Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary information

Indole-7-carbaldehyde thiosemicarbazone as a flexidentate ligand toward Zn^{II}, Cd^{II}, Pd^{II} and Pt^{II} ions: cytotoxic and apoptosis-inducing properties of the Pt^{II} complex.

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Table S1 Selected bond lengths (Å) and angles (°) for the zinc(II) and cadmium(II) complexes.

$[ZnBr_2(LH_2)_2]$. 2MeOH		**$[CdCl_2(LH_2)_2]$. MeOH**		**$[Cd(OAc)_2(LH_2)_2]$. 2MeOH**	
bond lengths					
Zn(1)-Br(1)	2.3816(5)	Cd(1)-Cl(2)	2.4651(14)	Cd(1)-O(3)	2.219(8)
Zn(1)-Br(2)	2.4154(6)	Cd(1)-S(2)	2.5080(11)	Cd(1)-O(1)	2.319(8)
Zn(1)-S(2)	2.3398(10)	Cd(1)-Cl(1)	2.5137(11)	Cd(1)-O(2)	2.488(7)
Zn(1)-S(1)	2.3650(11)	Cd(1)-S(1)	2.5245(12)	Cd(1)-S(2)	2.510(3)
S(1)-C(10)	1.719(4)	S(1)-C(10)	1.724(3)	Cd(1)-S(1)	2.583(3)
S(2)-C(20)	1.712(3)	S(2)-C(20)	1.717(3)	S(1)-C(10)	1.727(10)
N(2)-C(9)	1.277(5)	N(2)-C(9)	1.289(3)	S(2)-C(20)	1.727(10)
N(2)-N(3)	1.384(4)	N(2)-N(3)	1.396(3)	O(1)-C(21)	1.209(11)
N(3)-C(10)	1.324(5)	N(3)-C(10)	1.337(3)	O(2)-C(21)	1.247(9)
N(4)-C(10)	1.312(5)	N(4)-C(10)	1.316(4)	O(3)-C(23)	1.240(12)
N(6)-C(19)	1.284(4)	N(6)-C(19)	1.295(3)	O(4)-C(23)	1.241(12)
N(6)-N(7)	1.380(3)	N(6)-N(7)	1.393(3)	N(2)-C(9)	1.287(12)
N(7)-C(20)	1.335(4)	N(7)-C(20)	1.342(3)	N(2)-N(3)	1.388(10)
N(8)-C(20)	1.308(4)	N(8)-C(20)	1.293(4)	N(3)-C(10)	1.342(11)
				N(4)-C(10)	1.299(11)
				N(6)-C(19)	1.282(11)
				N(6)-N(7)	1.403(10)
				N(7)-C(20)	1.312(11)
				N(8)-C(20)	1.315(12)
bond angles					
S(2)-Zn(1)-S(1)	110.59(4)	Cl(2)-Cd(1)-S(2)	112.08(3)	O(3)-Cd(1)-O(1)	90.2(3)
S(2)-Zn(1)-Br(1)	107.04(3)	Cl(2)-Cd(1)-Cl(1)	102.72(2)	O(3)-Cd(1)-O(2)	85.6(3)
S(1)-Zn(1)-Br(1)	112.03(3)	S(2)-Cd(1)-Cl(1)	110.00(4)	O(1)-Cd(1)-O(2)	53.6(2)
S(2)-Zn(1)-Br(2)	113.14(3)	Cl(2)-Cd(1)-S(1)	117.44(3)	O(3)-Cd(1)-S(2)	132.8(2)
S(1)-Zn(1)-Br(2)	100.26(3)	S(2)-Cd(1)-S(1)	103.32(3)	O(1)-Cd(1)-S(2)	127.99(19)
Br(1)-Zn(1)-Br(2)	113.80(2)	Cl(1)-Cd(1)-S(1)	111.39(4)	O(2)-Cd(1)-S(2)	95.76(16)
C(10)-S(1)-Zn(1)	106.96(13)	C(10)-S(1)-Cd(1)	105.07(9)	O(3)-Cd(1)-S(1)	101.0(2)
C(20)-S(2)-Zn(1)	108.16(11)	C(20)-S(2)-Cd(1)	108.44(10)	O(1)-Cd(1)-S(1)	93.07(18)
				O(2)-Cd(1)-S(1)	146.33(16)
				S(2)-Cd(1)-S(1)	103.07(10)
				C(10)-S(1)-Cd(1)	105.4(4)
				C(20)-S(2)-Cd(1)	103.0(3)

Table S2 Selected bond lengths (Å) and angles (°) for the palladium(II) and platinum(II) complexes.

[Pd(L)(LH$_2$)]		**[Pd(L)(PPh$_3$)] . DMF**		**[Pt(L)(PPh$_3$)] . 0.75 MeOH**	
bond lengths					
Pd(1)-N(1)	2.0306(17)	Pd(1)-N(1)	2.0452(15)	Pt(1)-N(1)	2.043(3)
Pd(1)-N(2)	2.0245(16)	Pd(1)-N(2)	2.0676(16)	Pt(1)-N(2)	2.065(3)
Pd(1)-S(1)	2.2496(5)	Pd(1)-S(1)	2.2560(5)	Pt(1)-S(1)	2.2567(10)
Pd(1)-S(2)	2.2980(5)	Pd(1)-P(1)	2.2658(5)	Pt(1)-P(1)	2.2482(8)
S(1)-C(10)	1.746(2)	S(1)-C(10)	1.752(2)	S(1)-C(10)	1.754(4)
S(2)-C(20)	1.717(2)	N(2)-C(9)	1.296(3)	N(2)-C(9)	1.320(5)
N(2)-C(9)	1.296(3)	N(2)-N(3)	1.398(2)	N(2)-N(3)	1.390(5)
N(2)-N(3)	1.401(2)	N(3)-C(10)	1.303(3)	N(3)-C(10)	1.296(5)
N(3)-C(10)	1.301(3)	N(4)-C(10)	1.350(3)	N(4)-C(10)	1.354(5)
N(4)-C(10)	1.354(3)				
N(6)-C(19)	1.284(3)				
N(6)-N(7)	1.376(2)				
N(7)-C(20)	1.339(3)				
N(8)-C(20)	1.315(3)				
bond angles					
N(2)-Pd(1)-N(1)	92.43(7)	N(1)-Pd(1)-N(2)	91.89(6)	N(1)-Pt(1)-N(2)	90.91(12)
N(2)-Pd(1)-S(1)	84.58(5)	N(1)-Pd(1)-S(1)	175.59(4)	N(1)-Pt(1)-S(1)	173.89(9)
N(1)-Pd(1)-S(1)	176.77(5)	N(2)-Pd(1)-S(1)	83.73(5)	N(2)-Pt(1)-S(1)	83.58(10)
N(2)-Pd(1)-S(2)	169.53(5)	N(1)-Pd(1)-P(1)	94.30(4)	N(1)-Pt(1)-P(1)	93.85(8)
N(1)-Pd(1)-S(2)	95.25(5)	N(2)-Pd(1)-P(1)	173.16(5)	N(2)-Pt(1)-P(1)	174.02(9)
S(1)-Pd(1)-S(2)	87.86(2)	S(1)-Pd(1)-P(1)	90.092(18)	P(1)-Pt(1)-S(1)	91.82(3)
C(20)-S(2)-Pd(1)	108.61(7)				

Table S3 Hydrogen-bond geometry for the crystal structures. *Cg*(1)-*Cg*(5) are the centroids of the N5-C11-12-C13-C18, N1-C1-C2-C3-C8, C17-C22, C23-C28 and C3-C8 rings, respectively.

	D-H...A	H…A (Å)	D...A (Å)	D-H…A (°)
[Zn(LH$_2$)Br$_2$].2MeOH				
	N(1)-H(1N)...N(2)	2.57(5)	2.955(5)	109(4)
	N(1)-H(1N)...O(1)	2.07(3)	2.867(6)	155(5)
	N(3)-H(3N)...Br(1)	2.61(2)	3.456(3)	171(4)
	N(4)-H(4A)...O(1)	2.02(3)	2.804(6)	151(4)
	N(4)-H(4B)...O(2)	2.09(2)	2.904(6)	166(5)
	N(5)-H(5N)...N(6)	2.37(3)	2.930(4)	124(3)
	N(5)-H(5N)...Br(2)#1	2.82(3)	3.361(3)	123(3)
	N(7)-H(7N)...Br(2)	2.58(2)	3.399(3)	167(3)
	N(8)-H(8A)...Br(2)#1	2.74(3)	3.434(3)	139(3)
	N(8)-H(8B)...Br(1)#1	2.90(3)	3.625(3)	145(3)
[Cd(LH$_2$)$_2$Cl$_2$].MeOH				
	N(1)-H(1N)...N(2)	2.50	2.970(3)	115.5
	N(1)-H(1N)...Cl(2)#2	2.69	3.340(3)	133.6
	N(3)-H(3N)...O(1)	2.003(19)	2.861(4)	165(3)
	N(3)-H(3N)...O(1')	2.09(3)	2.919(19)	157(3)
	N(4)-H(4A)...Cl(2)#2	2.51(3)	3.230(3)	143(3)
	N(4)-H(4B)...Cl(1)	2.521(19)	3.360(3)	170(3)
	N(5)-H(5N)...N(6)	2.40	2.891(3)	116.6
	N(5)-H(5N)...Cl(1)#3	2.80	3.449(2)	133.2
	N(7)-H(7N)...Cl(1)#4	2.44(2)	3.237(3)	154(2)
	N(8)-H(8A)...Cl(1)#3	2.52(3)	3.174(3)	134(3)
	N(8)-H(8B)...Cl(2)	2.521(18)	3.366(2)	169(3)
[Cd(LH2)$_2$(OAc)$_2$].2MeOH				
	N(1)-H(1N)...O(6)	2.17	2.891(10)	141.3
	N(1)-H(1N)...N(2)	2.49	2.964(12)	115.6
	N(3)-H(3N)...O(11)	1.96	2.811(16)	168.5
	N(4)-H(4A)...O(6)	2.11	2.849(11)	143.5
	N(4)-H(4B)...O(3)	1.97	2.816(10)	169.2

	N(5)-H(5N)...O(10)#5	2.26	2.917(15)	132.7
	N(5)-H(5N)...N(6)	2.44	2.898(12)	114.3
	N(7)-H(7N)...O(5)#1	2.00	2.807(10)	155.9
	N(8)-H(8A)...O(10)#5	2.16	2.925(13)	147.4
	N(8)-H(8B)...O(4)	1.97	2.810(12)	166.8
	N(9)-H(9A)...O(9)#6	2.27	2.937(14)	134.7
	N(9)-H(9A)...N(10)	2.46	2.931(11)	115.2
	N(11)-H(11N)...O(1)	1.98	2.789(9)	157.2
	N(12)-H(12A)...O(9)#6	2.17	2.932(12)	148.3
	N(12)-H(12B)...O(8)	2.00	2.844(12)	168.4
	N(13)-H(13N)...O(2)#7	2.18	2.891(11)	140.1
	N(13)-H(13N)...N(14)	2.48	2.959(11)	116.1
	N(15)-H(15N)...O(12)	1.99	2.830(12)	165.0
	N(16)-H(16A)...O(2)#7	2.13	2.869(10)	143.8
	N(16)-H(16B)...O(7)	1.98	2.823(10)	166.7
	O(9)-H(9B)...O(8)	1.99	2.766(12)	158.4
	O(10)-H(10)...O(4)	1.91	2.706(13)	162.5
[Pd(L)(LH$_2$)]				
	N(5)-H(5N)...N(6)	2.40	2.900(3)	116.0
	N(8)-H(8A)...N(3)#8	2.109(15)	2.928(2)	155(2)
	N(4)-H(4B)...*Cg*(1)#9	2.78	3.619(2)	160
	C(19)-H(19)...*Cg*(2)#10	2.79	3.689(3)	158
[Pd(L)(PPh$_3$)].DMF				
	N(4)-H(4B)...N(3)#11	2.129(18)	3.001(3)	172(3)
	N(4)-H(4A)...O(1)	2.18(2)	2.982(4)	156(3)
	N(4)-H(4A)...O(2)	1.851(18)	2.695(4)	168(3)
	C(15)-H(15)...*Cg*(3)#4	2.92	3.497(2)	120
	C(19)-H(19)...*Cg*(4)#12	2.73	3.609(2)	154
	C(20)-H(20)...*Cg*(5)#13	2.77	3.505(2)	135
	C(21)-H(21)...*Cg*(2)#13	2.64	3.457(2)	144
	C(25)-H(25)...*Cg*(2)#1	2.63	3.439(2)	144
	C(25)-H(25)...*Cg*(5)#1	2.96	3.648(2)	131

[Pt(L)(PPh$_3$)].0.75MeOH

C(27)-H(27)...*Cg*(2)#14	2.85	3.382(5)	117
C(15)-H(15)...*Cg*(5)#15	2.91	3.647(5)	135
N(4)-H(4A)...O(1)#16	2.14(5)	3.044(6)	154(4)
N(4)-H(4B)...O(1)#17	2.16(5)	2.939(5)	144(4)
O(1)-H(1A)...N(3)	1.98	2.816(5)	178.6

Symmetry transformations used to generate equivalent atoms: #1 x-1,y,z; #2 x,-y+1/2,z+1/2; #3 x,-y+1/2,z-1/2; #4 -x+2,-y+1,-z+1; #5 -x,-y+1,-z; #6 -x+1,-y,-z+1; #7 x+1,y,z; #8 -x,-y+1,-z+1; #9 x-1/2,-y+1/2,z+1/2; #10 -x,-y,-z+1; #11 -x+2,-y,-z; #12 -x+1,-y+1,-z+1; #13 -x+2,-y,-z+1; #14 x,y,z-1; #15 x-y+1/3,x-1/3,-z+2/3; #16 -x+y+2/3,-x+1/3,z-2/3; #17 -y+1/3,x-y-1/3,z-1/3

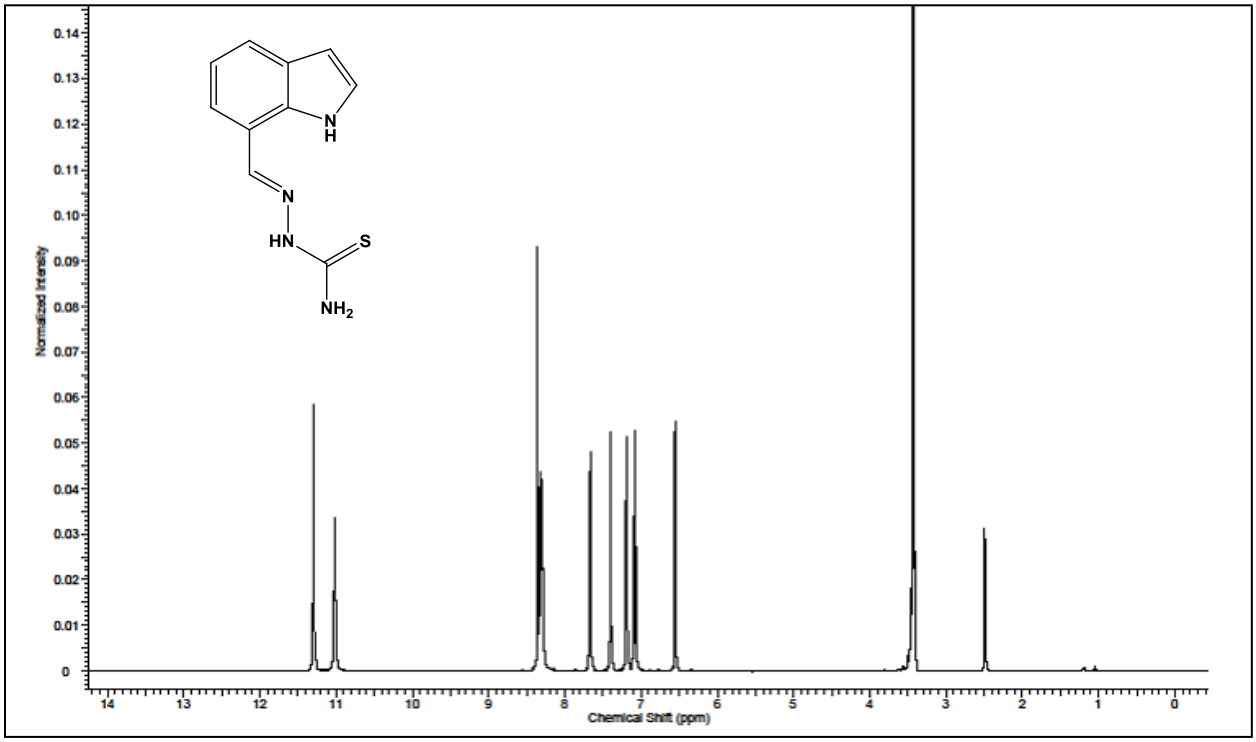
Table S4 Crystal data and refinement parameters for the zinc(II) and cadmium(II) complexes

	$[ZnBr_2(LH_2)_2]$. 2 MeOH	**$[CdCl_2(LH_2)_2]$. MeOH**	**$[Cd(OAc)_2(LH_2)_2]$. 2 MeOH**
Empirical formula	$C_{22}\,H_{28}\,Br_2\,N_8\,O_2\,S_2\,Zn$	$C_{21}\,H_{24}\,Cd\,Cl_2\,N_8\,O\,S_2$	$C_{26}\,H_{34}\,Cd\,N_8\,O_6\,S_2$
Formula weight	725.83	651.90	731.13
Temperature (K)	296(2)	296(2)	296(2)
Crystal system , Space group	Triclinic, *P -1*	Monoclinic, *P21/c*	Triclinic, *P -1*
Unit cell dimensions			
a (Å)	8.2989(11)	14.293(7)	12.223(7)
b (Å)	12.4402(16)	15.549(8)	14.649(9)
c (Å)	14.7088(19)	12.519(6)	19.869(11)
α (°)	74.448(2)		83.91(3)
β (°)	83.939(2)	91.673(9)	80.87(3)
γ (°)	85.086(2)		77.10(4)
Volume ($Å^3$)	1452.2(3)		3415(3)
Z, Density (calculated) ($g\,cm^{-3}$)	2, 1.660	4, 1.557	4, 1.422
F(000)	728	1312	1496
θ range for data collection (°)	1.92 to 25.25	2.09 to 27.50	1.04 to 25.25
Reflections collected / unique	7763, 5109 [R_{int} = 0.0141]	16726, 6313 [R_{int} = 0.0289]	19610, 12116 [R_{int} = 0.0908]
Observed reflections [$I > 2\sigma$ (I)]	4116	4827	5051
Completeness	To θ = 25.25°: 97.4 %	To θ = 27.50°: 98.7 %	To θ = 25.25°: 97.8 %
Data / restraints / parameters	5109 / 9 / 362	6313 / 6 / 357	12116 / 3 / 787
Goodness-of-fit on F^2	1.050	1.013	0.964
Final *R* indices [$I>2\sigma$ (I)]	R_1 = 0.0322, wR_2 = 0.0837	R_1 = 0.0292, wR_2 = 0.0705	R_1 = 0.0800, wR_2 = 0.1848
R indices (all data)	R_1 = 0.0430, wR_2 = 0.0881	R_1 = 0.0455, wR_2 = 0.0815	R_1 = 0.1902, wR_2 = 0.2349
Largest diff. peak and hole ($e.Å^{-3}$)	0.734 and -0.688	0.476 and -0.482	0.94 and -0.84

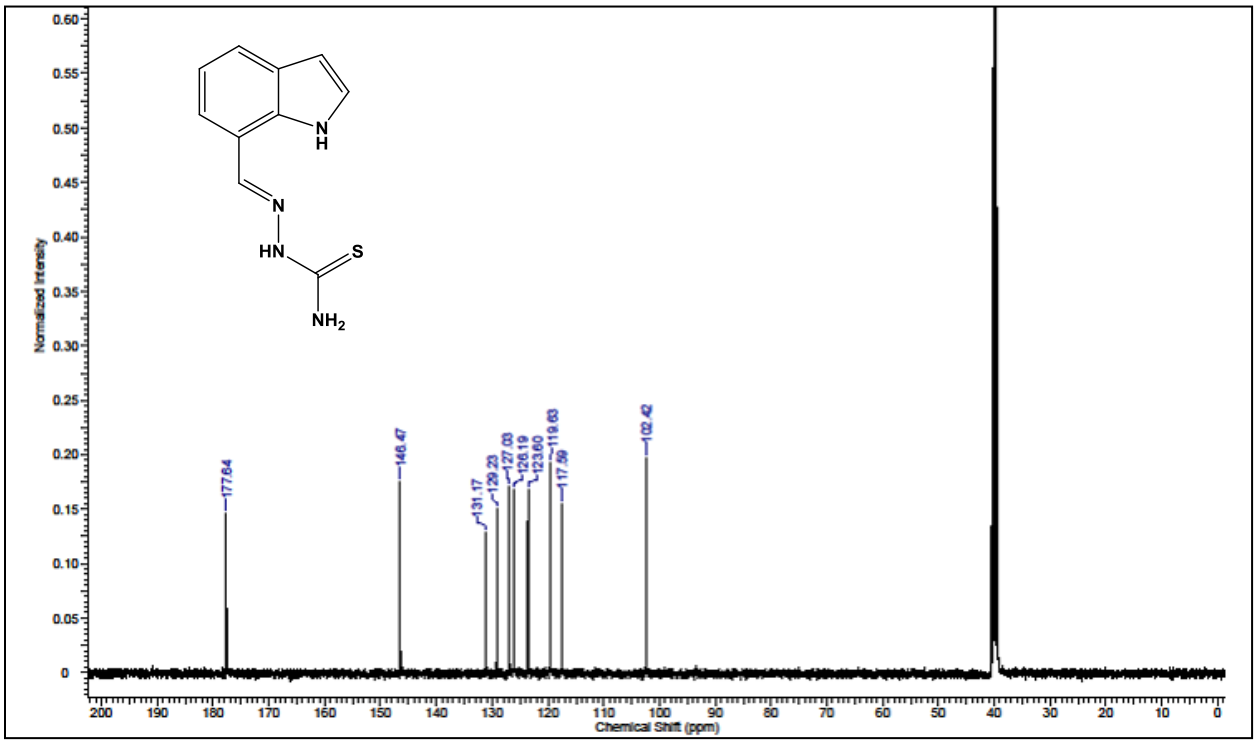
Table S5 Crystal data and refinement parameters for the palladium(II) and platinum(II) complexes

	[Pd(L)(LH$_2$)]	**[Pd(L)(PPh$_3$)] . DMF**	**[Pt(L)(PPh$_3$)] . 0.75 MeOH**
Empirical formula	C_{20} H_{18} N_8 Pd S_2	C_{31} H_{30} N_5 O P Pd S	$C_{28.75}$ H_{26} N_4 $O_{0.75}$ P Pt S
Formula weight	540.94	658.03	697.66
Temperature (K)	100(2)	100(2)	100(2)
Crystal system , Space group	Monoclinic, *P*21/*n*	Triclinic, *P* -1	Trigonal, *R*-3
Unit cell dimensions			
a (Å)	12.2138(2)	9.6267(5)	39.5689(12)
b (Å)	11.6637(2)	10.0243(5)	39.5689(12)
c (Å)	18.0652(3)	15.6913(8)	9.2324(3)
α (°)		80.642(3)	
β (°)	94.385(3)	87.833(3).	
γ (°)		73.852(3)	
Volume (Å^3)	2566.00(7)	1435.08(13)	12518.5(7)
Z, Density (calculated) (g cm^{-3})	4, 1.400	2, 1.523	18, 1.666
F(000)	1088	672	6147
θ range for data collection (°)	2.08 to 27.49	1.32 to 25.25	2.06 to 27.49
Reflections collected / unique	18756, 5866 [R_{int} = 0.0299]	8518, 5094 [R_{int} = 0.0111]	40144, 6380 [R_{int} = 0.0305]
Observed reflections [$I > 2\sigma$ (I)]	5136	4821	5556
Completeness	To θ = 27.49°: 99.8 %	To θ = 25.25°: 98.3 %	To θ = 27.49°: 100.0 %
Data / restraints / parameters	5866 / 3 / 289	5094 / 2 / 399	6380 / 0 / 342
Goodness-of-fit on F^2	1.072	1.020	1.044
Final *R* indices [$I>2\sigma$ (I)]	R_1 = 0.0265, wR_2 = 0.0704	R_1 = 0.0208, wR_2 = 0.0526	R_1 = 0.0248, wR_2 = 0.0585
R indices (all data)	R_1 = 0.0312, wR_2 = 0.0722	R_1 = 0.0223, wR_2 = 0.0538	R_1 = 0.0319, wR_2 = 0.0618
Largest diff. peak and hole (e.Å^{-3})	0.835 and -0.377 e.Å-3	0.333 and -0.537	2.009 and -0.978

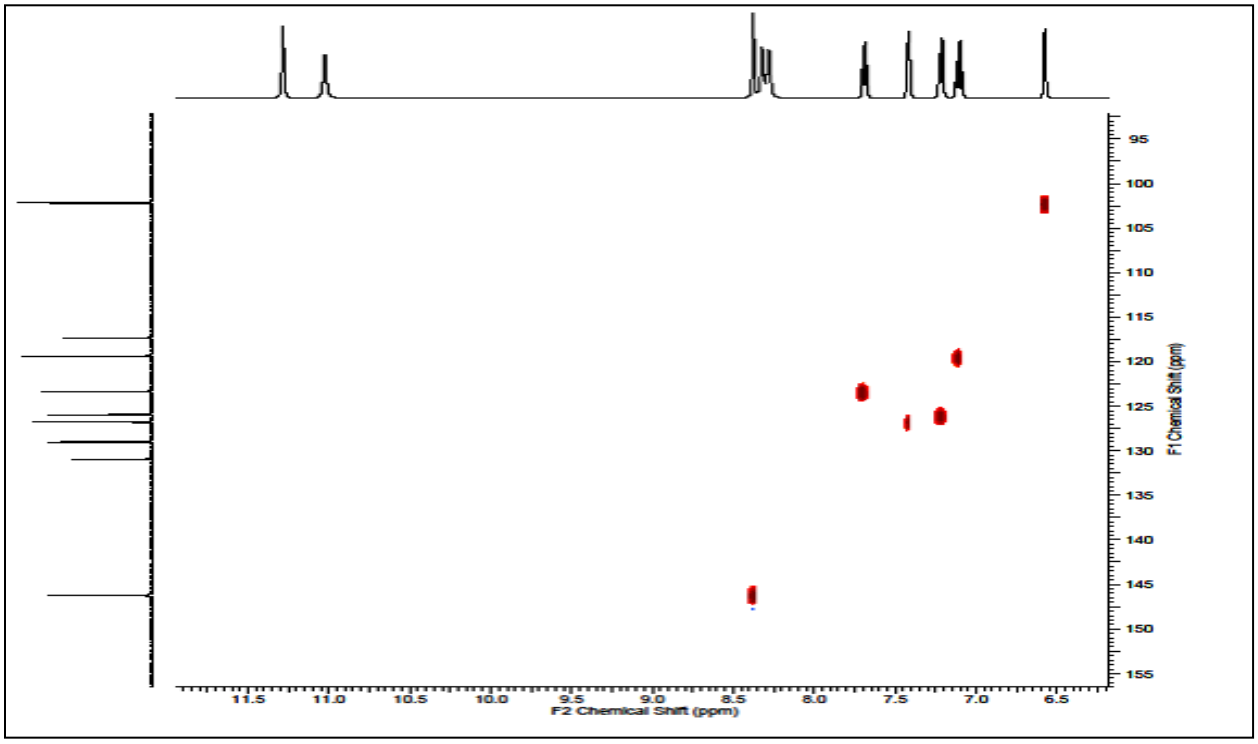
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of LH_2



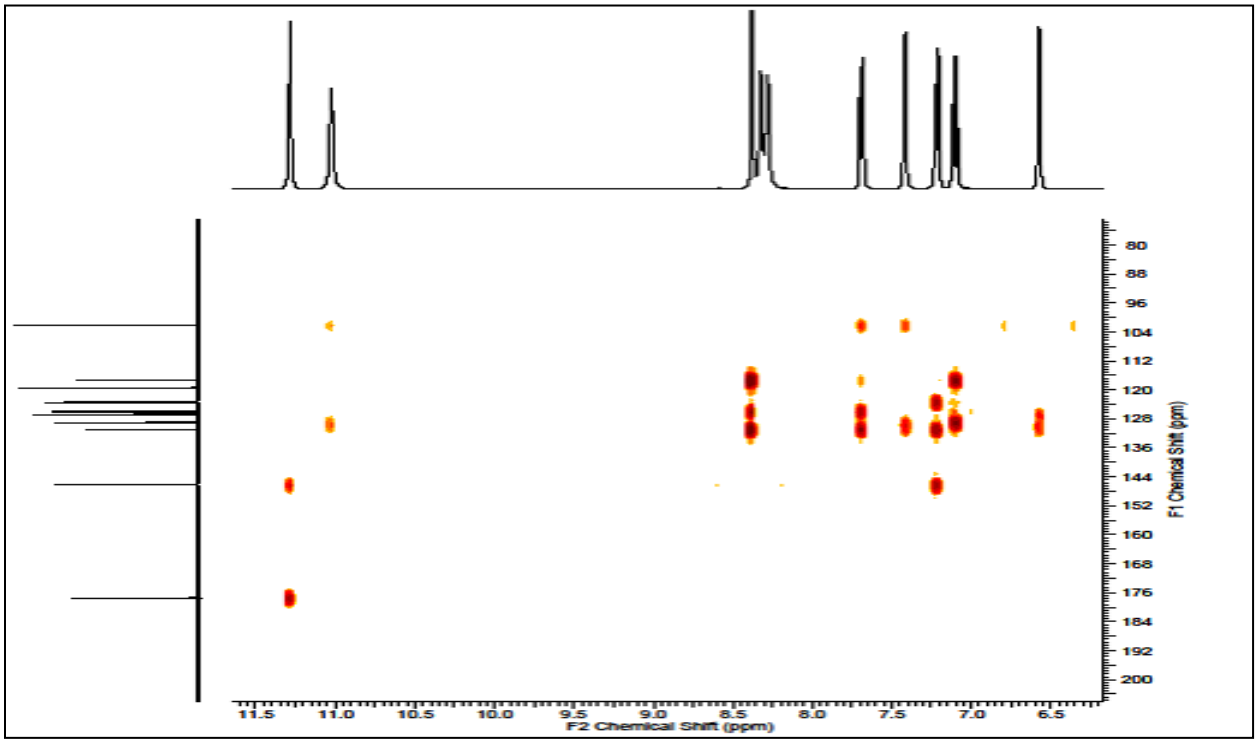
^{13}C NMR spectrum (100 MHz, DMSO-d_6) of LH_2



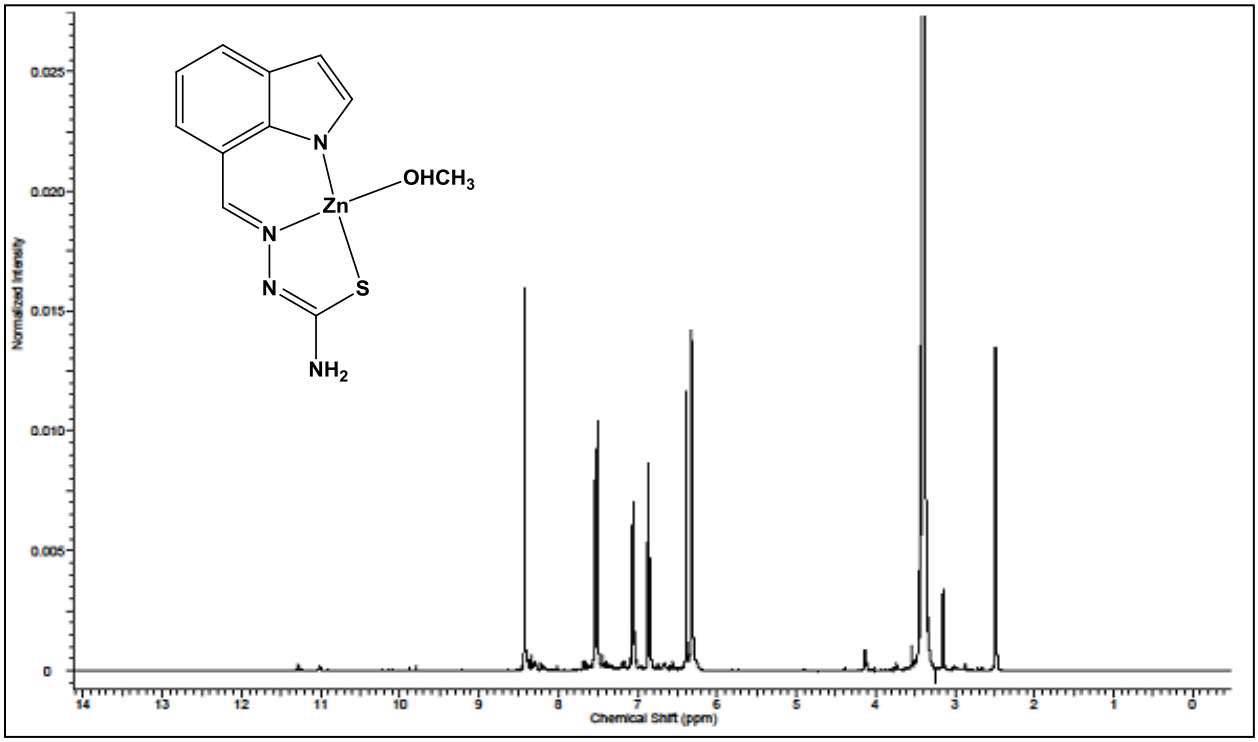
HSQC spectrum (in DMSO-d_6) of LH_2



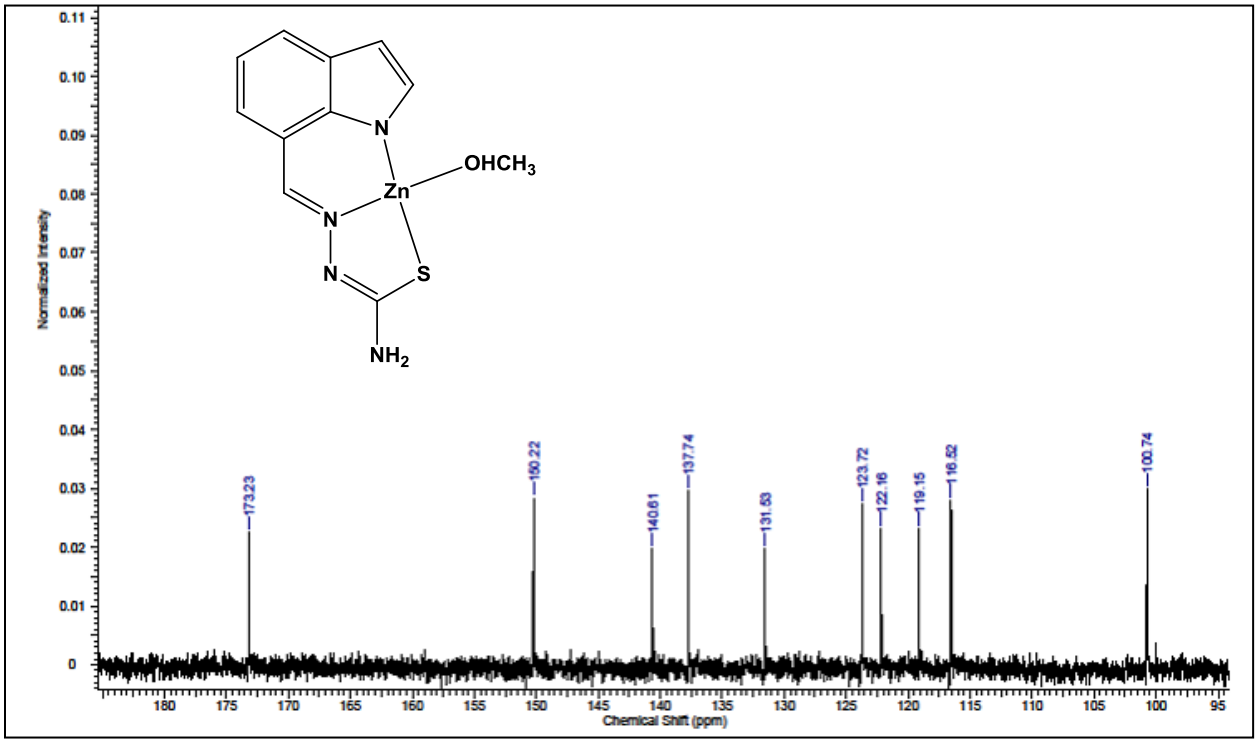
HMBC spectrum (in DMSO-d_6) of LH_2



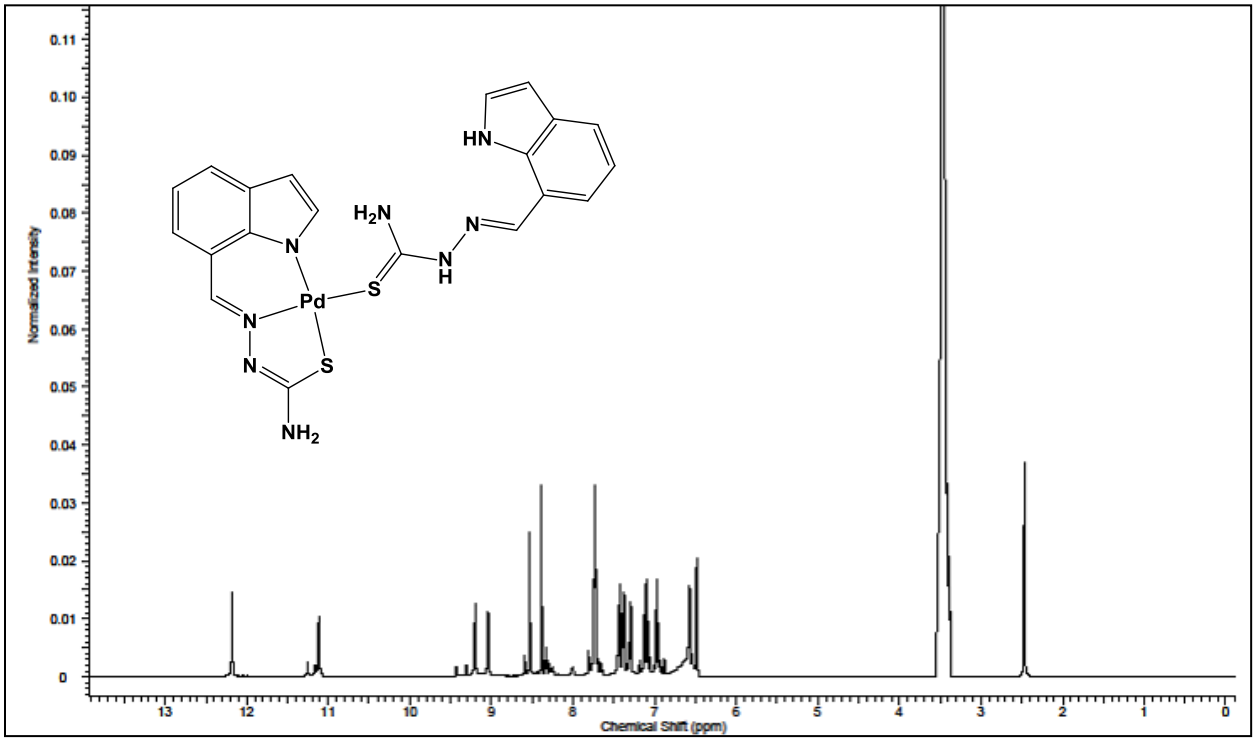
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of [Zn(L)(CH$_3$OH)]



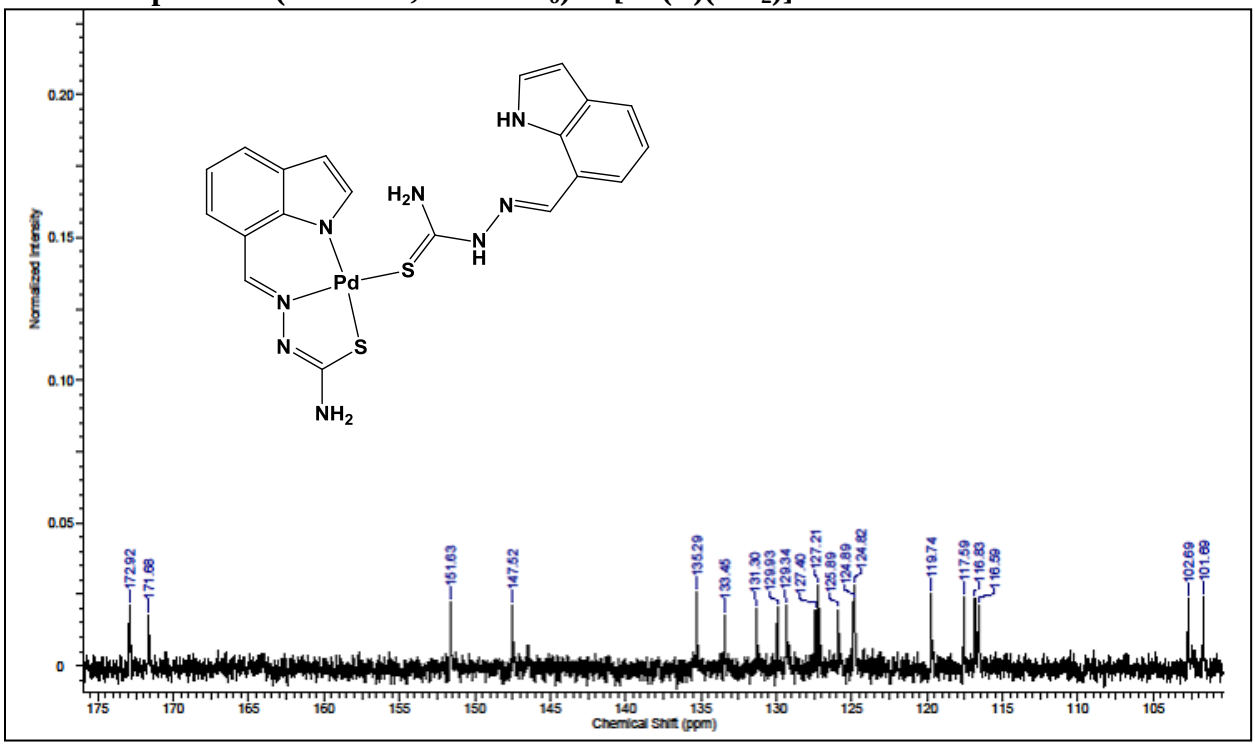
^{13}C NMR spectrum (100 MHz, DMSO-d_6) of [Zn(L)(CH$_3$OH)]



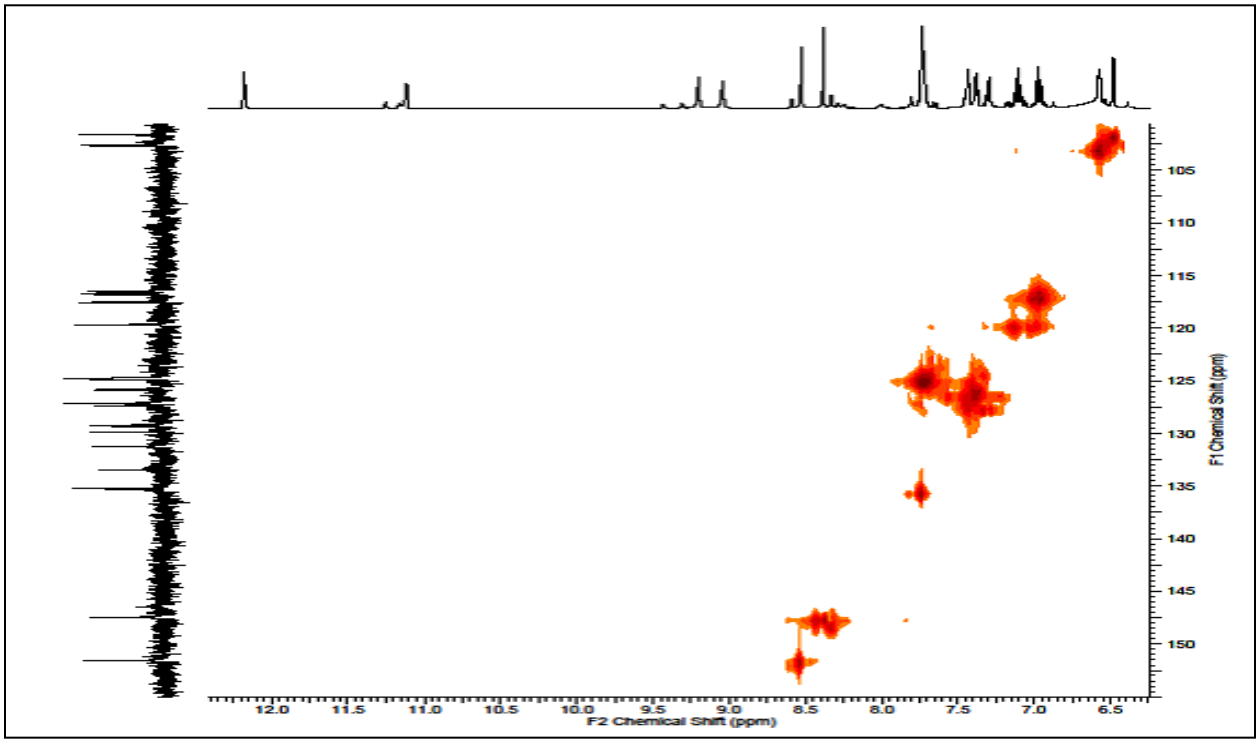
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of [Pd(L)(LH$_2$)]



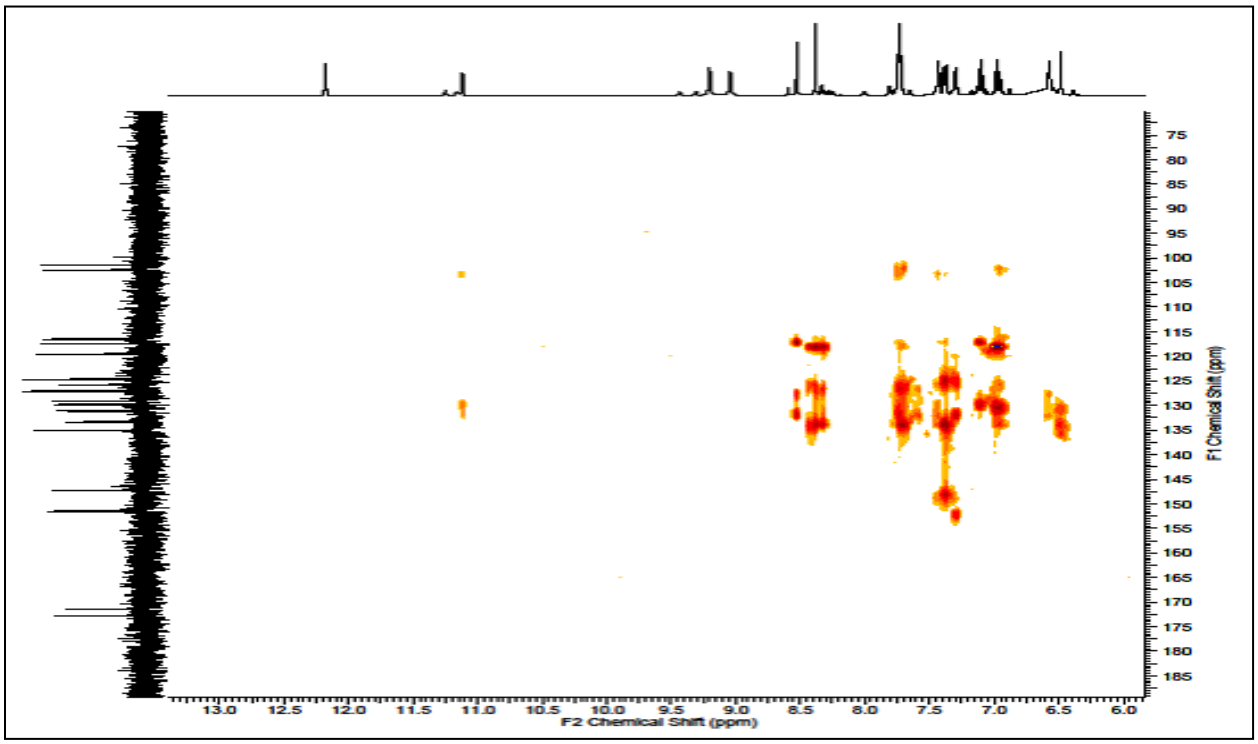
^{13}C NMR spectrum (100 MHz, DMSO-d_6) of [Pd(L)(LH$_2$)]



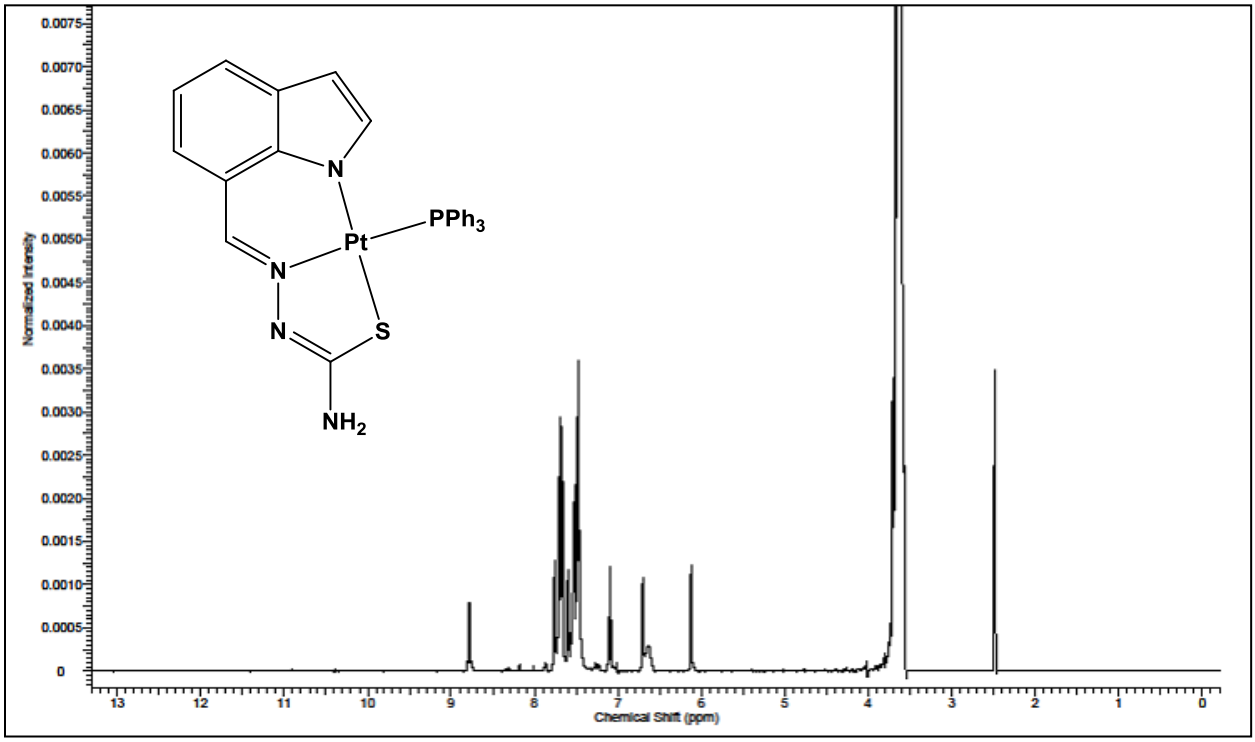
HSQC spectrum (in DMSO-d_6) of [Pd(L)(LH_2)]



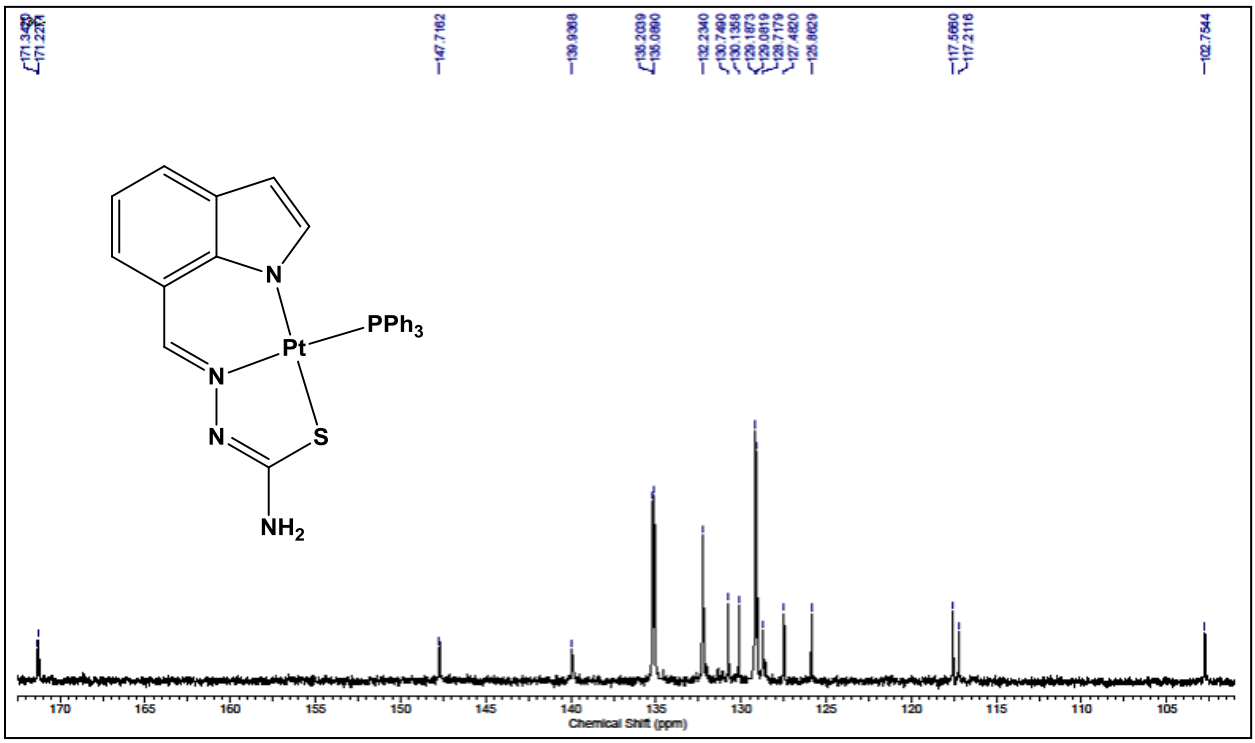
HMBC spectrum (in DMSO-d_6) of [Pd(L)(LH_2)]



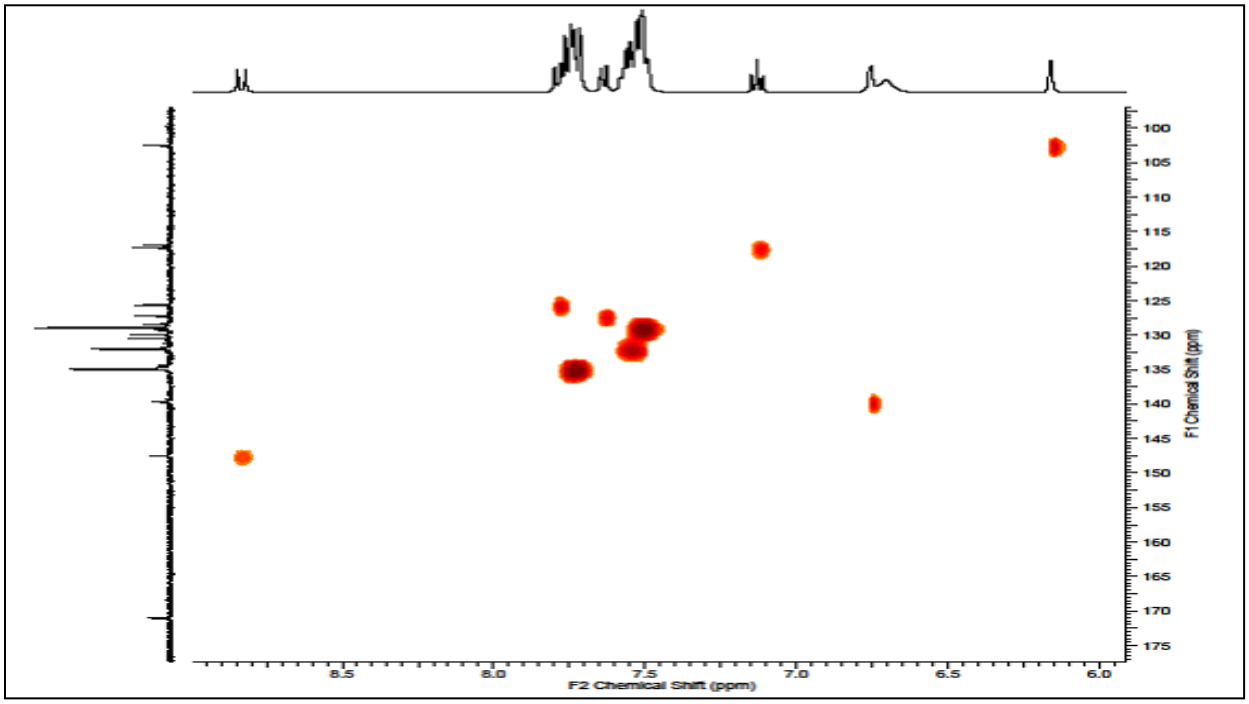
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of [Pt(L)(PPh$_3$)]



^{13}C NMR spectrum (100 MHz, DMSO-d_6) of [Pt(L)(PPh$_3$)]



HSQC spectrum (in DMSO-d_6) of [Pt(L)(PPh_3)]



HMBC spectrum (in DMSO-d_6) of [Pt(L)(PPh_3)]