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Electronic Supplementary Information

Investigation of the cytotoxic potential of methyl imidazole-derived thiosemicarbazones and their copper(II) complexes with dichloroacetate as co-ligand

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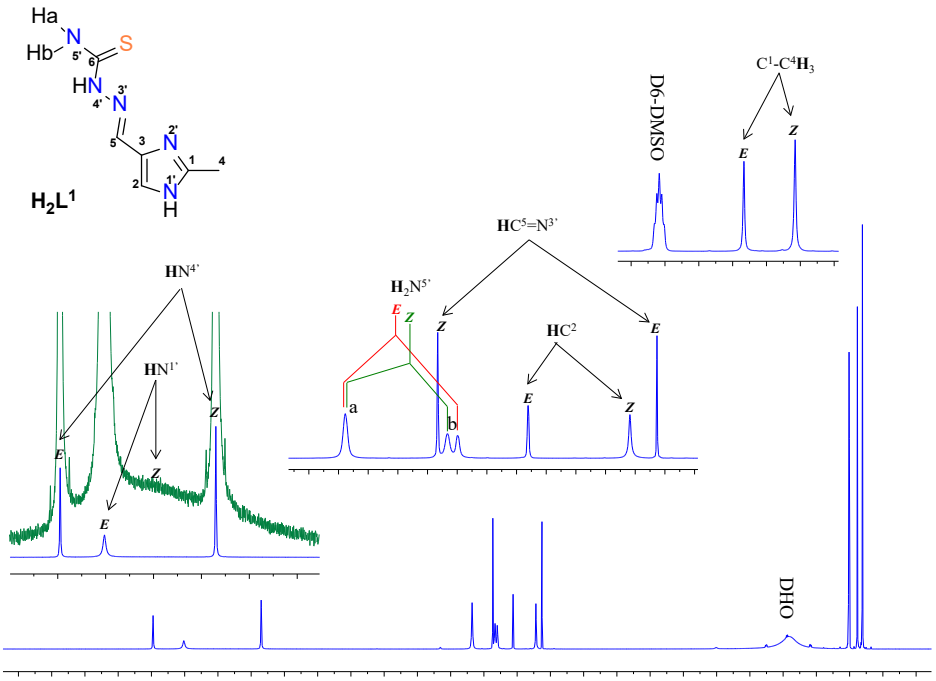

Fig. S1a ^{1}H NMR (500 MHz) spectra of **HL^{1}** in DMSO-d$_6$ (Z : E = 1.5 : 1)

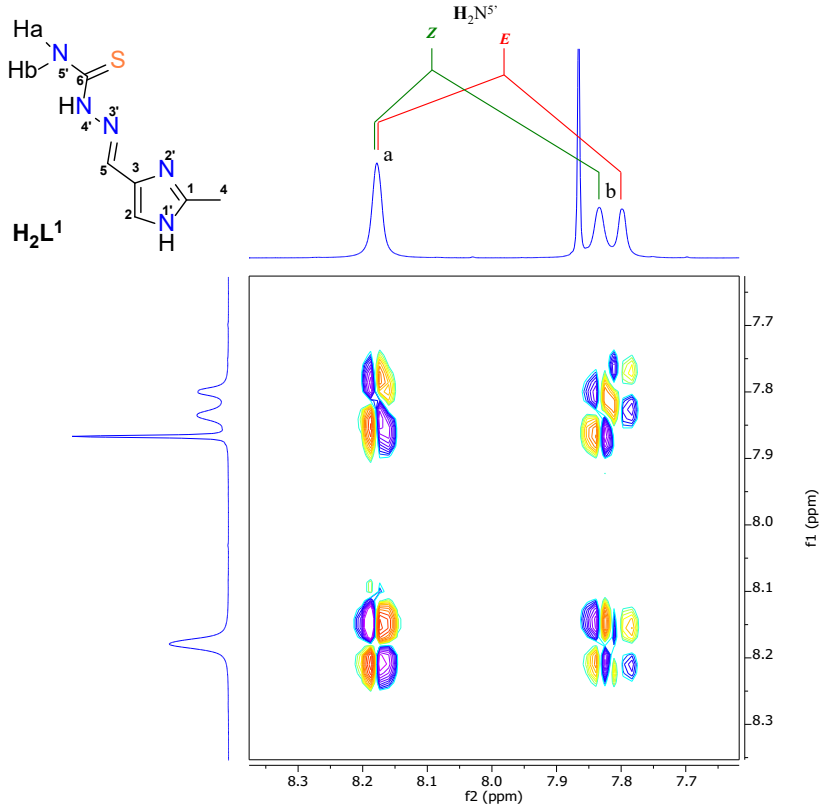

Fig. S1b ^{1}H,^{1}H COSY NMR spectrum of **HL^{1}** in DMSO-d$_6$.

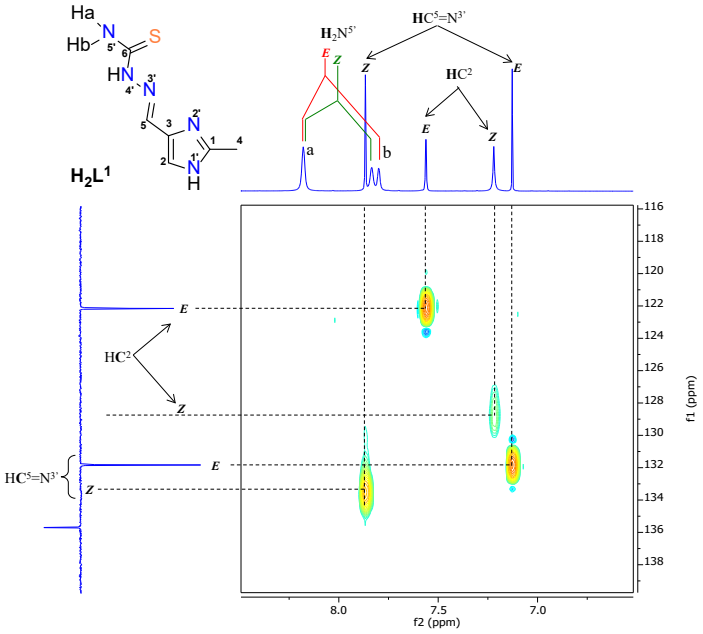

Fig. S1c $^{1}H,^{13}C$ HSQC NMR spectrum of **HL^{1}** in DMSO-d$_6$.

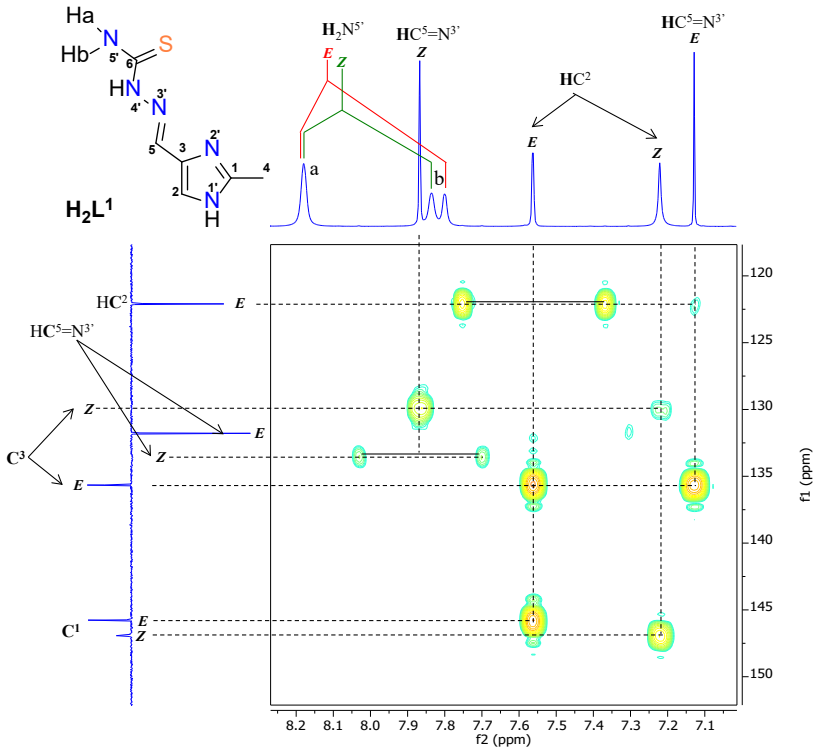

Fig. S1d Fragment of $^{1}H,^{13}C$ HMQC NMR spectrum of **HL^{1}** in DMSO-d$_6$.

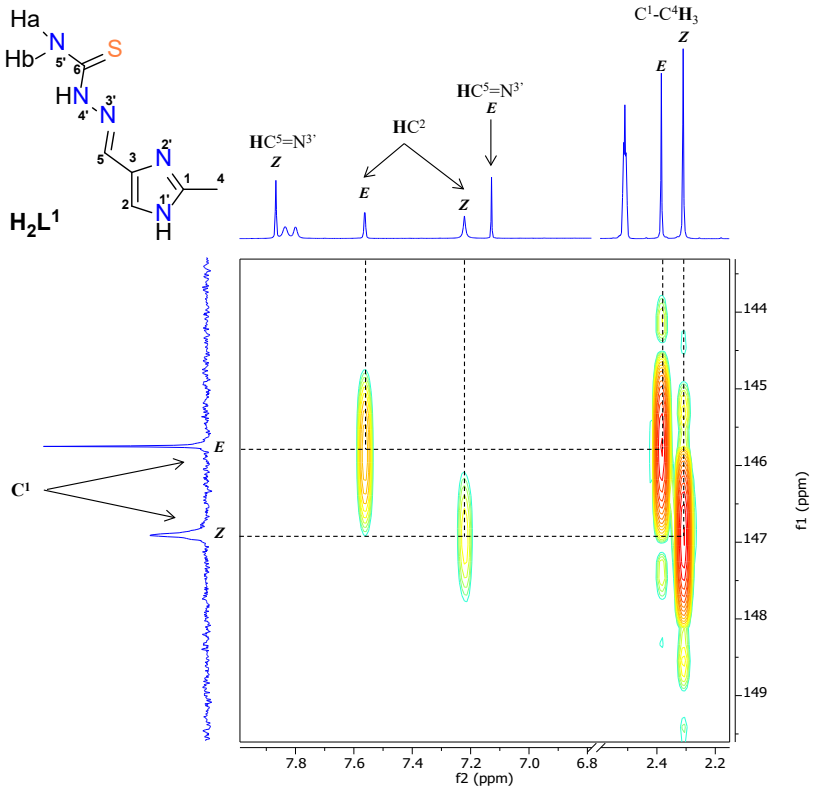

Fig. S1e Fragment of $^{1}H,^{13}C$ HMQC NMR spectrum of **HL^{1}** in DMSO-d$_6$.

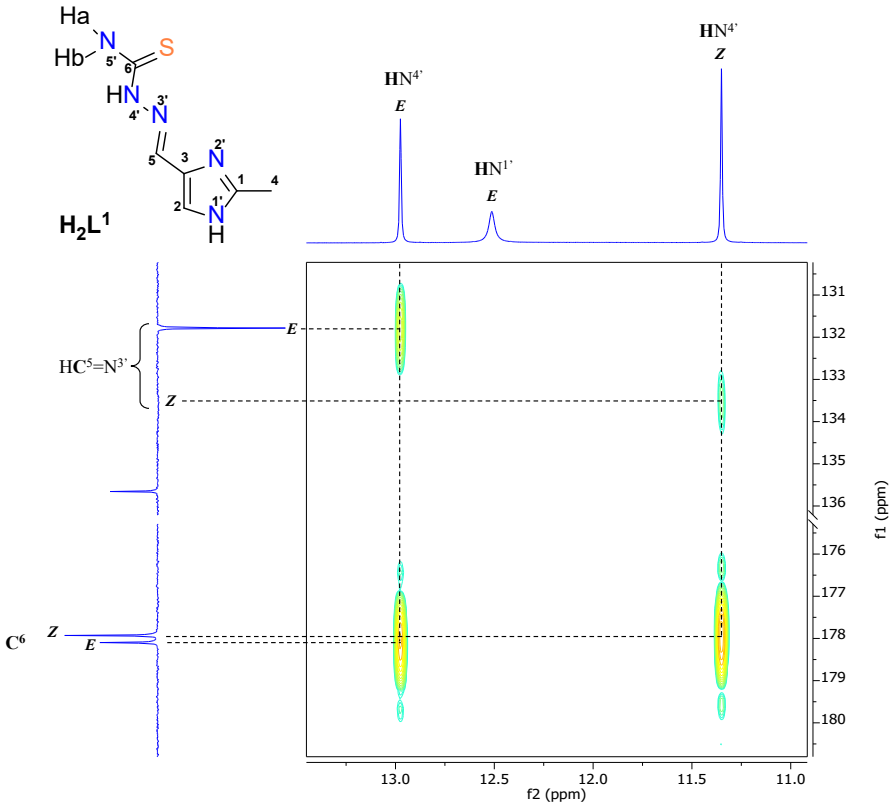

Fig. S1f Fragment of $^{1}H,^{13}C$ HMQC NMR spectrum of **HL^{1}** in DMSO-d$_6$.

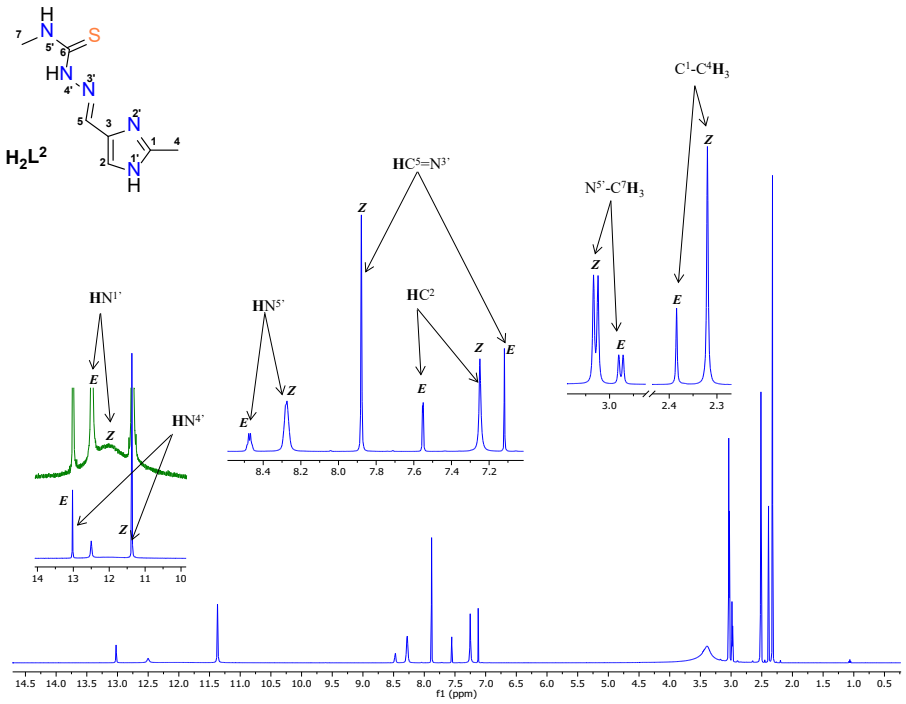

Fig. S2a ^{1}H NMR (500 MHz) spectra of **HL^{2}** in DMSO-d$_{6}$ (Z:E=3.9:1).

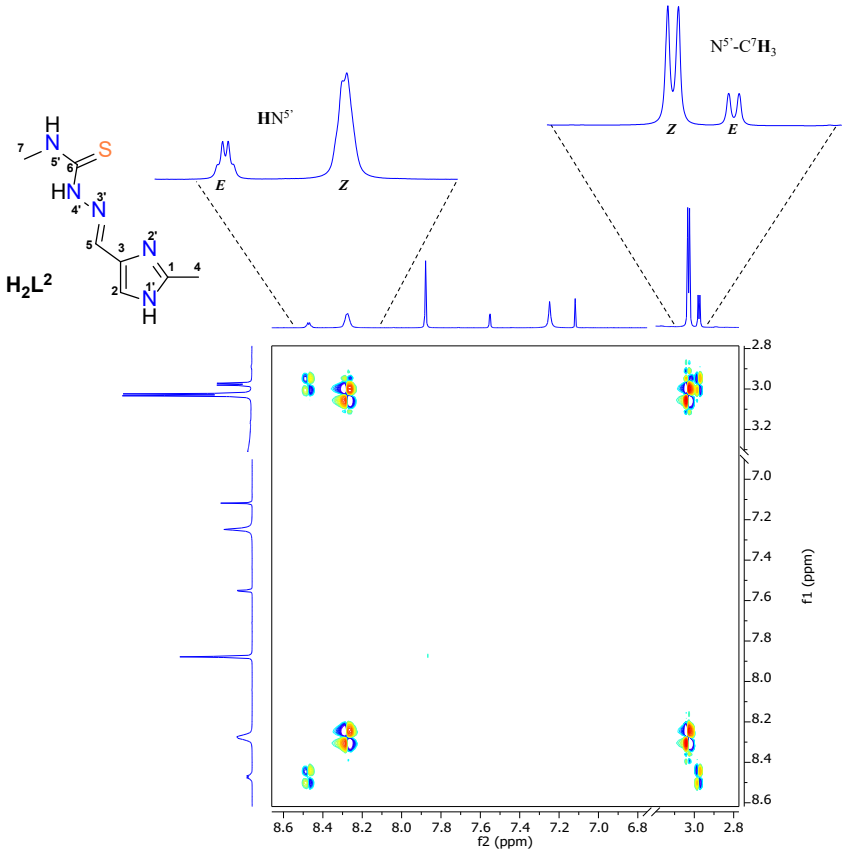

Fig. S2b ^{1}H,^{1}H COSY NMR spectrum of **HL^{2}** in DMSO-d$_{6}$.

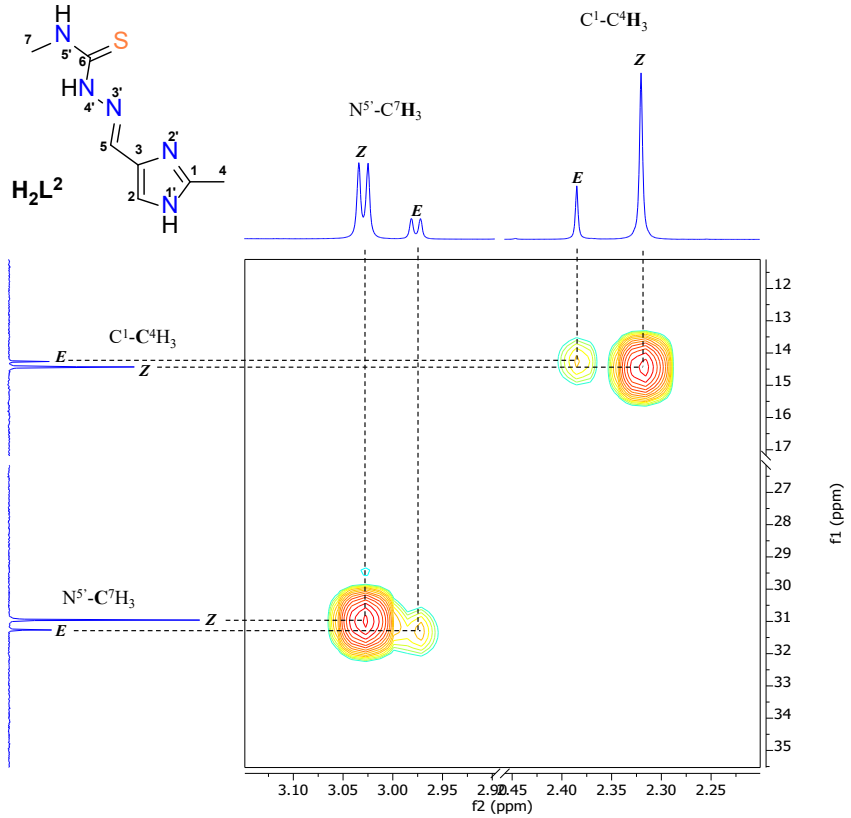

Fig. S2c Fragment of $^{1}H,^{13}C$ HSQC NMR spectrum of **HL²** in DMSO-d6.

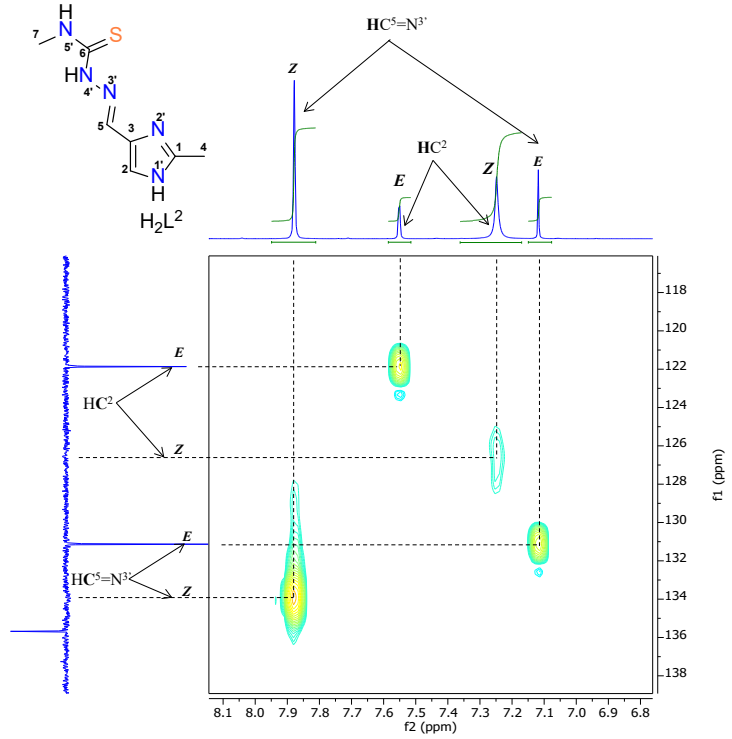

Fig. S2d. Fragment of $^{1}H,^{13}C$ HSQC NMR spectrum of **HL²** in DMSO-d6.

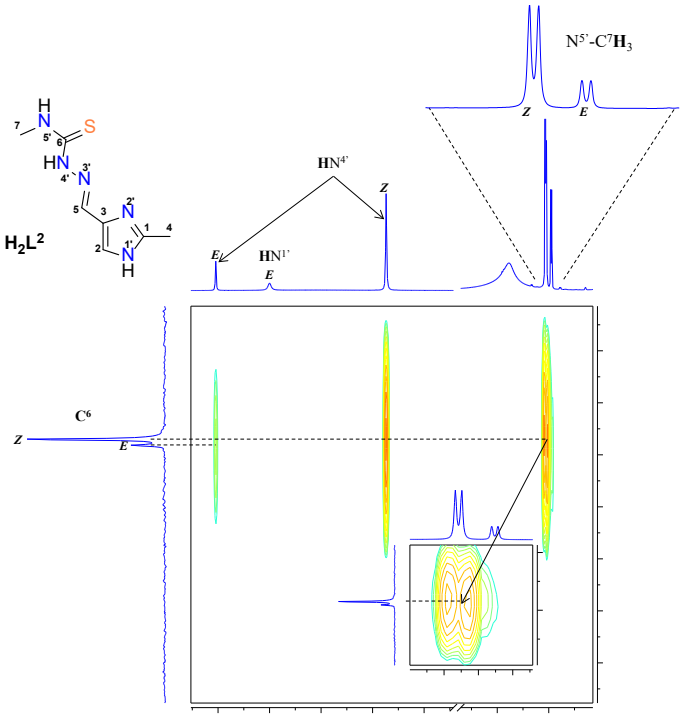

Fig. S2e Fragment of $^{1}H,^{13}C$ HMQC NMR spectrum of **HL²** in DMSO-d6.

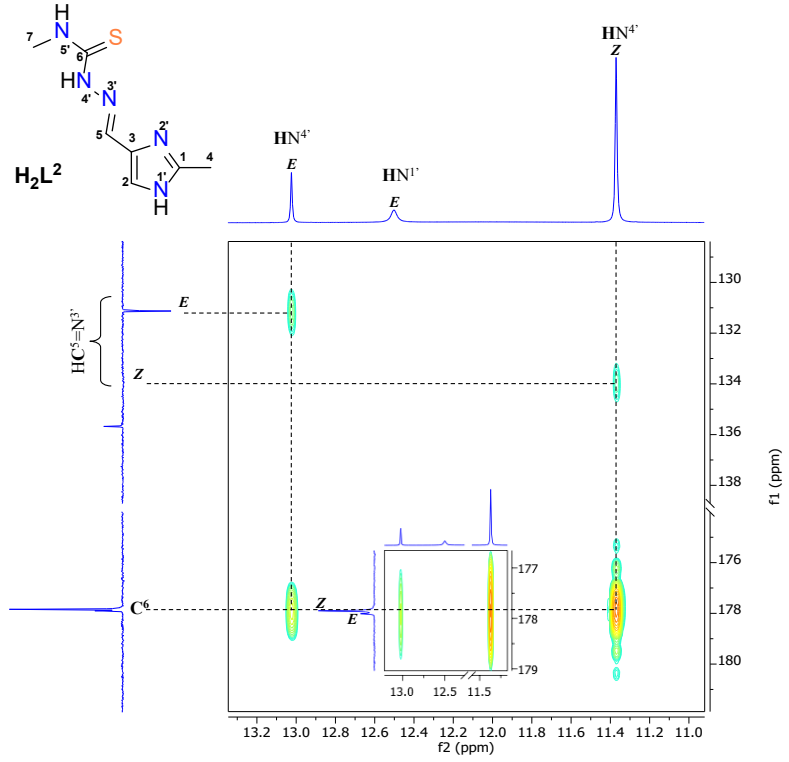

Fig. S2f Fragment of $^{1}H,^{13}C$ HMQC NMR spectrum of **HL²** in DMSO-d6.

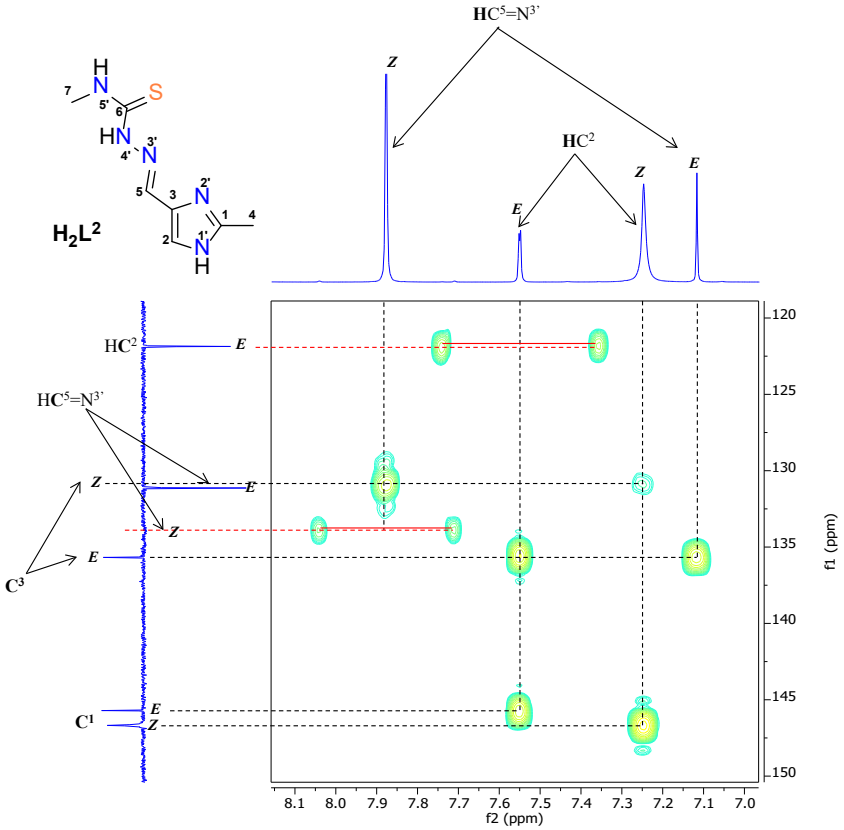

Fig. S2g Fragment of $^{1}H,^{13}C$ HMQC NMR spectrum of **HL²** in DMSO-d6.

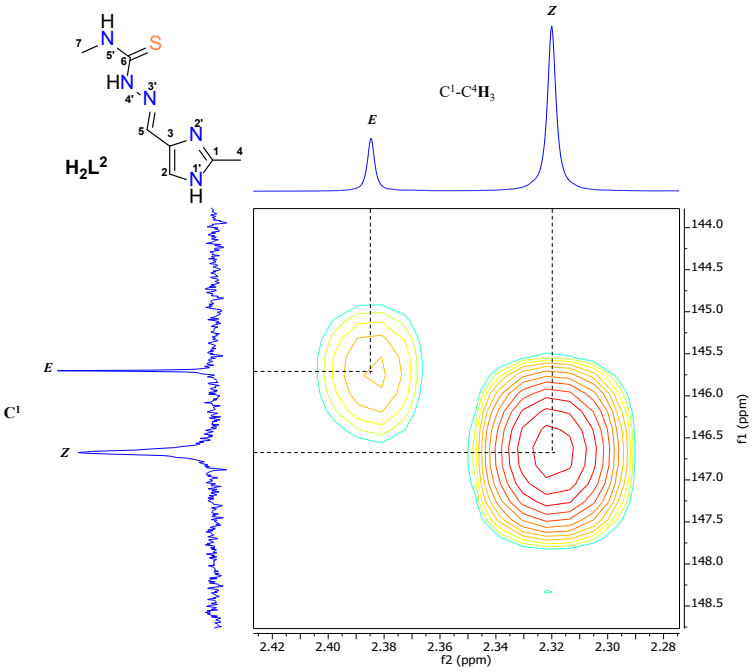

Fig. S2h Fragment of $^{1}H,^{13}C$ HMQC NMR spectrum of **HL²** in DMSO-d6.

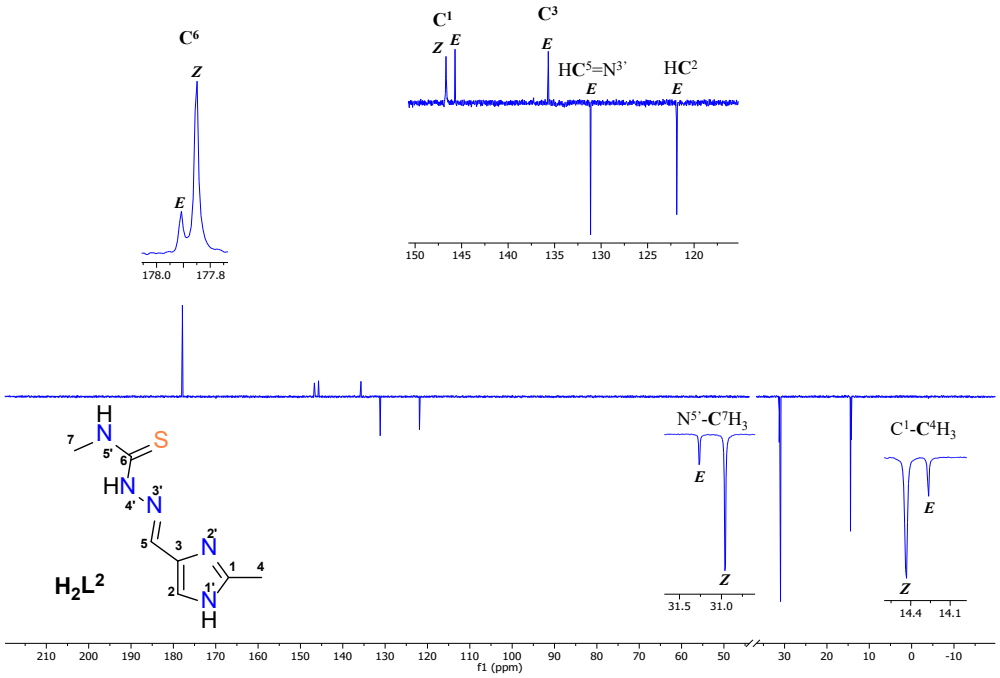

Fig. S2i ^{13}C NMR spectra of **HL^2** in DMSO-d$_6$

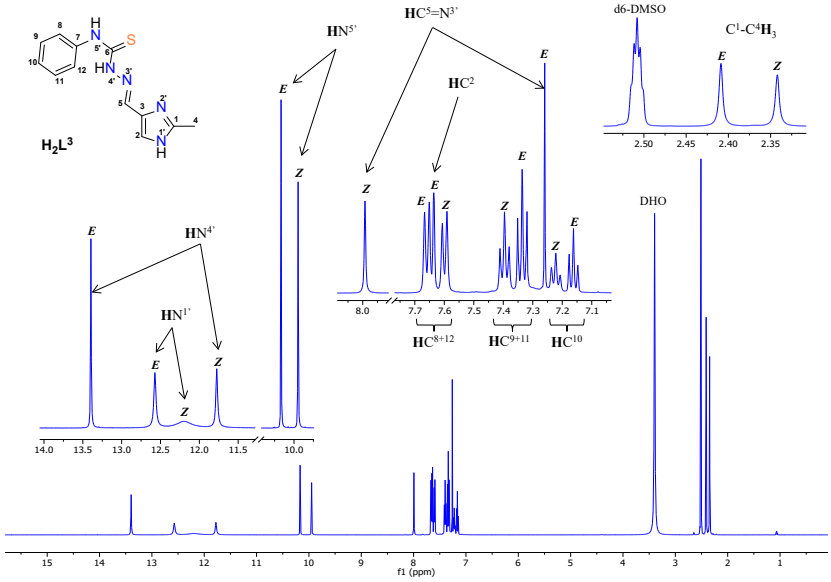

Fig. S3a ^{1}H NMR (500 MHz) spectra of **HL^3** in DMSO-d$_6$ (Z:E~0.8:1).

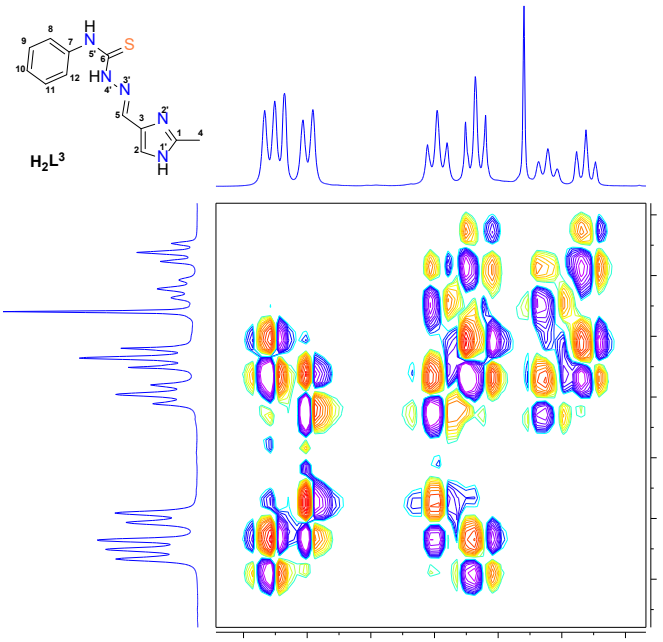

Fig. S3b ^{1}H,^{1}H COSY NMR spectrum of **HL^{3}** in DMSO-d$_6$.

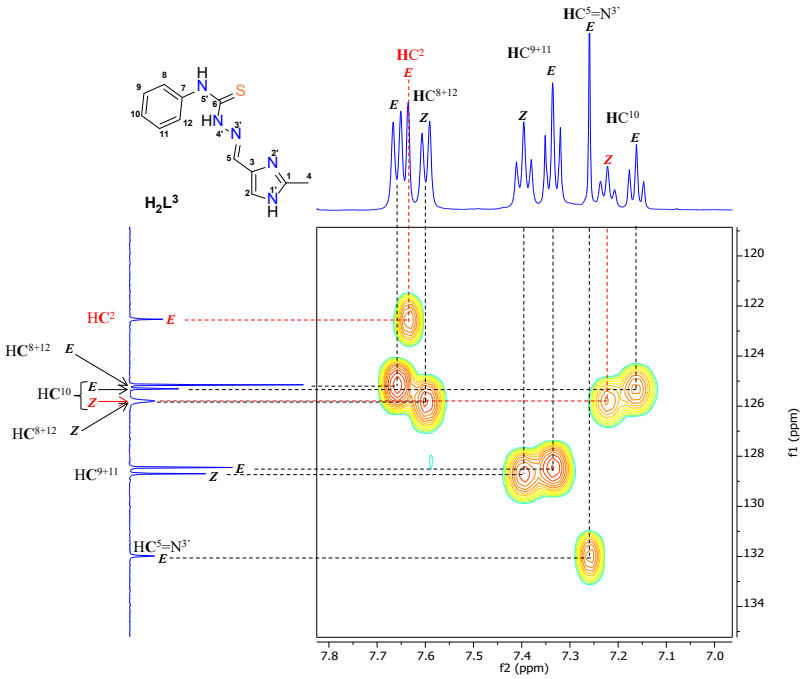

Fig. S3c Fragment of ^{1}H,^{13}C HSQC NMR spectrum of **HL^{3}** in DMSO-d$_6$.

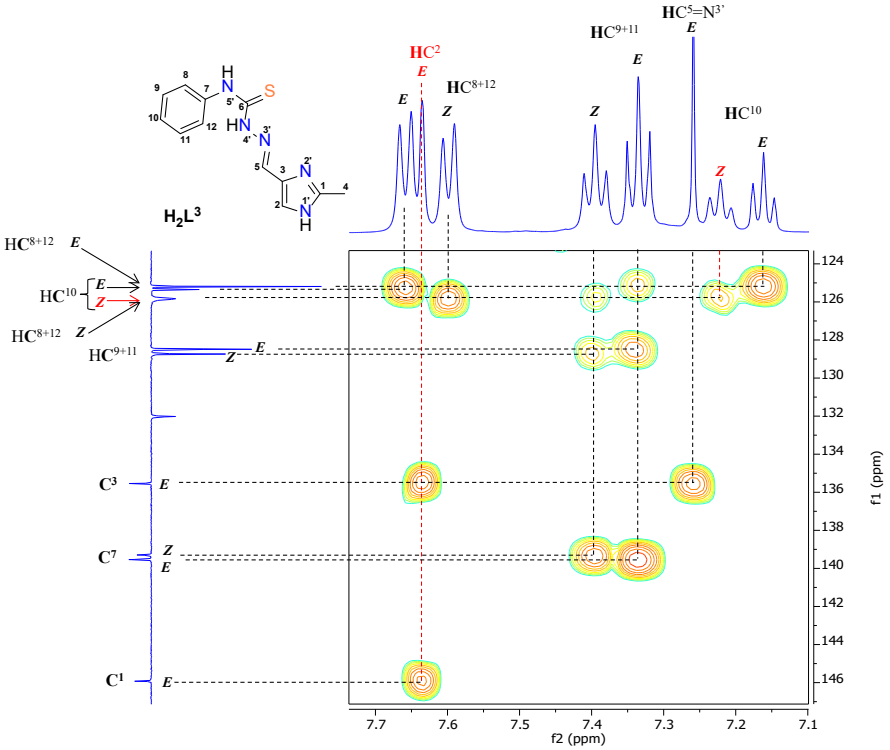

Fig. S3d Fragment of $^{1}H,^{13}C$ HMQC NMR spectrum of **HL^{3}** in DMSO-d$_6$.

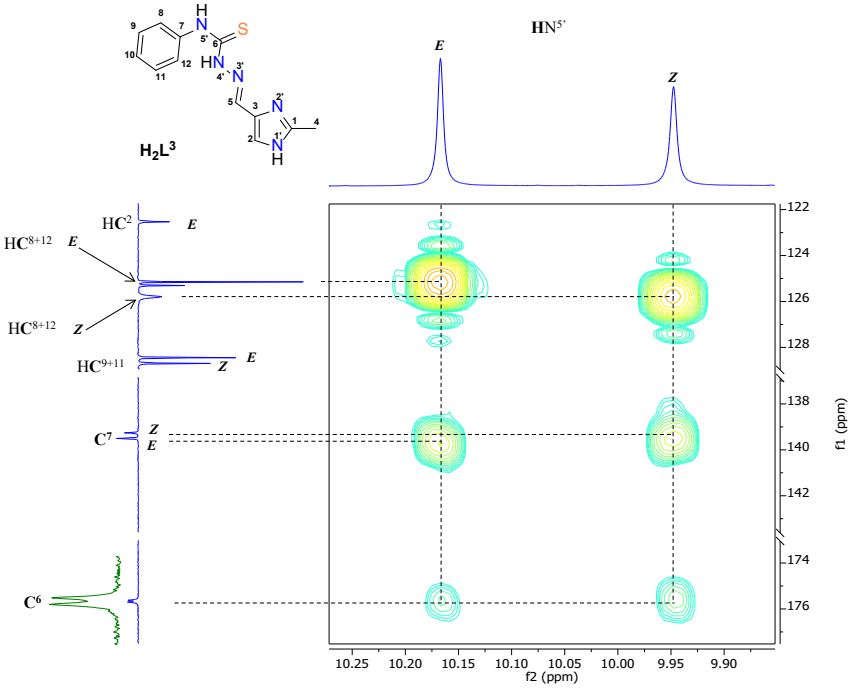

Fig. S3e Fragment of $^{1}H,^{13}C$ HMQC NMR spectrum of **HL^{3}** in DMSO-d$_6$.

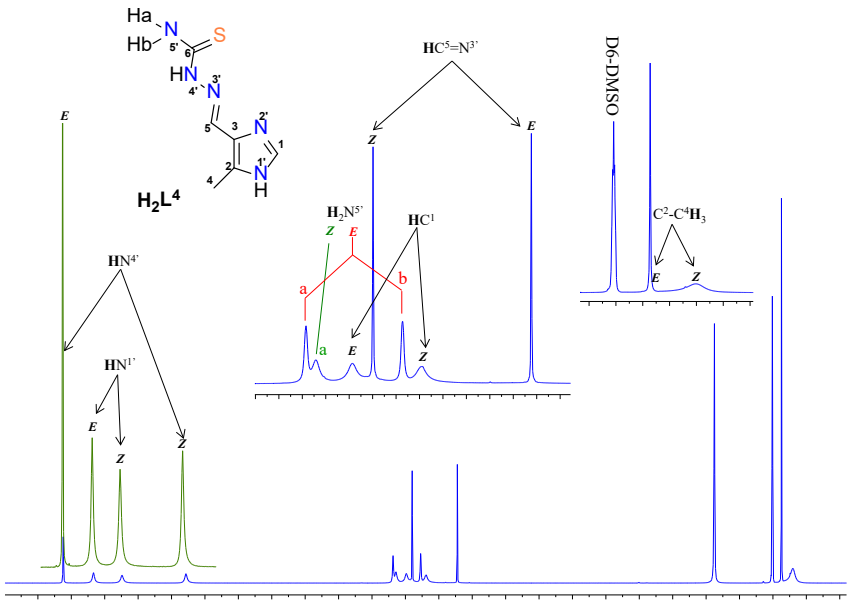

Fig. S4a ^{1}H NMR (500 MHz) spectra of **HL^{4}** in DMSO-d$_6$ (Z:E = 1:1).

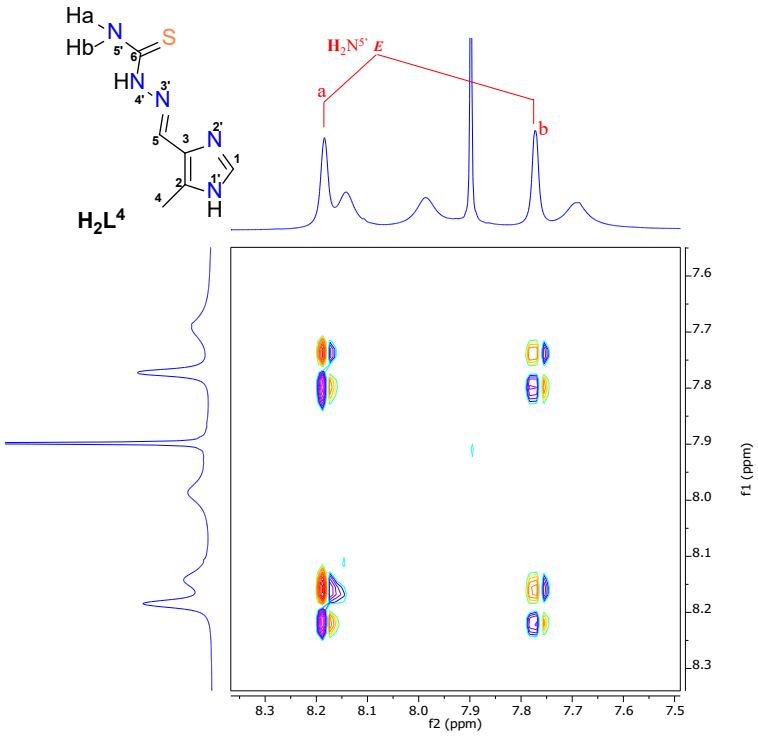

Fig. S4b ^{1}H,^{1}H COSY NMR spectrum of **HL^{4}** in DMSO-d$_6$.

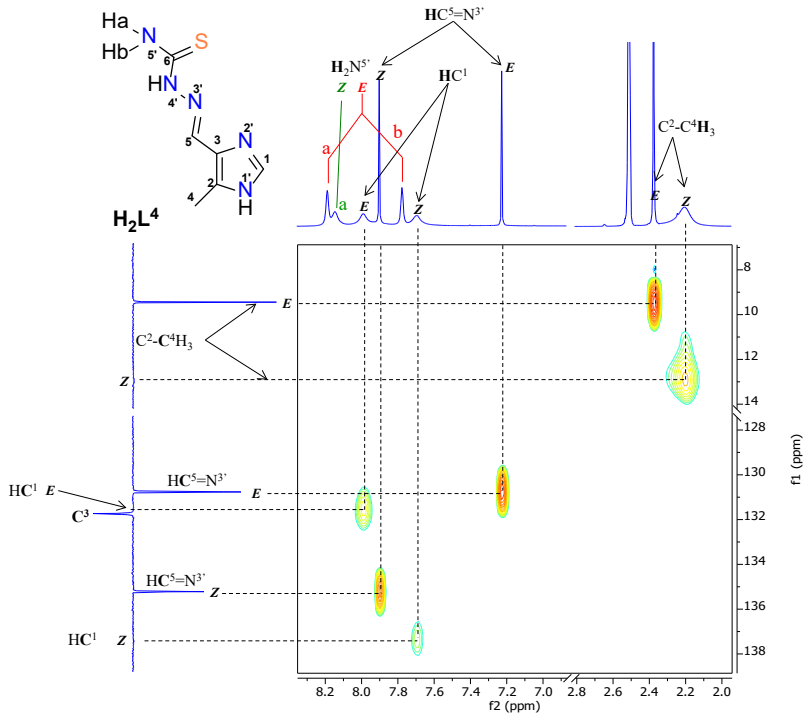

Fig. S4c $^{1}H,^{13}C$ HSQC NMR spectrum of **HL^{4}** in DMSO-d$_6$.

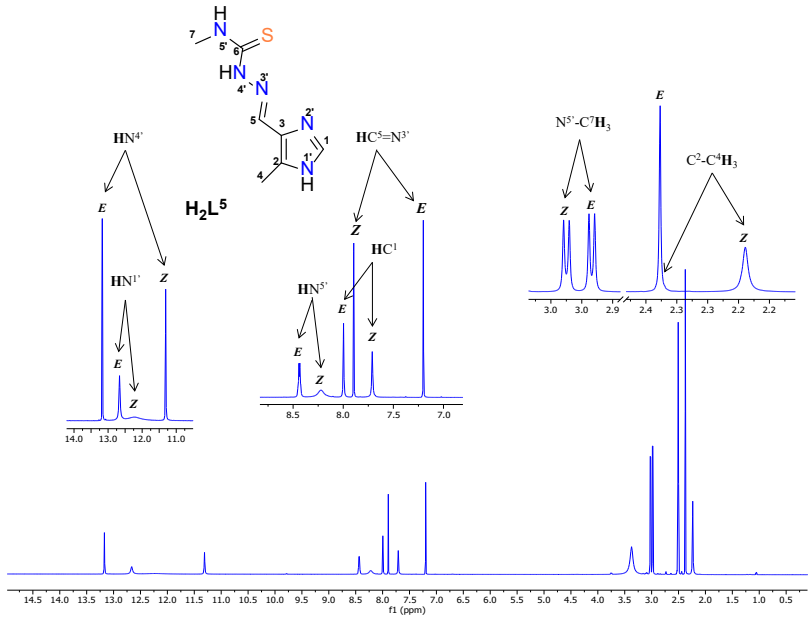

Fig. S5a ^{1}H NMR (500 MHz) spectra of **HL^{5}** in DMSO-d$_6$ (Z:E=1:1).

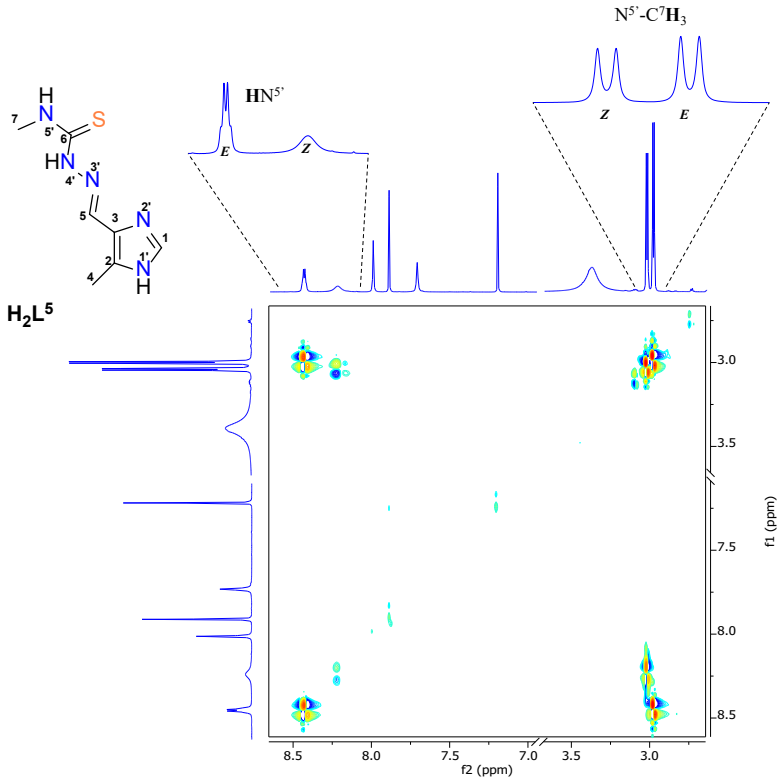

Fig. S5b ^{1}H,^{1}H COSY NMR spectrum of **HL^{5}** in DMSO-d$_6$.

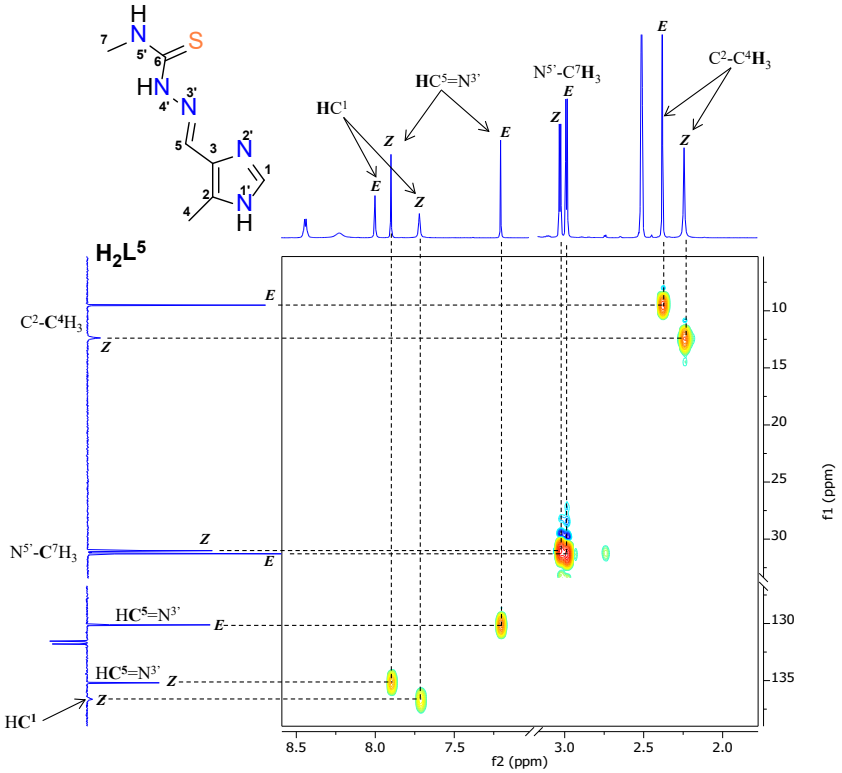

Fig. S5c ^{1}H,^{13}C HSQC NMR spectrum of **H$_2$L^{5}**in DMSO-d$_6$.

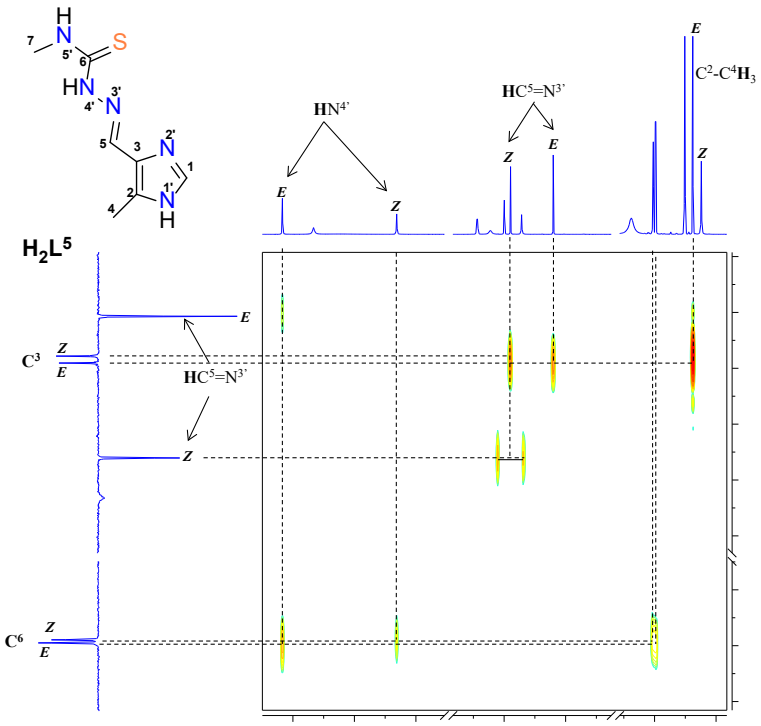

Fig. S5d $^{1}H,^{13}C$ HMQC NMR spectrum of **HL^{5}** in DMSO-d_6.

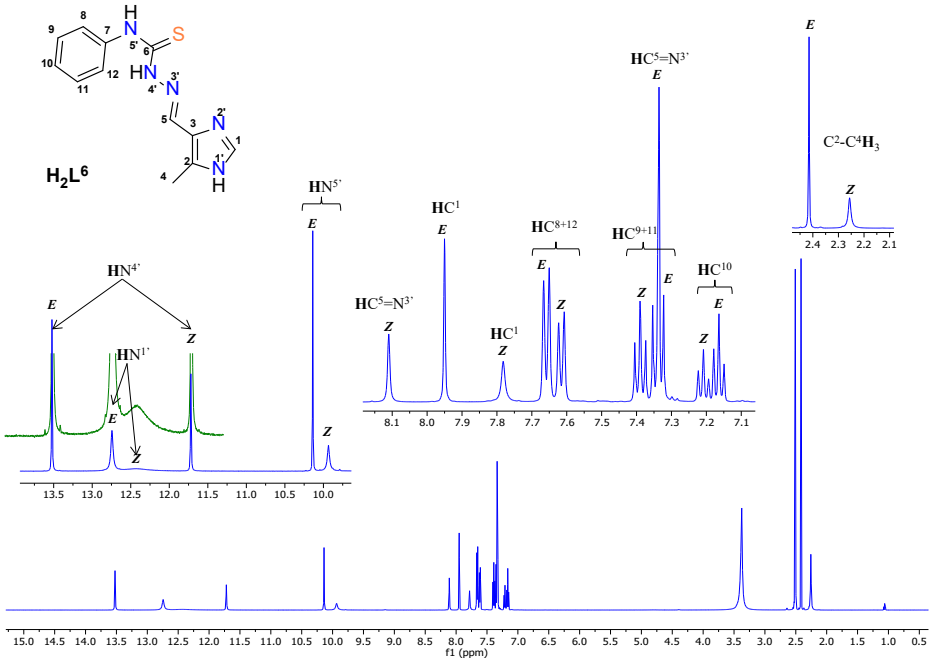

Fig. S6a ^{1}H NMR (500 MHz) spectra of **HL^{6}** in DMSO-d_6 (Z:E = 0.7:1).

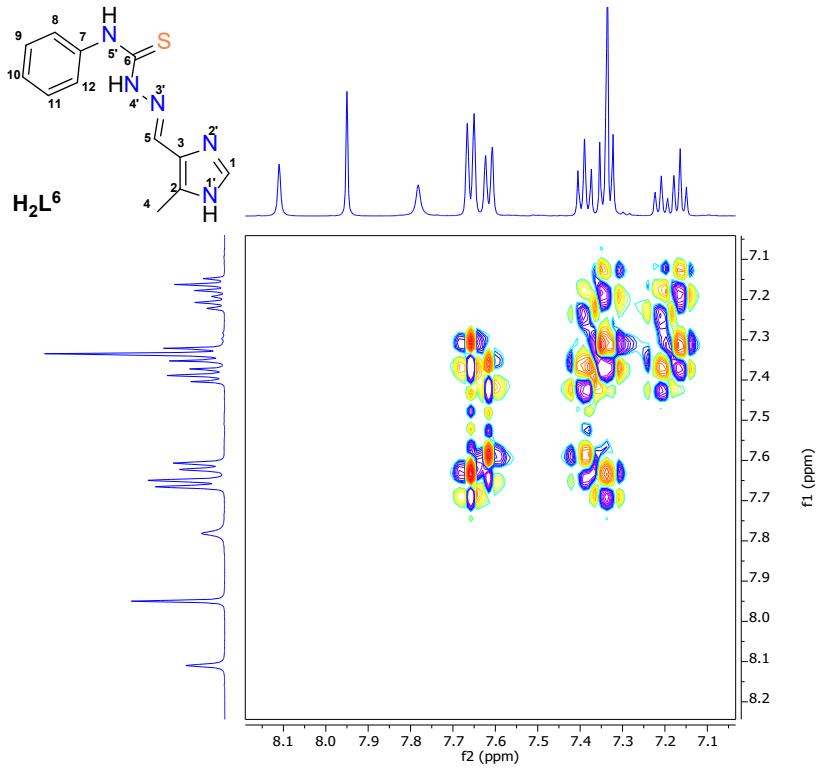

Fig. S6b $^{1}H,^{1}H$ COSY NMR spectrum of **HL^{6}** in DMSO-d_6.

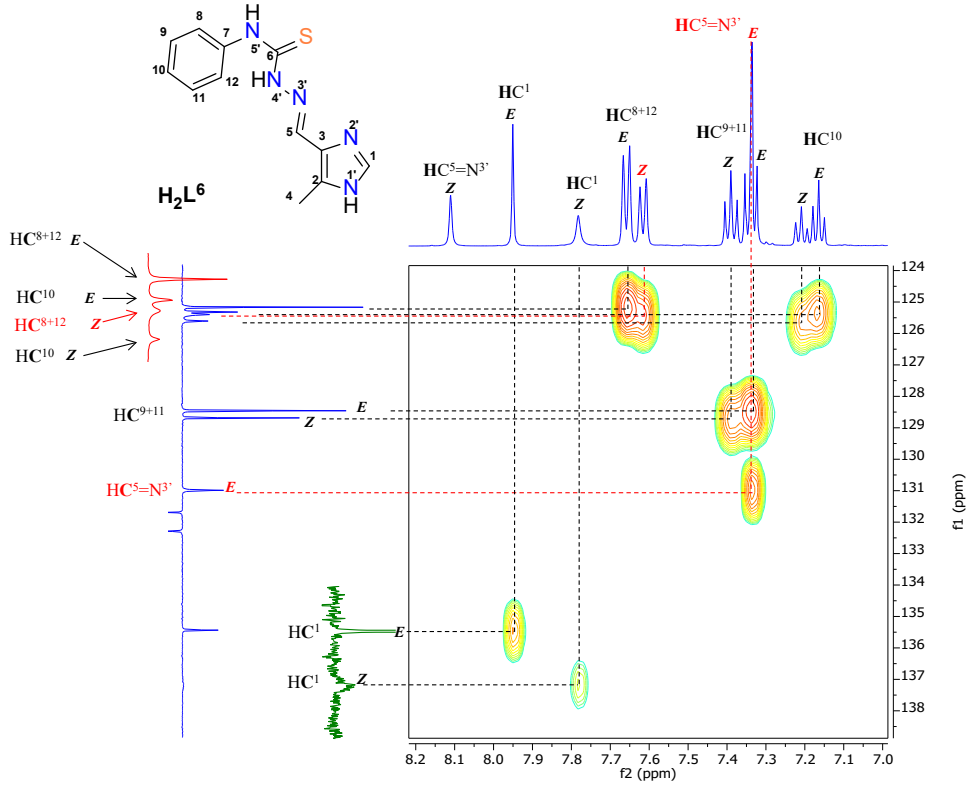

Fig. S6c $^{1}H,^{13}C$ HSQC NMR spectrum of **HL^{6}** in DMSO-d_6.

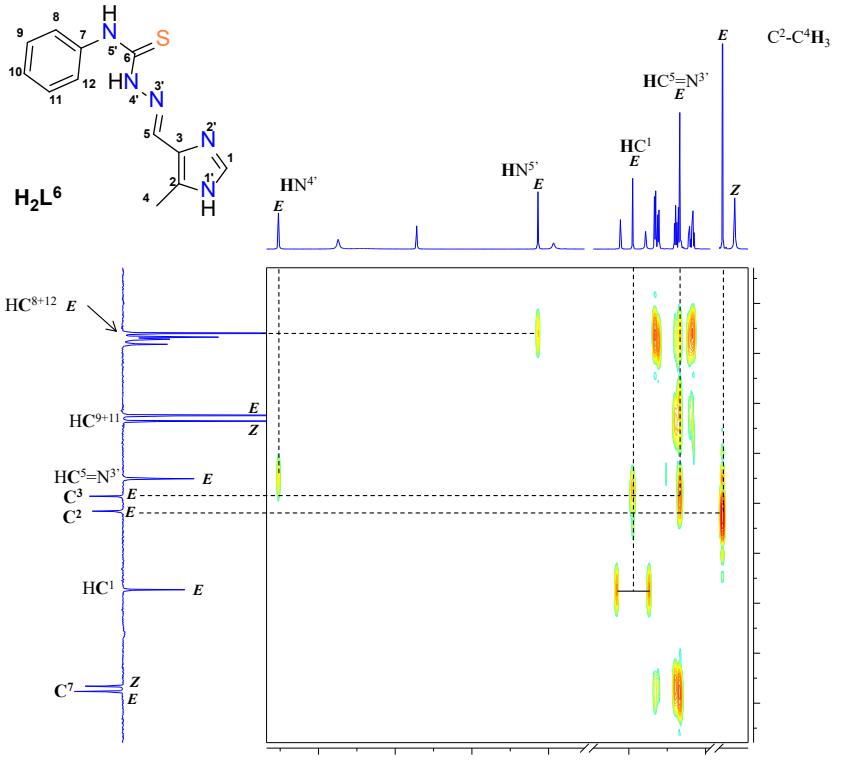

Fig. S6d $^{1}H,^{13}C$ HMQC NMR spectrum of **HL^{6}** in DMSO-d_6.

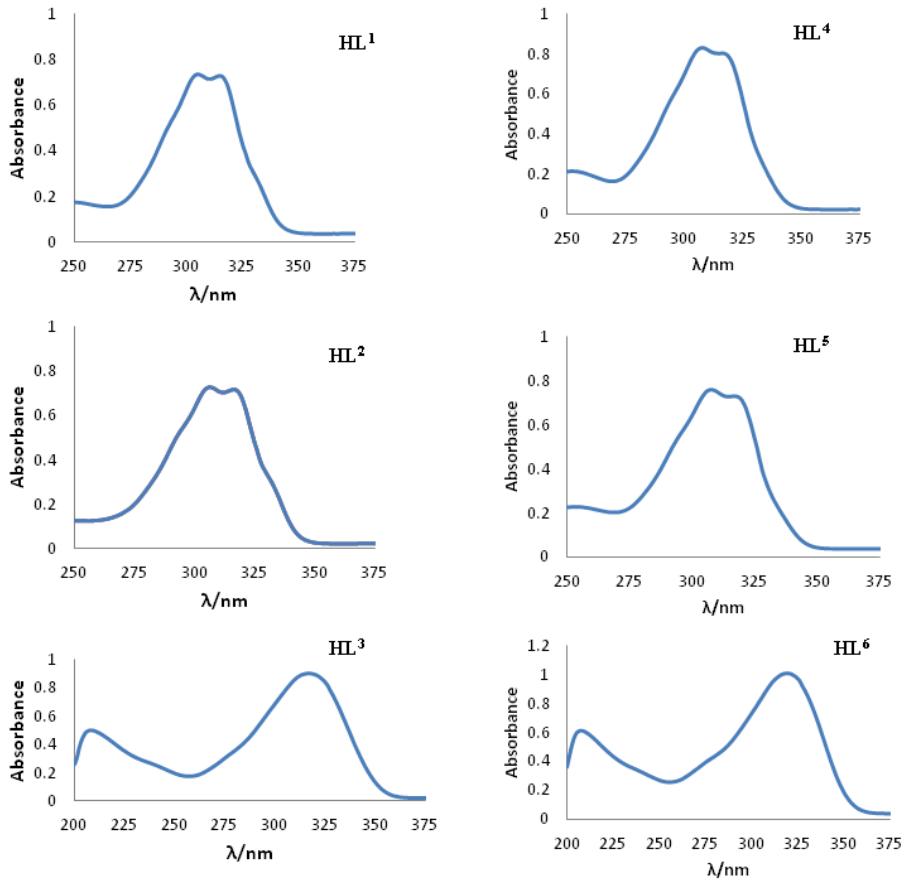

Fig. S7 UV-vis spectra of **HL^{1}**–**HL^{6}**.

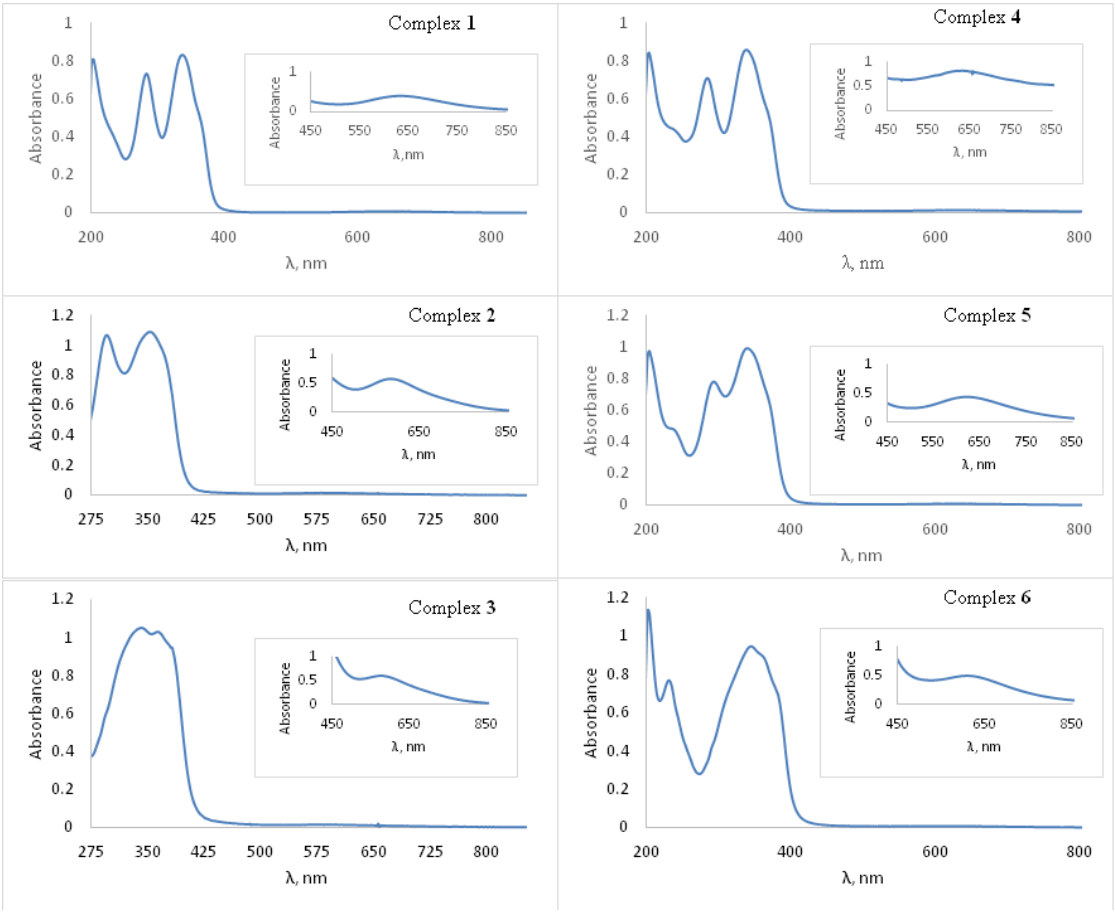

Fig. S8 UV-vis spectra of **1**−**6**.

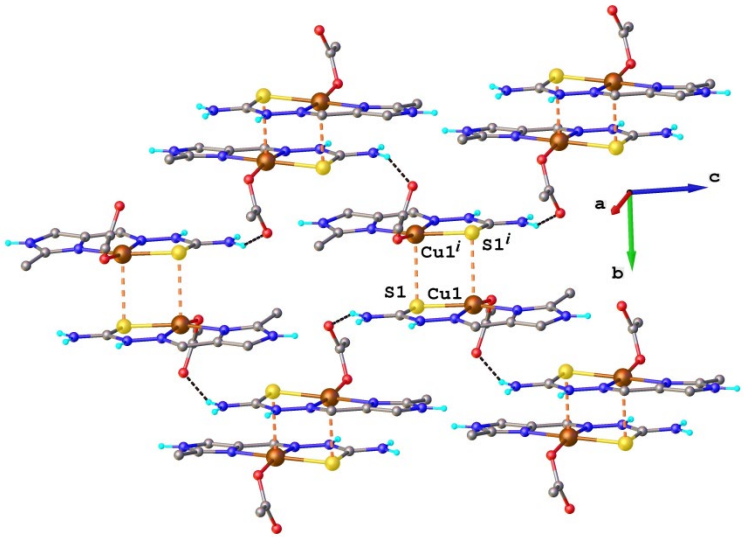

Fig. S9 View of the part of the crystal structure in **1**.

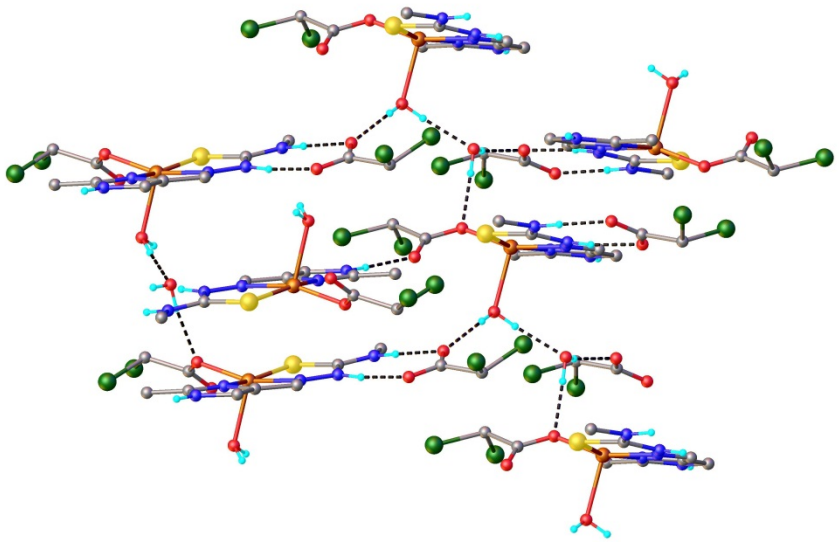

Fig. S10 View of the part of the crystal structure in **2**.

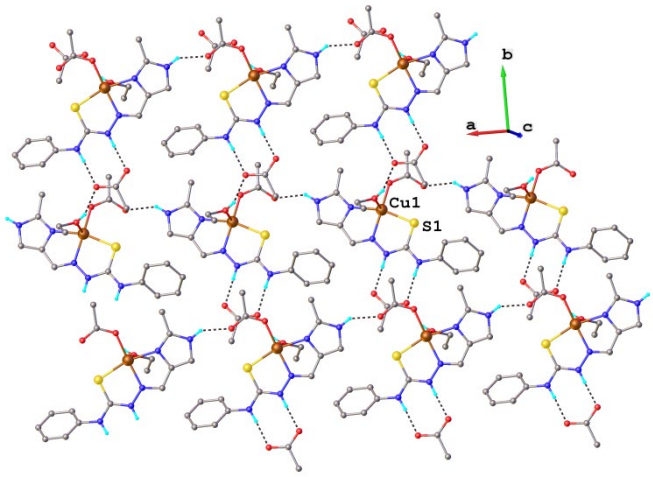

Fig. S11 View of the part of the crystal structure in **3**.

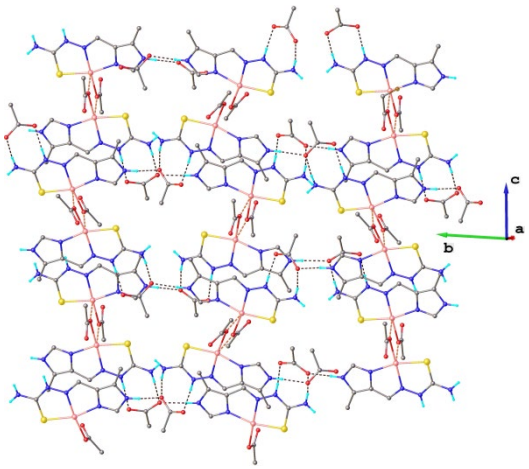

Fig. S12 View of the part of the crystal structure in **4**.

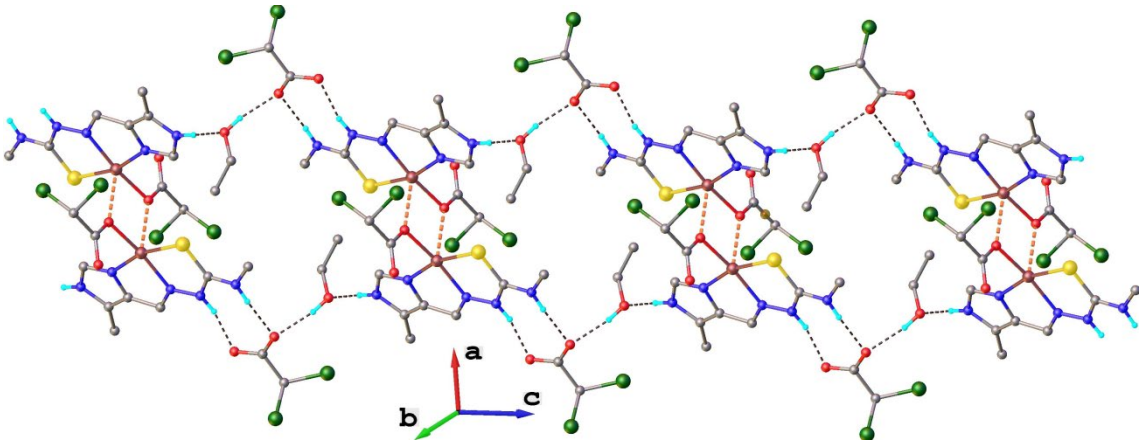

Fig. S13 H-bonded ribbon in the crystal structure of **5**.

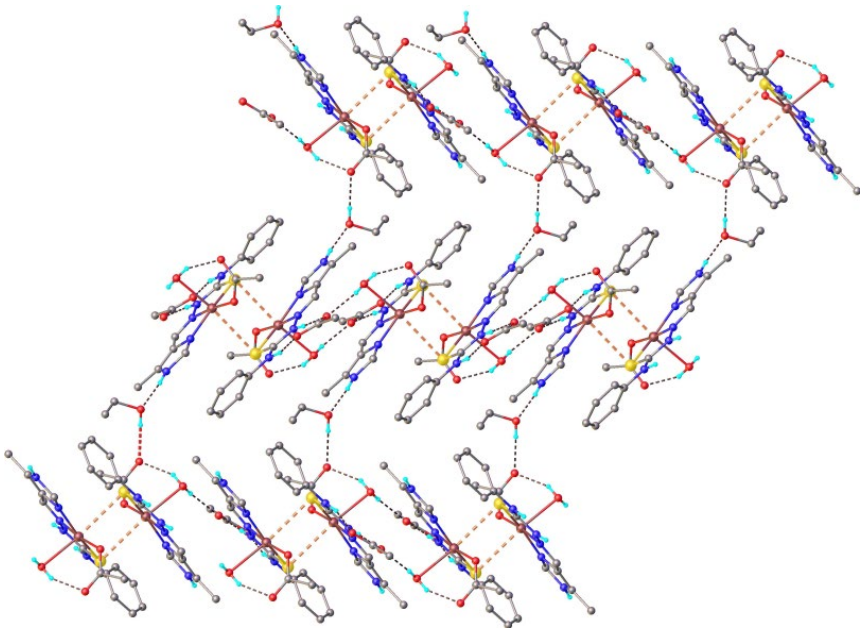

Fig. S14 View of the part of the crystal structure in **6**.

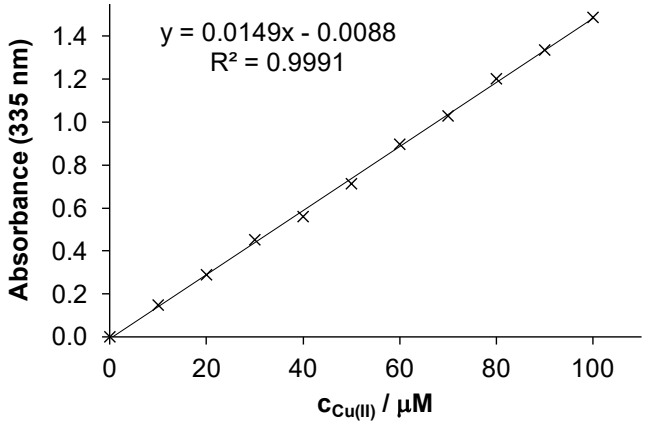

Fig. S15 Calibration curve for the Cu(II) – H_2L^1 system at λ = 335 nm. ($c_{(ligand}$ = 145 µM; I = 0.10 M KCl, pH = 4.07).

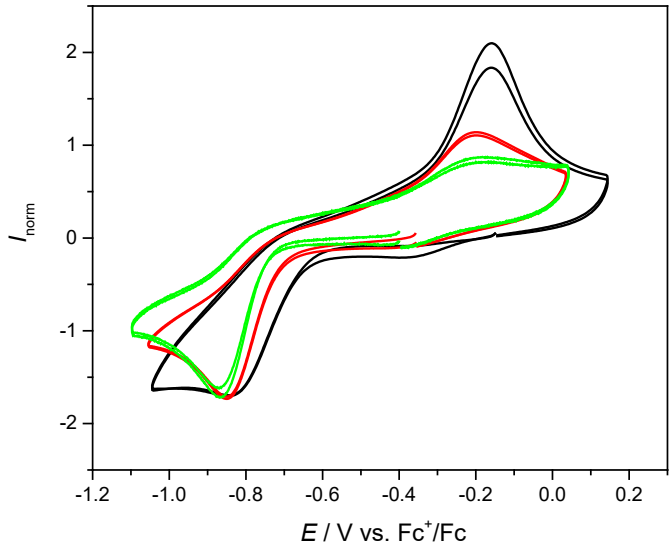

Fig. S16 The cyclic voltammograms of **1** (black trace), **2** (red trace), **3** (green trace) in DMSO/nBu$_4$NPF$_6$ at scan rate of 100 mV s^{-1}.

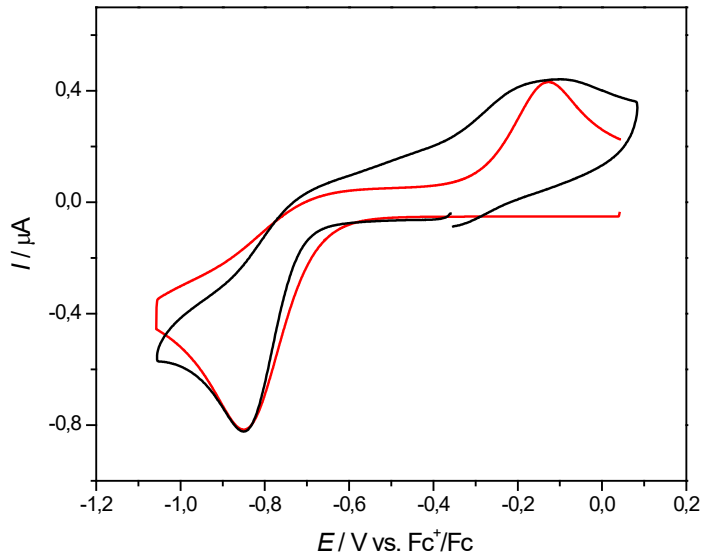

Fig. S17 Digital simulations of cyclic voltammograms for one-electron reduction of Cu(II) complex **6** (red lines) compared to the experimental traces in DMSO/nBu$_4$NPF$_6$ at scan rate of 100 mV s^{-1} (black lines). Formal redox potential $E^{o'}$ = –0.48 V vs. Fc^+/Fc, $k_s = 0.9 \times 10^{-5}$ cm s^{-1}, $\Gamma_{max} = 3.7 \times 10^{-9}$.

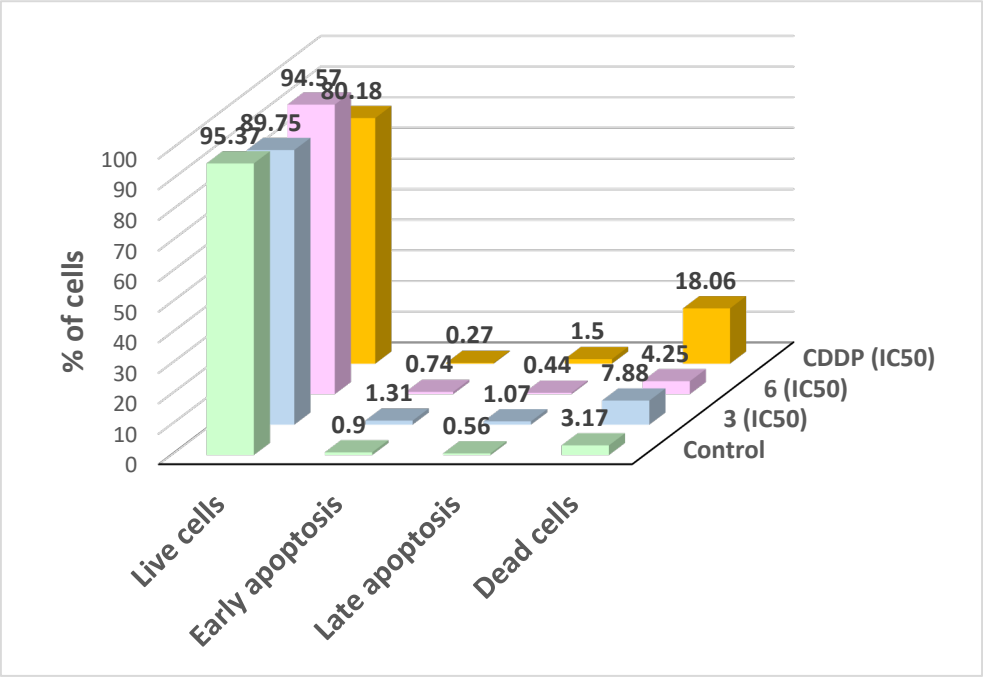

Fig. S18 Analysis of apoptotic potential of investigated complexes **3** and **6** in comparison to cisplatin (CDDP). The A549 cells were exposed for 24 h to investigated agents and apoptosis was determined by flow cytometry using Annexin V-FITC /PI staining.

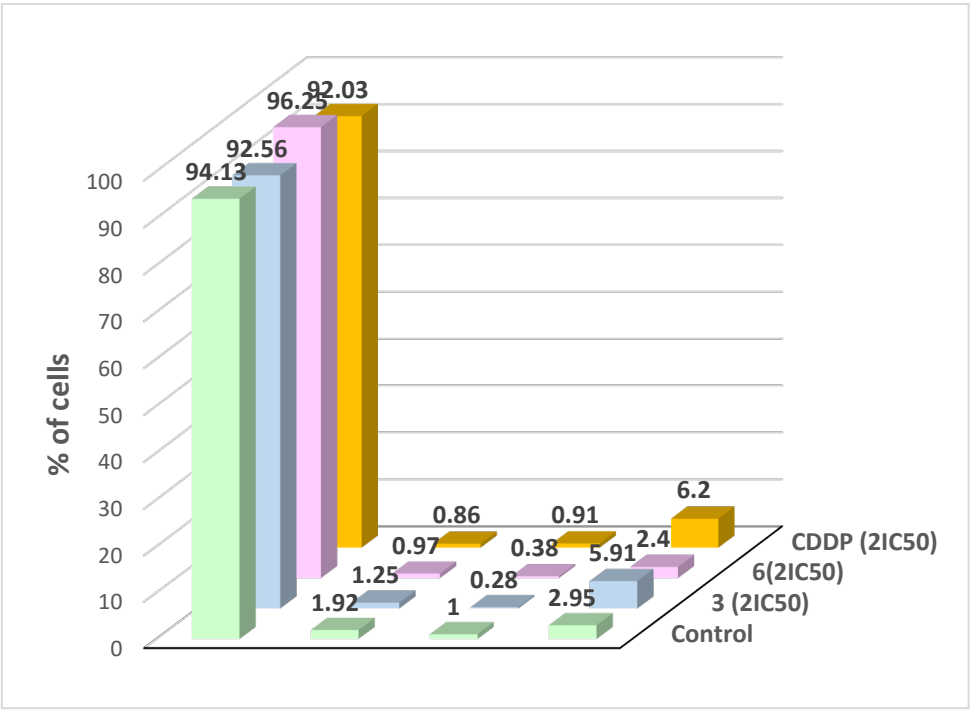

Fig. S19 Analysis of apoptotic potential of investigated complexes **3** and **6** in comparison to cisplatin. The A549 cells were exposed for 24 h to investigated agents and apoptosis was determined by flow cytometry using annexin V-FITC /PI staining.

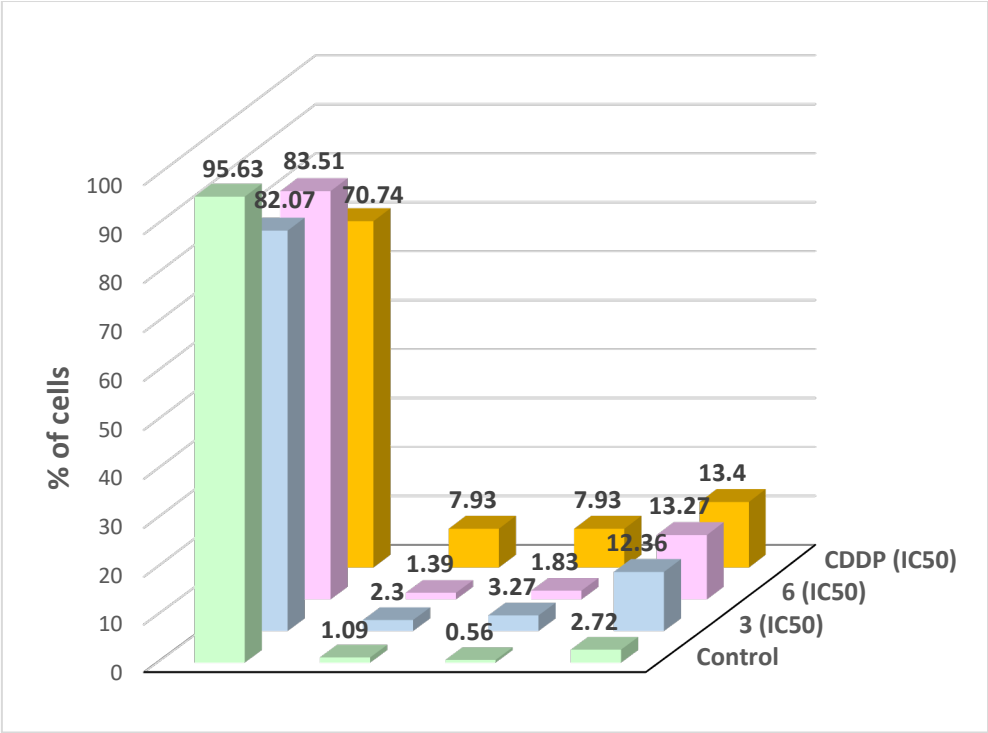

Fig. S20 Analysis of apoptotic potential of investigated complexes **3** and **6** in comparison to cisplatin. The A549 cells were exposed for 48 h to investigated agents and apoptosis was determined by flow cytometry using annexin V-FITC /PI staining.

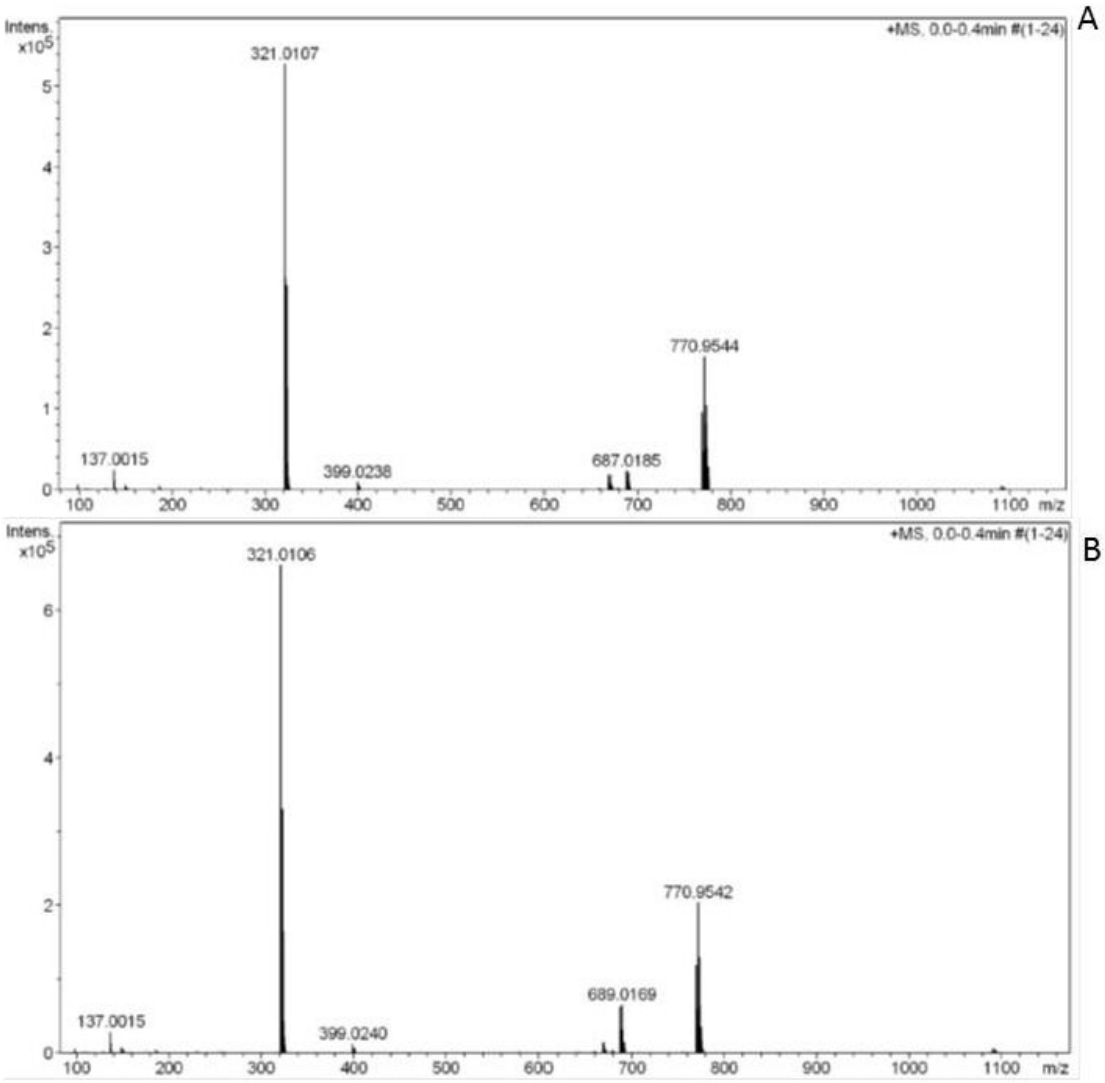

Fig. S21 ESI mass spectra (in positive mode) of a methanolic solution of **6** with an excess of DMSO measured immediately (A) and 24 h (B) after sample preparation. The *m*/*z* values of 321, 399 and 771 were attributed to $[Cu^{II}(L^6)]^+$, $[Cu^{II}(L^6)DMSO]^+$ and $[Cu^{II}_2(L^6)_2(CHCl_2CO_2)]^+$, respectively.

Table S1. Bond distances (Å) and angle (deg.) for **1**.

C1-C3	1.355(3)	C7-O2	1.229(2)
C1-C5	1.442(2)	C8-Cl1	1.779(2)
C1-N1	1.396(2)	C8-Cl2	1.765(2)
C2-C4	1.486(2)	Cu1-N1	2.0171(15)
C2-N1	1.320(2)	Cu1-N3	1.9778(15)
C2-N2	1.356(3)	Cu1-O1	1.9294(12)
C3-N2	1.370(2)	Cu1-S1	2.3186(5)
C5-N3	1.288(2)	N3-N4	1.367(2)
C6-N4	1.337(2)	C9-C10	1.536(3)
C6-N5	1.320(2)	C9-O3	1.252(2)
C6-S1	1.7335(18)	C9-O4	1.248(2)
C7-C8	1.536(2)	C10-Cl3	1.7745(17)
C7-O1	1.277(2)	C10-Cl4	1.780(5)

C3-C1-C5	134.27(18)	O1-Cu1-N1	100.69(6)
C3-C1-N1	109.52(16)	O1-Cu1-N3	169.70(6)
N1-C1-C5	116.17(16)	O1-Cu1-S1	94.48(4)
N1-C2-C4	126.26(17)	C1-N1-Cu1	111.28(11)
N1-C2-N2	110.20(16)	C2-N1-C1	105.99(15)
N2-C2-C4	123.52(16)	C2-N1-Cu1	142.74(13)
C1-C3-N2	105.79(17)	C2-N2-C3	108.49(15)
N3-C5-C1	113.72(17)	C5-N3-Cu1	118.29(12)
N4-C6-S1	121.39(13)	C5-N3-N4	120.43(16)
N5-C6-N4	117.36(16)	N4-N3-Cu1	121.21(12)
N5-C6-S1	121.24(14)	C6-N4-N3	117.13(15)
O1-C7-C8	111.68(16)	C7-O1-Cu1	119.32(11)
O2-C7-C8	120.49(17)	C6-S1-Cu1	96.31(6)
O2-C7-O1	127.74(16)	O3-C9-C10	113.05(16)
C7-C8-Cl1	106.02(12)	O4-C9-C10	119.74(15)
C7-C8-Cl2	112.49(14)	O4-C9-O3	127.17(17)
Cl2-C8-Cl1	110.36(11)	C9-C10-Cl3	112.33(13)
N1-Cu1-S1	163.60(4)	C9-C10-Cl4	107.0(4)
N3-Cu1-N1	80.33(6)	Cl3-C10-Cl4	106.5(4)
N3-Cu1-S1	83.63(4)		

Table S2. Bond distances (Å) and angle (deg.) for **2**.

Cu1-S1	2.2980(6)	N3-N4	1.367(2)
Cu1-O1	1.9820(14)	N3-C5	1.292(3)
Cu1-O1*w*	2.1874(14)	N4-C6	1.353(3)
Cu1-N1	2.0404(17)	N5-C6	1.319(3)
Cu1-N3	2.0070(17)	N5-C7	1.456(3)
Cl1-C9	1.782(2)	C1-C2	1.366(3)
Cl2-C9	1.765(2)	C1-C5	1.436(3)
S1-C6	1.712(2)	C3-C4	1.481(3)
O1-C8	1.279(2)	C8-C9	1.543(3)
O2-C8	1.227(2)	Cl3-C10	1.766(2)
N1-C1	1.392(3)	Cl4-C10	1.758(2)

N1-C3	1.328(3)	O3-C11	1.242(3)
N2-C2	1.368(3)	O4-C11	1.251(3)
N2-C3	1.354(3)	C10C11	1.550(3

O1-Cu1-S1	97.30(4)	C2-C1-N1	109.35(18)
O1-Cu1-O1*w*	91.47(6)	C2-C1-C5	133.5(2)
O1-Cu1-N1	96.22(6)	C1-C2-N2	105.56(18)
O1-Cu1-N3	160.86(6)	N1-C3-N2	109.79(18)
O1*w*-Cu1-S1	102.54(4)	N1-C3-C4	126.29(19)
N1-Cu1-S1	160.88(5)	N2-C3-C4	123.85(18)
N1-Cu1-O1*w*	90.55(6)	N3-C5-C1	113.62(19)
N3-Cu1-S1	83.22(5)	N4-C6-S1	121.04(16)
N3-Cu1-O1*w*	107.15(6)	N5-C6-S1	122.77(16)
N3-Cu1-N1	79.59(7)	N5-C6-N4	116.19(19)
C6-S1-Cu1	97.94(7)	O1-C8-C9	112.72(17)
C8-O1-Cu1	122.10(13)	O2-C8-O1	127.14(19)
C1-N1-Cu1	111.16(13)	O2-C8-C9	120.12(18)
C3-N1-Cu1	142.35(15)	Cl2-C9-Cl1	108.76(12)
C3-N1-C1	106.28(17)	C8-C9-Cl1	110.23(14)
C3-N2-C2	109.01(17)	C8-C9-Cl2	112.85(14)
N4-N3-Cu1	120.60(12)	Cl4-C10-Cl3	111.26(12)
C5-N3-Cu1	118.29(14)	C11-C10-Cl3	112.08(15)
C5-N3-N4	121.11(17)	C11-C10-Cl4	111.76(15)
C6-N4-N3	116.82(17)	O3-C11-O4	126.3(2)
C6-N5-C7	123.80(18)	O3-C11-C10	117.66(19)
N1-C1-C5	117.20(18)	O4-C11-C10	115.90(18

Table S3. Bond distances (Å) and angle (deg.) for **3**.

Cu1-S1	2.2939(9)	N5-C6	1.330(4)
Cu1-O1	1.935(2)	N5-C7	1.431(4)
Cu1-O3	2.263(2)	C1-C2	1.361(5)
Cu1-N1	2.028(3)	C1-C5	1.429(5)
Cu1-N3	1.993(3)	C3-C4	1.483(5)
Cl1-C14	1.770(3)	C7-C8	1.384(5)
Cl2-C14	1.774(3)	C7-C12	1.387(5)
S1-C6	1.713(3)	C8-C9	1.386(5)
O1-C13	1.260(4)	C9-C10	1.369(6)
O2-C13	1.264(6)	C10-C11	1.387(6)
O2X-C13	1.270(6)	C11-C12	1.386(5)
O3-C17	1.410(5)	C13-C14	1.532(5)
N1-C1	1.394(4)	C17-C18	1.493(6)
N1-C3	1.329(4)	Cl3-C16	1.776(4)
N2-C2	1.372(5)	Cl4-C16	1.758(4)
N2-C3	1.350(4)	O4-C15	1.244(4)
N3-N4	1.372(4)	O5-C15	1.262(4)
N3-C5	1.289(4)	C15-C16	1.536(5)
N4-C6	1.351(4)		

O1-Cu1-S1	100.00(7)	N2-C3-C4	124.3(3)
O1-Cu1-O3	97.01(9)	N3-C5-C1	114.0(3)
O1-Cu1-N1	95.17(10)	N4-C6-S1	121.2(2)

O1-Cu1-N3	167.46(11)	N5-C6-S1	123.2(2)
O3-Cu1-S1	96.12(7)	N5-C6-N4	115.5(3)
N1-Cu1-S1	163.21(8)	C8-C7-N5	118.2(3)
N1-Cu1-O3	89.07(10)	C8-C7-C12	120.5(3)
N3-Cu1-S1	83.68(8)	C12-C7-N5	121.1(3)
N3-Cu1-O3	94.49(10)	C7-C8-C9	119.6(4)
N3-Cu1-N1	80.00(11)	C10-C9-C8	120.4(4)
C6-S1-Cu1	97.39(12)	C9-C10-C11	119.9(4)
C13-O1-Cu1	129.3(2)	C12-C11-C10	120.5(4)
C17-O3-Cu1	131.4(2)	C11-C12-C7	119.0(3)
C1-N1-Cu1	110.7(2)	O1-C13-O2	125.0(5)
C3-N1-Cu1	140.8(2)	O1-C13-O2X	125.3(5)
C3-N1-C1	106.4(3)	O1-C13-C14	113.2(3)
C3-N2-C2	109.3(3)	O2-C13-C14	117.8(4)
N4-N3-Cu1	120.5(2)	Cl1-C14-Cl2	109.07(17)
C5-N3-Cu1	117.9(2)	C13-C14-Cl1	112.9(2)
C5-N3-N4	121.5(3)	C13-C14-Cl2	109.4(2)
C6-N4-N3	116.7(3)	O3-C17-C18	113.6(4)
C6-N5-C7	125.1(3)	O4-C15-O5	126.5(3)
N1-C1-C5	116.8(3)	O4-C15-C16	119.1(3)
C2-C1-N1	109.4(3)	O5-C15-C16	114.4(3)
C2-C1-C5	133.7(3)	Cl4-C16-Cl3	109.45(19)
C1-C2-N2	105.4(3)	C15-C16-Cl3	107.6(2)
N1-C3-N2	109.5(3)	C15-C16-Cl4	113.2(2)
N1-C3-C4	126.2(3)		

Table S4. Bond distances (Å) and angle (deg.) for **4**.

Cu1A-S1A	2.2862(6)	Cu1B-S1B	2.2861(5)
Cu1A-O1A	1.9549(13)	Cu1B-O1B	1.9586(13)
Cu1A-N1A	1.9951(16)	Cu1B-N1B	1.9921(16)
Cu1A-N3A	1.9739(16)	Cu1B-N3B	1.9740(16)
Cl1A-C8A	1.783(2)	Cl1B-C8B	1.785(2)
Cl2A-C8A	1.779(2)	Cl2B-C8B	1.775(2)
Cl3A-C10A	1.776(2)	Cl3B-C10B	1.771(2)
Cl4A-C10A	1.777(2)	Cl4B-C10B	1.779(2)
S1A-C6A	1.711(2)	S1B-C6B	1.720(2)
O1A-C7A	1.283(2)	O1B-C7B	1.283(2)
O2A-C7A	1.227(2)	O2B-C7B	1.228(2)
O3A-C9A	1.249(2)	O3B-C9B	1.241(2)
O4A-C9A	1.247(2)	O4B-C9B	1.259(3)
N1A-C1A	1.394(2)	N1B-C1B	1.392(2)
N1A-C4A	1.313(3)	N1B-C4B	1.313(2)
N2A-C2A	1.378(3)	N2B-C2B	1.378(3)
N2A-C4A	1.350(3)	N2B-C4B	1.350(3)
N3A-N4A	1.370(2)	N3B-N4B	1.370(2)
N3A-C5A	1.290(3)	N3B-C5B	1.292(2)
N4A-C6A	1.341(3)	N4B-C6B	1.336(3)
N5A-C6A	1.330(3)	N5B-C6B	1.326(3)
C1A-C2A	1.374(3)	C1B-C2B	1.374(3)
C1A-C5A	1.436(3)	C1B-C5B	1.445(3)
C2A-C3A	1.485(3)	C2B-C3B	1.486(3)
C7A-C8A	1.527(3)	C7B-C8B	1.534(3)

C9A-C10A	1.538(3)	C9B-C10B	1.542(3)

O1A-Cu1A-S1A	94.93(4)	O1B-Cu1B-S1B	102.12(4)
O1A-Cu1A-N1A	99.59(6)	O1B-Cu1B-N1B	92.65(6)
O1A-Cu1A-N3A	176.95(6)	O1B-Cu1B-N3B	173.00(6)
O1A-C7A-C8A	117.42(18)	O1B-C7B-C8B	117.86(17)
O2A-C7A-O1A	125.59(18)	O2B-C7B-O1B	125.40(18)
O2A-C7A-C8A	116.91(17)	O2B-C7B-C8B	116.73(17)
O3A-C9A-C10A	114.00(17)	O3B-C9B-C10B	118.43(18)
O4A-C9A-O3A	127.58(19)	O3B-C9B-O4B	127.26(19)
O4A-C9A-C10A	118.38(17)	O4B-C9B-C10B	114.24(17)
N1A-Cu1A-S1A	164.70(5)	N1B-Cu1B-S1B	163.17(5)
N3A-Cu1A-S1A	84.73(5)	N3B-Cu1B-S1B	84.62(5)
N3A-Cu1A-N1A	80.52(6)	N3B-Cu1B-N1B	80.41(6)
C6A-S1A-Cu1A	96.23(7)	C6B-S1B-Cu1B	96.22(7)
C7A-O1A-Cu1A	108.58(12)	C7B-O1B-Cu1B	110.22(12)
C1A-N1A-Cu1A	111.19(12)	C1B-N1B-Cu1B	111.78(12)
C4A-N1A-Cu1A	141.23(14)	C4B-N1B-Cu1B	140.84(14)
C4A-N1A-C1A	106.04(16)	C4B-N1B-C1B	106.41(16)
C4A-N2A-C2A	108.54(16)	C4B-N2B-C2B	108.79(16)
N4A-N3A-Cu1A	120.06(12)	N4B-N3B-Cu1B	120.14(12)
C5A-N3A-Cu1A	118.00(13)	C5B-N3B-Cu1B	118.17(13)
C5A-N3A-N4A	121.90(16)	C5B-N3B-N4B	121.69(16)
C6A-N4A-N3A	116.50(16)	C6B-N4B-N3B	116.72(16)
C7A-C8A-Cl1A	108.33(15)	C7B-C8B-Cl1B	112.05(13)
C7A-C8A-Cl2A	112.33(15)	C7B-C8B-Cl2B	110.13(14)
C9A-C10A-Cl3A	111.25(14)	C9B-C10B-Cl3B	112.52(14)
C9A-C10A-Cl4A	107.40(14)	C9B-C10B-Cl4B	110.40(15)
N1A-C1A-C5A	116.34(16)	N1B-C1B-C5B	115.78(16)
C2A-C1A-N1A	109.45(17)	C2B-C1B-N1B	109.31(16)
C2A-C1A-C5A	134.11(18)	C2B-C1B-C5B	134.91(18)
N2A-C2A-C3A	123.64(18)	N2B-C2B-C3B	122.49(17)
C1A-C2A-N2A	104.98(17)	C1B-C2B-N2B	104.90(16)
C1A-C2A-C3A	131.29(18)	C1B-C2B-C3B	132.57(18)
N1A-C4A-N2A	110.99(18)	N1B-C4B-N2B	110.59(17)
N3A-C5A-C1A	113.25(17)	N3B-C5B-C1B	113.14(17)
N4A-C6A-S1A	122.47(15)	N4B-C6B-S1B	122.14(15)
N5A-C6A-S1A	120.94(15)	N5B-C6B-S1B	121.10(15)
N5A-C6A-N4A	116.58(18)	N5B-C6B-N4B	116.76(18)
Cl2A-C8A-Cl1A	110.48(12)	Cl2B-C8B-Cl1B	110.45(11)
Cl3A-C10A-Cl4A	110.27(11)	Cl3B-C10B-Cl4B	110.76(11)

Table S5. Bond distances (Å) and angle (deg.) for **5**.

Cu1-S1	2.2903(4)	N4-C6	1.3524(18)
Cu1-O2	1.9670(9)	N5-C6	1.3196(18)
Cu1-N1	1.9923(11)	N5-C7	1.4554(18)
Cu1-N3	1.9863(11)	C1-C2	1.3690(19)
Cl1-C9	1.7873(14)	C1-C5	1.4389(19)
Cl2-C9	1.7706(14)	C2-C3	1.4870(19)
S1-C6	1.7165(13)	C8-C9	1.5371(18)

O1-C8	1.2274(17)	Cl3-C11	1.7719(14)
O2-C8	1.2784(17)	Cl4-C11	1.7892(14)
N1-C1	1.3944(17)	O3-C10	1.2506(17)
N1-C4	1.3114(18)	O4-C10	1.2442(17)
N2-C2	1.3754(18)	C10-C11	1.5423(18)
N2-C4	1.3522(18)	O5-C12	1.4293(18)
N3-N4	1.3666(15)	C12-C13	1.500(2)
N3-C5	1.2881(18)		

O2-Cu1-S1	95.73(3)	C1-C2-N2	105.07(12)
O2-Cu1-N1	98.90(4)	C1-C2-C3	131.89(13)
O2-Cu1-N3	171.15(4)	N1-C4-N2	110.72(12)
N1-Cu1-S1	164.29(3)	N3-C5-C1	113.21(12)
N3-Cu1-S1	84.31(3)	N4-C6-S1	121.54(10)
N3-Cu1-N1	80.35(5)	N5-C6-S1	122.34(10)
C6-S1-Cu1	96.88(5)	N5-C6-N4	116.12(12)
C8-O2-Cu1	110.61(8)	O1-C8-O2	126.60(12)
C1-N1-Cu1	111.77(9)	O1-C8-C9	116.45(12)
C4-N1-Cu1	141.42(10)	O2-C8-C9	116.92(11)
C4-N1-C1	106.12(11)	Cl2-C9-Cl1	110.78(7)
C4-N2-C2	108.61(11)	C8-C9-Cl1	107.84(9)
N4-N3-Cu1	120.29(8)	C8-C9-Cl2	112.55(9)
C5-N3-Cu1	118.11(9)	O3-C10-C11	117.99(12)
C5-N3-N4	121.57(11)	O4-C10-O3	127.73(13)
C6-N4-N3	116.84(11)	O4-C10-C11	114.23(12)
C6-N5-C7	124.17(12)	Cl3-C11-Cl4	110.47(7)
N1-C1-C5	116.31(11)	C10-C11-Cl3	112.24(9)
C2-C1-N1	109.48(12)	C10-C11-Cl4	106.86(9)
C2-C1-C5	134.16(12)	O5-C12C13	108.55(13)
N2-C2-C3	122.95(12)		

Table S6. Bond distances (Å) and angle (deg.) for **6**.

Cu1-S1	2.3075(5)	N5-C7	1.425(3)
Cu1-O1	1.9474(13)	C1-C2	1.367(3)
Cu1-O1w	2.4381(14)	C1-C5	1.434(3)
Cu1-N1	2.0055(16)	C2-C3	1.492(3)
Cu1-N3	1.9718(16)	C7-C8	1.392(3)
Cl1-C14	1.777(2)	C7-C12	1.389(3)
Cl2-C14	1.769(2)	C8-C9	1.386(3)
S1-C6	1.717(2)	C9-C10	1.384(3)
O1-C13	1.267(2)	C10-C11	1.383(3)
O2-C13	1.234(2)	C11-C12	1.386(3)
N1-C1	1.392(3)	C13-C14	1.530(3)
N1-C4	1.314(3)	O5-C17	1.428(3)
N2-C2	1.371(3)	C17-C18	1.493(3)
N2-C4	1.351(3)	Cl3-C16	1.784(2)
N3-N4	1.364(2)	Cl4-C16	1.772(2)
N3-C5	1.290(3)	O3-C15	1.247(2)
N4-C6	1.348(3)	O4-C15	1.246(2)
N5-C6	1.336(3)	C15-C16	1.544(3)

S1-Cu1-O1W	99.42(4)	N1-C4-N2	110.93(18)
O1-Cu1-S1	96.12(4)	N3-C5-C1	113.87(17)
O1-Cu1-O1W	94.36(5)	N4-C6-S1	120.65(15)
O1-Cu1-N1	98.51(6)	N5-C6-S1	125.31(15)
O1-Cu1-N3	173.62(6)	N5-C6-N4	114.04(17)
N1-Cu1-S1	162.86(5)	C8-C7-N5	115.92(18)
N1-Cu1-O1W	88.34(6)	C12-C7-N5	123.88(18)
N3-Cu1-S1	83.62(5)	C12-C7-C8	120.09(19)
N3-Cu1-O1W	91.96(6)	C9-C8-C7	119.7(2)
N3-Cu1-N1	80.85(7)	C10-C9-C8	120.4(2)
C6-S1-Cu1	97.11(7)	C11-C10-C9	119.6(2)
C13-O1-Cu1	123.55(12)	C10-C11-C12	120.7(2)
C1-N1-Cu1	110.92(12)	C11-C12-C7	119.5(2)
C4-N1-Cu1	143.49(14)	O1-C13-C14	112.25(17)
C4-N1-C1	105.54(16)	O2-C13-O1	128.11(18)
C4-N2-C2	108.63(17)	O2-C13-C14	119.61(17)
N4-N3-Cu1	120.92(12)	Cl2-C14-Cl1	109.48(11)
C5-N3-Cu1	117.67(13)	C13-C14-Cl1	106.86(14)
C5-N3-N4	121.39(16)	C13-C14-Cl2	112.46(15)
C6-N4-N3	117.31(16)	O5-C17-C18	112.65(19)
C6-N5-C7	129.36(17)	O3-C15-C16	119.08(18)
N1-C1-C5	116.59(17)	O4-C15-O3	126.71(19)
C2-C1-N1	109.98(17)	O4-C15-C16	114.21(17)
C2-C1-C5	133.43(19)	Cl4-C16-Cl3	109.94(11)
N2-C2-C3	123.39(18)	C15-C16-Cl3	108.41(14)
C1-C2-N2	104.92(17)	C15-C16-Cl4	113.25(14)
C1-C2-C3	131.65(19)		

Table S7. Bond distances (Å) and angle (deg.) for Cu(II) atom.

	3	**6**
Cu1-S1	2.2939(9)	2.3075(5)
Cu1-O1	1.935(2)	1.9474(13)
Cu1-O3(O1*w*)*	2.263(2)	2.4381(14)
Cu1-N1	2.028(3)	2.0055(16)
Cu1-N3	1.993(3)	1.9718(16)

O1-Cu1-S1	100.00(7)	96.12(4)
O1-Cu1-O3(O1*w*)*	97.01(9)	94.36(5)
O1-Cu1-N1	95.17(10)	98.51(6)
O1-Cu1-N3	167.46(11)	173.62(6)
O3-Cu1-S1	96.12(7)	99.42(4)
N1-Cu1-S1	163.21(8)	162.86(5)
N1-Cu1-O3	89.07(10)	88.34(6)
N3-Cu1-S1	83.68(8)	83.62(5)
N3-Cu1-O3	94.49(10)	91.96(6)
N3-Cu1-N1	80.00(11)	80.85(7)

*complex **6**

	1	2	4		5
			Molecule A	Molecule B	
Cu1-N1	2.0171(15)	2.022(2)	1.9951(16)	1.9921(16)	1.9923(11)
Cu1-N3	1.9778(15)	1.978(2)	1.9739(16)	1.9740(16)	1.9863(11)
Cu1-O1	1.9294(12)	-	1.9549(13)	1.9586(13)	1.9670(9)
Cu1-S1	2.3186(5)	2.2877(7)	2.2862(6)	2.2861(5)	2.2903(4)
Cu1-Cl1	-	2.2244(7)	-	-	-

	1	2	4		5
			Molecule A	Molecule B	
O1-Cu1-N1	100.69(6)	-	99.59(6)	92.65(6)	98.90(4)
O1-Cu1-N3	169.70(6)	-	176.95(6)	173.00(6)	171.15(4)
O1-Cu1-S1	94.48(4)	-	94.93(4)	102.12(4)	95.73(3)
N1-Cu1-S1	163.60(4)	161.55(6)	164.70(5)	163.17(5)	164.29(3)
N3-Cu1-N1	80.33(6)	80.56(8)	80.52(6)	80.41(6)	80.35(5)
N3-Cu1-S1	83.63(4)	83.81(6)	84.73(5)	84.62(5)	84.31(3)
Cl1-Cu1-S1	-	93.89(2)	-	-	-
N1-Cu1-Cl1	-	102.09(6)	-	-	-
N3-Cu1-Cl1	-	176.74(6)	-	-	-

Table S8. Formal redox potential, heterogeneous rate constant and surface excess values for all studied complexes obtained from simulation.

	E / V vs. Fc^+/Fc	E / V vs. NHE	k_s / 10^{-5} cm s^{-1}	Γ_{max} / 10^{-8}
1	-0.52	0.12	2.3	8.80
2	-0.52	0.12	2.0	1.30
3	-0.50	0.14	1.4	0.25
4	-0.51	0.13	2.9	9.00
5	-0.51	0.13	5.0	17.00
6	-0.48	0.16	0.9	0.37