Electronic Supplementary Material (ESI) for Dalton Transactions.

# SUPPORTING INFORMATION

# Photoswitchable transition metal complexes with azobenzene-functionalized imine-based ligands: structural and kinetic analysis

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## Contents

# 1. NMR data

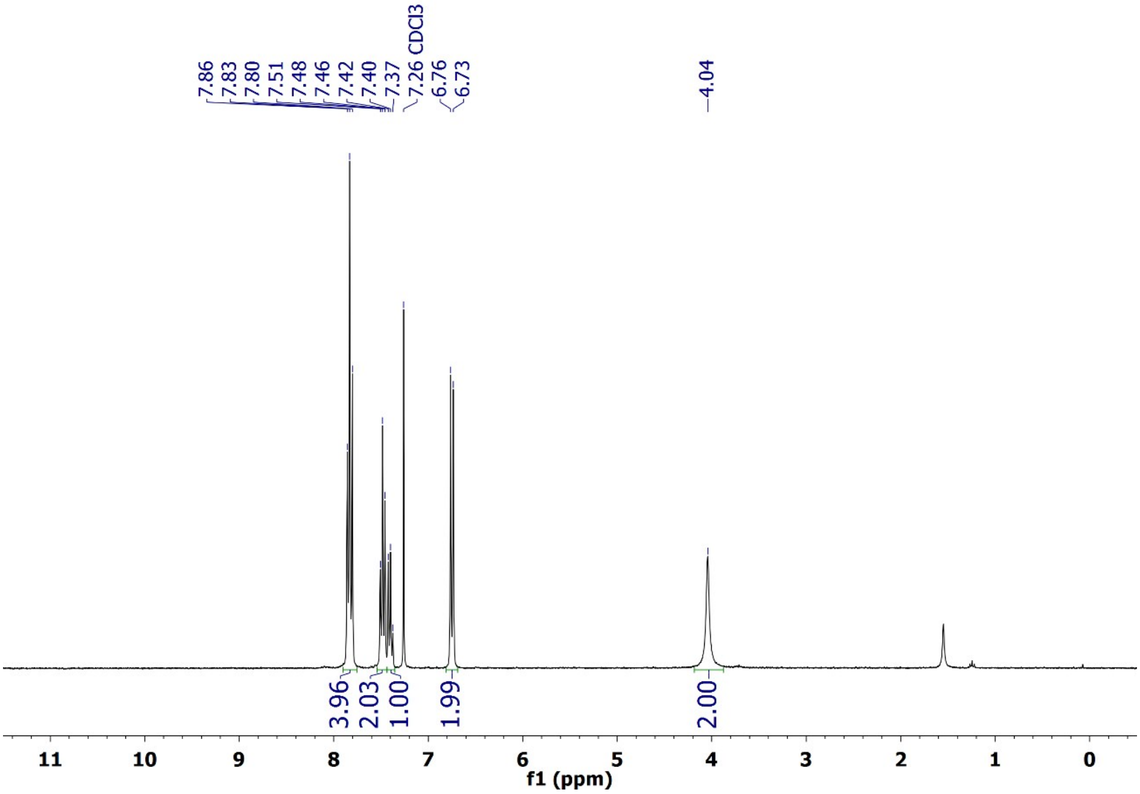

**Figure S1.** $^1$H NMR (300 MHz $CDCl_3$) spectrum of 4-aminoazobenzene.

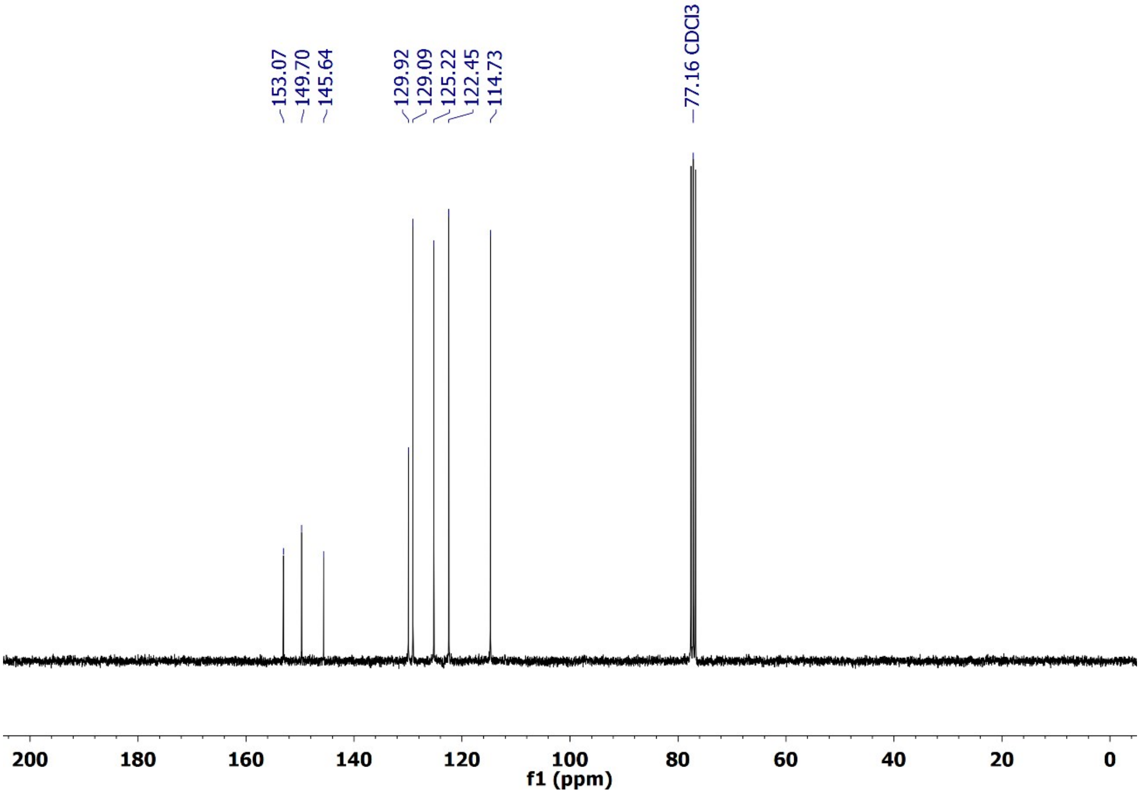

**Figure S2**. $^{13}$C NMR (75 MHz $CDCl_3$) spectrum of 4-aminoazobenzene.

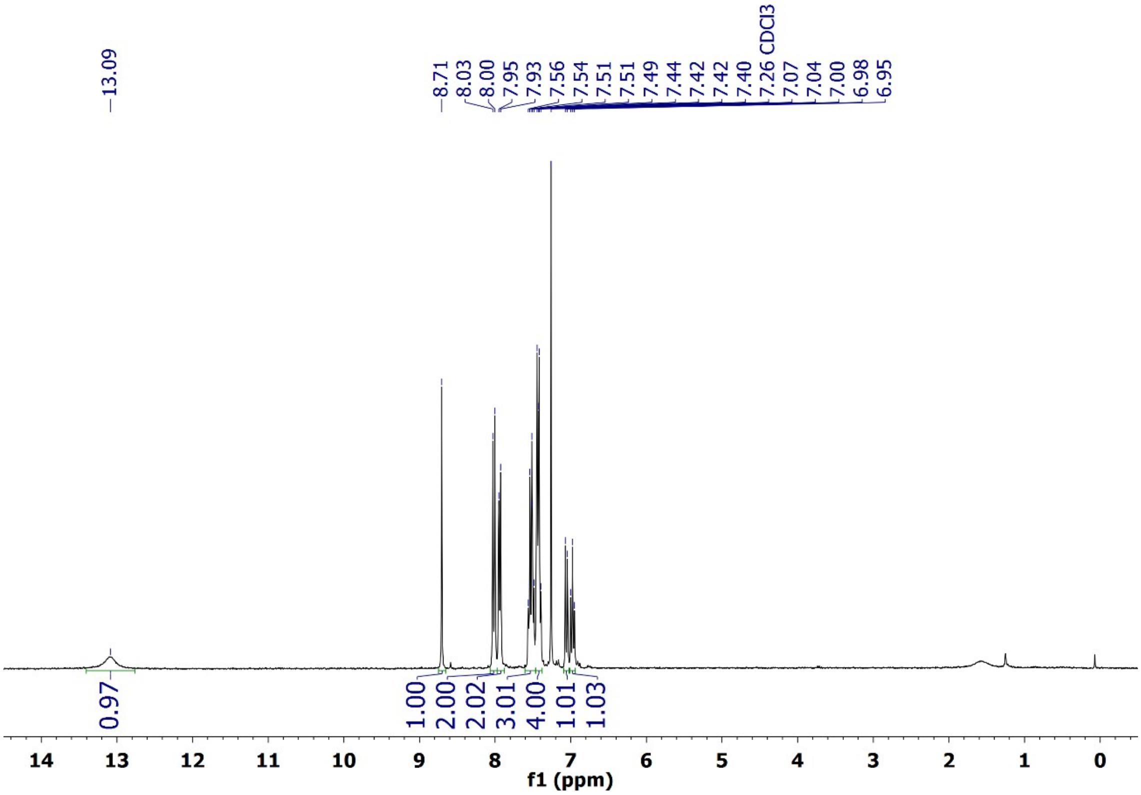

**Figure S3.** $^1$H NMR (300 MHz CDCl$_3$) spectrum of **L1**.

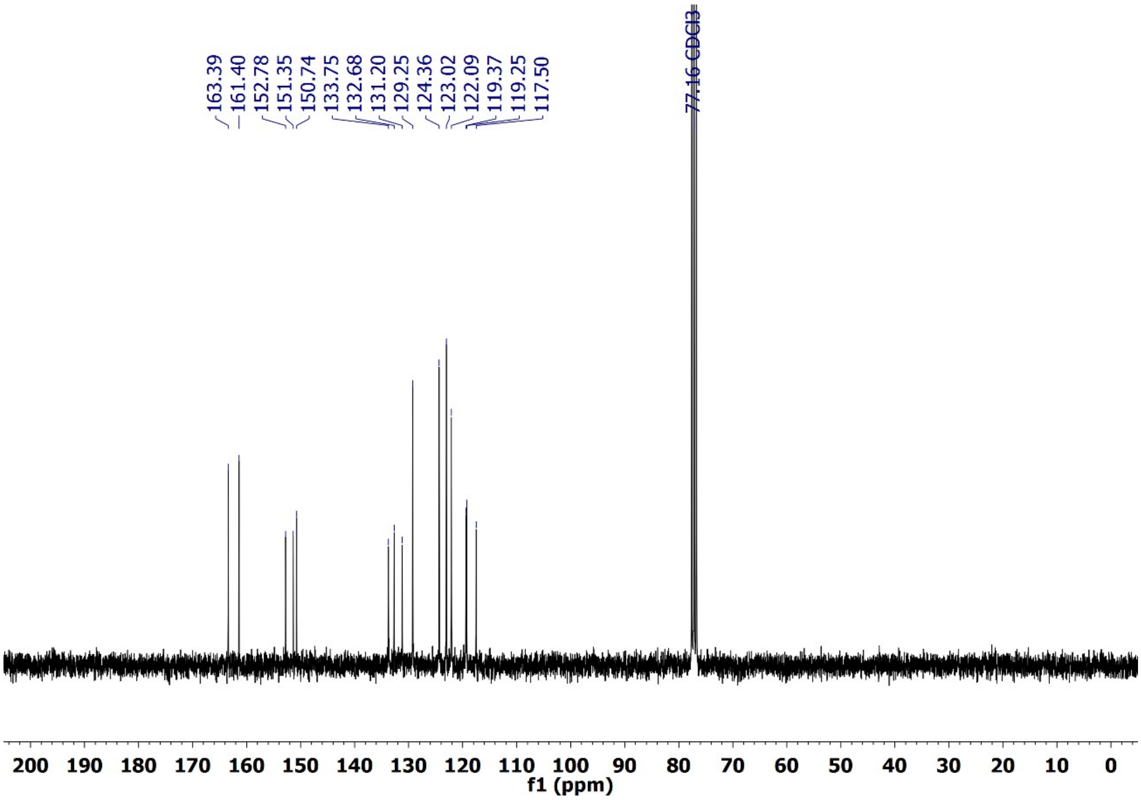

**Figure S4**. $^{13}$C NMR (75 MHz CDCl$_3$) spectrum of **L1.**

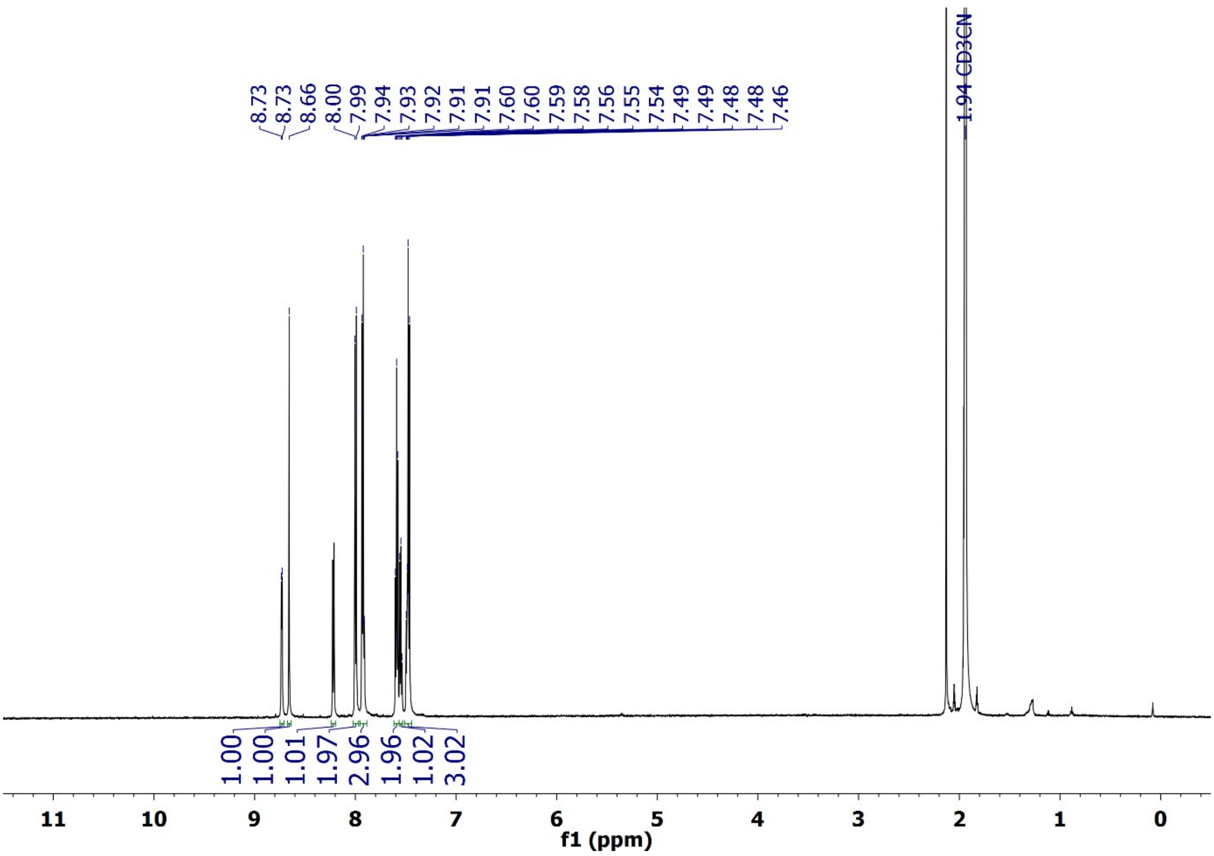

**Figure S5.** $^{1}$H NMR (600 MHz $CD_3CN$) spectrum of **L2**.

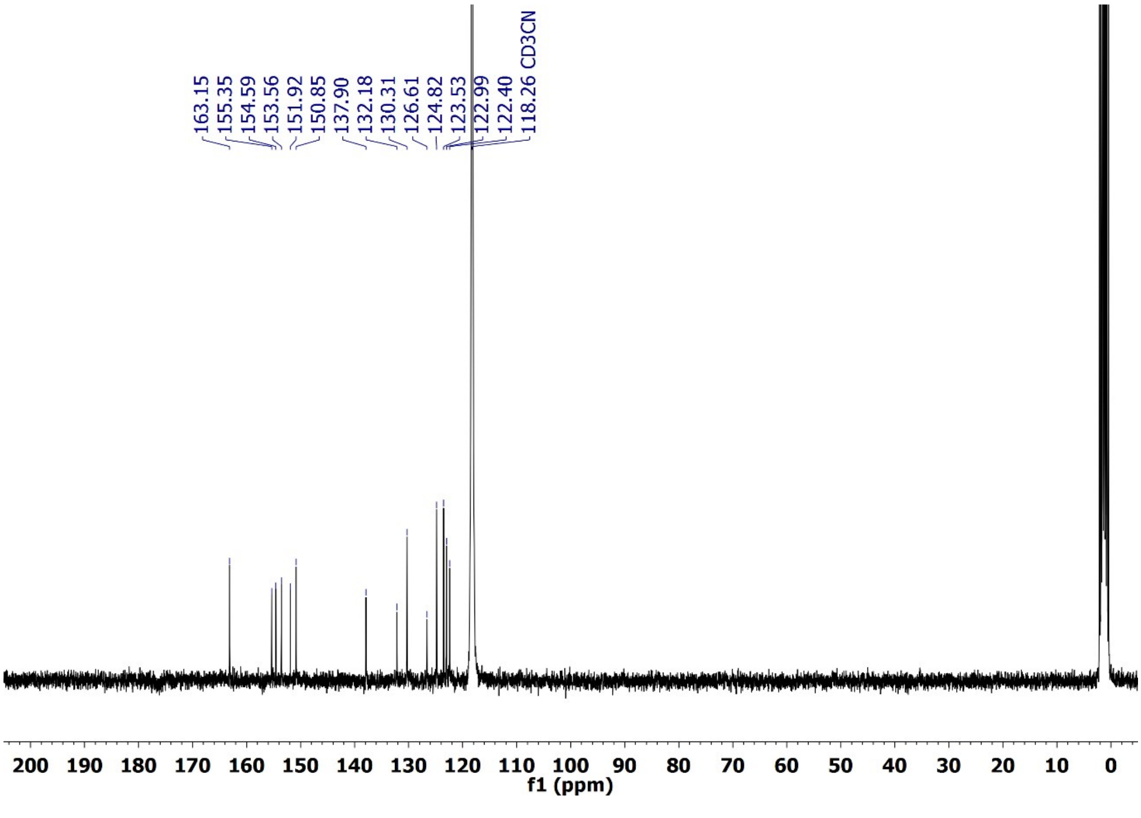

**Figure S6**. $^{13}$C NMR (75 MHz $CD_3CN$) spectrum of **L2.**

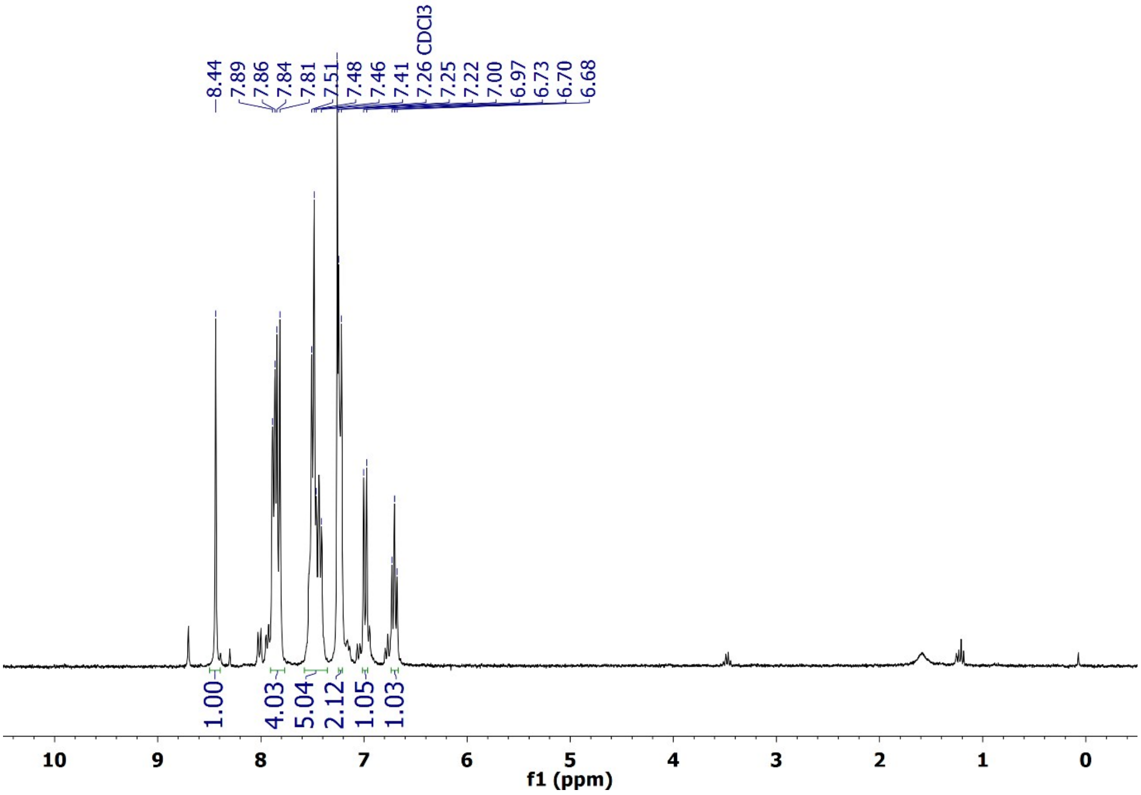

**Figure S7.** $^1$H NMR (300 MHz $CDCl_3$) spectrum of Zn(**L1**-H)$_2$.

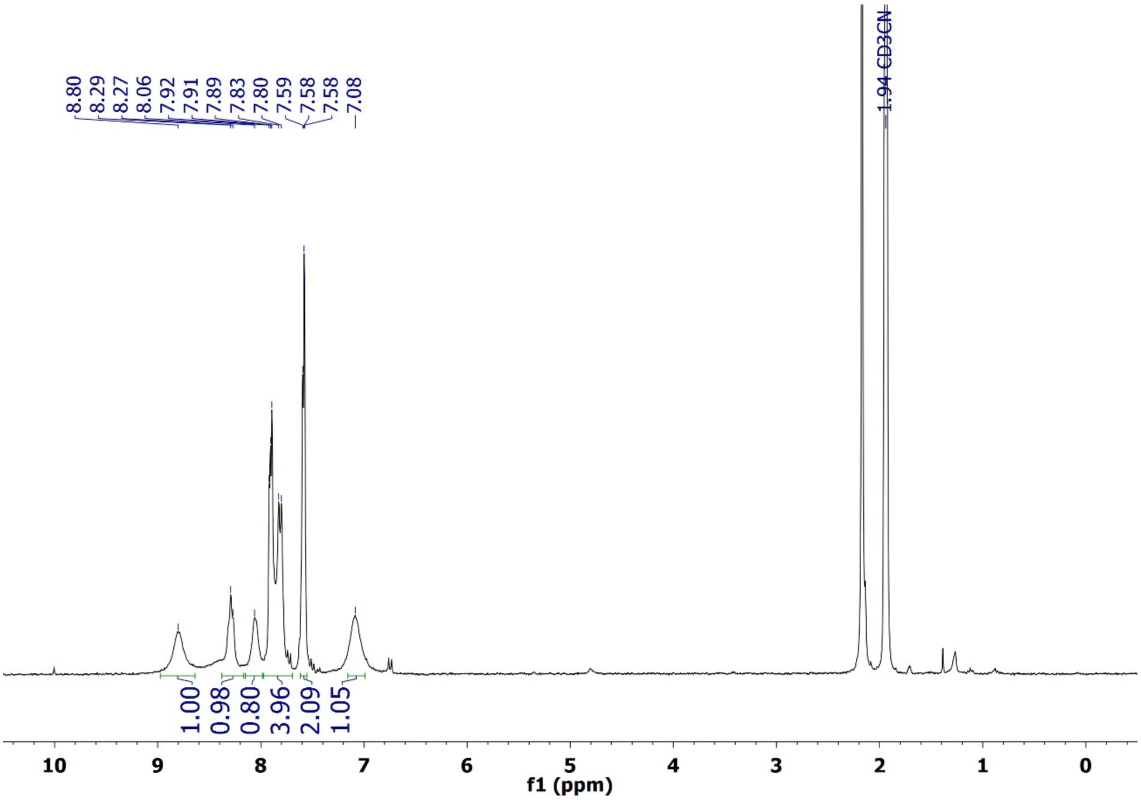

**Figure S8.** $^1$H NMR (300 MHz $CD_3CN$) spectrum of [Zn(**L2**)$_3$]($ClO_4$)$_2$.

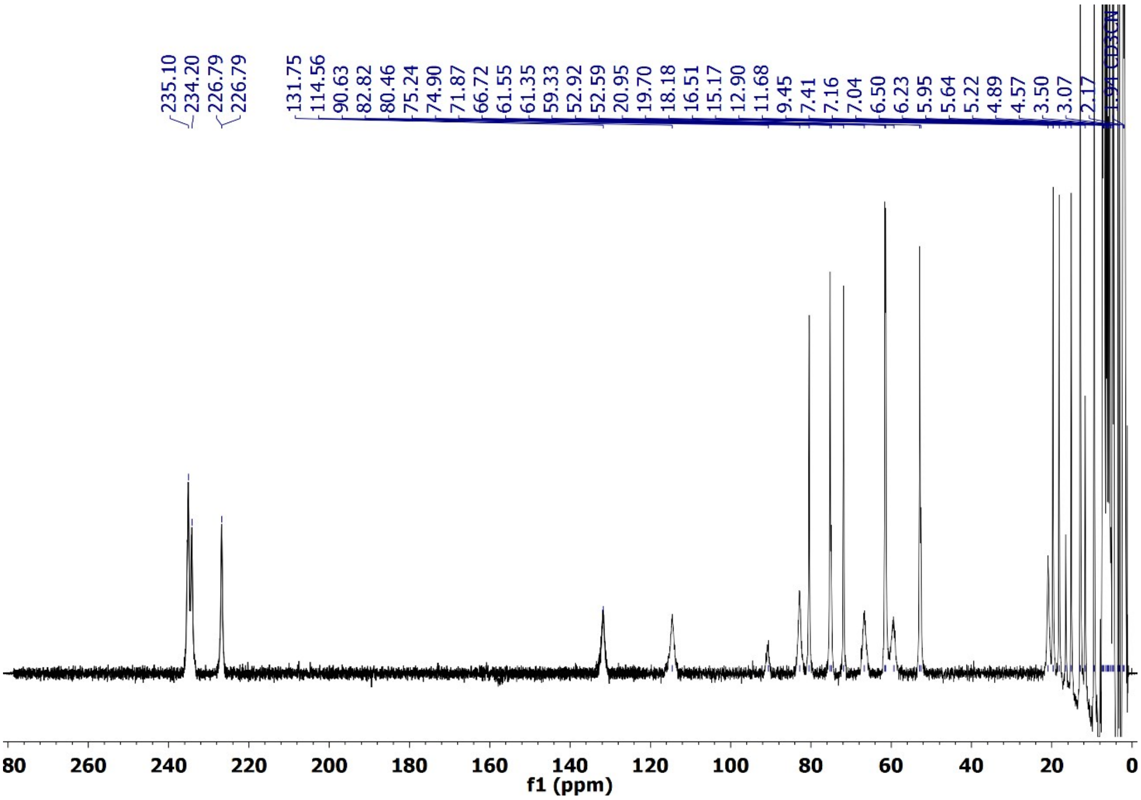

**Figure S9.** $^1$H NMR (300 MHz $CD_3CN$) spectrum of $[Co(\mathbf{L2})_3](ClO_4)_2$.

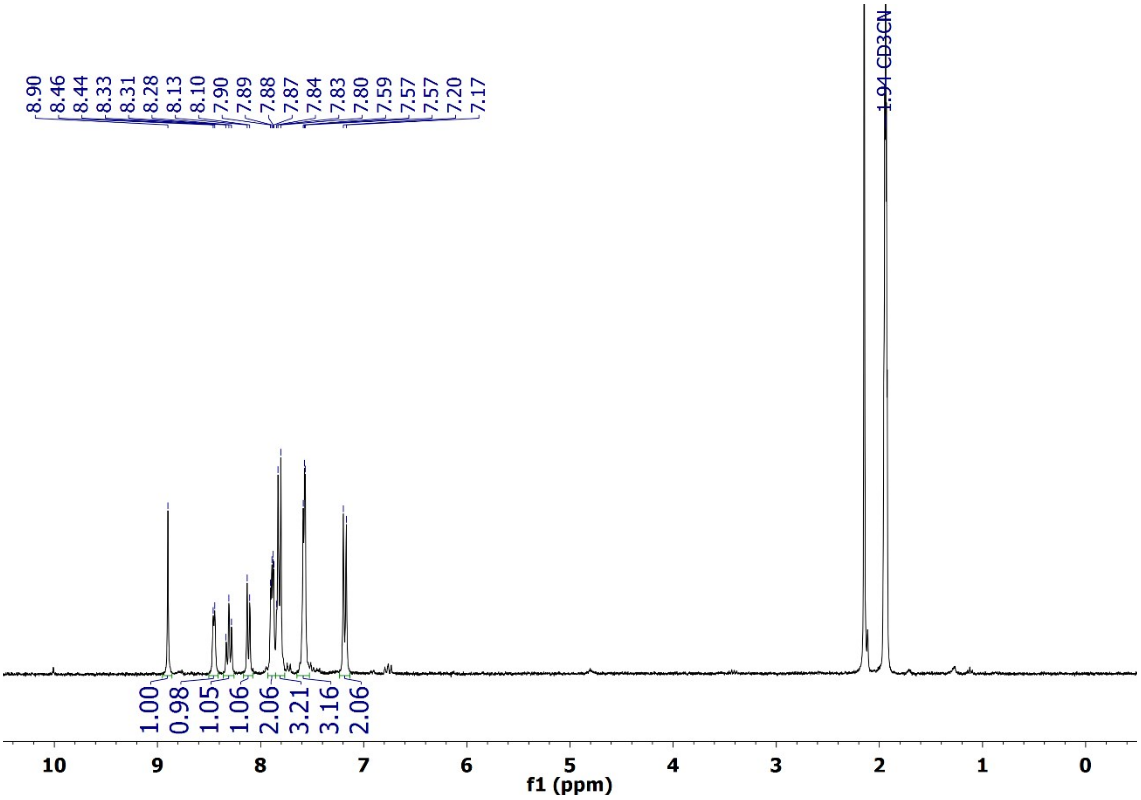

**Figure S10.** $^1$H NMR (300 MHz $CD_3CN$) spectrum of $[Cd(\mathbf{L2})_3](ClO_4)_2$.

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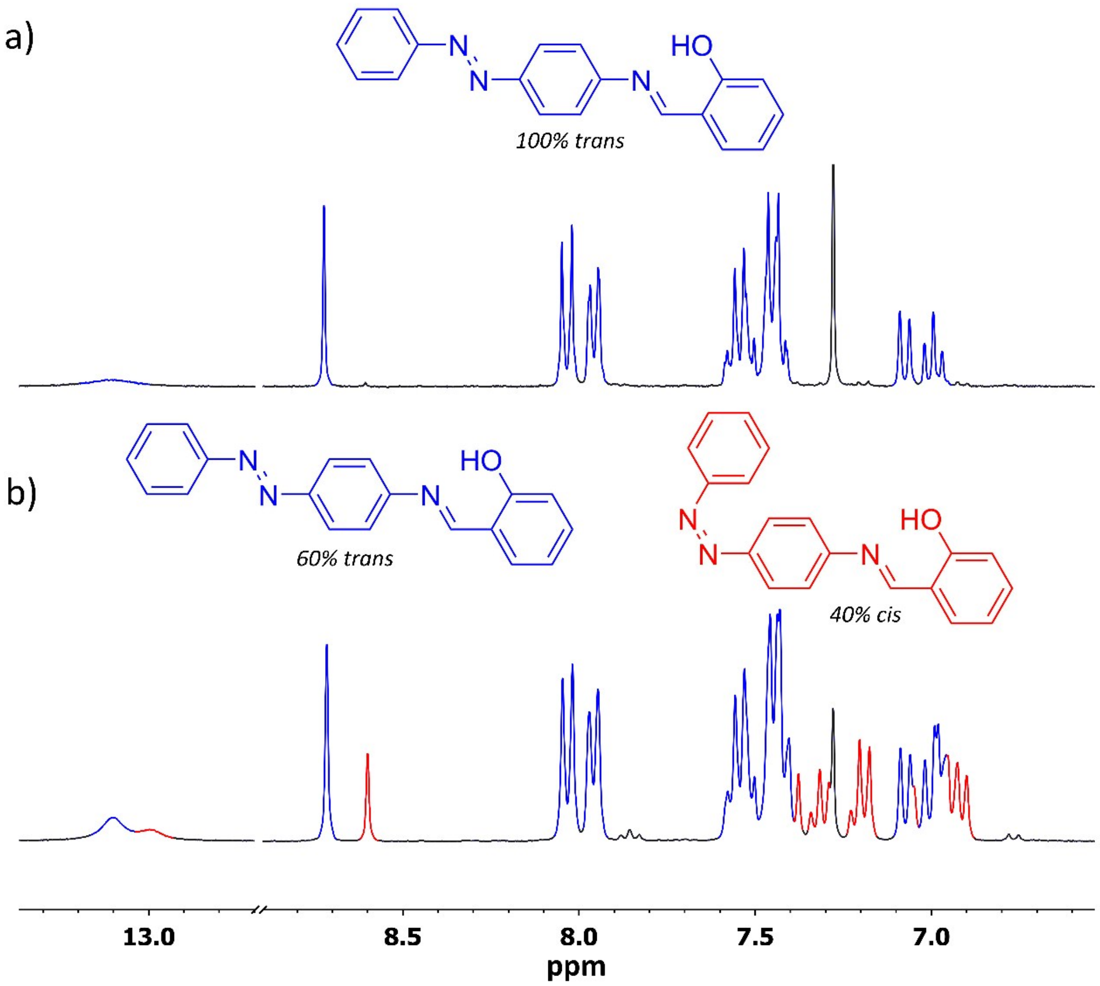

**Figure S11**. $^1$H NMR (300 MHz $CDCl_3$) spectra of **L1** ligand. a) before irradiation (100% *trans*- blue signals) b) after irradiation with UV (365 nm). (PSS at 40% of *cis* isomer-red signals). Inside: structures of L1 in *trans* and *cis* forms.

# 2. ESI-MS data

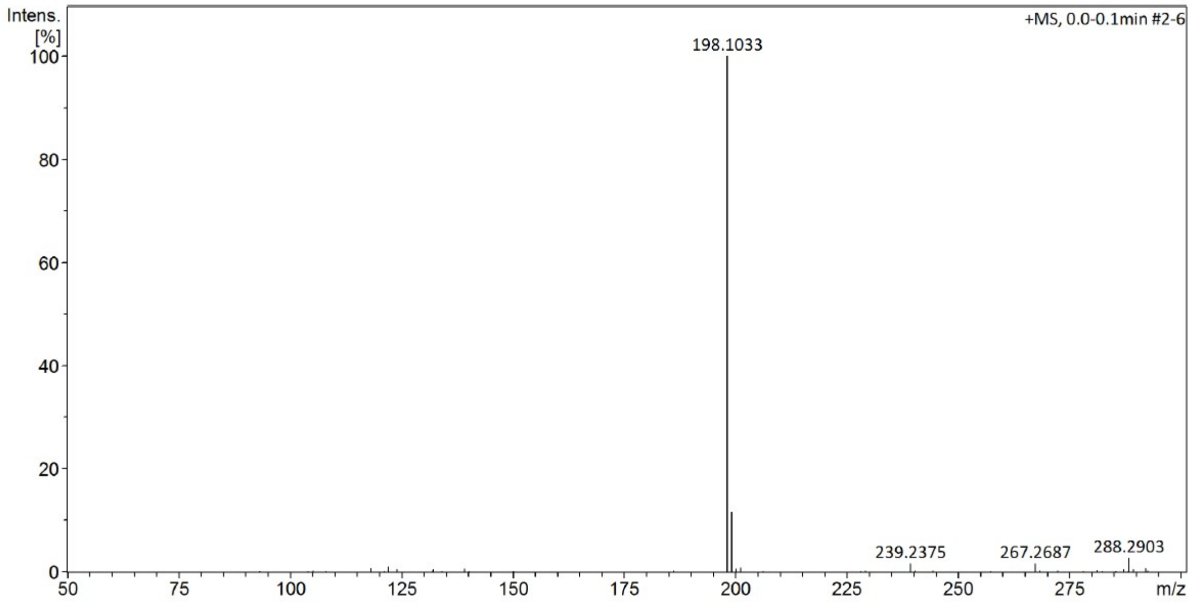

**Figure S12.** ESI-MS spectrum of 4-aminoazobenzene. Calcd for $C_{12}H_{12}N_3$: 198.1026 m/z, Found: $[M+H]^+$= 198.1033 m/z.

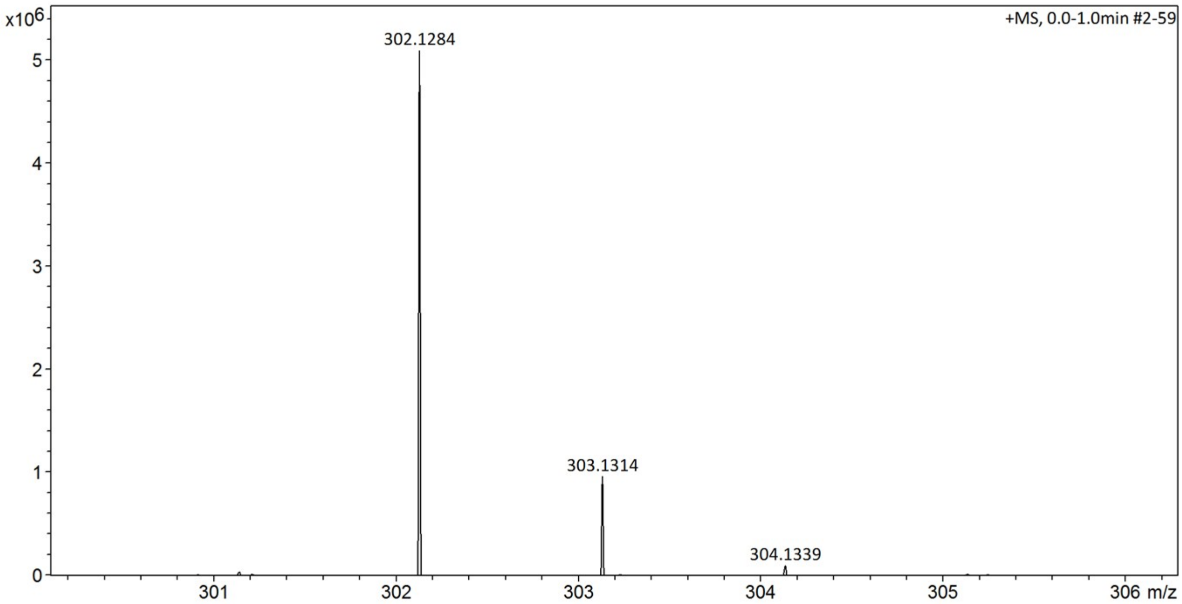

**Figure S13.** ESI-MS spectrum of **L1.** Calcd for $C_{19}H_{16}N_3O$: 302.1293 m/z, Found: $[M+H]^+$= 302.1284 m/z

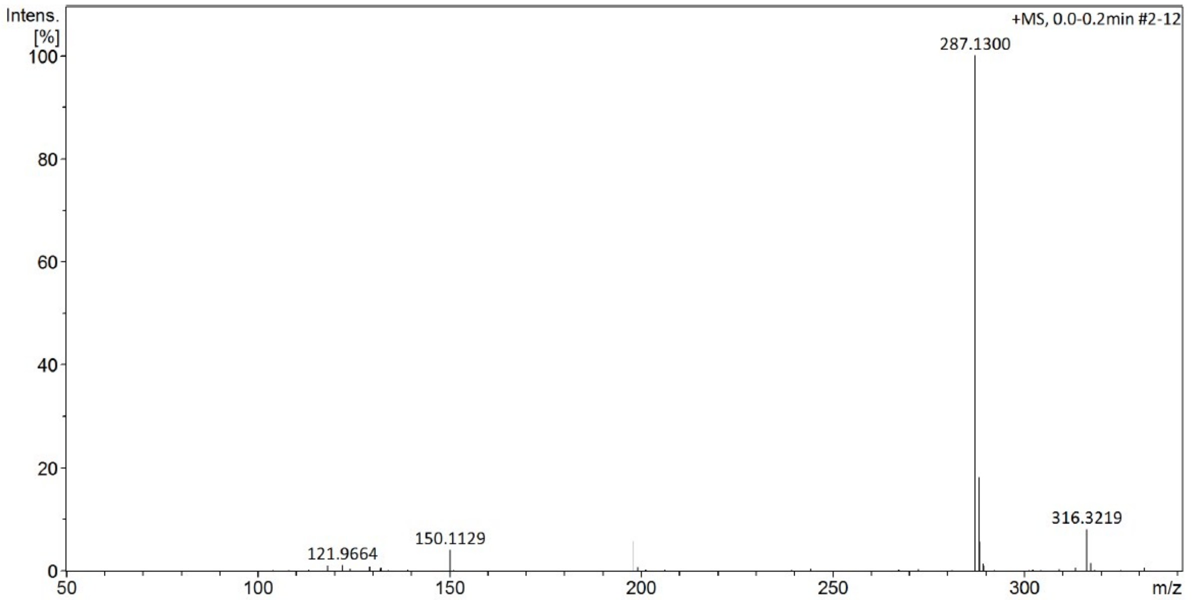

**Figure S14.** ESI-MS spectrum of **L2**. Calcd for $C_{18}H_{15}N_4$: 287.1291 m/z, Found: $[M+H]^+$= 287.1300 m/z.

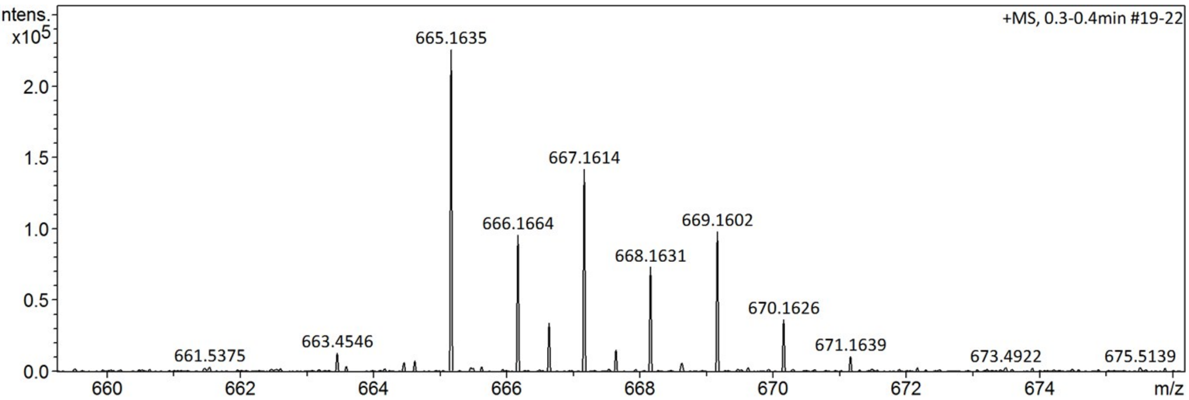

**Figure S15.** ESI-MS spectrum of Zn(**L1**-H)$_2$. Calcd for $C_{38}H_{29}N_6O_2Zn$: 665.1643 m/z, $[M+H]^+$= 665.1635 m/z

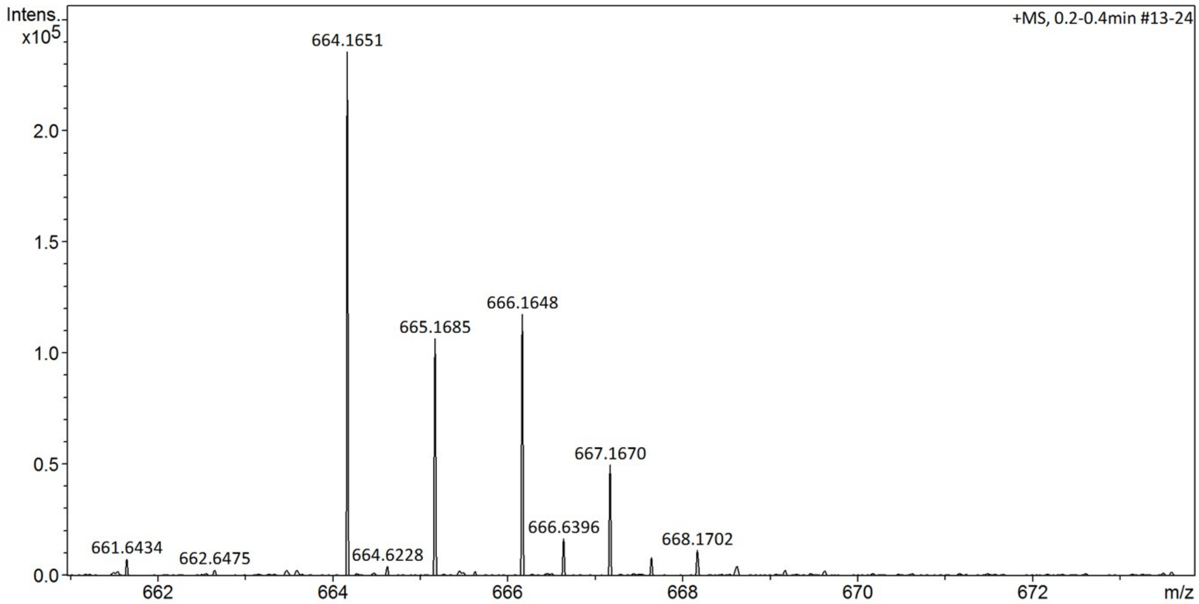

**Figure S16.** ESI-MS spectrum of Cu(**L1**-H)$_2$. ESI-MS: Calcd for $C_{38}H_{29}N_6O_2Cu$: 664.1647 m/z, Found $[M+H]^+$= 664.1650 m/z.

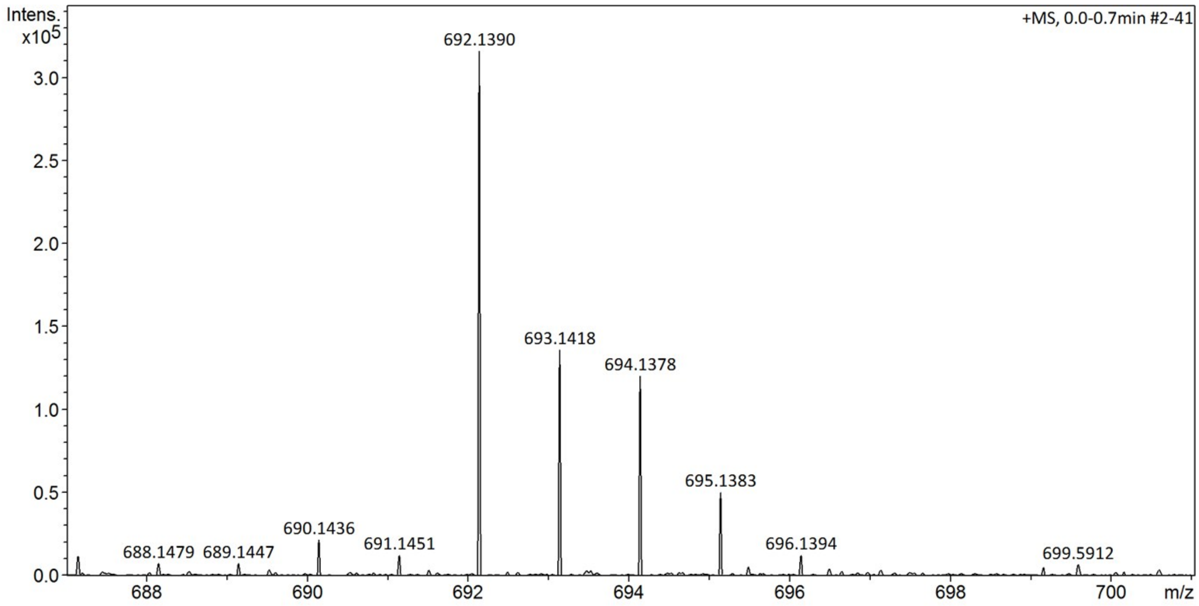

**Figure S17.** ESI-MS spectrum of Fe(**L1**-H)$_2$Cl. ESI-MS: Calcd for $C_{38}H_{29}ClFeN_6O_2$: 692.1389 m/z, Found $[M+H]^+$= 692.1390 m/z.

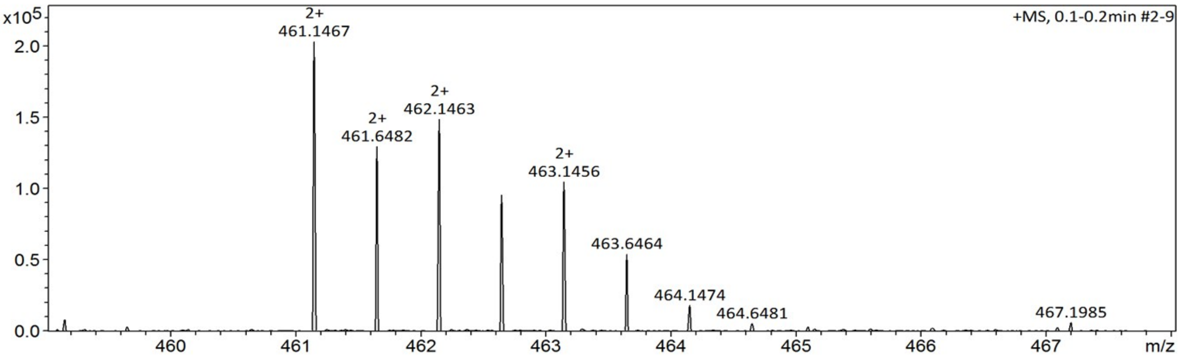

**Figure S18.** ESI-MS spectrum of [Zn(**L2**)$_3$](ClO$_4$)$_2$ ESI-MS: Calcd for $C_{54}H_{42}N_{12}Zn$: 461.1468m/z, Found [M-2ClO$_4^-$]$^{2+}$= 461.1467 m/z.

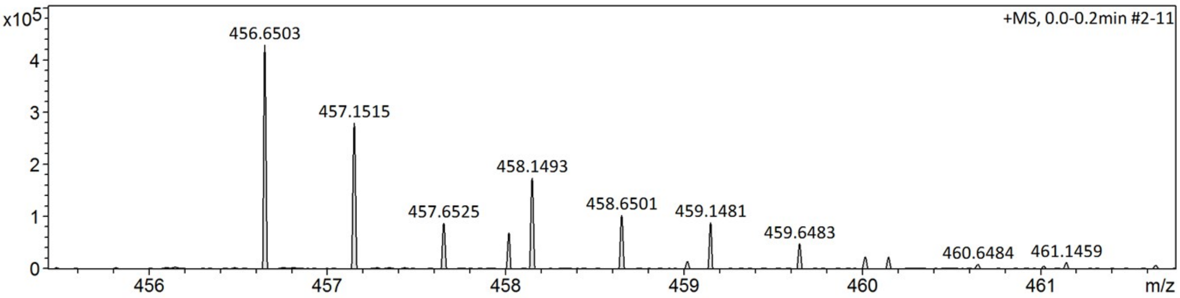

**Figure S19.** ESI-MS spectrum of [Mn(**L2**)$_3$](ClO$_4$)$_{2.}$ Calcd for $C_{54}H_{42}N_{12}Mn$: 456.6518 m/z, Found [M-2ClO$_4^-$]$^{2+}$= 456.6503 m/z.

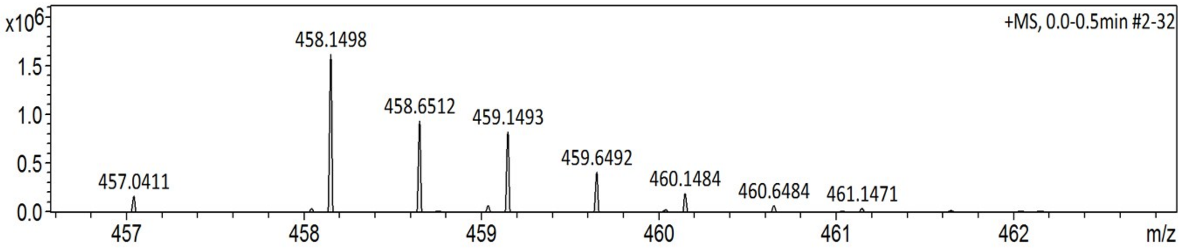

**Figure S20**. ESI-MS spectrum of [Ni(**L2**)$_3$](ClO$_4$)$_{2.}$ ESI-MS: Calcd for $C_{54}H_{42}N_{12}Ni$: 458.1504 m/z, Found [M-2ClO$_4^-$]$^{2+}$= 458.1498 m/z.

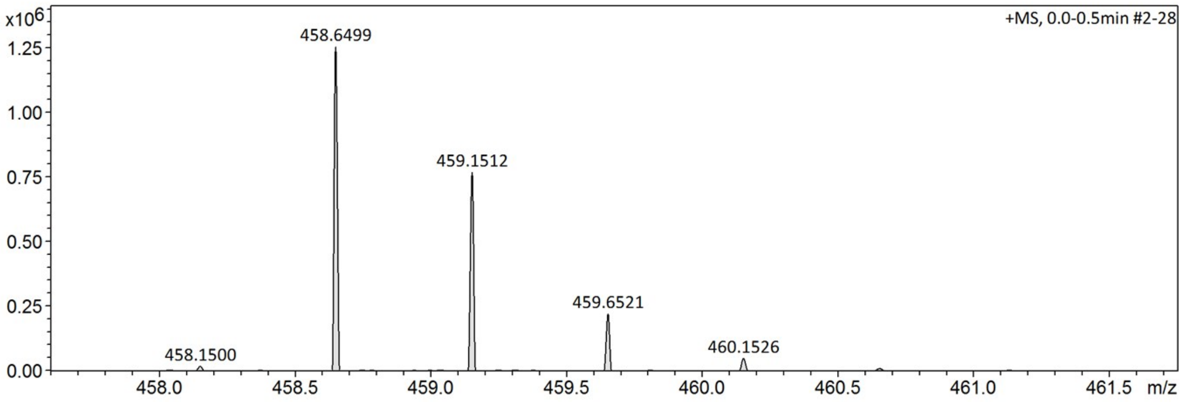

**Figure S21.** ESI-MS spectrum of [Co(**L2**)$_3$](ClO$_4$)$_{2.}$ ESI-MS: Calcd for $C_{54}H_{42}N_{12}Co$: 458.6494 m/z, Found [M-2ClO$_4^-$]$^{2+}$= 458.6499 m/z.

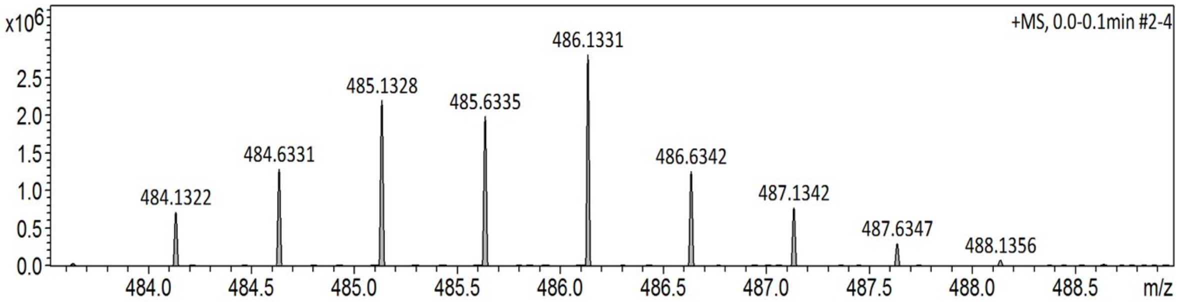

**Figure S22.** ESI-MS spectrum of [Cd(**L2**)$_3$](ClO$_4$)$_2$. ESI-MS: Calcd for $C_{54}H_{42}N_{12}Cd$: 486.1344 m/z, Found [M-2ClO$_4^-$]$^{2+}$= 486.1331 m/z.

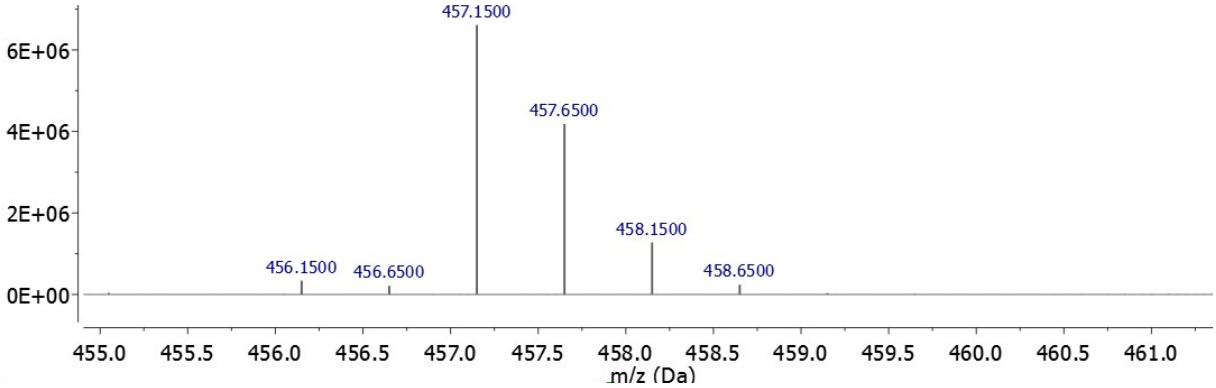

**Figure S23.** ESI-MS spectrum of [Fe(**L2**)$_3$](BF$_4$)$_2$. Calcd for $C_{54}H_{42}N_{12}Fe$: 457,1497 m/z,
Found [M-2BF$_4^-$]$^{2+}$= 457,1500 m/z.

# 3. Spectrophotometric data

Photoisomerization kinetic data were fitted to the equation:

$$ln\frac{A_0 - A_{eq}}{A_t - A_{eq}} = kt$$

Where $A_0$, $A_t$ and $A_{eq}$ represent absorbance before irradiation, at irradiation time t and at the photostationary state, t represents the time, and k is defined as:

$$k = (k_f + k_b) \text{ or } (k_{tc} + k_{ct}),$$

where tc refers to the forward reaction and ct to its reverse and each constant is the sum of rate constants for the thermal and photocatalysed reactions.

Assuming that the rate constants for the thermal reactions can be ignored compared to the photocatalysed processes $k_{tc}$ and $k_{ct}$ must both depend on the light intensity $I_0$, the quantum yields for excitation of the two isomers and the rate constants for isomerisation in the excited state and thus are composite parameters which vary depending upon the particular reaction conditions. To obtain their separate values, it is necessary to know the value of the apparent equilibrium constant K, which is defined by

$$K = k_{tc}/k_{ct}$$

In the case of ligand **2**, for example, $K = 58/42 = 1.4$ and since $k = 5.9 \times 10^{-2}$ $s^{-1}$, $k_{tc} = kK/(K+1) = 3.4 \times 10^{-2}$ and $k_{ct} = 2.5 \times 10^{-2}$ $s^{-1}$.

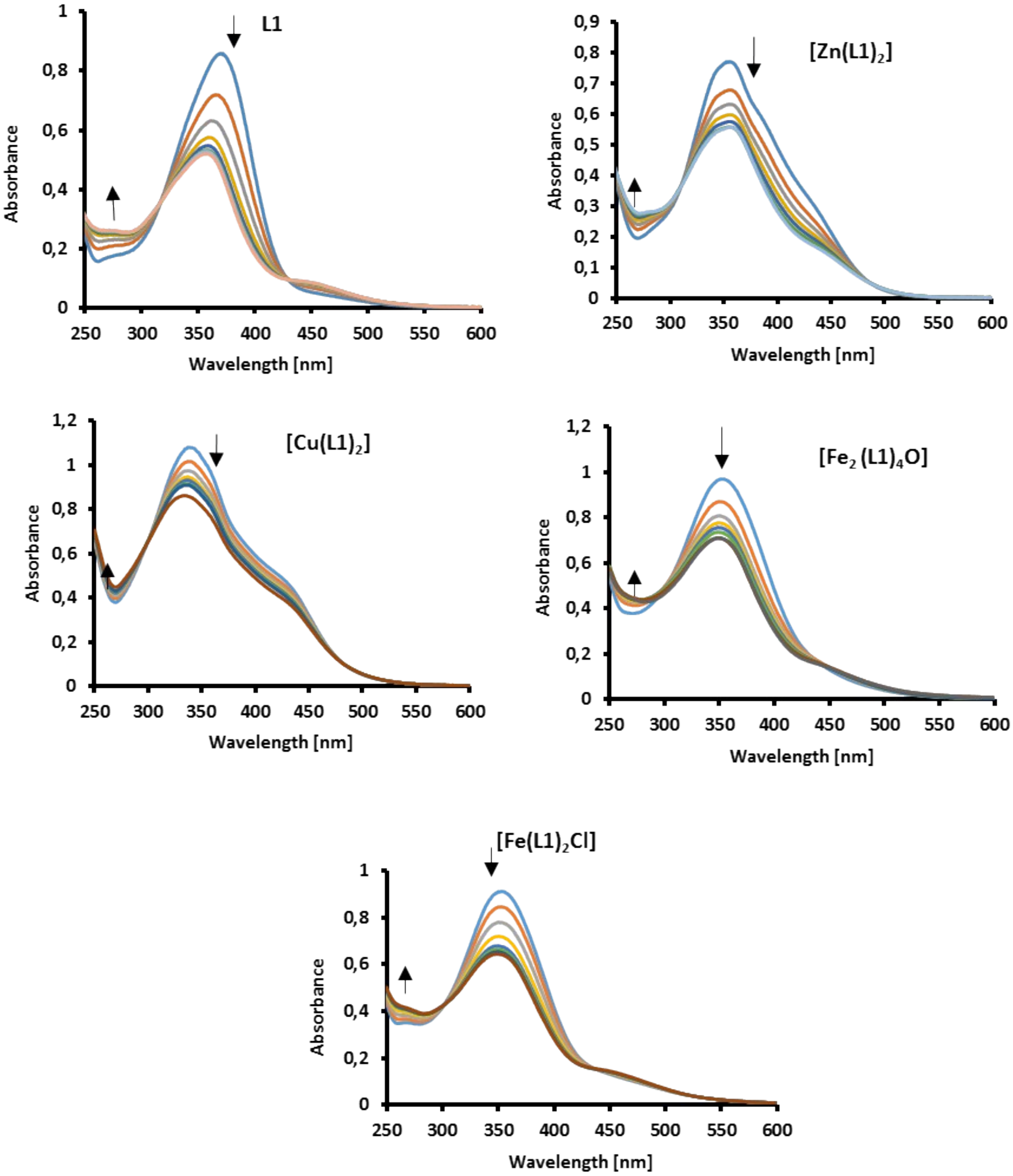

**Figure S24.** UV-Vis spectra obtained during UV irradiations of **L1** ligand and **L1** complexes.

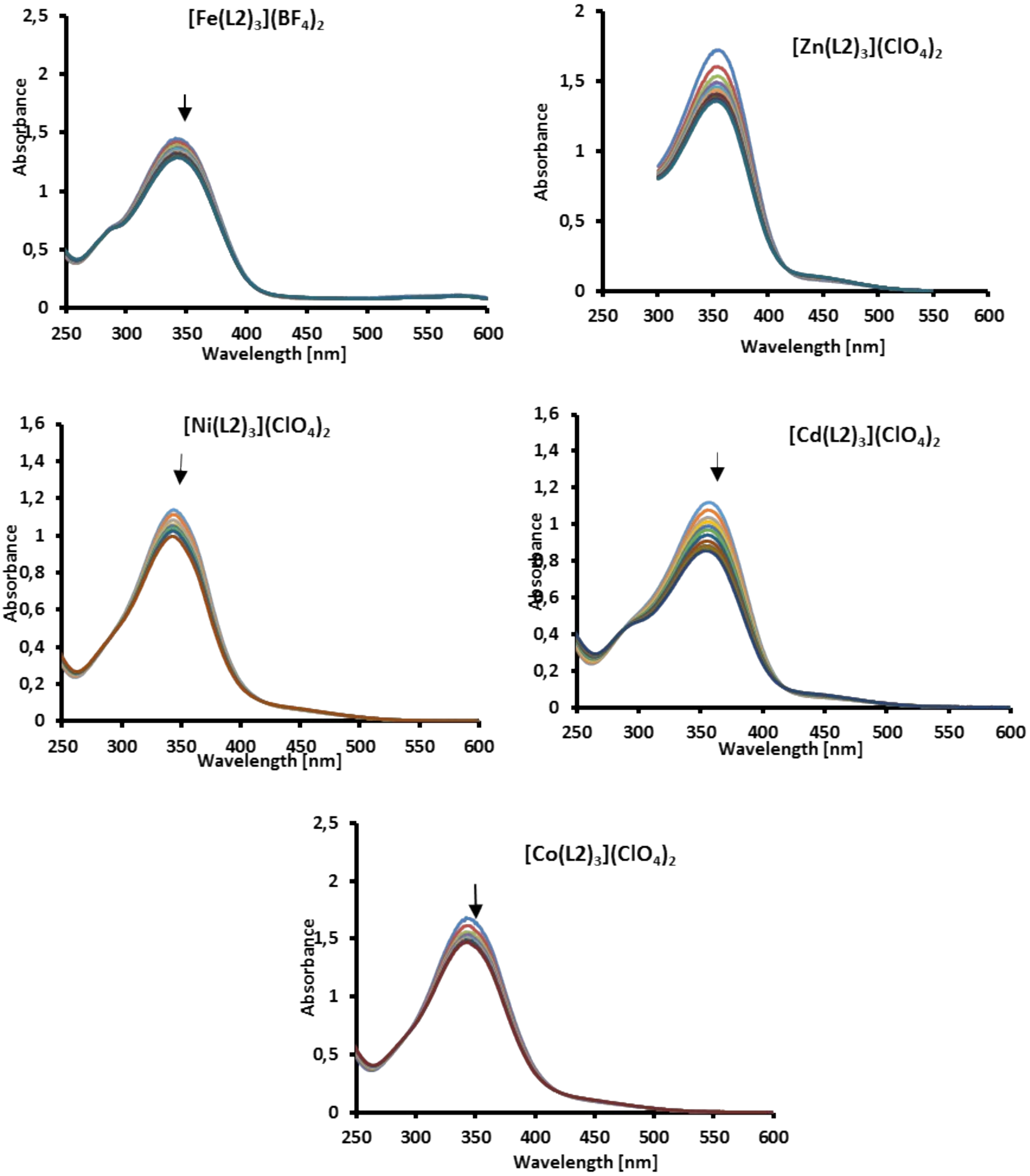

**Figure S25.** UV-Vis spectra obtained during UV irradiations of **L2** ligand and **L2** complexes.

# 4. X-ray Crystallography data

The diffraction data for **L1**, Zn(**L1**-H)$_2$, Cu(**L1**-H)$_2$, Fe(**L1-H**)$_2$Cl and Fe$_2$(**L1-H**)$_4$O were collected on a New Xcalibur EosS2 diffractometer, equipped with a CCD detector, with graphite monochromated Mo Kα radiation ($\lambda\alpha$ = 0.71073 Å). X-ray data were collected at room temperature with the ω-scan technique. For data reduction, UB-matrix determination and absorption correction CrysAlisPro software was used. Using Olex2, the structure were solved with the SHELXT structure solution program using Intrinsic Phasing and refined by full-matrix least-square minimization against F2 utilizing with the SHELXL. All non-hydrogen atoms were refined with anisotropically displacement parameters. Hydrogen atoms were located in idealized positions by molecular geometry and refined as rigid groups. The positions of $U_{iso}$ of hydrogen atoms were set as 1.2 (for C-carries) times $U_{eq}$ of the corresponding carrier atom.