, 64.11; H, 8.52; N, 8.35. Calc. for C<sub>54</sub>H<sub>86</sub>CuN<sub>6</sub>O<sub>8</sub> (1010.84): C, 64.13; H, 8.57; N, 8.32%.

For **IV-14**. mp 62.6 °C. Found: C, 64.16; H, 8.59; N, 8.33. Calc. for C<sub>54</sub>H<sub>86</sub>CuN<sub>6</sub>O<sub>8</sub> (1010.84): C, 64.16; H, 8.58; N, 8.31%.

## Results.

### Two dimensional correlation NMR spectra

The structures of the compounds studied were confirmed by the use of DEPT, *g*-HSQC and *g*-HMBC NMR techniques. Also the vicinal <sup>3</sup>J<sub>HC</sub> couplings which by analogy to <sup>3</sup>J<sub>HH</sub> couplings obey the Karplus-type relationship<sup>4</sup> were of help. The main problem in spectra analyses was that many crucial signals were closely positioned; for example, three signals appeared at 149 ppm, the difference between them in some cases being smaller than 0.1 ppm.

In the first step the <sup>1</sup>H and <sup>13</sup>C spectra of the parent compound **III-1** were evaluated (Table 1). As follows from the DEPT spectrum of this molecule the signals at 97.17 and 149.88 ppm belong to the carbon atoms bearing one hydrogen atom only. The signal at 97.17 ppm was assigned to the aromatic carbon atom 2 (or 2') and that at 149.88 ppm to the vinylic carbon atom 4 (or 4').<sup>5</sup> This allows one to assign two signals appearing in the aromatic/ vinylic range of the proton spectrum of **III-1** since that at 6.60 ppm is correlated through one-bond coupling to carbon 2 and that at 7.80 ppm to carbon 4.

**Table 1.** <sup>1</sup>H and <sup>13</sup>C NMR data of **III-1** (δ in ppm vs. TMS and *J* in Hz); an arbitrary numbering of the carbon atoms has been applied

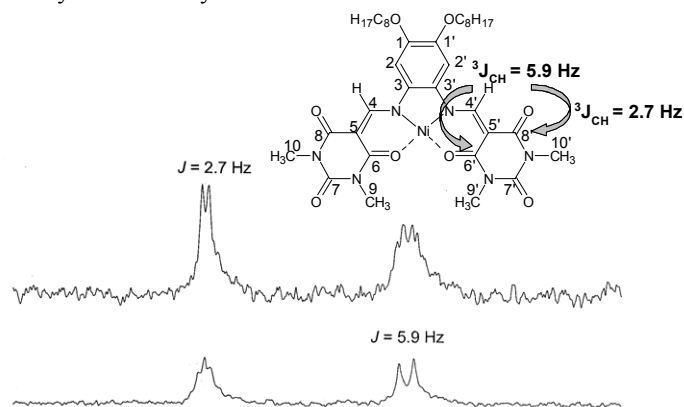
C no	<sup>13</sup> C NMR (DEPT)	<sup>1</sup> H NMR	HSQC correlations	HMBC correlations
C1/C1'	148.98	–	–	–
C2/C2'	97.17 (CH)	6.60 s	x	C1 (C1'), C3 (C3')
C3/C3'	135.06	–	–	–
C4/C4'	149.88 (CH)	7.80 s	x	C3 (C3'), C5 (C5'), C6 (C6'), C8 (C8')
C5/C5'	93.40	–	–	–
C6/C6'	160.91	–	–	<sup>3</sup> J (C6H4) = 5.9 Hz
C7/C7'	149.84	–	–	–
C8/C8'	161.75	–	–	<sup>3</sup> J (C8H4) = 2.7 Hz
C9/C9'	27.95 (CH <sub>3</sub> )	3.08 s	x	C6 (C6'), C7 (C7')
C10/C10'	28.00 (CH <sub>3</sub> )	3.24 s	x	C7 (C7'), C8 (C8')
C11/C11'	69.39 (CH <sub>3</sub> )	3.79 t	x	C1 (C1')

The coupling between the vinylic proton 4 (or 4') with the carbon atom at 160.91 ppm, <sup>3</sup>J<sub>HC</sub> = 5.9 Hz, is two-times larger than the coupling between the same proton and the carbon atom at 161.75 ppm, <sup>3</sup>J<sub>HC</sub> = 2.7 Hz. This result strongly indicates that the first carbon atom is *trans* arranged towards the proton coupled (C6/C6' in Figure 1), whereas the second one must be *cis* positioned (C8/C8'). The unambiguous assignment of the signals belonging to these two carbon atoms allowed subsequently an assignment of the signals corresponding to the protons of the two methyl groups attached to the nitrogen atoms.

<sup>4</sup> K. Kamienska-Trela, J. Wojcik, *A specialist Periodical Report, NMR*, **2005**, *34*, 187.

<sup>5</sup> H. O. Kalinowski, S. Berger, S. Braun in *Carbon-13 NMR Spectroscopy*, Wiley, 1994.



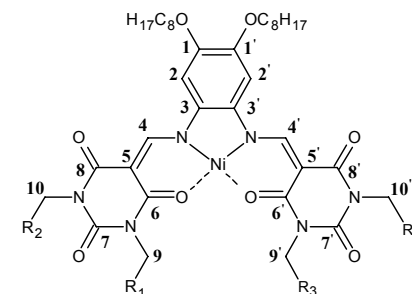


**Figure 1.** An analysis of  $^3J_{\text{CH}}$  coupling constants.

Thus, the signal appearing at 3.08 ppm which gives in the HMBC spectrum the crosspeak with the carbon signal at 160.91 ppm (C6/C6') must correspond to the methyl group as 9 (or 9'), whereas that at 3.24 ppm which correlates with the signal at 161.75 ppm (C8/C8') belongs to the methyl group 10 (or 10'). Out of two signals appearing in the carbon spectrum at ca. 149 ppm, the one at 149.84 ppm gave in the HMBC spectrum two crosspeaks correlating it with the protons of the both methyl groups and therefore corresponds to the carbon atom 7 (or 7'). The other signal (at 148.98 ppm) ascribed to C1 (or C1') shows two crosspeaks, one with the proton H2 (or H2') and the second one with the protons of the OCH<sub>2</sub> moiety which absorb at 3.79 ppm. The analysis of the crosspeaks observed for the signals at 93.4 and 135.06 ppm allows one to assign them to the carbons C5 (or C5') and C3 (or C3'), respectively. The results obtained for the compound **III-1** provided a good basis for the structure elucidation of the four compounds **III-13.1**, **III-13.2**, **III-13.3** and **III-14** for which similar sets of the spectra have been obtained; the crucial <sup>13</sup>C and <sup>1</sup>H NMR data are presented in Table 2. It should be indicated at this point that it was impossible to separate the chromatographically uniform mixture of three isomeric compounds **III-13.1-3** into individual components and therefore quite a number of the signals in the spectra overlap. Although the assignment of the particular signals had to be in some cases arbitrary or can be interchanged, the spectra as a whole are easy to interpret and provide an unequivocal proof of the structures of the compounds studied. In particular, an integration of the signals of the NCH<sub>3</sub> protons allowed an estimation of the ratio of the isomers **III-13.1** (32 %), **III-13.2** (14 %) and **III-13.3** (54 %) in the mixture obtained. The result has been confirmed by the integration of the aromatic C2H2 (C2'H2') protons.

**Table 2.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of III-13.1-3 and III-14 compounds (in ppm vs TMS); an arbitrary numbering of the carbon atoms has been applied.

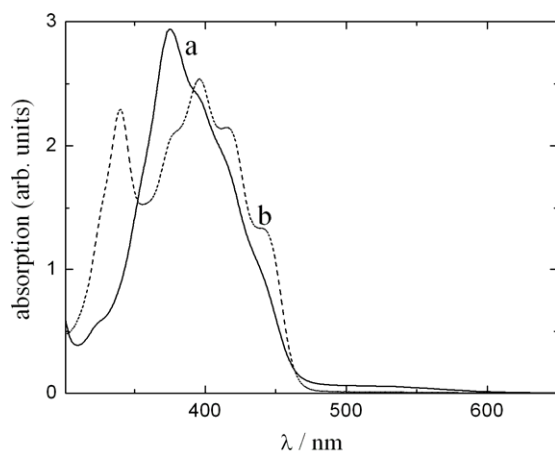
III-13.1			III-13.2			III-13.3			III-14			General structure of Ni(II) complexes						
$\text{R}_1=\text{R}_3=\text{H}; \text{R}_2=\text{R}_4=\text{C}_9\text{H}_{19}$			$\text{R}_1=\text{R}_3=\text{C}_9\text{H}_{19}; \text{R}_2=\text{R}_4=\text{H}$			$\text{R}_1=\text{R}_4=\text{H}; \text{R}_2=\text{R}_3=\text{C}_9\text{H}_{19}$			$\text{R}_1=\text{R}_2=\text{H}; \text{R}_3=\text{R}_4=\text{C}_9\text{H}_{19}$									
Cno	$\delta(^{13}\text{C})$	$\delta(^1\text{H})$	Cno	$\delta(^{13}\text{C})$	$\delta(^1\text{H})$	Cno	$\delta(^{13}\text{C})$	$\delta(^1\text{H})$	Cno	$\delta(^{13}\text{C})$	$\delta(^1\text{H})$	Cno	$\delta(^{13}\text{C})$	$\delta(^1\text{H})$	Cno	$\delta(^{13}\text{C})$	$\delta(^1\text{H})$	
C1/C1'	148.99	–	C1/C1'	149.02	–	C1	149.10	–	C1'	148.99	–	C1	148.94 <sup>a</sup>	–	C1'	149.10 <sup>a</sup>	–	
C2/C2'	97.22	6.69	C2/C2'	97.97	6.72	C2	97.92	6.71	C2'	97.74	6.70	C2	97.70	6.78	C2'	97.97	6.80	
C3/3'	135.14	–	C3/3'	135.26	–	C3	135.20 <sup>c</sup>	–	C3'	135.21 <sup>c</sup>	–	C3	135.10 <sup>b</sup>	–	C3'	135.30 <sup>b</sup>	–	
C4/C4'	150.24	7.91	C4/C4'	150.36	7.94	C4	150.24	7.91	C4'	150.24	7.93	C4	150.28	7.98	C4'	150.20	8.00	
C5/C5'	93.71 <sup>d</sup>	–	C5/C5'	93.77 <sup>d</sup>	–	C5	93.77 <sup>d</sup>	–	C5'	93.71 <sup>d</sup>	–	C5	93.77	–	C5'	93.61	–	
C6/C6'	161.22	–	C6/C6'	161.10	–	C6	161.07	–	C6'	161.22	–	C6	161.18	–	C6'	161.09	–	
C7/7'	149.95	–	C7/7'	150.02	–	C7	149.95	–	C7'	149.93	–	C7	150.28	–	C7'	149.68	–	
C8/8'	161.86	–	C8/8'	162.20	–	C8	162.10	–	C8'	161.92	–	C8	162.04	–	C8'	161.95	–	
C9/9'	28.05	3.15	C9/9'	42.09	3.80 <sup>e</sup>	C9	42.37	3.70 <sup>t</sup>	C9'	28.05	3.14	C9	28.03	3.22	C9'	42.27	3.76	
C10/10'	41.74	3.80 <sup>e</sup>	C10/10'	28.05	3.25	C10	27.95	3.22	C10'	41.77	3.80 <sup>e</sup>	C10	28.03	3.31	C10'	41.71	3.89	



**a-e)** the assignments can be interchanged; **d)** the signals overlap; **e)** a multiplet of the overlapping signals

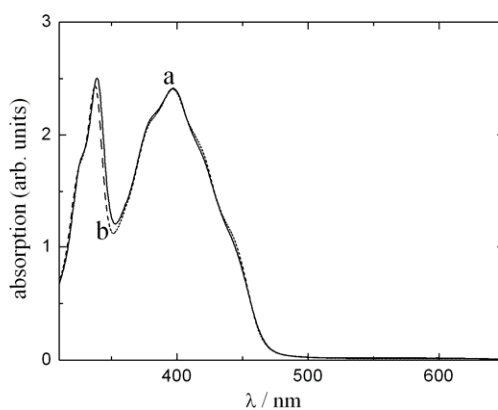
### UV-VIS studies

UV-VIS spectra of the mixture of pyridine and **III-9** compound confirmed that the additional substitution of the ligands in axial positions changes the complex geometry. The maximum of absorption is shifted and additional signals appear after adding pyridine (Figure 3).

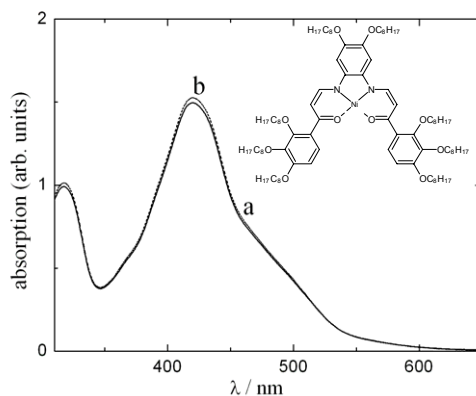


**Figure 3.** UV-VIS absorption spectra of unsubstituted **III-9** compound (**a**) and **III-9** substituted with pyridine (**b**).

Contrary, in case of **IV-9** Cu(II) complex and related cis-enaminoketone Ni(II) complex no changes in the UV-VIS spectra were observed upon adding the pyridine (see Figure 4 and Figure 5).



**Figure 4.** UV-VIS absorption spectra of **IV-9** Cu(II) complex before (**a**) and after (**b**) adding the pyridine.



**Figure 5.** UV-VIS absorption spectra of cis-enaminoketone Ni(II) complex before (**a**) and after (**b**) adding the pyridine.