# Supporting Information

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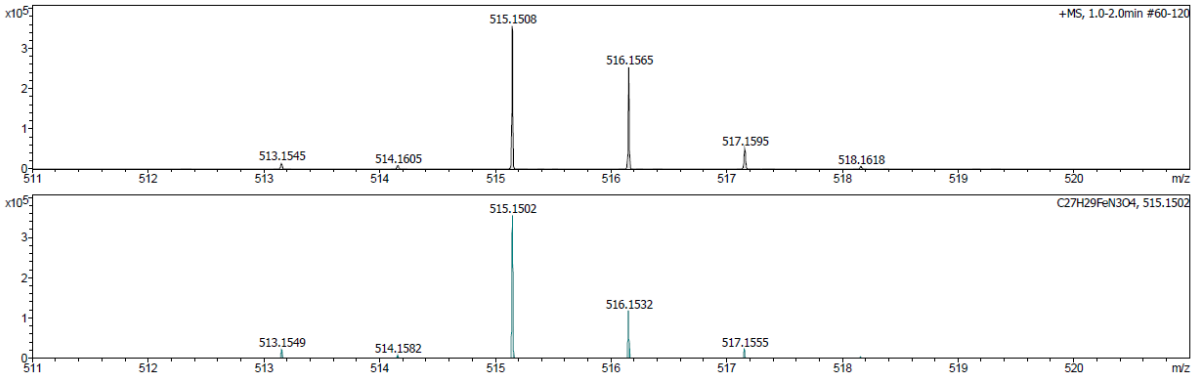


**Figure S1.** HRMS ESI$^+$: experimental (top) and simulated (bottom) ion peaks of compound **2**.

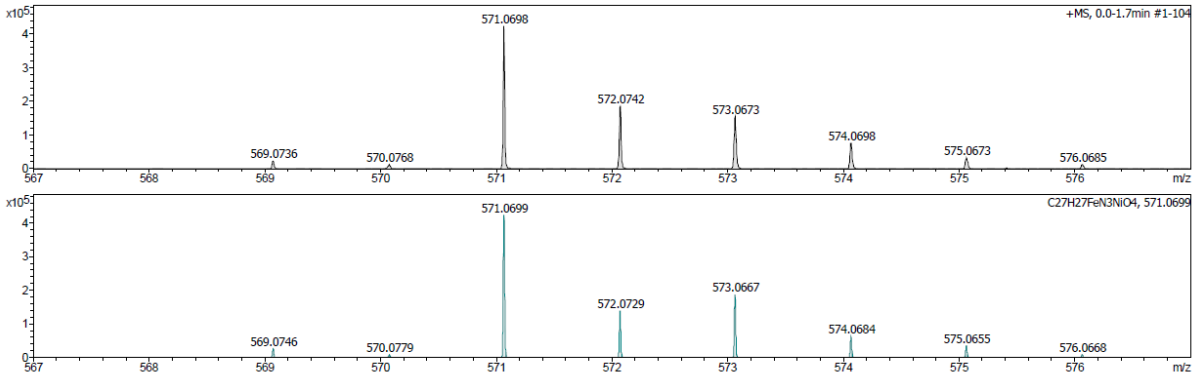


**Figure S2.** HRMS ESI$^+$: experimental (top) and simulated (bottom) ion peaks of the bimetallic complex **3**.

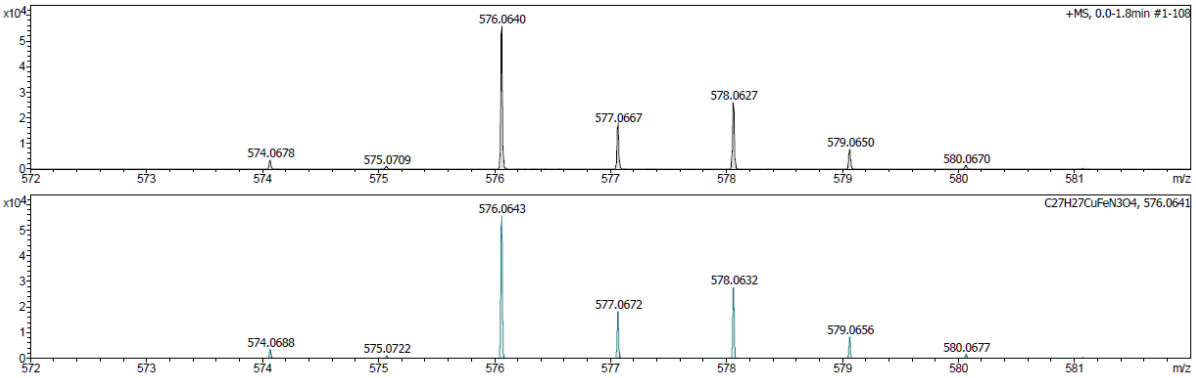


**Figure S3.** HRMS ESI$^+$: experimental (top) and simulated (bottom) ion peaks of the bimetallic complex **4**.

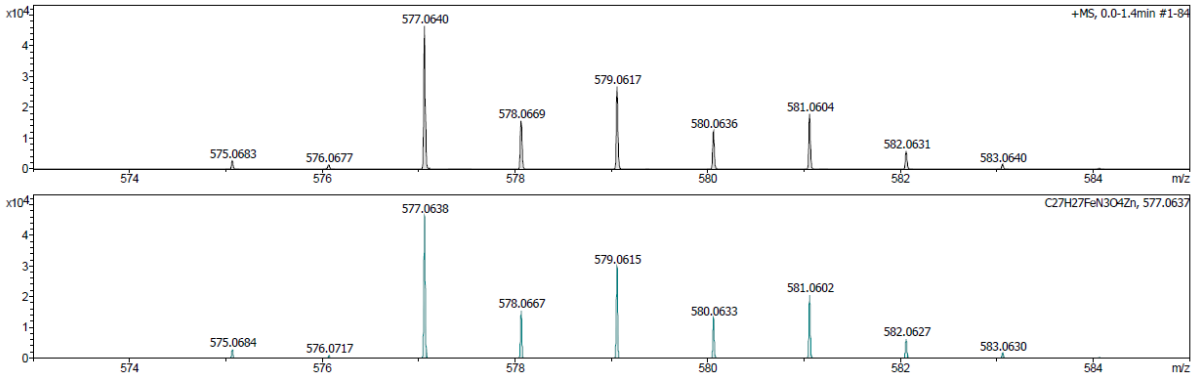


**Figure S4.** HRMS ESI$^+$: experimental (top) and simulated (bottom) ion peaks of the bimetallic complex **5**.

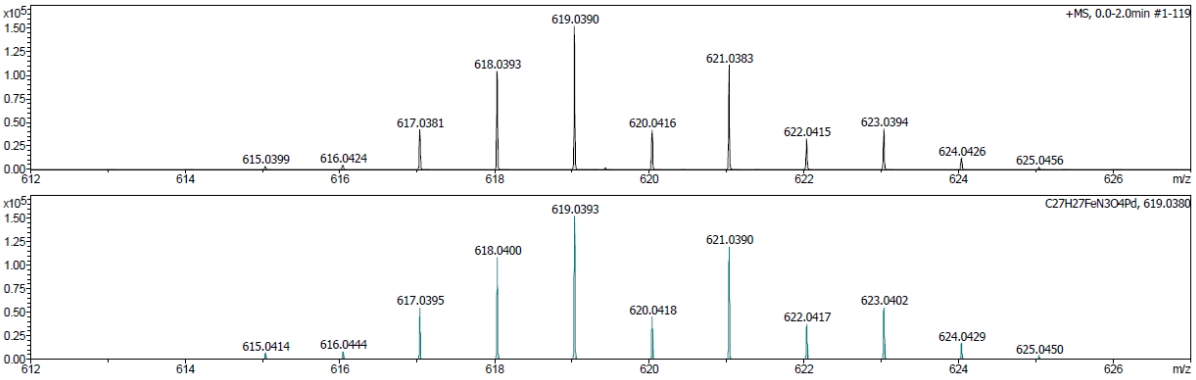


**Figure S5.** HRMS ESI$^+$: experimental (top) and simulated (bottom) ion peaks of the bimetallic complex **6**.

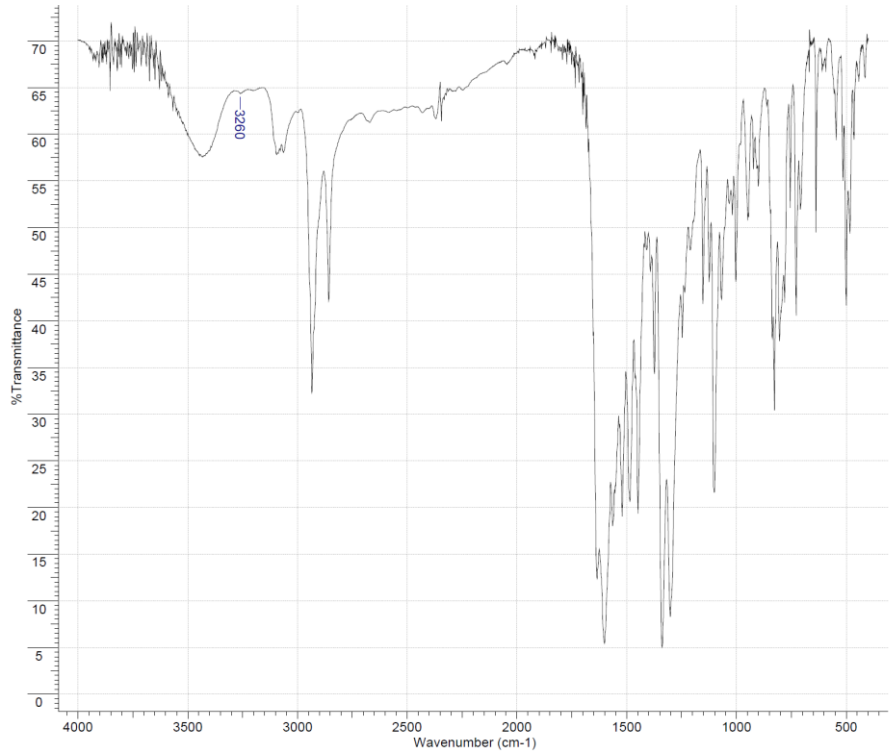


**Figure S6.** FT-IR solid-state spectrum (KBr disk) of metalloligand **2**.

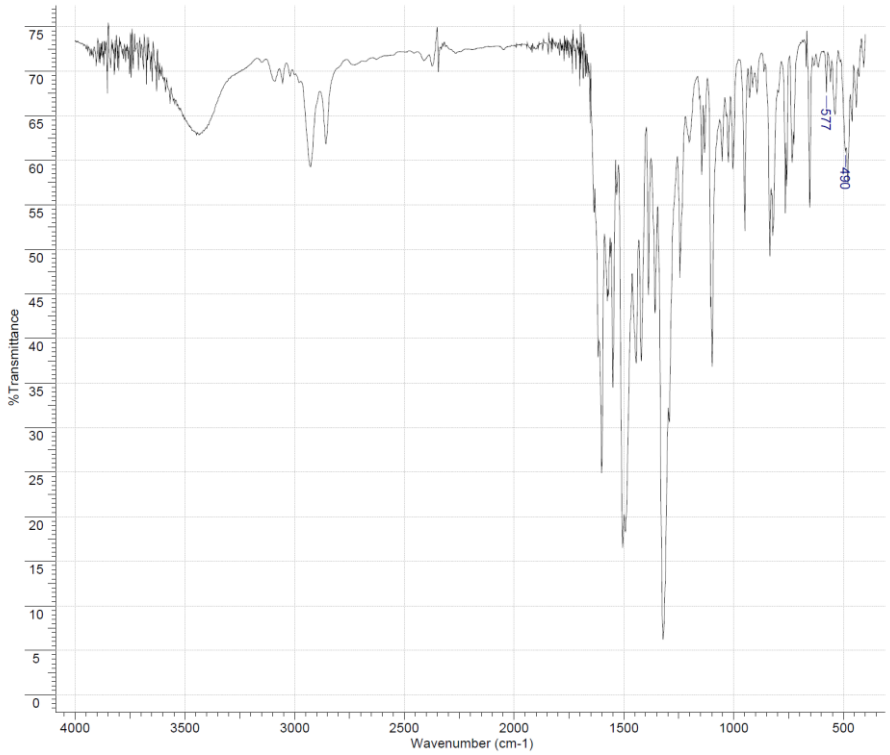


**Figure S7.** FT-IR solid-state spectrum (KBr disk) of bimetallic complex **3**.

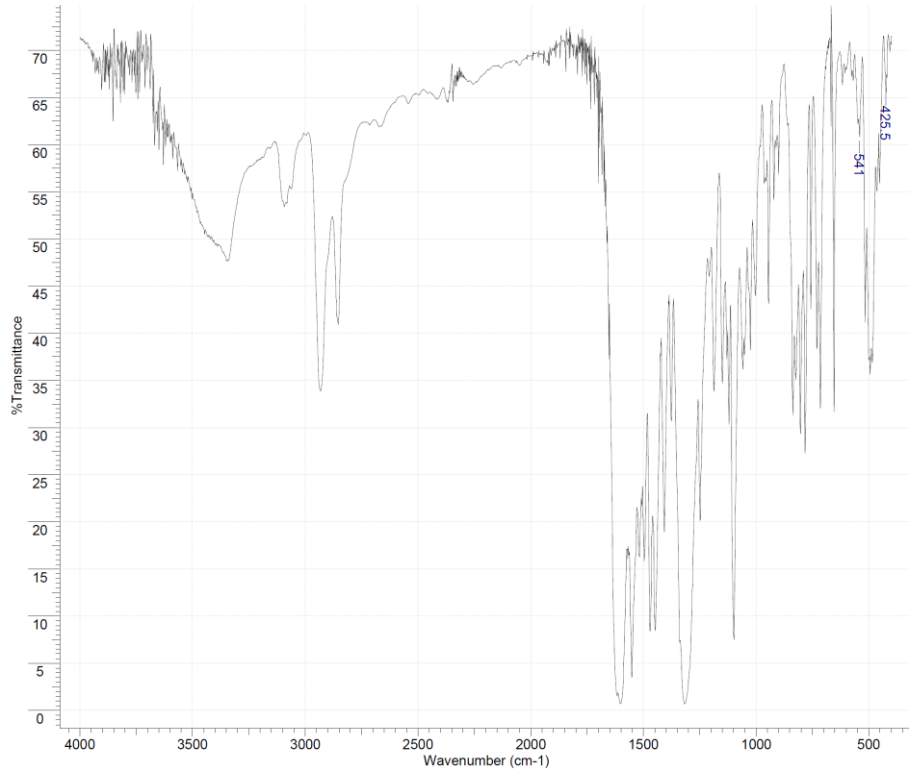


**Figure S8.** FT-IR solid-state spectrum (KBr disk) of bimetallic complex **4**.

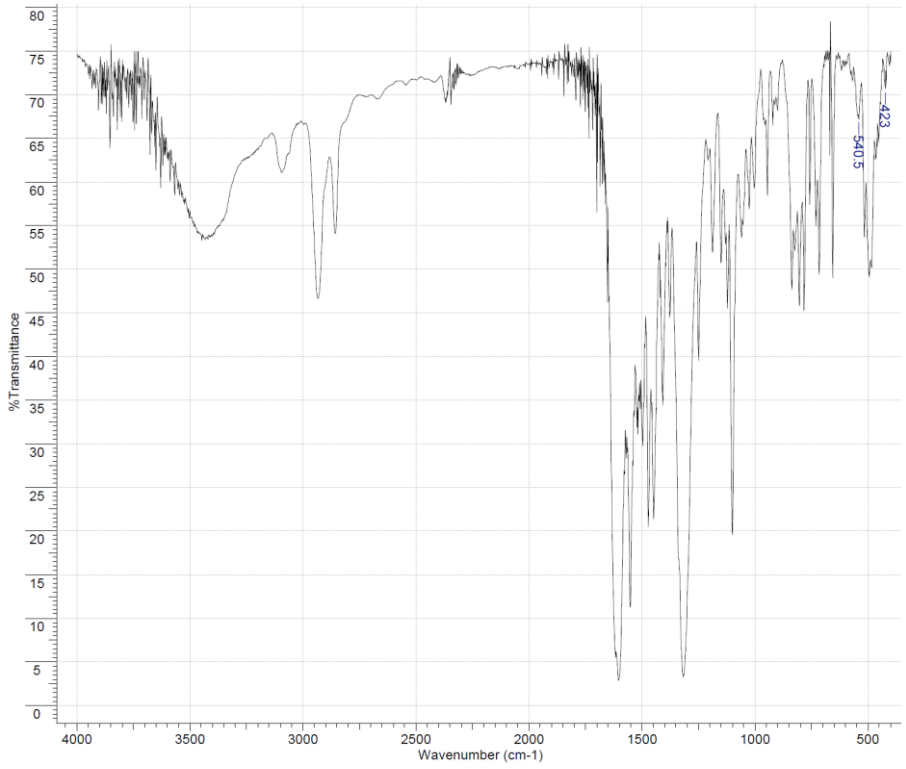


**Figure S9.** FT-IR solid-state spectrum (KBr disk) of bimetallic complex **5**.

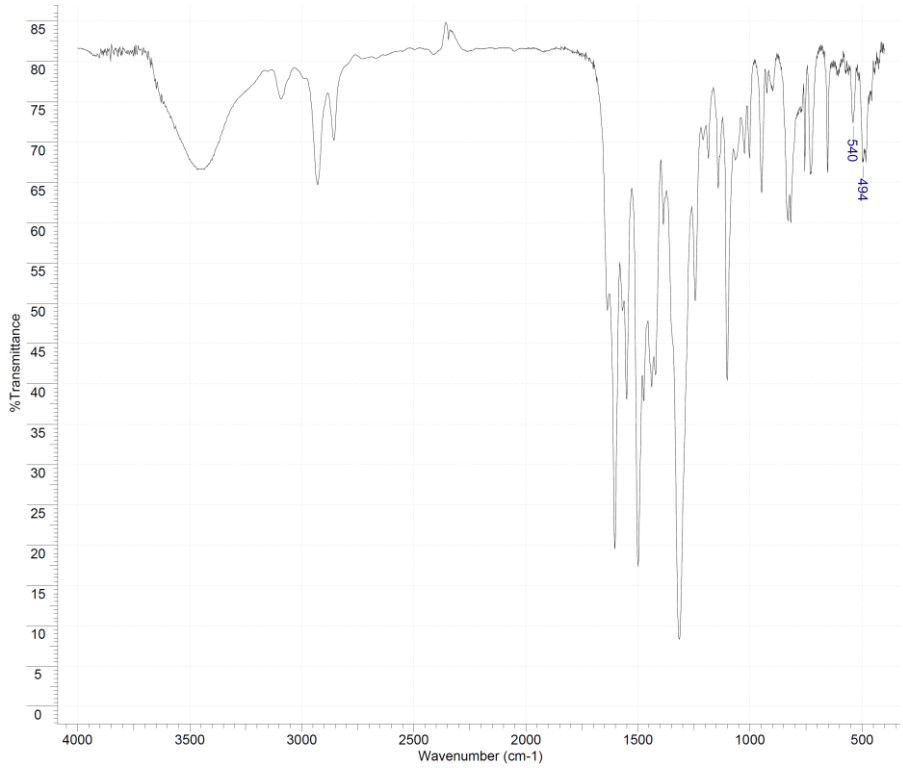


**Figure S10.** FT-IR solid-state spectrum (KBr disk) of bimetallic complex **6**.

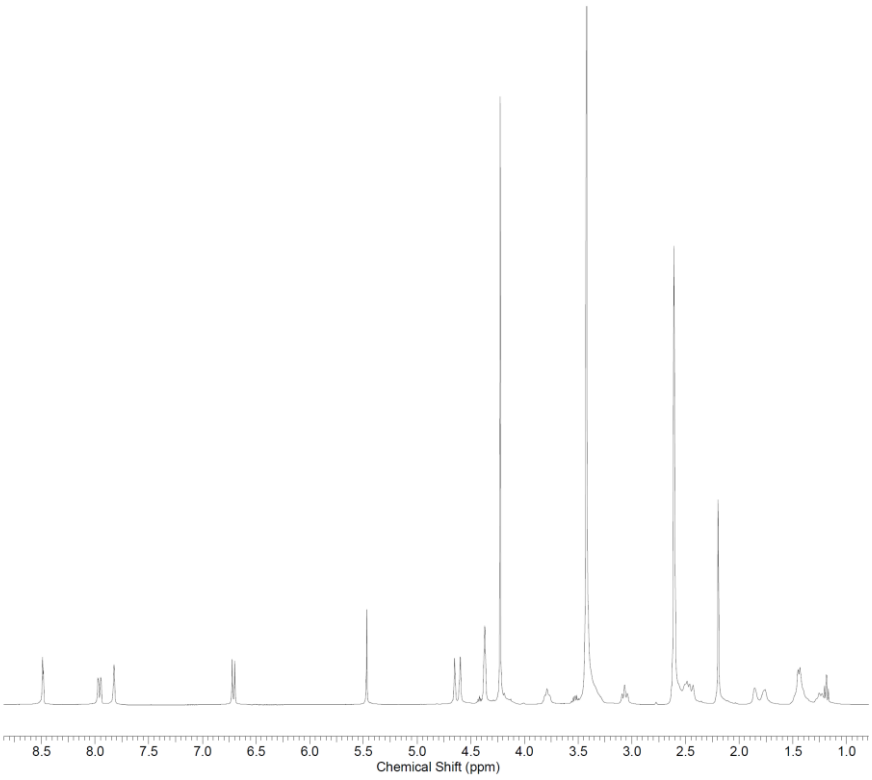


**Figure S11.** $^{1}$H NMR spectrum of bimetallic complex **3** recorded in DMSO-$d_6$ at 298 K.

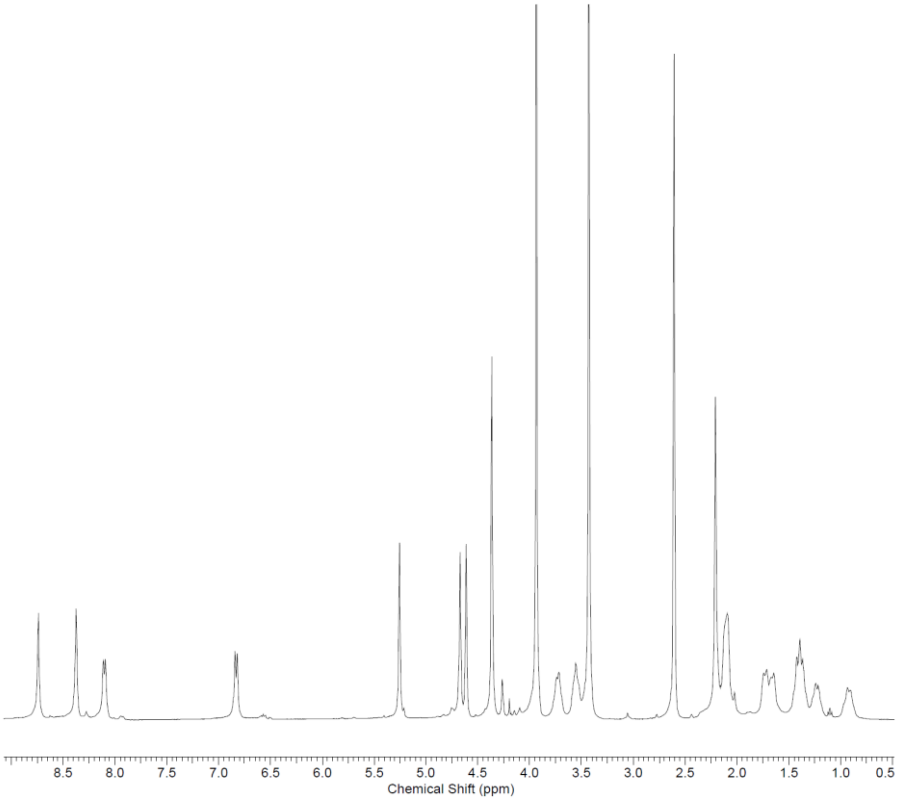


**Figure S12.** $^{1}$H NMR spectrum of bimetallic complex **5** recorded in DMSO-$d_6$ at 298 K.

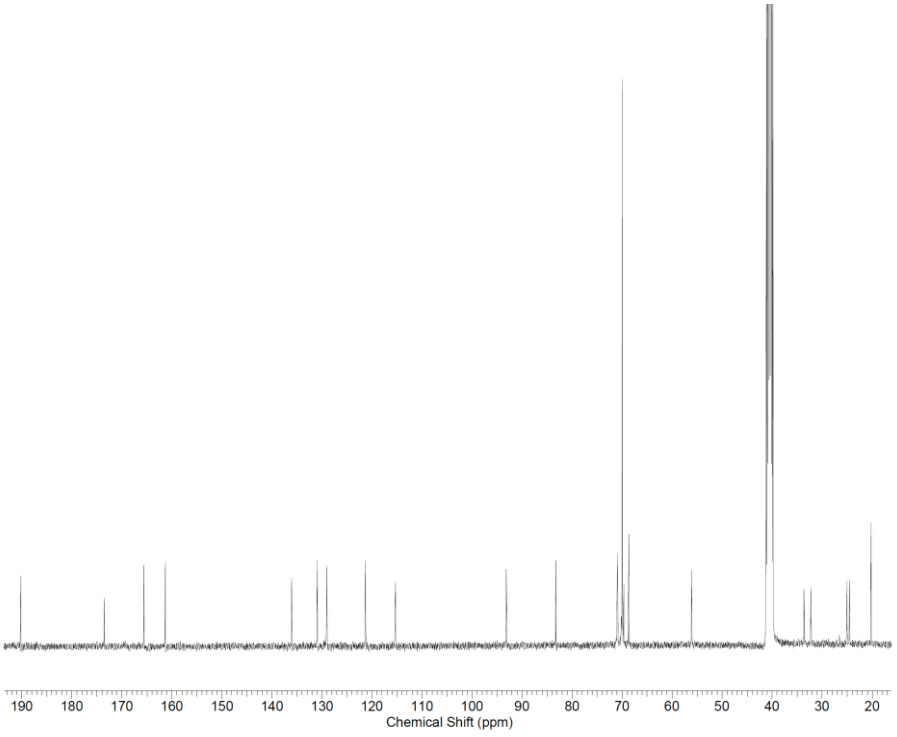


**Figure S13.** $^{13}$C{$^{1}$H} NMR spectrum of metalloligand **2** recorded in DMSO-$d_6$ at 298 K.

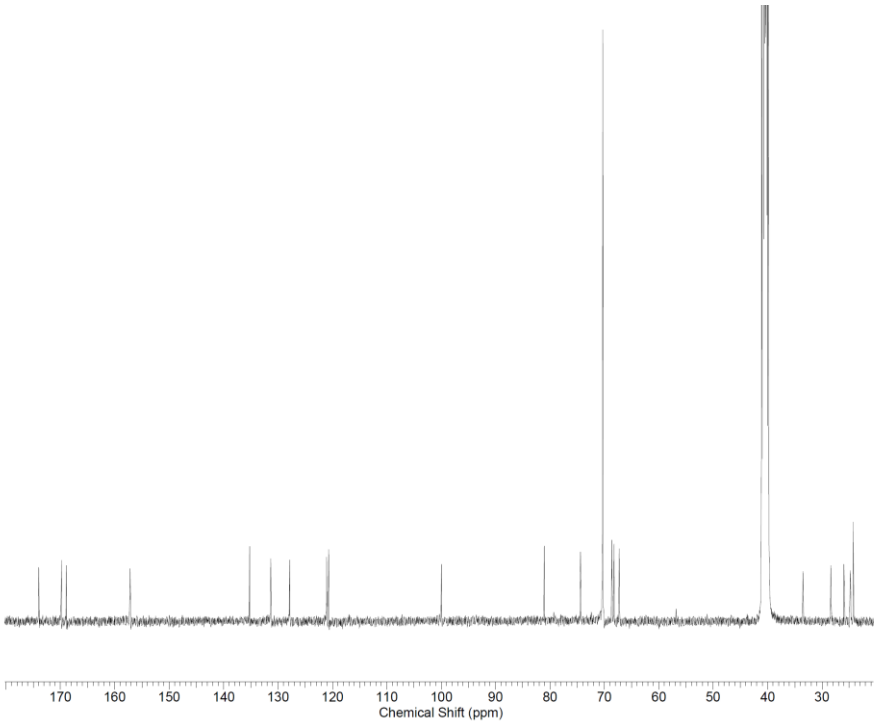


**Figure S14.** $^{13}C\{^{1}H\}$ NMR spectrum of bimetallic complex **3** recorded in DMSO-$d_6$ at 298 K.

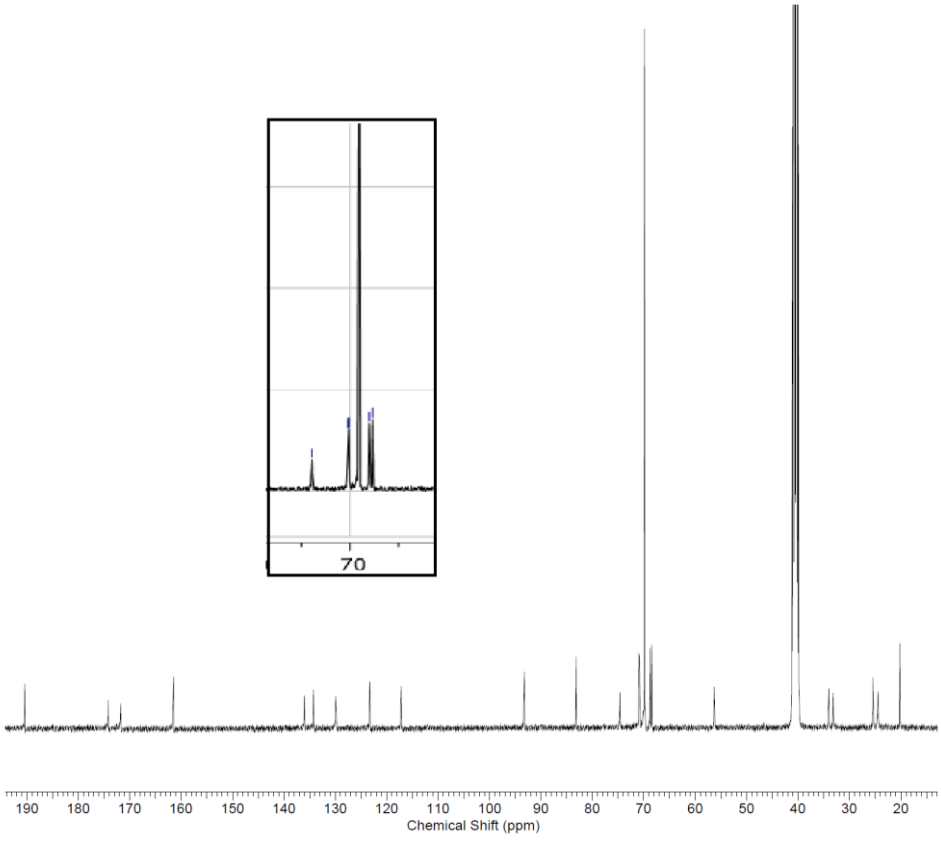


**Figure S15.** $^{13}C\{^{1}H\}$ NMR spectrum of bimetallic complex **5** recorded in DMSO-$d_6$ at 298 K. Inser: resonance pattern of the substituted Cp carbons.

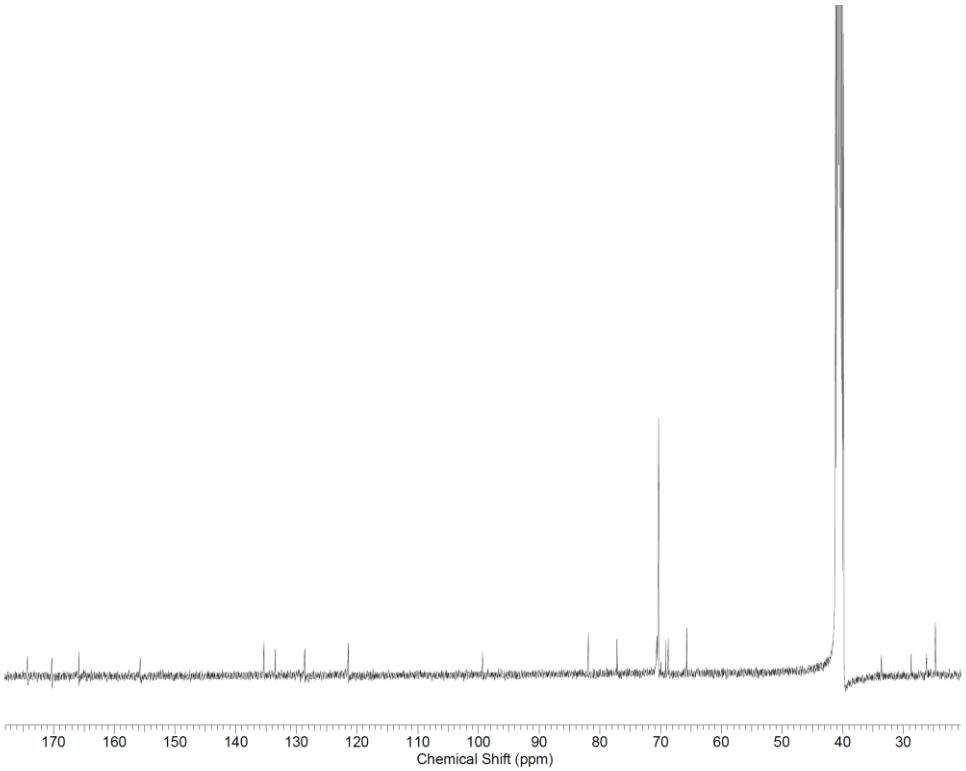


**Figure S16.** $^{13}C\{^{1}H\}$ NMR spectrum of bimetallic complex **6** recorded in DMSO-$d_6$ at 298 K.

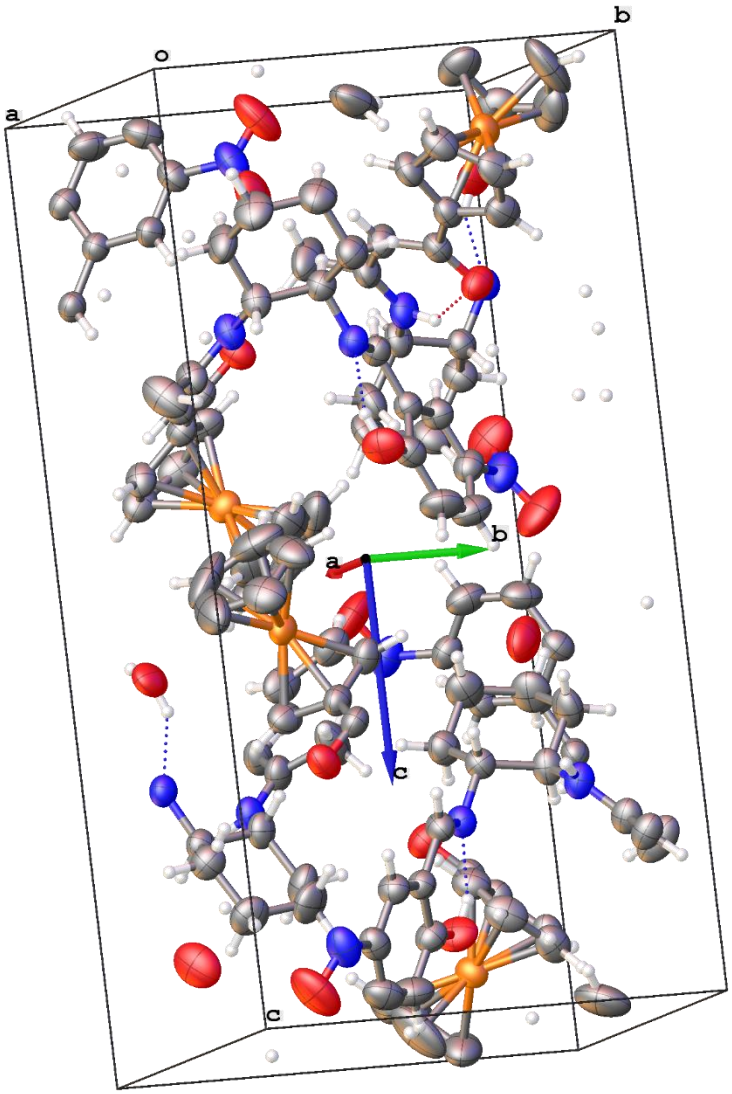


**Figure S17.** Packing diagram of complex **2** showing the molecular arrangement and hydrogen-bond interactions. Thermal ellipsoids are drawn at 50% probability.

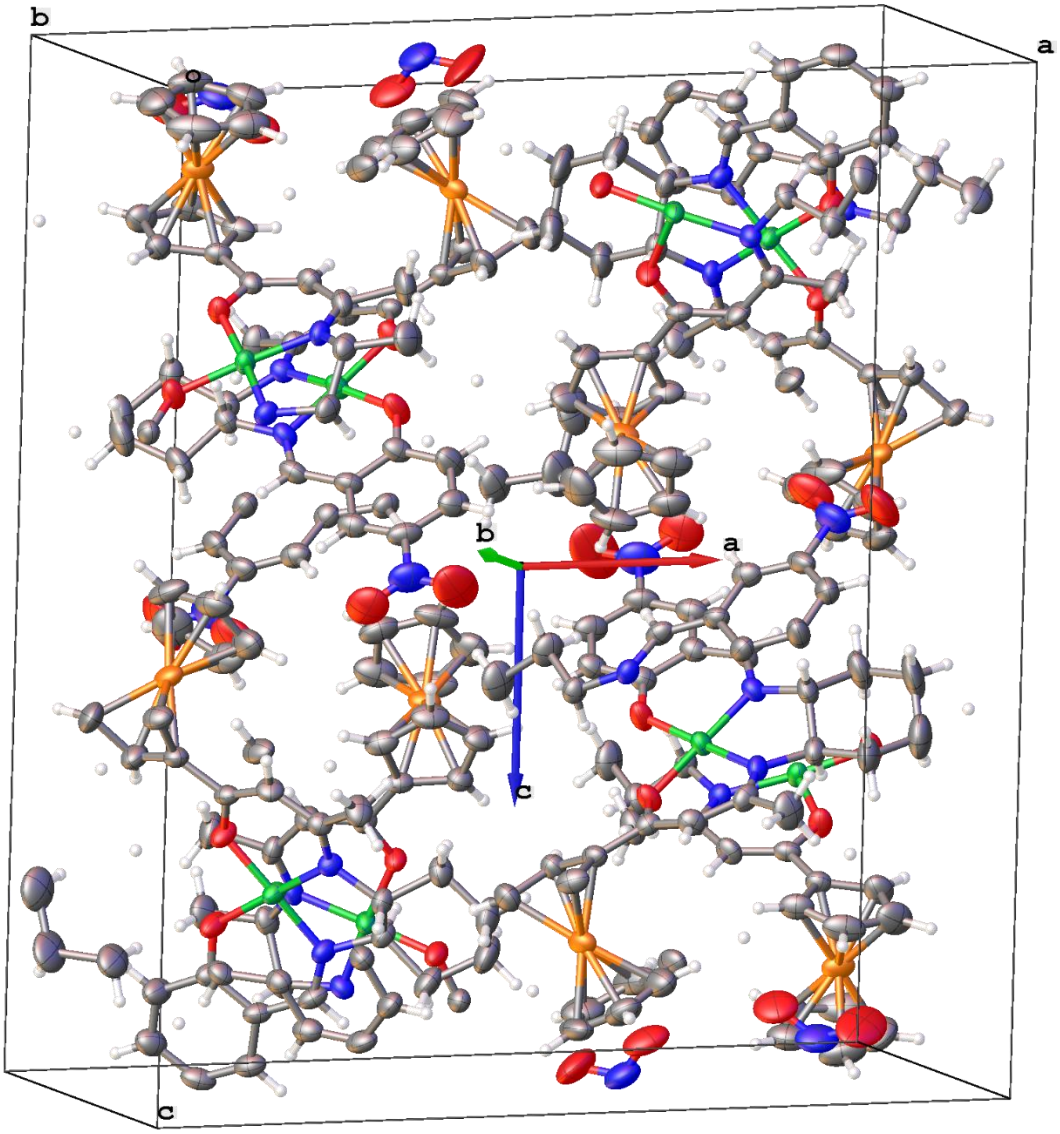


**Figure S18.** Packing diagram of bimetallic complex **3** showing the molecular arrangement and hydrogen-bond interactions. Thermal ellipsoids are drawn at 50% probability.

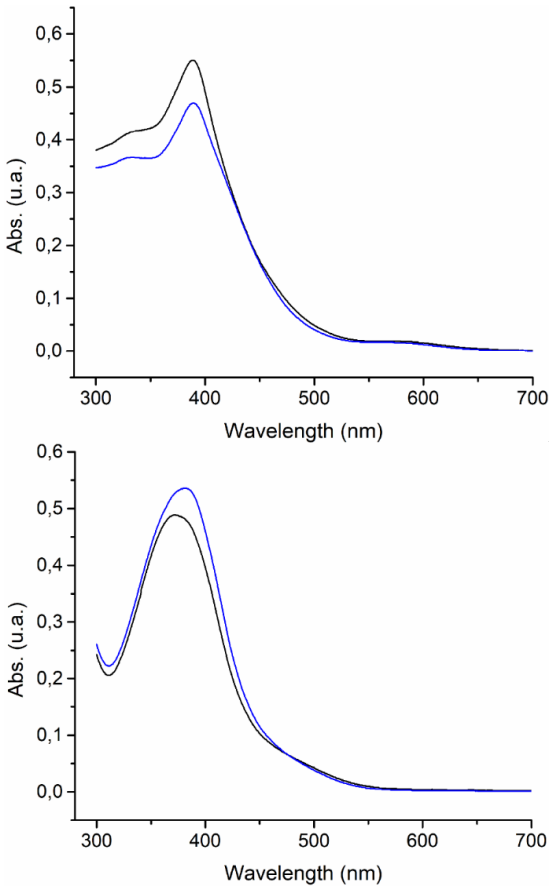


**Figure S19.** UV-vis spectra of complexes **4** (top) and **5** (bottom) recorded in DCM (black line) and DMF (blue line) solutions.

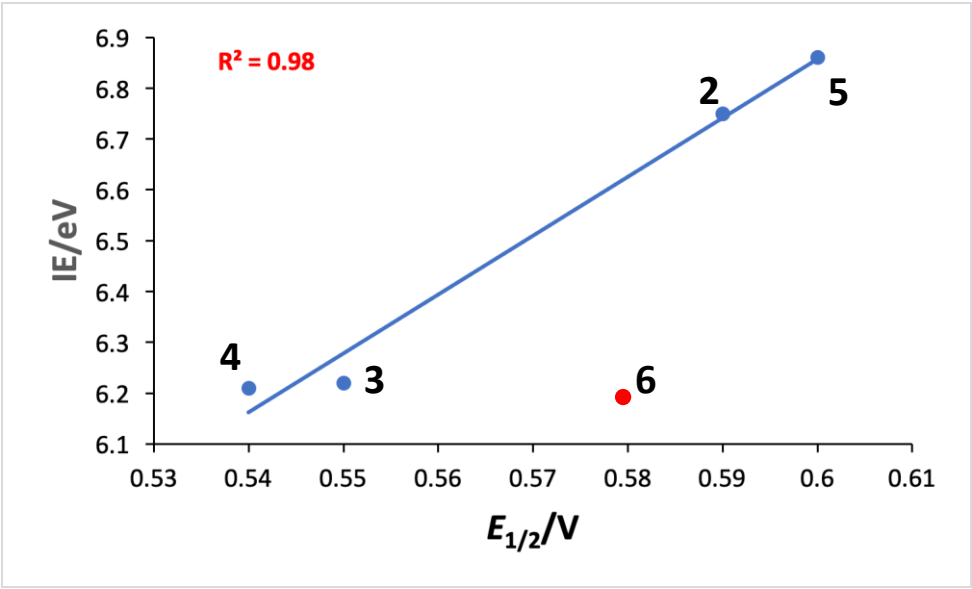


**Figure S20.** The linear correlation between the electrochemical $E_{1/2}$ and the computed ionization energies of complexes **2**, **3**, **4** and **5**. Complex **6** is added for comparison.

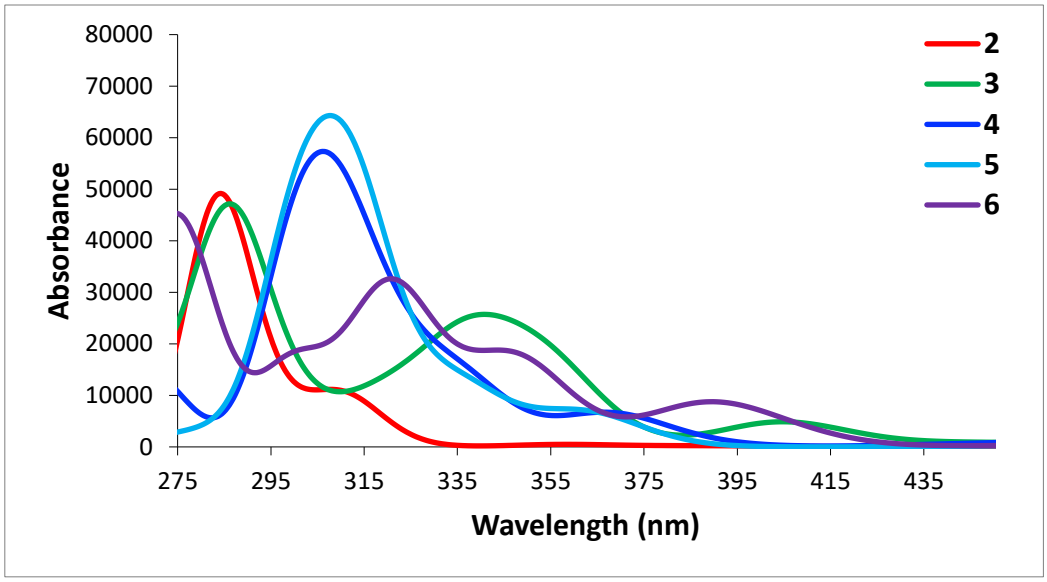


**Figure S21.** TD-DFT-simulated UV-vis spectra of complexes **2**-**6**.

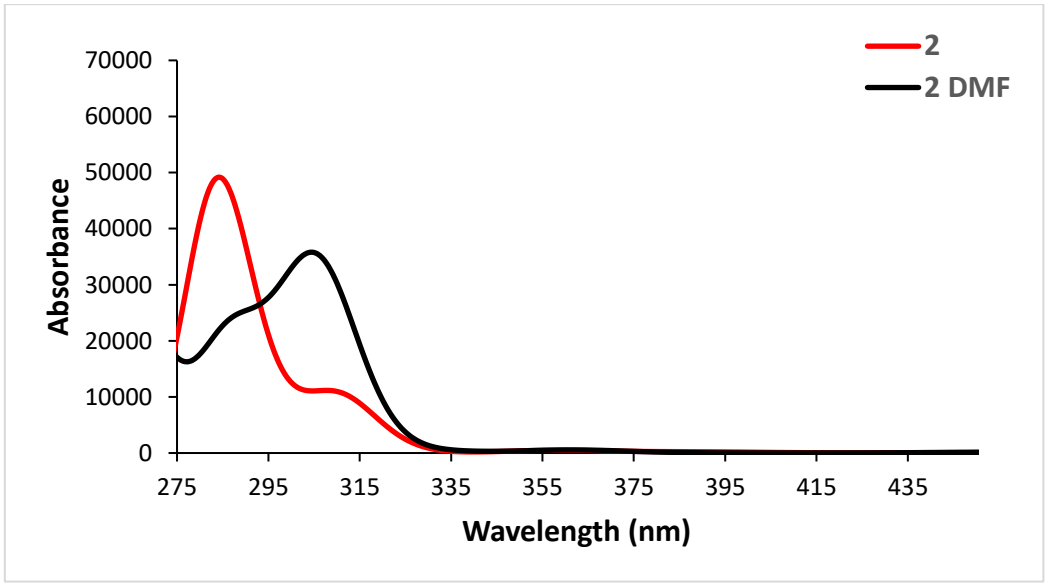


**Figure S22. The** TD-DFT-simulated UV-vis spectra of complexe **2** in vacuum (red curve) and in DMF (black curve).

**Table S1.** Selected bond distances (Å) and angles (°) for compounds **2** and **3**.

| | **1** | **2** | **3A** | **3B** |
|---|---|---|---|---|
| Bond distances | | | | |
| C(11)-O(1) | 1.248(4) | 1.248(4) | 1.284(7) | 1.290(7) |
| C(13)-N(1) | 1.321(5) | 1.332(4) | 1.323(7) | 1.309(7) |
| C(11)-C(12) | 1.412(5) | 1.411(5) | 1.360(9) | 1.361(8) |
| C(12)-C(13) | 1.381(5) | 1.373(5) | 1.414(7) | 1.404(8) |
| N(1)-C(15) | 1.468(4) | 1.458(4) | 1.494(6) | 1.492(6) |
| C(15)-C(16) | 1.526(5) | 1.538(5) | 1.516(6) | 1.524(7) |
| C(16)-N(2) | 1.458(6) | 1.461(4) | 1.478(6) | 1.481(6) |
| N(2)-C(21) | - | 1.273(4) | 1.287(6) | 1.284(7) |
| C(21)-C(22) | - | 1.448(5) | 1.446(8) | 1.428(7) |
| C(22)-C(23) | - | 1.387(4) | 1.421(7) | 1.415(7) |
| O(1)-C(23) | - | 1.320(4) | 1.287(6) | 1.282(6) |
| C(26)-N(3) | - | 1.464(4) | 1.447(8) | 1.450(8) |
| N(3)-O(3) | - | 1.211(4) | 1.212(8) | 1.184(9) |
| N(3)-O(4) | - | 1.206(5) | 1.204(8) | 1.214(8) |
| Bond angles | | | | |
| O(1)-C(11)-C(12) | 123.7(3) | 118.3(3) | 124.5(5) | 123.3(5) |
| N(1)-C(13)-C(12) | 121.10(3) | 121.10(3) | 122.40(5) | 122.30(5) |
| C(11)-C(12)-C(13) | 123.8(3) | 123.9(3) | 125.8(5) | 126.0(5) |
| O(2)-C(23)-C(22) | - | 121.30(3) | 124.00(5) | 123.60(5) |
| N(2)-C(21)-C(22) | - | 120.90(3) | 124.40(5) | 126.00(5) |
| C(21)-C(22)-C(23) | - | 120.20(3) | 120.80(5) | 121.20(5) |
| O(3)-N(3)-C(26) | - | 117.7(4) | 117.8(7) | 119.1(8) |
| O(3)-N(3)-O(4) | - | 119.7(3) | 122.1(7) | 122.0(7) |
| Ni(1)-O(1)-C(11) | - | - | 125.60(4) | 124.50(4) |
| Ni(1)-O(2)-C(23) | - | - | 128.20(4) | 128.30(3) |
| Ni(1)-N(1)-C(13) | - | - | 122.80(4) | 122.70(4) |
| Ni(1)-N(1)-C(15) | - | - | 112.60(3) | 108.60(3) |
| Ni(1)-N(2)-C(16) | - | - | 127.70(4) | 112.40(3) |
| Ni(1)-N(2)-C(21) | - | - | 127.70(4) | 125.50(4) |

**Table S2.** Selected metrical parameters of the ferrocenyl units in compounds **2** and **3**.

| Compd | Fe-$Cp_{CNT}$ (Å) | Fe-$Cp'_{CNT}$ (Å) | $Cp_{CNT}$-Fe-$Cp'_{CNT}$(°) | Cp/Cp' (°) |
|---|---|---|---|---|
| **2** | 1.647 | 1.639 | 178.5 | 2.4(4) |
| **3A** | 1.647 | 1.650 | 178.1 | 10.3(9) |
| **3B** | 1.658 | 1.659 | 179.3 | 9.3(9) |

Abbreviations: Cp = $C_5H_5$, Cp' = $C_5H_4$, CNT = centroid.

**Table S3.** Intra- and intermolecular hydrogen bond interactions in metalloligand **2**.

| Natur | D-H···A | D−H (Å) | H···A (Å) | D···A (Å) | ∢ D−H···A (°) |
|---|---|---|---|---|---|
| Intra | N(1)-H···O(1) | 0.86 | 1.98 | 2.648(3) | 134 |
| Intra | O(2)-H···N(2) | 0.82 | 1.81 | 2.540(4) | 148 |
| Inter | C(2)-h(2A)···O(3)$^{\#1}$ | 0.93 | 2.57 | 3.433(9) | 155 |
| Inter | C(23)-H(23)···O(1)$^{\#2}$ | 0.93 | 2.55 | 3.345(4) | 143 |
| Inter | C(26)-H(26)···O(3)$^{\#3}$ | 0.93 | 2.48 | 3.206(5) | 135 |

Symmetry transformations used to generate equivalent atoms: #1 = 1/2+x,3/2-y,1-z; #2 = 1-x,1/2+y,1/2-z; #3 = -1/2+x,3/2-y,1-z.

**Table S4.** Intermolecular hydrogen bond interactions in complex **3**.

| D-H···A | D−H (Å) | H···A (Å) | D···A (Å) | ∢ D−H···A (°) |
|---|---|---|---|---|
| C(18A)-H(18A)···O(3A)$^{\#1}$ | 0.97 | 2.42 | 3.360(9) | 164 |
| C(18B)-H(18C)···O(3B)$^{\#2}$ | 0.97 | 2.45 | 3.341(11) | 153 |

Symmetry transformations used to generate equivalent atoms: #1 = 1/2+x,1/2-y,2-z; #2 = -1/2+x,-1/2-y,2-z.