

Ternary Copper (II) complexes of 1,10-phenanthroline and coumarin-based oxylacetates as pro-apoptotic UPR CHOP inducer

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SUPPLEMENTARY INFORMATION

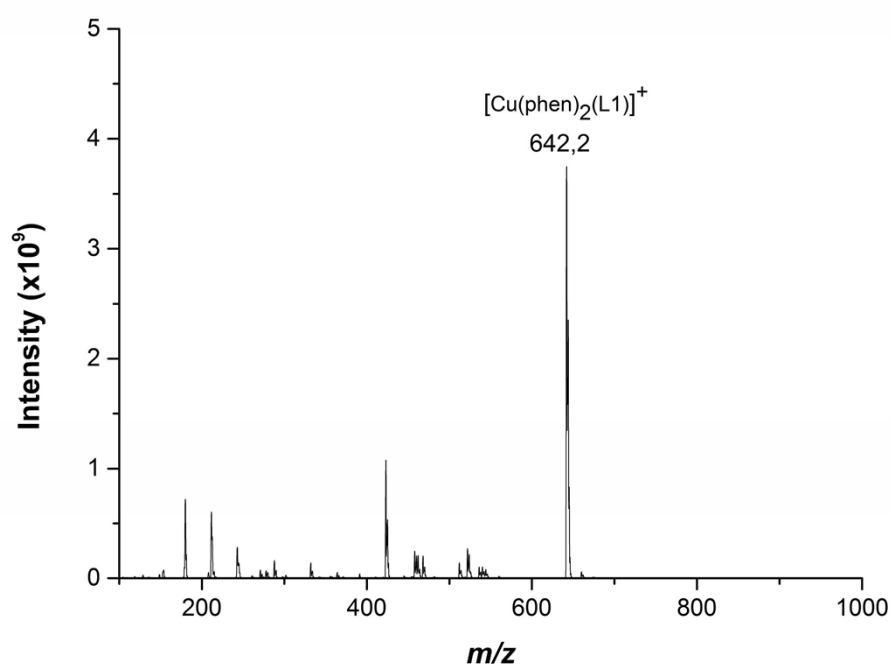


Figure S1. ESI mass spectrum of D1, $[\text{Cu}(\text{phen})_2(\text{L}^1)](\text{ClO}_4)$.

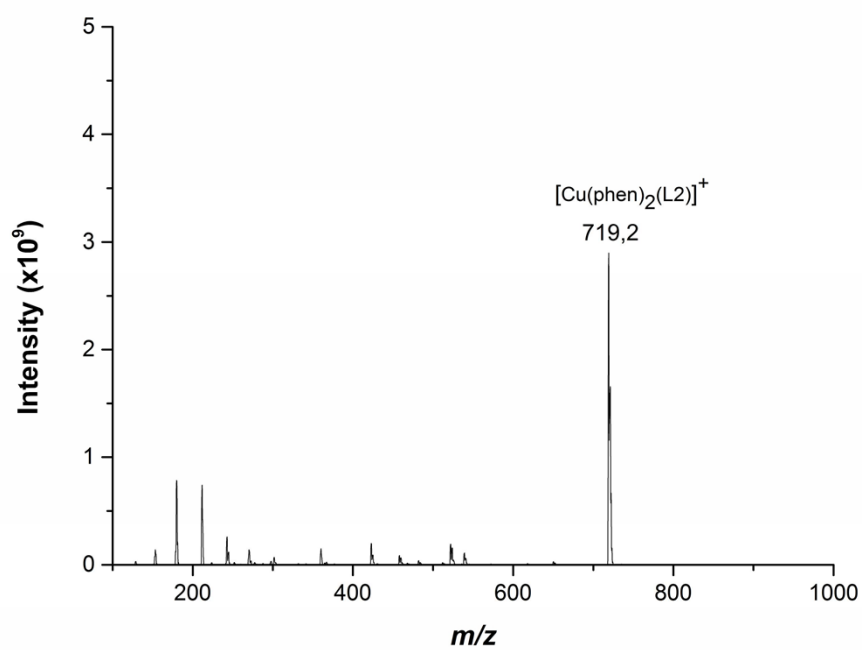


Figure S2. ESI mass spectrum of D2, $[\text{Cu}(\text{phen})_2(\text{L}^2)](\text{ClO}_4)$.

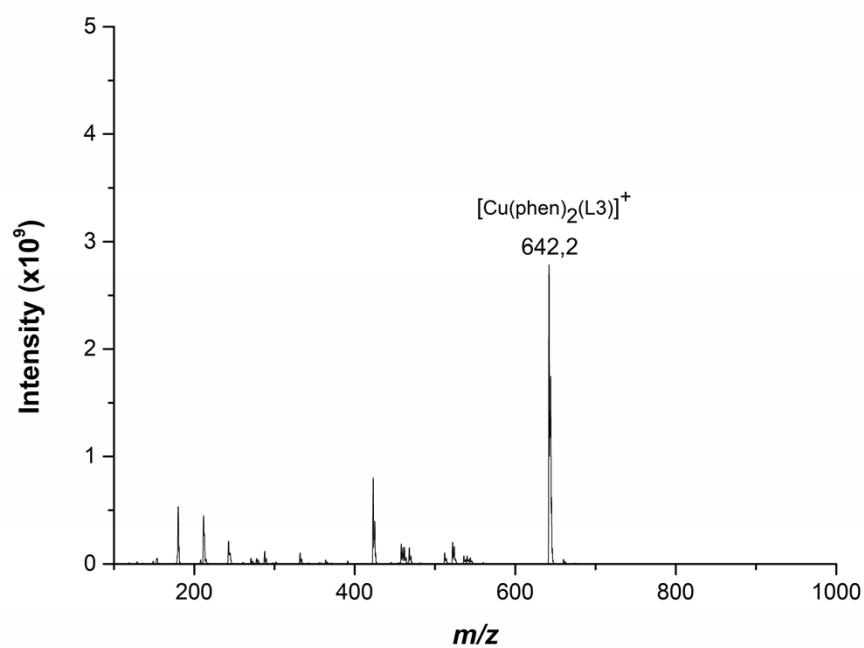


Figure S3. ESI mass spectrum of D3, $[\text{Cu}(\text{phen})_2(\text{L}^3)](\text{ClO}_4)$.

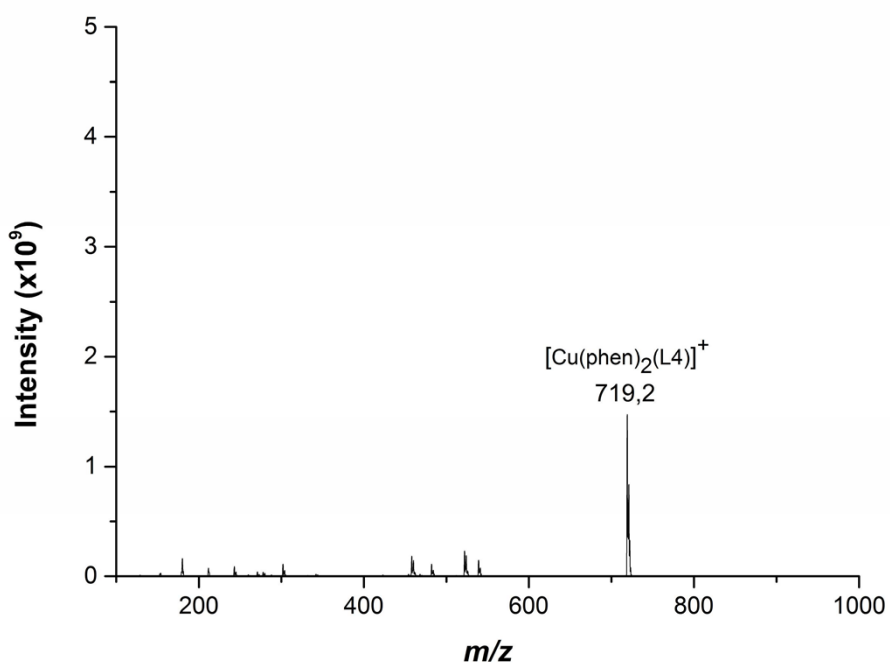


Figure S4. ESI mass spectrum of D4, $[\text{Cu}(\text{phen})_2(\text{L}^4)](\text{ClO}_4)$.

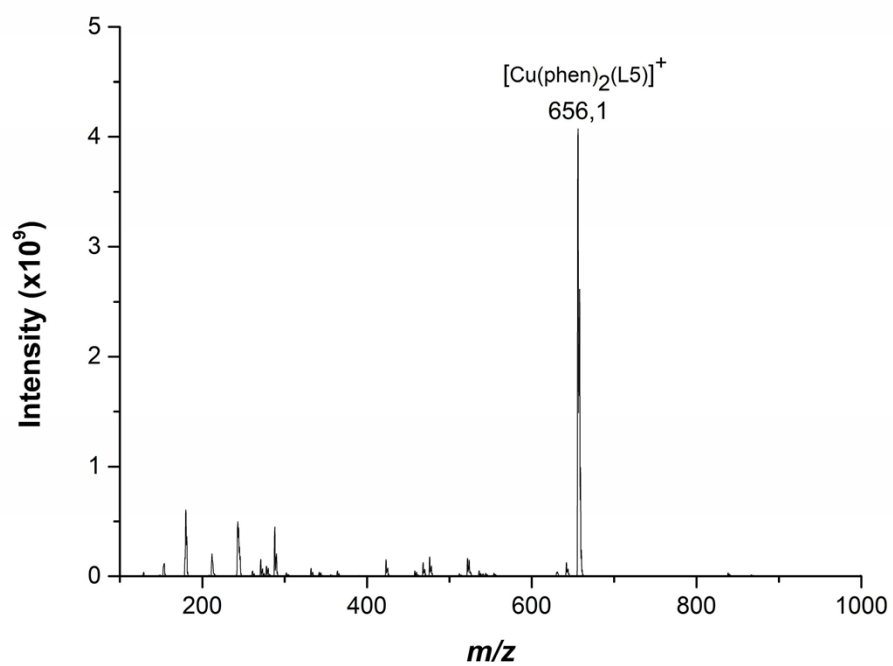


Figure S5. ESI mass spectrum of D5, $[\text{Cu}(\text{phen})_2(\text{L}^5)](\text{ClO}_4)$.

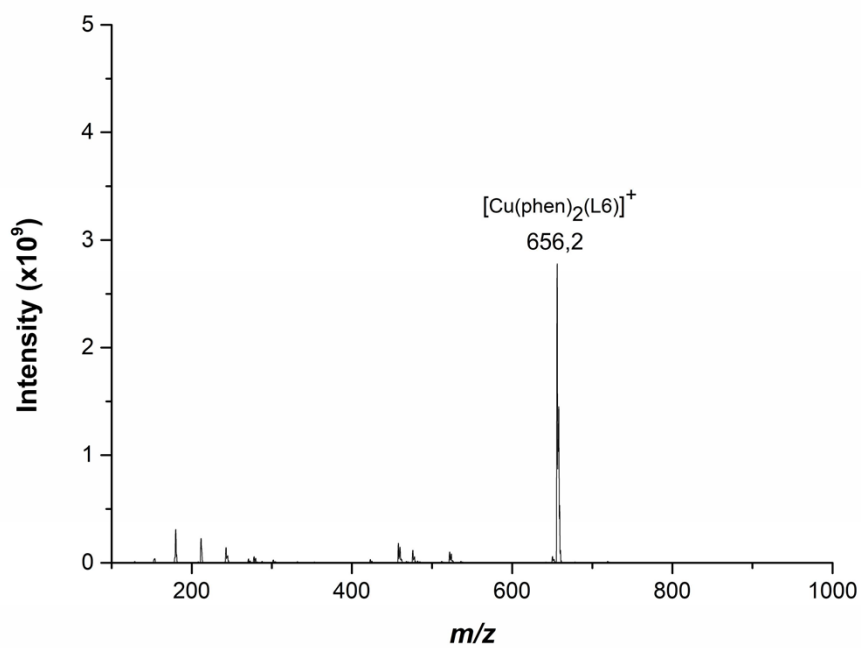


Figure S6. ESI mass spectrum of D6, $[\text{Cu}(\text{phen})_2(\text{L}^6)](\text{ClO}_4)$.

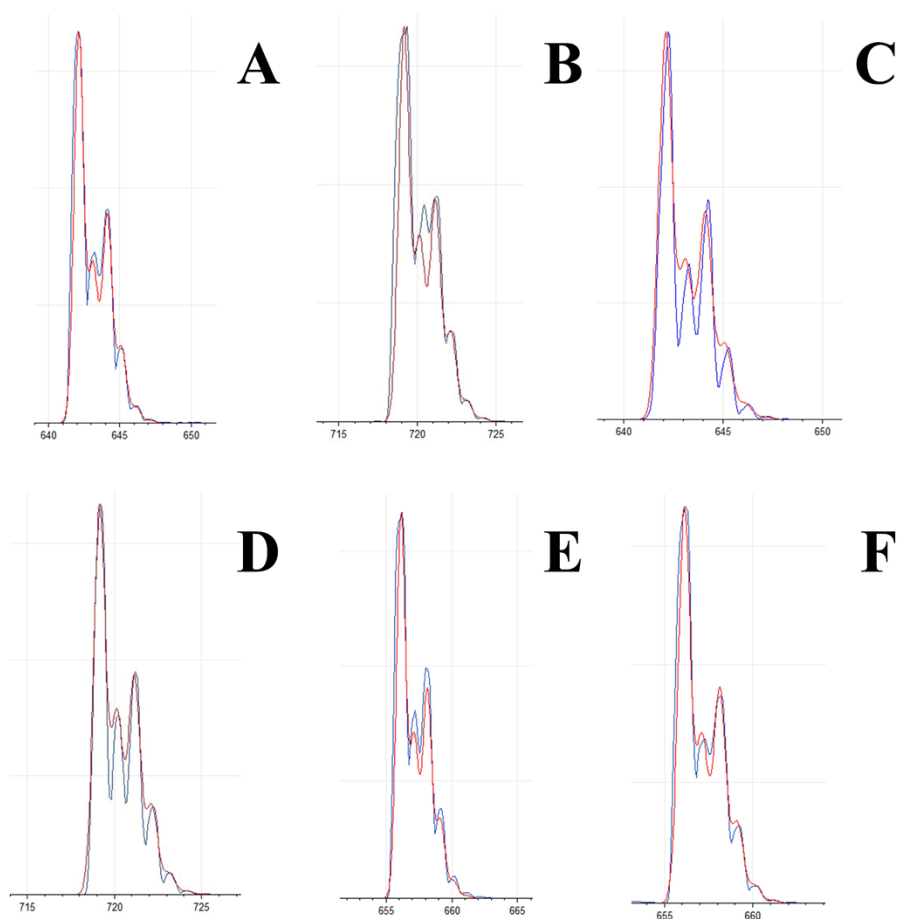


Figure S7. Experimental (blue line) and calculated (red line) isotopic patterns of m/z (A) 642 $[\text{Cu}(\text{phen})_2(\text{L}^1)]^+$, (B) 719 $[\text{Cu}(\text{phen})_2(\text{L}^2)]^+$, (C) 642 $[\text{Cu}(\text{phen})_2(\text{L}^3)]^+$ (D) 642 $[\text{Cu}(\text{phen})_2(\text{L}^4)]^+$, (E) 656 $[\text{Cu}(\text{phen})_2(\text{L}^5)]^+$, (F) 656 $[\text{Cu}(\text{phen})_2(\text{L}^6)]^+$.

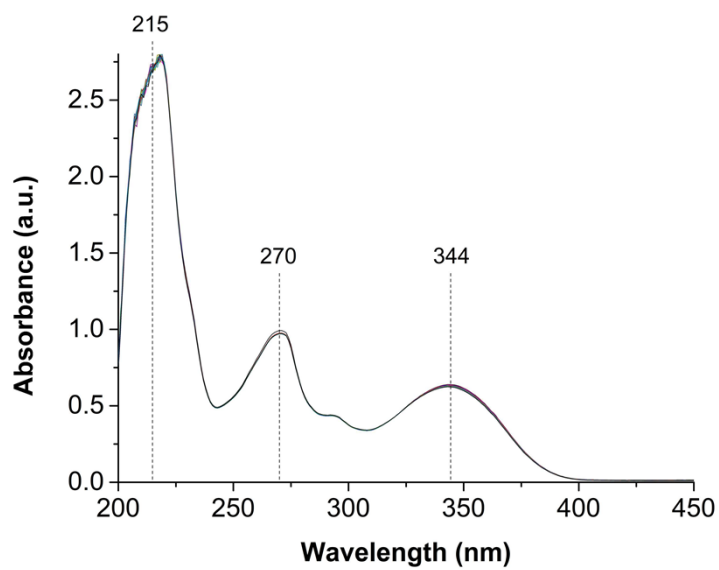


Figure S8. UV-Vis spectra of D2 ($6.00 \cdot 10^{-6}$ M), in the 200-450 nm range, recorded in 24 hrs. Each spectrum was acquired every 60 minutes, PB 0.05 M, pH 7.4, 25°C, 1 cm optical path length.

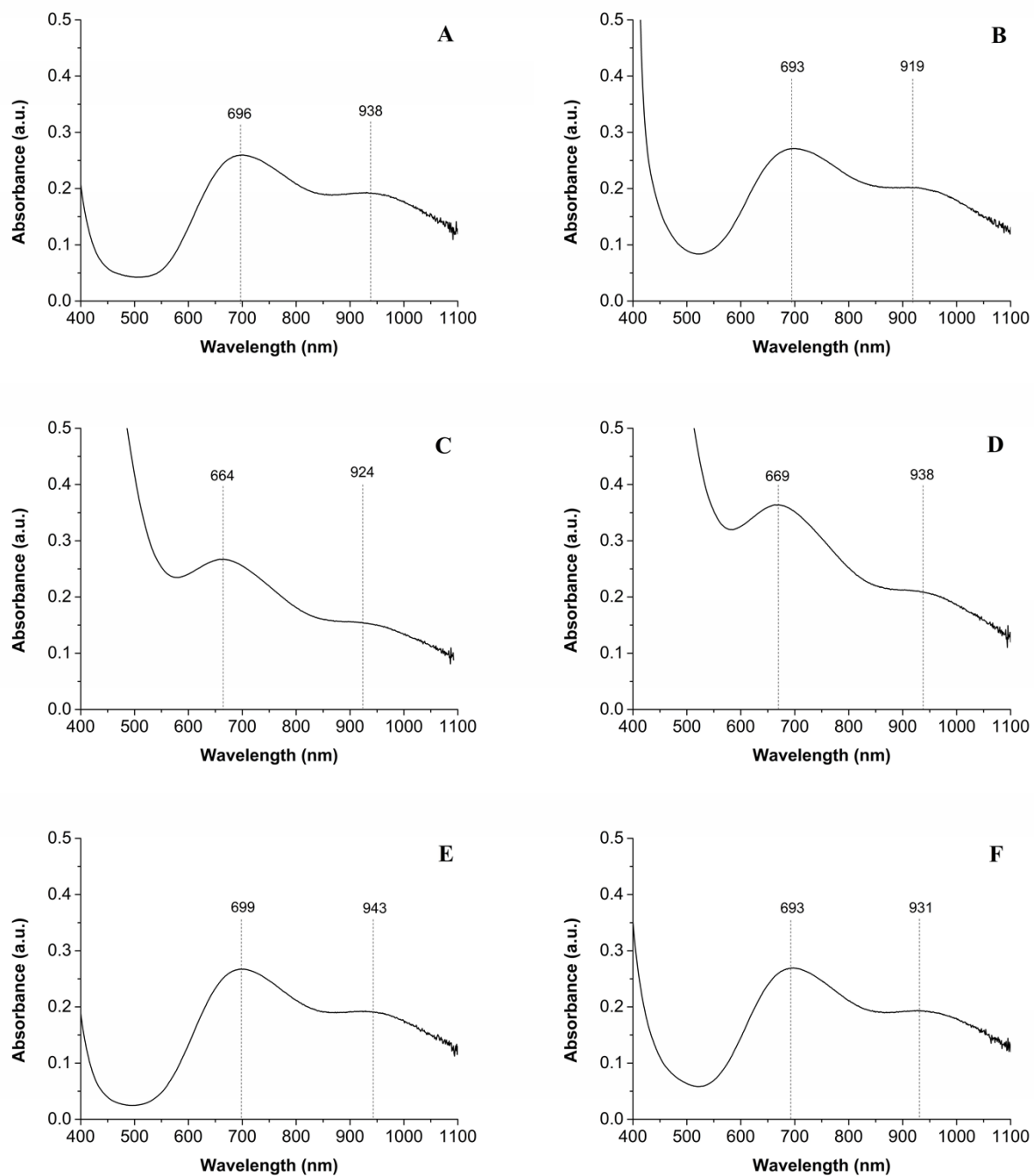


Figure S9. Vis-NIR spectra of (A) D1 ($7.14 \cdot 10^{-3}$ M), (B) D2 ($5.93 \cdot 10^{-3}$ M), (C) D3 ($7.00 \cdot 10^{-3}$ M), (D) D4 ($6.19 \cdot 10^{-3}$ M), (E) D5 ($6.40 \cdot 10^{-3}$ M), (F) D6 ($6.05 \cdot 10^{-3}$ M), $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (1:1), 25 °C, 1 cm optical path length.

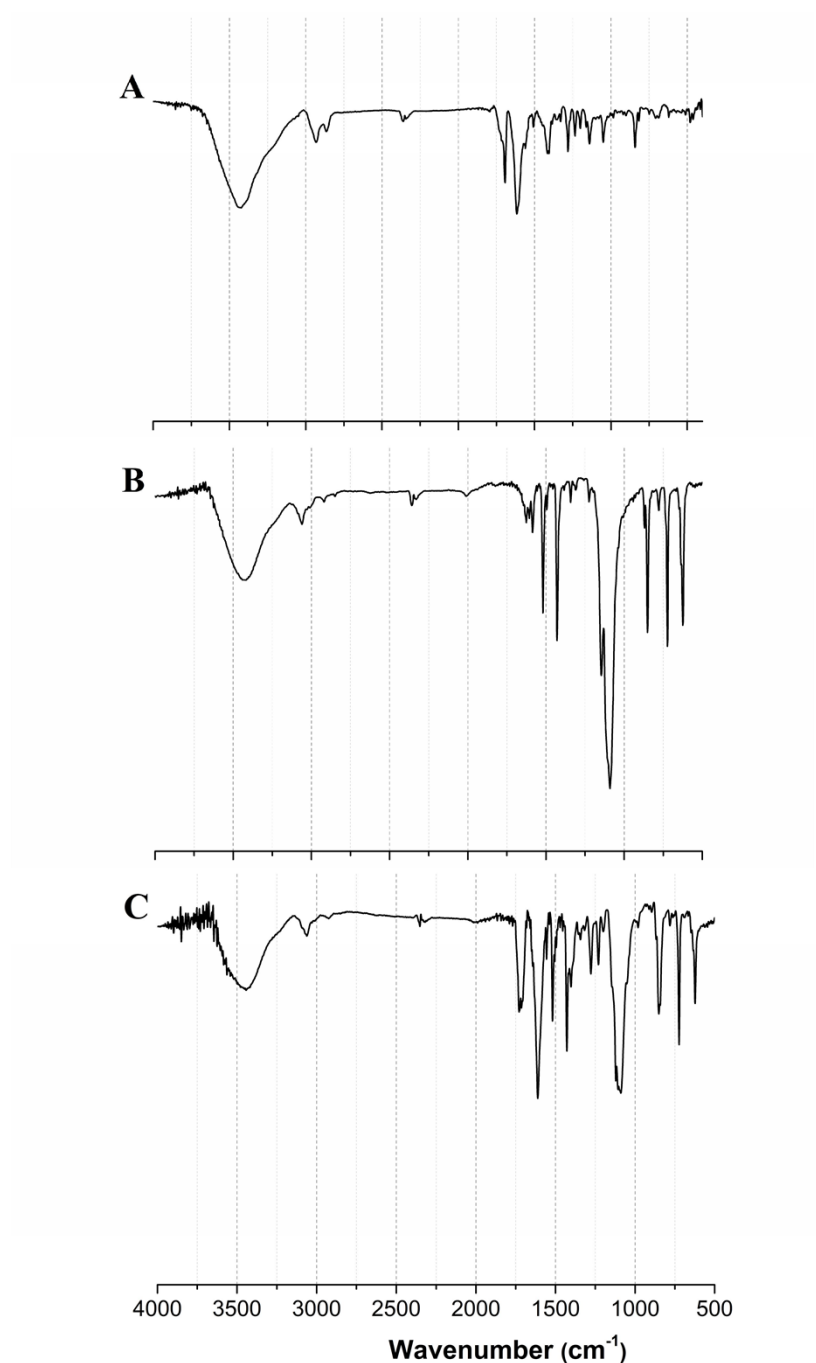


Figure S10. FT-IR spectrum of NaL1 (A), C0 (B) and D1 (C).

In the FT-IR spectrum of NaL¹ (Figure S24A), asymmetric and symmetric stretching peaks of oxygen carboxylate group ($\nu_{\text{Inn1}}(\text{COO})$ and $\nu_{\text{nn1}}(\text{COO})$) fall at 1615 and 1406 cm⁻¹ respectively, with a $\Delta(\text{COO})_{\text{nIn}}$ value of 199 cm⁻¹. In the D1 complex (Figure S24C), the same bands fall at 1611 and 1362 cm⁻¹ respectively, with a $\Delta(\text{COO})_{\text{In}}$ of 249 cm⁻¹. Since $\Delta(\text{COO})_{\text{In}} > \Delta(\text{COO})_{\text{nIn}}$, we can conclude that the carboxylic group coordinates the metal centre in D1 in a monodentate fashion. Considering the structural similarity of the other HL²⁻⁶ auxiliary ligands and the same stoichiometry determined for D2-6 complexes

$[\text{Cu}(\text{phen})_2(\text{Lx})](\text{ClO}_4)$), the same considerations are extended to the remaining Cu(II) complexes reported in this work. The signals observed in the FT-IR spectrum of D1 at 1521, 1429, 851, 724 and 623 cm^{-1} are due to the phenanthroline moieties (see the FT-IR spectrum of C0 for comparison), while the band centred at around 1100 cm^{-1} derive from the perchlorate anion. The signal observed at 1725 cm^{-1} corresponds to the stretching of the lactonic carbonyl in the 2-H-chromen-2-one backbone.

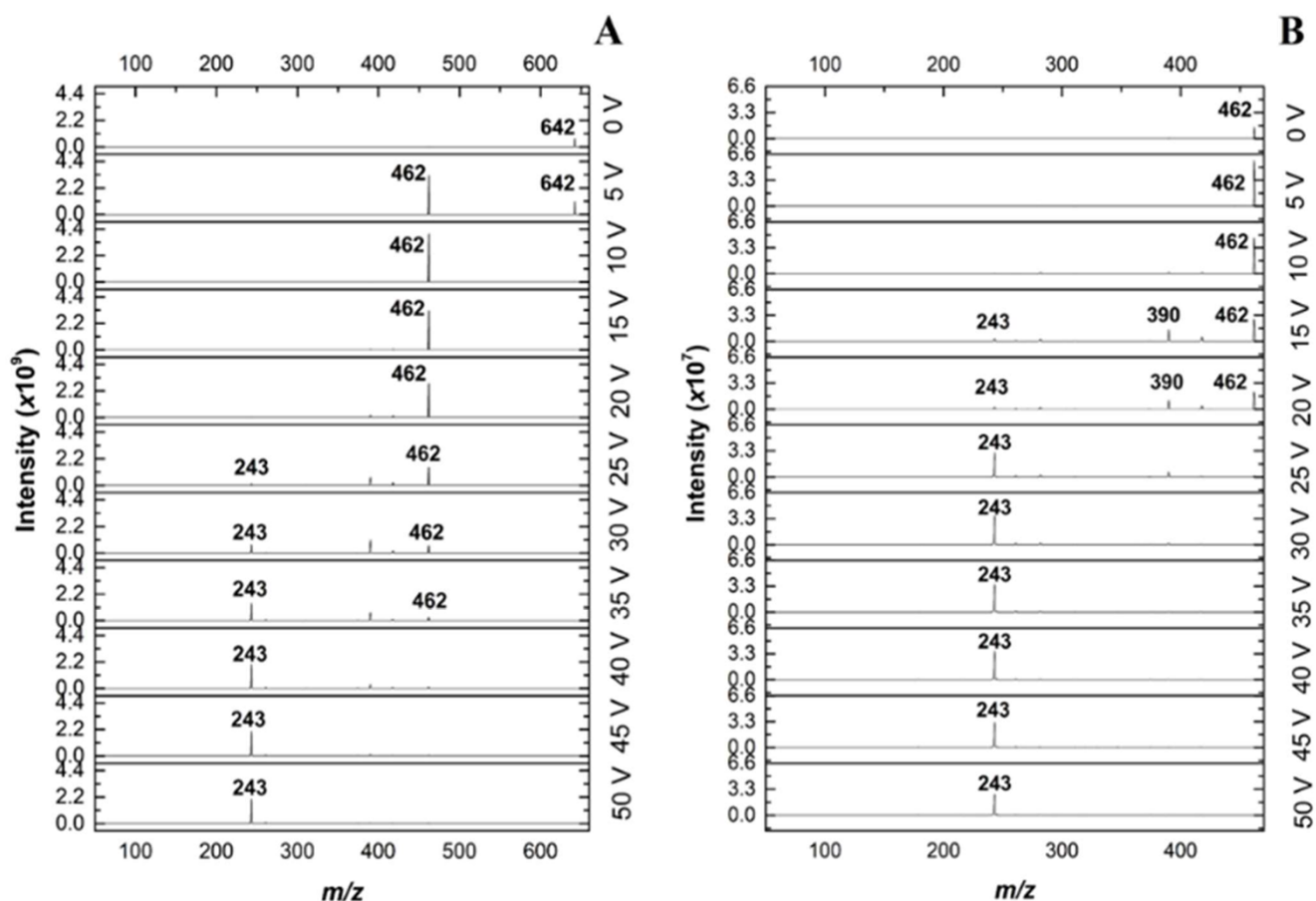
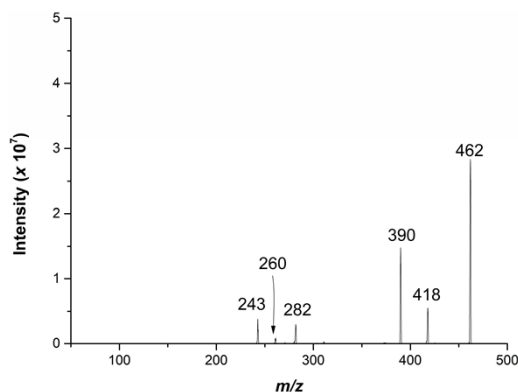


Fig. S11. Tandem MS fragmentations at different collision energies of the peaks at (A) m/z 642 ($[\text{Cu}(\text{phen})_2(\text{L}^1)]^+$) and (B) 462 ($[\text{Cu}(\text{phen})(\text{L}^1)]^+$). All the mass values are expressed as monoisotopic masses, computed as the sum of the masses of the primary isotope of each atom in the molecule (note that the monoisotopic mass may differ from the nominal molecular mass, especially for big molecules).

Comments:

Taking the CID experiments of the D1's parent ion at 642 m/z ($[\text{Cu}(\text{phen})_2(\text{L}^1)]^+$) as example it is possible to observe the loss of one phenanthroline unit and the formation of the product ion at 462 m/z ($[\text{Cu}(\text{phen})(\text{L}^1)]^+$). A gradual decrease in intensity for the peak at m/z 642 is observed as the CE is increased, a feature consistent with further fragmentation processes of the related ion. At $\text{CE} \geq 25$ V, a peak at m/z 243 due to the species $[\text{Cu}(\text{phen})]^+$ is obtained for the loss of the L1 moiety as radical, with subsequent reduction of Cu(II) centre, as previously reported 16,25. This fragmentation scheme is confirmed by CID experiments of the 462 m/z ion. In addition, minor ion peaks at $15 \text{ V} \leq \text{CE} \leq 20$ V are observed:

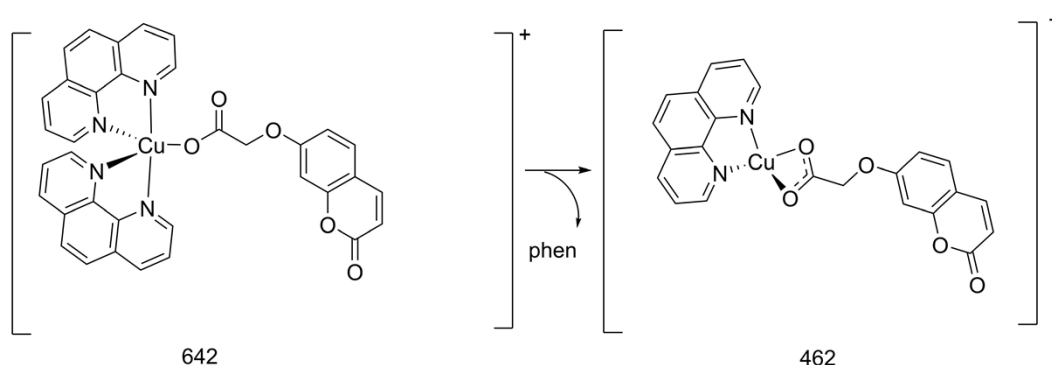


CID experiment on the peak at 462 m/z (CE 15 V, Ar 1.8 psi)

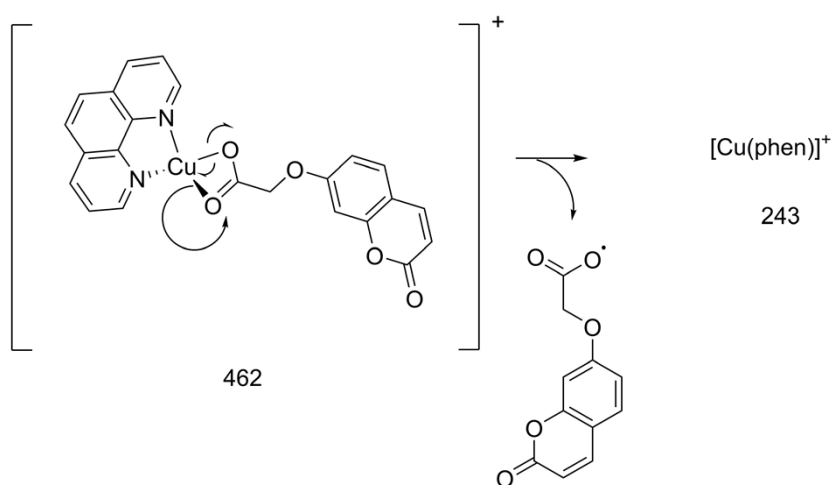
The ion at 418 m/z comes from CO_2 loss from the coumarin moiety, while that at 390 m/z originates from 418 m/z by loss of CO from the carboxylate coordinating moiety. The product ion at 282 m/z derives from the loss of the phen unit while the signal at 260 m/z arises from transposition of an H α from the auxiliary ligand and subsequent closure of a C α =C carbonyl double bond with loss of a neutral ketene.

The proposed fragmentation patterns for product ions at 462 (A), 243 (B) m/z generated from 642 m/z under CID conditions (all the mass values are expressed as monoisotopic masses) are:

A)

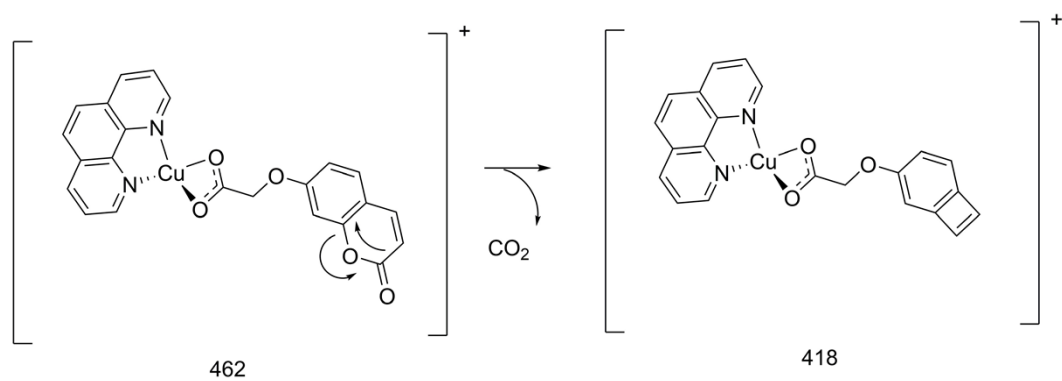


B)

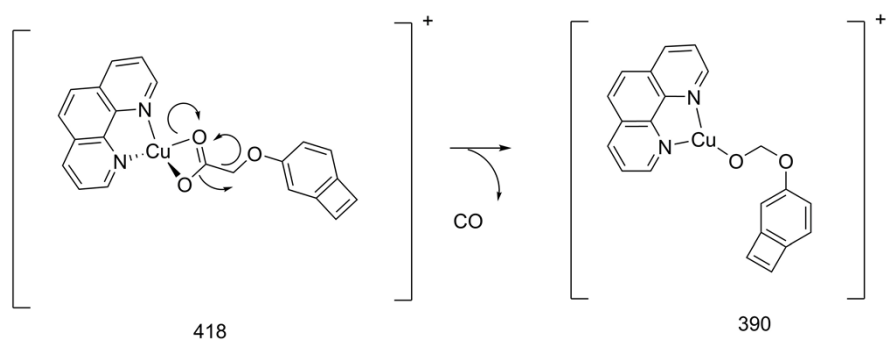


The proposed fragmentation patterns for product ions at 418 (A), 390 (B), 282 (C), 260 (D) m/z generated from 462 m/z under CID conditions (all the mass values are expressed as monoisotopic masses) are:

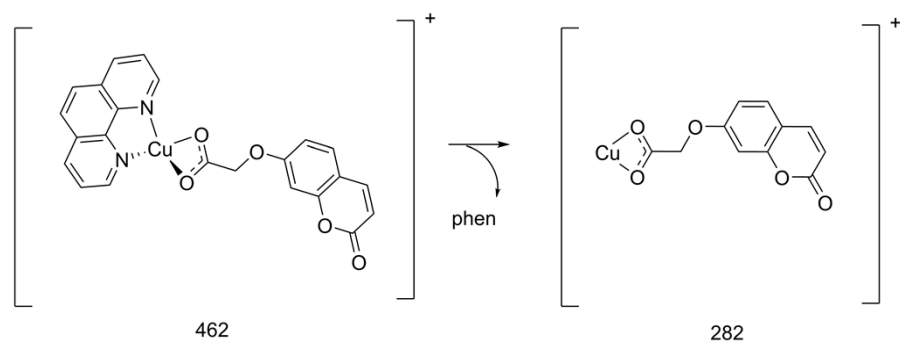
A)



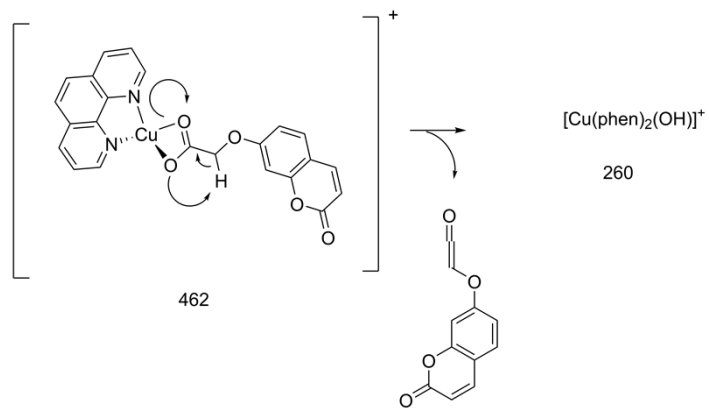
B)



C)



D)



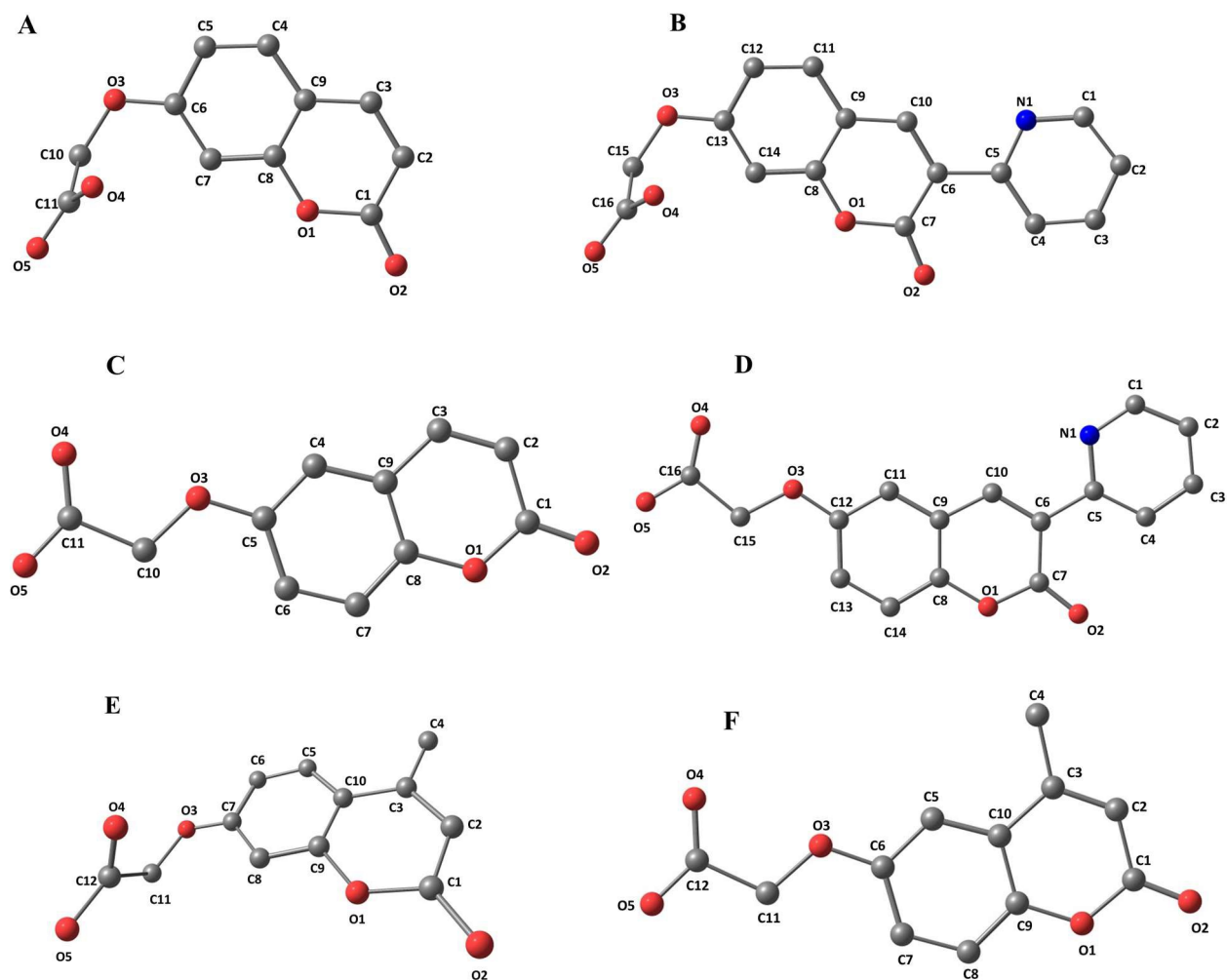
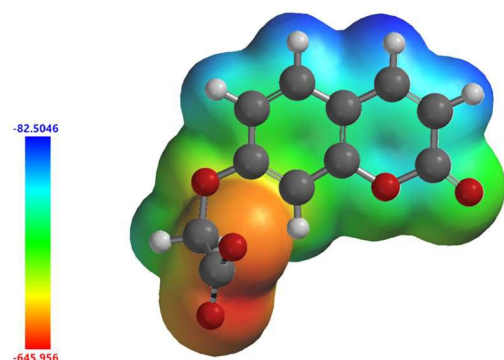
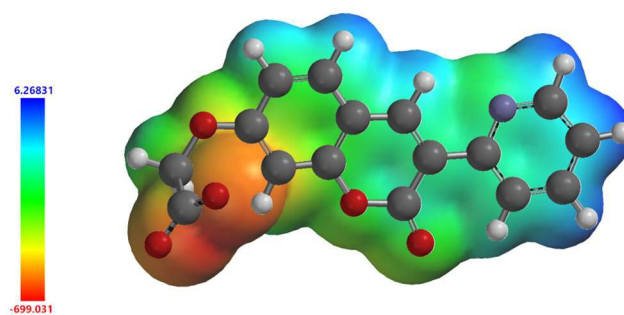


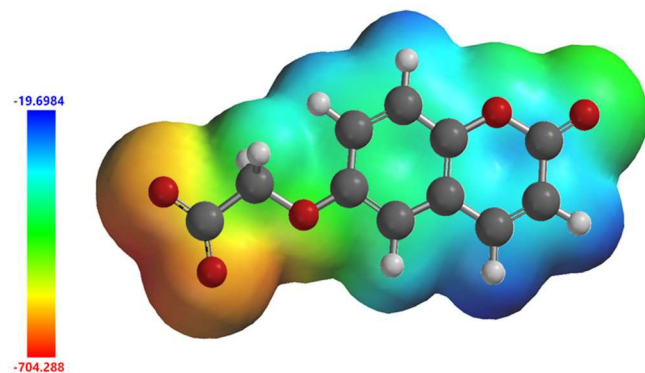
Figure S12. Molecular drawings and atom labelling scheme for L^1 (A), L^2 (B), L^3 (C), L^4 (D), L^5 (E), L^6 (F) at the DFT-optimized geometries (gas phase).



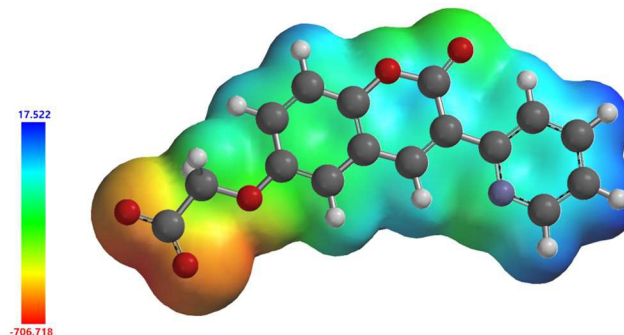
L1



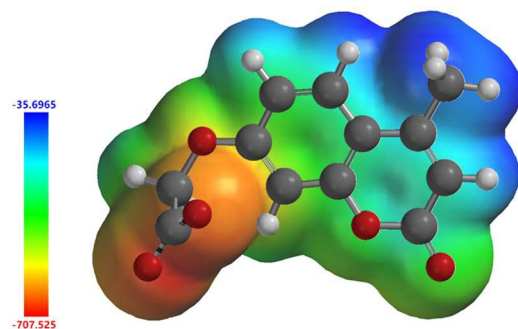
L2



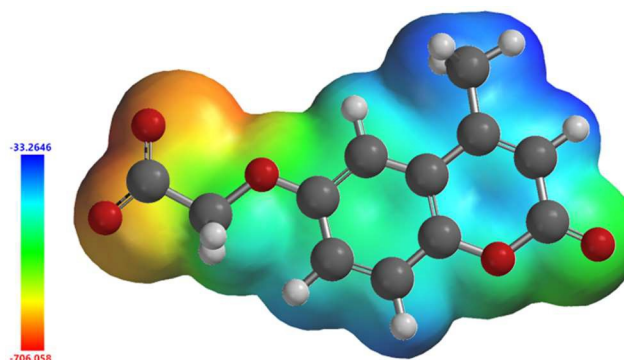
L3



L4



L5



L6

Figure S13. Mep surfaces for ligands (isovalue 0.002)

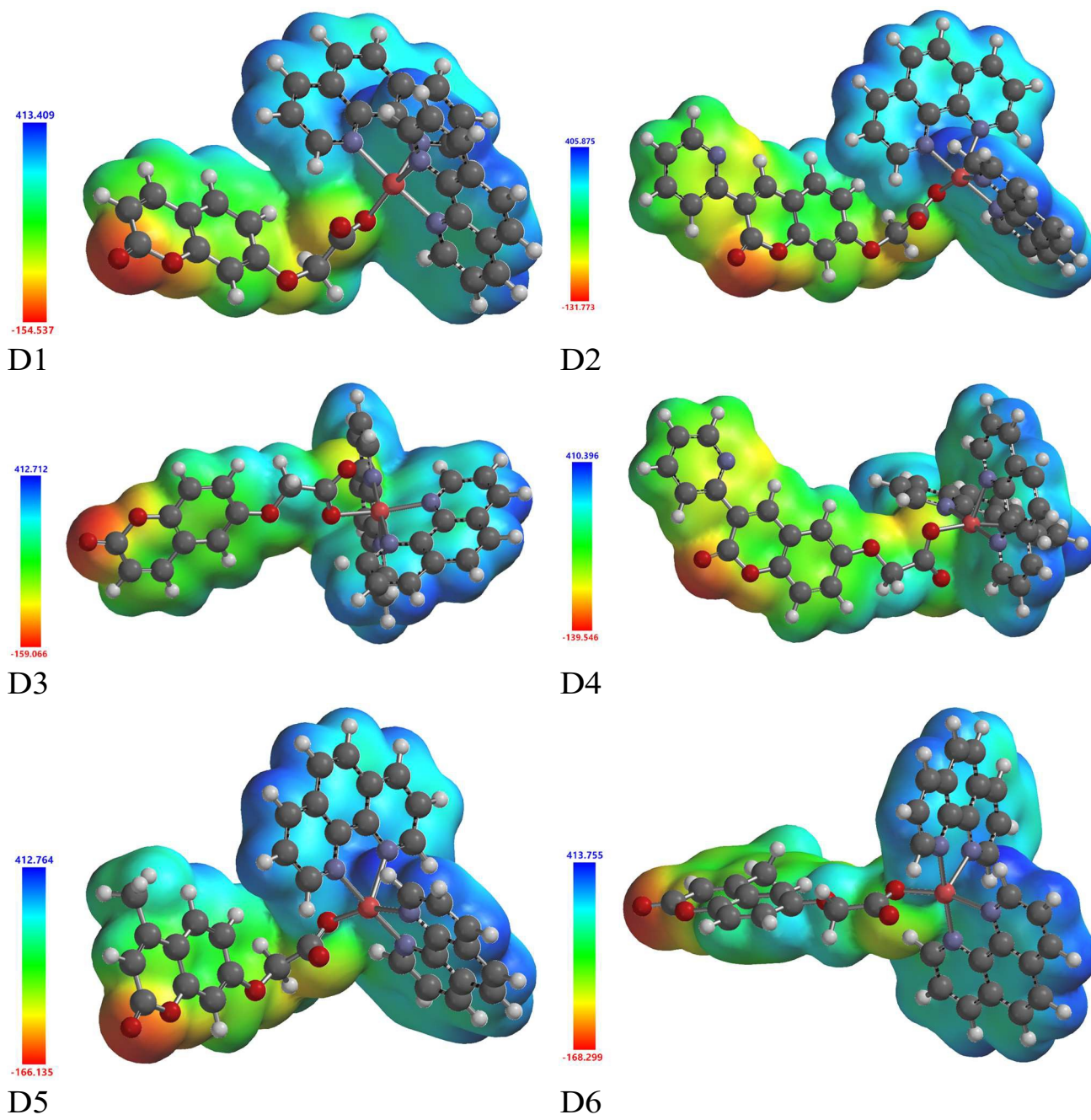


Figure S14: Mep surfaces for complexes (isovalue 0.002)

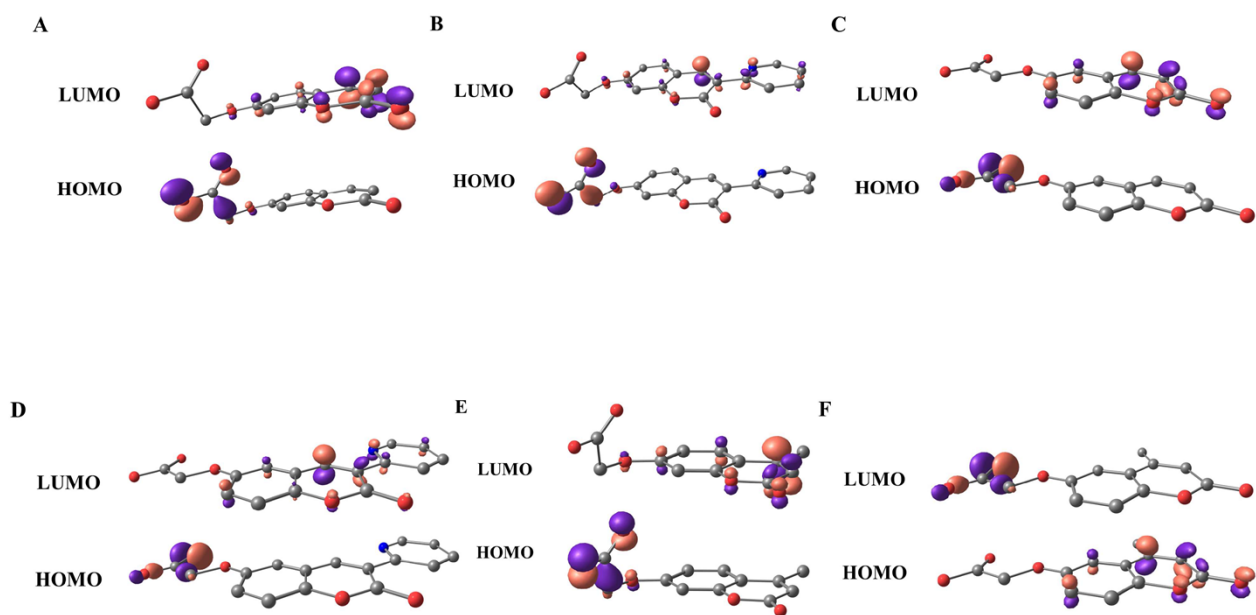


Figure S15. Gas-phase frontier Molecular Orbitals plots (contour value: 0.1) for L¹ (A), L² (B), L³ (C), L⁴ (D), L⁵ (E), L⁶ (F) at the DFT-optimized geometries (gas phase).

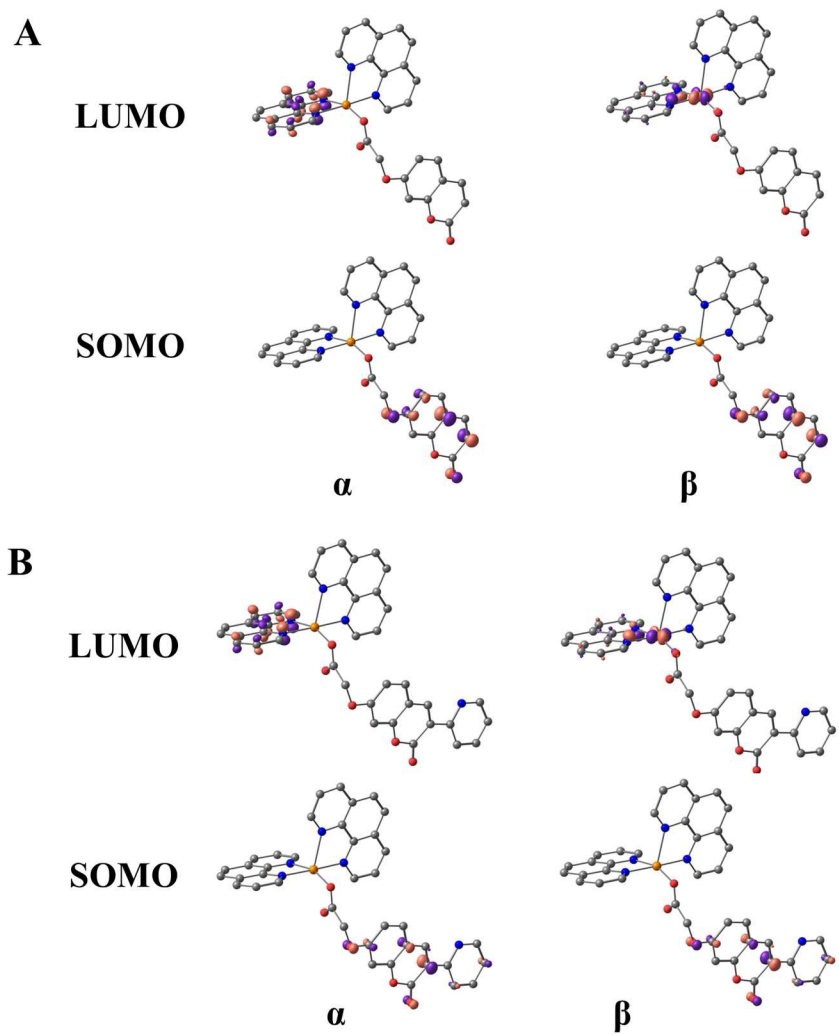


Figure S16. Gas-phase frontier Molecular Orbitals plots (contour value: 0.1) of $[\text{Cu}(\text{phen})_2(\text{L}^1)]^+$ (A) and $[\text{Cu}(\text{phen})_2(\text{L}^2)]^+$ (B).

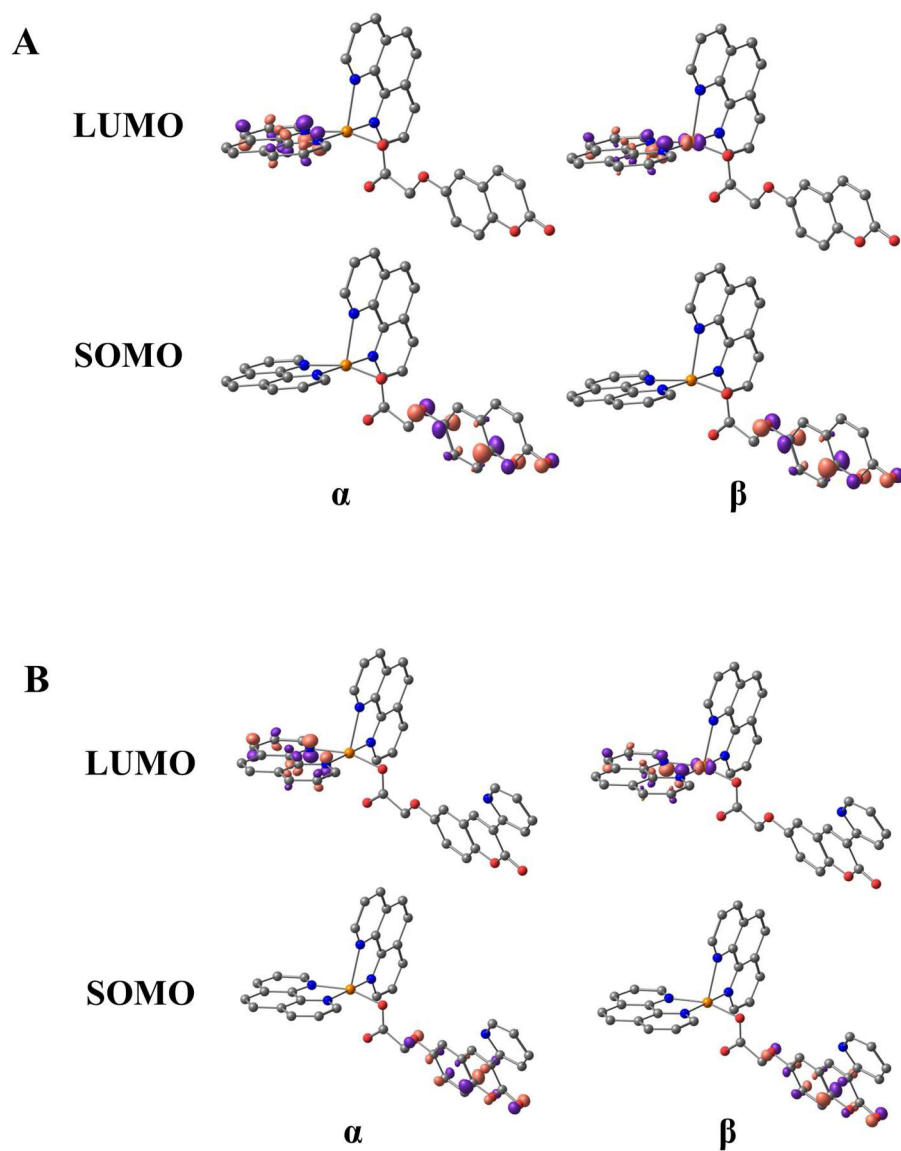


Figure S17. Gas-phase frontier Molecular Orbitals plots (contour value: 0.1) of [Cu(phen)₂(L³)]⁺ (A) and [Cu(phen)₂(L⁴)]⁺ (B).

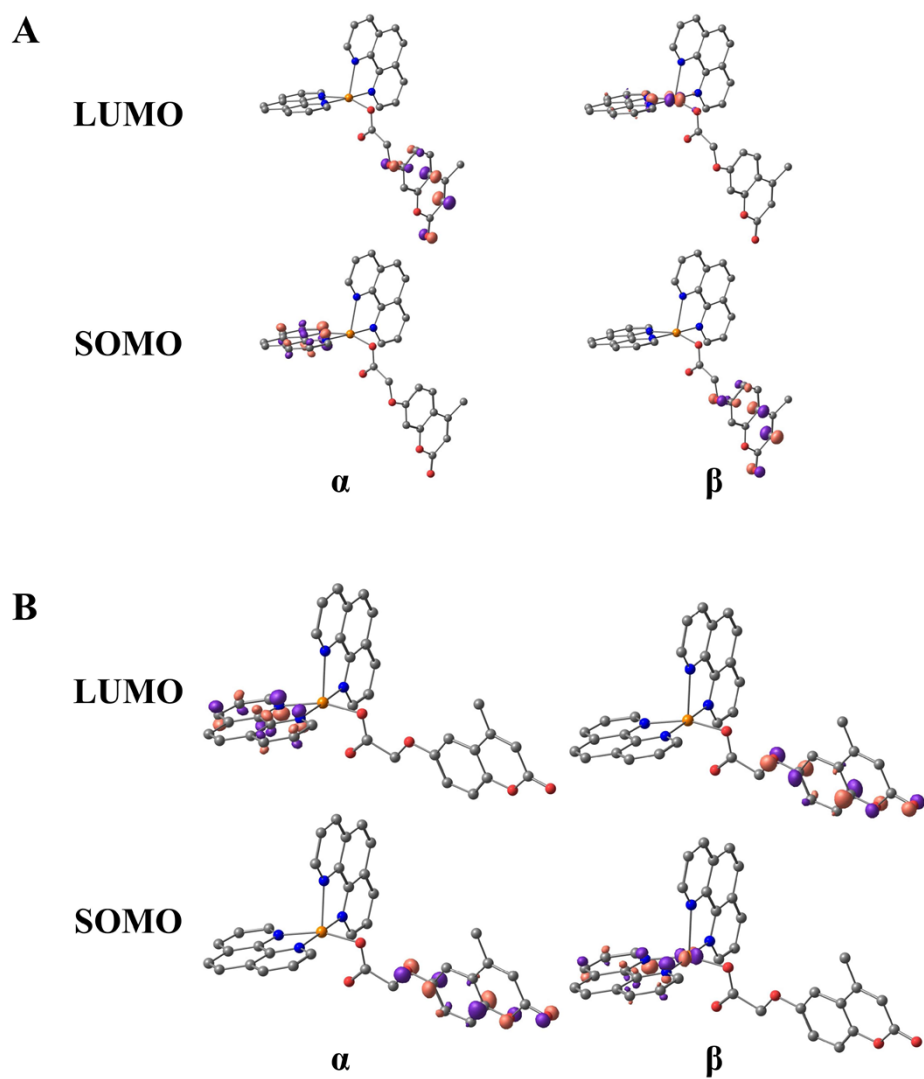


Figure S18. Gas-phase frontier Molecular Orbitals plots (contour value: 0.1) of [Cu(phen)₂(L⁵)]⁺ (A) and [Cu(phen)₂(L⁶)]⁺ (B).

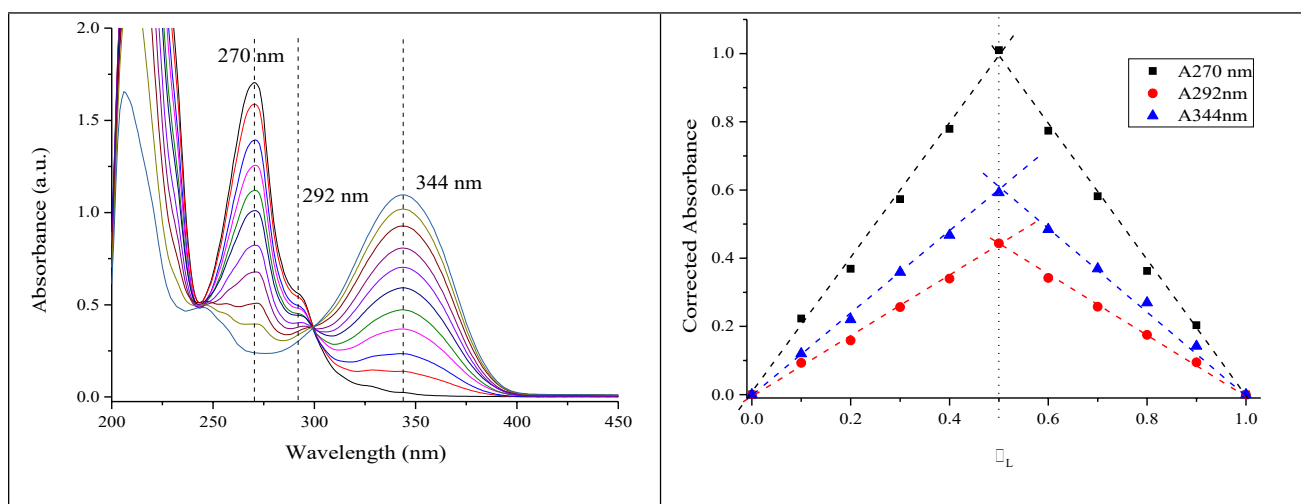


Figure S19. Absorption spectra collected varying the ligand molar fraction from 0 to 1, for the system C0 (4.37·10⁻⁵ M) - HL² (4.37·10⁻⁵ M) in PB 0.05 M, pH 7.4, 25 °C, 1 cm optical path length (A). Job's plot of C0 and L²H (B) at 270 nm (black), 292 nm (red) and 344 nm (bleu).

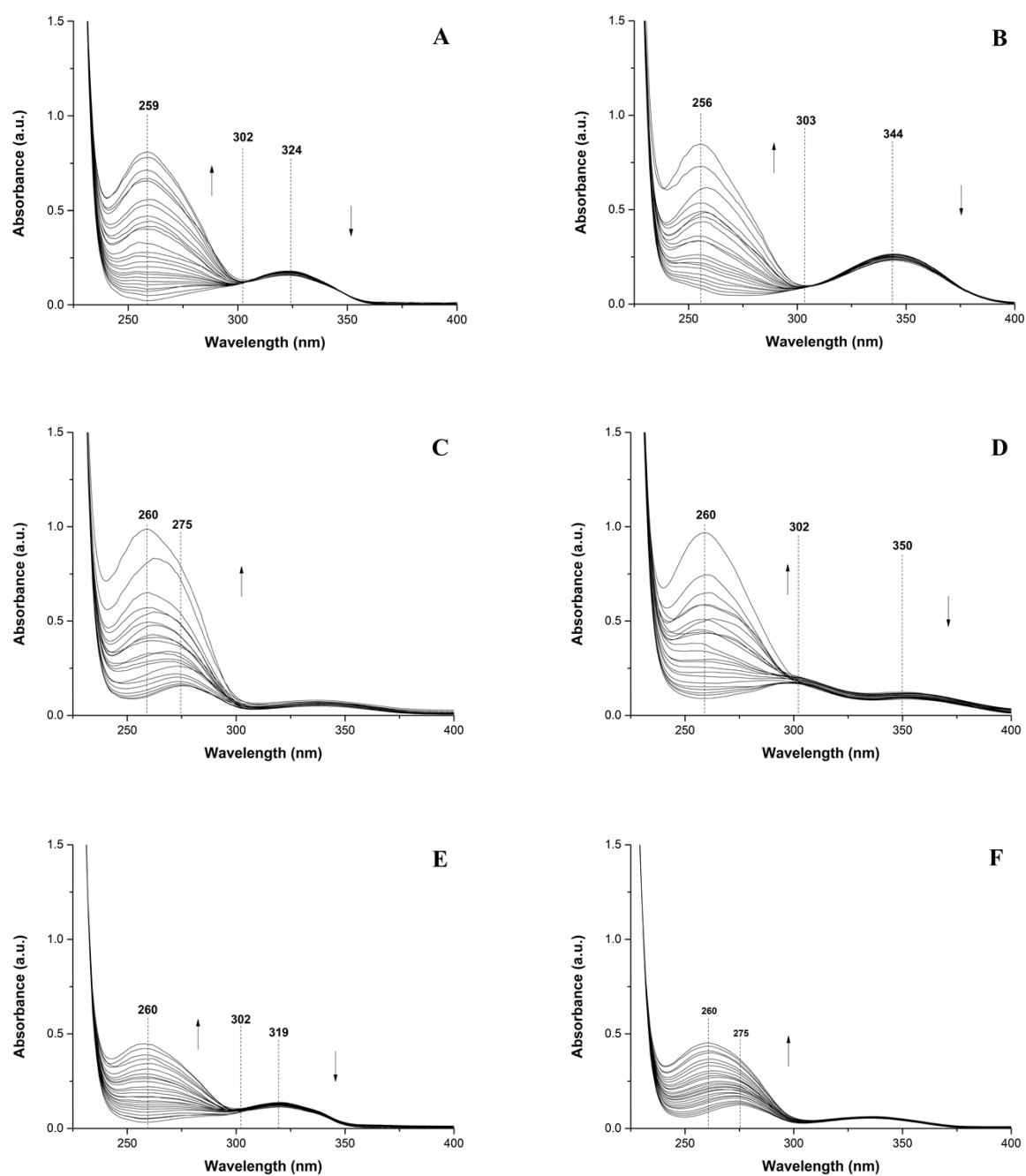


Figure S20. Selected spectra collected during the spectrophotometric titration of (A) HL¹ $1.235 \cdot 10^{-5}$ M, (B), HL² $1.208 \cdot 10^{-5}$ M, (C), HL³ $1.042 \cdot 10^{-5}$ M, (D), HL⁴ $1.216 \cdot 10^{-5}$ M, (E) HL⁵ $9.780 \cdot 10^{-6}$ M, (F) HL⁶ $1.121 \cdot 10^{-5}$ M with ct-DNA $2.270 \cdot 10^{-4}$ M; TRIS-HCl buffer (TRIS-HCl 0.05 M, NaCl 0.05 M), pH 7.1, 25 °C, 1 cm optical path length.

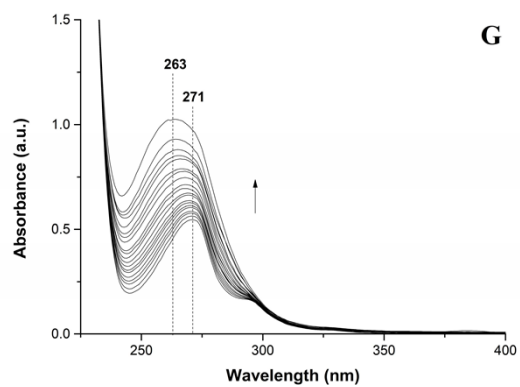
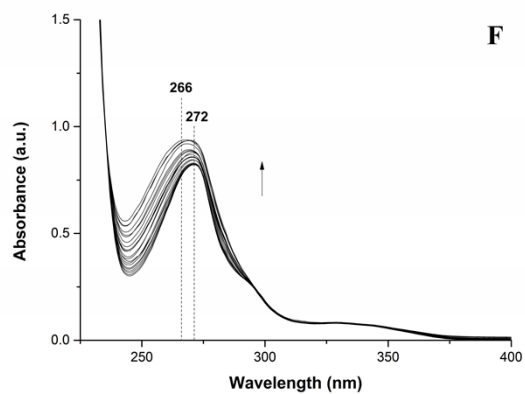
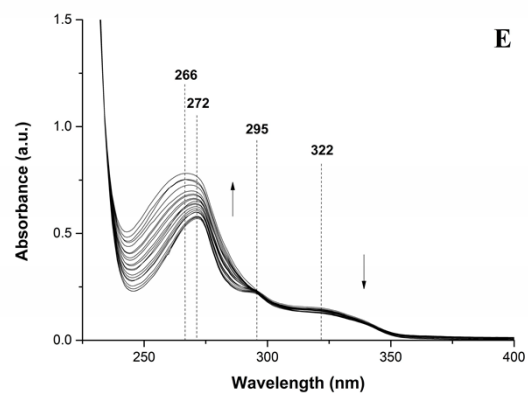
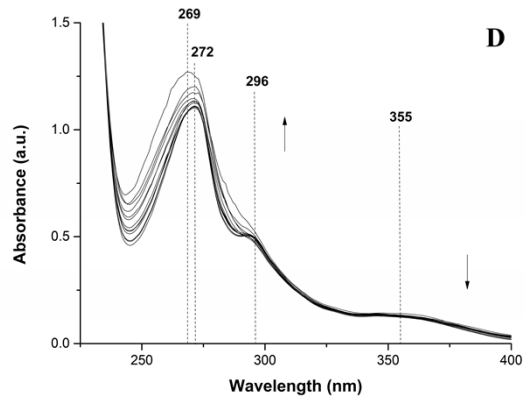
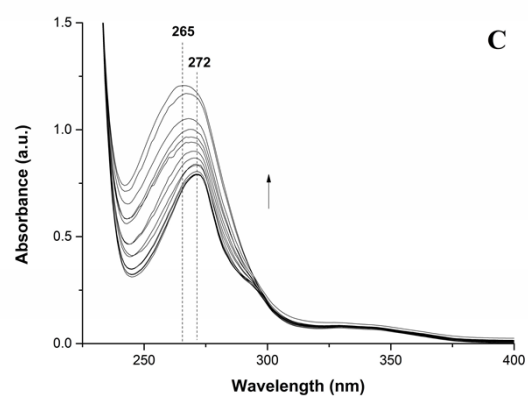
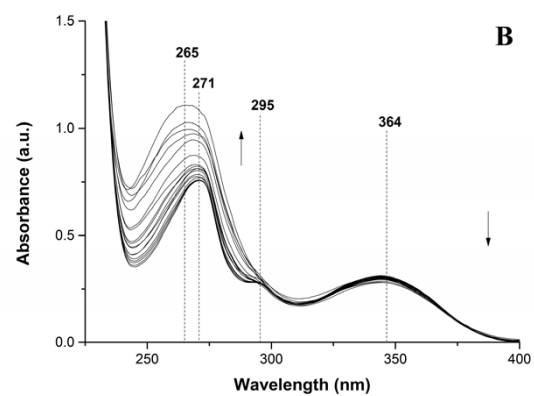
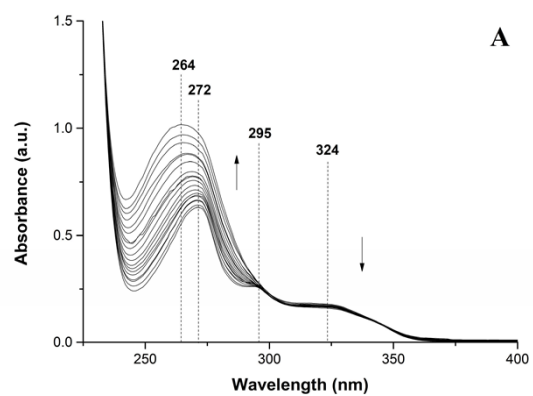


Figure S21. Selected spectra collected during the spectrophotometric titration of (A) D1 $1.144 \cdot 10^{-5}$ M, (B), D2 $1.031 \cdot 10^{-5}$ M, (C), D3 $1.105 \cdot 10^{-5}$ M, (D), D4 $1.213 \cdot 10^{-5}$ M, (E) D5 $1.002 \cdot 10^{-5}$ M, (F) D6 $1.244 \cdot 10^{-5}$ M, (G) C0 $1.061 \cdot 10^{-5}$ M with ct-DNA $2.270 \cdot 10^{-4}$ M; TRIS-HCl buffer (TRIS-HCl 0.05 M, NaCl 0.05 M), pH 7.1, 25 °C, 1 cm optical path length.

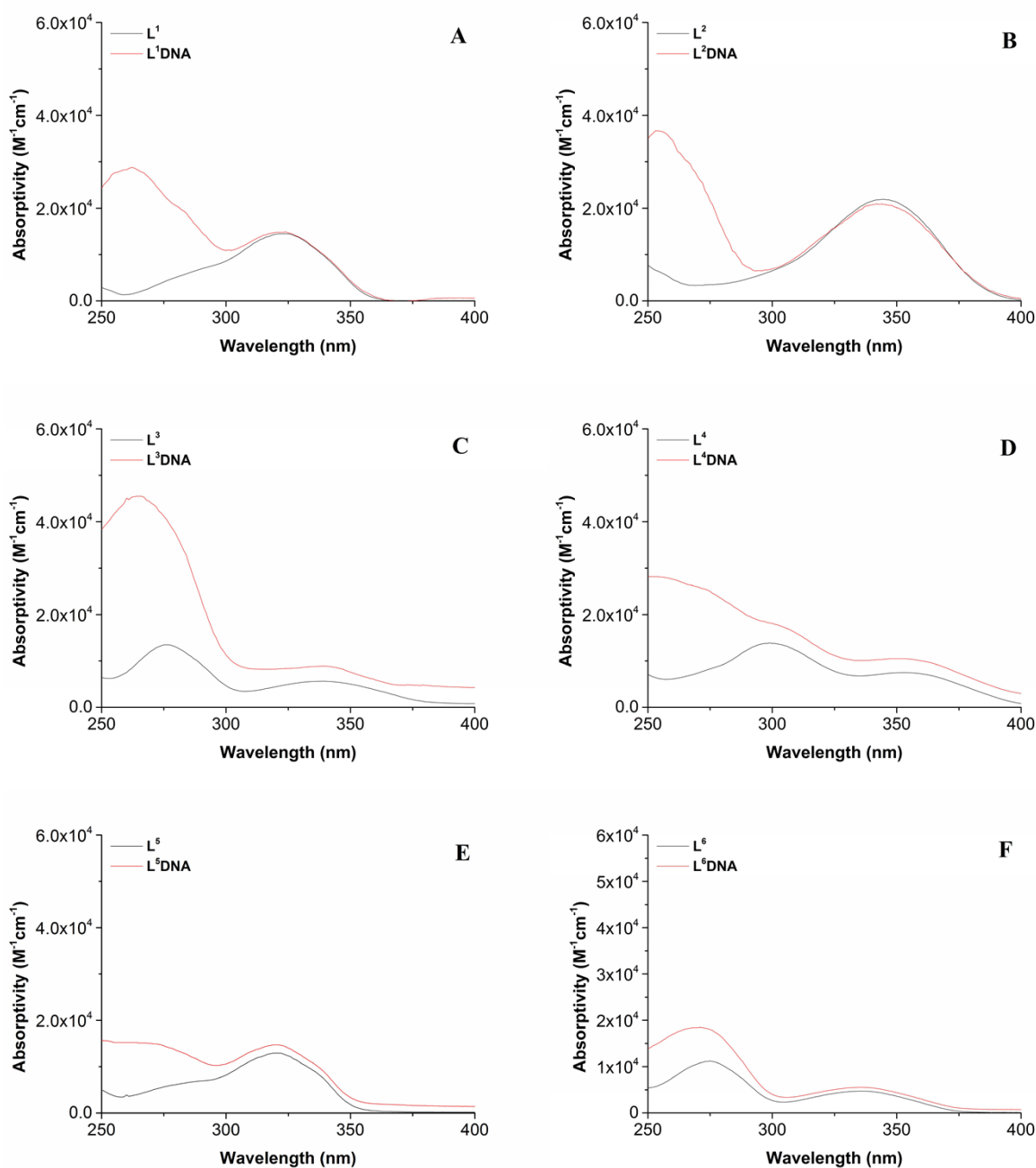


Figure S22. Absorbance spectra of the adducts between ct-DNA and the L¹⁻⁶ compounds.

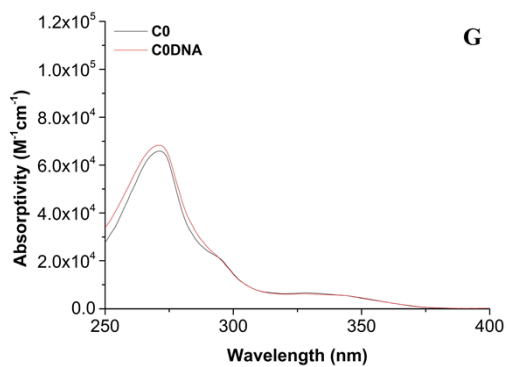
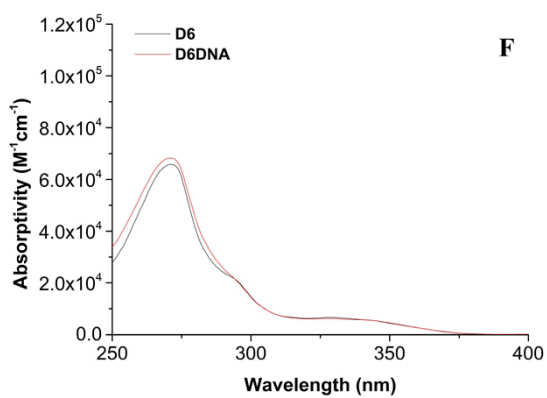
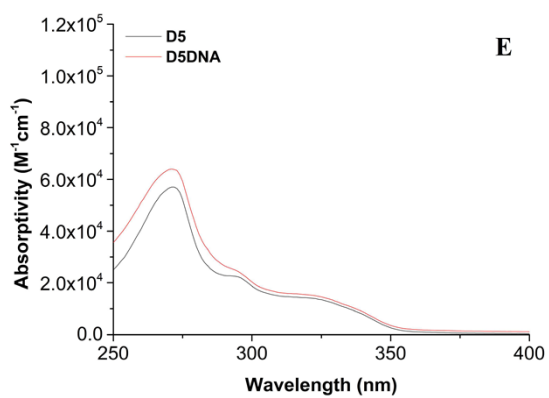
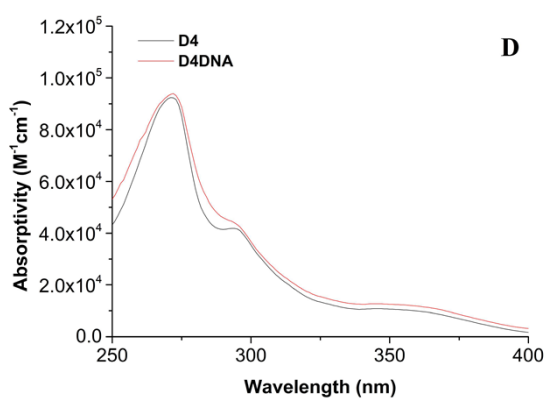
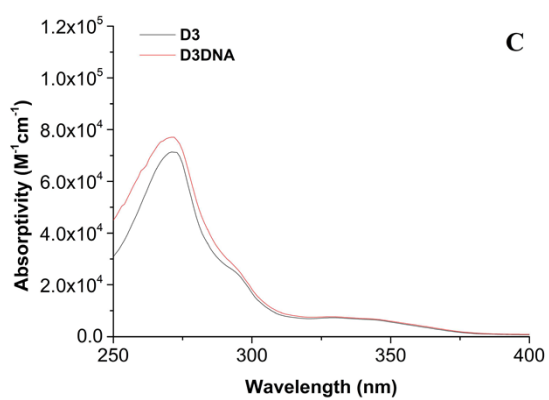
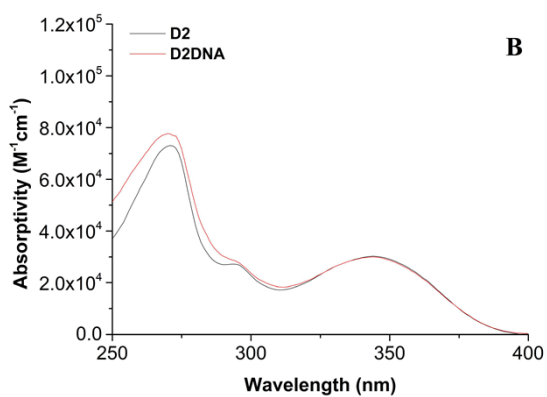
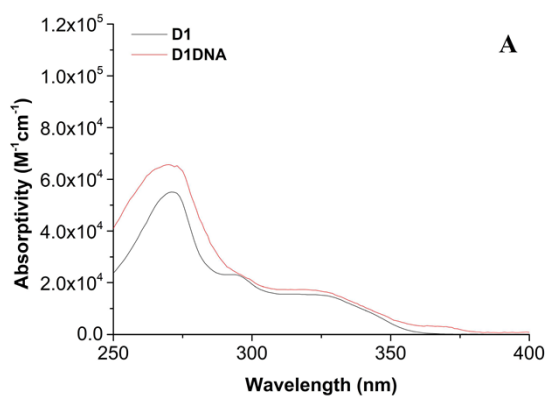


Figure S23. Absorptivity spectra of the adducts between ct-DNA and the Cu(II) complexes D1-6 and C0.

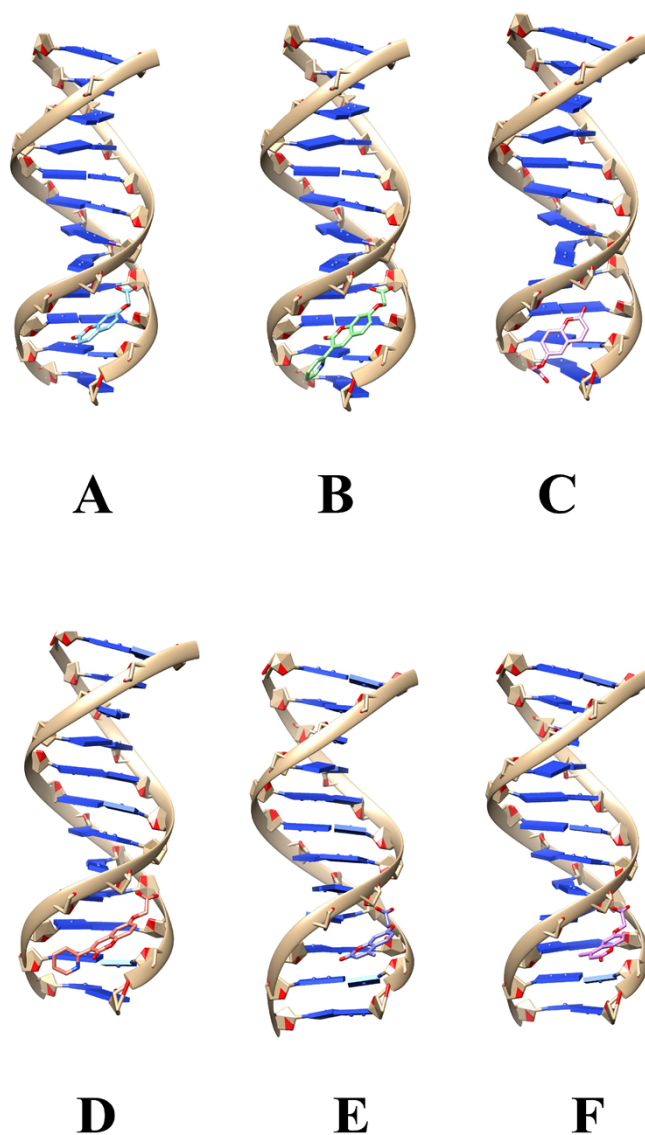


Figure S24. Full view of the complex between the highest-ranking score of deprotonated HL^{1-6} (L^{1-6} , charges are omitted for simplicity) and BDNA.

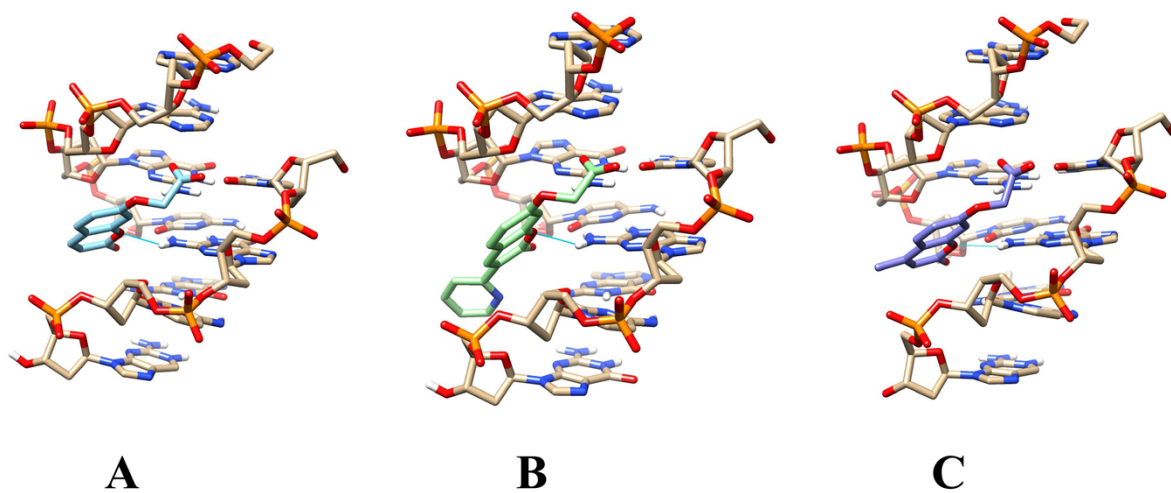


Figure S25. Hydrogen bonding profile between the highest-ranking score of L¹ (A), L² (B), L⁵ (C) and BDNA.

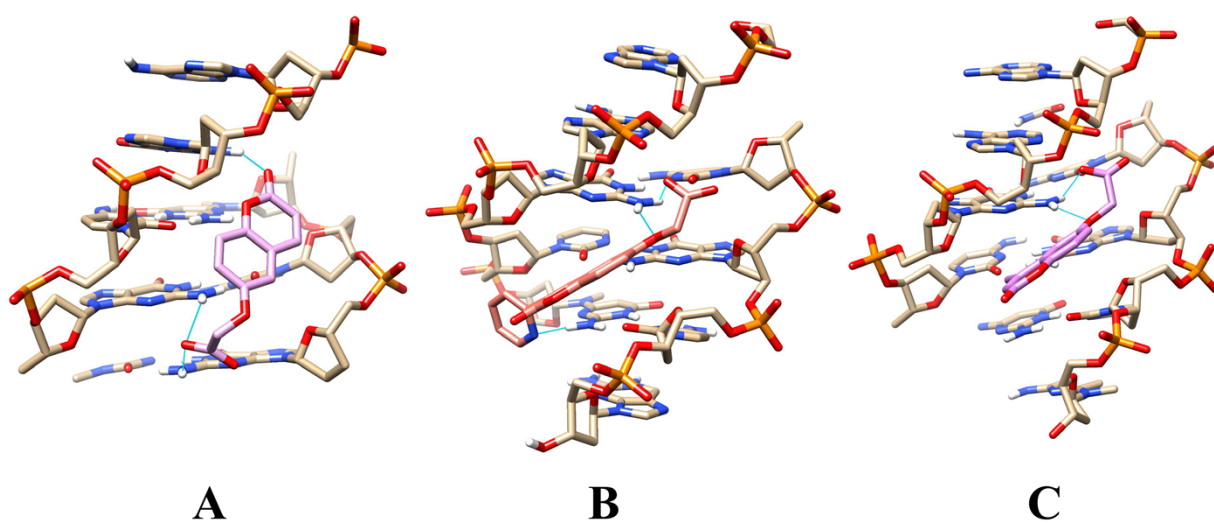


Figure S26. Hydrogen bonding profile between the highest-ranking score of L³ (A), L⁴ (B), L⁶ (C) and BDNA.

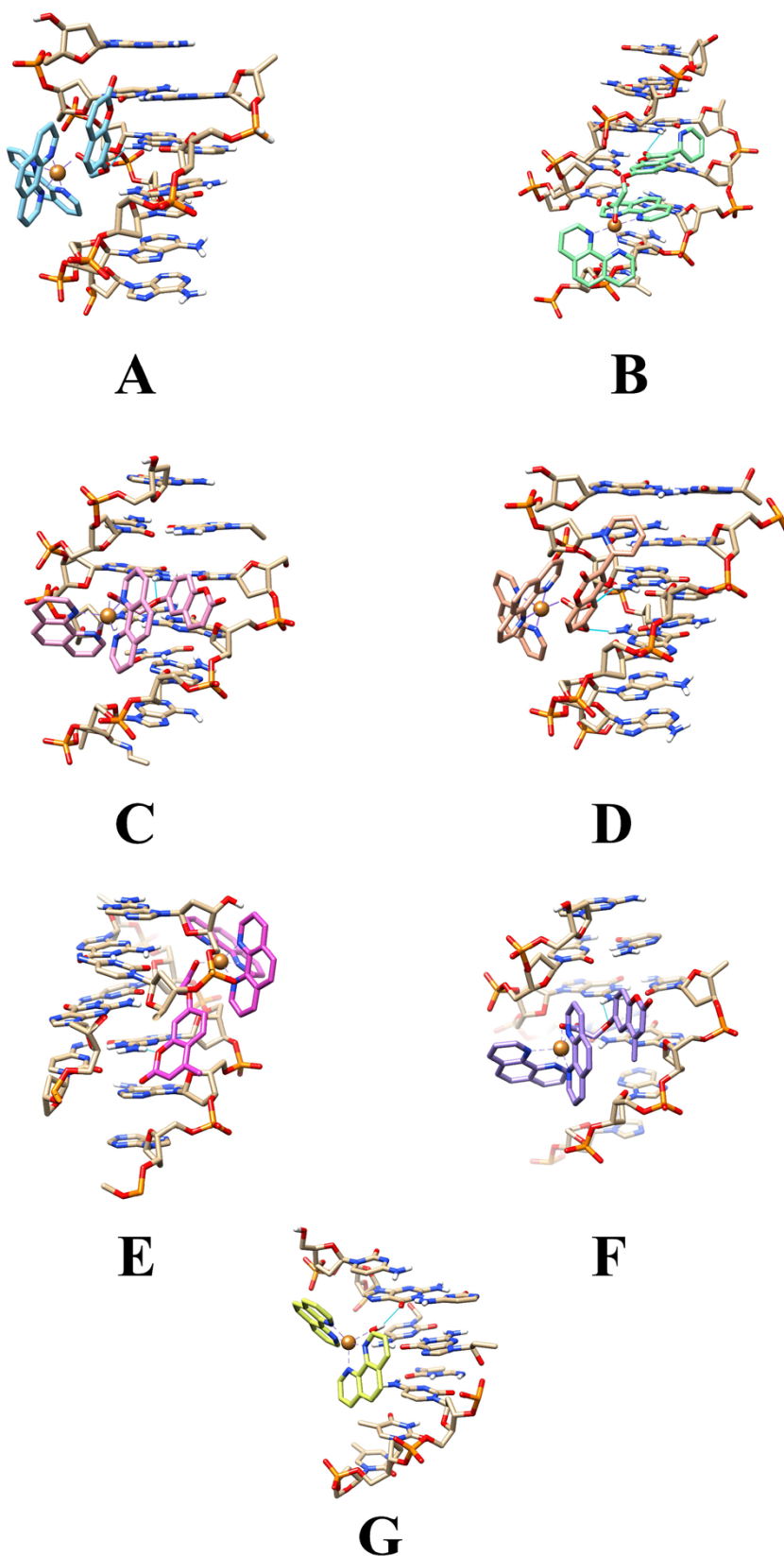


Figure S27. Hydrogen bonding profile between the highest-ranking score of $[\text{Cu}(\text{phen})_2(\text{L}^1)]^+$ (A), $[\text{Cu}(\text{phen})_2(\text{L}^2)]^+$ (B), $[\text{Cu}(\text{phen})_2(\text{L}^3)]^+$ (C), $[\text{Cu}(\text{phen})_2(\text{L}^4)]^+$ (D), $[\text{Cu}(\text{phen})_2(\text{L}^5)]^+$ (E), $[\text{Cu}(\text{phen})_2(\text{L}^6)]^+$ (F), $[\text{Cu}(\text{phen})_2(\text{OH}_2)]^{2+}$ (g) and BDNA.

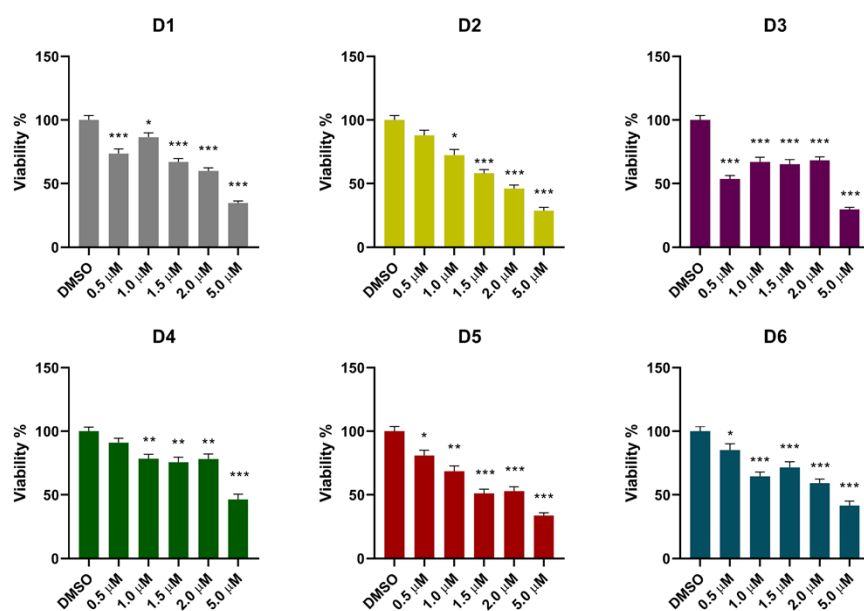


Figure S28. Viability (% compared to the control) of SKOV-3 cells after 24 hrs, in presence of D1-6 at different concentrations or DMSO (control), determined by means of MTT assay. Results are expressed as Mean $\pm$ SEM from 3 independent experiments done in technical hexaplicates. Asterisks indicate statistical significance (with respect to the control) at $p < 0.05$ (*), $p < 0.01$ (**), $p < 0.001$ (***)).

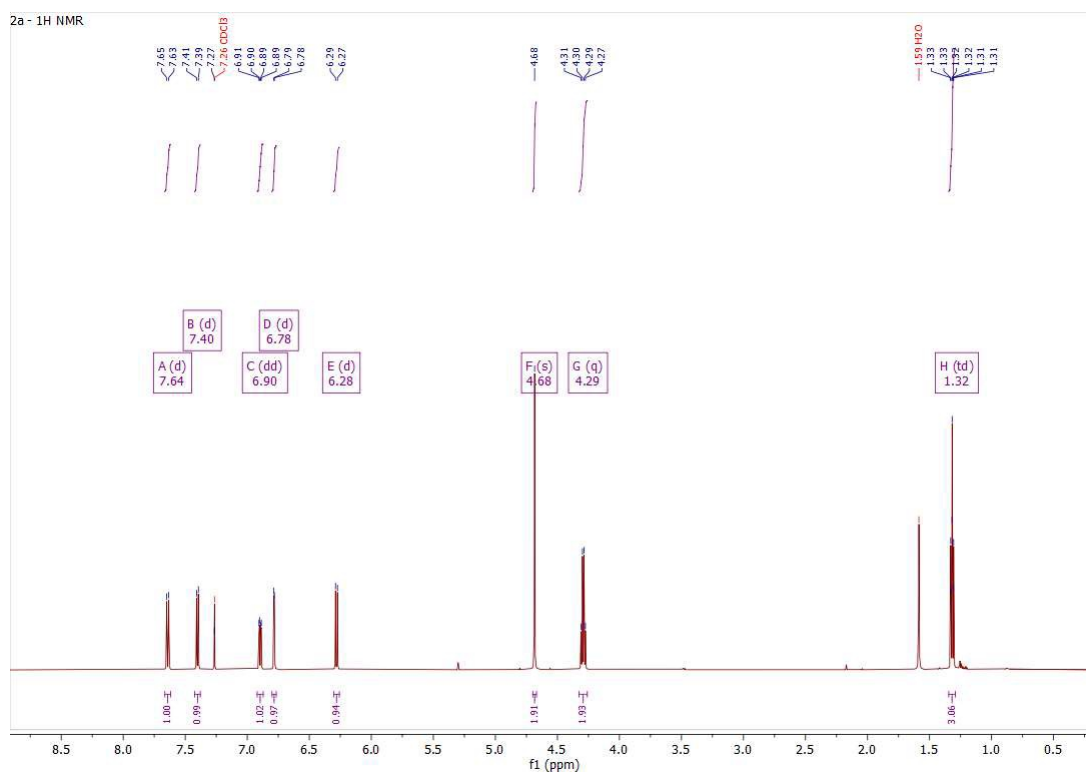


Figure S29. ¹H-NMR of 2a, Ethyl 2-((2-oxo-2H-chromen-7-yl)oxy)acetate (600 MHz, CDCl₃).

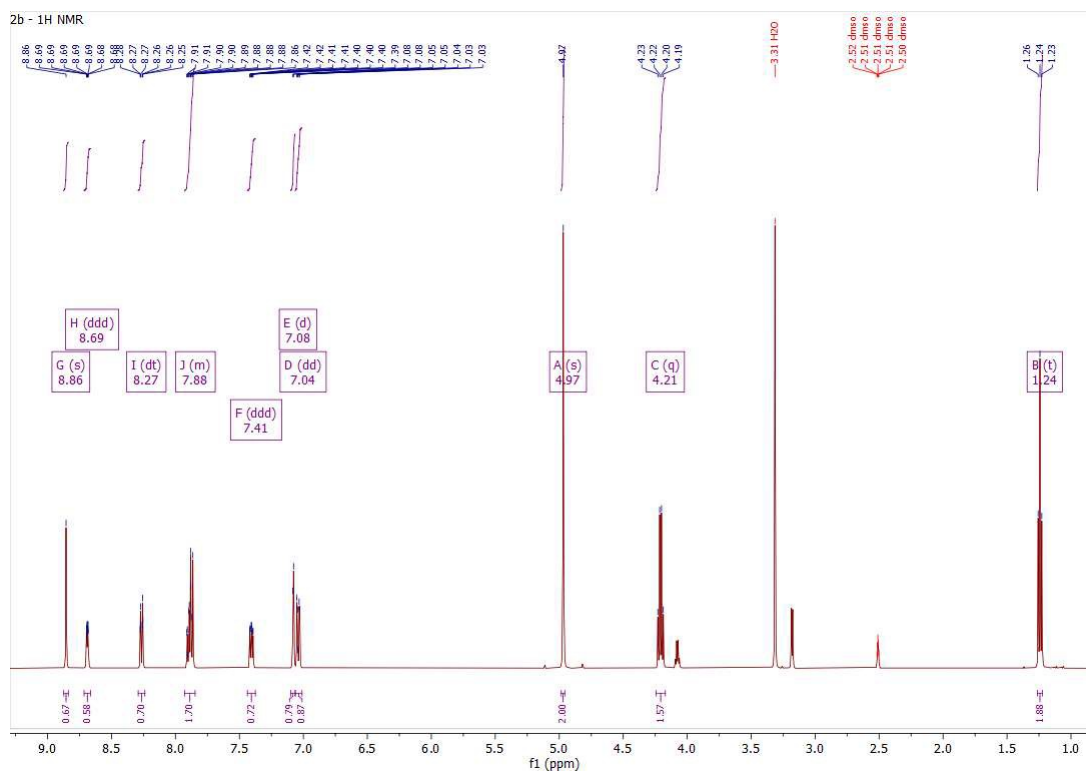


Figure S30 ¹H-NMR of 2b, Ethyl 2-((2-oxo-3-(pyridin-2-yl)-2H-chromen-7-yl)oxy)acetate (500 MHz, DMSO d₆).

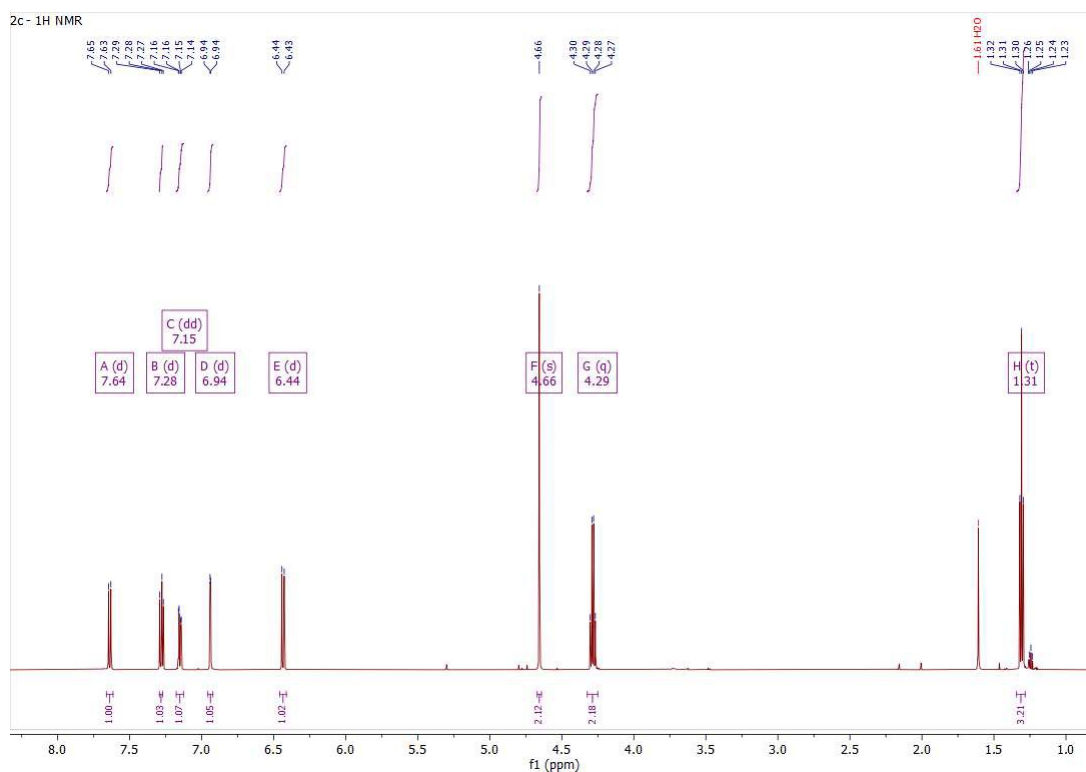


Figure S31. ¹H-NMR of 2c, Ethyl 2-((2-oxo-2H-chromen-6-yl)oxy)acetate (600 MHz, CDCl₃).

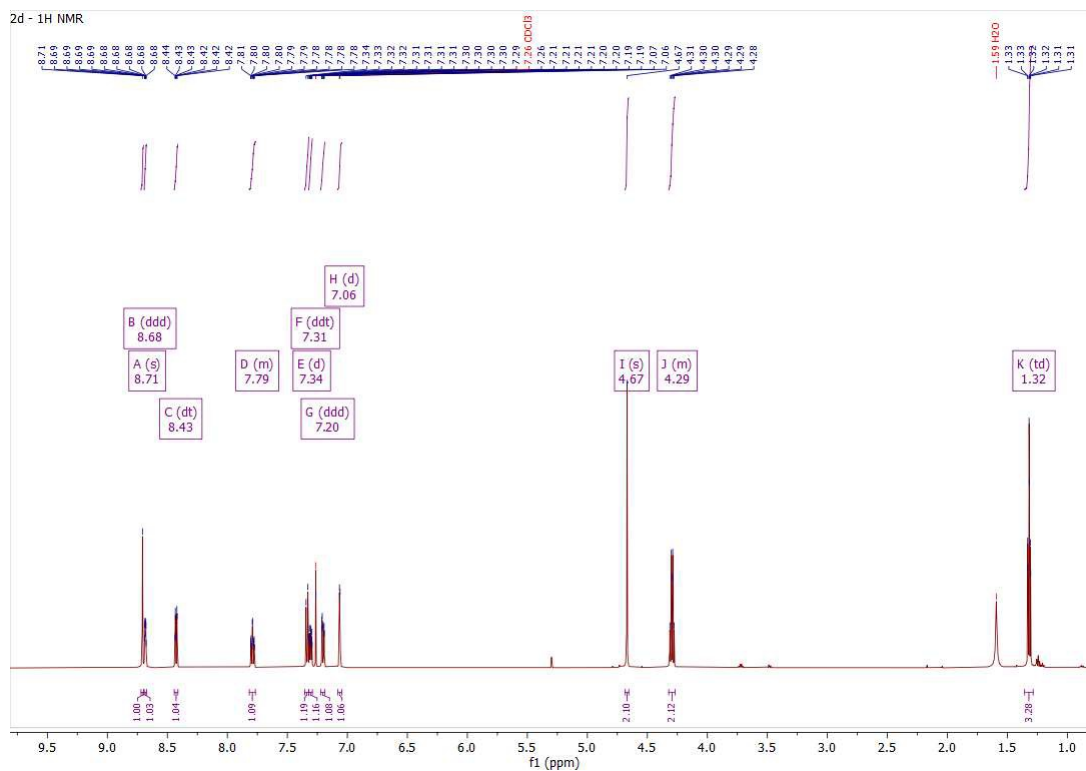


Figure S32. ¹H-NMR of 2d, Ethyl 2-((2-oxo-3-(pyridin-2-yl)-2H-chromen-6-yl)oxy)acetate (600 MHz, CDCl₃).

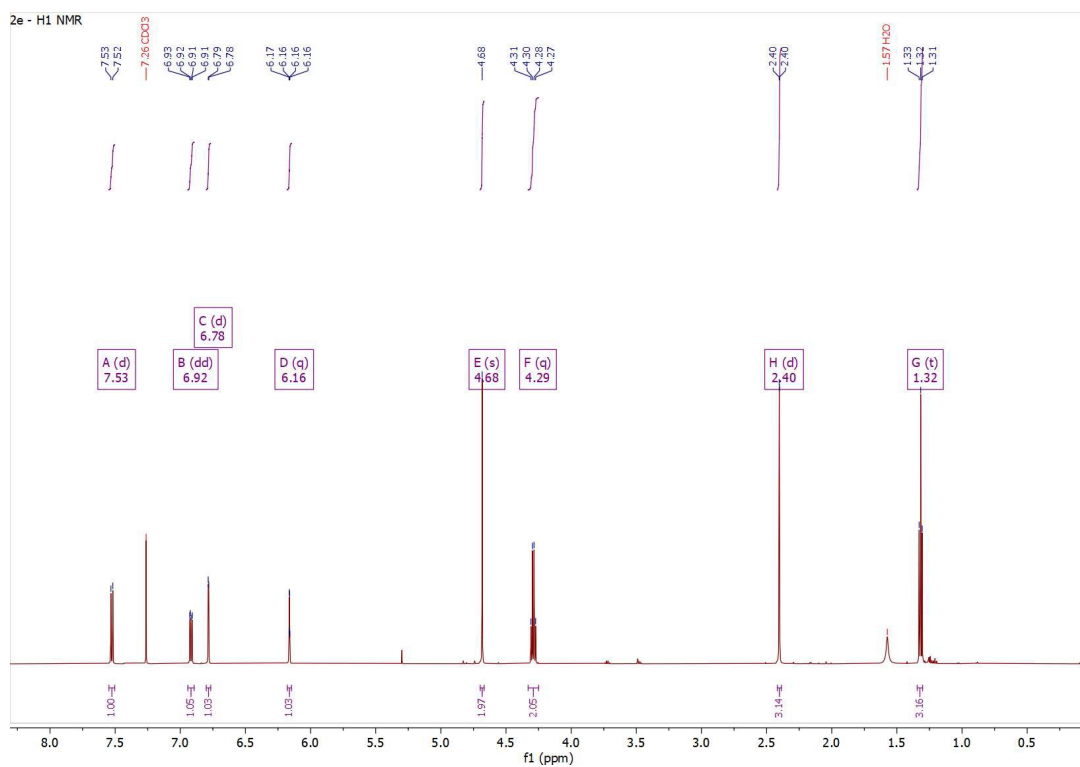


Figure S33. ¹H-NMR of 2e, Ethyl 2-(4-methyl-2-oxo-2H-chromen-7-yl)oxy)acetate (600 MHz, CDCl₃).

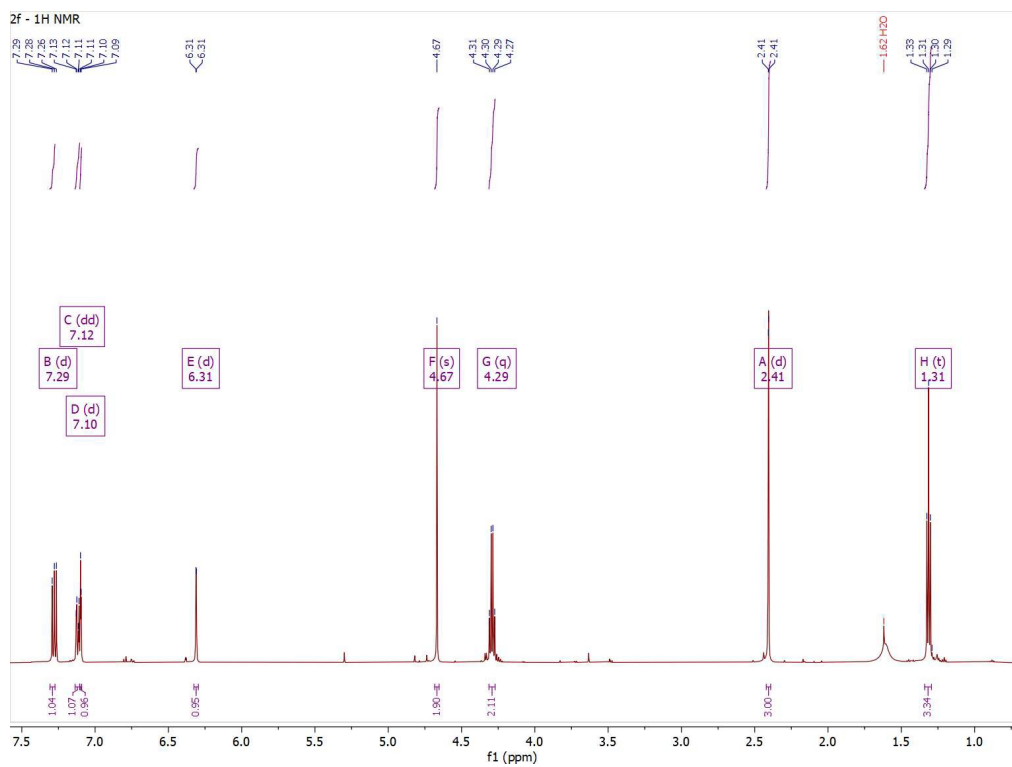


Figure S34. ¹H-NMR of 2f, Ethyl 2-(4-methyl-2-oxo-2H-chromen-6-yl)oxy)acetate (600 MHz, CDCl₃).

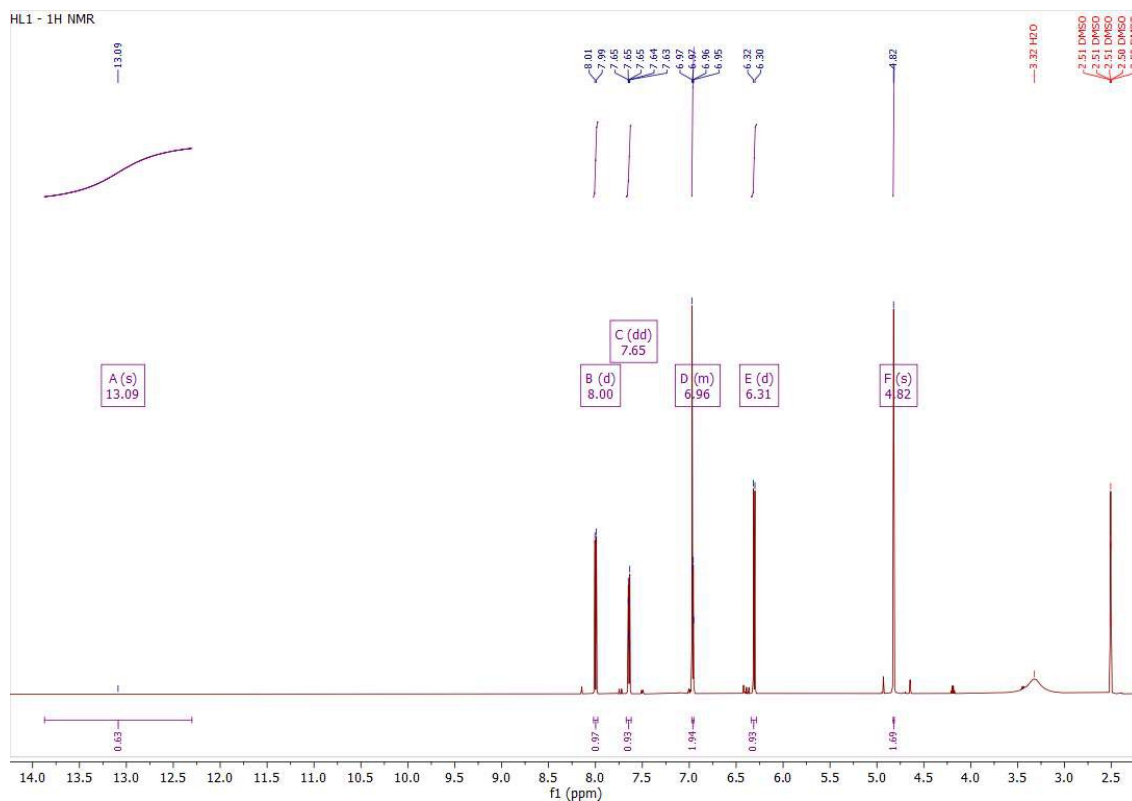


Figure S35 ¹H-NMR of HL¹, 2-((2-oxo-2H-chromen-7-yl)oxy)acetic acid (600 MHz, DMSO d₆).

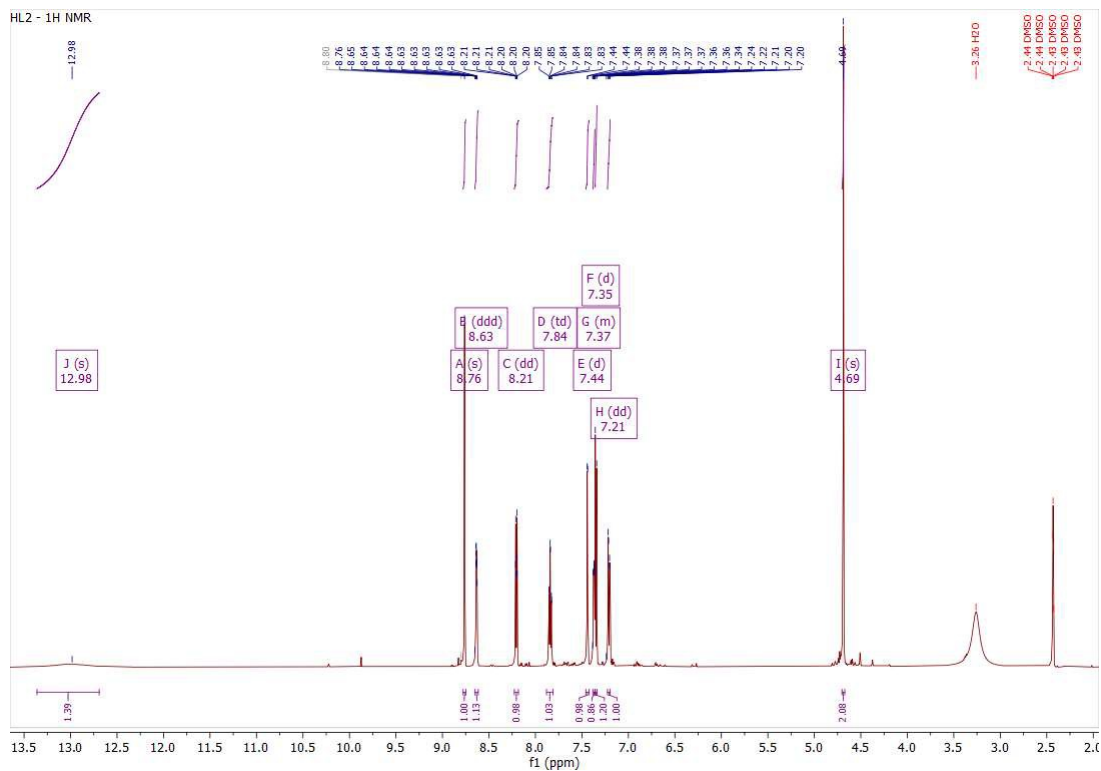


Figure S36. ¹H-NMR of HL², 2-((2-oxo-3-(pyridin-2-yl)-2H-chromen-7-yl)oxy)acetic acid (600 MHz, DMSO d₆).

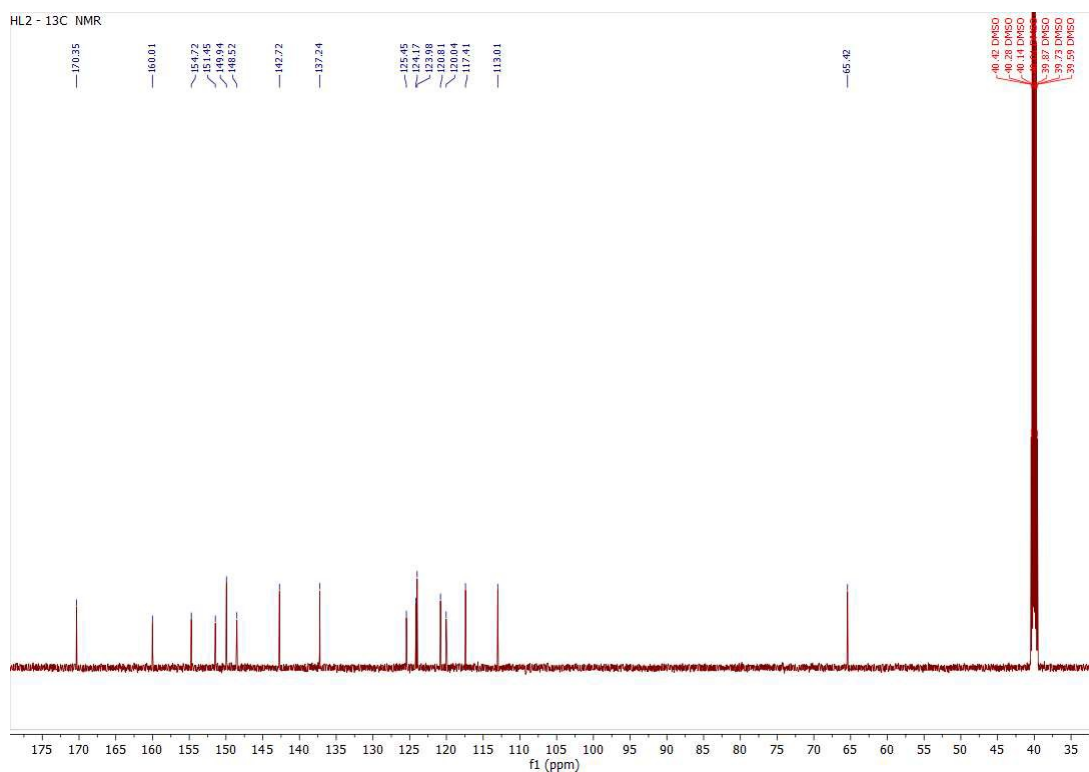


Figure S37. ^{13}C -NMR of HL², 2-((2-oxo-3-(pyridin-2-yl)-2H-chromen-7-yl)oxy)acetic acid (151 MHz, DMSO d₆).

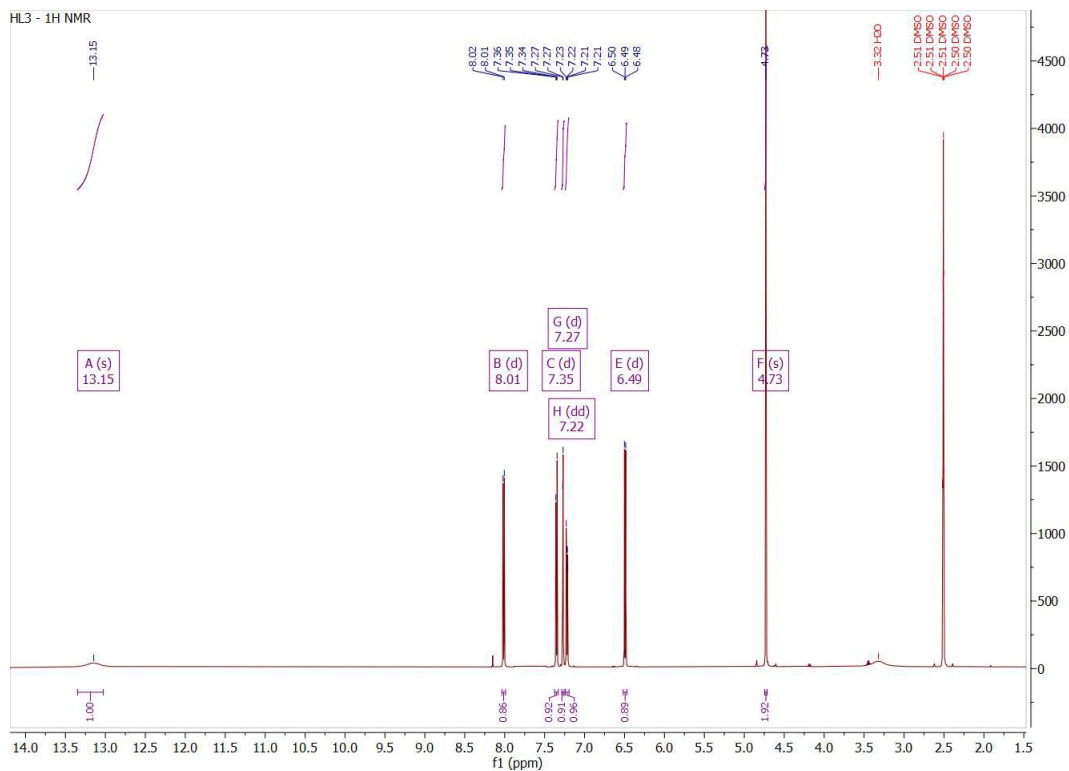


Figure S38. ^1H -NMR of HL³, 2-((2-oxo-2H-chromen-6-yl)oxy)acetic acid (600 MHz, DMSO d₆).

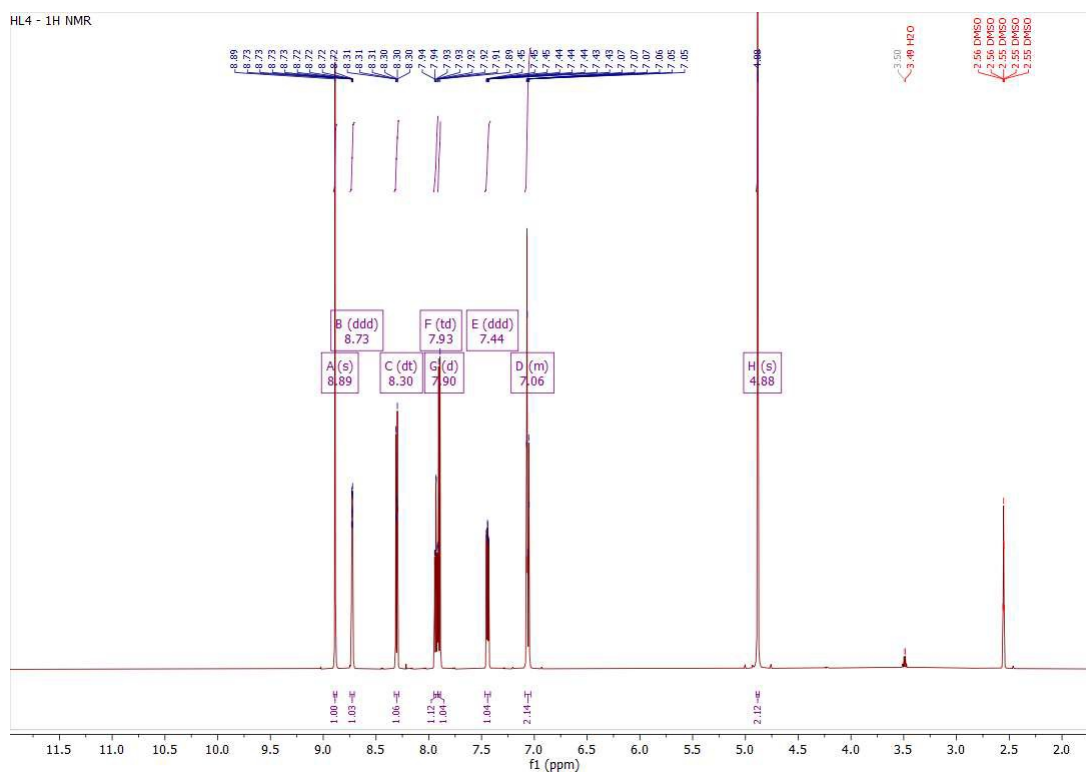


Figure S39. ¹H-NMR of HL⁴, 2-((2-oxo-3-(pyridin-2-yl)-2H-chromen-6-yl)oxy)acetic acid (600 MHz, DMSO d₆).

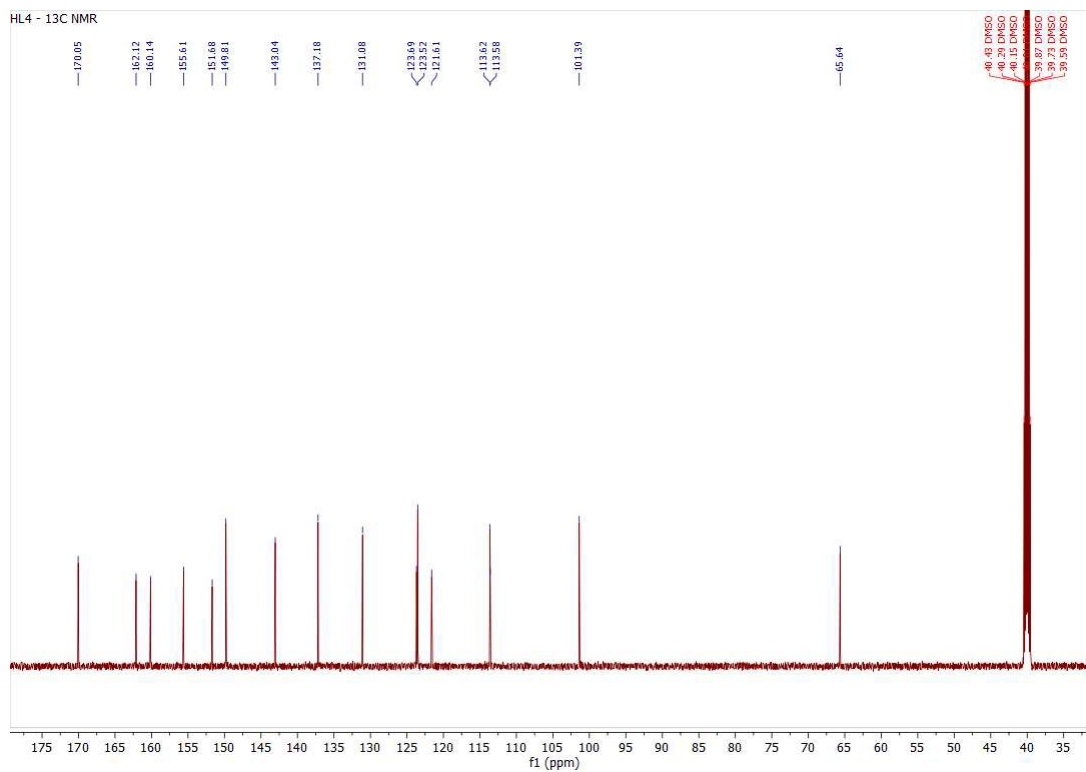


Figure S40. ¹³C-NMR of HL⁴, 2-((2-oxo-3-(pyridin-2-yl)-2H-chromen-6-yl)oxy)acetic acid (151 MHz, DMSO d₆).

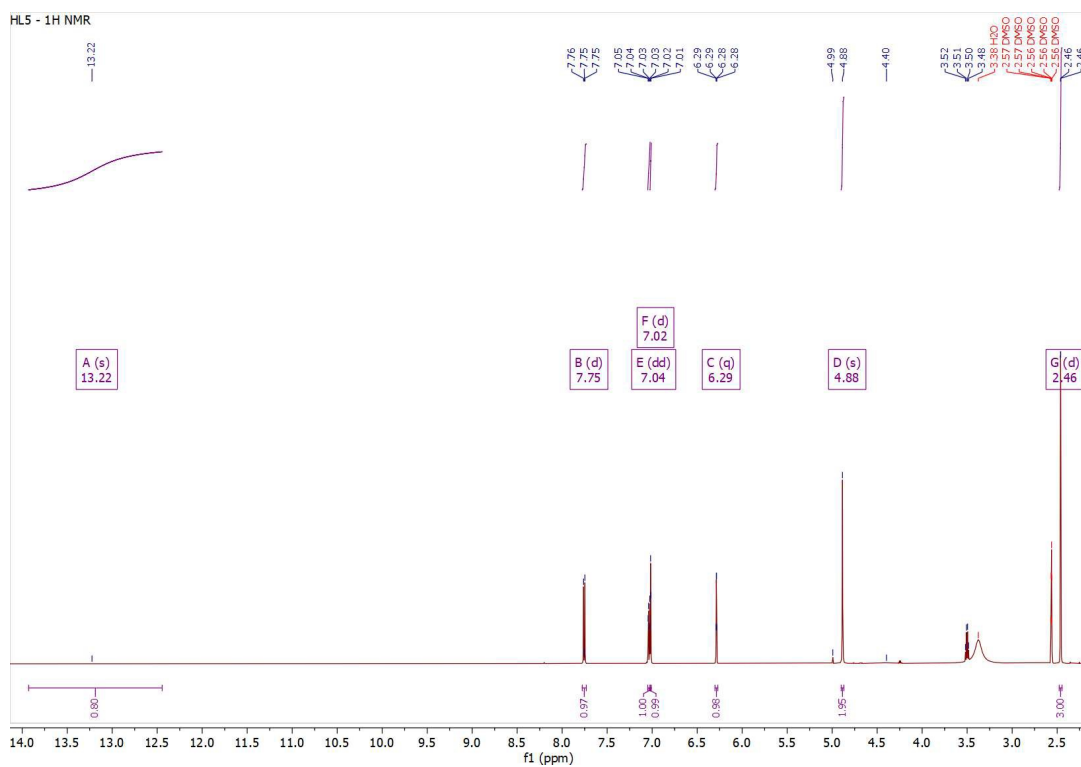


Figure S41. ¹H-NMR of HL⁵, 2-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)acetic acid (600 MHz, DMSO d₆).

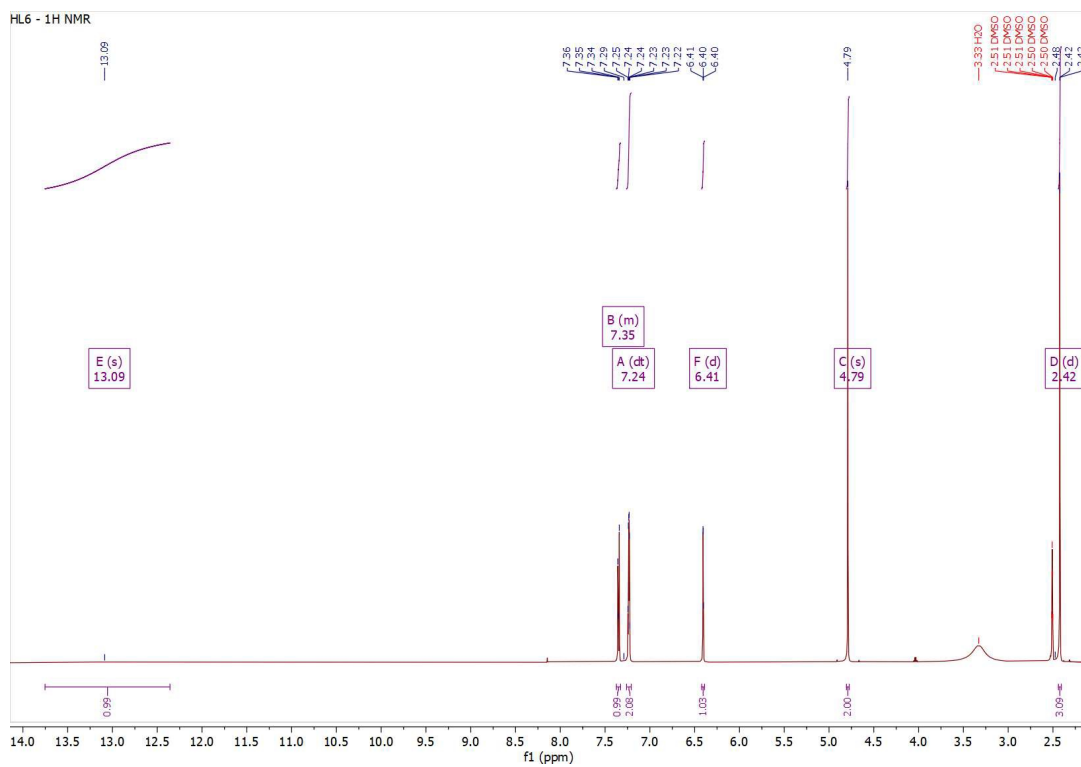


Figure S42. ¹H-NMR of HL⁶, 2-((4-methyl-2-oxo-2H-chromen-6-yl)oxy)acetic acid (600 MHz, DMSO d₆).

Table S1. Selected optimized bond distances (Å) and angles (°) for DFT-optimized structure of L¹ (gas phase) and corresponding X-Ray structural parameters. Atom labelling scheme as in Figure S12.

L ¹		
	Structural parameters	DFT-optimized
C1-O1	1.378	1.376
O1-C8	1.378	1.359
C1-O2	1.210	1.206
C6-O3	1.361	1.322
O3-C10	1.429	1.430
C11-O4	1.238	1.238
C11-O5	1.249	1.242
O1-C1-C2	117.12	116.38
C8-O1-C1	122.27	123.40
C6-O3-C10	117.88	119.56
C10-C11-O4	119.36	116.70
C10-C11-O5	113.51	111.44
O4-C11-O5	127.03	131.86
C8-O1-C1-C2	3.45	0.98
O3-C10-C11-O4	18.65	1.23
O3-C10-C11-O5	-164.68	-178.76

Table S2. Selected optimized bond distances (Å) and angles (°) for DFT-optimized structure of L² (gas phase). Atom labelling scheme as in Figure S12.

L ²			
C8-O1	1.353	C6-C5-N1	115.87
O1-C7	1.373	C7-C6-C5	121.74
C7-O2	1.207	C5-N1-C1	119.21
C7-C6	1.456	O1-C7-C6	116.80
C6-C5	1.473	C15-C16-O4	116.61
C5-N1	1.342	C15-C16-O5	111.37
N1-C1	1.321	O4-C16-O5	132.02

C13-O3	1.319	C7-C6-C5-N1	175.44
O3-C15	1.430	C8-O1-C7-O2	-178.76
C16-O4	1.238	C13-O3-C15-C16	68.61
C16-O5	1.241	O3-C15-C16-O4	2.36
C8-O1-C7	124.49	O3-C15-C16-O5	-177.86

Table S3. Selected optimized bond distances (Å) and angles (°) for DFT-optimized structure of L³ (gas phase). Atom labelling scheme as in Figure S12.

L ³			
C1-O1	1.364	C5-O3-C10	119.15
O1-C8	1.366	C10-C11-O4	118.04
C1-O2	1.206	C10-C11-O5	110.38
C5-O3	1.326	O4-C11-O5	131.59
O3-C10	1.431	C8-O1-C1-C2	0.06
C11-O4	1.235	O3-C10-C11-O4	0.63
C11-O5	1.245	O3-C10-C11-O5	-179.41
C8-O1-C1	122.78		

Table S4. Selected optimized bond distances (Å) and angles (°) for DFT-optimized structure of L⁴ (gas phase). Atom labelling scheme as in Figure S12.

L ⁴			
C8-O1	1.360	C6-C5-N1	115.47
O1-C7	1.362	C7-C6-C5	121.49
C7-O2	1.208	C5-N1-C1	119.24
C7-C6	1.465	O1-C7-C6	116.77
C6-C5	1.480	C15-C16-O4	118.04
C5-N1	1.340	C15-C16-O5	110.31
N1-C1	1.321	O4-C16-O5	131.64
C12-O3	1.326	C7-C6-C5-N1	-178.21
O3-C15	1.432	C8-O1-C7-O2	-179.68
C16-O4	1.235	C12-O3-C15-C16	-179.48
C16-O5	1.245	O3-C15-C16-O4	-0.60
C8-O1-C7	124.01	O3-C15-C16-O5	179.44

Table S5. Selected optimized bond distances (Å) and angles (°) for DFT-optimized structure of L⁵ (gas phase). Atom labelling scheme as in Figure S12.

L⁵

C1-O1	1.371	C7-O3-C11	119.50
O1-C9	1.356	C11-C12-O4	116.74
C1-O2	1.206	C11-C12-O5	111.44
C7-O3	1.322	O4-C12-O5	131.81
O3-C11	1.430	C9-O1-C1-C2	1.14
C12-O4	1.238	O3-C11-C12-O4	-1.04
C12-O5	1.242	O3-C110-C12-O5	178.90
C9-O1-C1	122.86		

Table S6. Selected optimized bond distances (Å) and angles (°) for DFT-optimized structure of L⁶ (gas phase). Atom labelling scheme as in Figure S12.

L⁶

C1-O1	1.363	C6-O3-C11	119.14
O1-C9	1.347	C11-C12-O4	118.03
C1-O2	1.207	C11-C12-O5	110.42
C6-O3	1.327	O4-C12-O5	131.55
O3-C11	1.431	C9-O1-C1-C2	0.02
C12-O4	1.235	O3-C11-C12-O4	0.71
C12-O5	1.246	O3-C110-C12-O5	-179.34
C9-O1-C1	122.23		

Table S7. Selected atomic charges, calculated at NPA level of L¹, L³ and L⁵. Atomic scheme as in Figure S12.

L ¹		L ³		L ⁵	
	NPA		NPA		NPA
O1	-0.428	O1	-0.576	O1	-0.427
O2	-0.579	O2	-0.724	O2	-0.582
O3	-0.429	O3	-0.421	O3	-0.431
O4	-0.728	O4	-0.724	O4	-0.729
O5	-0.742	O5	-0.757	O5	-0.743

Table S8. Selected atomic charges, calculated at NPA level, of L², L⁴ and L⁶. Atomic scheme as in Figure S12.

L ²	L ⁴	L ⁶
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	charges		charges		charges
O1	-0.423	O1	-0.422	O1	-0.427
O2	-0.591	O2	-0.592	O2	-0.581
O3	-0.423	O3	-0.419	O3	-0.422
O4	-0.726	O4	-0.723	O4	-0.725
O5	-0.738	O5	-0.757	O5	-0.757
N1	-0.436	N1	-0.425		

Table S9. Energy values (eV) of the frontier Molecular Orbitals of L¹⁻⁶ in gas phase at the DFT level (PBE0, def-2 TZVP).

compound	HOMO	LUMO
L ¹	-2.22	1.02
L ²	-2.36	0.41
L ³	-2.11	0.34
L ⁴	-2.13	-0.17
L ⁵	-2.18	1.08
L ⁶	-2.11	0.47

Table S10. Selected optimized bond distances (Å) and angles (°) for DFT-optimized structure of [Cu(phen)₂(L¹)]⁺ (gas phase). Atom labelling scheme as in Figure 3.

[Cu(phen) ₂ (L ¹)] ⁺			
Cu-N1	2.045	N3-Cu-O4	90.76
Cu-N2	2.285	N4-Cu-O4	160.08
Cu-N3	2.030	N1-Cu-N2	77.41
Cu-N4	2.087	N1-Cu-N3	176.12
Cu-O4	1.986	N1-Cu-N4	95.79
O4-C25	1.282	N1-Cu-O4-C25	-84.24
C25- O5	1.229	N1-Cu-N3-C13	-172.01
Cu-O4-C25	100.92	N1-Cu-N3-C24	10.36
Cu-N1-C1	123.63	N2-Cu-N3-C13	-82.31
Cu-N1-C12	116.68	N1-Cu-N3-C24	99.53
Cu-N2-C10	132.01	N3-Cu-N1-C1	-90.78
Cu-N2-C11	109.25	N3-Cu-N1-C12	92.08
Cu-N3-C13	126.95	N3-Cu-N2-C11	-178.12
Cu-N3-C24	113.66	N3-Cu-N2-C10	4.87
Cu-N4-C22	129.76	N4-Cu-N2-C11	-96.02

Cu-N4-C23	111.62	N4-Cu-N2-C10	86.97
N1-Cu-O4	93.06	Cu-O4-C25-O5	1.27
N2-Cu-O4	100.12		

Table S11. Selected optimized bond distances (Å) and angles (°) for DFT-optimized structure of $[\text{Cu}(\text{phen})_2(\text{L}^2)]^+$ (gas phase). Atom labelling scheme as in Figure 3.

$[\text{Cu}(\text{phen})_2(\text{L}^2)]^+$			
Cu-N1	2.043	N3-Cu-O4	90.57
Cu-N2	2.283	N4-Cu-O4	159.62
Cu-N3	2.029	N1-Cu-N2	77.47
Cu-N4	2.089	N1-Cu-N3	175.91
Cu-O4	1.991	N1-Cu-N4	95.58
O4-C25	1.281	N1-Cu-O4-C25	-83.87
C25- O5	1.223	N1-Cu-N3-C13	-175.22
Cu-O4-C25	100.46	N1-Cu-N3-C24	7.33
Cu-N1-C1	123.68	N2-Cu-N3-C13	-82.09
Cu-N1-C12	116.67	N1-Cu-N3-C24	100.46
Cu-N2-C10	132.03	N3-Cu-N1-C1	-86.68
Cu-N2-C11	109.24	N3-Cu-N1-C12	95.71
Cu-N3-C13	126.89	N3-Cu-N2-C11	-177.46
Cu-N3-C24	113.70	N3-Cu-N2-C10	5.20
Cu-N4-C22	129.77	N4-Cu-N2-C11	-95.40
Cu-N4-C23	111.57	N4-Cu-N2-C10	87.44
N1-Cu-O4	93.40	Cu-O4-C25-O5	0.59
N2-Cu-O4	99.93		

Table S12. Selected optimized bond distances (Å) and angles (°) for DFT-optimized structure of $[\text{Cu}(\text{phen})_2(\text{L}^3)]^+$ (gas phase). Atom labelling scheme as in Figure 3.

$[\text{Cu}(\text{phen})_2(\text{L}^3)]^+$			
Cu-N1	2.045	N3-Cu-O4	90.22
Cu-N2	2.286	N4-Cu-O4	161.64
Cu-N3	2.032	N1-Cu-N2	77.40
Cu-N4	2.080	N1-Cu-N3	177.00
Cu-O4	1.964	N1-Cu-N4	96.65
O4-C25	1.276	N1-Cu-O4-C25	-84.90
C25- O5	1.234	N1-Cu-N3-C13	165.29
Cu-O4-C25	103.00	N1-Cu-N3-C24	-12.46
Cu-N1-C1	123.57	N2-Cu-N3-C13	-82.98

Cu-N1-C12	116.59	N1-Cu-N3-C24	-99.27
Cu-N2-C10	132.00	N3-Cu-N1-C1	-68.48
Cu-N2-C11	109.11	N3-Cu-N1-C12	116.72
Cu-N3-C13	127.01	N3-Cu-N2-C11	178.49
Cu-N3-C24	113.55	N3-Cu-N2-C10	4.01
Cu-N4-C22	129.61	N4-Cu-N2-C11	-99.12
Cu-N4-C23	111.75	N4-Cu-N2-C10	86.40
N1-Cu-O4	92.37	Cu-O4-C25-O5	3.43
N2-Cu-O4	97.93		

Table S13. Selected optimized bond distances (Å) and angles (°) for DFT-optimized structure of $[\text{Cu}(\text{phen})_2(\text{L}^4)]^+$ (gas phase). Atom labelling scheme as in Figure 3.

$[\text{Cu}(\text{phen})_2(\text{L}^4)]^+$			
Cu-N1	2.047	N3-Cu-O4	89.78
Cu-N2	2.285	N4-Cu-O4	162.05
Cu-N3	2.034	N1-Cu-N2	77.35
Cu-N4	2.080	N1-Cu-N3	176.55
Cu-O4	1.959	N1-Cu-N4	96.46
O4-C25	1.277	N1-Cu-O4-C25	-84.93
C25- O5	1.233	N1-Cu-N3-C13	154.56
Cu-O4-C25	103.56	N1-Cu-N3-C24	-23.07
Cu-N1-C1	123.56	N2-Cu-N3-C13	-83.81
Cu-N1-C12	116.63	N1-Cu-N3-C24	-23.07
Cu-N2-C10	131.92	N3-Cu-N1-C1	-58.67
Cu-N2-C11	109.22	N3-Cu-N1-C12	126.18
Cu-N3-C13	127.00	N3-Cu-N2-C11	179.17
Cu-N3-C24	113.55	N3-Cu-N2-C10	4.32
Cu-N4-C22	129.53	N4-Cu-N2-C11	-98.54
Cu-N4-C23	111.84	N4-Cu-N2-C10	86.62
N1-Cu-O4	92.89	Cu-O4-C25-O5	5.74
N2-Cu-O4	98.02		

Table S14. Selected optimized bond distances (Å) and angles (°) for DFT-optimized structure of $[\text{Cu}(\text{phen})_2(\text{L}^5)]^+$ (gas phase). Atom labelling scheme as in Figure 3.

$[\text{Cu}(\text{phen})_2(\text{L}^5)]^+$			
Cu-N1	2.045	N3-Cu-O4	90.72
Cu-N2	2.284	N4-Cu-O4	159.92
Cu-N3	2.030	N1-Cu-N2	77.42

Cu-N4	2.087	N1-Cu-N3	95.86
Cu-O4	1.986	N1-Cu-N4	-84.47
O4-C25	1.283	N1-Cu-O4-C25	-173.38
C25- O5	1.229	N1-Cu-N3-C13	9.17
Cu-O4-C25	100.80	N1-Cu-N3-C24	-82.85
Cu-N1-C1	123.62	N2-Cu-N3-C13	99.70
Cu-N1-C12	116.68	N1-Cu-N3-C24	-89.55
Cu-N2-C10	132.01	N3-Cu-N1-C1	93.42
Cu-N2-C11	109.25	N3-Cu-N1-C12	-178.18
Cu-N3-C13	126.95	N3-Cu-N2-C11	4.73
Cu-N3-C24	113.66	N3-Cu-N2-C10	-96.07
Cu-N4-C22	129.76	N4-Cu-N2-C11	86.85
Cu-N4-C23	111.61	N4-Cu-N2-C10	1.50
N1-Cu-O4	93.00	Cu-O4-C25-O5	
N2-Cu-O4	100.27		

Table S15. Selected optimized bond distances (Å) and angles (°) for DFT-optimized structure of $[\text{Cu}(\text{phen})_2(\text{L}^6)]^+$ (gas phase). Atom labelling scheme as in Figure 3.

$[\text{Cu}(\text{phen})_2(\text{L}^6)]^+$			
Cu-N1	2.046	N3-Cu-O4	90.21
Cu-N2	2.289	N4-Cu-O4	161.75
Cu-N3	2.032	N1-Cu-N2	77.38
Cu-N4	2.080	N1-Cu-N3	176.96
Cu-O4	1.965	N1-Cu-N4	96.61
O4-C25	1.276	N1-Cu-O4-C25	-84.87
C25- O5	1.234	N1-Cu-N3-C13	165.49
Cu-O4-C25	102.91	N1-Cu-N3-C24	-12.24
Cu-N1-C1	123.56	N2-Cu-N3-C13	-83.13
Cu-N1-C12	116.62	N1-Cu-N3-C24	99.13
Cu-N2-C10	132.00	N3-Cu-N1-C1	-68.83
Cu-N2-C11	109.12	N3-Cu-N1-C12	116.26
Cu-N3-C13	127.01	N3-Cu-N2-C11	178.68
Cu-N3-C24	113.55	N3-Cu-N2-C10	4.02
Cu-N4-C22	129.61	N4-Cu-N2-C11	-98.97
Cu-N4-C23	111.76	N4-Cu-N2-C10	86.38
N1-Cu-O4	92.43	Cu-O4-C25-O5	3.49
N2-Cu-O4	98.01		

Table S16. Tau ($\tau = \frac{\ln I}{\sigma}$) parameters calculated from the DFT-optimized structures (gas phase) of $[\text{Cu}(\text{phen})_2(\text{L}^x)]^+$ (x = 1 - 6). Atom labelling scheme as in Figure 3.

	τ (N1 - N2 - N3)	τ (N1 - N4 - N5)	τ
$[\text{Cu}(\text{phen})_2(\text{L}^1)]^+$	176.12	160.08	0.27
$[\text{Cu}(\text{phen})_2(\text{L}^2)]^+$	175.91	159.62	0.27
$[\text{Cu}(\text{phen})_2(\text{L}^3)]^+$	177.00	161.64	0.26
$[\text{Cu}(\text{phen})_2(\text{L}^4)]^+$	176.55	162.05	0.24
$[\text{Cu}(\text{phen})_2(\text{L}^5)]^+$	177.00	161.64	0.26
$[\text{Cu}(\text{phen})_2(\text{L}^6)]^+$	176.97	161.75	0.25

Table S17. Selected atomic charges, calculated at NPA level, of $[\text{Cu}(\text{phen})_2(\text{L}^1)]^+$, $[\text{Cu}(\text{phen})_2(\text{L}^3)]^+$ and $[\text{Cu}(\text{phen})_2(\text{L}^5)]^+$. Atomic scheme as in Figure 3.

$[\text{Cu}(\text{phen})_2(\text{L}^1)]^+$		$[\text{Cu}(\text{phen})_2(\text{L}^3)]^+$		$[\text{Cu}(\text{phen})_2(\text{L}^5)]^+$	
	charges		charges		charges
Cu	1.396	Cu	1.394	Cu	1.396
N1	-0.501	N1	-0.499	N1	-0.501
N2	-0.481	N2	-0.481	N2	-0.486
N3	-0.489	N3	-0.484	N3	-0.481
N4	-0.489	N4	-0.490	N4	-0.489
O1	-0.427	O1	-0.424	O1	-0.427
O2	-0.523	O2	-0.525	O2	-0.531
O3	-0.424	O3	-0.442	O3	-0.425
O4	-0.774	O4	-0.750	O4	-0.774
O5	-0.687	O5	-0.705	O5	-0.687

Table S18. Selected atomic charges, calculated at NPA level, of $[\text{Cu}(\text{phen})_2(\text{L}^2)]^+$, $[\text{Cu}(\text{phen})_2(\text{L}^4)]^+$ and $[\text{Cu}(\text{phen})_2(\text{L}^6)]^+$. Atomic scheme as in Figure 3.

$[\text{Cu}(\text{phen})_2(\text{L}^2)]^+$		$[\text{Cu}(\text{phen})_2(\text{L}^4)]^+$		$[\text{Cu}(\text{phen})_2(\text{L}^6)]^+$	
	charges		charges		charges
Cu	1.396	Cu	1.393	Cu	1.394

N1	-0.503	N1	-0.490	N1	-0.169
N2	-0.482	N2	-0.481	N2	-0.480
N3	-0.489	N3	-0.490	N3	-0.489
N4	-0.489	N4	-0.490	N4	-0.490
N5	-0.432	N5	-0.427	O1	-0.424
O1	-0.424	O1	-0.420	O2	-0.531
O2	-0.543	O2	-0.547	O3	-0.443
O3	-0.424	O3	-0.444	O4	-0.750
O4	-0.773	O4	-0.751	O5	-0.705
O5	-0.689	O5	-0.701		

Table S19. Energy values (eV) of the frontier Molecular Orbitals of $[\text{Cu}(\text{phen})_2(\text{L}^x)]^+$ ($x = 1 - 6$) in gas phase at the DFT level (PBE0, def-2 TZVP).

compound	α -SOMO	α -LUMO	β -SOMO	β -LUMO
$[\text{Cu}(\text{phen})_2(\text{L}^1)]^+$	-8.78	-8.04	-8.79	-8.05
$[\text{Cu}(\text{phen})_2(\text{L}^2)]^+$	-8.04	-5.29	-8.04	-5.32
$[\text{Cu}(\text{phen})_2(\text{L}^3)]^+$	-7.88	-5.27	-7.88	-5.28
$[\text{Cu}(\text{phen})_2(\text{L}^4)]^+$	-7.71	-5.22	-7.71	-5.23
$[\text{Cu}(\text{phen})_2(\text{L}^5)]^+$	-7.94	-5.28	-7.95	-5.31
$[\text{Cu}(\text{phen})_2(\text{L}^6)]^+$	-7.80	-5.27	-7.80	-5.28