Supporting Information

Cyclometalated iridium (III) complexes of (aryl)ethenyl functionalized 2, 2'-bipyridine: synthesis, photophysical properties and *trans-cis* isomerization behavior

Soumalya Sinha, Soumik Mandal, Parna Gupta*

Department of Chemical Sciences,
Indian Institute of Science Education and Research (IISER) Kolkata,
Mohanpur, Nadia, 741246, India
Email: parna@iiserkol.ac.in

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Figure S1. Time-dependent ^{1}H NMR spectra of **L2** under photoirradiation

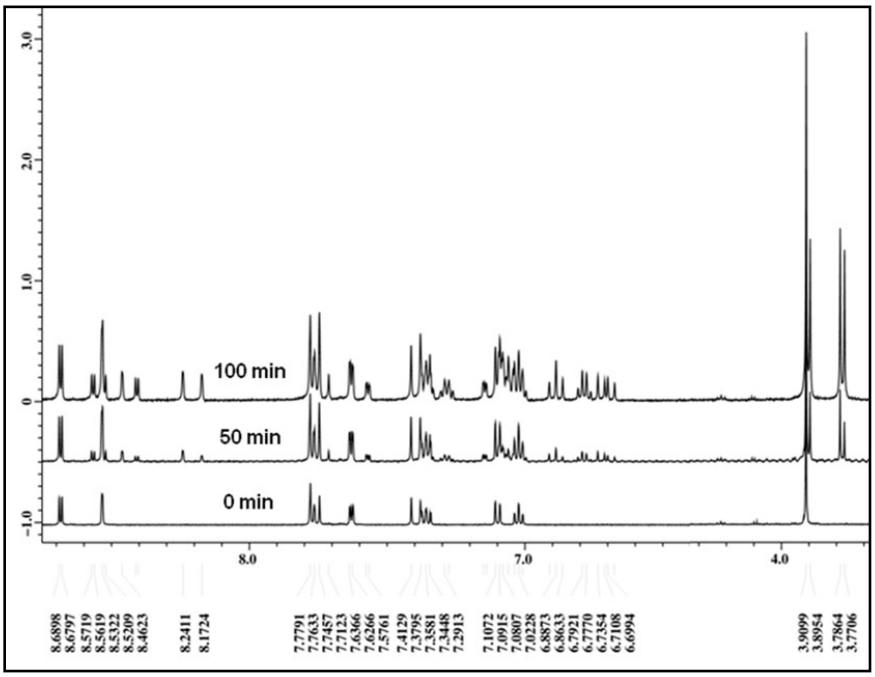
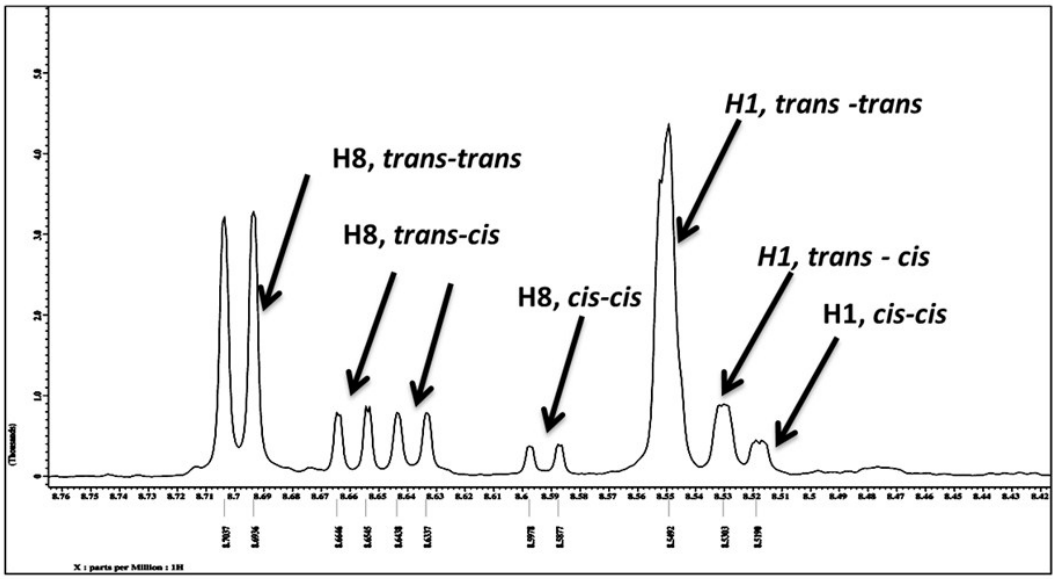
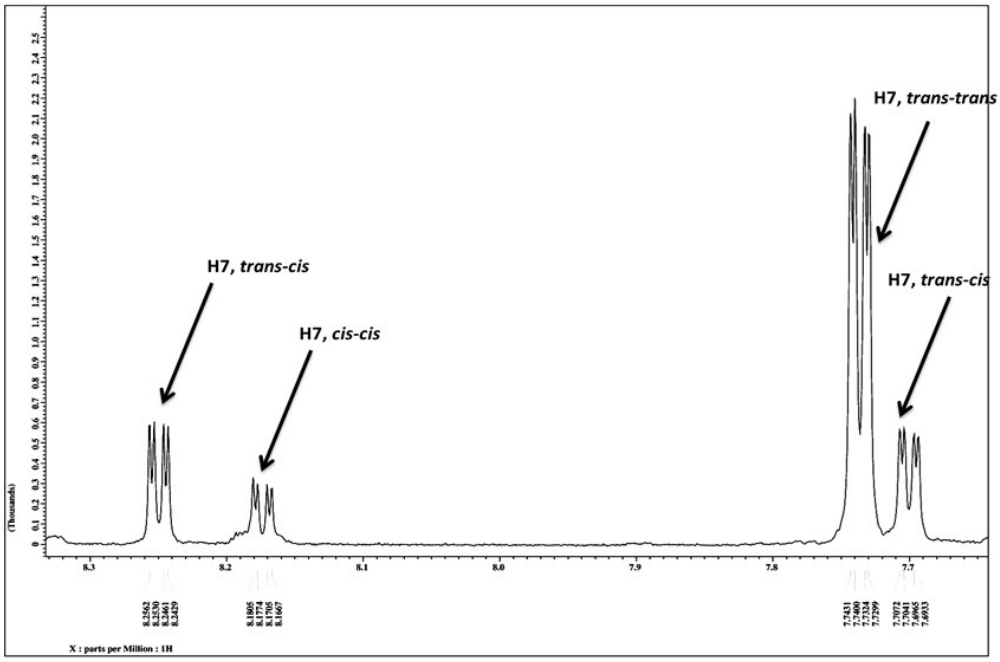


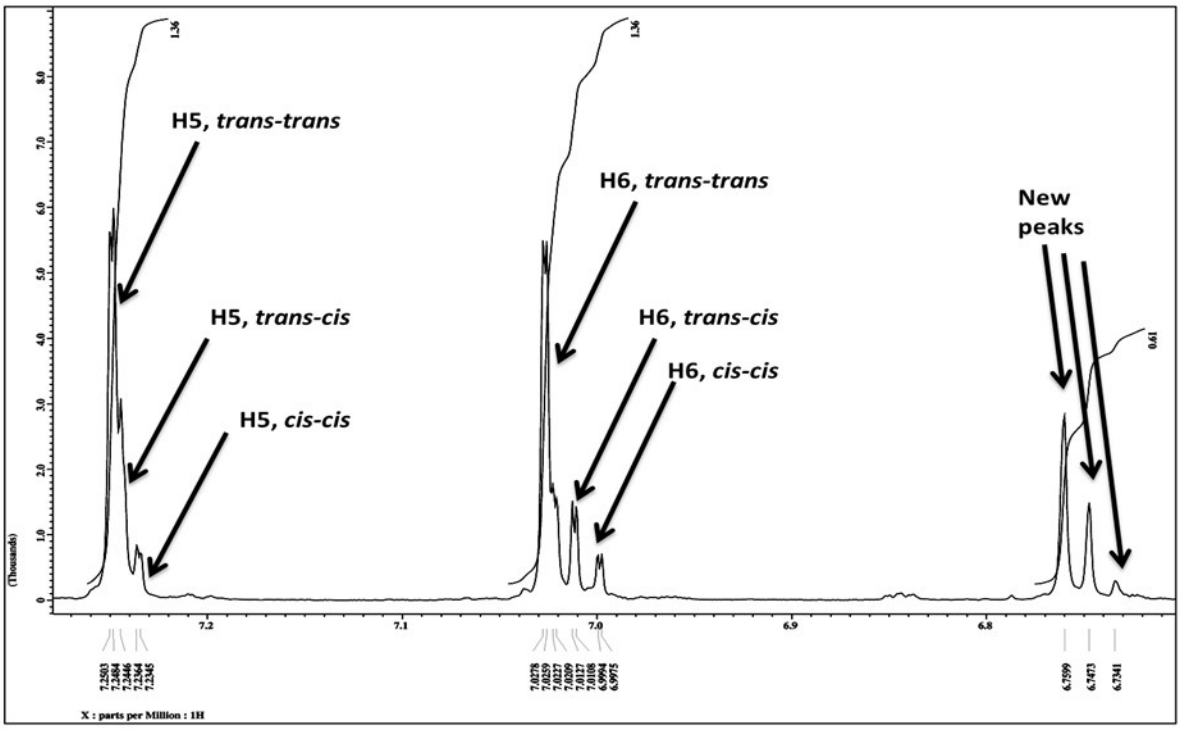
Figure S2: Expanded ^{1}H NMR data of **L1**



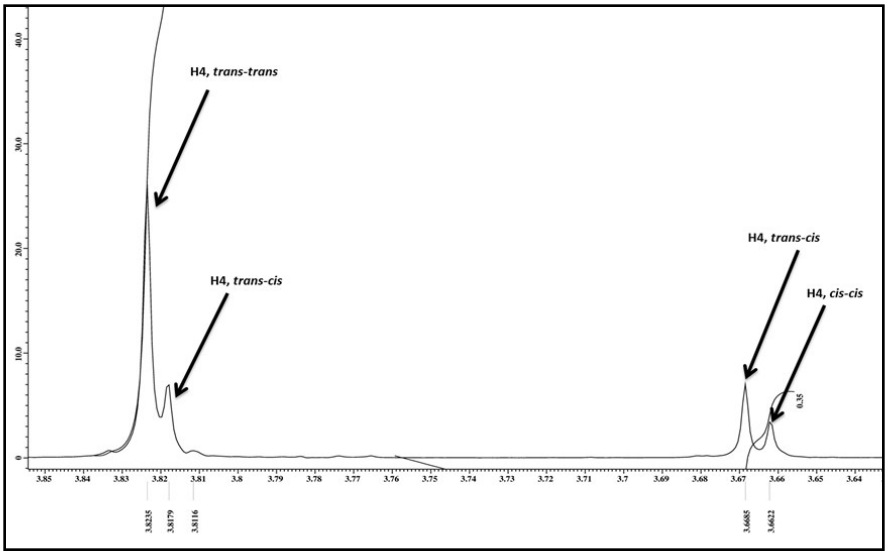
Note: H8, H1 (*tt, tc, cc*)



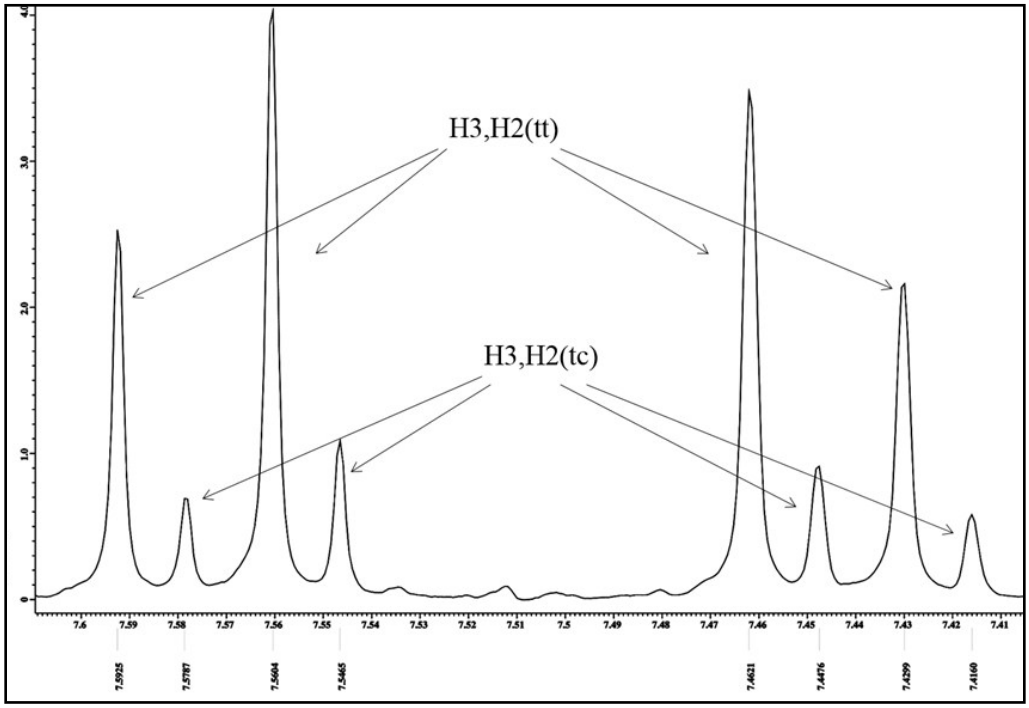
Note: H7(*tt, tc, cc*)



Note: H5(*tt, tc, cc*), H6(*tt, tc, cc*), H2-H3(*tc*, *cc*)



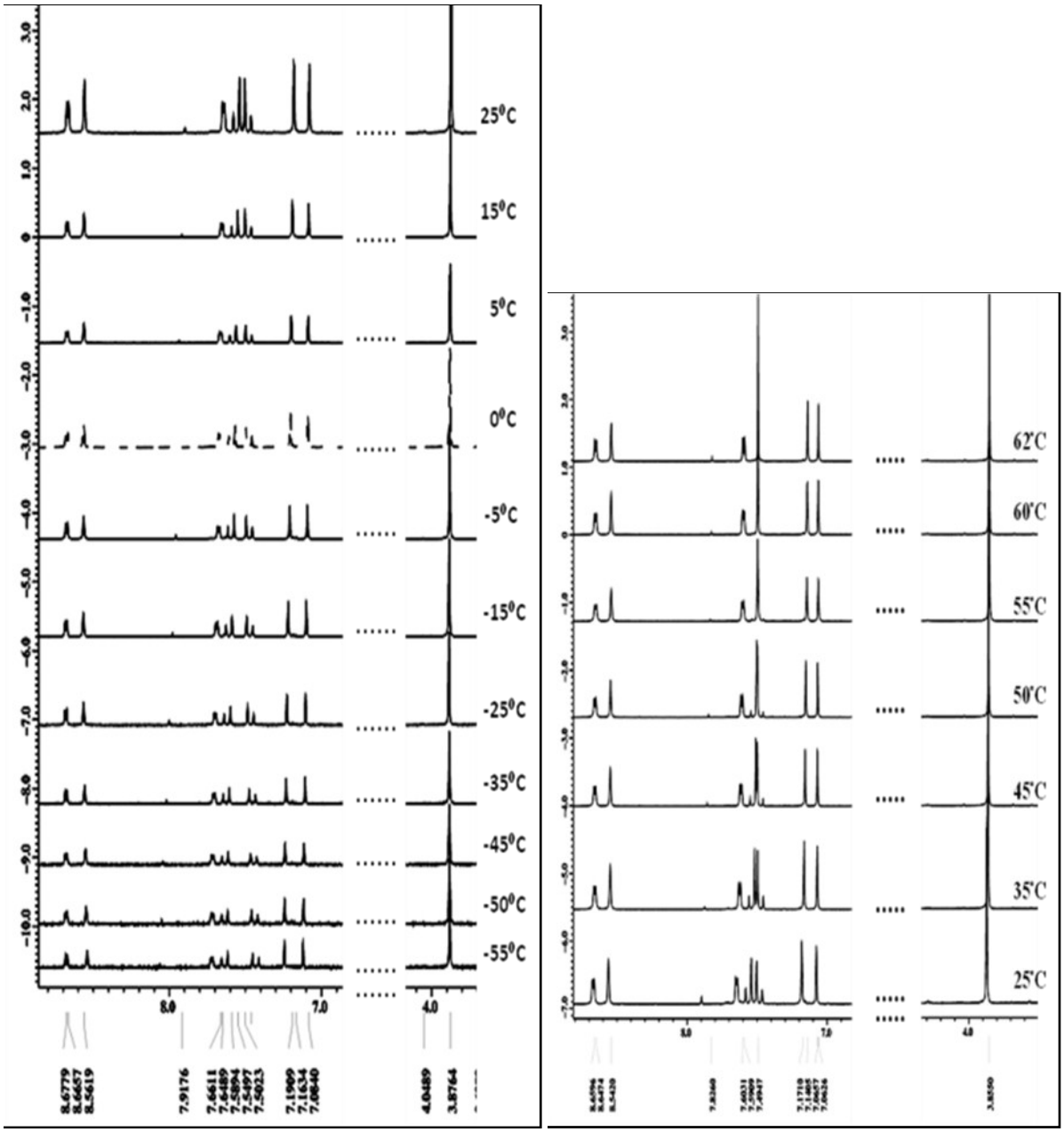
Note: H4(*tt, tc, cc*)



Note: H2-H3(*tt, tc*)

Figure S3: Variable temperature ^{1}H NMR spectra in Methanol-d_4

L1:



L2:

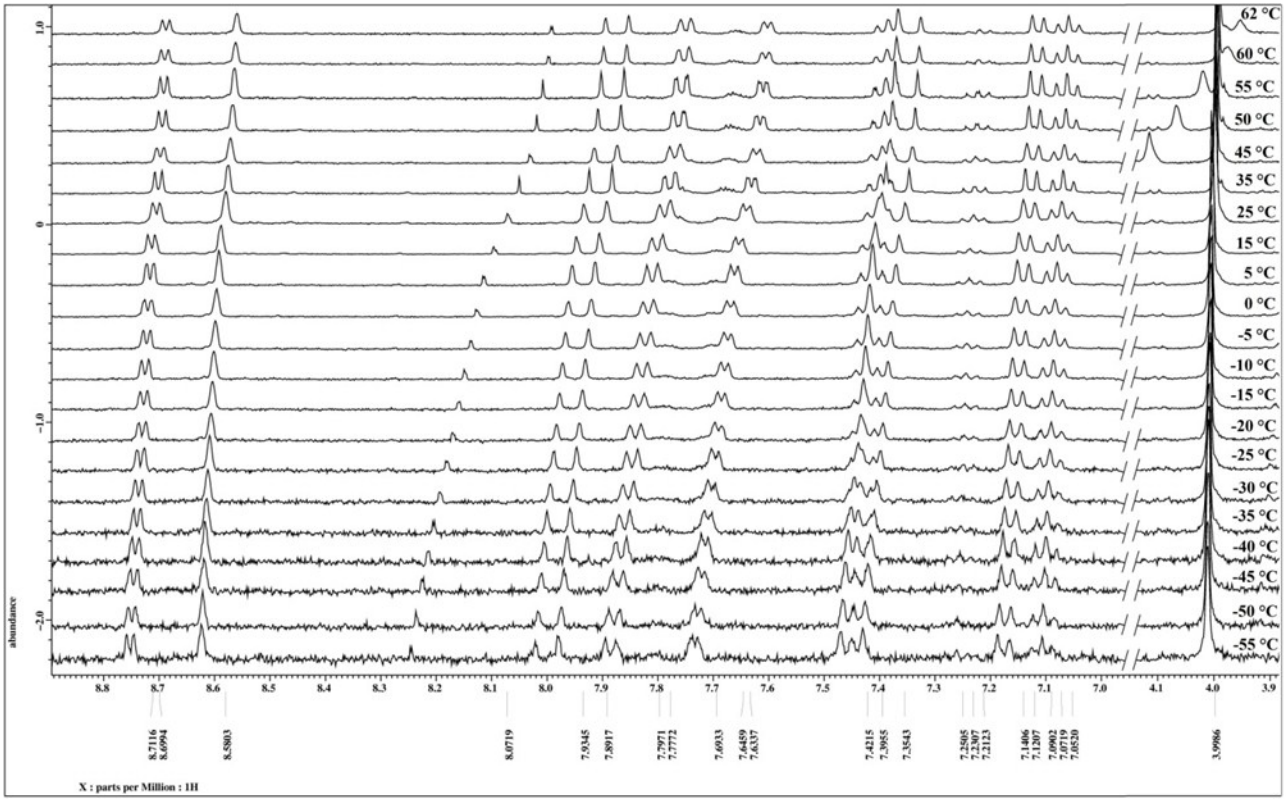
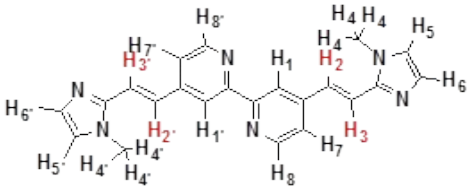
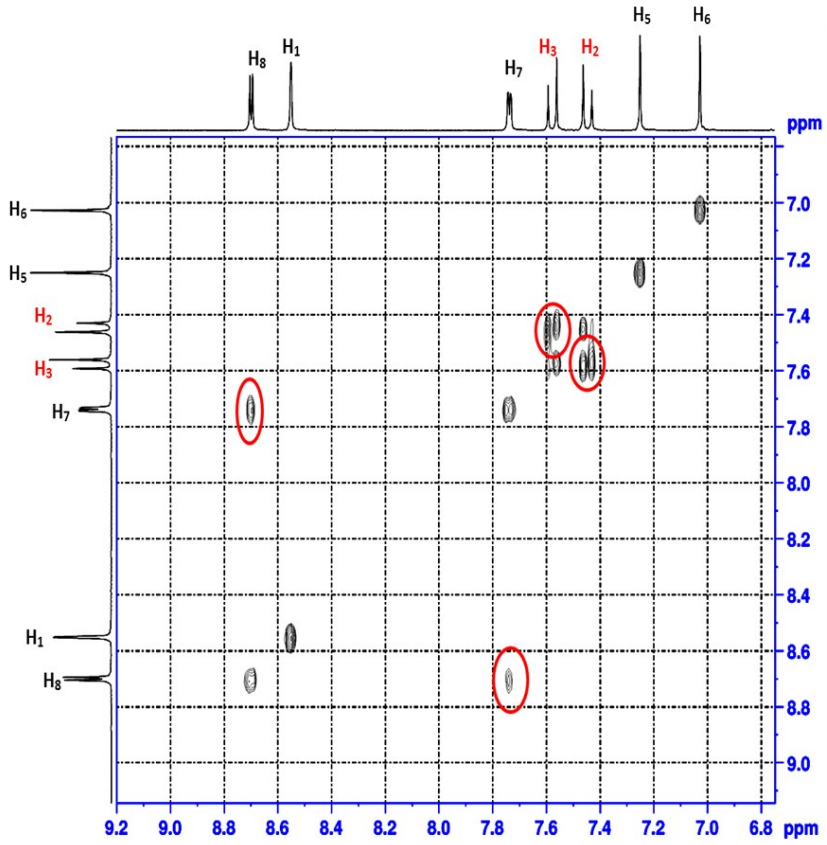

62 °C
60 °C
55 °C
50 °C
45 °C
35 °C
25 °C
15 °C
5 °C
0 °C
-5 °C
-10 °C
-15 °C
-20 °C
-25 °C
-30 °C
-35 °C
-40 °C
-45 °C
-50 °C
-55 °C
abundance
X : parts per Million : 1H

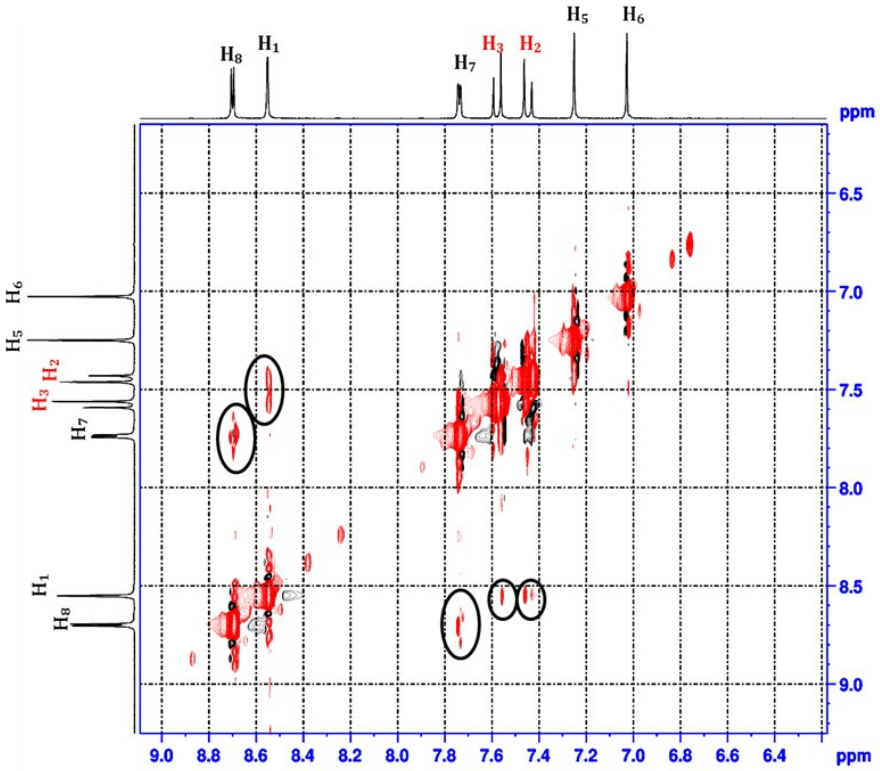
Figure S4: ^{1}H - ^{1}H COSY and ^{1}H - ^{1}H NOESY NMR spectra of **L1**
Before photoirradiation:



^{1}H – ^{1}H COSY NMR:

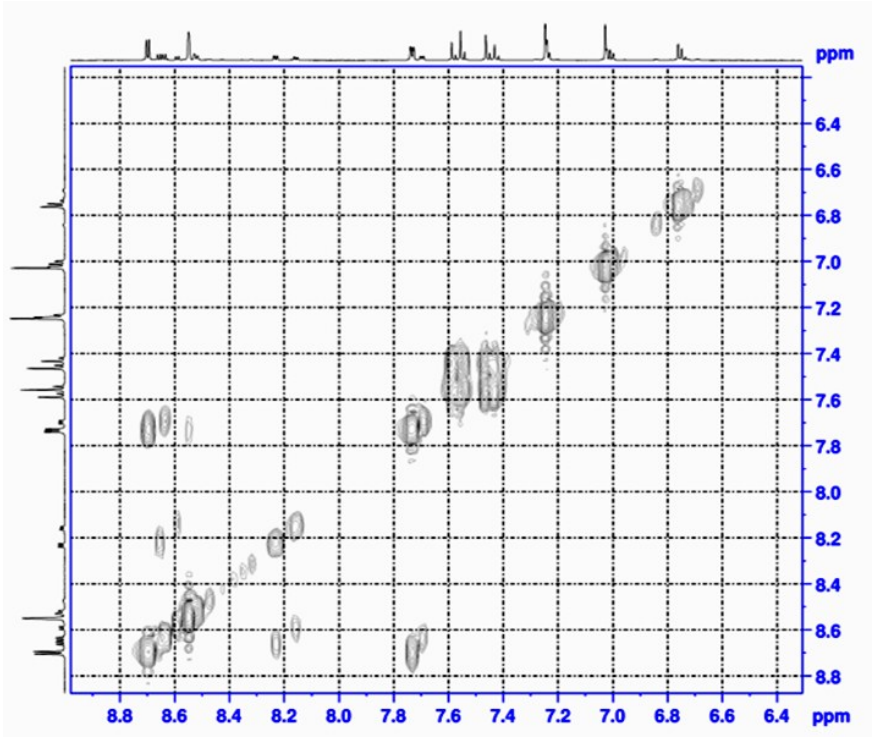


^{1}H – ^{1}H NOESY NMR:



After photoirradiation:

^{1}H – ^{1}H COSY NMR:



$^{1}H - {}^{1}H$ NOESY NMR:

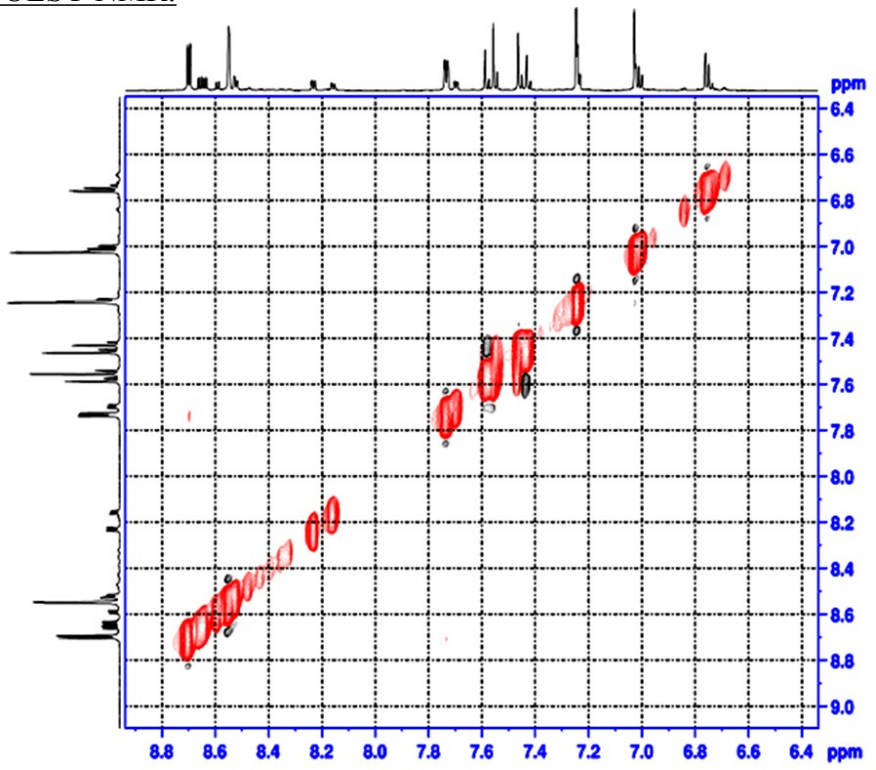


Figure S5: Time dependent absorption spectra of **L1** under photoirradiation

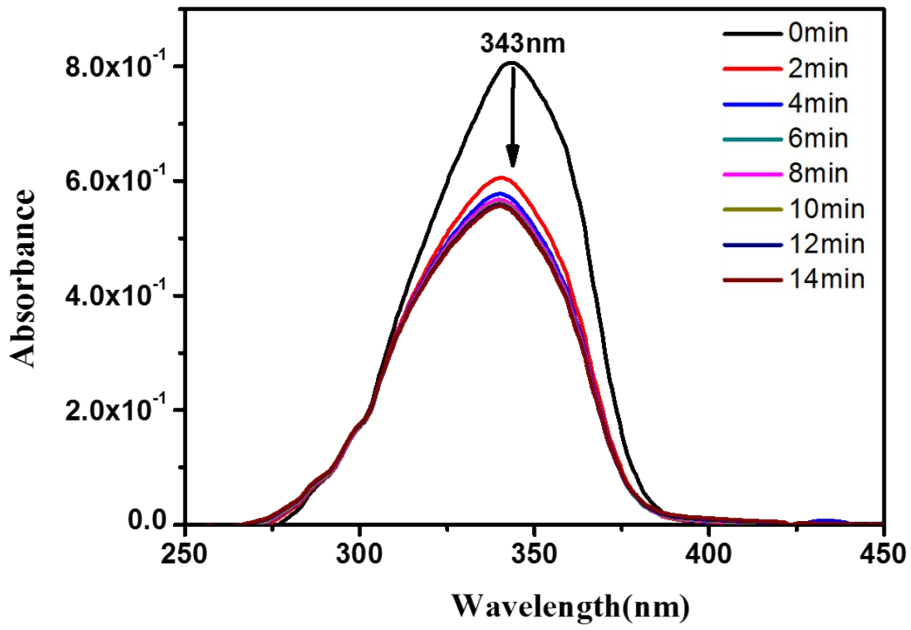
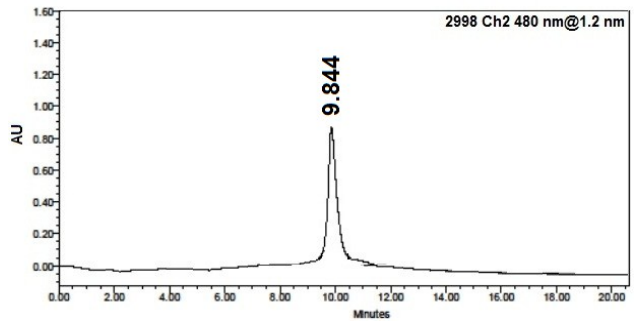


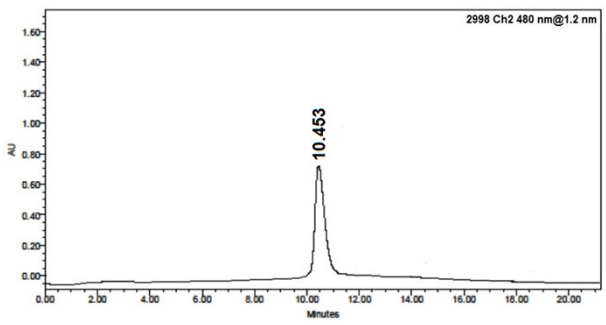
Figure S6: HPLC of complex for (A) **1** (*trans, trans*) and **2** (*trans, trans*) (B) **1** and **2** after photoirradiation

Retention Time

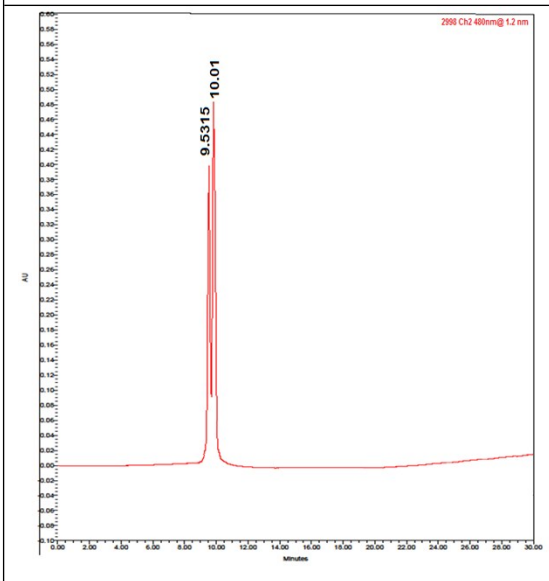
Complex	Retention Time (pure *trans-trans*) (minutes)	Retention Time (After photoirradiation)
1	9.84	10.45
2	9.53, 10.01	10.39

A.





B



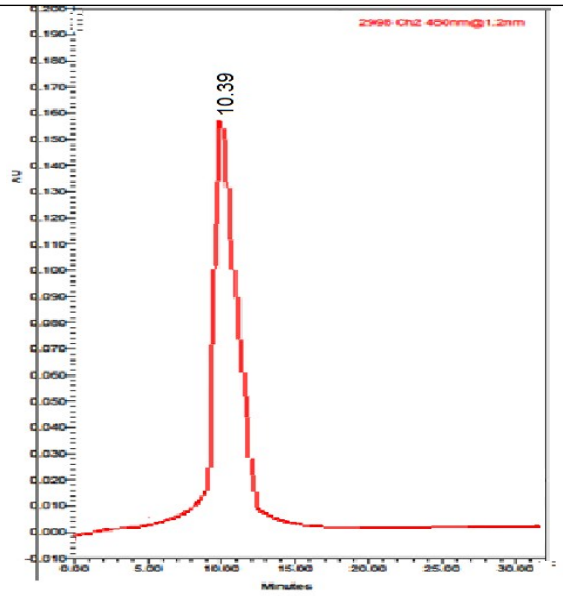
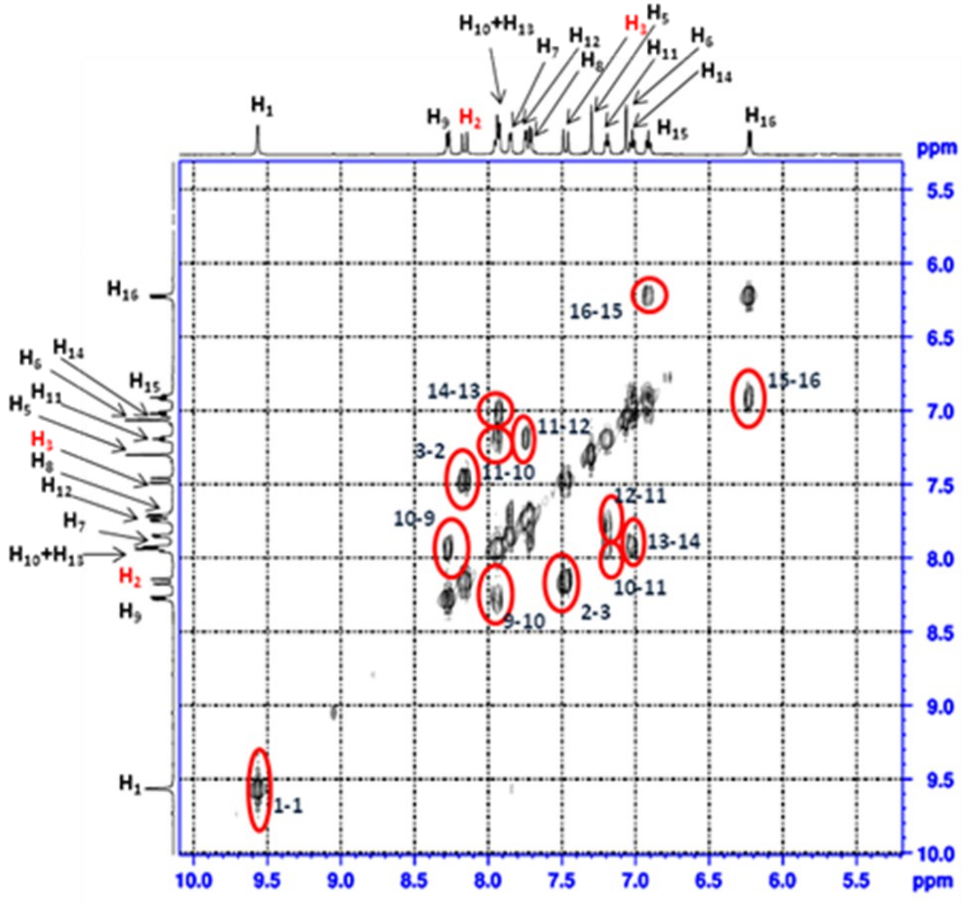


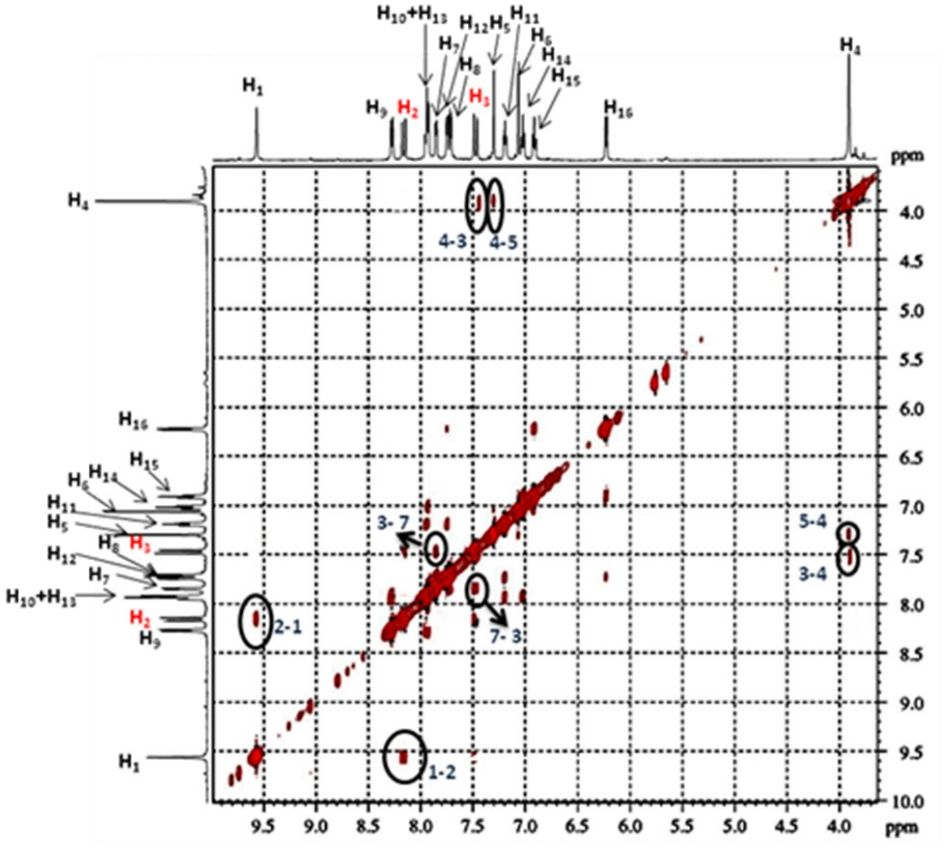
Figure S7: ^{1}H - ^{1}H COSY and ^{1}H - ^{1}H NOESY NMR spectra of Complex **1**

A. Before photoirradiation:

^{1}H – ^{1}H COSY NMR:

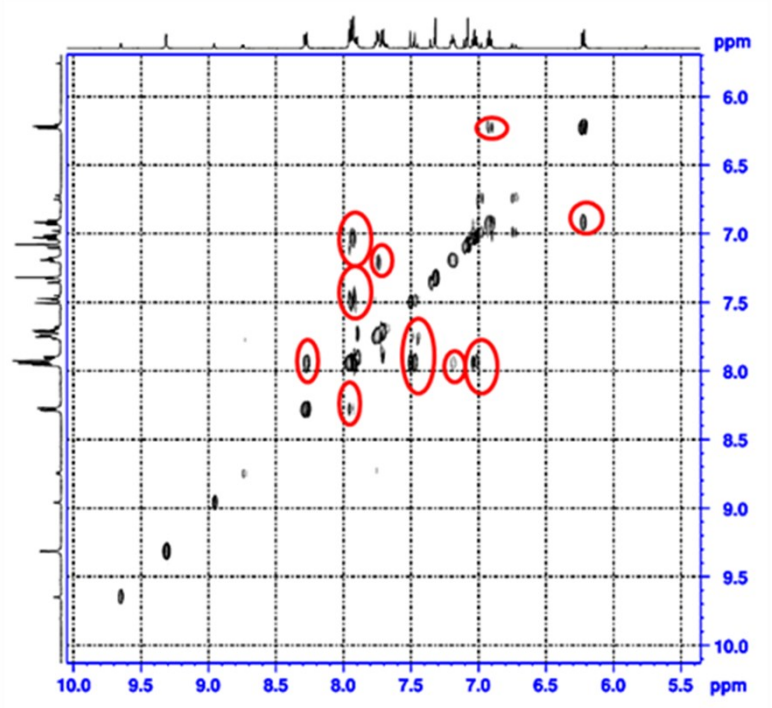


$^{1}H - {}^{1}H$ NOESY NMR:



B. After photoirradiation:

$^{1}H - {}^{1}H$ COSY NMR:



^{1}H – ^{1}H NOESY NMR:

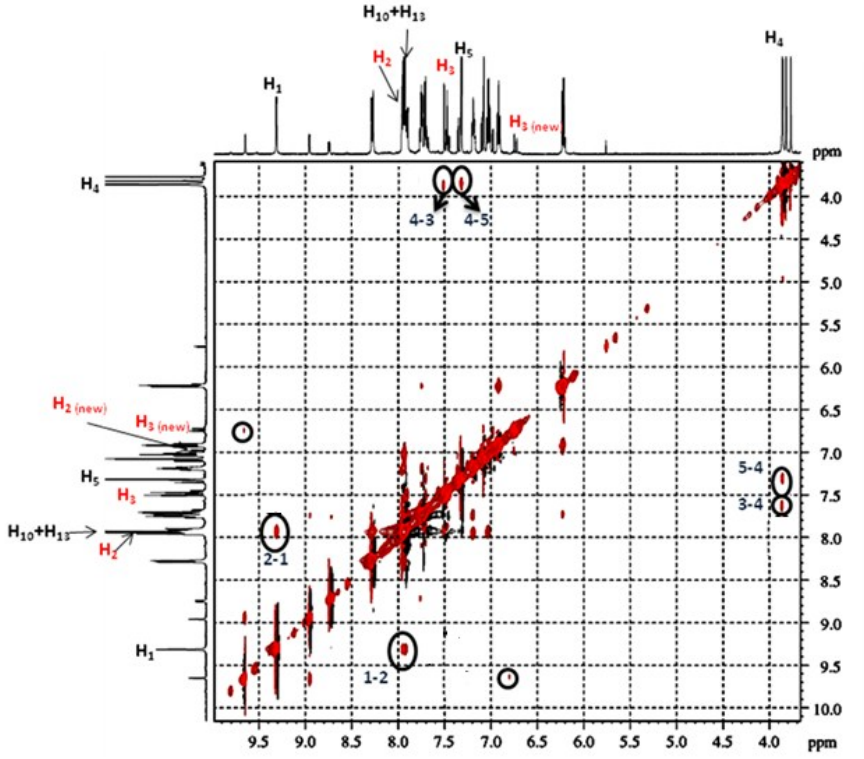
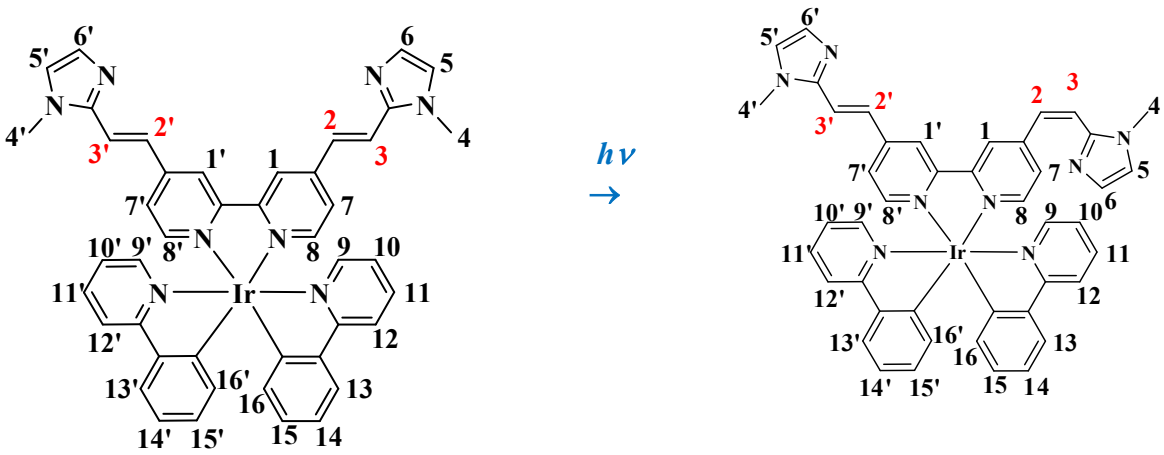
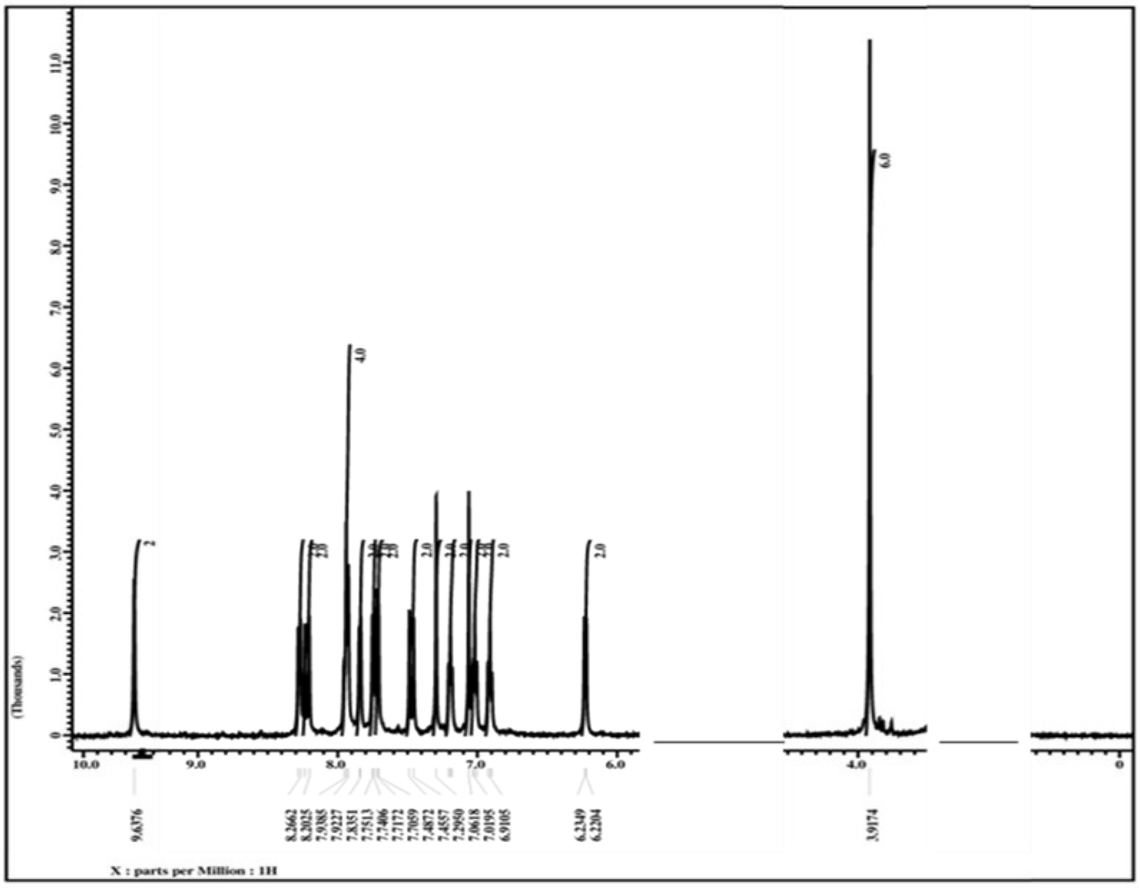
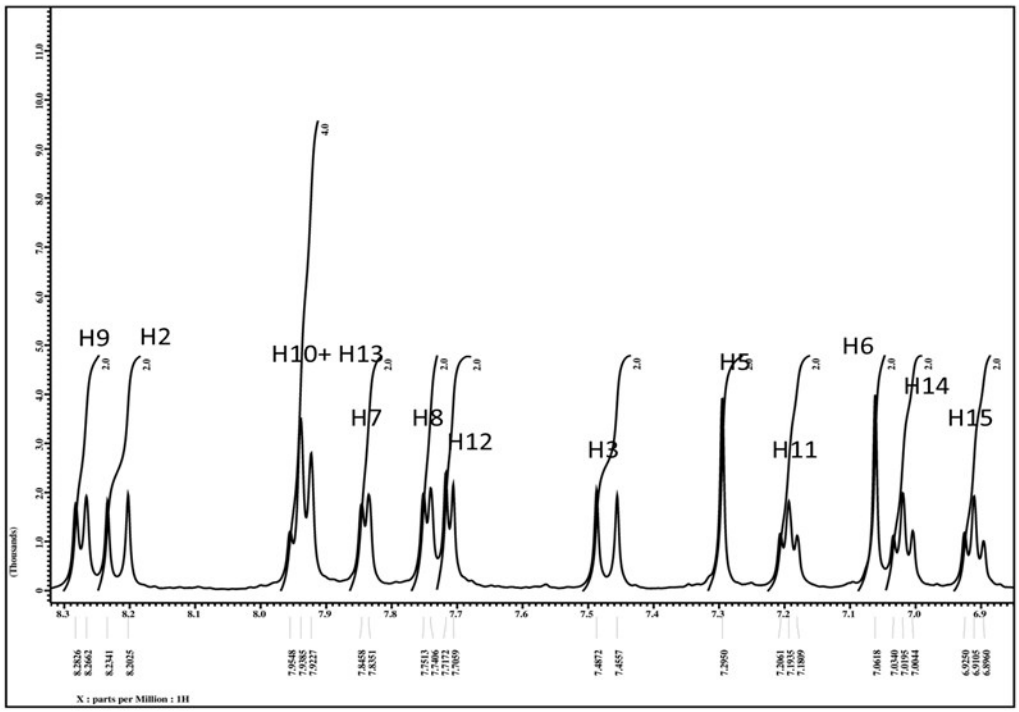


Figure S8: Expanded ^{1}H NMR of complex **1**(*trans,trans*) and **2**(*trans,trans*) in DMSO-d_6.
Complex **1**:

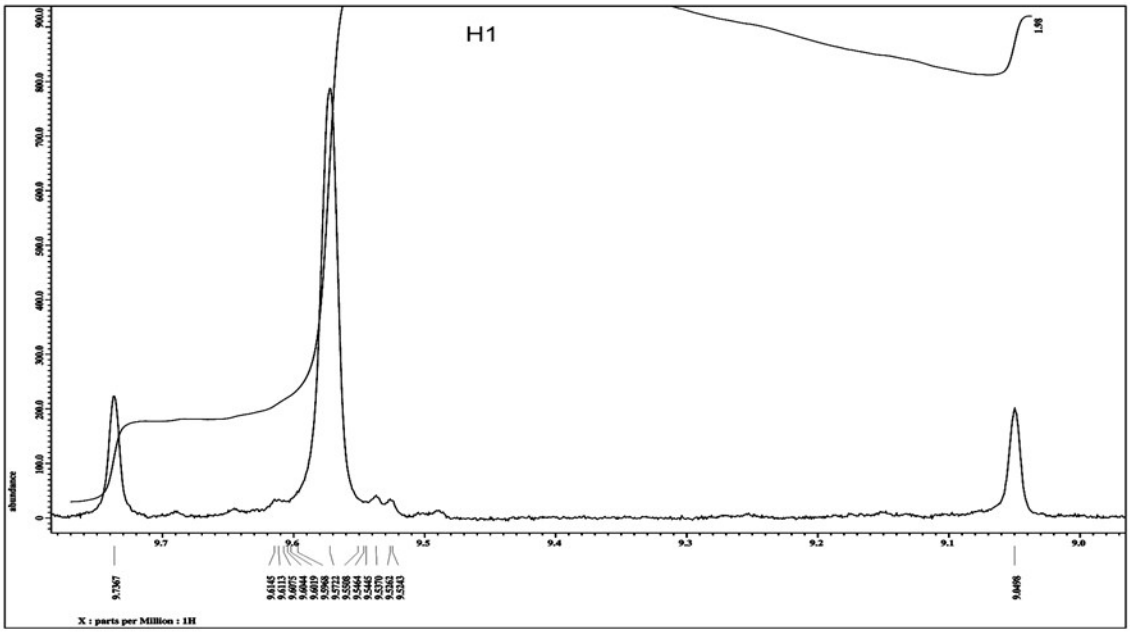


^{1}H NMR spectrum of **1** (entire spectrum)

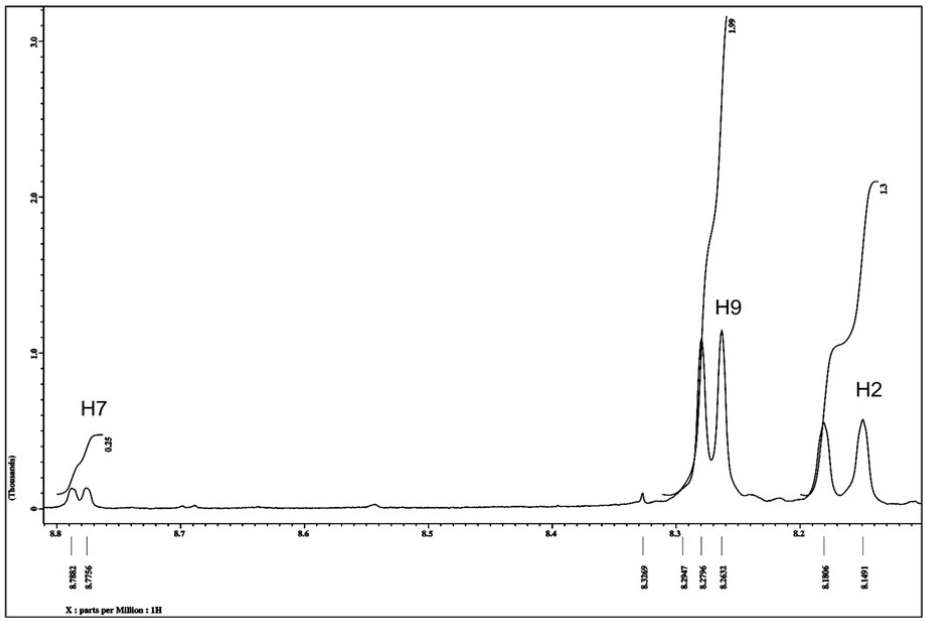




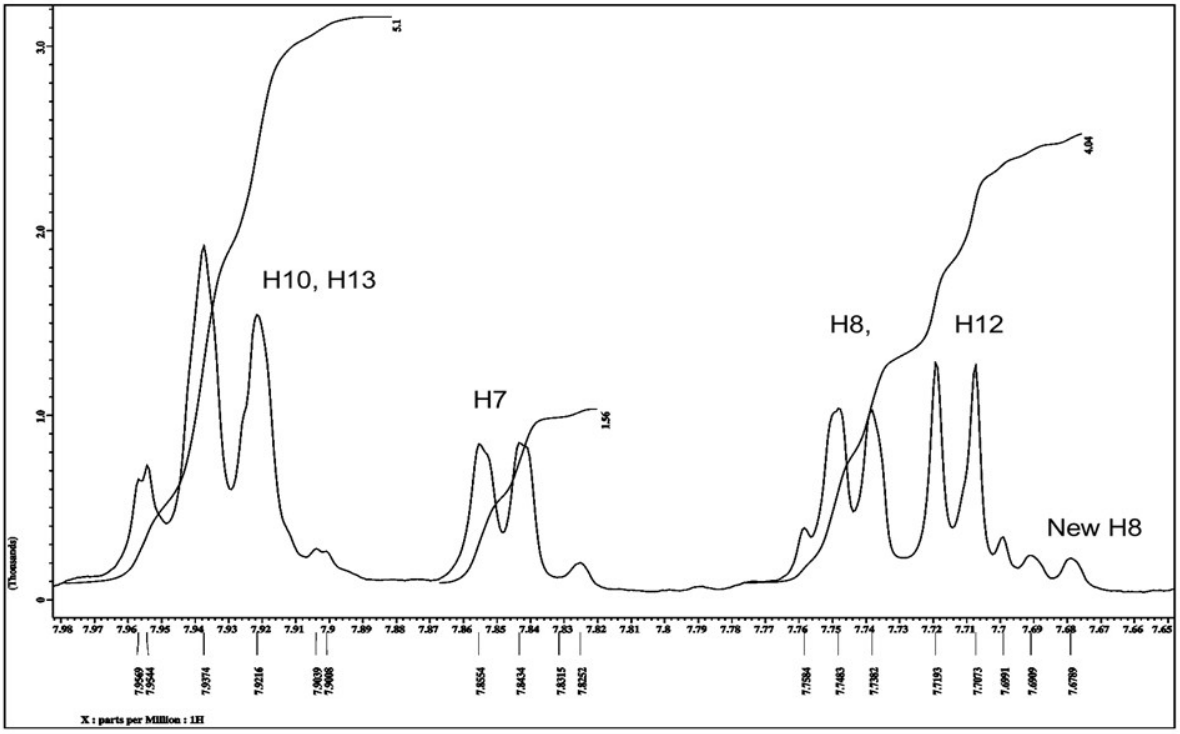
^{1}H NMR spectrum of **1** (Part A)



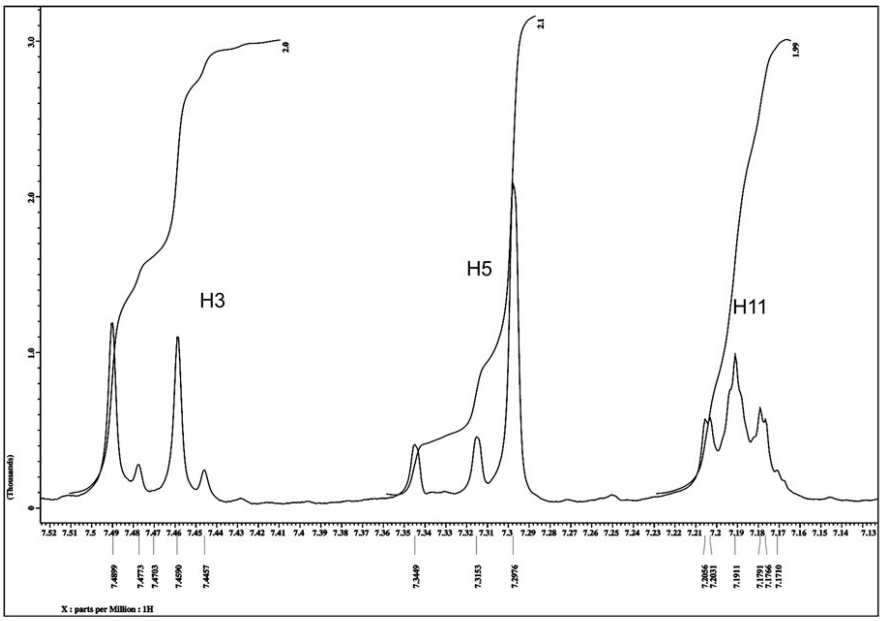
^{1}H NMR spectrum of **1** (Part B)



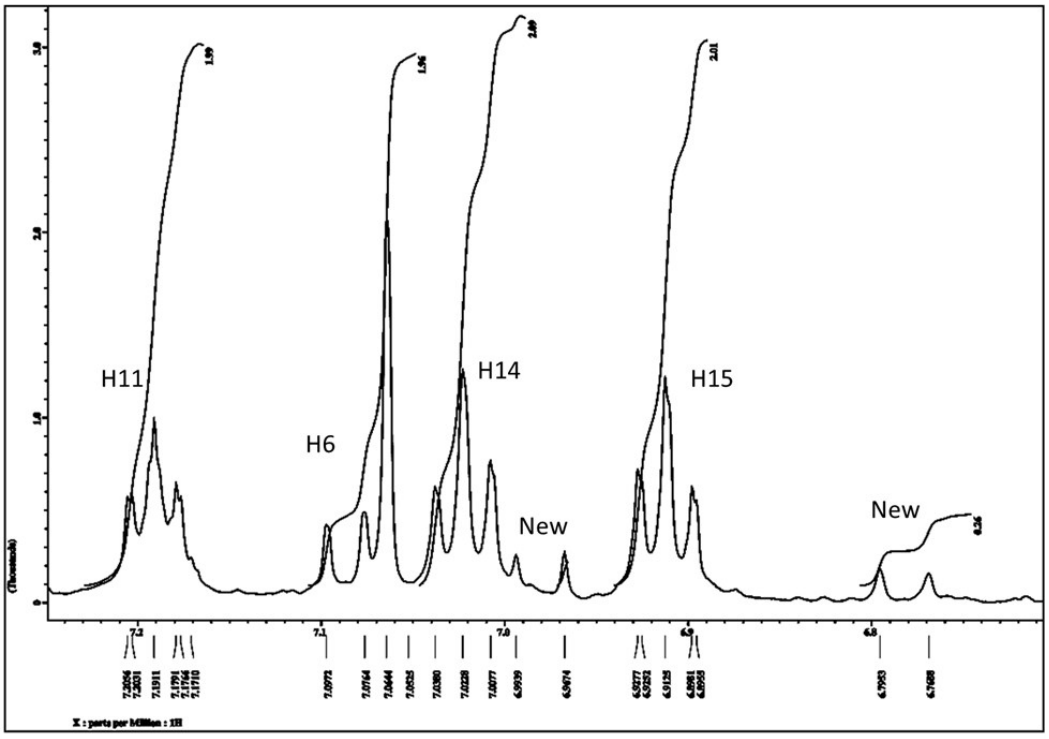
^{1}H NMR spectrum of **1** (Part C)



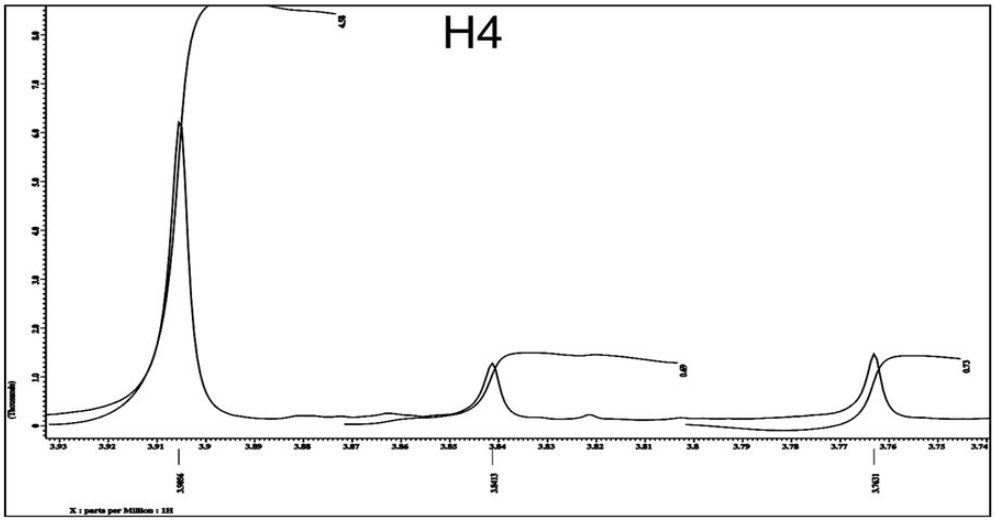
^{1}H NMR spectrum of **1** (Part D)



^{1}H NMR spectrum of **1** (Part E)

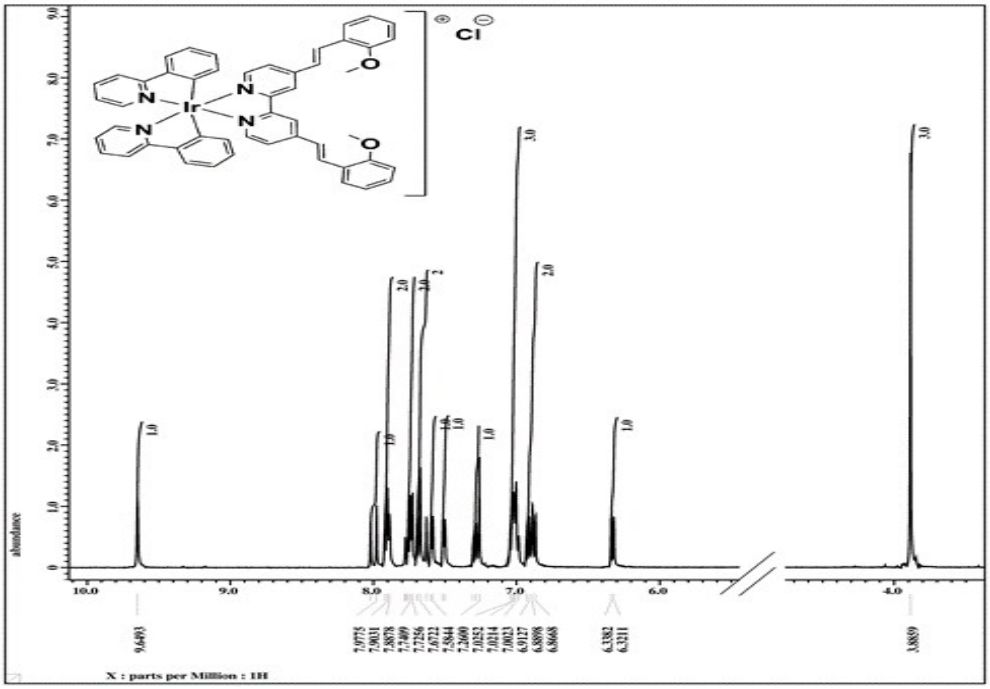


^{1}H NMR spectrum of **1** (Part F)

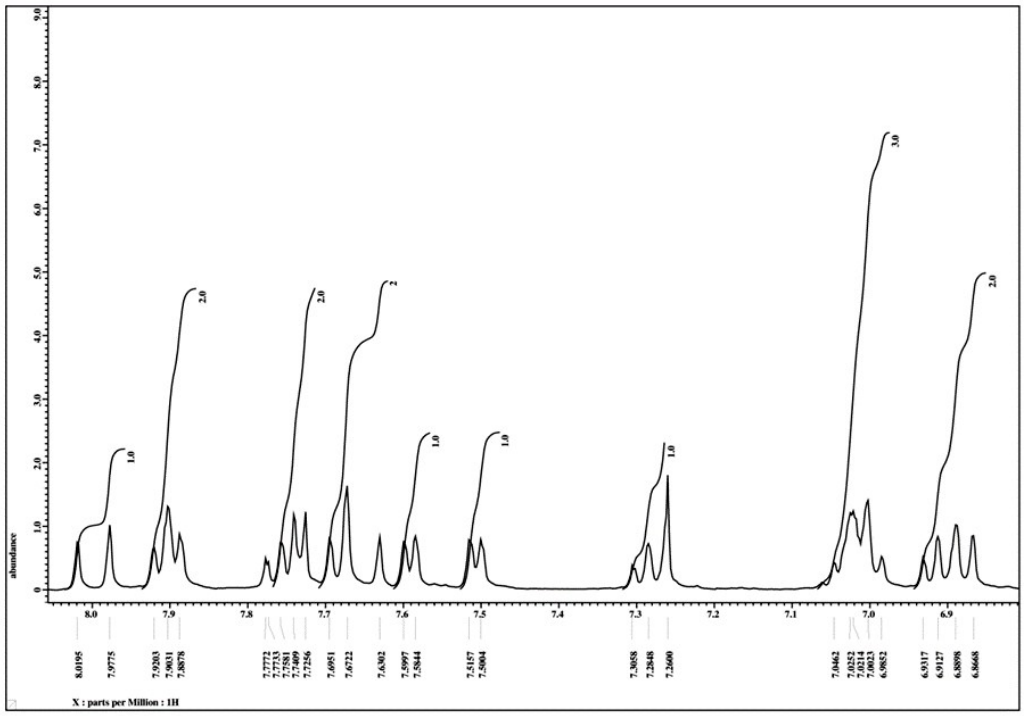


^{1}H NMR spectrum of **1** (Part E)

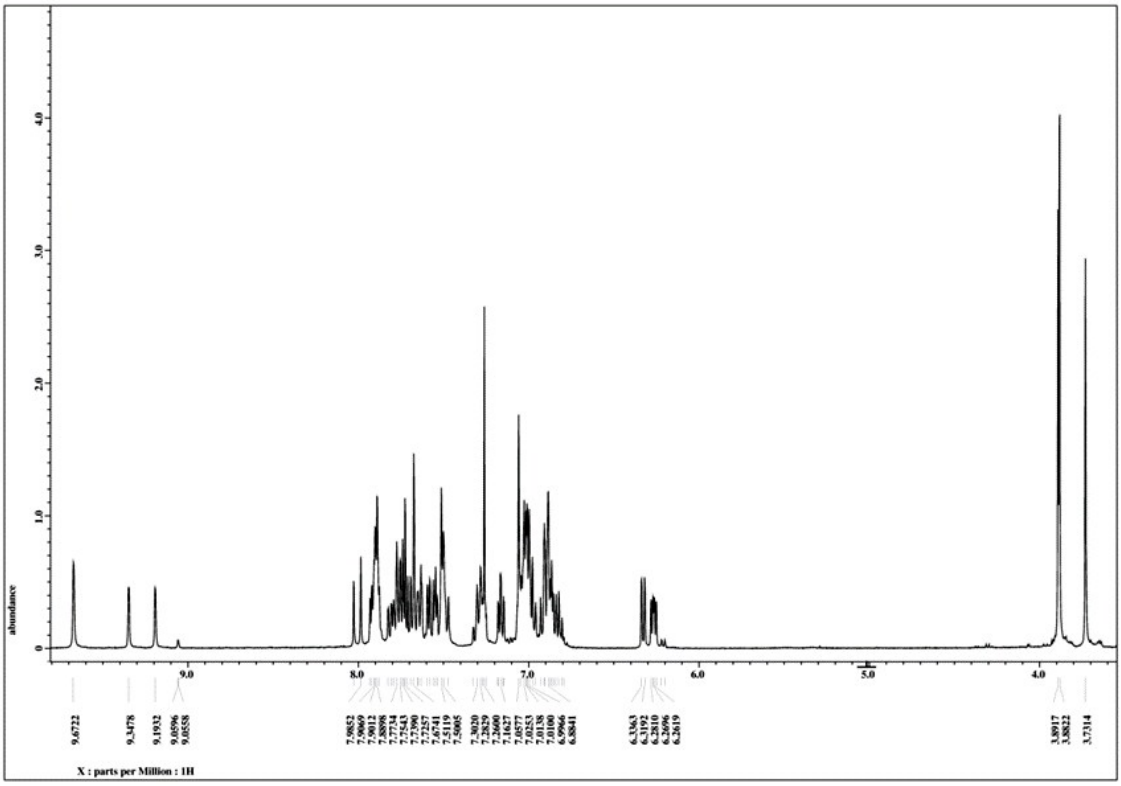
Complex **2**:



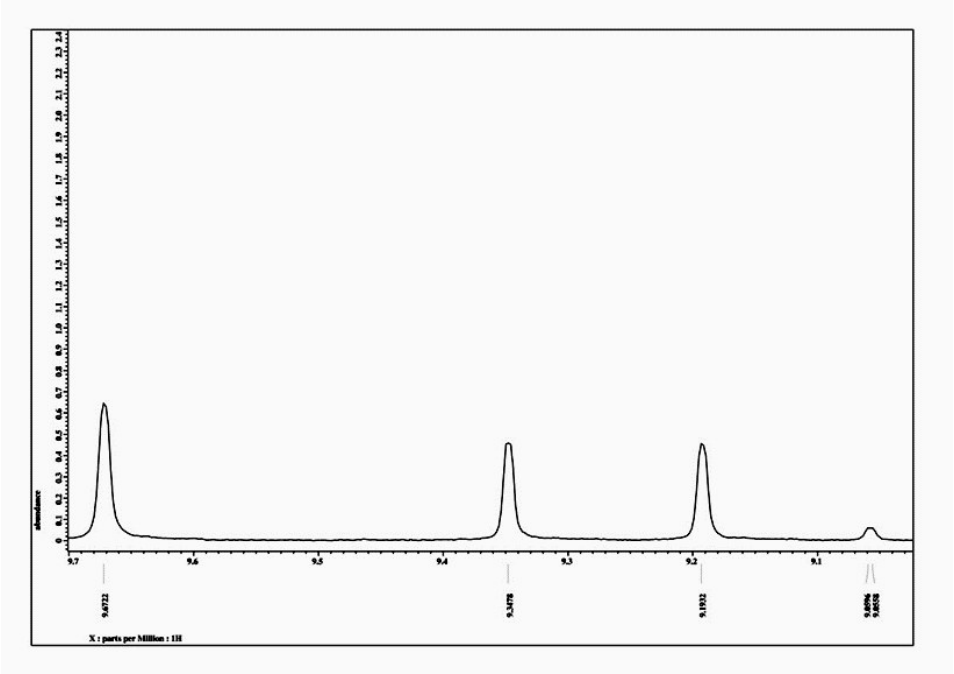
^{1}H NMR spectrum of **2** (entire spectrum)



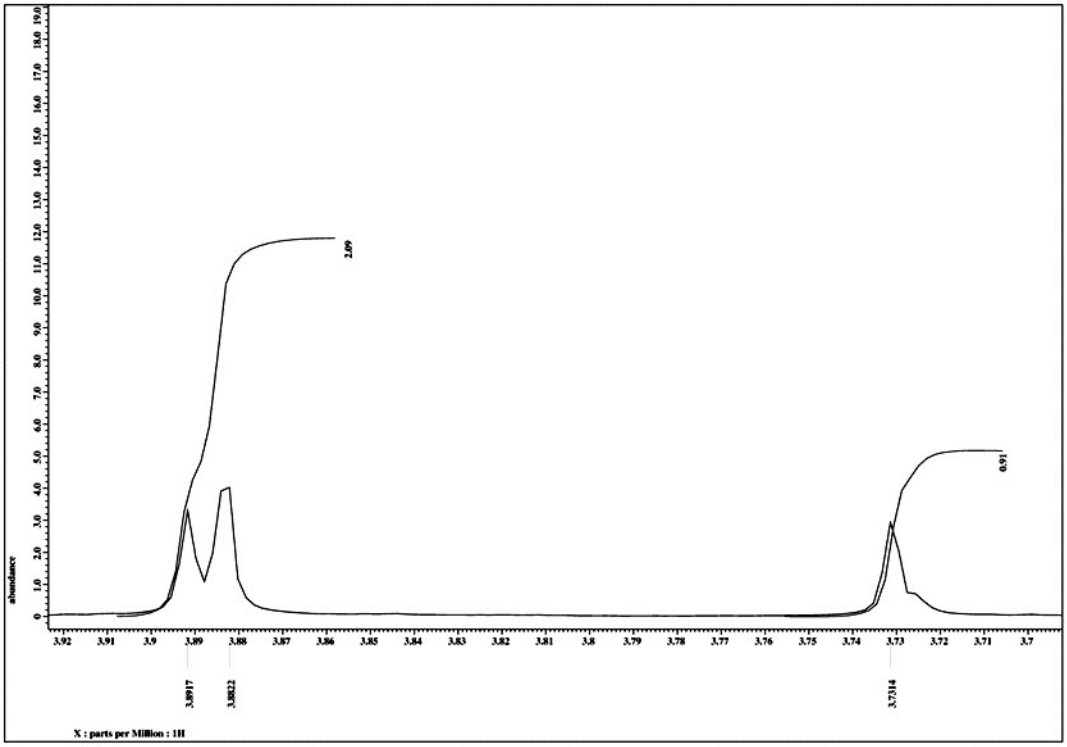
^{1}H NMR spectrum of **2** (Part A)



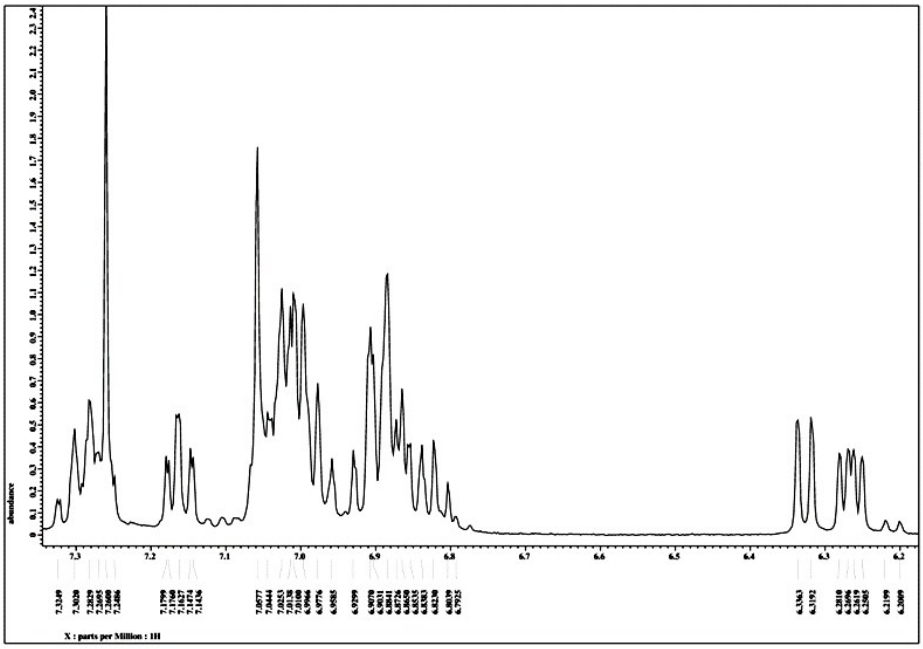
^{1}H NMR spectrum of **2** (Part B)



^{1}H NMR spectrum of **2** (Part C)



^{1}H NMR spectrum of **2** (Part D)



^{1}H NMR spectrum of **2** (Part E)

Figure S9: Time-dependent ^{1}H NMR spectra of **2**

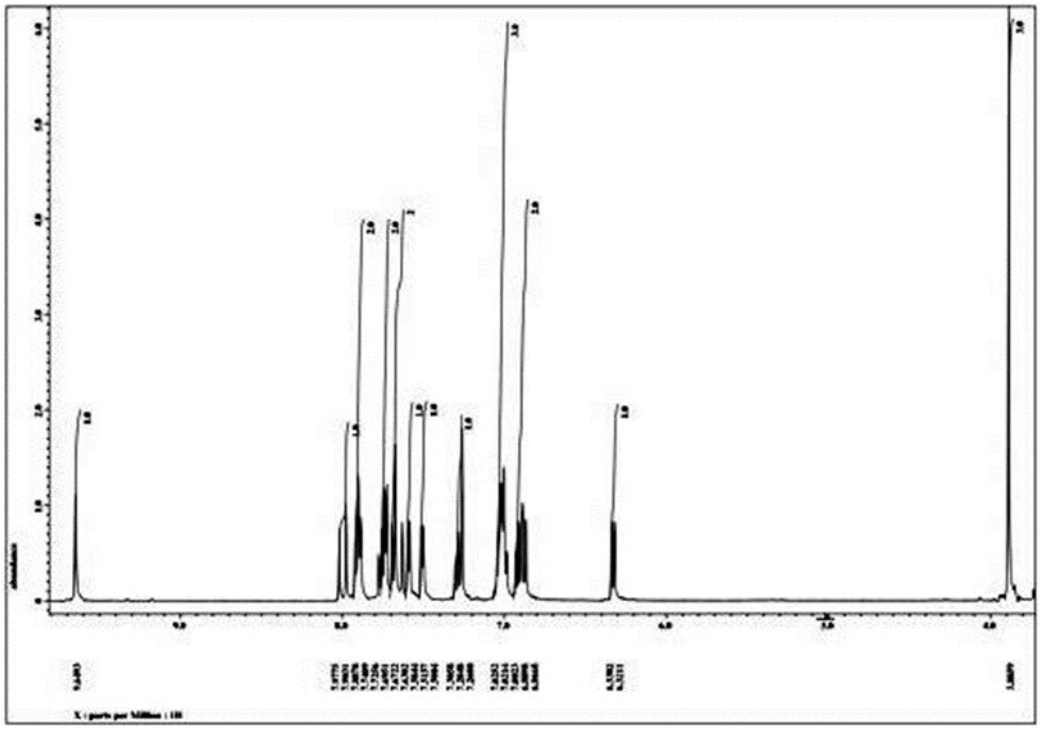
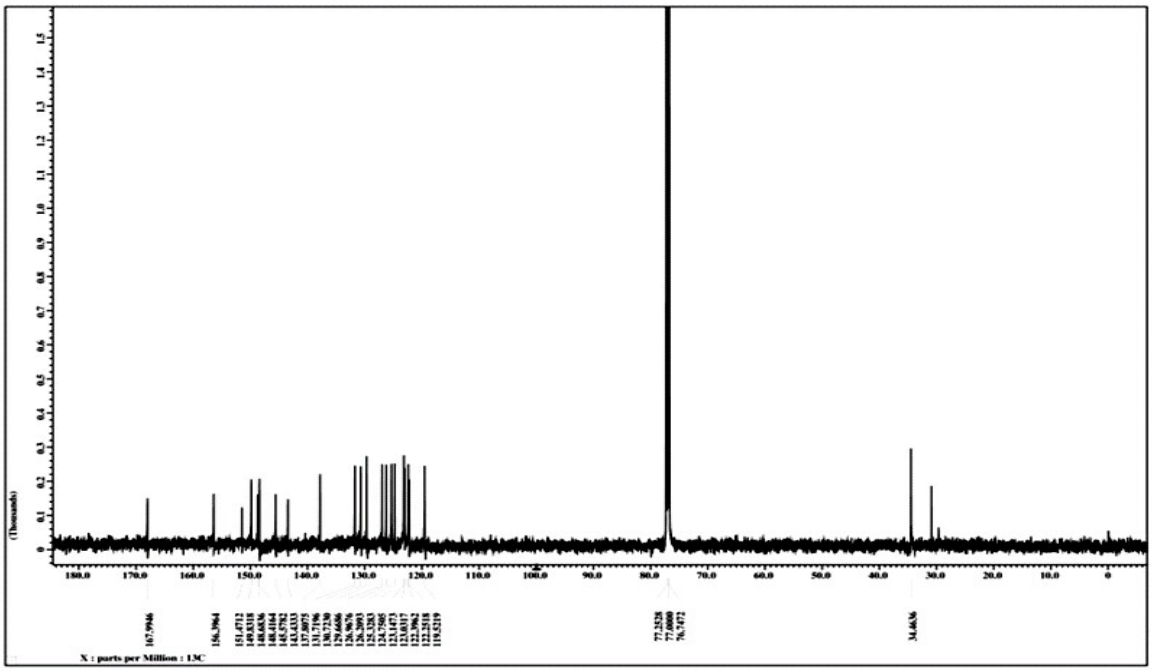


Figure S10: ^{13}C NMR spectra of complexes **1** and **2**

Complex **1**:



Complex **2**:

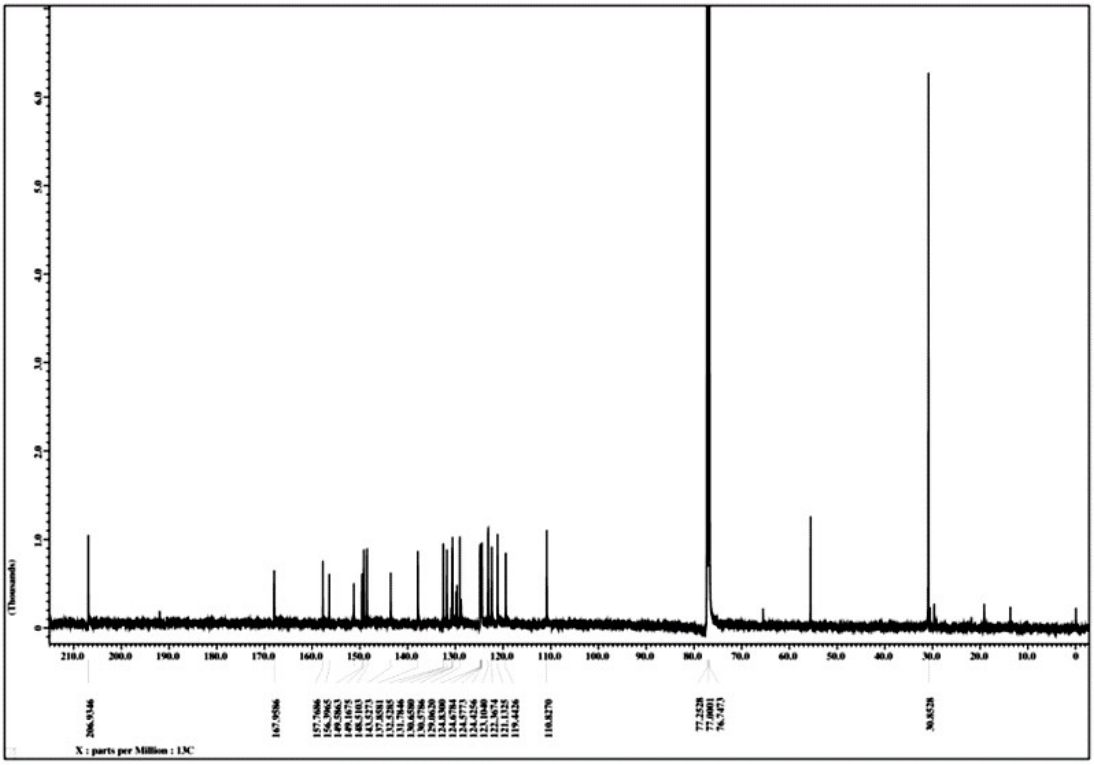
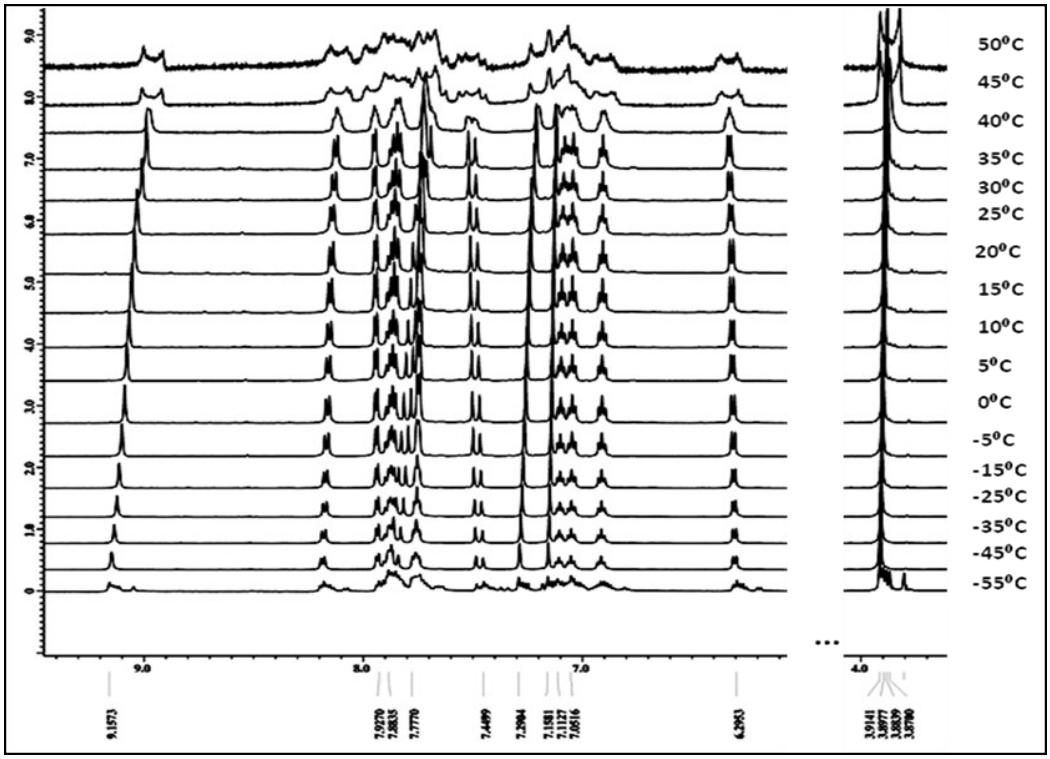


Figure S11: Temperature dependent ^{1}H NMR of **1** and **2** in Methanol-d_4

Complex **1**:



Complex **2**:

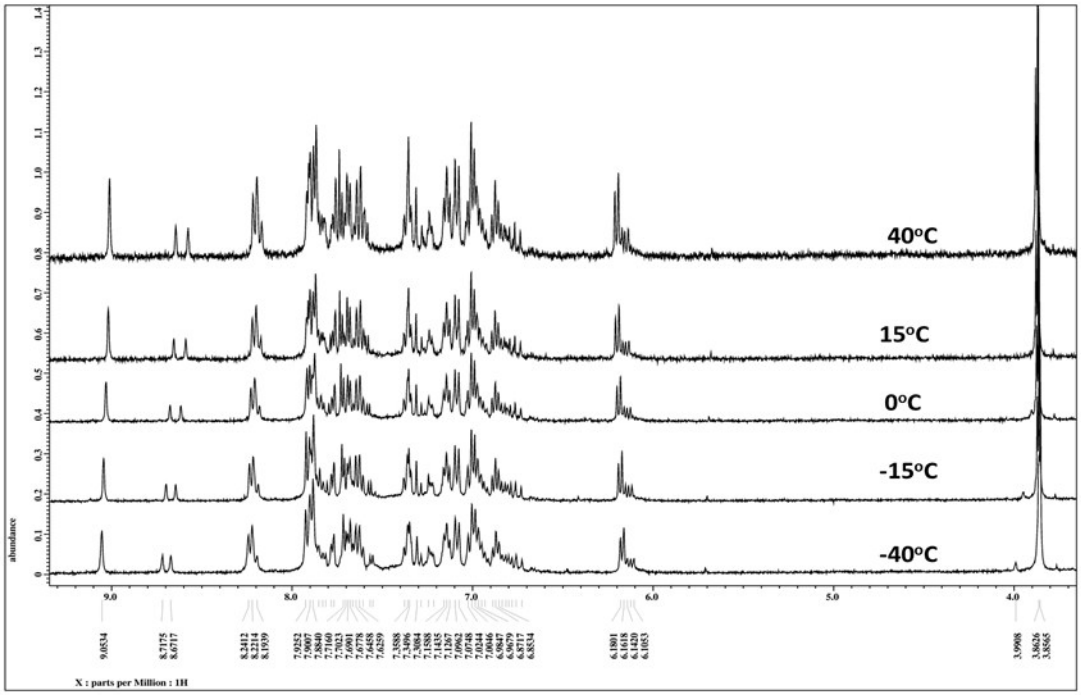
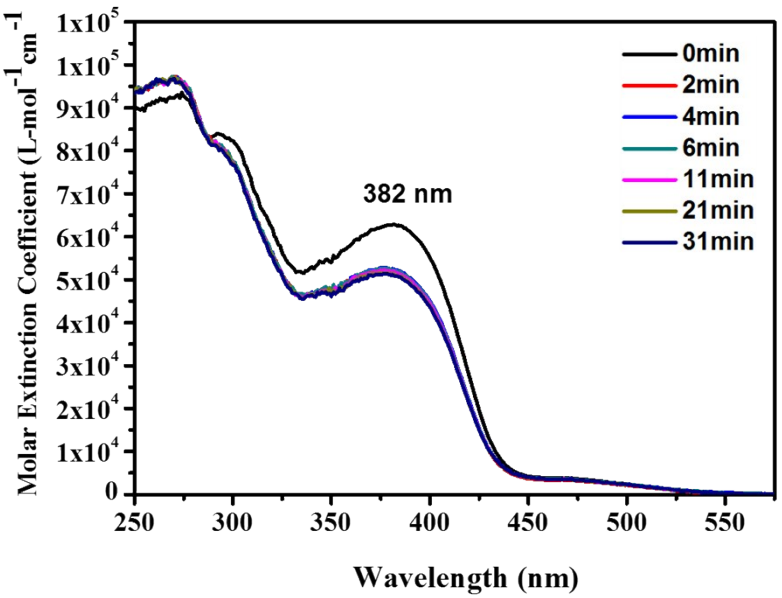


Figure S12: Time dependent electronic spectra of **2** (10 μM in dry DCM) under 366nm light exposure.

A. Absorption spectra:



B. Emission spectra(λ_{ex} = 350 nm):

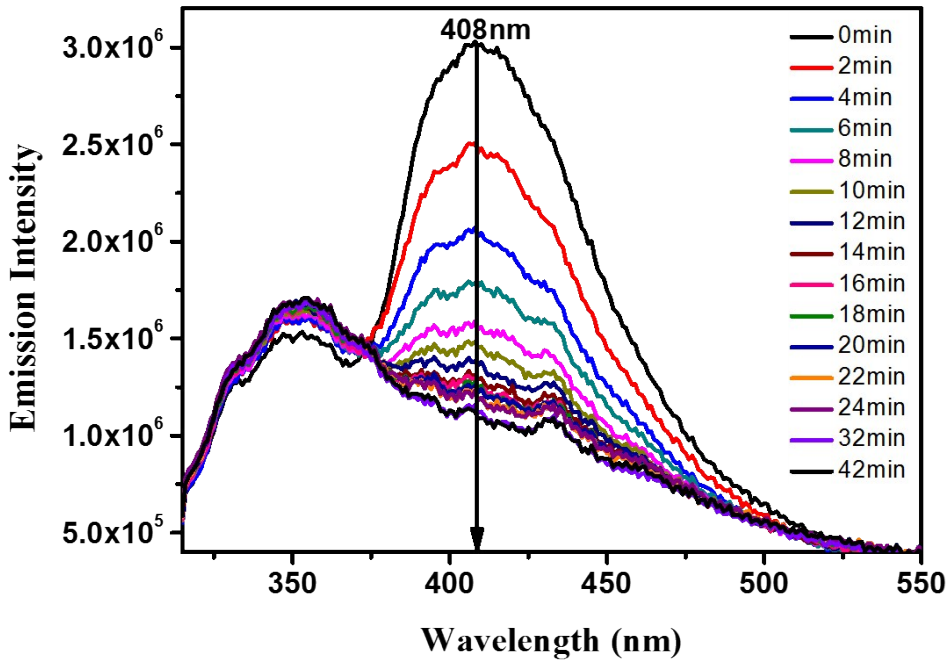


Figure S13: Energy levels of the ground and excited state for the ligands **L1**, **L2** and complexes **1**, **2**

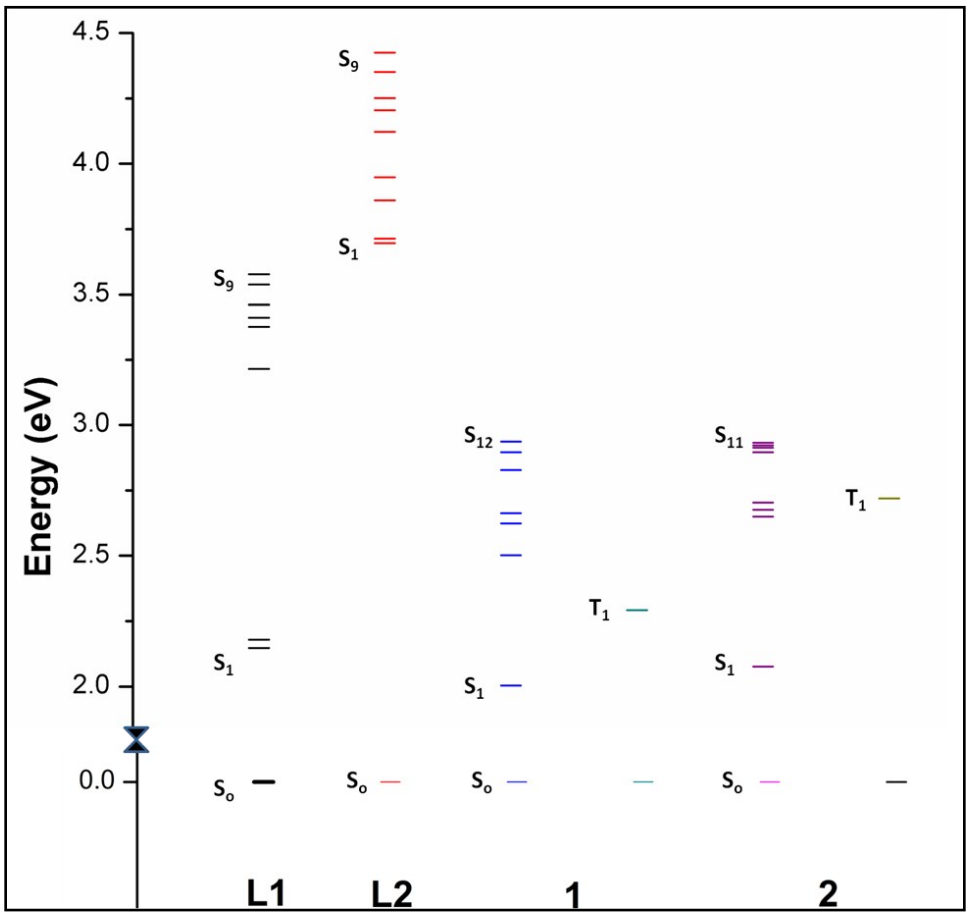
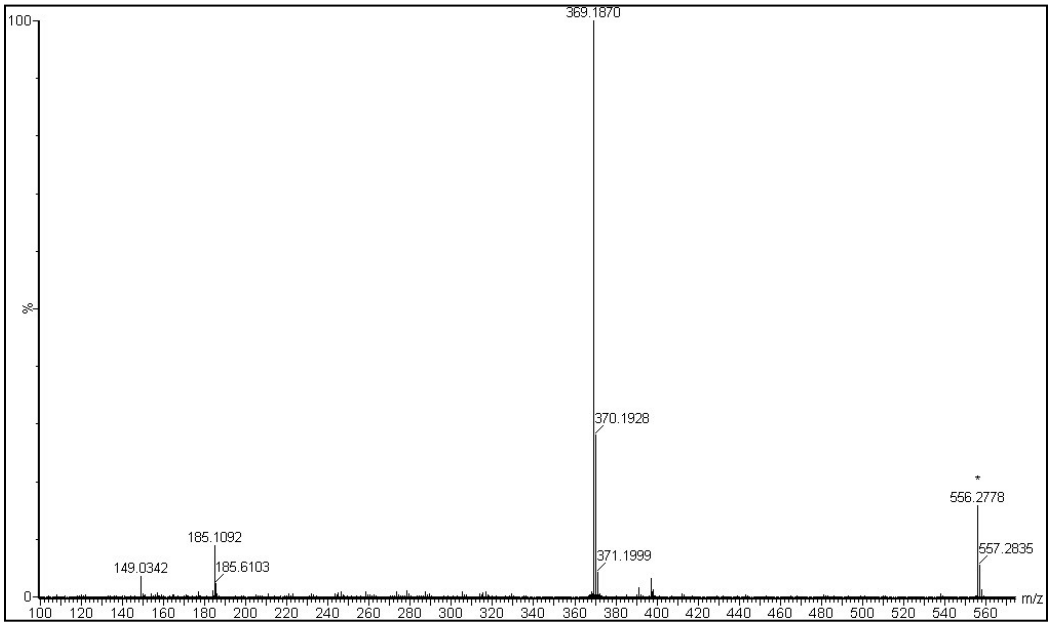


Figure S14: ESI-MS of ligands **L1** and**L2**

L1:



L2:

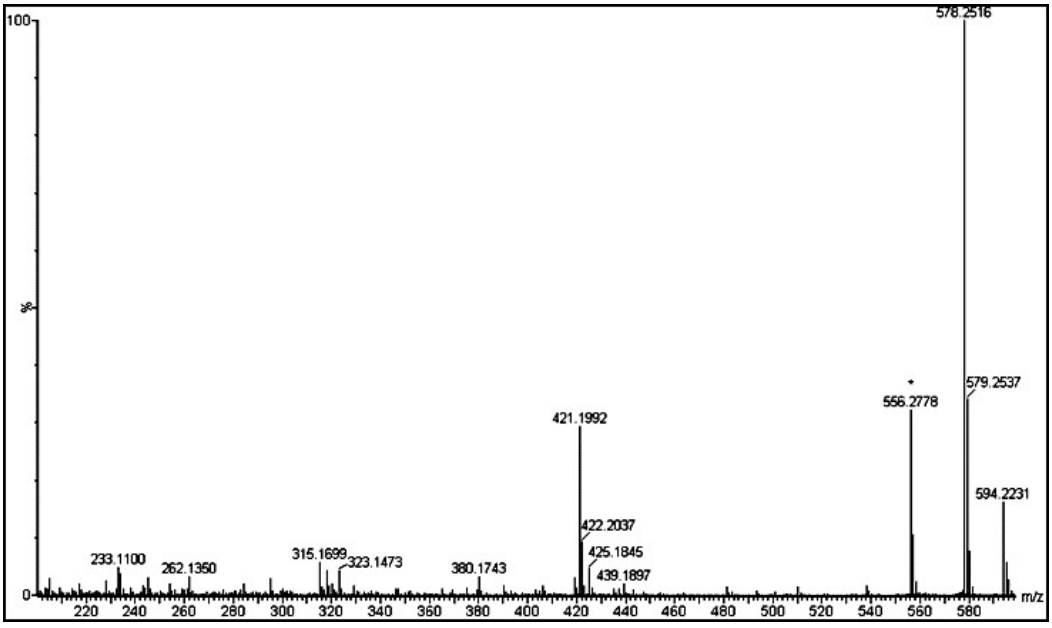
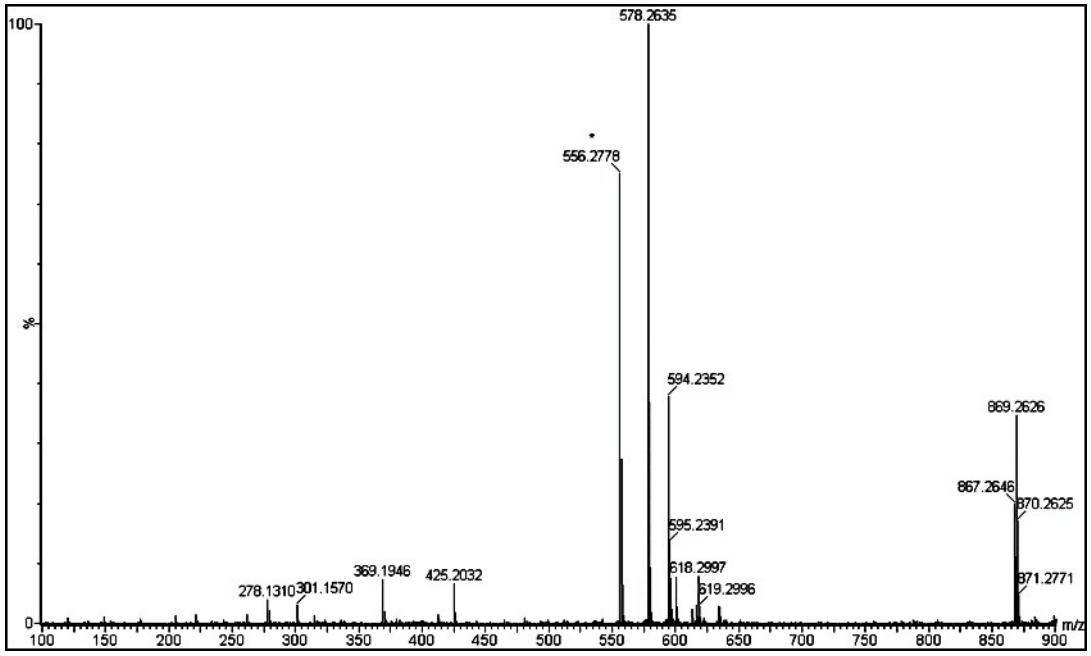


Figure S15: ESI-MS of complexes**1**and **2**

Complex **1**:



Complex **2**.

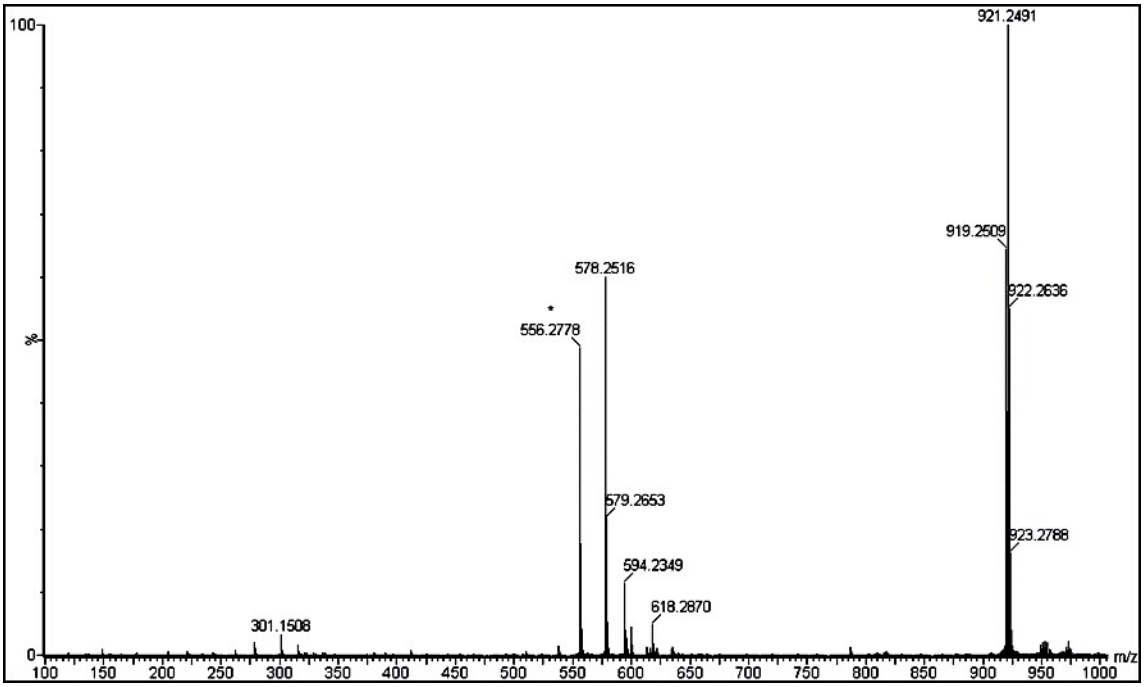


Table S1: Selected Bond Distances and Bond Angles for **1**, **2**, and $\mathbf{2_{final}}$

Bond lengths(Å)	Bond angles(°)	Bond angles(°)
1		
Ir1 - N1 2.030(10)	N1 - Ir1 - N2 172.9(4)	N2 - Ir1 - C22 80.4(4)
Ir1 - N2 2.052(9)	N1 - Ir1 - N3 90.8(4)	N3 - Ir1 - N4 76.0(4)
Ir1 - N3 2.148(9)	N1 - Ir1 - N4 96.0(4)	N3 - Ir1 - C11 97.8(4)
Ir1 - N4 2.143(9)	N1 - Ir1 - C11 81.1(4)	N3 - Ir1 - C22 174.3(4)
Ir1 - C11 2.005(10)	N1 - Ir1 - C22 93.7(4)	N4 - Ir1 - C11 173.3(4)
Ir1 - C22 1.995(11)	N2 - Ir1 - N3 95.5(4)	N4 - Ir1 - C22 99.8(4)
	N2 - Ir1 - N4 88.9(3)	C11 - Ir1 - C22 86.5(4)
	N2 - Ir1 - C11 94.6(4)	
2		
Ir1 - N1 2.04(2)	N1 - Ir1 - N2 174.6(9)	N2 - Ir1 - C12 80.6(9)
Ir1 - N2 2.06(2)	N1 - Ir1 - N3 89.1(9)	N3 - Ir1 - N475.7(10)
Ir1 - N3 2.15(2)	N1 - Ir1 - N496.2(10)	N3 - Ir1 - C1 97.6(11)
Ir1 - N42.11(3)	N1 - Ir1 - C1 80.1(12)	N3 - Ir1 - C12172.1(9)
Ir1 - C11.96(3)	N1 - Ir1 - C12 95.5(9)	N4 - Ir1 - C1172.5(10)
Ir1 - C122.026(14)	N2 - Ir1 - N3 95.3(9)	N4 - Ir1 - C12 97.4(9)
	N2 - Ir1 - N4 88.0(9)	C1 - Ir1 - C12 89.5(10)
	N2 - Ir1 - C196.1(11)	
$\mathbf{2_{Final}}$		
Ir1 - N1 1.936(18)	N1 - Ir1 - N2 173.6(7)	N2 - Ir1 - C22 81.8(8)
Ir1 - N2 2.014(19)	N1 - Ir1 - N3 96.6(7)	N3 - Ir1 - N475.9(7)
Ir1 - N3 2.132(18)	N1 - Ir1 - N4 89.6(7)	N3 - Ir1 - C11 175.5(8)
Ir1 - N4 2.127(17)	N1 - Ir1 - C11 82.5(9)	N3 - Ir1 - C22 99.9(8)
Ir1 - C11 2.00(2)	N1 - Ir1 - C22 92.7(8)	N4 - Ir1 - C1199.7(8)
Ir1 - C22 2.04(2)	N2 - Ir1 - N3 87.6(7)	N4 - Ir1 - C22 175.4(8)
	N2 - Ir1 - N4 96.1(7)	C11 - Ir1 - C22 84.5(9)
	N2 - Ir1 - C11 93.7(8)	