**Electronic Supplementary Information:**

# Anion Directed Structural Diversity in Zinc Complexes with Conformationally Flexible Quinazoline Ligand: Structural, Spectral and Theoretical Studies

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## Supplementary Materials

**Section 1:** Mechanistic aspects.

We have studied another similar compound, 2-hydroxyquinazoline (Fig. S1) separately and observed that O-H adjacent to N1 appears at 13.90 as singlet. Since H of OH prefers to interact with more basic nitrogen, it indicates that N1 is more basic than N2 in quinazoline ring.

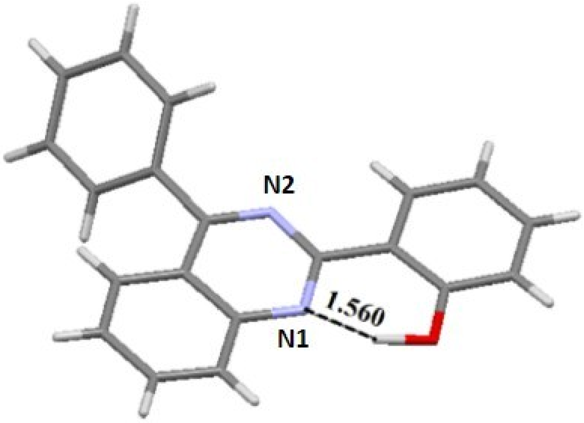
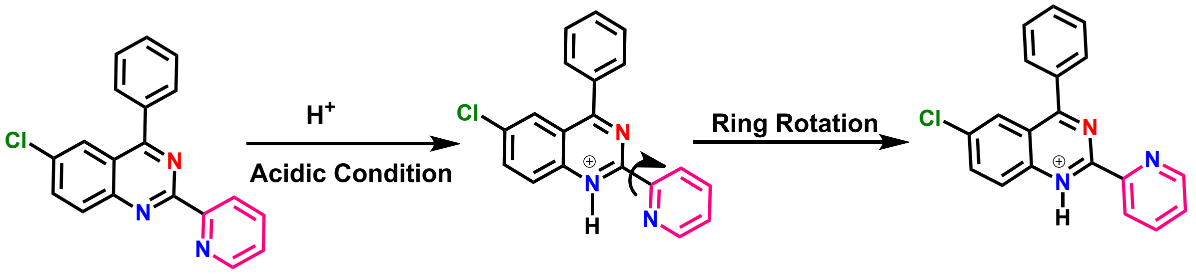


**Fig. S1:** Chemical structure of 2-hydroxyquinazoline. Atoms of our interest are numbered.

This knowledge helps us to understand that N1 should be protonated under acidic condition preferably over N2. Once N1 is protonated, it remains unavailable for complexation. We have observed on pH dependent studies for our system presented here that the pH of the solution having $Zn(OAc)_2$ is basic (pH: ~6.8) while that of $Zn(NO_3)_2$ is acidic (pH:~ 4.2). Therefore, it appears that anion is basically fine controlling the pH of reaction mixture. It is established that at neutral condition, conformer **A** is more favourable than conformer **B** for metal complexation. However when Zn metal-anion is changed to $Zn(NO_3)_2$, the acidity of reaction mixture enhances leading to protonation of N1. Once it is protonated, the N1 remains unavailable leading to rotation of the pyridine ring for complexation through availabe N2. This sequence is shown in Scheme S1.



**Conformer A**

**Conformer B**

**Scheme S1:** The possible sequences which leads to twisting of pyridine ring attached with quinazoline ring.

Acidic condition induced conformational changes is also reported for a flexible dimine molecule. (Ref: *Phys. Chem. Chem. Phys., 2016, 18, 7055-7067*).

**Section 2:** Selected bond lengths (Å) and angles (°) and hydrogen bond table for Ligand and complexes **1, 2, 3 & 4** obtained from X-ray diffraction

**Table S1:** Selected bond lengths (Å) and angles (°) for Ligand and complexes **1, 2, 3 & 4** obtained from X-ray diffraction

| | | | |
|---|---|---|---|
| | | **L** | |
| | | **Bond lengths** | |
| Cl(1)-C(4) | 1.7412(19) | N(1)-C(8) | 1.368(2) |
| N(2)-C(2) | 1.316(2) | N(1)-C(1) | 1.312(2) |

| | | | |
|---|---|---|---|
| N(2)-C(1) | 1.368(2) | N(3)-C(16) | 1.331(2) |
| N(3)-C(15) | 1.337(2) | Cl(1)-C(4) | 1.7412(19) |

**Bond angles**

| | | | |
|---|---|---|---|
| C(2)-N(2)-C(1) | 117.79(14) | N(1)-C(1)-C(15) | 118.58(15) |
| C(1)-N(1)-C(8) | 116.61(14) | N(2)-C(1)-C(15) | 115.21(14) |
| C(16)-N(3)-C(15) | 117.01(16) | N(1)-C(8)-C(7) | 121.93(14) |
| N(1)-C(1)-N(2) | 126.17(16) | N(1)-C(8)-C(6) | 119.03(16) |
| N(2)-C(2)-C(9) | 116.96(14) | N(1)-C(1)-C(15) | 118.58(15) |

**$[Zn_2(L)_2(\mu\text{-}N_3)_2(CH_3COO)_2]$ 1**

**Bond lengths**

| | | | |
|---|---|---|---|
| Zn(1)-O(1) | 2.477(4) | Zn(1)-N(3) | 2.106(3) |
| Zn(1)-O(2) | 2.034(3) | Zn(1)-N(4) | 2.054(3) |
| Zn(1)-N(1) | 2.218(3) | Zn(1)-N(4)#1 | 2.190(3) |

**Bond angles**

| | | | |
|---|---|---|---|
| O(2)-Zn(1)-N(4) | 105.70(14) | N(3)-Zn(1)-N(1) | 76.88(12) |
| O(2)-Zn(1)-N(3) | 143.14(13) | N(4)-Zn(1)-N(1)#1 | 165.74(13) |
| N(4)-Zn(1)-N(3) | 111.15(14) | O(2)-Zn(1)-O(1) | 56.23(12) |
| O(2)-Zn(1)-N(4)#1 | 92.98(13) | N(4)-Zn(1)-O(1) | 161.86(14) |
| N(4)-Zn(1)-N(4)#1 | 80.55(14) | N(3)-Zn(1)-O(1) | 86.96(13) |
| N(3)-Zn(1)-N(4)#1 | 92.02(13) | N(4)-Zn(1)-O(1)#1 | 100.50(13) |
| O(2)-Zn(1)-N(1) | 101.28(12) | N(1)-Zn(1)-O(1) | 87.99(11) |
| N(4)-Zn(1)-N(1) | 94.98(12) | | |

**$[Zn_2(L)(Cl)_2]$ 2**

**Bond lengths**

| | | | |
|---|---|---|---|
| Zn(1)-N(3) | 2.077(3) | Zn(1)-Cl(2) | 2.2067(16) |
| Zn(1)-N(1) | 2.159(3) | Zn(1)-Cl(3) | 2.2094(15) |

**Bond angles**

| | | | |
|---|---|---|---|
| N(3)-Zn(1)-N(1) | 78.11(13) | N(3)-Zn(1)-Cl(3) | 119.52(11) |
| N(3)-Zn(1)-Cl(2) | 111.12(11) | N(1)-Zn(1)-Cl(3) | 98.66(10) |
| N(1)-Zn(1)-Cl(2) | 103.97(10) | Cl(2)-Zn(1)-Cl(3) | 127.63(6) |

**$[Zn_2(L)_2(N_3)_4]$ 3**

**Bond lengths**

| | | | |
|---|---|---|---|
| Zn(1)-N(2) | 2.259(3) | Zn(1)-N(7) | 2.023(4) |
| Zn(1)-N(3) | 2.065(3) | Zn(1)-N(7)#1 | 2.180(3) |
| Zn(1)-N(4) | 1.940(3) | | |

**Bond angles**

| | | | |
|---|---|---|---|
| N(4)-Zn(1)-N(7) | 132.71(16) | N(3)-Zn(1)-N(7)#1 | 94.81(12) |
| N(4)-Zn(1)-N(3) | 123.88(16) | N(4)-Zn(1)-N(2) | 96.27(13) |
| N(7)-Zn(1)-N(3) | 103.38(12) | N(7)-Zn(1)-N(2) | 96.10(13) |
| N(4)-Zn(1)-N(7)#1 | 93.22(14) | N(3)-Zn(1)-N(2) | 76.37(12) |

| | | | |
|---|---|---|---|
| N(7)-Zn(1)-N(7)#1 | 80.44(16) | N(2)-Zn(1)-N(7)#1 | 169.61(11) |

**$[Zn_2(L)(Cl)_2]$ 4**

**Bond lengths**

| | | | |
|---|---|---|---|
| Zn(1)-N(3) | 2.060(6) | Zn(1)-Cl(2) | 2.200(3) |
| Zn(1)-N(2) | 2.083(6) | Zn(1)-Cl(3) | 2.205(3) |

**Bond angles**

| | | | |
|---|---|---|---|
| N(3)-Zn(1)-N(2) | 79.7(2) | N(3)-Zn(1)-Cl(3) | 114.9(2) |
| N(3)-Zn(1)-Cl(2) | 106.87(19) | N(2)-Zn(1)-Cl(3) | 107.32(19) |
| N(2)-Zn(1)-Cl(2) | 122.06(19) | Cl(2)-Zn(1)-Cl(3) | 119.46(10) |

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

**Table S2:** Hydrogen bond length (Å) and bond angle (°) in ligand and complexes **1-4**

| **D-H···A** | **d(D-H) / Å** | **d(H···A) / Å** | **d(D···A) / Å** | **<(DHA) / °** |
|---|---|---|---|---|
| **L** | | | | |
| C(5)-H(5)···N(3)#1 | 0.93 | 2.62 | 3.419(2) | 144.2 |
| **1** | | | | |
| C(5)-H(5)···O(2)#1 | 0.93 | 2.62 | 3.422(5) | 144.8 |
| C(16)-H(16)···N(4)#2 | 0.93 | 2.59 | 3.174(6) | 121.6 |
| **2** | | | | |
| C(16)-H(16)···Cl(2)#1 | 0.93 | 2.63 | 3.387(5) | 138.8 |
| **3** | | | | |
| C(17)-H(17)···N(6)#2 | 0.93 | 2.68 | 3.302(6) | 125.1 |
| C(6)-H(6)···N(5)#3 | 0.93 | 2.69 | 3.614(5) | 170.2 |
| C(6)-H(6)···N(6)#3 | 0.93 | 2.64 | 3.537(6) | 161.7 |
| **4** | | | | |
| C(6)-H(6)...Cl(1)#1 | 0.93 | 2.92 | 3.740(8) | 148.2 |

Symmetry transformations used to generate equivalent atoms: #1 -x, -y+1, -z for **L**; #1 -x+1/2, -y-1/2, -z; #2 -x+1/2, -y+1/2, -z for **1**; #1 -x+1, -y, -z+1 for **2**; #2 x, -y+1/2, z+1/2; #3 -x+1, -y, -z+2; #3 -x+1, -y, -z+2 for **3**; #1 x+1/2, -y+3/2, -z+1 for **4**.

**Section-3:** Hirshfeld 2D fingerprint plot diagrams for Ligand and complexes.

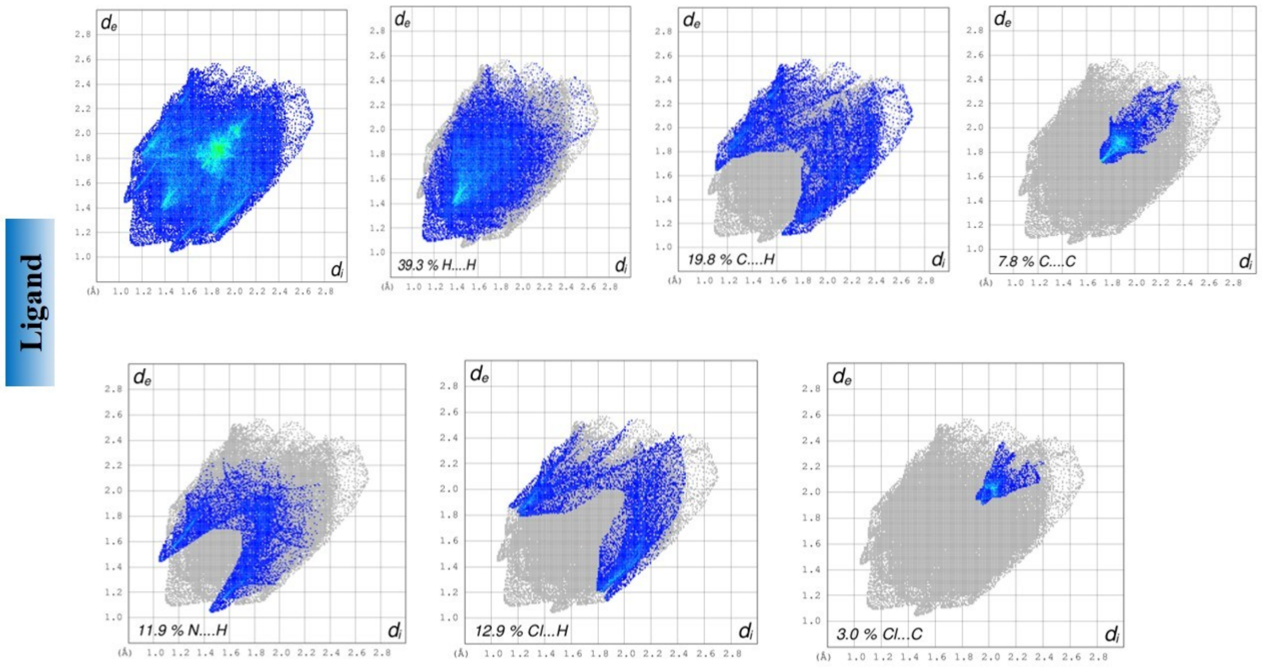


**Fig. S2**: 2D fingerprint plots for Ligand (**L**).

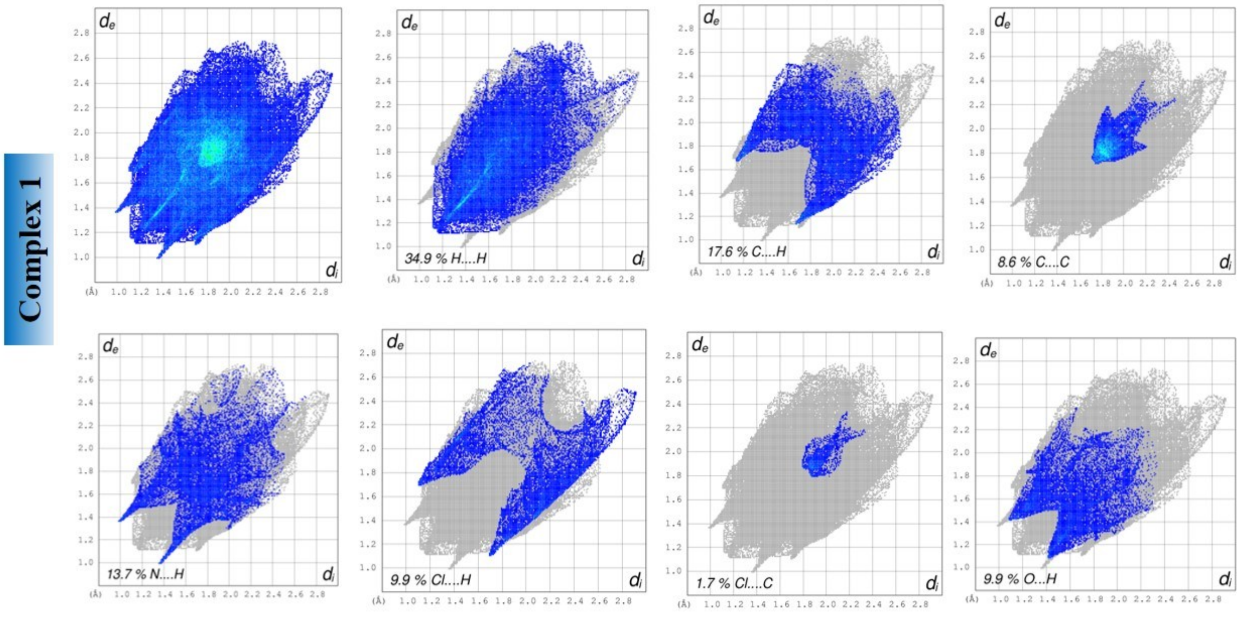


**Fig. S3**: 2D fingerprint plots for complex **1**.

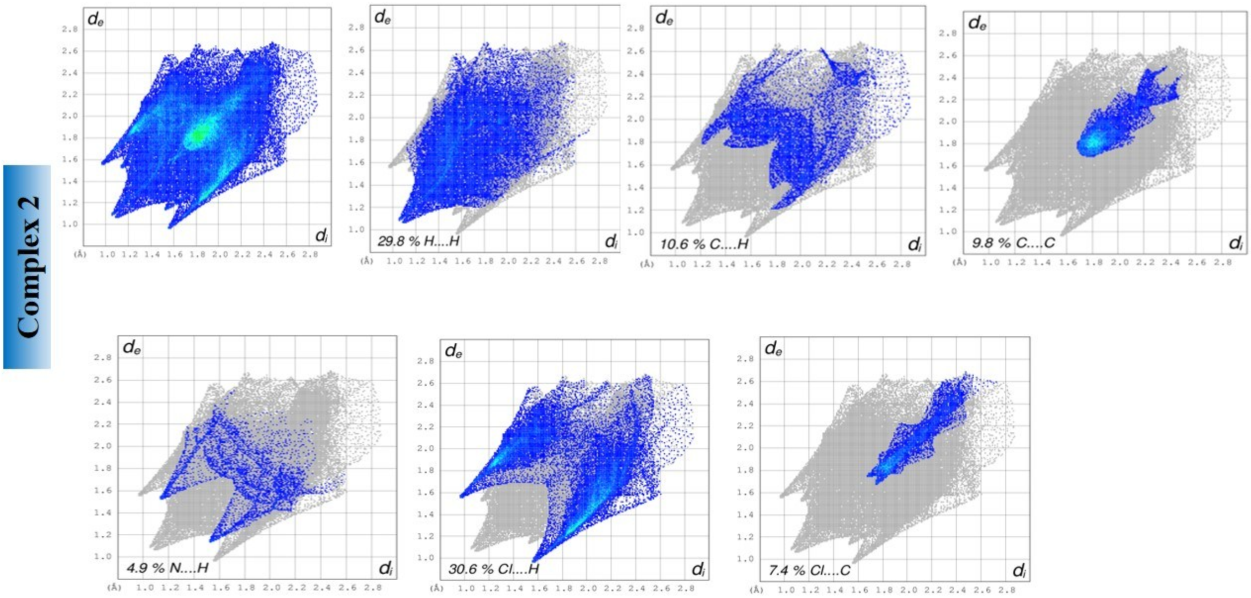


**Fig. S4**: 2D fingerprint plots for complex **2**.

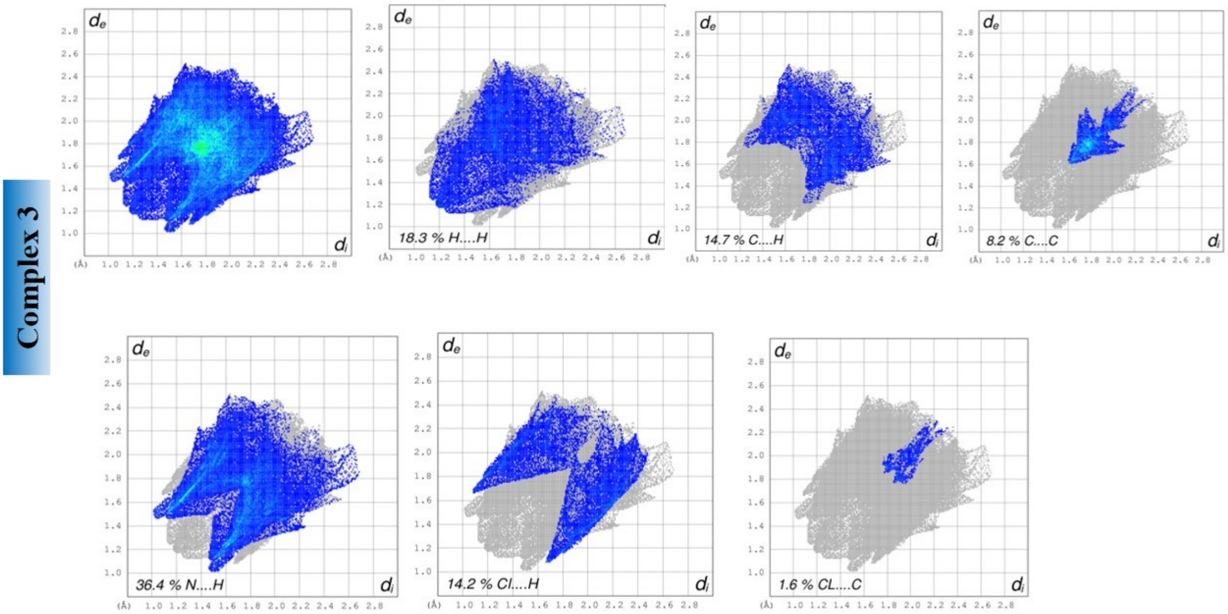


**Fig. S5**: 2D fingerprint plots for complex **3**.

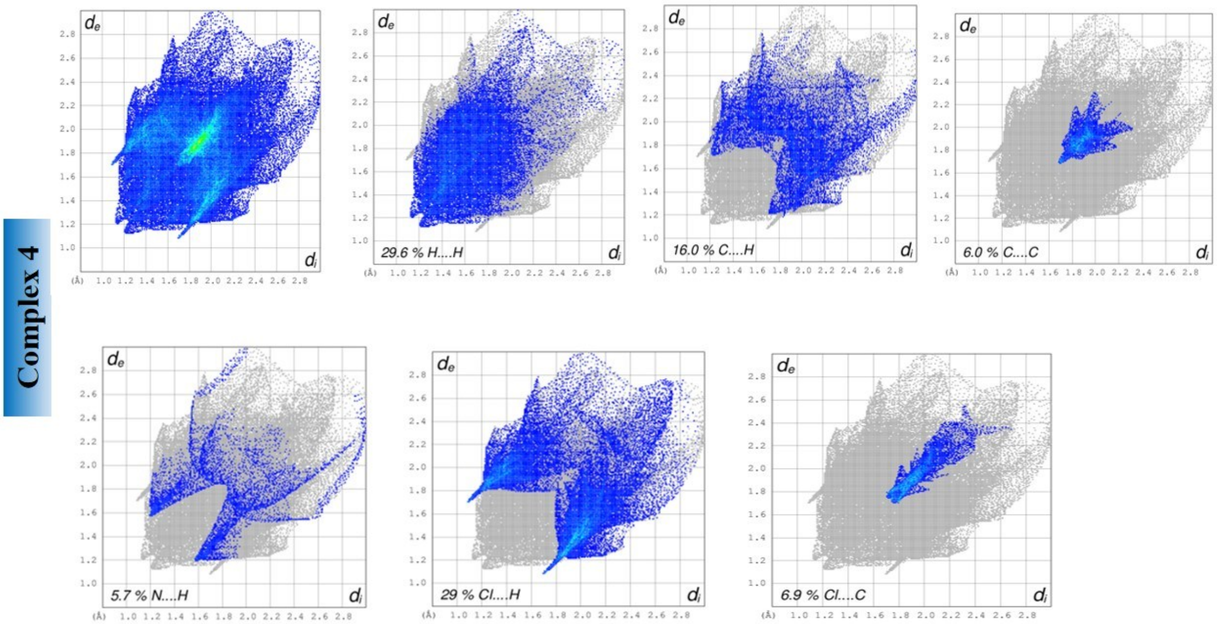


**Fig. S6**: 2D fingerprint plots for complex **4**.

**Section-4:** Theoretical calculations.

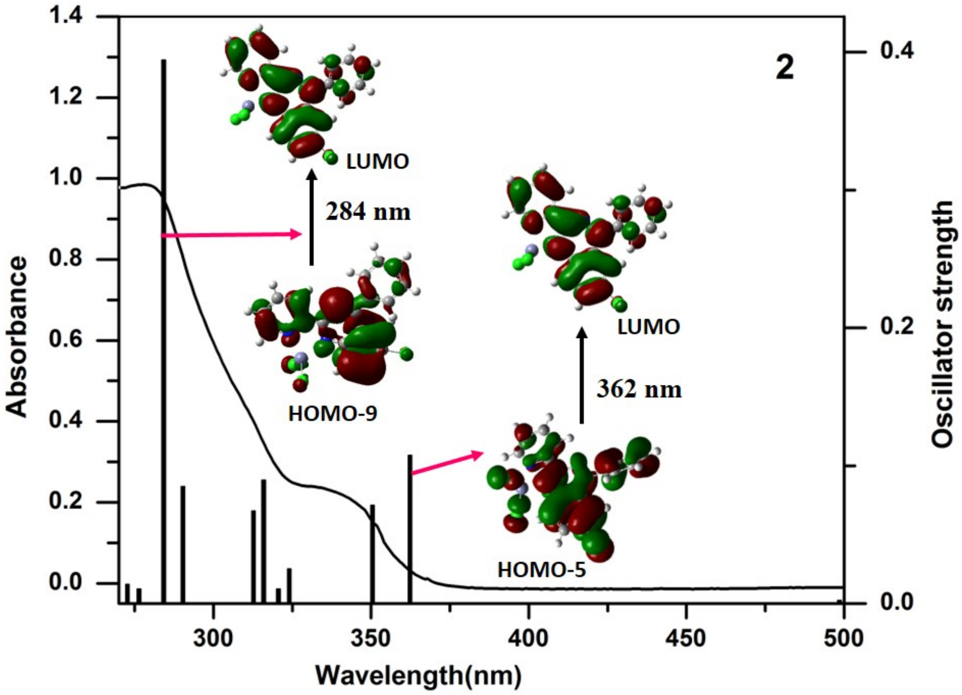


**Fig. S7**: UV-Visible spectrum of complex **2** in DMSO (curved line). Vertical lines correspond to TD-DFT calculated data. No correction is employed on the positions of calculated transition energies. The height of the lines indicate the strength of the transition. The orbitals associated with two important transitions are also shown in the figure.

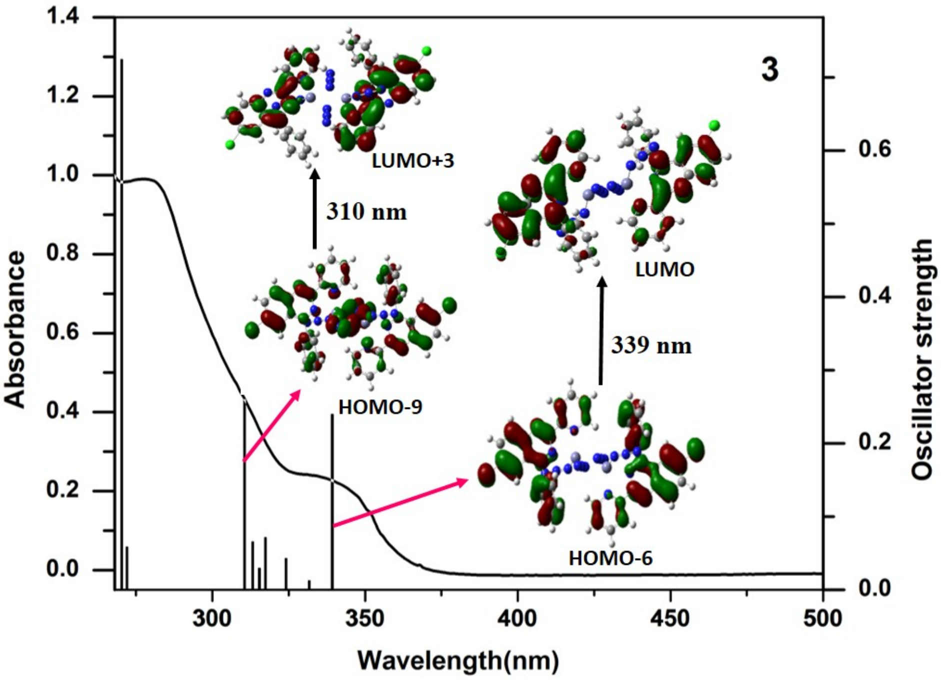


**Fig. S8**: UV-Visible spectrum of complex **3** in DMSO (curved line). Vertical lines correspond to TD-DFT calculated data. No correction is employed on the positions of calculated transition energies. The height of the lines indicate the strength of the transition. The orbitals associated with two important transitions are also shown in the figure.

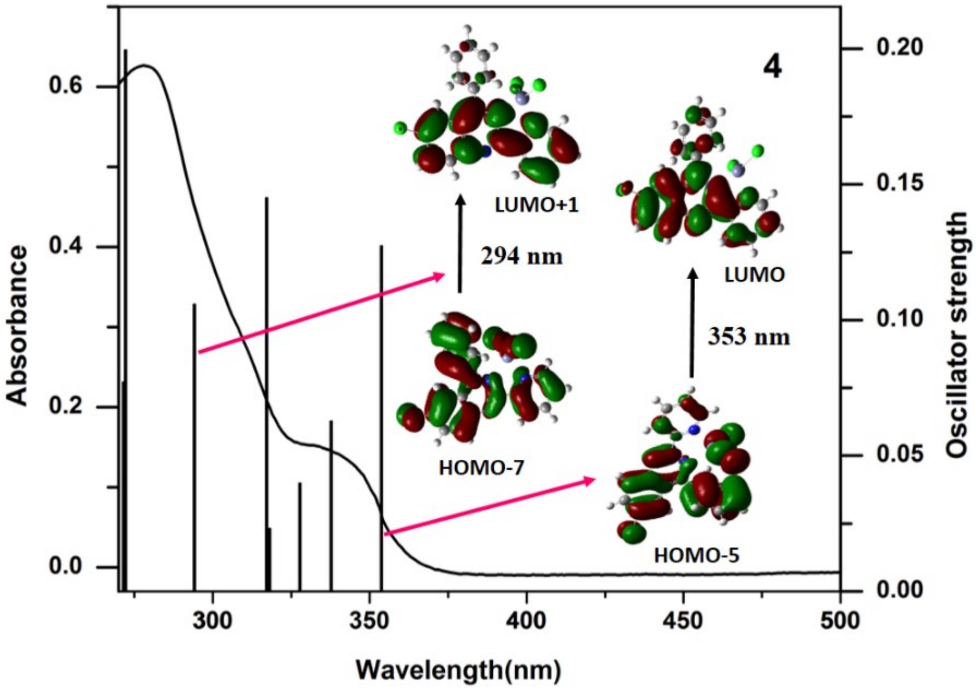


**Fig. S9**: UV-Visible spectrum of complex **4** in DMSO (curved line). Vertical lines correspond to TD-DFT calculated data. No correction is employed on the positions of calculated transition energies. The height of the lines indicate the strength of the transition. The orbitals associated with two important transitions are also shown in the figure.

**Section-3:** $^{1}$H NMR and $^{13}$C spectra for the ligand and complexes.

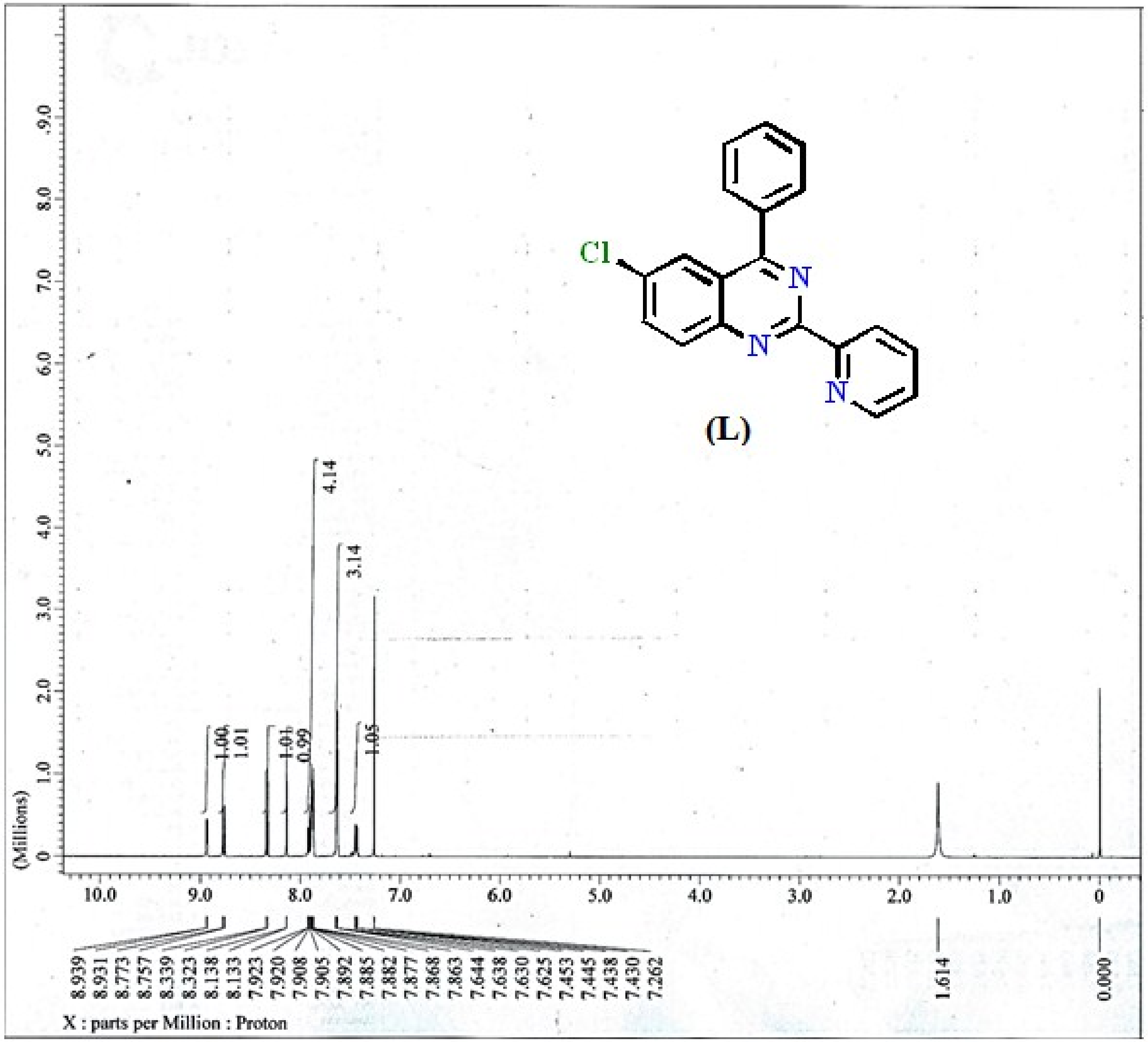


**Fig. S10**: $^{1}$H spectra of Ligand (**L**) in $CDCl_3$.

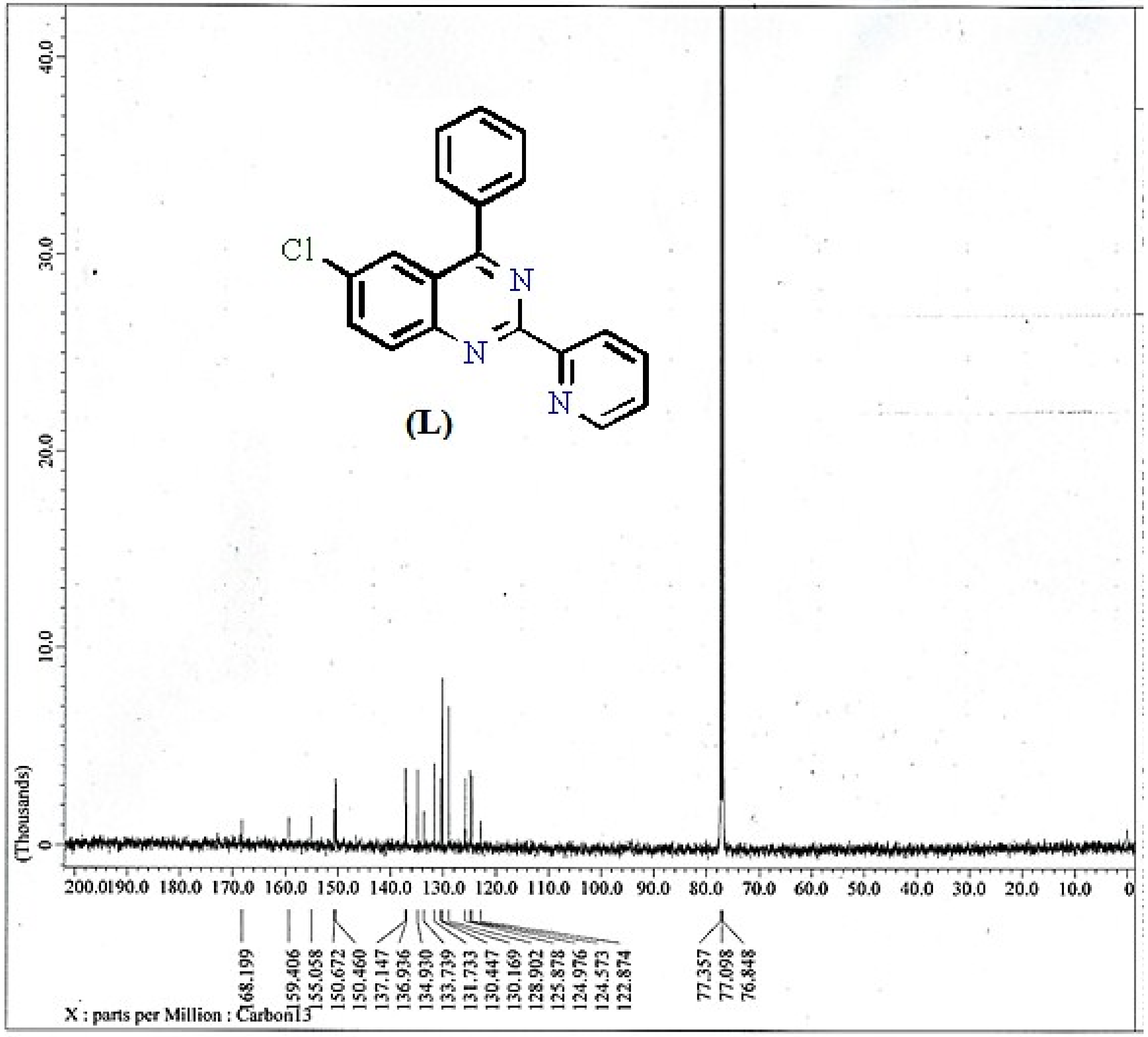


**Fig. S11**: $^{13}$C spectra of Ligand (**L**) in $CDCl_3$.

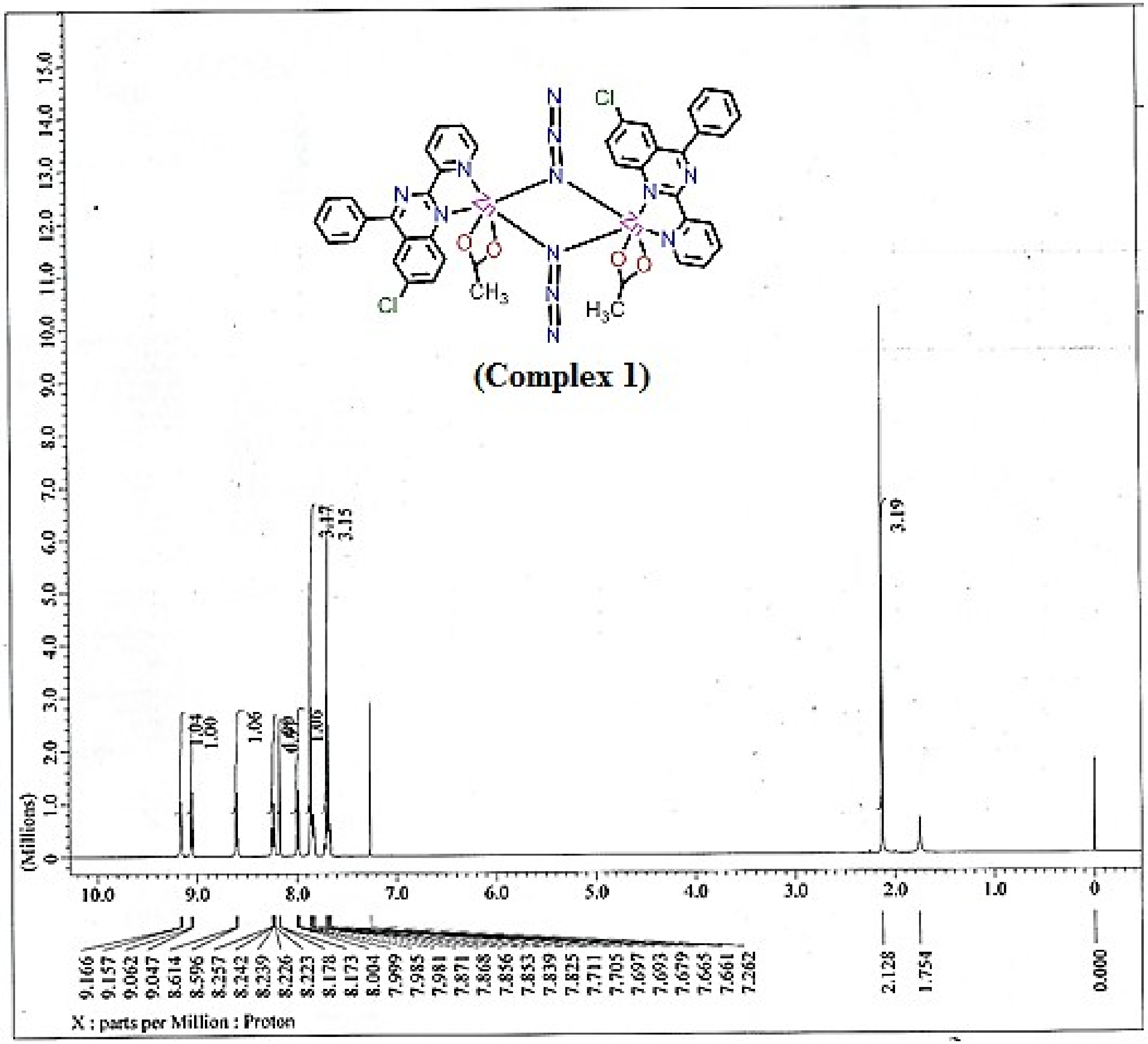


**Fig. S12**: $^1$H spectra of Complex **1** in $CDCl_3$

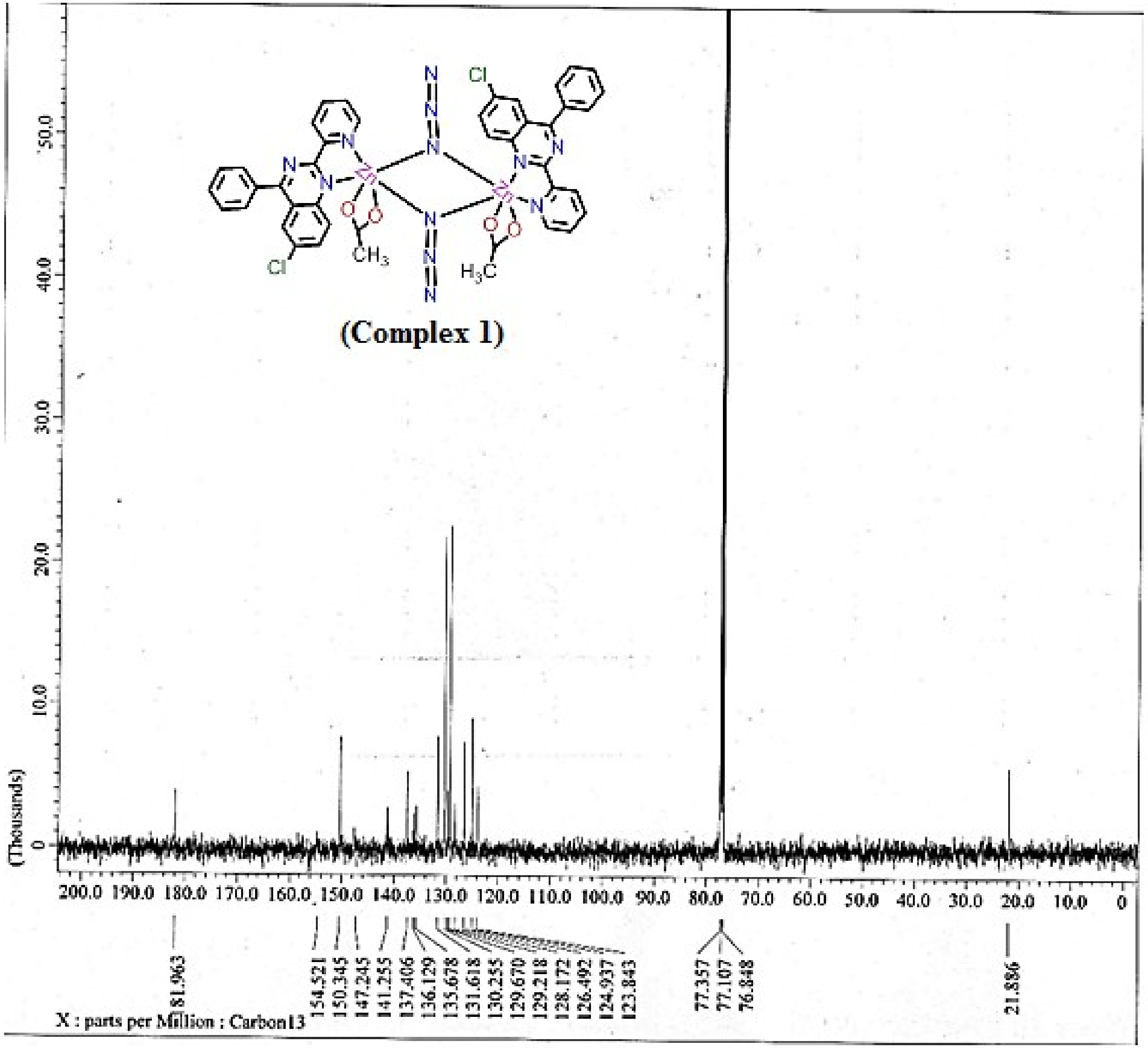


**Fig. S13**: $^{13}$C spectra of Complex **1** in $CDCl_3$

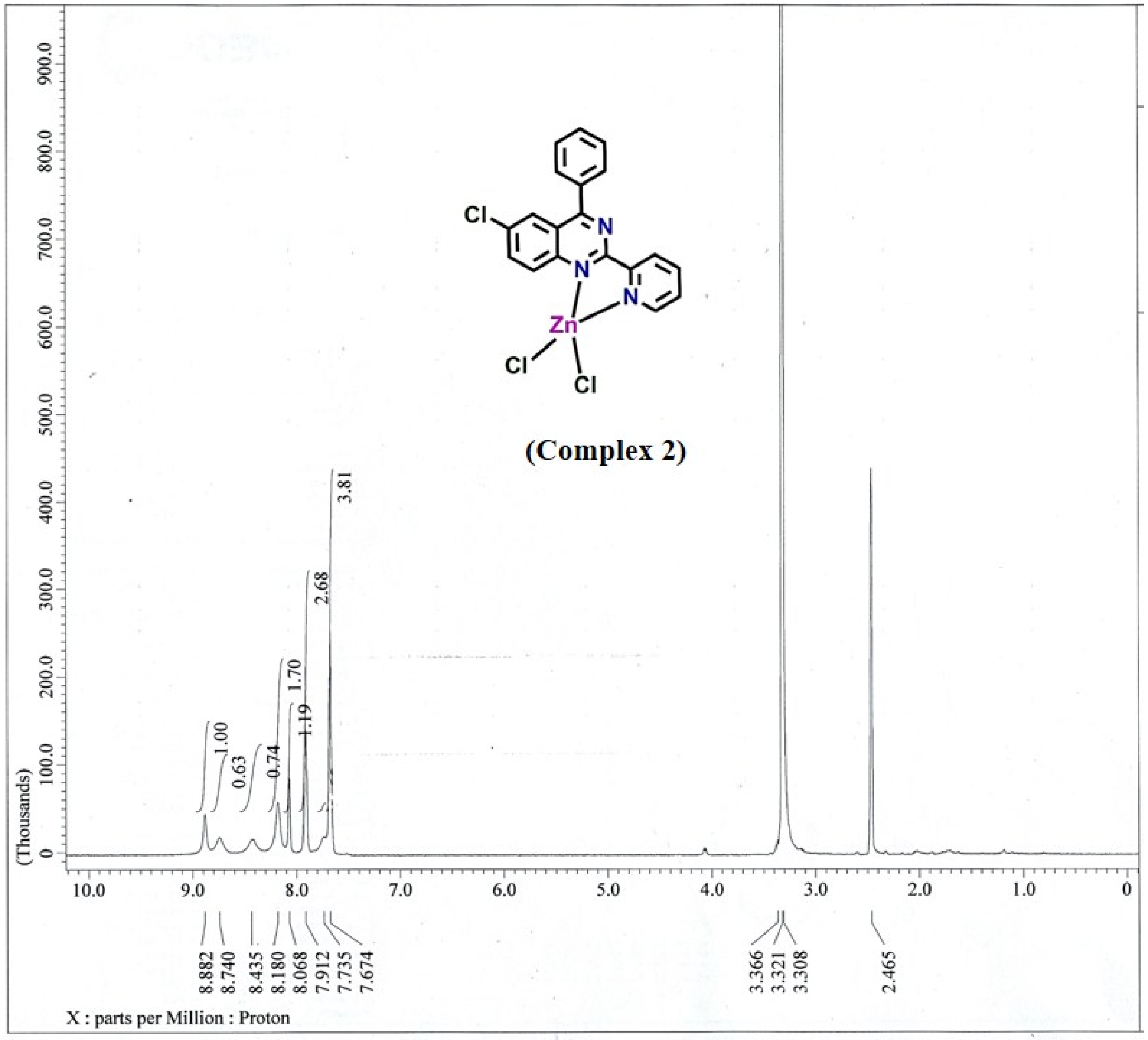


**Fig. S14**: $^1$H spectra of Complex **2** in DMSO-$d_6$

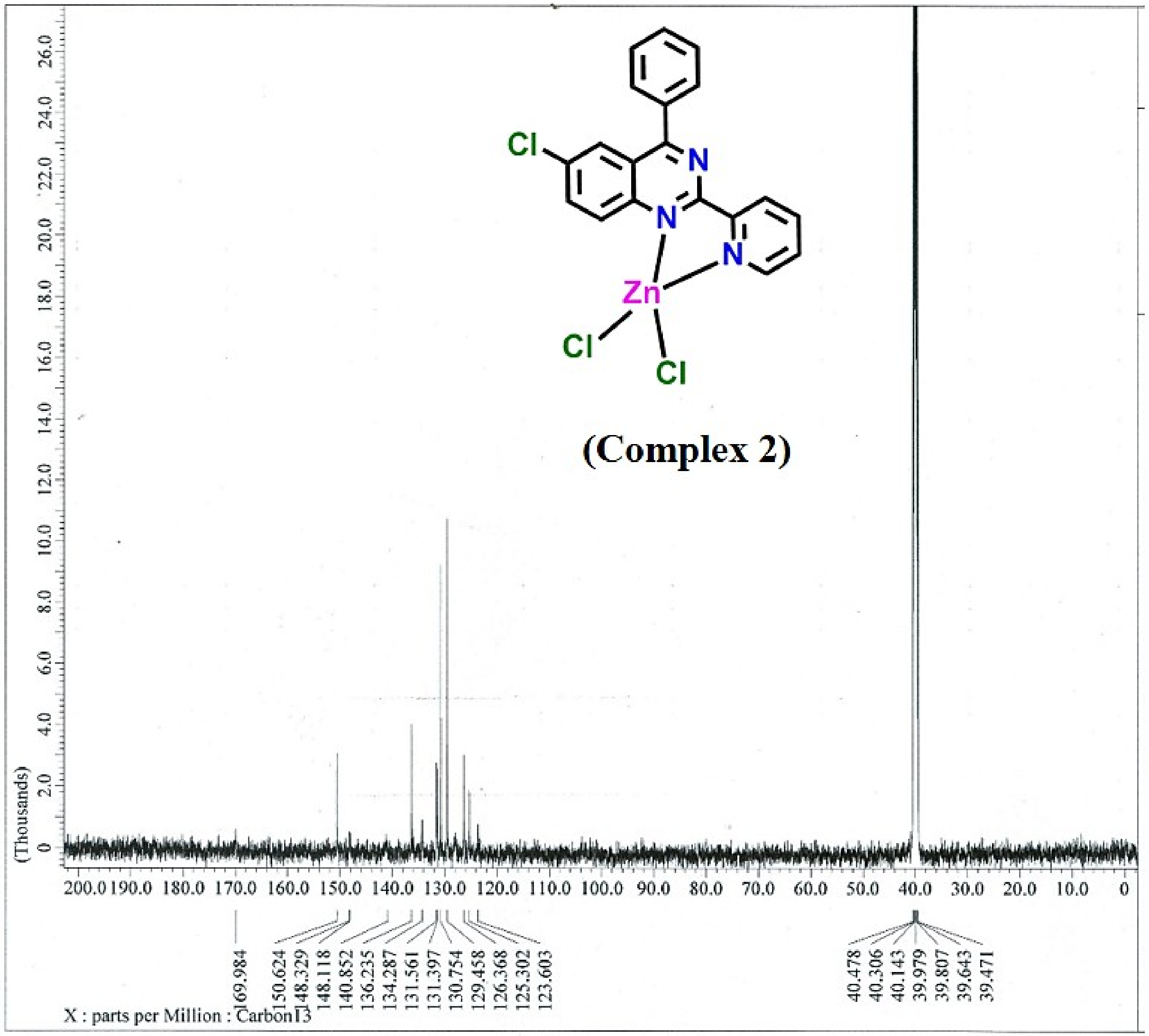


**Fig. S15**: $^{13}$C spectra of Complex **2** in DMSO-d$_6$

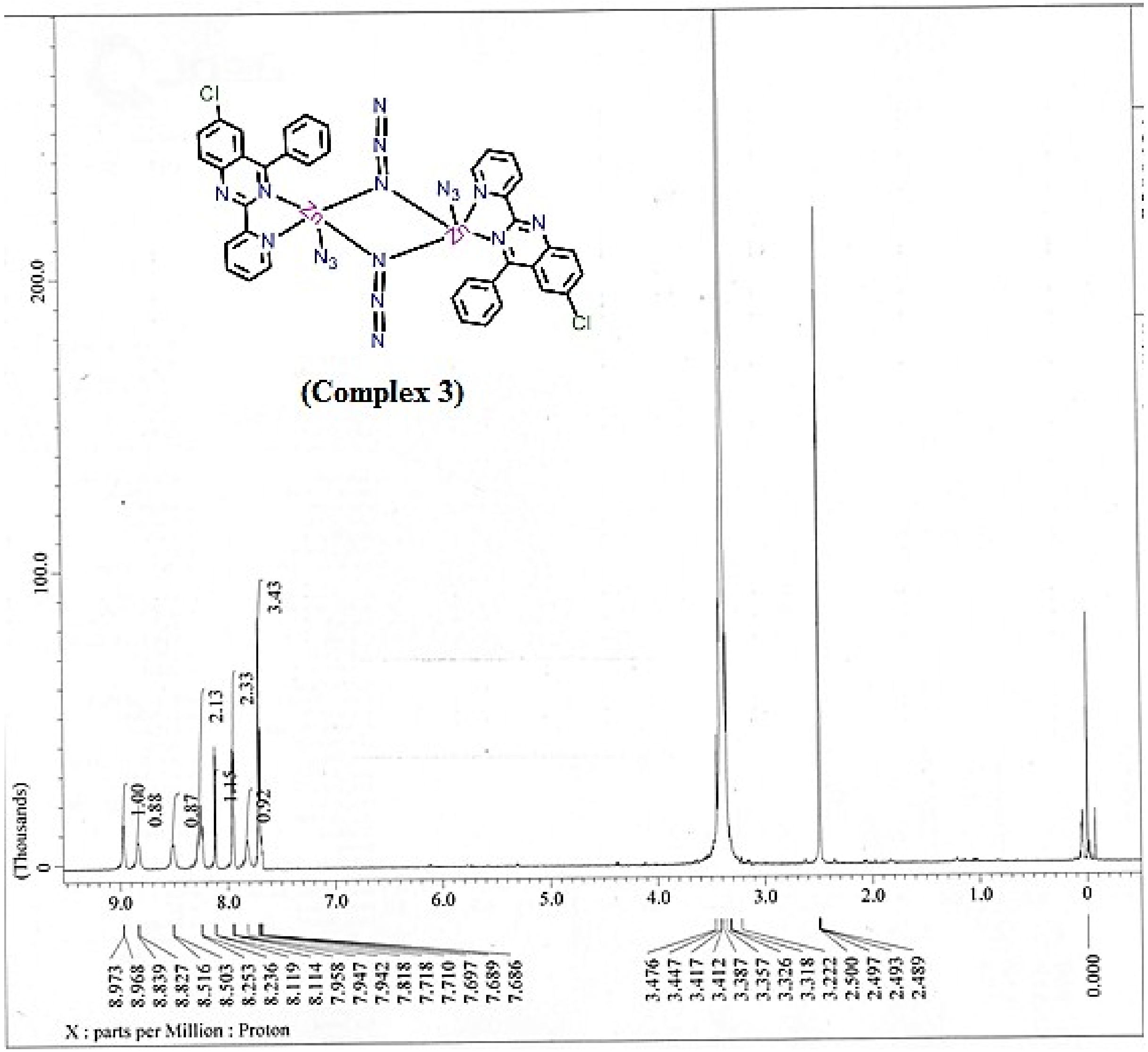


**Fig. S16**: $^{1}$H spectra of Complex **3** in DMSO-$d_6$

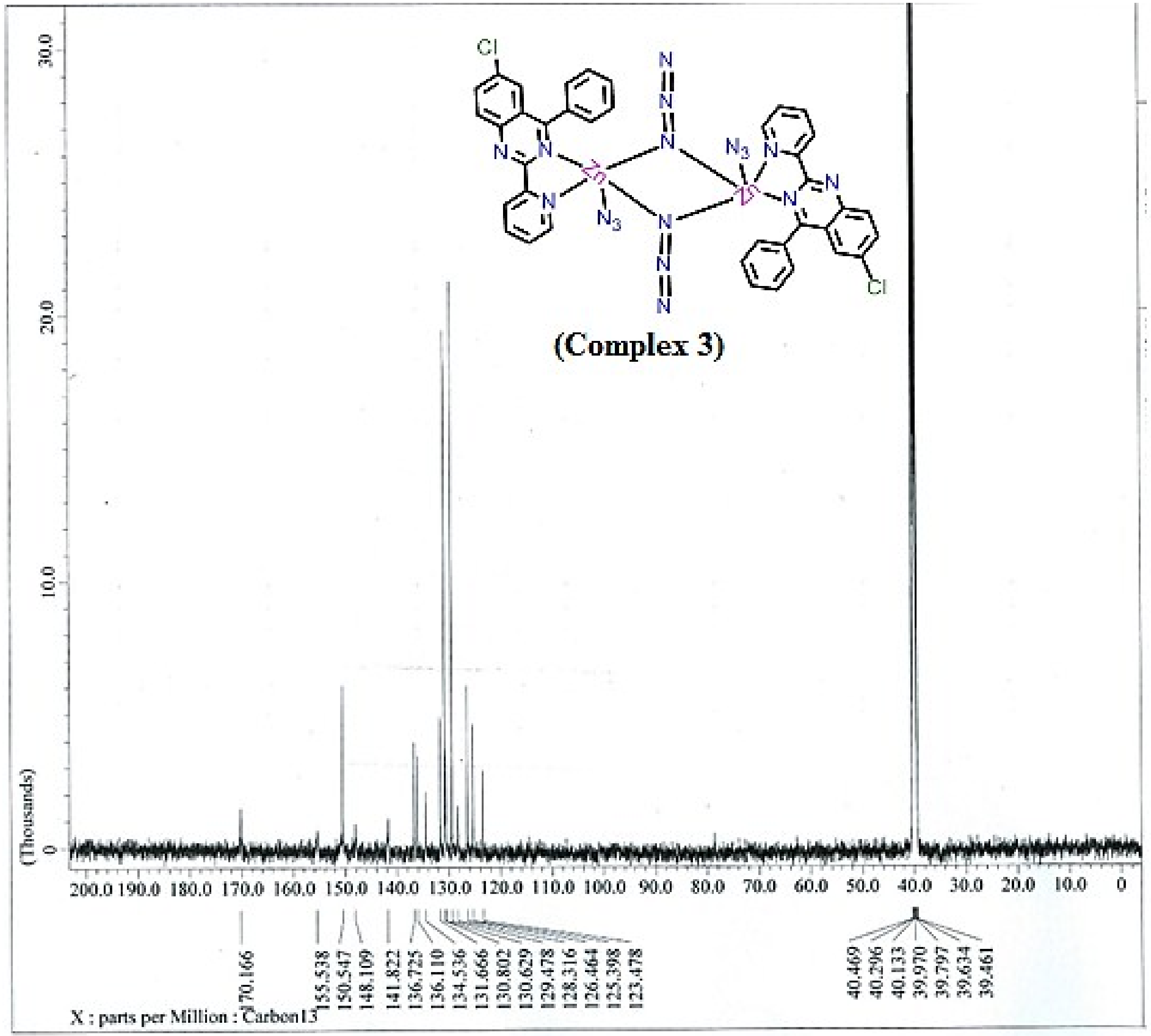


**Fig. S17**: $^{13}$C spectra of Complex **3** in DMSO-d$_6$

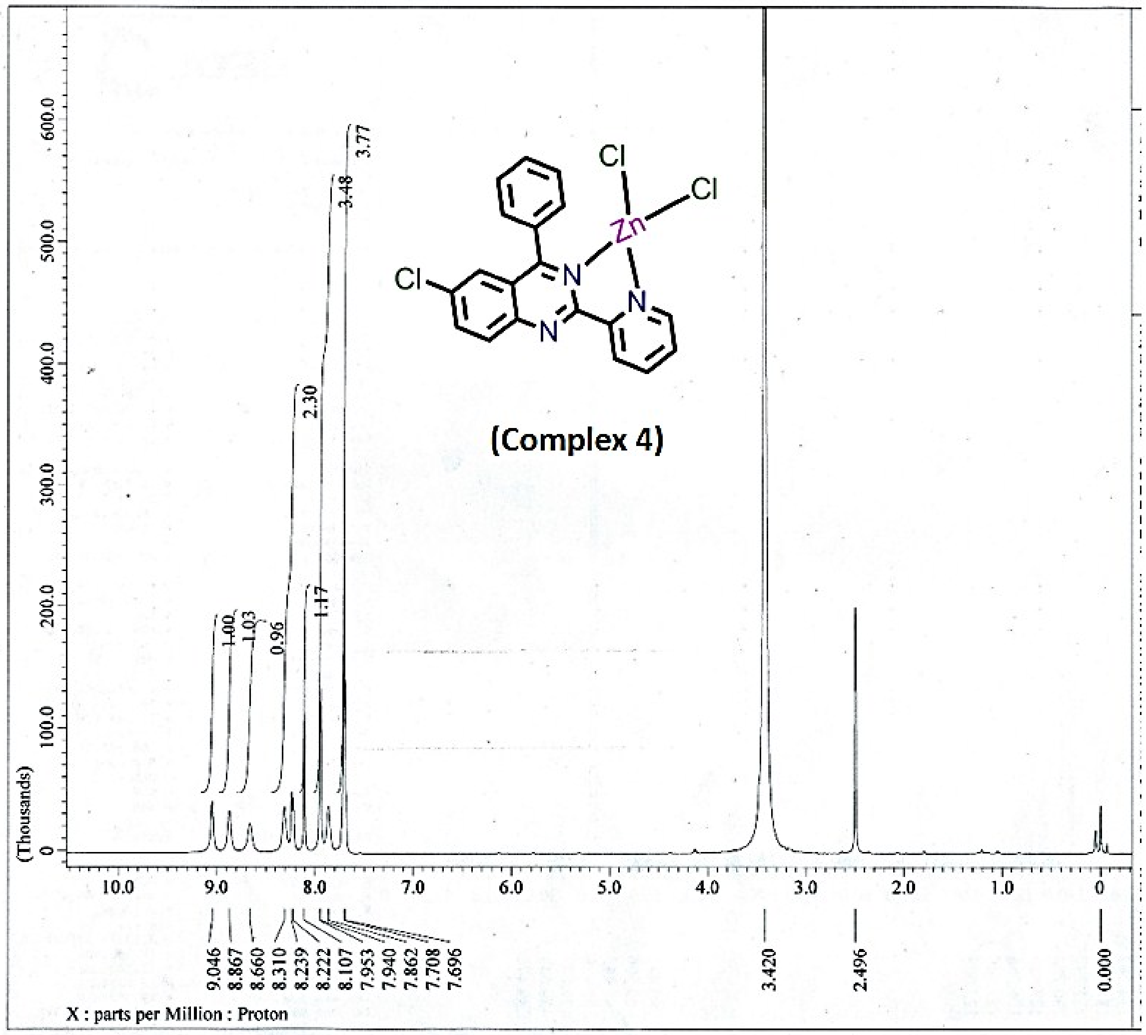


**Fig. S18**: $^1$H spectra of Complex **4** in DMSO-$d_6$

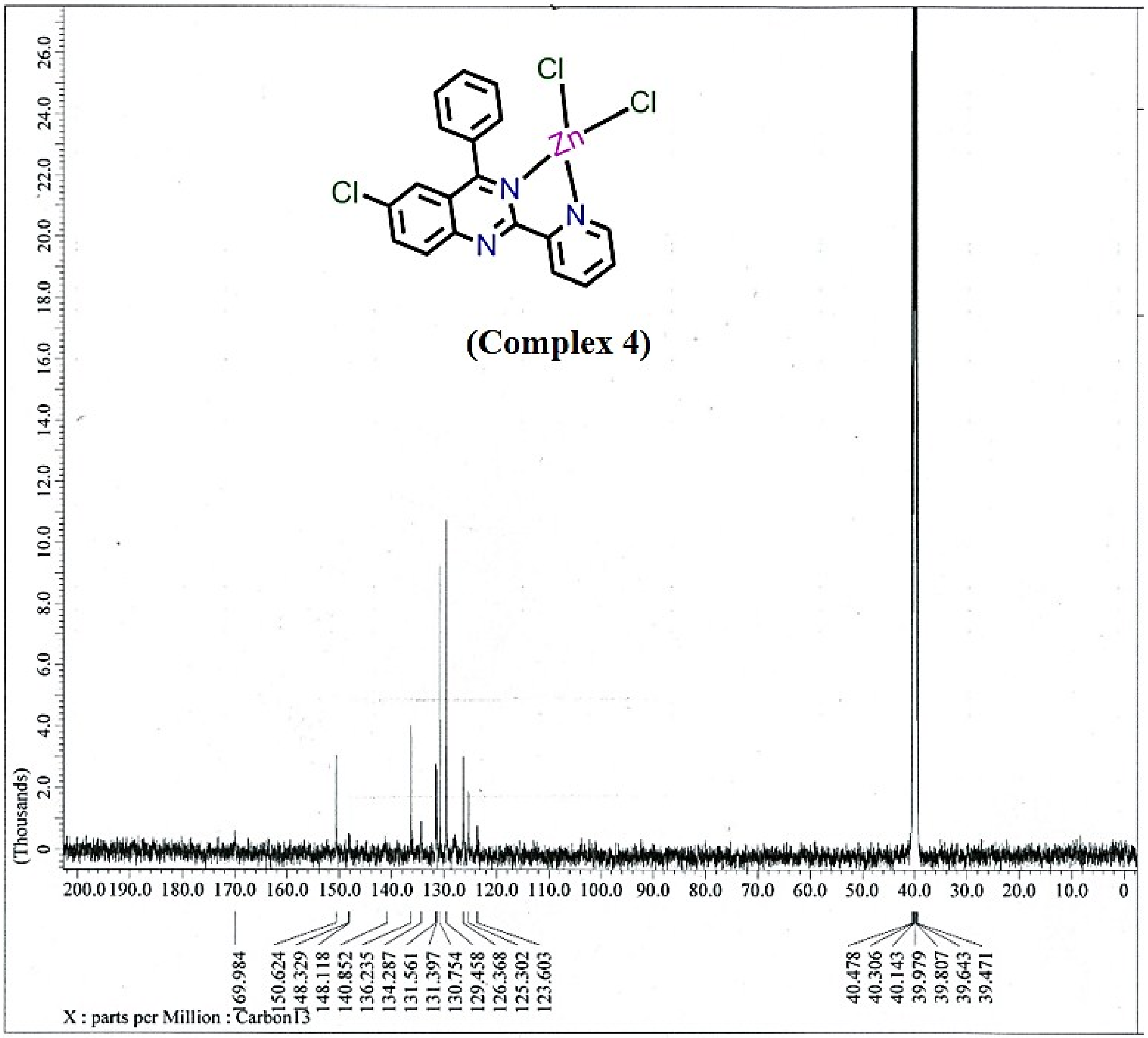


**Fig. S19**: $^{13}$C spectra of Complex **4** in DMSO-$d_6$