Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Supporting Information

for

Dual coordination in ditopic azabipyridines and azaterpyridines as a key for reversible switching

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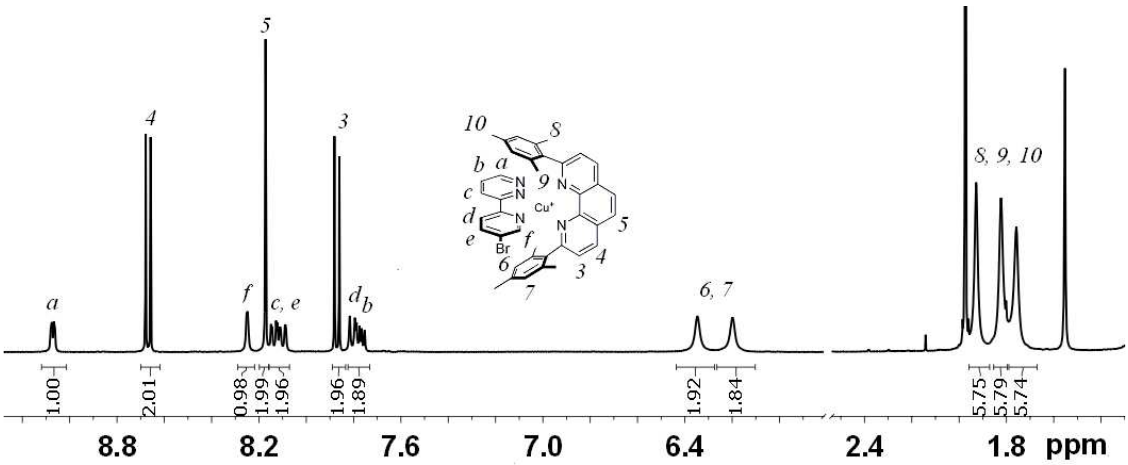

Figure S1: ^{1}H NMR spectrum (400 MHz) of complex **8** in CD_2Cl_2 at 298 K**.**

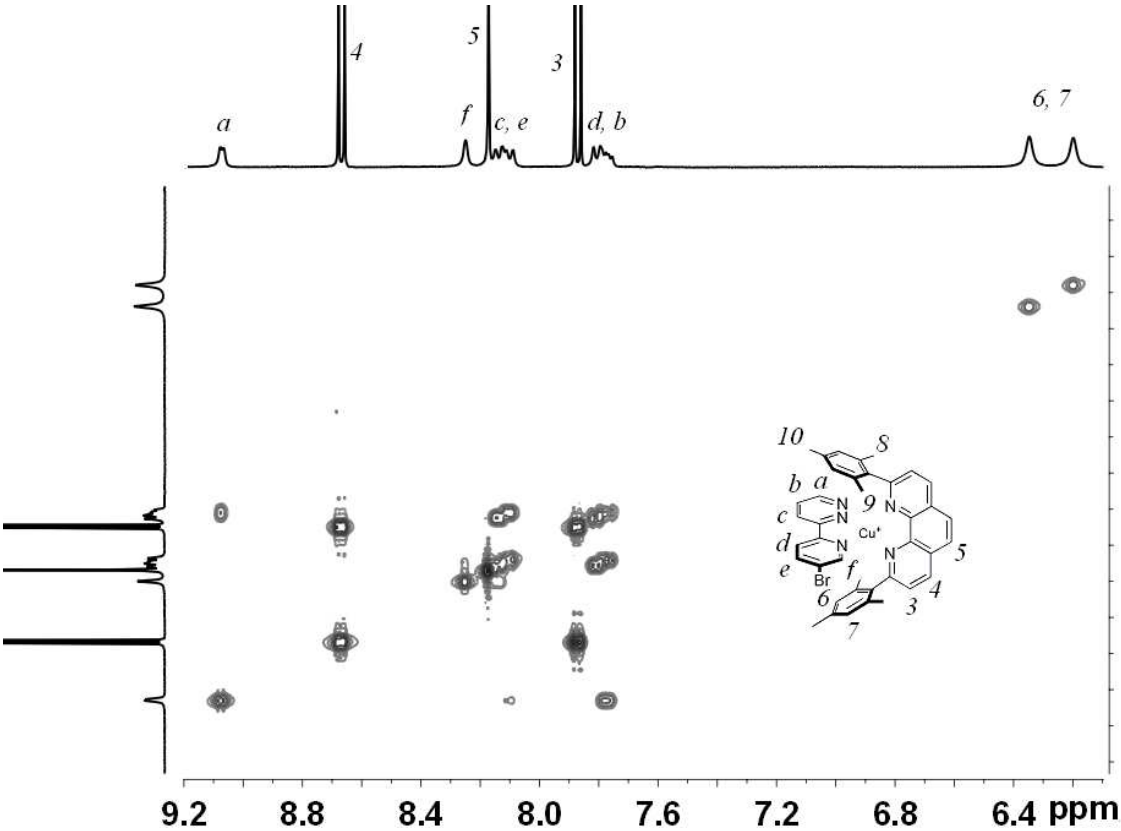

Figure S2: Partial ^{1}H-^{1}H COSY spectrum (400 MHz) of complex **8** in CD_2Cl_2 at 298 K**.**

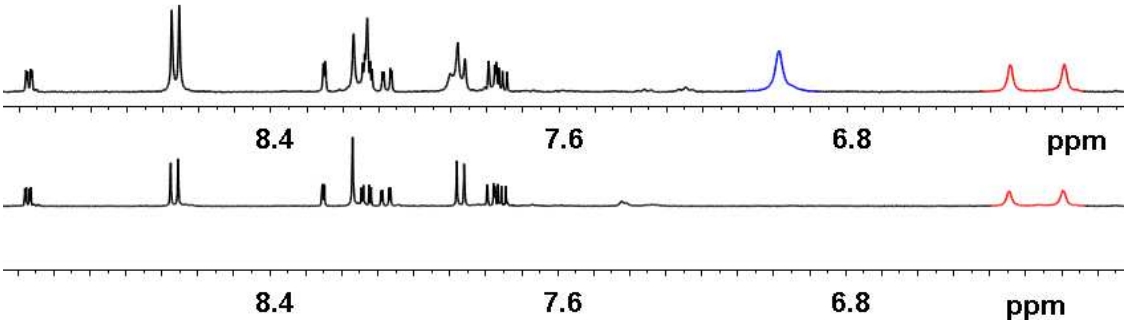

Figure S3: ^{1}H NMR spectra (400 MHz) of $[Cu(MeCN)_4]PF_6$ and **5** (1:1) in CD_2Cl_2 at 298 K with (top) 0.5 equiv. of **1** being added, and (bottom) with a total of 1.0 equiv. of **1** being added affording complex **8.**

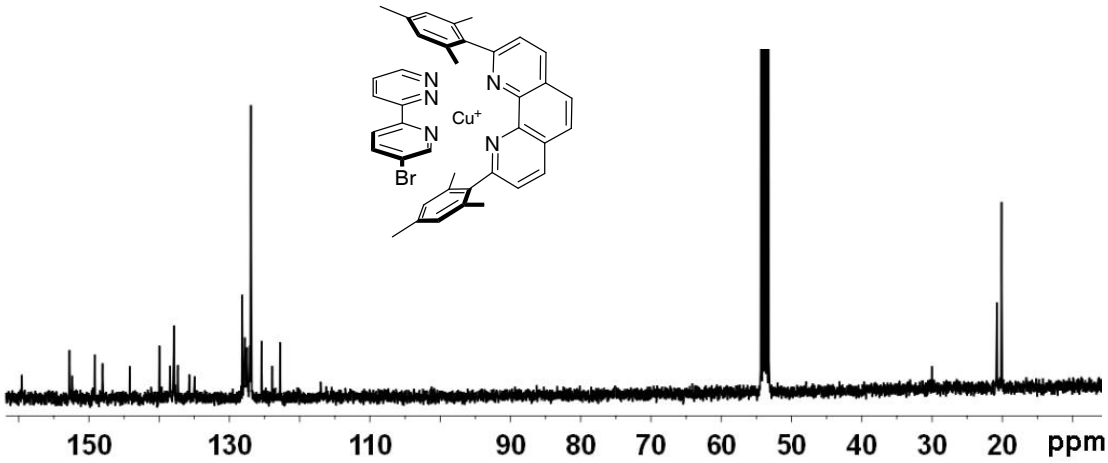

Figure S4: ^{13}C NMR spectrum (100 MHz) of complex **8** in CD_2Cl_2 at 298 K**.**

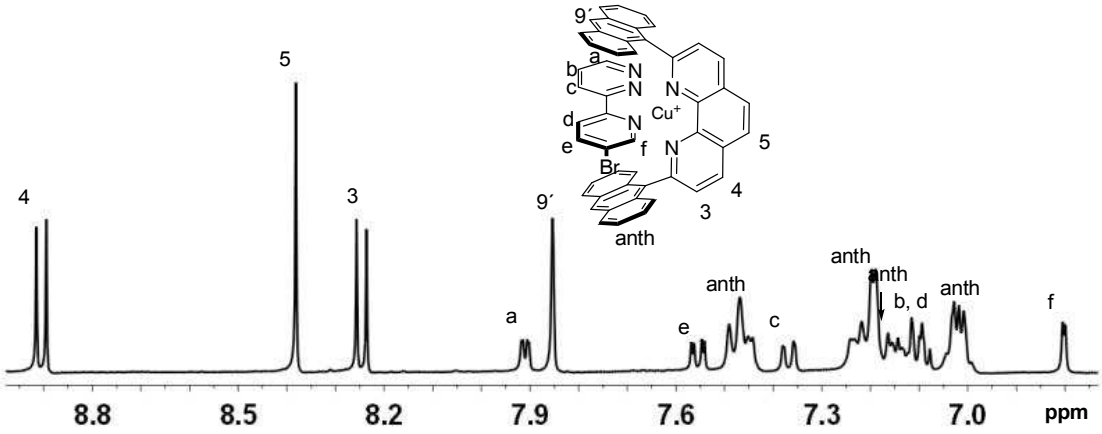

Figure S5: ^{1}H NMR spectrum (400 MHz) of complex **9** in CD_2Cl_2 at 298 K**.**

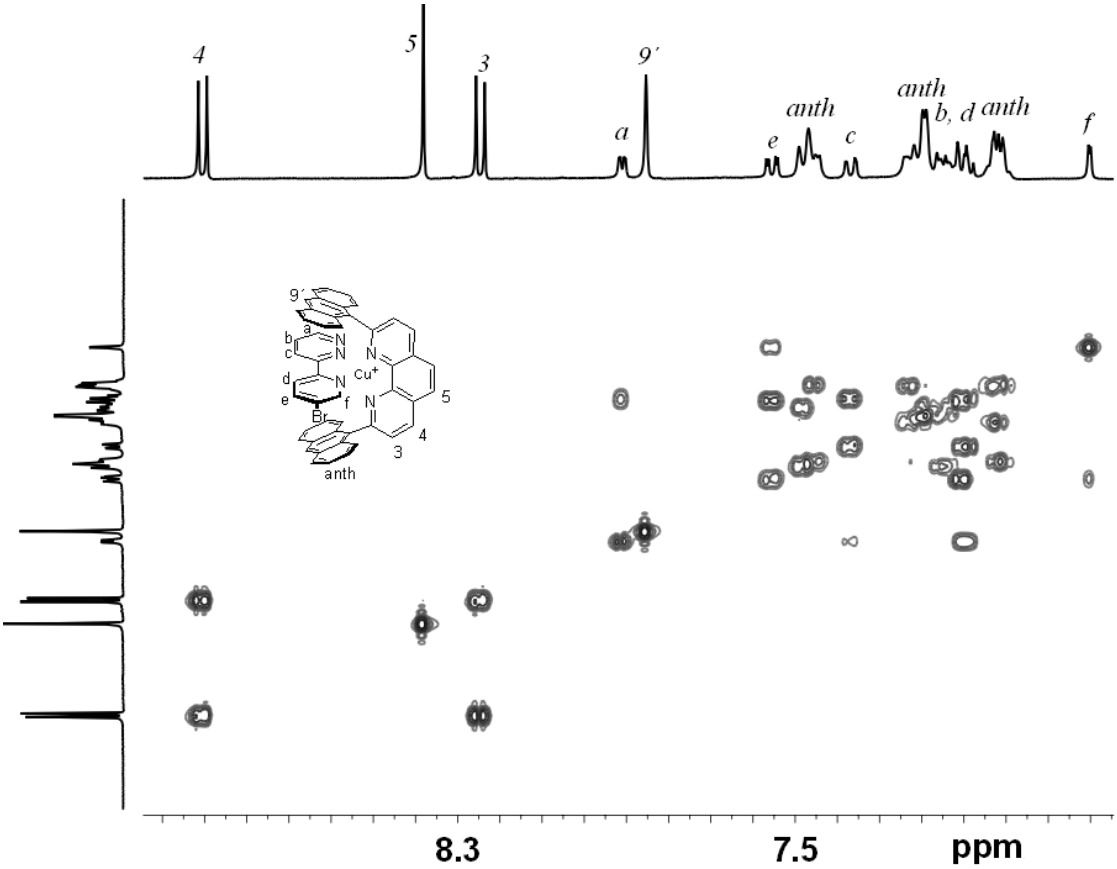

Figure S6: ^{1}H-^{1}H COSY spectrum (400 MHz) of complex **9** in CD_2Cl_2 at 298 K**.**

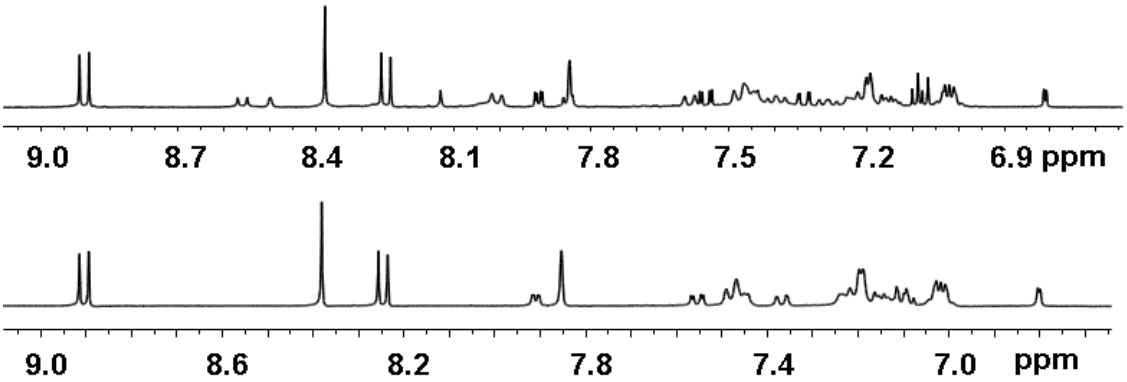

Figure S7: ^{1}H NMR spectra (400 MHz) of $[Cu(MeCN)_4]PF_6$ and **6** (1:1) in CD_2Cl_2 at 298 K with (top) 0.5 equiv. of **1** being added, and (bottom) with a total of 1.0 equiv. of **1** being added affording complex **9**.

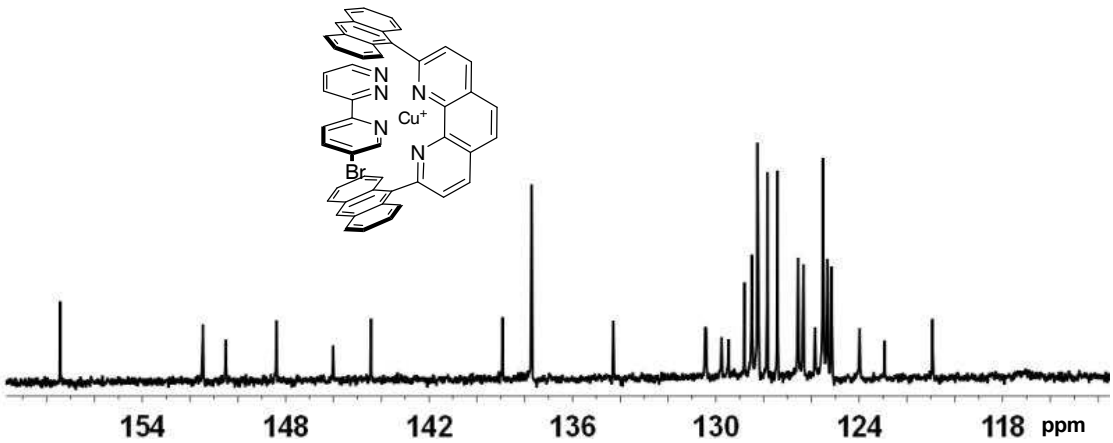

Figure S8: ^{13}C NMR spectrum (100 MHz) of complex **9** in CD_2Cl_2 at 298 K.

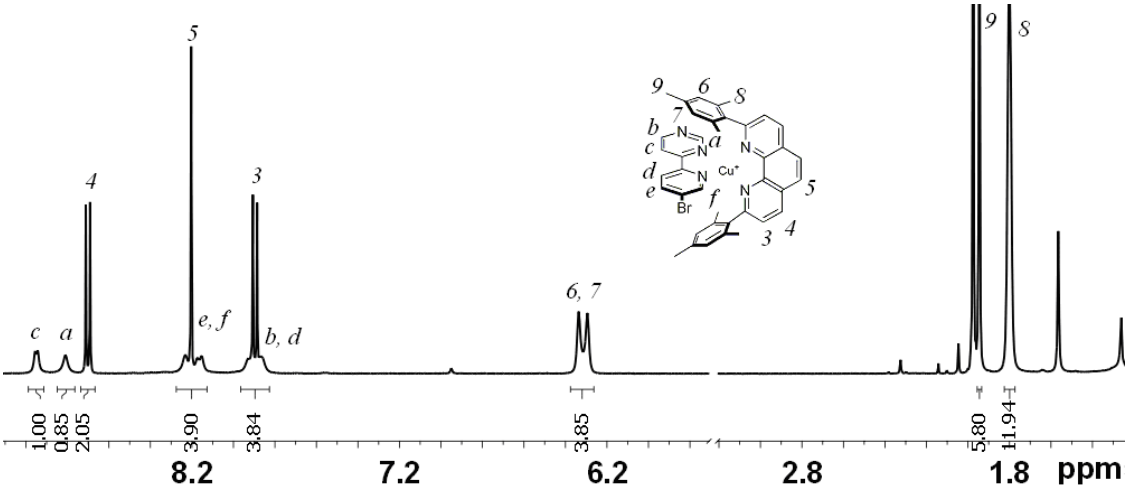

Figure S9: ^{1}H NMR spectrum (400 MHz) of complex **10** in CD_2Cl_2 at 298 K**.**

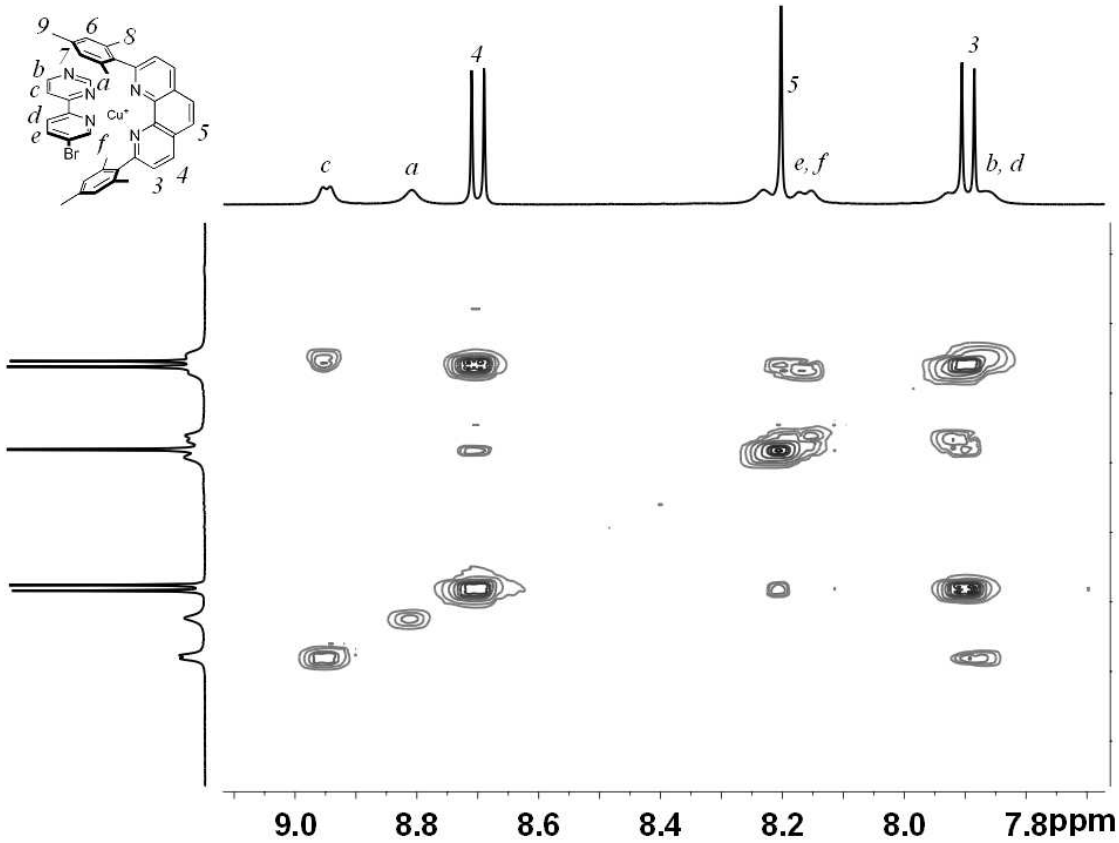

Figure S10: Partial ^{1}H-^{1}H COSY spectrum (400 MHz) of complex **10** in CD_2Cl_2 at 298 K**.**

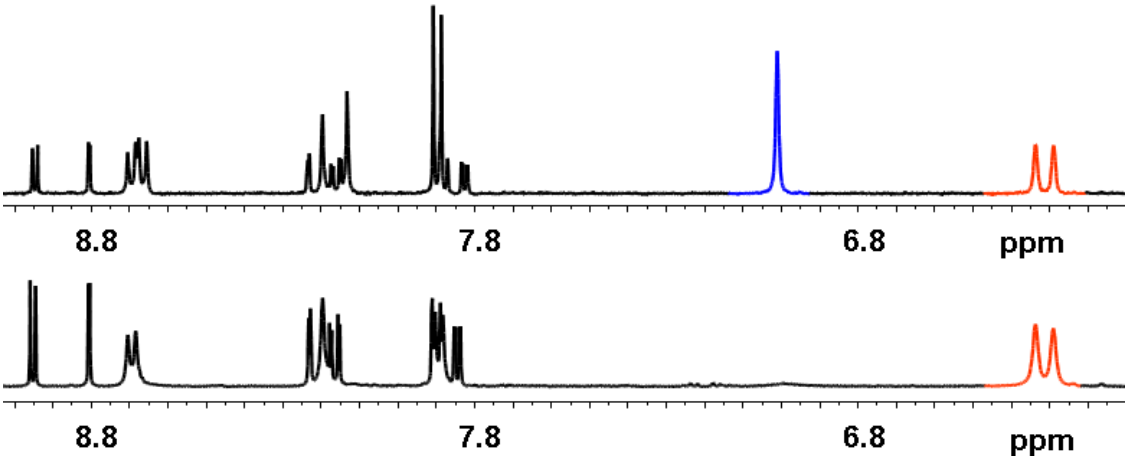

Figure S 11: ^{1}H NMR spectra (400 MHz) of $[Cu(MeCN)_4]PF_6$ and **5** (1:1) in CD_2Cl_2 at 298 K with (top) 0.5 equiv. of **2** being added, and (bottom) with a total of 1.0 equiv. of **2** being added affording complex **10**.

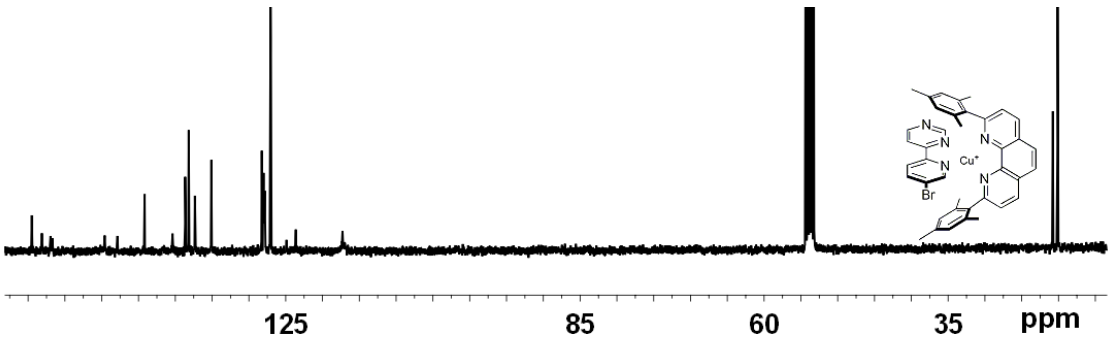

Figure S12: ^{13}C NMR spectrum (100 MHz) of complex **10** in CD_2Cl_2 at 298 K**.**

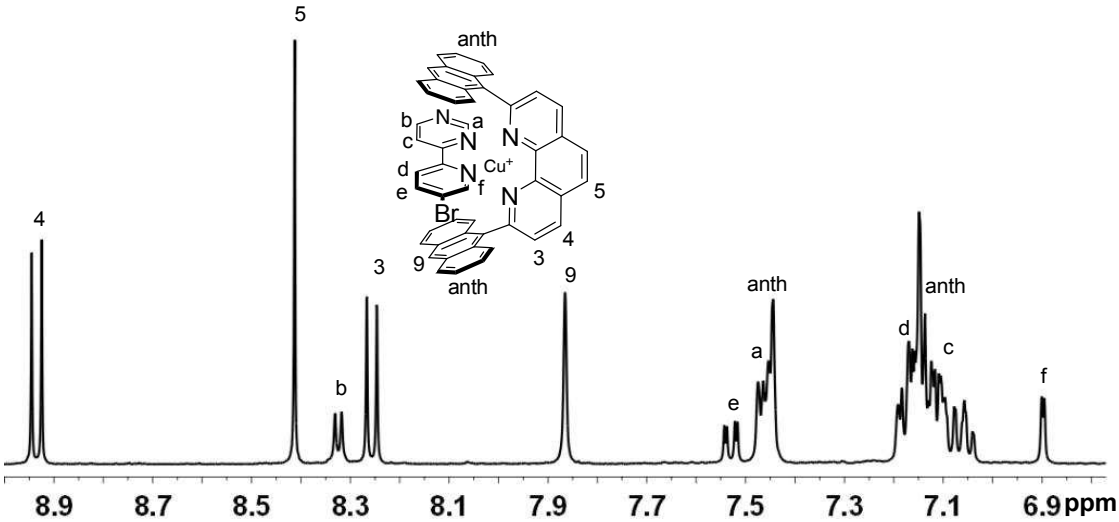

Figure S13: ^{1}H NMR spectrum of (400 MHz) complex **11** in CD_2Cl_2 at 298 K**.**

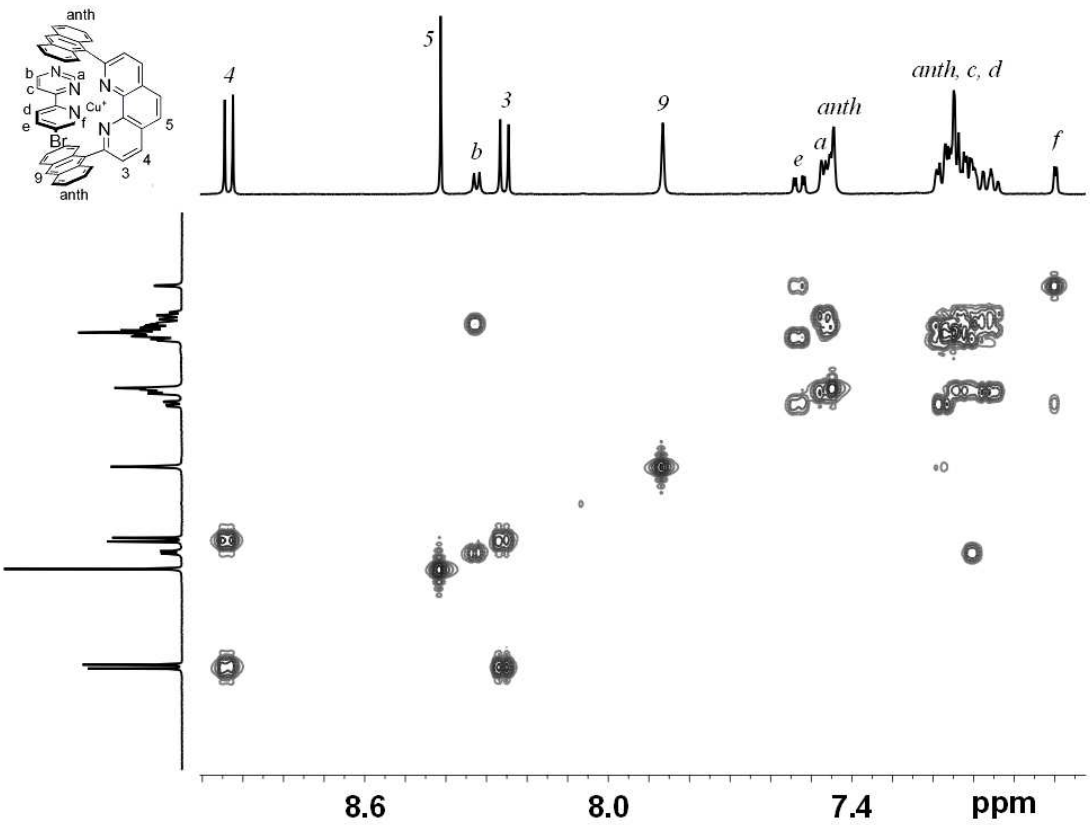

Figure S14: ^{1}H-^{1}H COSY spectrum (400 MHz) of complex **11** in CD_2Cl_2 at 298 K.

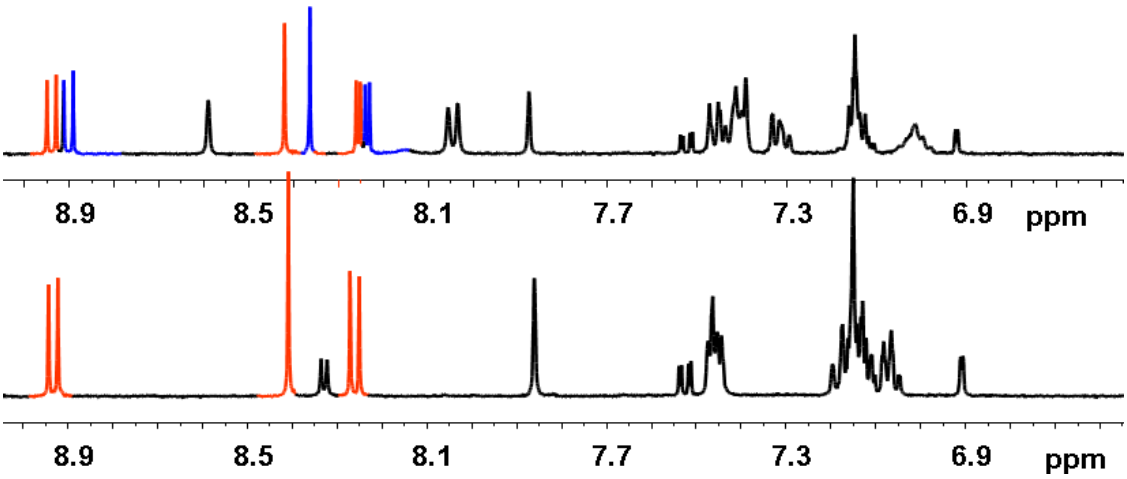

Figure S15: ^{1}H NMR spectra (400 MHz) of $[Cu(MeCN)_4]PF_6$ and **6** (1:1) in CD_2Cl_2 at 298 K with (top) 0.5 equiv. of **2** being added, and (bottom) with a total of 1.0 equiv. of **2** being added affording complex **11**.

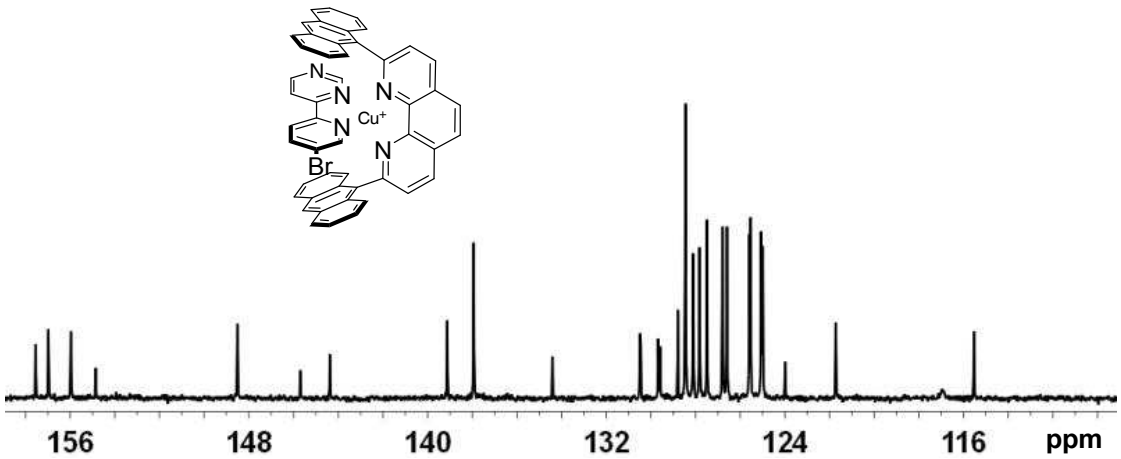

Figure S16: ^{13}C NMR spectrum (100 MHz) of complex **11** in CD_2Cl_2 at 298 K**.**

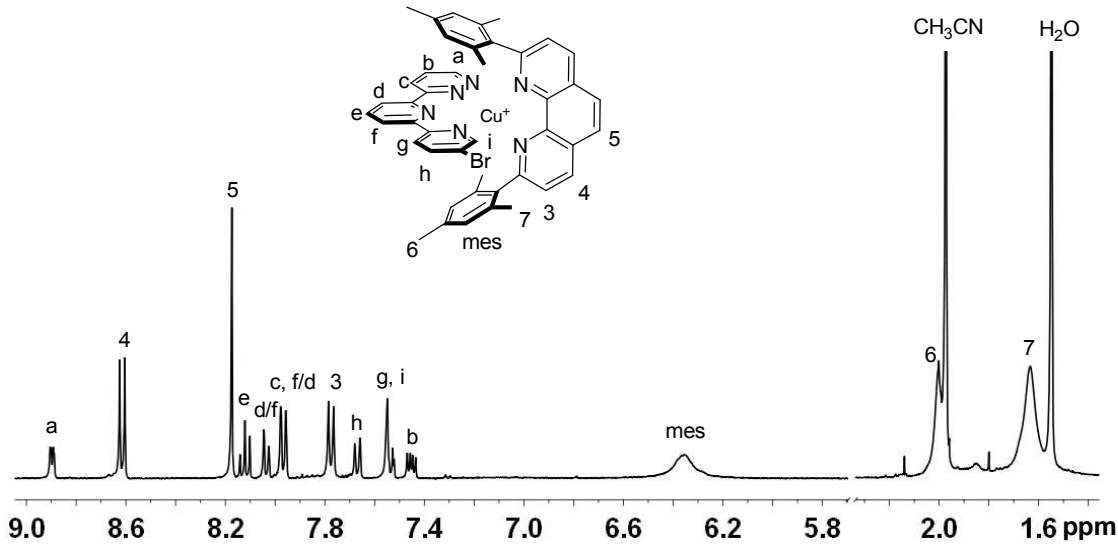

Figure S17: ^{1}H NMR spectrum (400 MHz) of complex **12** in CD_2Cl_2 at 298 K**.**

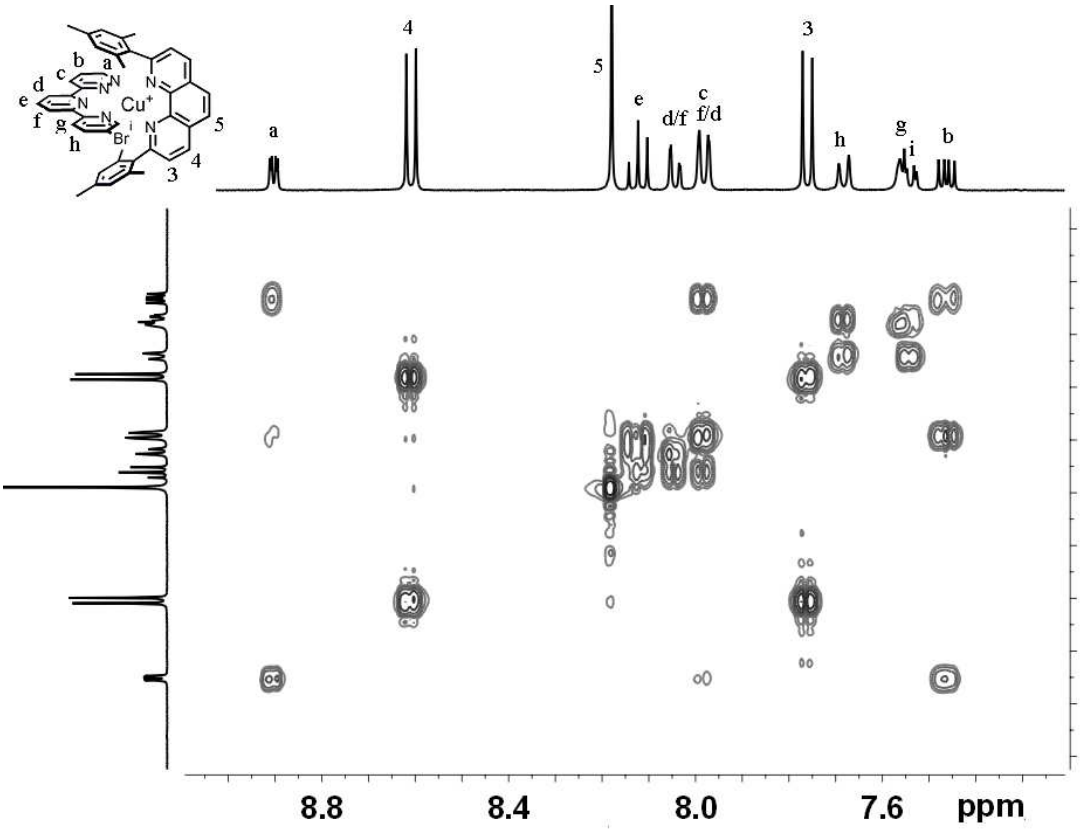

Figure S18: Partial ^{1}H-^{1}H COSY spectrum (400 MHz) of complex **12** in CD_2Cl_2 at 298 K**.**

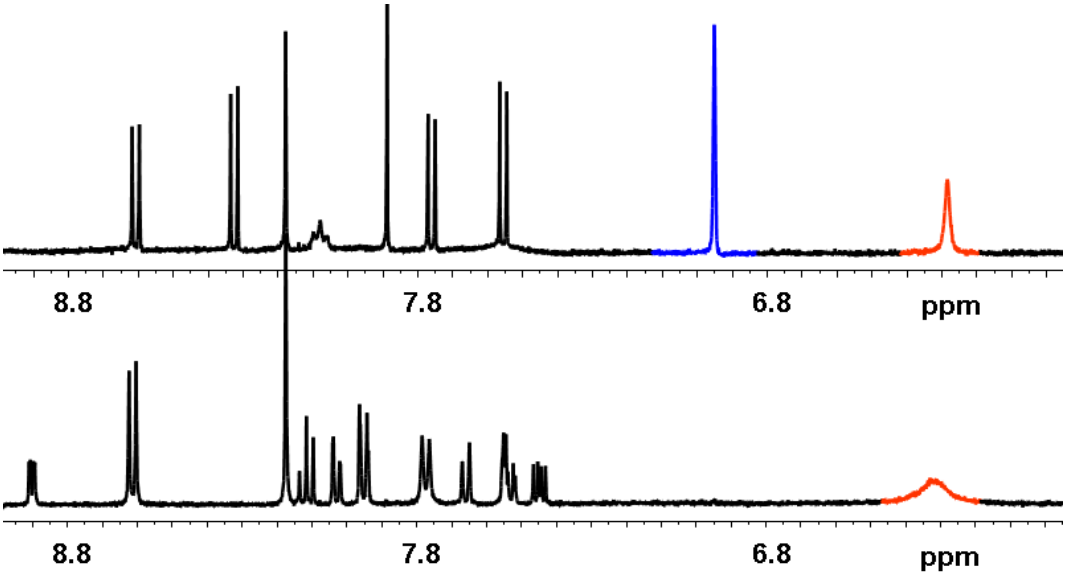

Figure S19: ^{1}H NMR spectra (400 MHz) of **3** and **5** (1:1) in CD_2Cl_2 at 298 K with (top) 0.5 equiv. of $[Cu(MeCN)_4]PF_6$ being added, and (bottom) with a total of 1.0 equiv. of $[Cu(MeCN)_4]PF_6$ being added affording complex **12**.

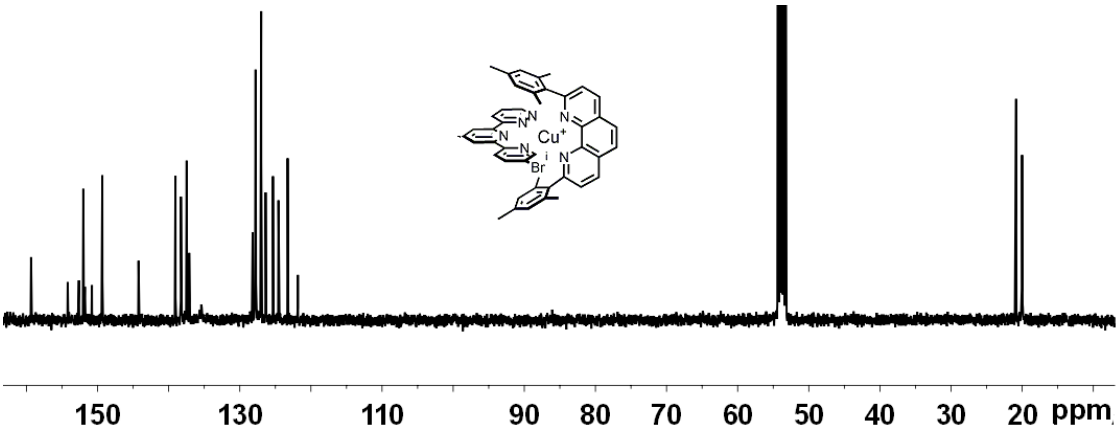

Figure S20: ^{13}C NMR spectrum (100 MHz) of complex **12** in CD_2Cl_2 at 298 K**.**

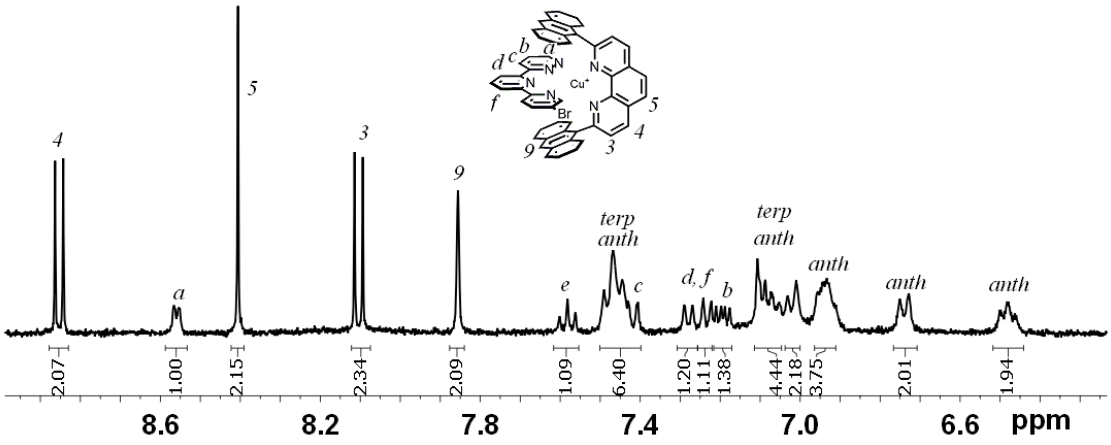

Figure S21: ^{1}H NMR spectrum (400 MHz) of complex **13** in CD_2Cl_2 at 298 K**.**

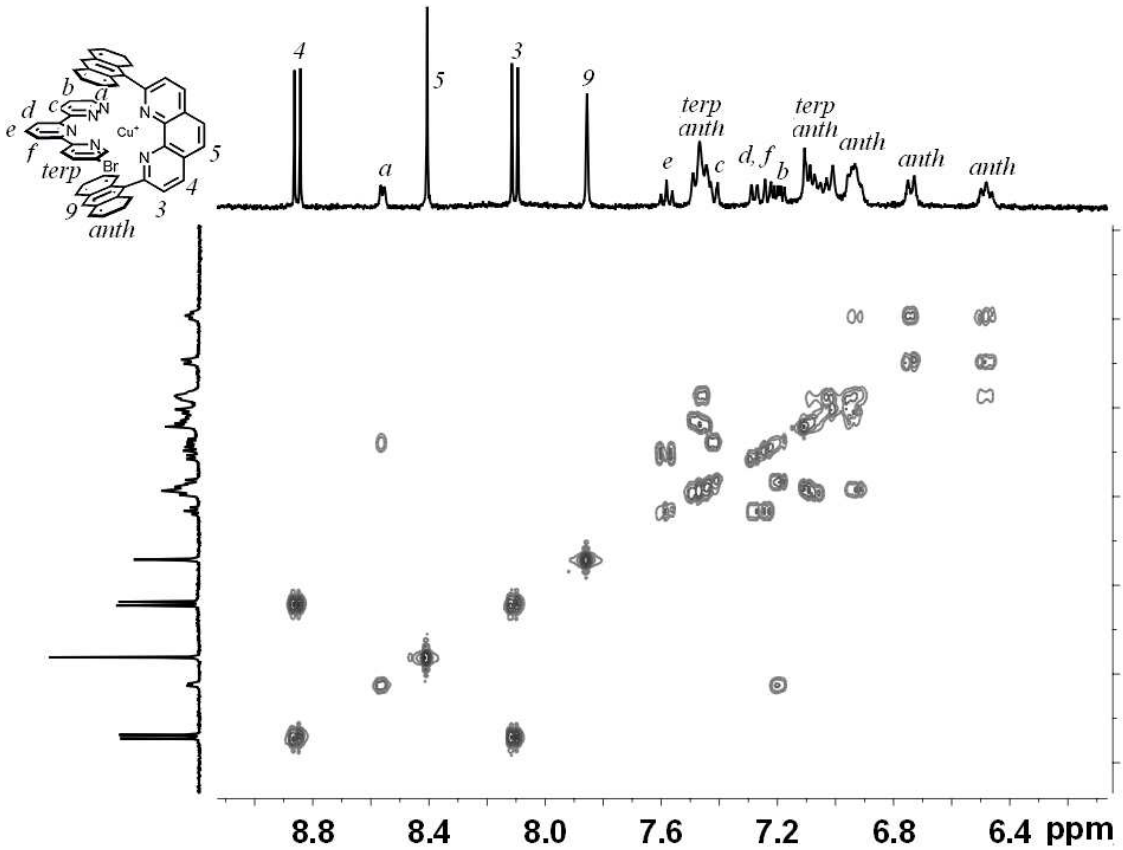

Figure S22: ^{1}H-^{1}H COSY spectrum (400 MHz) of complex **13** in CD_2Cl_2 at 298 K**.**

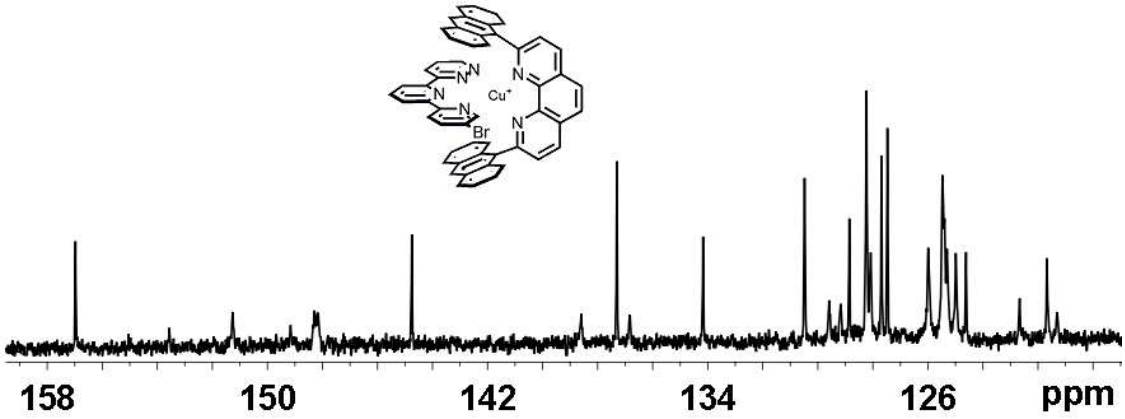

Figure S23: ^{13}C NMR spectrum (100 MHz) of complex **13** in CD_2Cl_2 at 298 K**.**

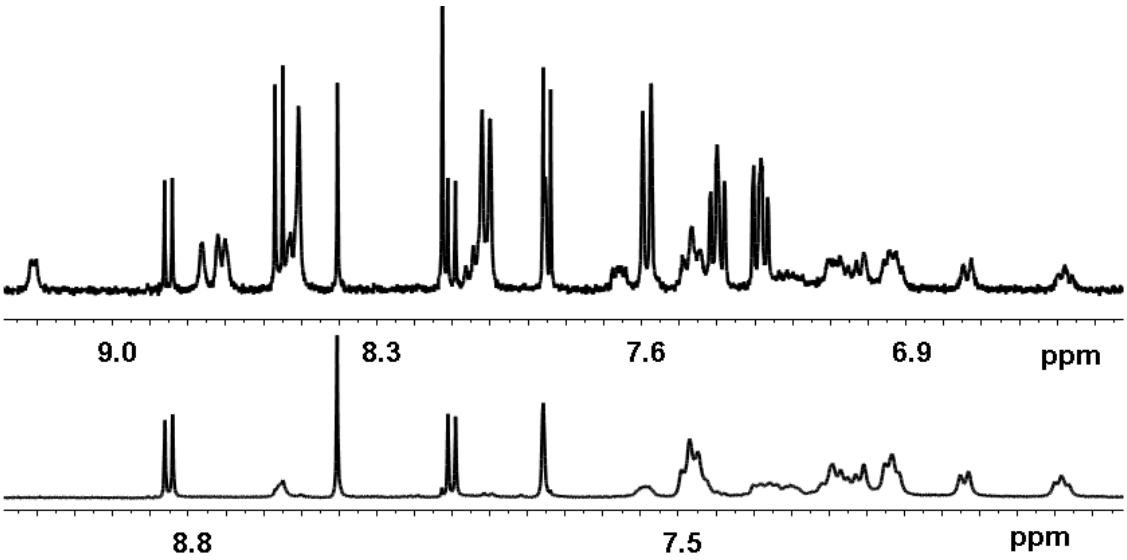

Figure S24: ^{1}H NMR spectra (400 MHz) of **3** and **6** (1:1) in CD_2Cl_2 at 298 K with (top) 0.5 equiv. of $[Cu(MeCN)_4]PF_6$ being added, and (bottom) with a total of 1.0 equiv. of $[Cu(MeCN)_4]PF_6$ being added affording complex **13**.

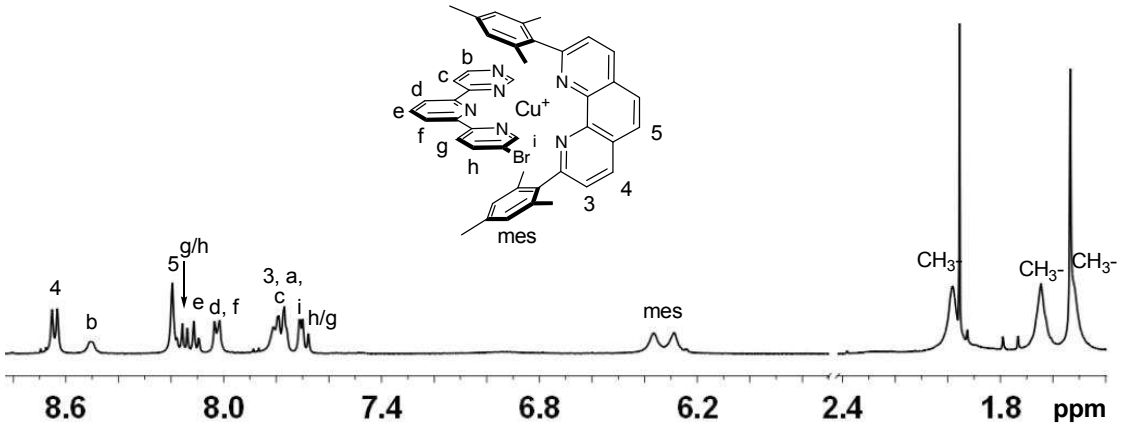

Figure S25: ^{1}H NMR spectrum (400 MHz) of complex **14** in CD_2Cl_2 at 298 K**.**

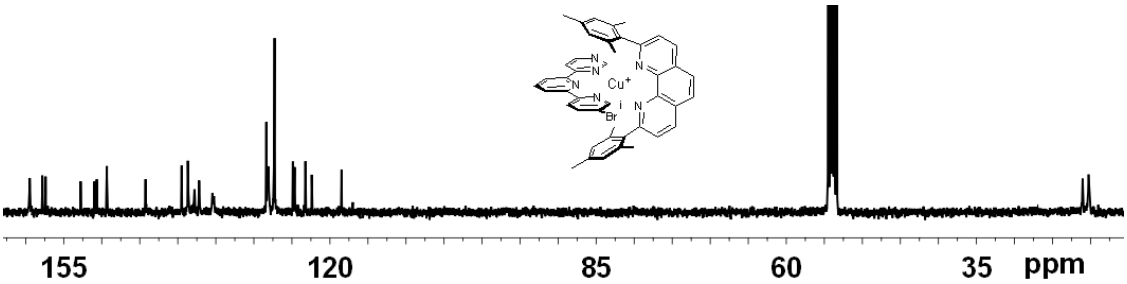

Figure S26: ^{13}C NMR spectrum (100 MHz) of complex **14** in CD_2Cl_2 at 298 K**.**

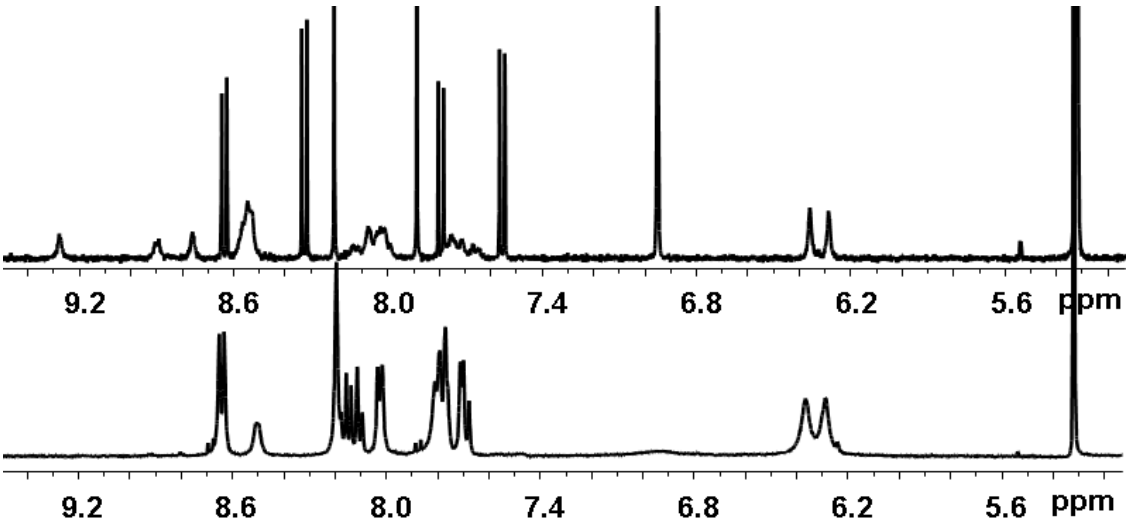

Figure S27: ^{1}H NMR spectra (400 MHz) of **4** and **5** (1:1) in CD_2Cl_2 at 298 K with (top) 0.5 equiv. of $[Cu(MeCN)_4]PF_6$ being added, and (bottom) with a total of 1.0 equiv. of $[Cu(MeCN)_4]PF_6$ being added affording complex **14**.

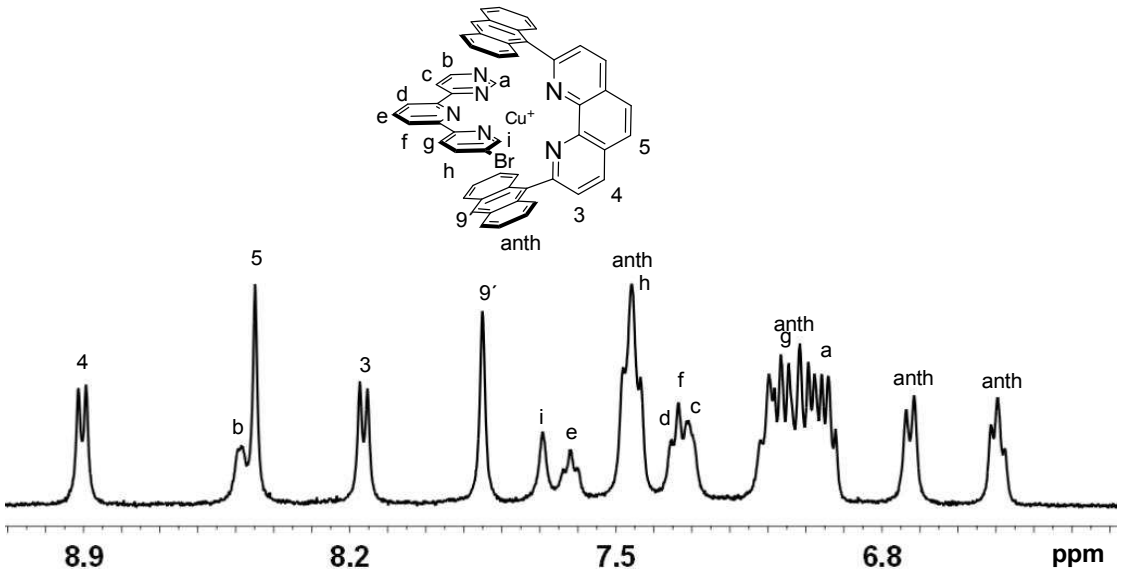

Figure S28: ^{1}H NMR spectrum (400 MHz) of complex **15** in CD_2Cl_2 at 298 K**.**

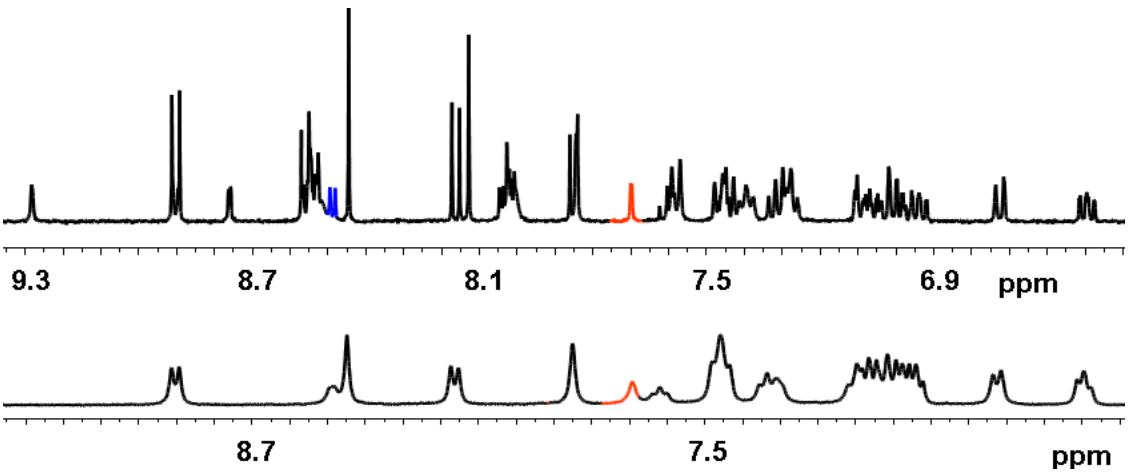

Figure S29: ^{1}H NMR spectra (400 MHz) of **4** and **6** (1:1) in CD_2Cl_2 at 298 K with (top) 0.5 equiv. of $[Cu(MeCN)_4]PF_6$ being added, and (bottom) with a total of 1.0 equiv. of $[Cu(MeCN)_4]PF_6$ being added affording complex **15**.

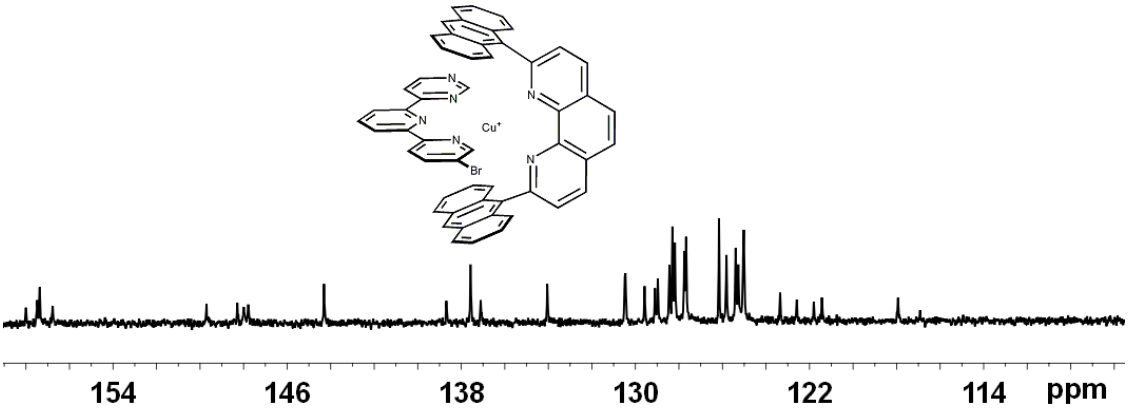

Figure S30: ^{13}C NMR spectrum (100 MHz) of complex **15** in CD_2Cl_2 at 298 K**.**

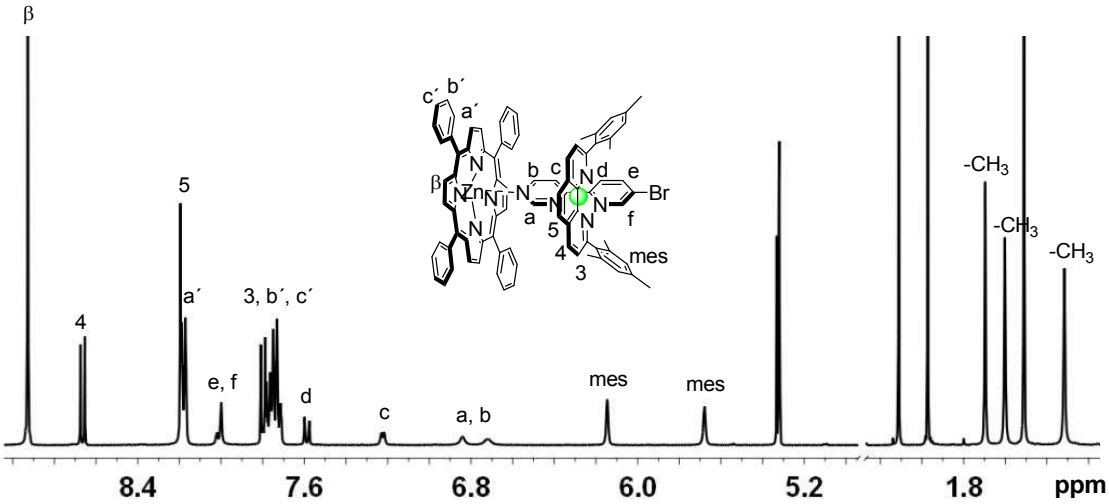

Figure S31: ^{1}H NMR spectrum (400 MHz) of complex **16** in CD_2Cl_2 at 298 K**.**

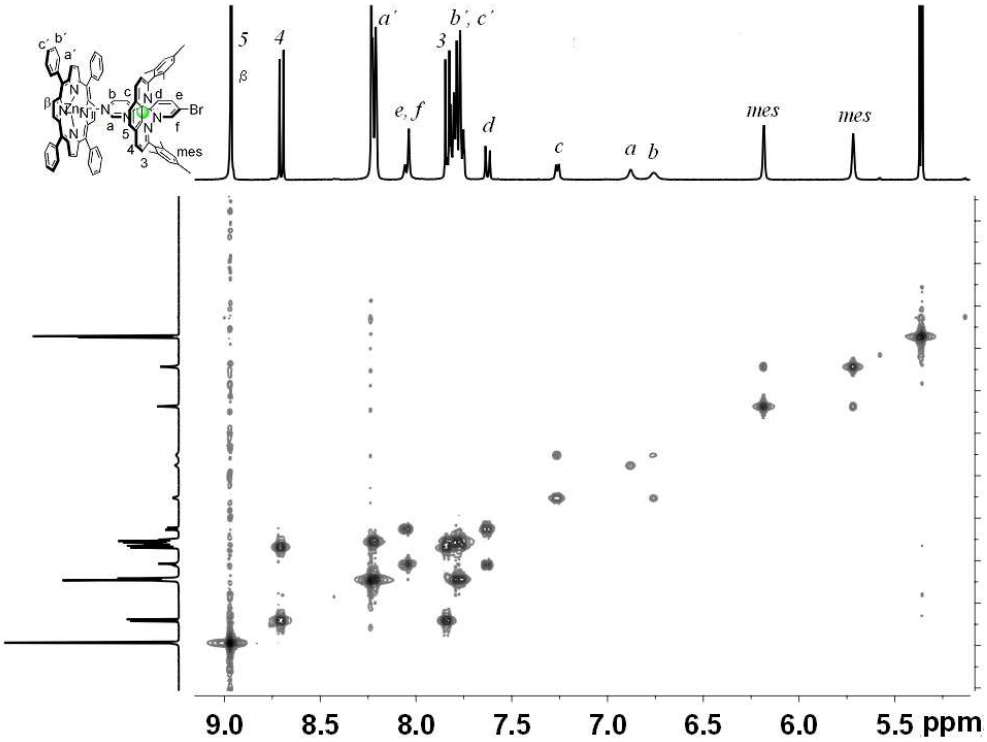

Figure S32: Partial ^{1}H-^{1}H COSY spectrum (400 MHz) of complex **16** in CD_2Cl_2 at 298 K**.**

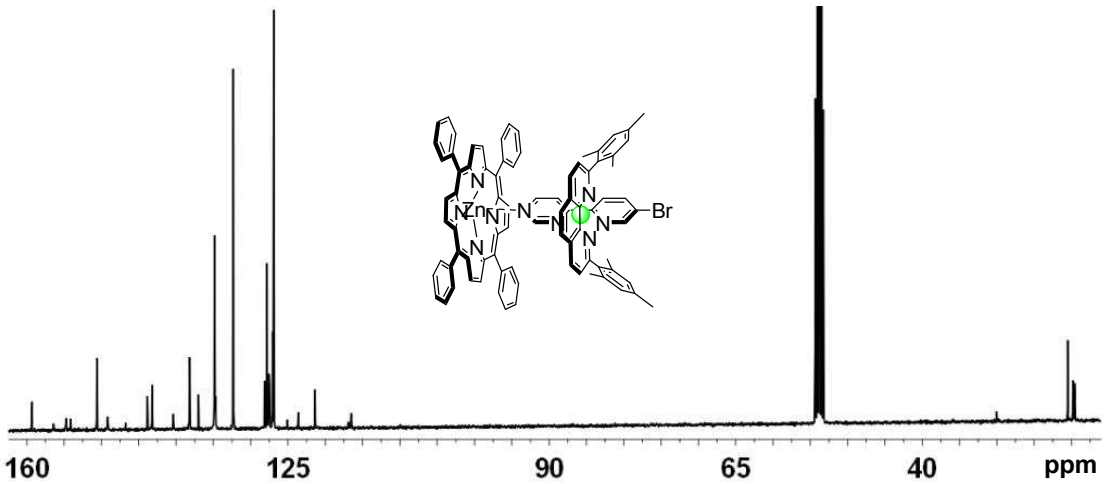

Figure S33: ^{13}C NMR spectrum (100 MHz) of complex **16** in CD_2Cl_2 at 298 K**.**

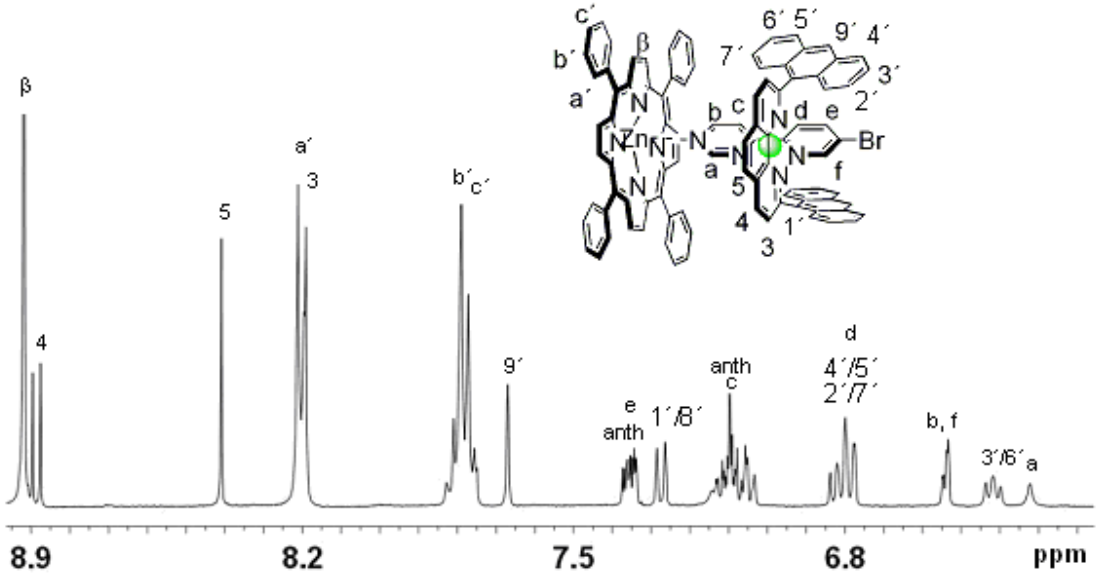

Figure S34: ^{1}H NMR spectrum (400 MHz) of complex **17** in CD_2Cl_2 at 298 K**.**

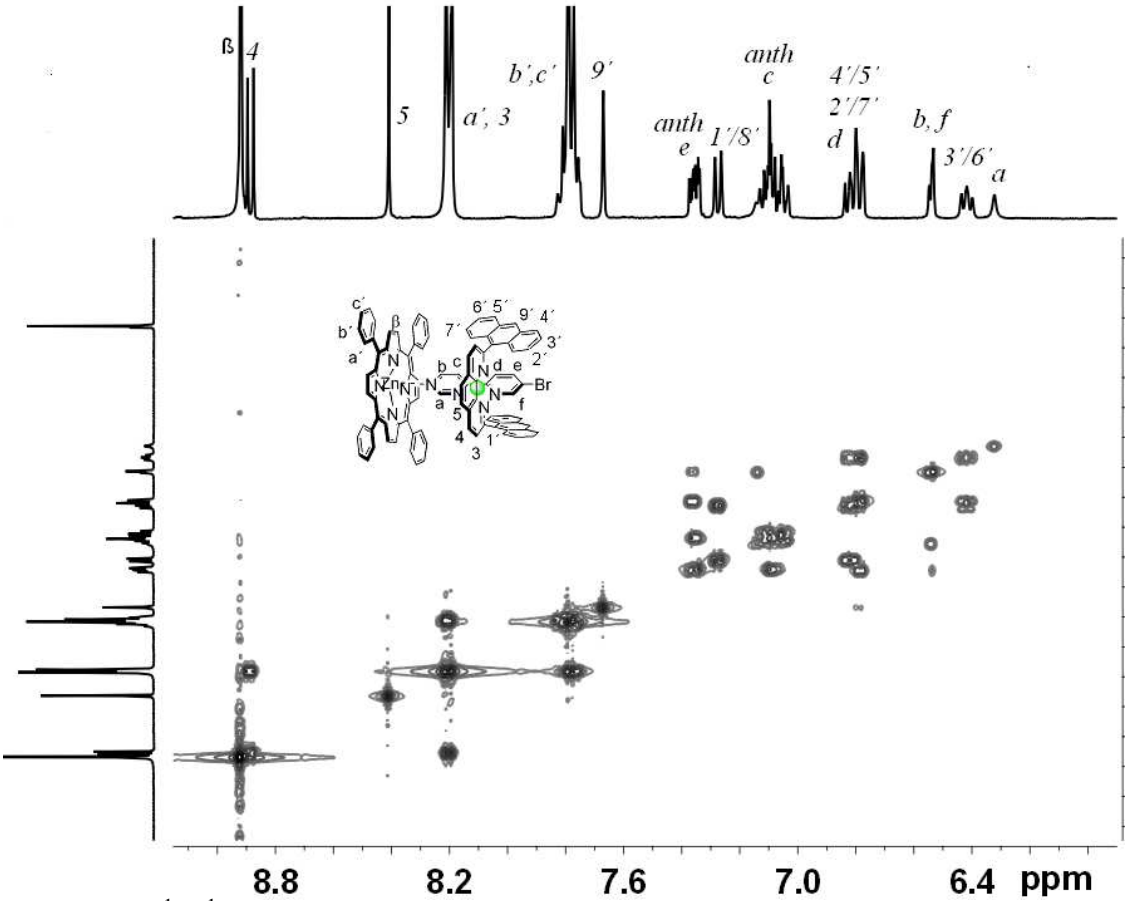

Figure S35: ^{1}H-^{1}H COSY spectrum of (400 MHz) complex **17** in CD_2Cl_2 at 298 K**.**

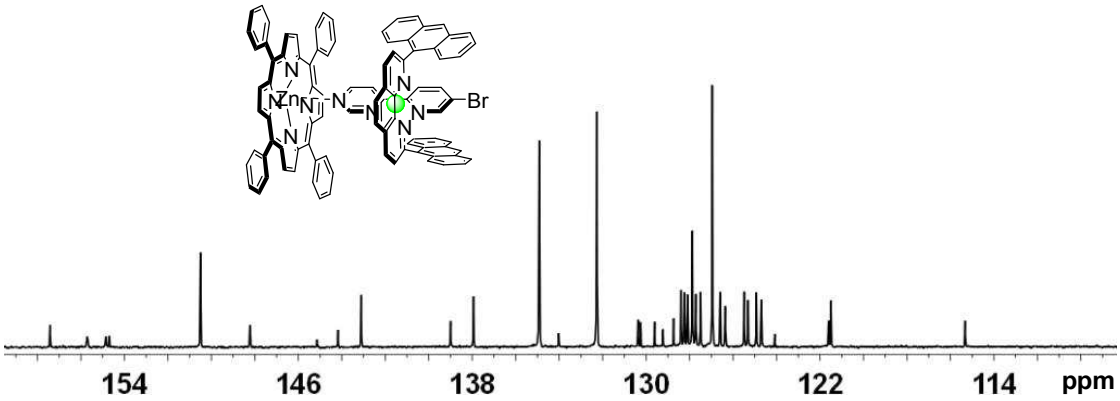

Figure S36: ^{13}C NMR spectrum (100 MHz) of complex **17** in CD_2Cl_2 at 298 K**.**

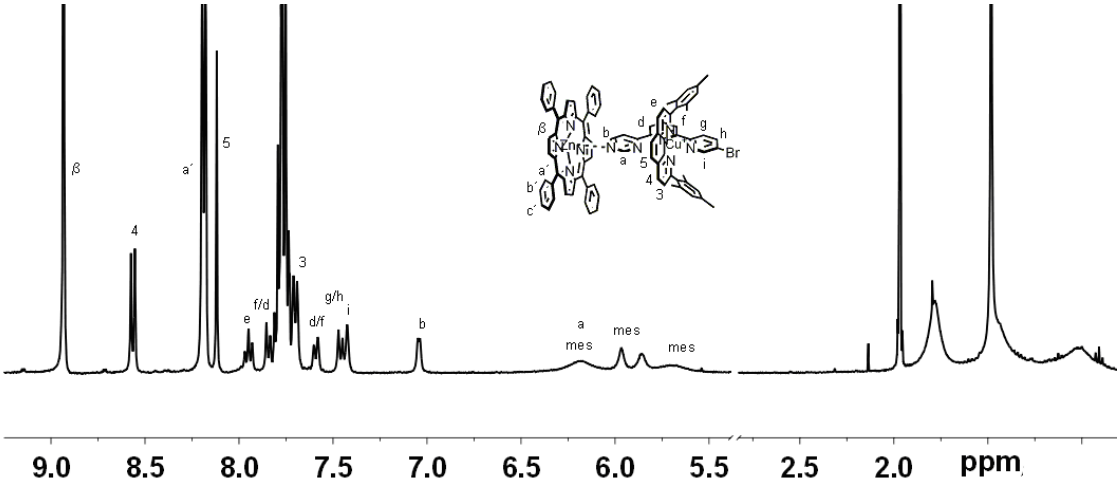

Figure S37: ^{1}H NMR spectrum (400 MHz) of complex **18** in CD_2Cl_2 at 298 K**.**

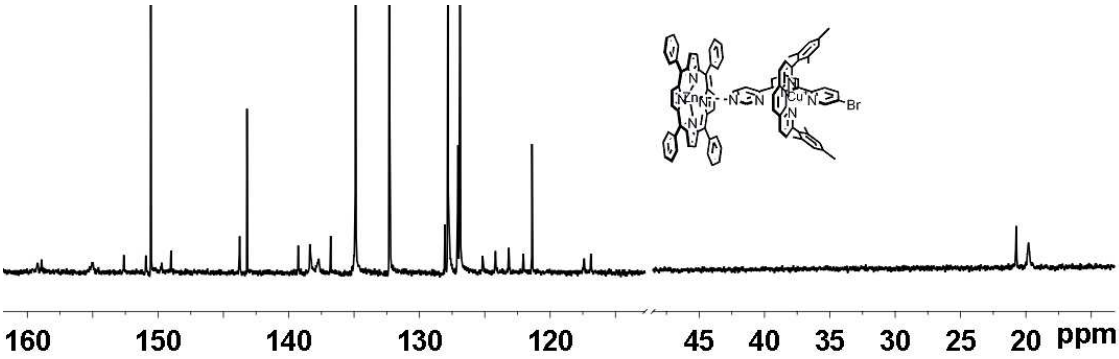

Figure S38: ^{13}C NMR spectrum (100 MHz) of complex **18** in CD_2Cl_2 at 298 K**.**

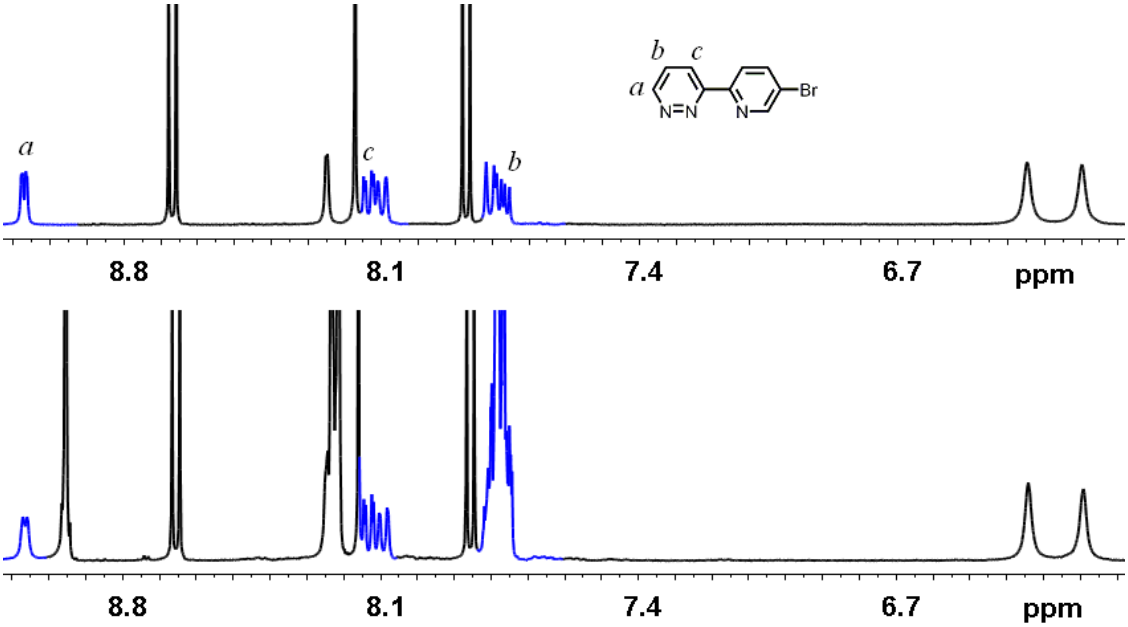

Figure S39: ^{1}H NMR spectra (400 MHz) in CD_2Cl_2 at 298 K of (top) complex **8**, and (bottom) complex **8** in presence of ZnTPP (**7**). Congruent blue coloured peaks for **1** in both spectra (see a-H and b-H) indicate that **1** is not axially coordinated to the added ZnTPP.

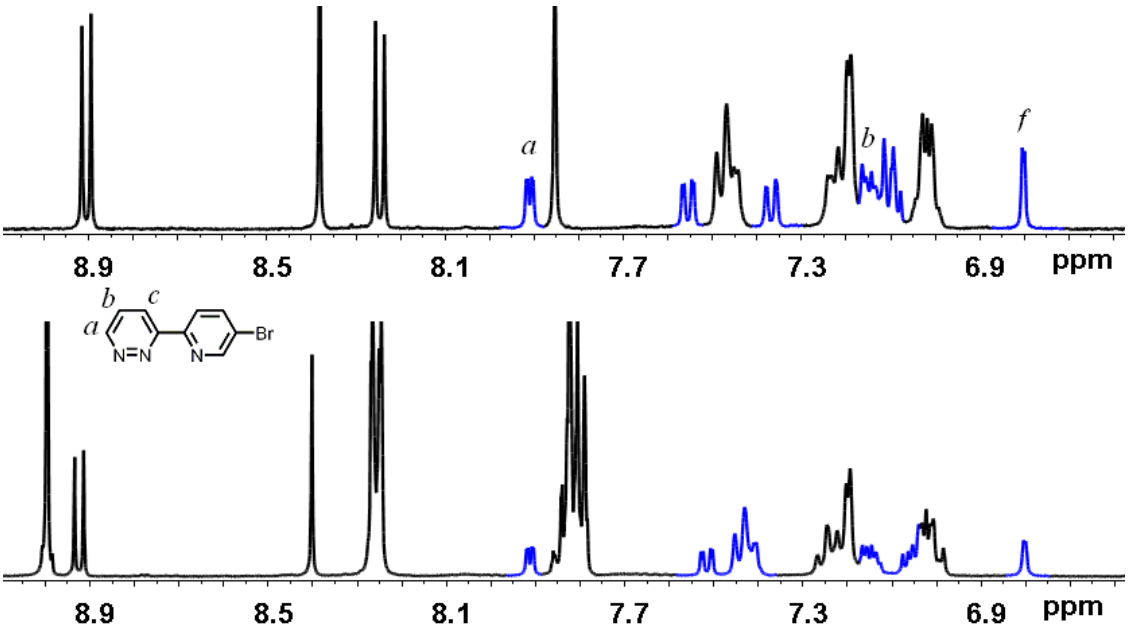

Figure S40: ^{1}H NMR spectra (400 MHz) in CD_2Cl_2 at 298 K of (top) complex **9**, and (bottom) complex **9** in presence of ZnTPP (**7**). Congruent blue coloured peaks for **1** in both spectra (see a-H and b-H) indicate that **1** is not axially coordinated to the added ZnTPP.

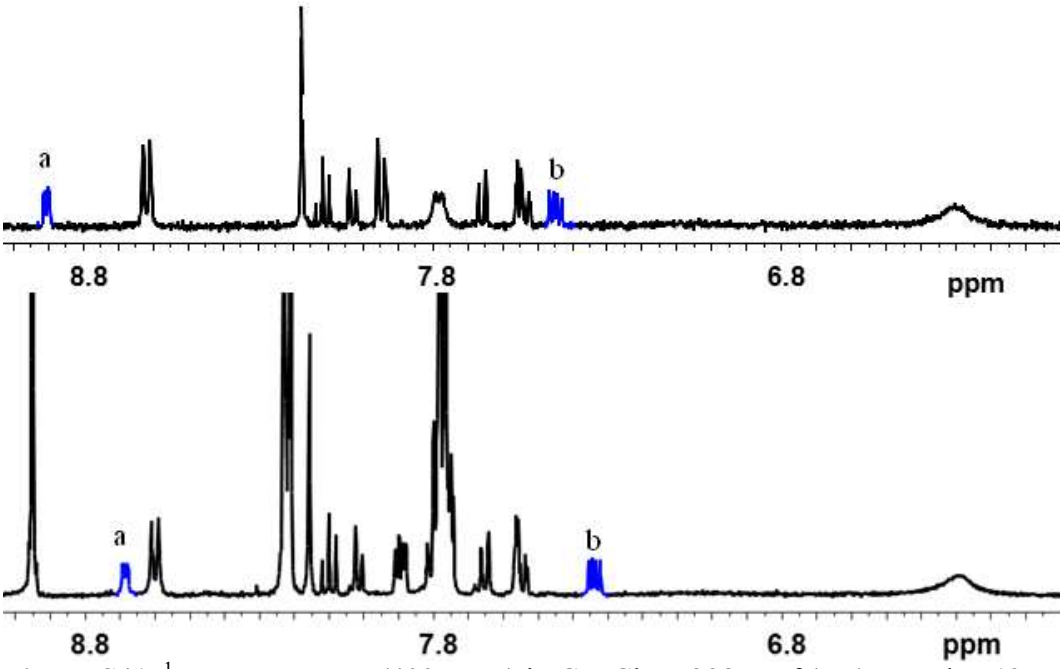

Figure S41: ^{1}H NMR spectra (400 MHz) in CD_2Cl_2 at 298 K of (top) complex **12**, and (bottom) complex **12** in presence of ZnTPP. The different shifts (blue colour) for **3** in both spectra (see a-H and b-H) indicate that **3** is axially coordinated to the added ZnTPP.

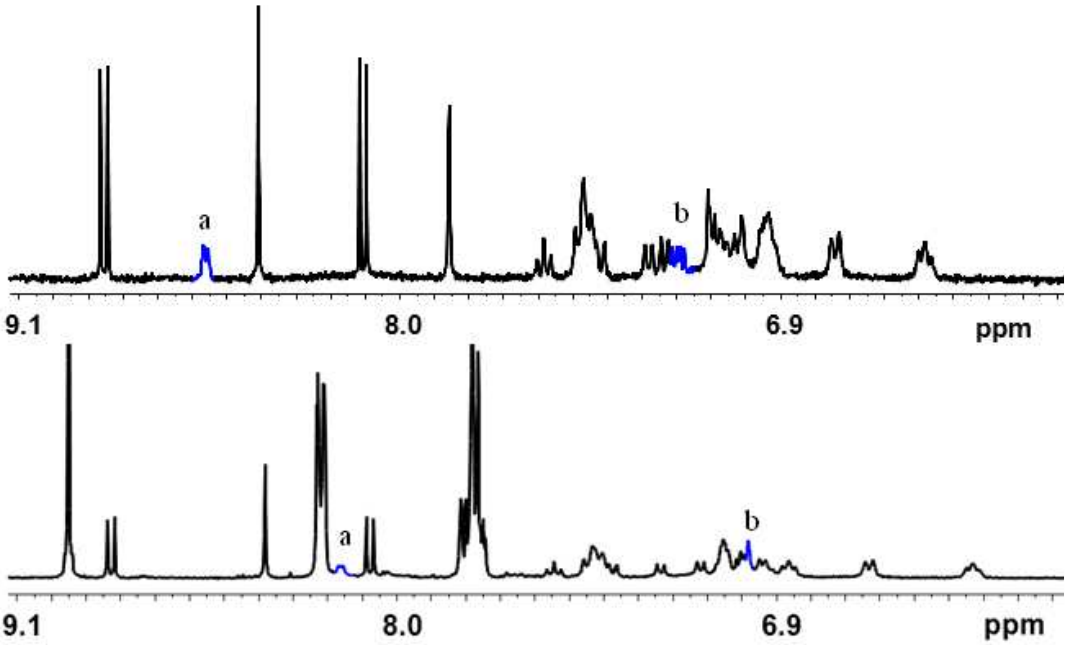

Figure S42: ^{1}H NMR spectra (400 MHz) in CD_2Cl_2 at 298 K of (top) complex **13**, and (bottom) complex **13** in presence of ZnTPP. The different shifts (blue colour) for **3** in both spectra (see a-H and b-H) indicate that **3** is axially coordinated to the added ZnTPP.

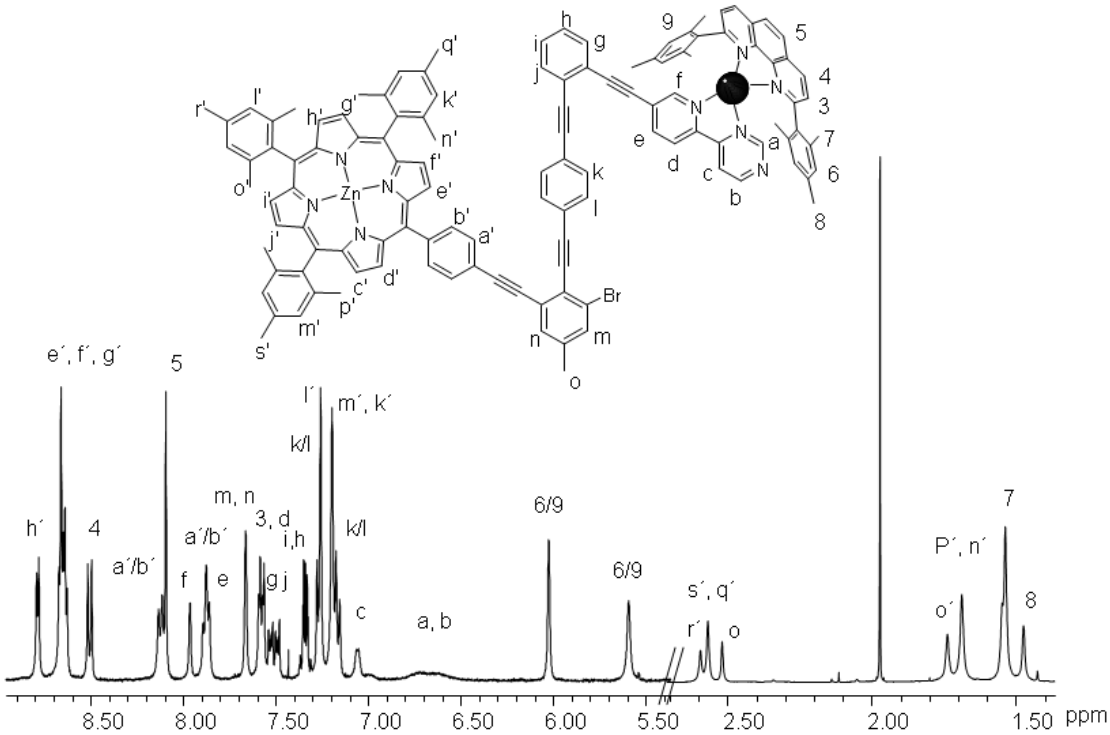

Figure S43: ^{1}H NMR spectrum (400 MHz) of complex **20** in CD_2Cl_2 at 298 K**.**

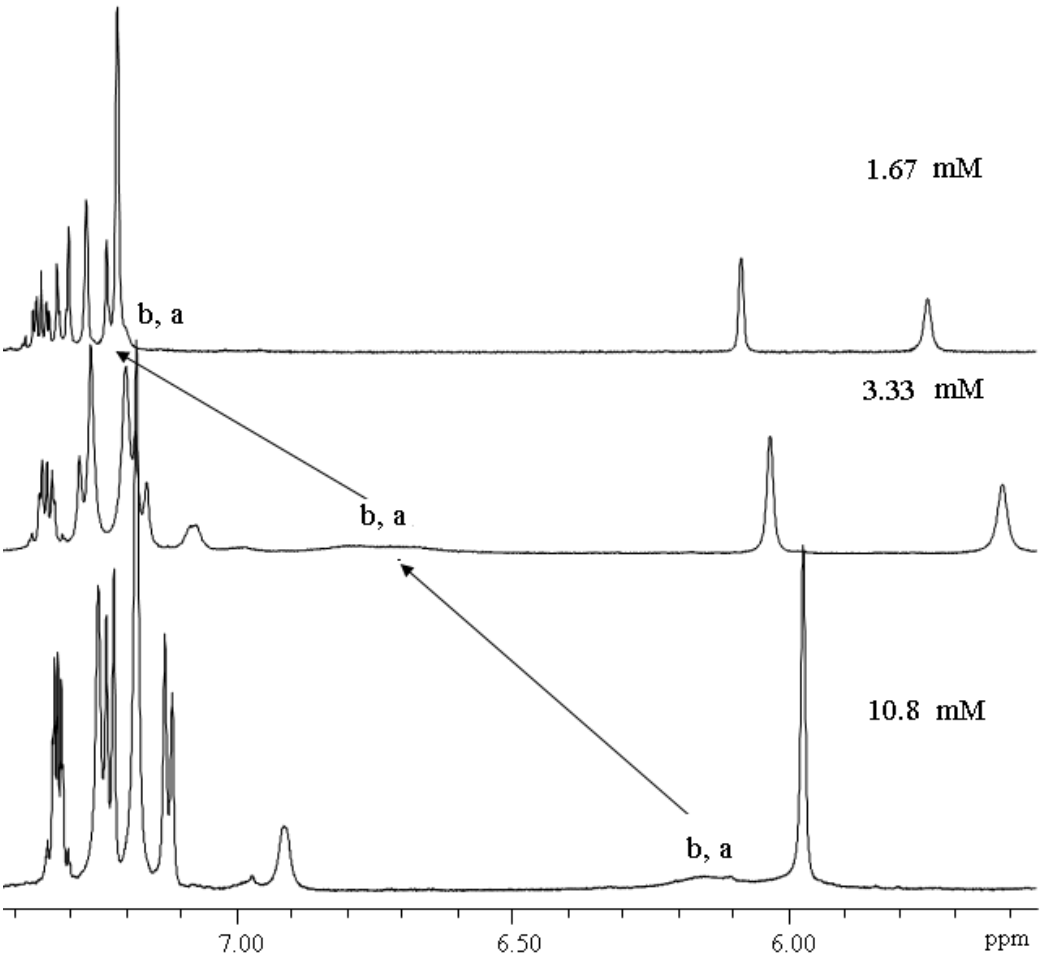

Figure S44: Concentration dependence of the ^{1}H NMR (400 MHz) shifts of protons a-H and b-H at the bipy unit in complex **20**. The downfield shift with decreasing concentration points to intermolecular coordination.

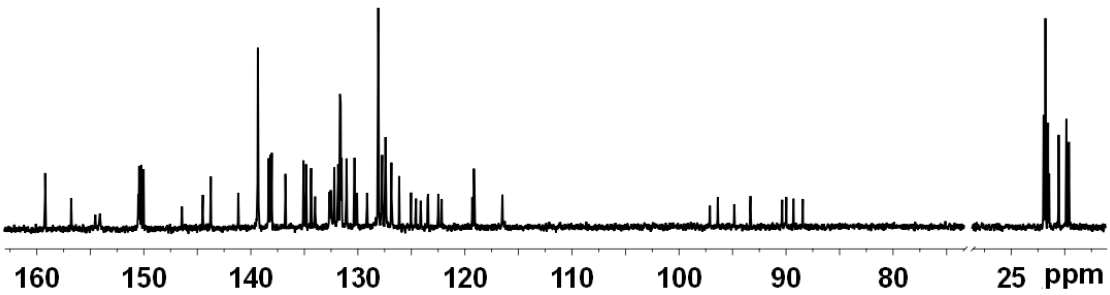

Figure S45: ^{13}C NMR spectrum (150 MHz) of unlocked complex **20** in CD_2Cl_2 at 298 K**.**

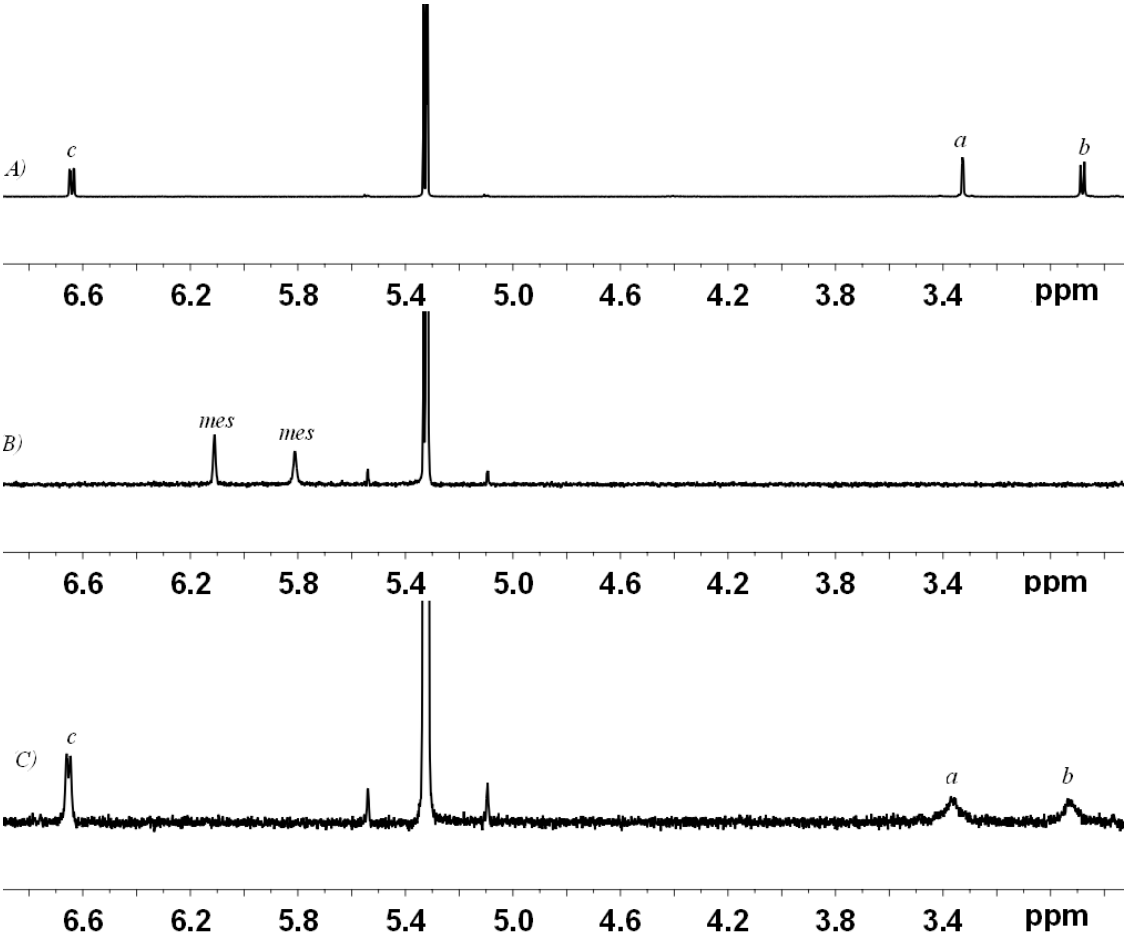

Figure S46: Partial ^{1}H NMR spectrum (400 MHz) showing reversible switching between the open and closed form. (A) Only nanoswitch **19**. (B) **19** after addition of one equivalent of [Cu(**5**)]$^{+}$. (C) After addition of one equivalent of cyclam to solution B. Only the characteristics protons a-H, b-H, and mes-H are shown.

DOSY Spectra of Complexes:

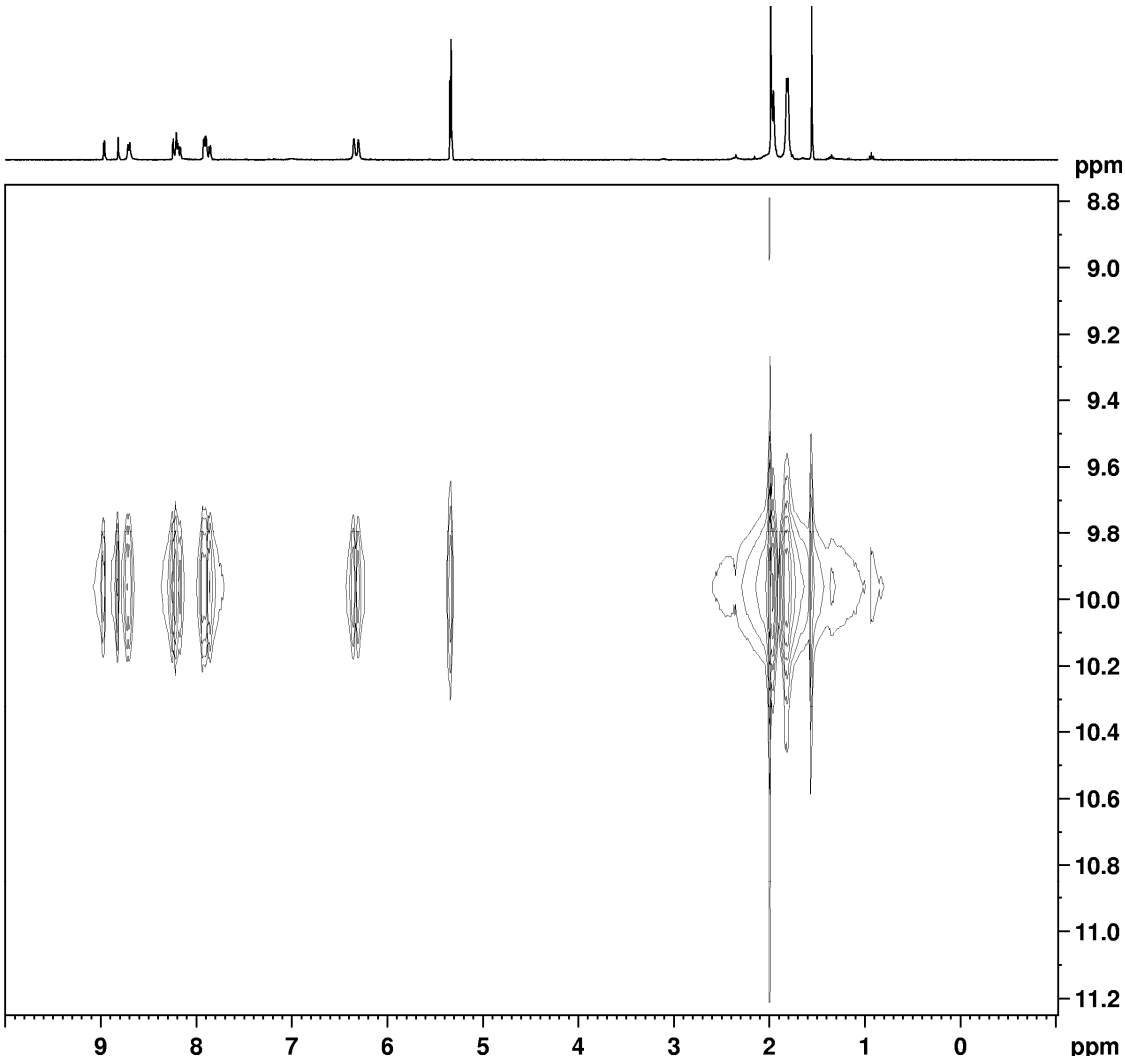

Figure S47: DOSY spectrum (400 MHz) of complex **10** at 298 K.

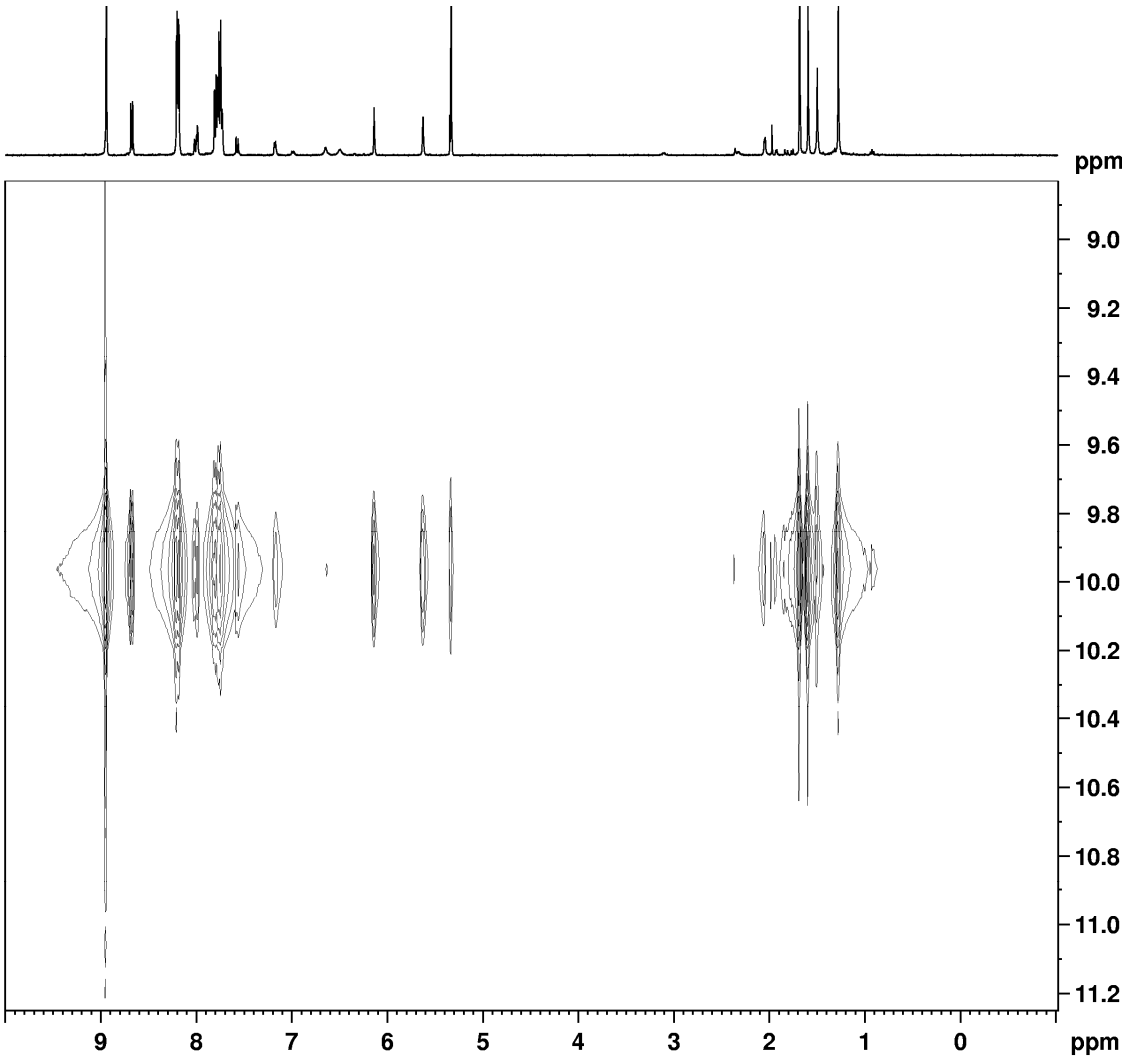

Figure S48: DOSY spectrum (400 MHz) of complex **16** at 298 K.

ESI-MS of Complexes:

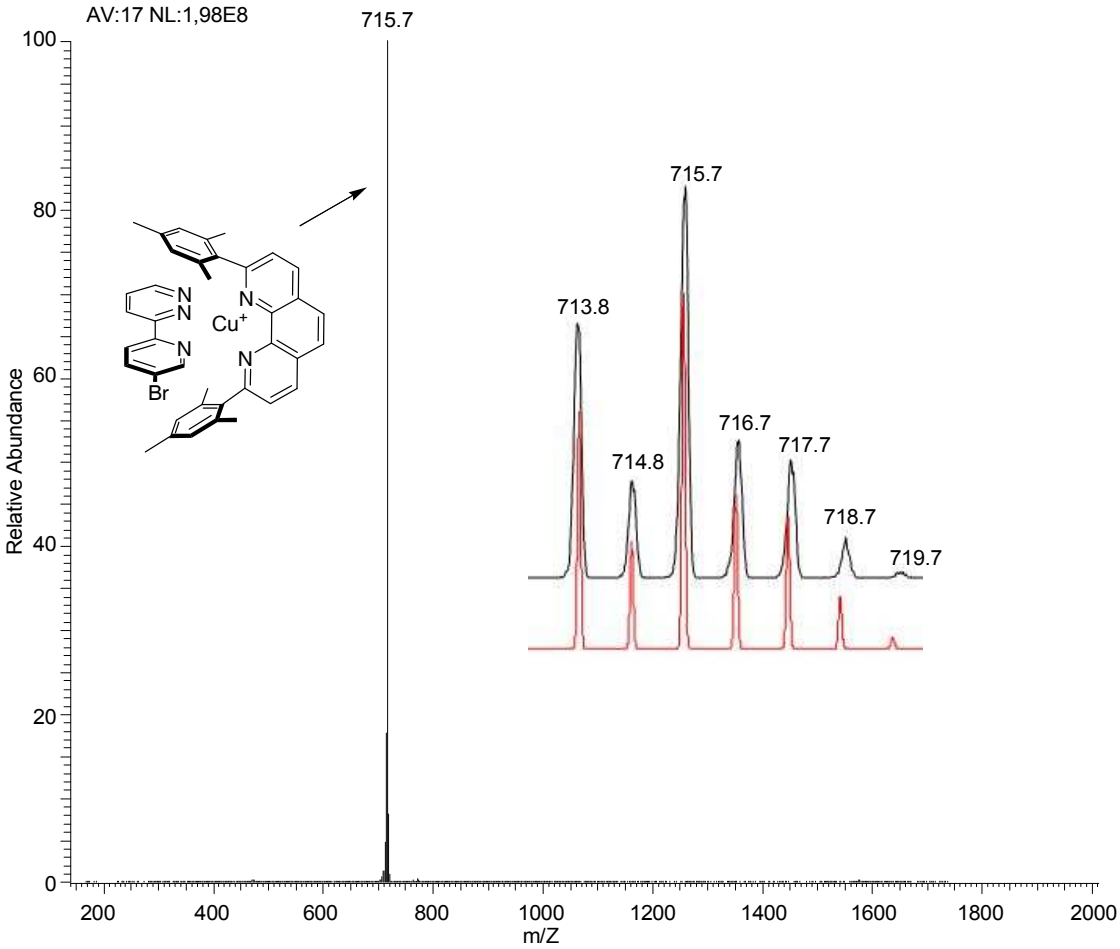

Figure S49: ESI-MS of complex **8.**

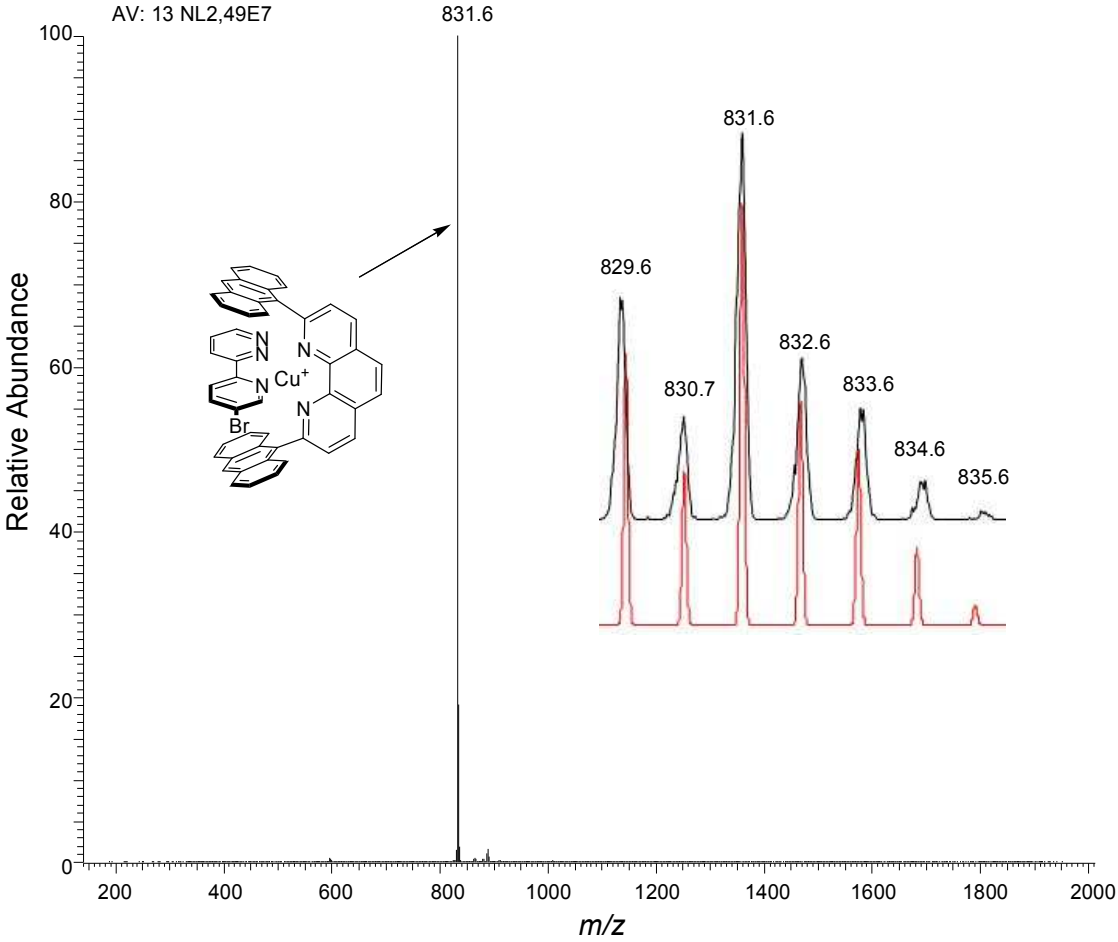

Figure S50: ESI-MS of complex **9.**

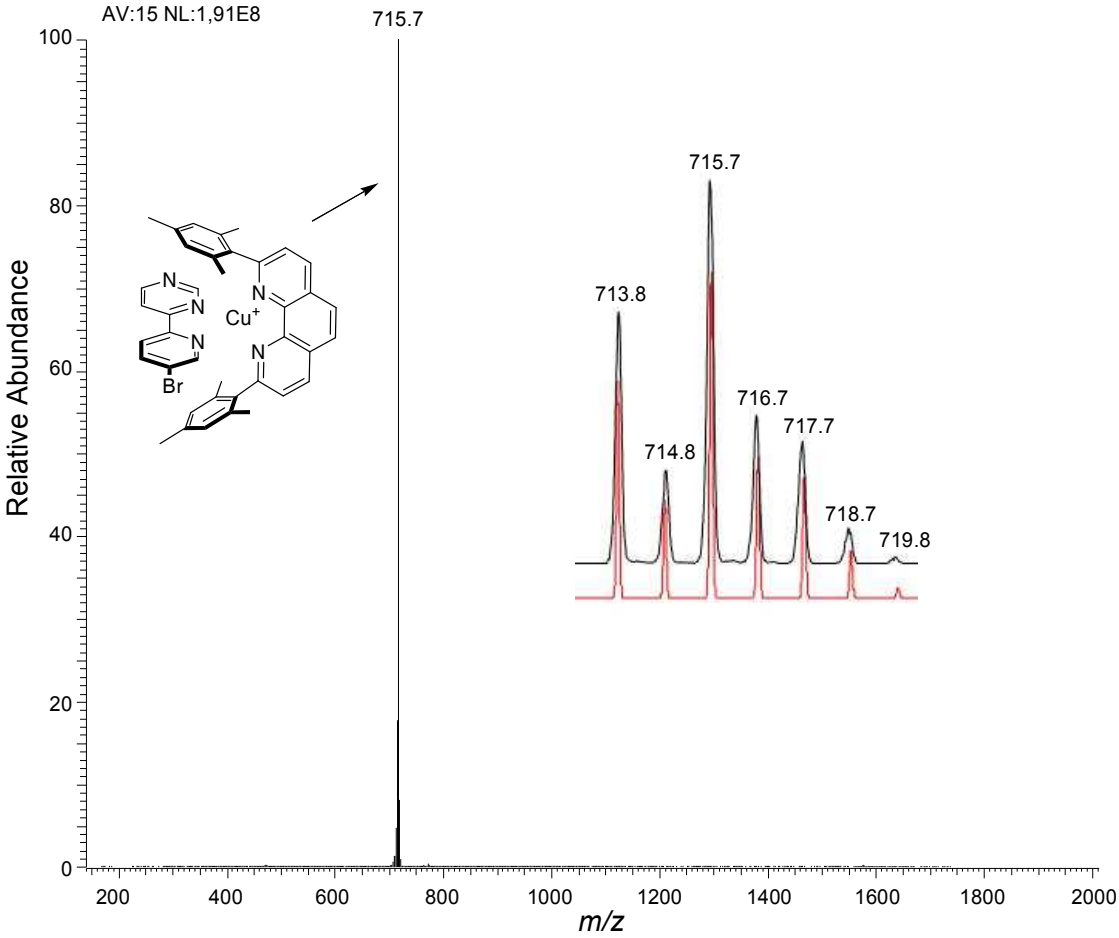

Figure S51: ESI-MS of complex **10.**

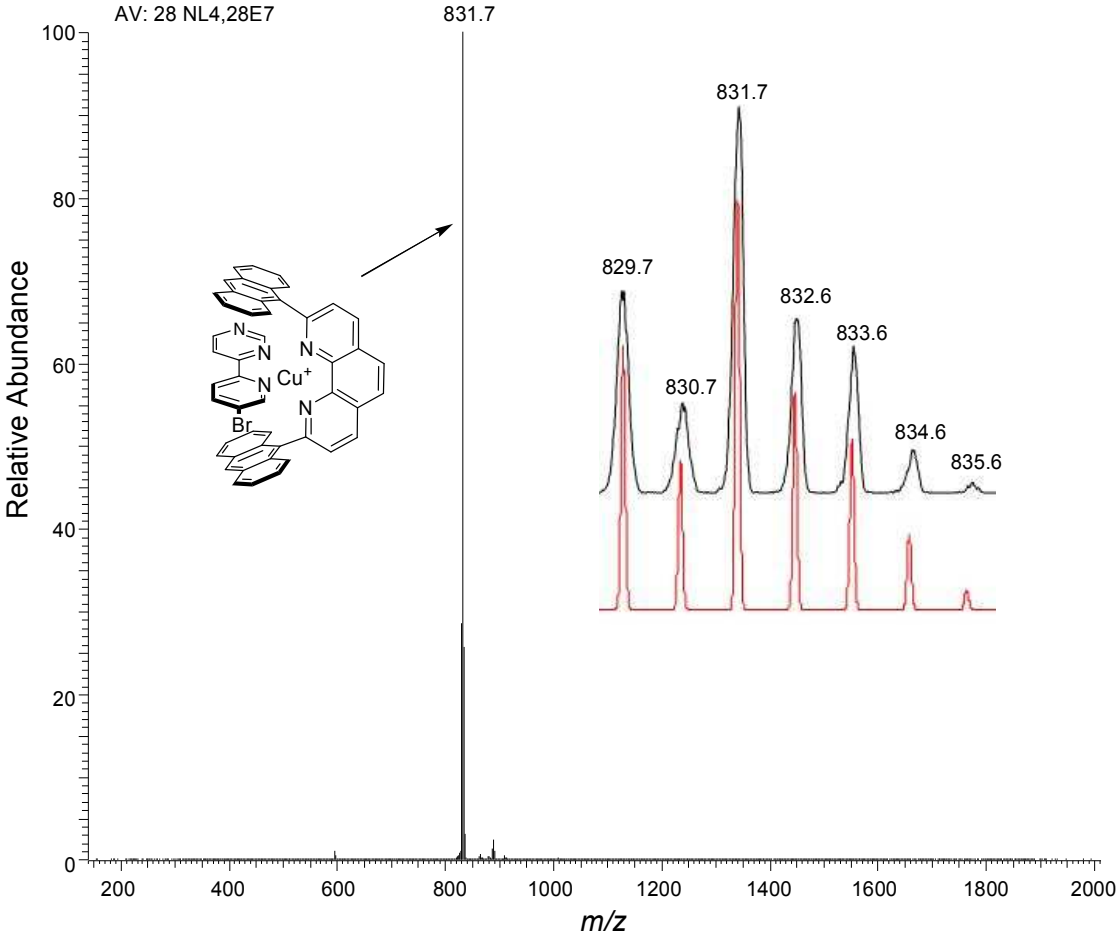

Figure S52: ESI-MS of complex **11.**

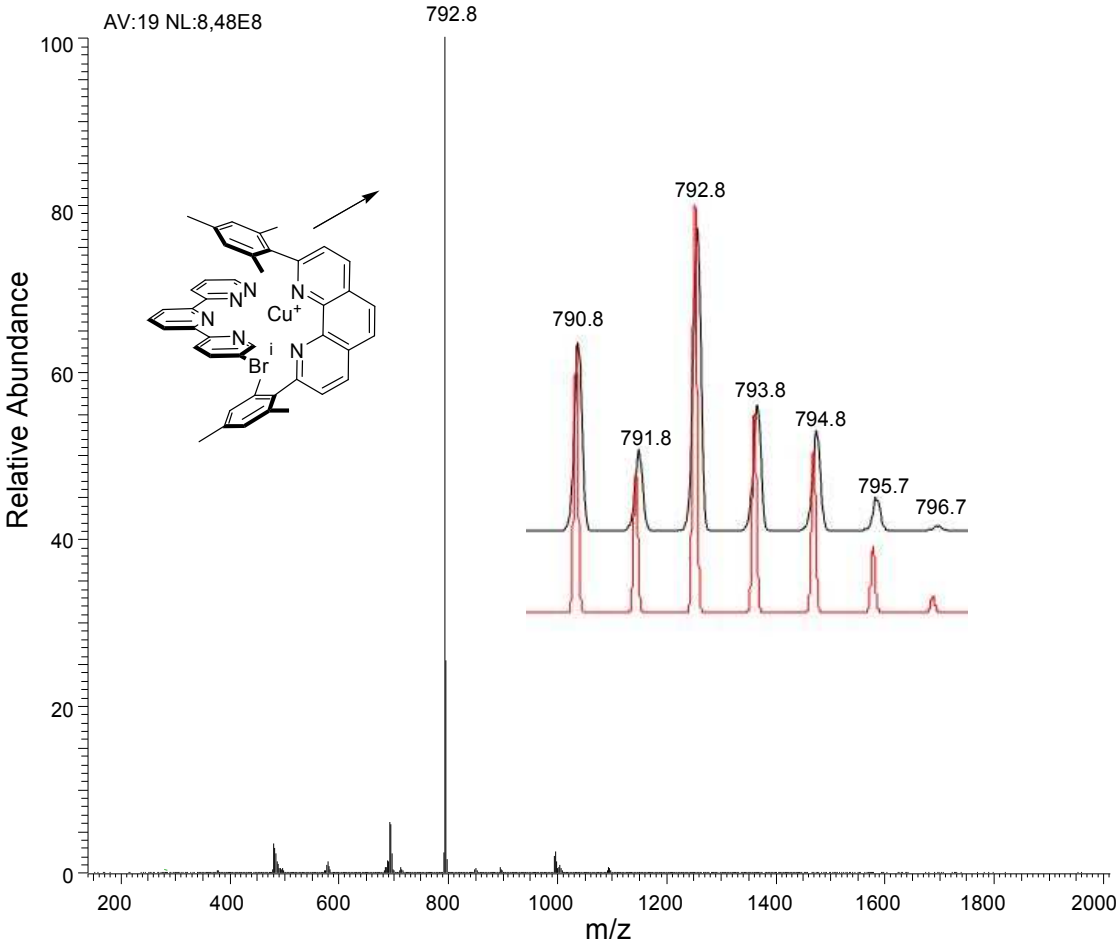

Figure S53: ESI-MS of complex **12.**

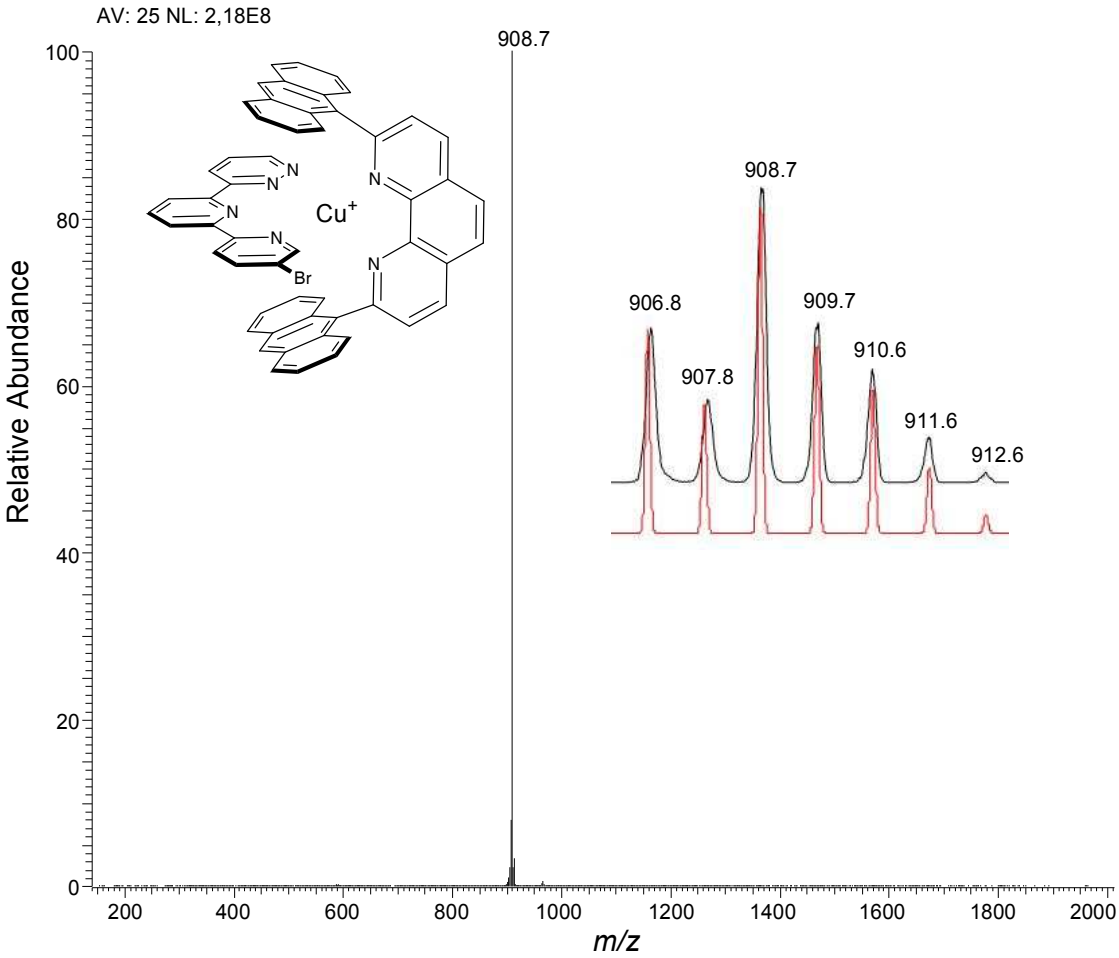

Figure S54: ESI-MS of complex **13.**

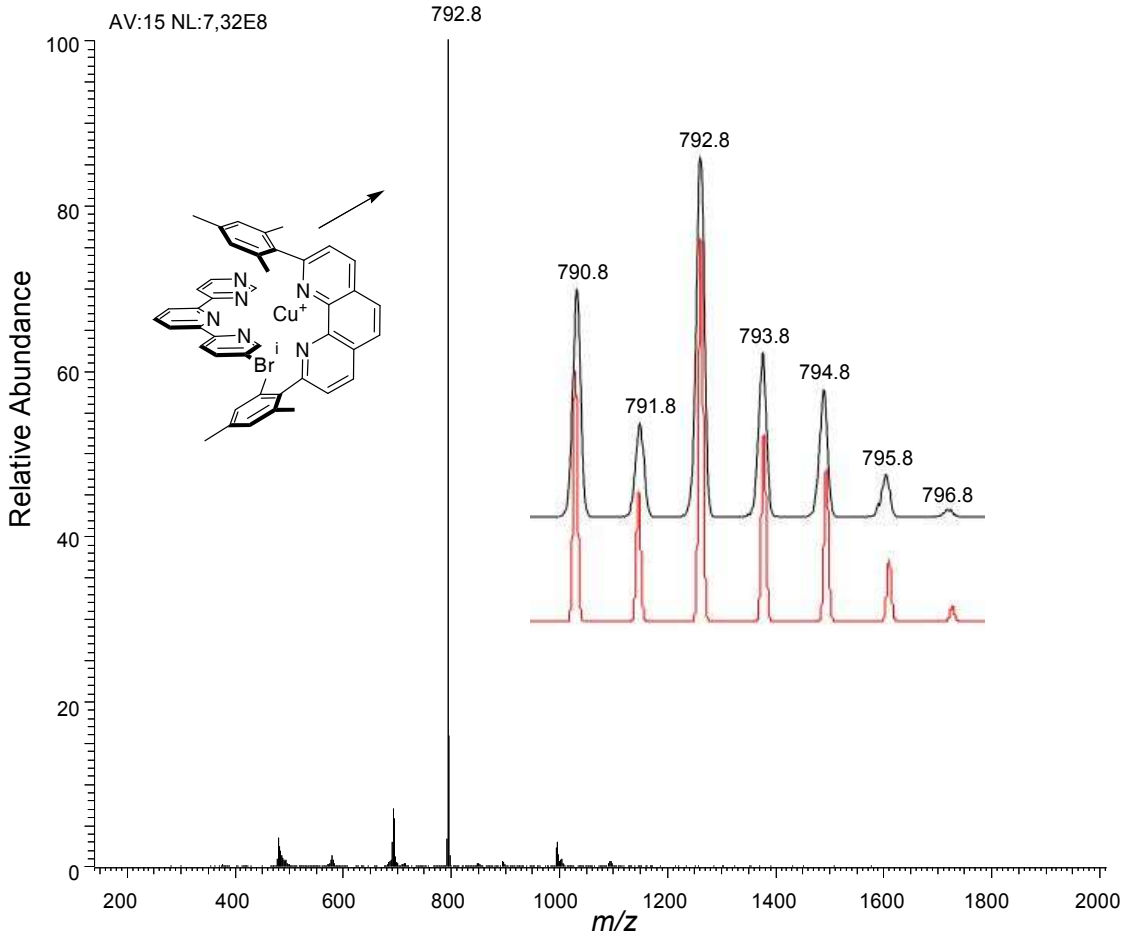

Figure S55: ESI-MS of complex **14.**

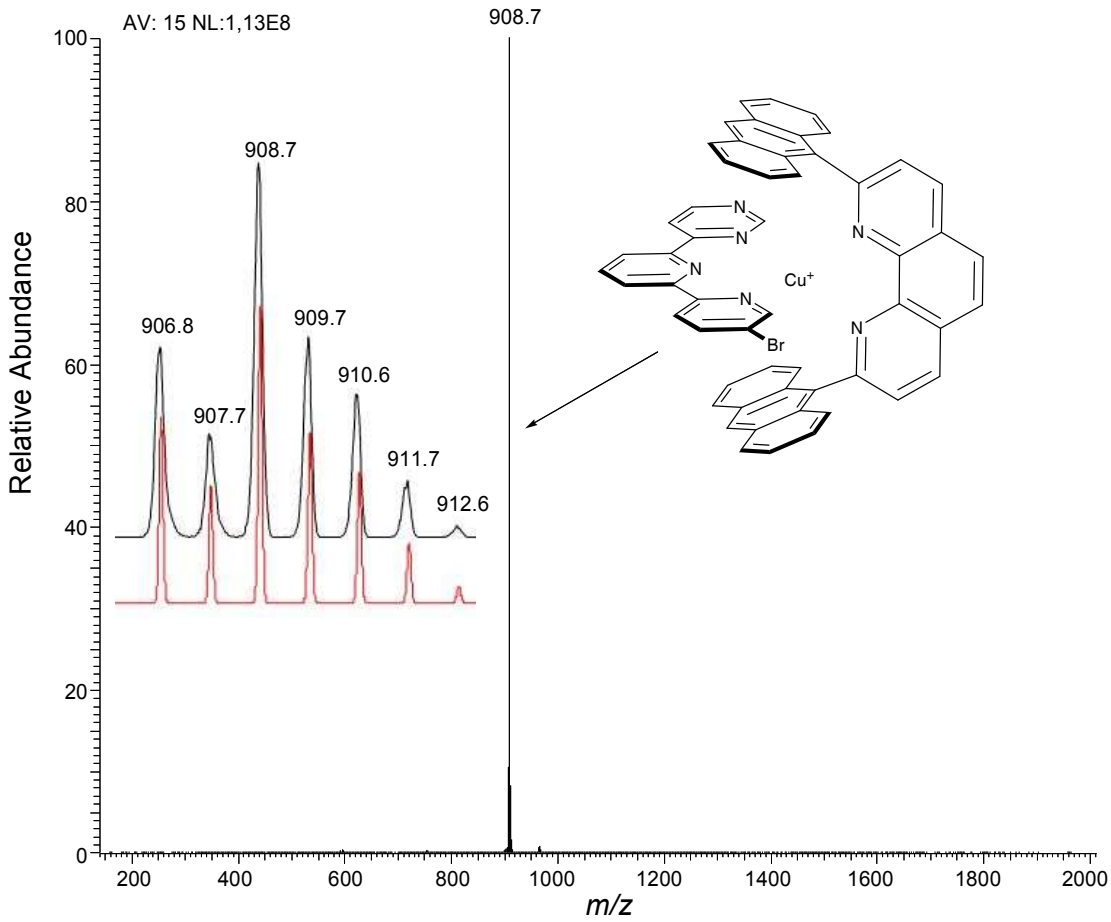

Figure S56: ESI-MS of complex **15.**