Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Kinetic and Mechanistic Studies of 1,3-Bis(2-pyridylimino)isoindolate Pt(II) Derivatives. Experimental and new Computational Approach.

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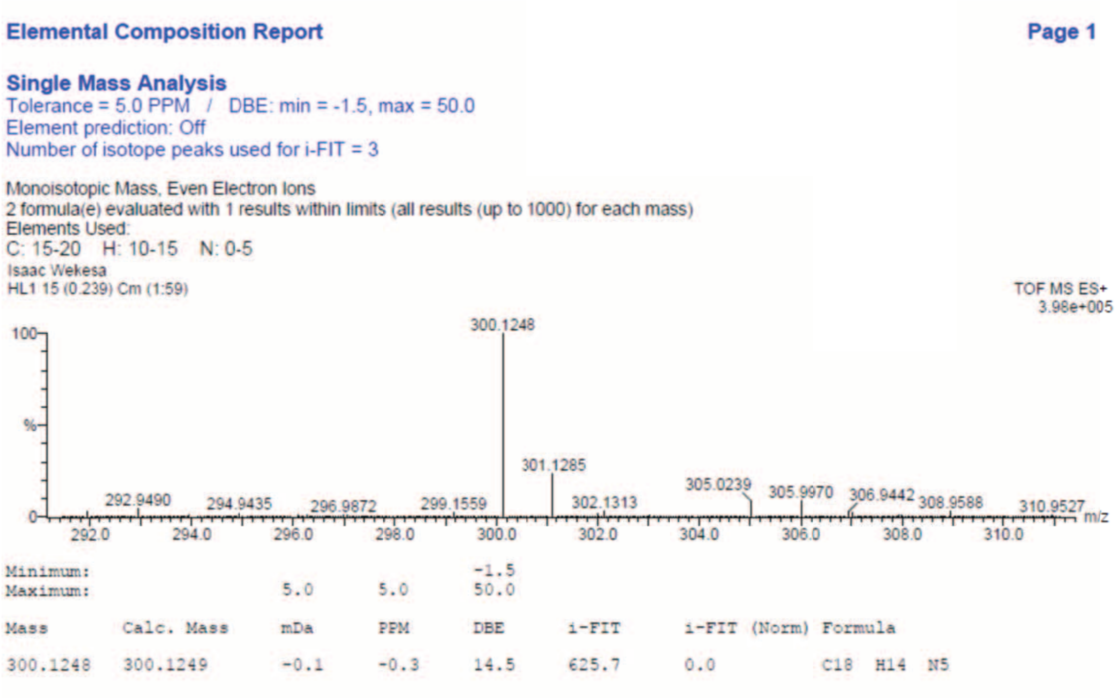
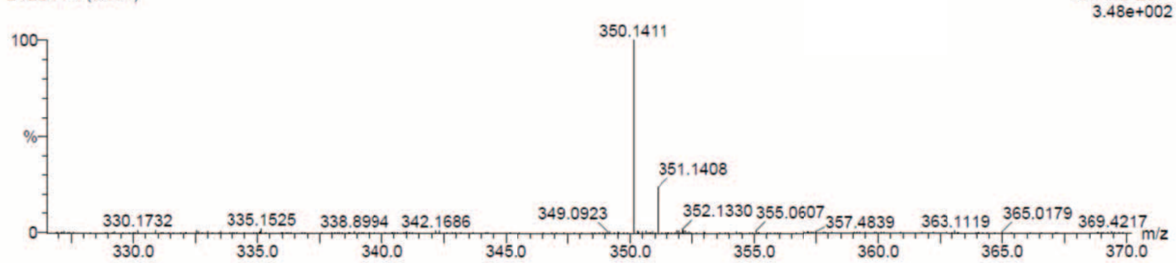


Figure SI 1 Mass spectrum of 1,3-Bis(2-pyridylimino)isoindoline

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 20-25 H: 10-20 N: 0-5
Isaac Wekesa
B1BB11 4 (0.051)



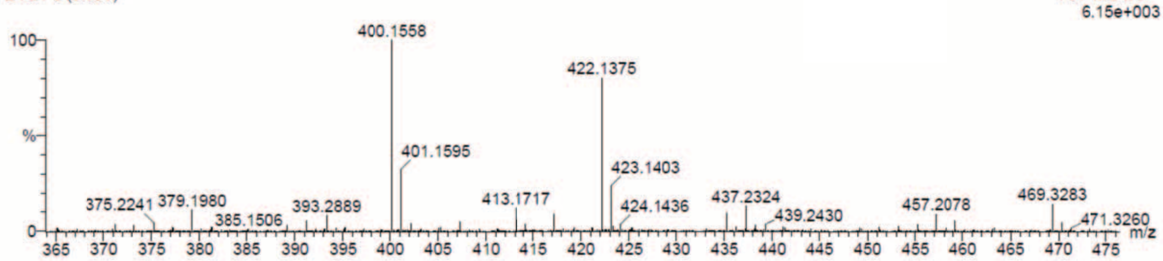
Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
350.1411	350.1406	0.5	1.4	17.5	53.1	0.0	C22 H16 N5

Figure SI 2 Mass spectrum of 1,3-Bis(2-pyridylimino)benz(f)isoindoline

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
4 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 25-30 H: 15-20 N: 0-5 Na: 0-1
Isaac Wekesa
B1Q1 6 (0.085)



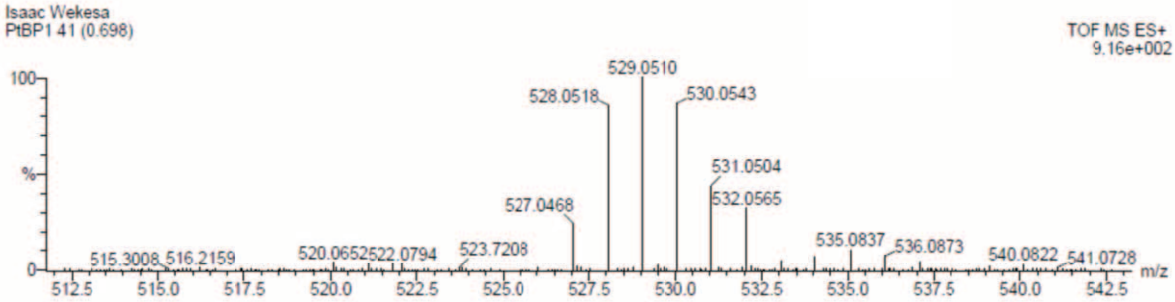
Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
400.1558	400.1562	-0.4	-1.0	20.5	114.2	0.0	C26 H18 N5

Figure SI 3 Mass spectrum of 1,3-Bis(1-isoquinolylimino))isoindoline

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
18 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 15-20 H: 10-15 N: 0-5 Cl: 0-1 Pt: 1-2



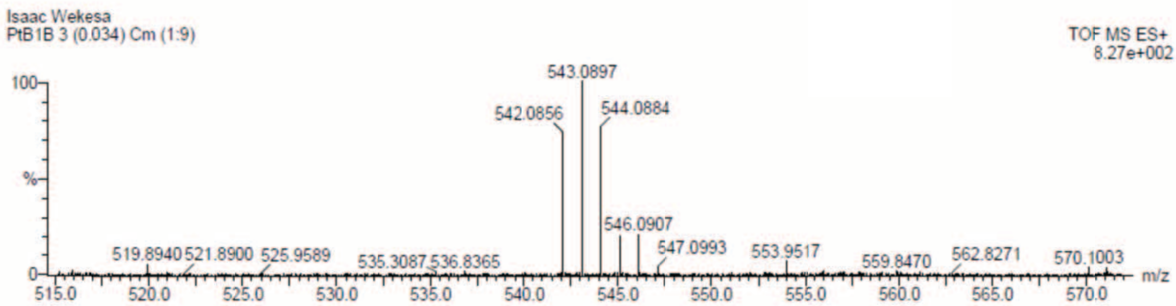
Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
529.0510	529.0507	0.3	0.6	15.5	105.0	0.0	C18 H13 N5 Cl Pt

Figure SI 4 Mass spectrum of 1,3-Bis(2-pyridylimino)isoindoline platinum(II) chloride

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
13 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 20-25 H: 10-15 N: 0-5 Pt: 0-2



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
543.0897	543.0897	0.0	0.0	19.5	153.4	0.0	C22 H14 N5 Pt

Figure SI 5 Mass spectrum of 1,3-Bis(2-pyridylimino)benz(f)isoindoline platinum(II) chloride

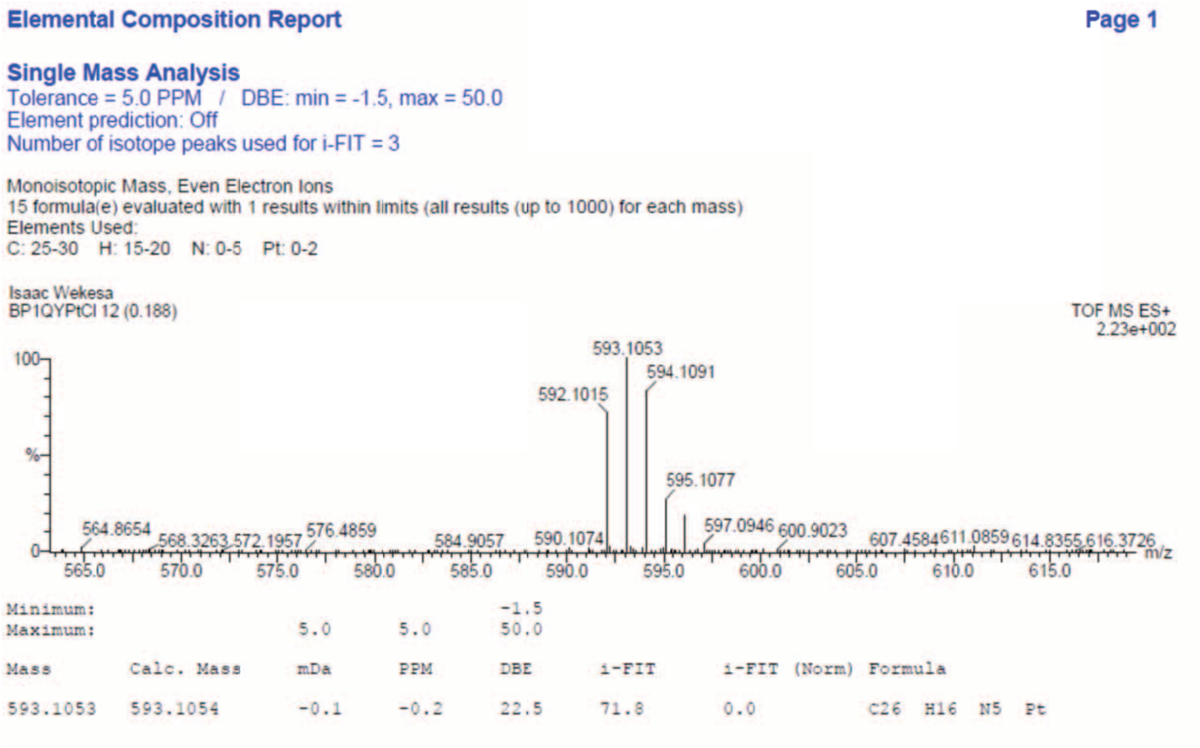


Figure SI 6 Mass spectrum of 1,3-Bis(1-isoquinolylimino))isoindoline platinum(II) chloride

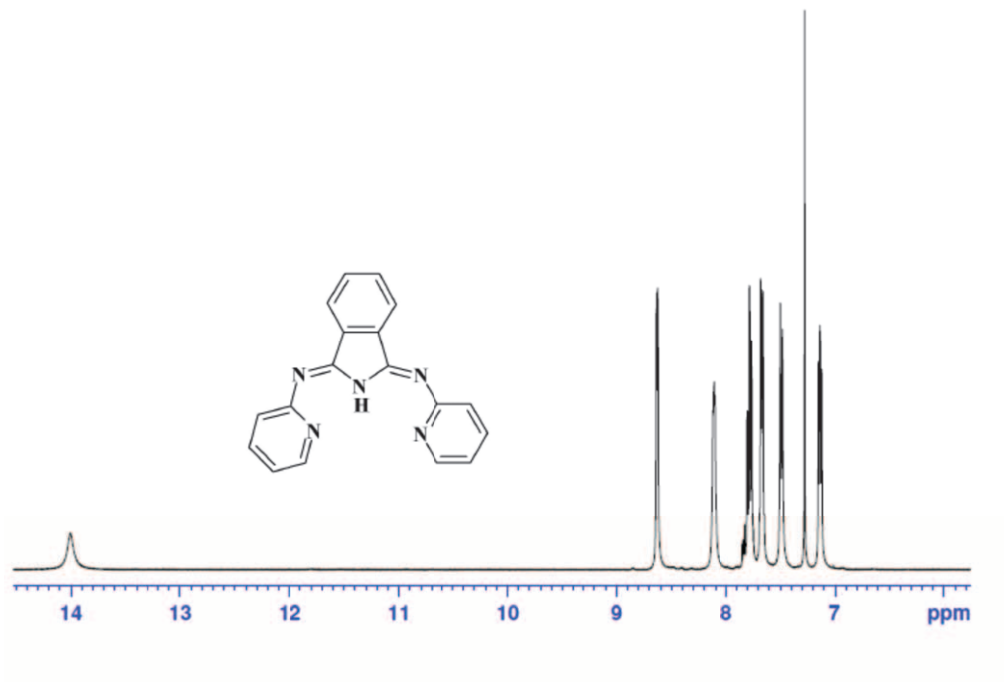


Figure SI 7 ^{1}H NMR spectrum of 1,3-Bis(2-pyridylimino)isoindoline

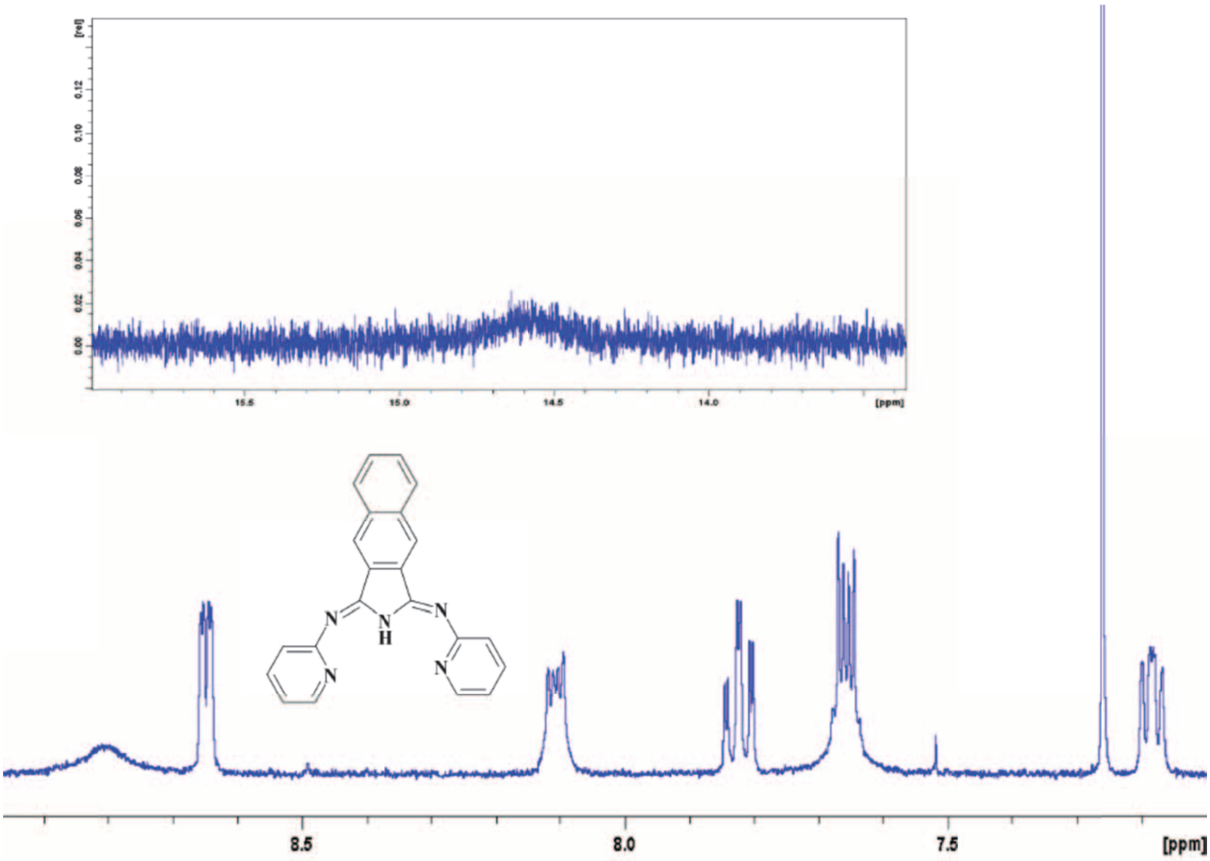


Figure SI 8 ^{1}H NMR spectrum of 1,3-Bis(2-pyridylimino)benz(f)isoindoline

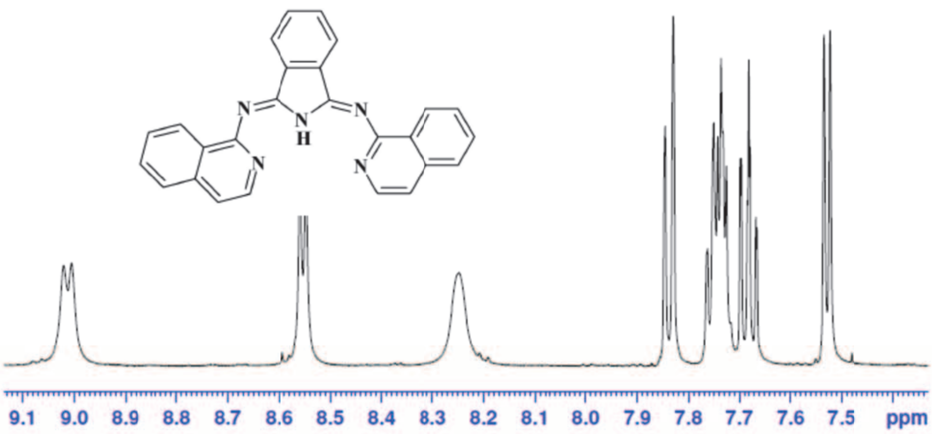


Figure SI 9 ^{1}H NMR spectrum of 1,3-Bis(1-isoquinolylimino))isoindoline

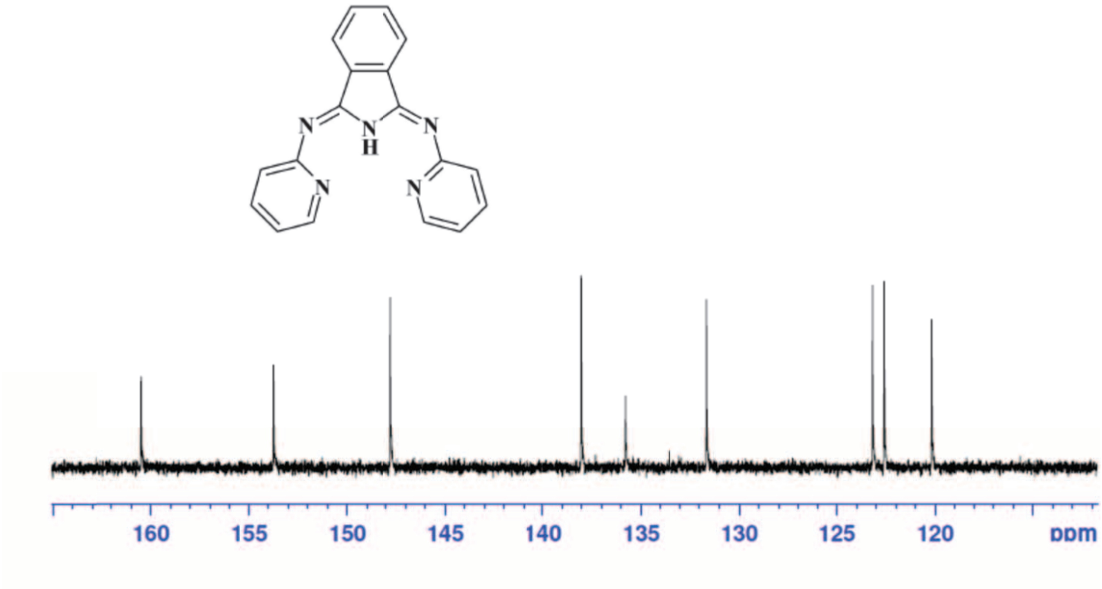


Figure SI 10 ^{13}C NMR spectrum of 1,3-Bis(2-pyridylimino)isoindoline

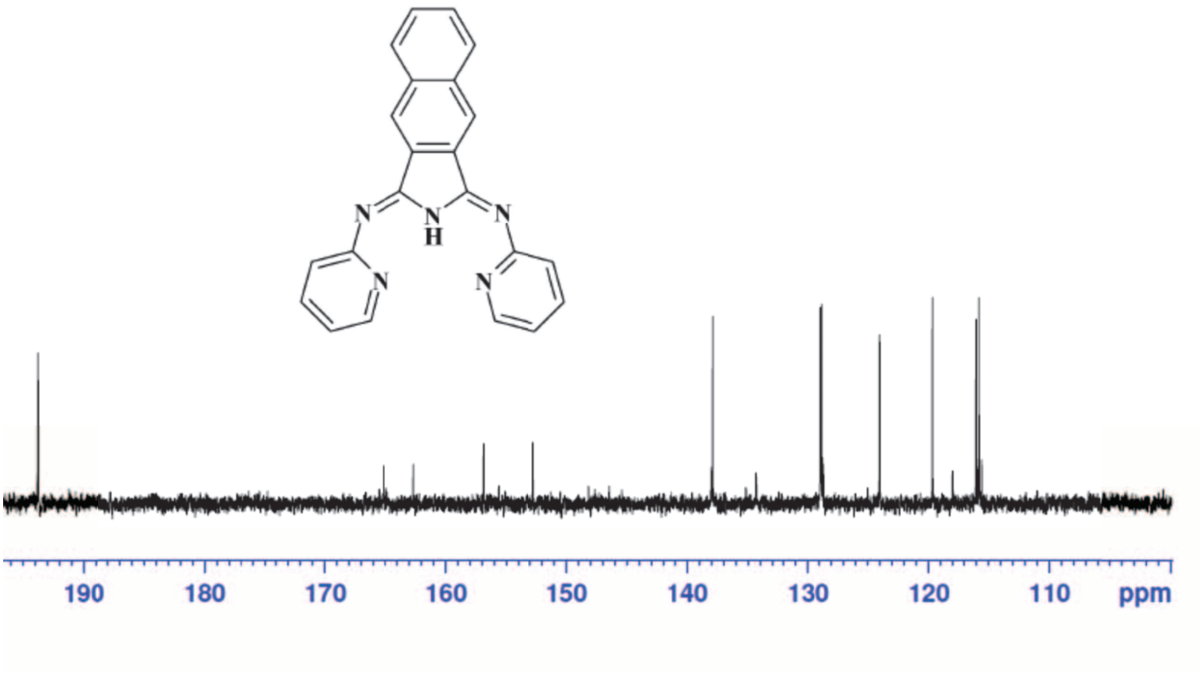


Figure SI 11 ^{13}C NMR spectrum of 1,3-Bis(2-pyridylimino)benz(f)isoindoline

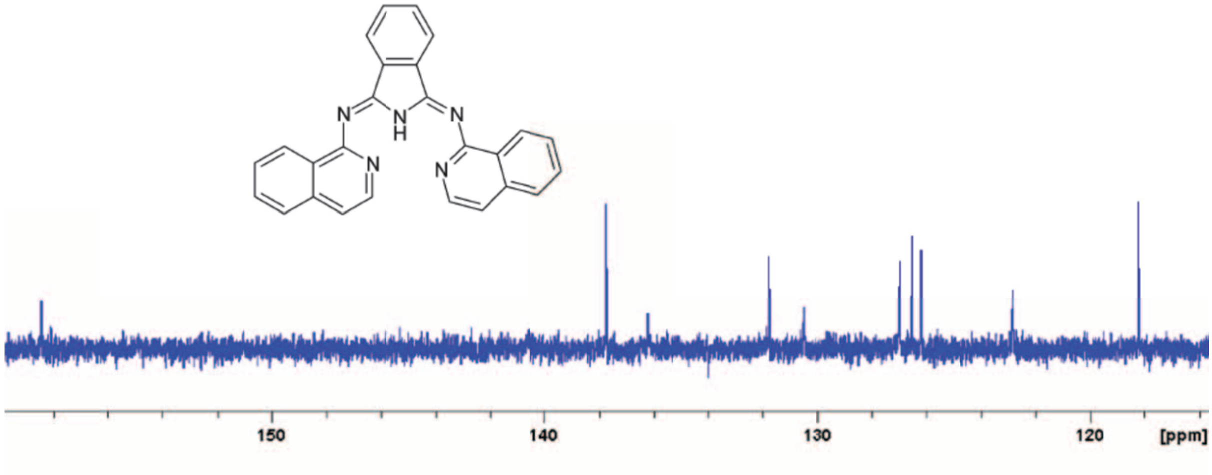


Figure SI 12 ^{13}C NMR spectrum of 1,3-Bis(1-isoquinolylimino))isoindoline

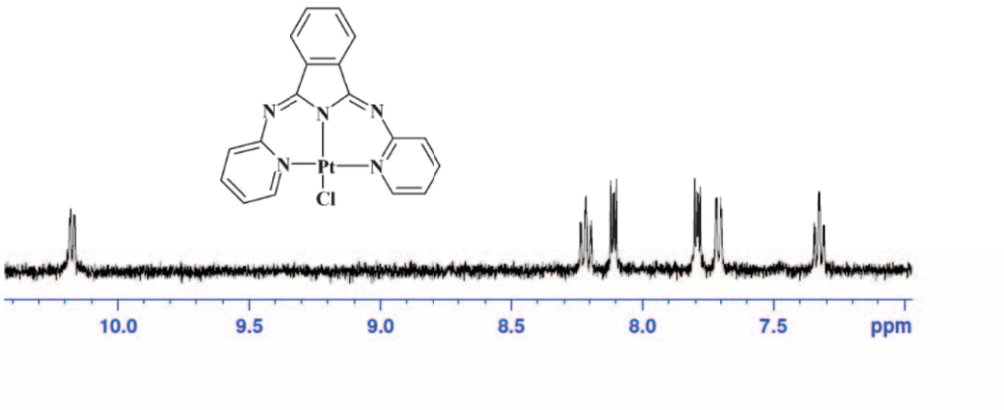


Figure SI 13 ^{1}H NMR spectrum of 1,3-Bis(2-pyridylimino)isoindoline platinum(II) chloride

Table SI 1: Summary of the wavelengths (nm) used for monitoring the reactions between Pt(II) complexes with neutral S-donor nucleophiles.

Complex	Nucleophiles	Wavelength, λ (nm)
Pt2	**Tu**	**443**
	Dmtu	**504**
	Tmtu	**483**
Pt3	**Tu**	**485**
	Dmtu	**434**
	Tmtu	**414**
Pt4	**Tu**	**310**
	Dmtu	**305**
	Tmtu	**369**

Table SI 2: Average observed rate constants, k_{obs}, s^{-1}, for the substitution of chloride from **Pt2** by thiourea nucleophiles, T = 298 K, I = 0.1 M ($NaClO_4$).

Tu (λ = 443 nm)		**Dmtu** (λ = 504nm)		**Tmtu** (λ = 483) nm	
Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}
0.000102	0.0158	0.000102	0.010	0.000102	0.00515
0.000204	0.0307	0.000204	0.016	0.000204	0.01024
0.000306	0.0485	0.000306	0.024	0.000306	0.01520
0.000408	0.0640	0.000408	0.030	0.000408	0.01741
0.000510	0.0785	0.000510	0.039	0.000510	0.02600

Table SI 3: Temperature dependence of k_2, $M^{-1}s^{-1}$, for substitution of chloride from **Pt2** by thiourea nucleophiiles at mid-fold excess [metal complex], T = 298 K, I = 0.1M ($NaClO_4$).

Tu (λ = 443 nm)		**Dmtu** (λ = 504 nm)		**Tmtu** (λ = 483) nm	
(1/T), K^{-1}	ln(k_2/T)	(1/T), K^{-1}	ln(k_2/T)	(1/T), K^{-1}	ln(k_2/T)
0.00341	-8.87	0.00341	-10.02	0.00341	-11.46
0.00335	-8.73	0.00335	-9.42	0.00335	-11.04
0.00330	-8.63	0.00330	-9.11	0.00330	-10.57
0.00324	-8.49	0.00324	-8.72	0.00324	-10.04
0.00319	-8.31	0.00319	-8.35	0.00319	-09.58

Table SI 4: Average observed rate constants, k_{obs}, s^{-1}, for the substitution of chloride from **Pt3** by thiourea nucleophiles, T = 298 K, I = 0.1 M ($NaClO_4$).

Tu (λ = nm)		**Dmtu** (λ = 434nm)		**Tmtu** (λ = nm)	
Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}
0.0020	0.0640	0.0020	0.0129	0.0020	0.0004161
0.0025	0.0770	0.0025	0.0155	0.0025	0.0005165
0.0030	0.0890	0.0030	0.0180	0.0030	0.0005980
0.0035	0.1010	0.0035	0.0220	0.0035	0.0007096
0.0040	0.1230	0.0040	0.0250	0.0040	0.0008330

Table SI 5: Temperature dependence of k_2, $M^{-1}s^{-1}$, for substitution of chloride from **Pt3** by thiourea nucleophiiles at mid-fold excess [metal complex], T = 298 K, I = 0.1M ($NaClO_4$).

Tu (λ = - nm)		**Dmtu** (λ = 434 nm)		**Tmtu** (λ = -) nm	
(1/T), K^{-1}	ln(k_2/T)	(1/T), K^{-1}	ln(k_2/T)	(1/T), K^{-1}	ln(k_2/T)
0.00341	-8.325	0.00341	-10.285	0.00341	-13.65
0.00335	-8.130	0.00335	-9.714	0.00335	-13.40
0.00330	-7.920	0.00330	-9.4026	0.00330	-13.02
0.00324	-7.620	0.00324	-9.111	0.00324	-12.88
0.00319	-7.210	0.00319	-8.847	0.00319	-12.68

Table SI 6: Average observed rate constants, k_{obs}, s^{-1}, for the substitution of chloride from **Pt4** by thiourea nucleophiles, T = 298 K, I = 0.1 M ($NaClO_4$).

Tu (λ = 310 nm)		**Dmtu** (λ = 305 nm)		**Tmtu** (λ = 369) nm	
[Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}	Conc., M	k_{obs}, s^{-1}] X 10^{-4}
1.02	1.075	1.02	0.729	1.02	0.570
2.04	2.190	2.04	1.330	2.06	1.140
3.06	3.030	3.06	2.020	3.06	1.630
4.08	3.870	4.08	2.450	4.08	2.340
5.10	5.300	5.10	3.500	5.10	3.005

Table SI 7: Temperature dependence of k_2, $M^{-1}s^{-1}$, for substitution of chloride from **Pt4** by thiourea nucleophiiles at mid-fold excess [metal complex], T = 298 K, I = 0.1M ($NaClO_4$).

Tu (λ = 310 nm)		**Dmtu** (λ = 305 nm)		**Tmtu** (λ = 369) nm	
(1/T), K^{-1}	ln(k_2/T)	(1/T), K^{-1}	ln(k_2/T)	(1/T), K^{-1}	ln(k_2/T)
0.00341	-14.43	0.00341	-14.70	0.00341	-15.16
0.00335	-14.26	0.00335	-14.50	0.00335	-14.89
0.00330	-13.98	0.00330	-14.26	0.00330	-14.77
0.00324	-13.74	0.00324	-13.93	0.00324	-14.42
0.00319	-13.55	0.00319	-13.66	0.00319	-14.17

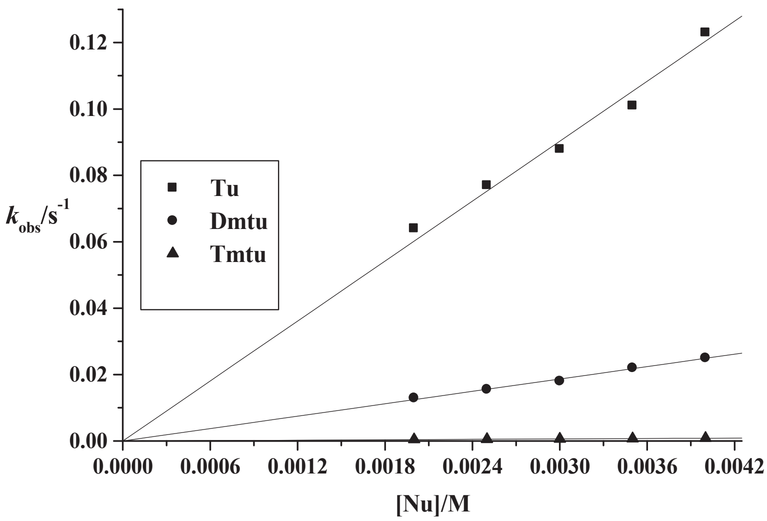


Figure SI 14 Dependence of the pseudo-first-order rate constants (k_{obs}) on the concentration of thiourea nucleophiles for chloride substitution on **Pt3** in ethanol, I=0.1 M ($NaClO_4$), T = 298 K

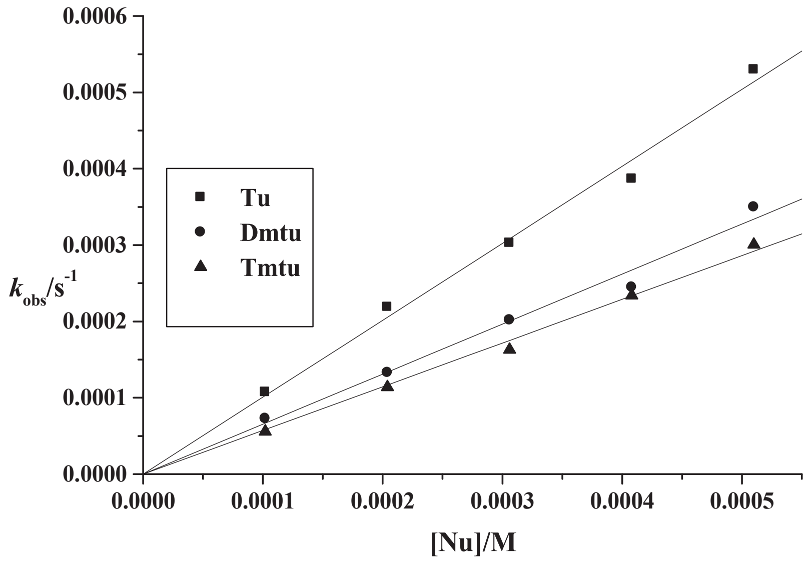


Figure SI 15 Dependence of the pseudo-first-order rate constants (k_{obs}) on the concentration of thiourea nucleophiles for chloride substitution on **Pt4** in ethanol, *I*=0.1 M ($NaClO_4$), T = 298 K

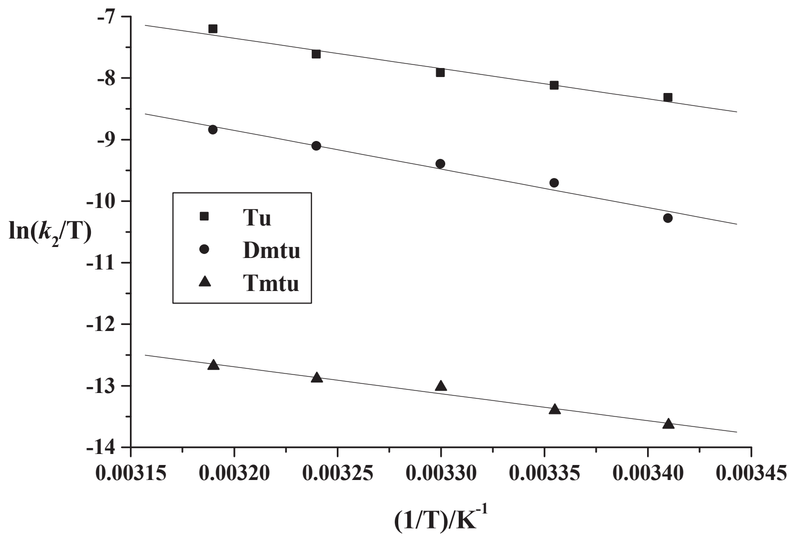


Figure SI 16 Eyring Plots of **Pt3** with thiourea nucleophiles at different temperatures

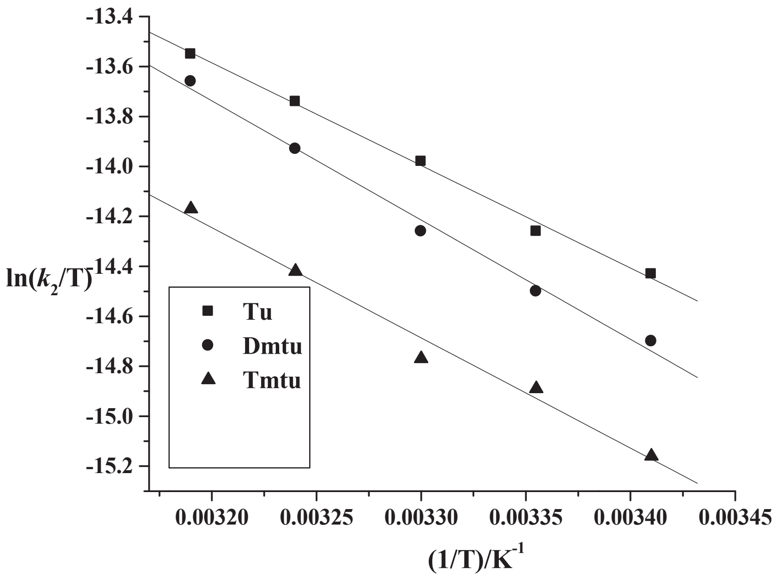


Figure SI 17 Eyring Plots of **Pt4** with thiourea nucleophiles at different temperatures

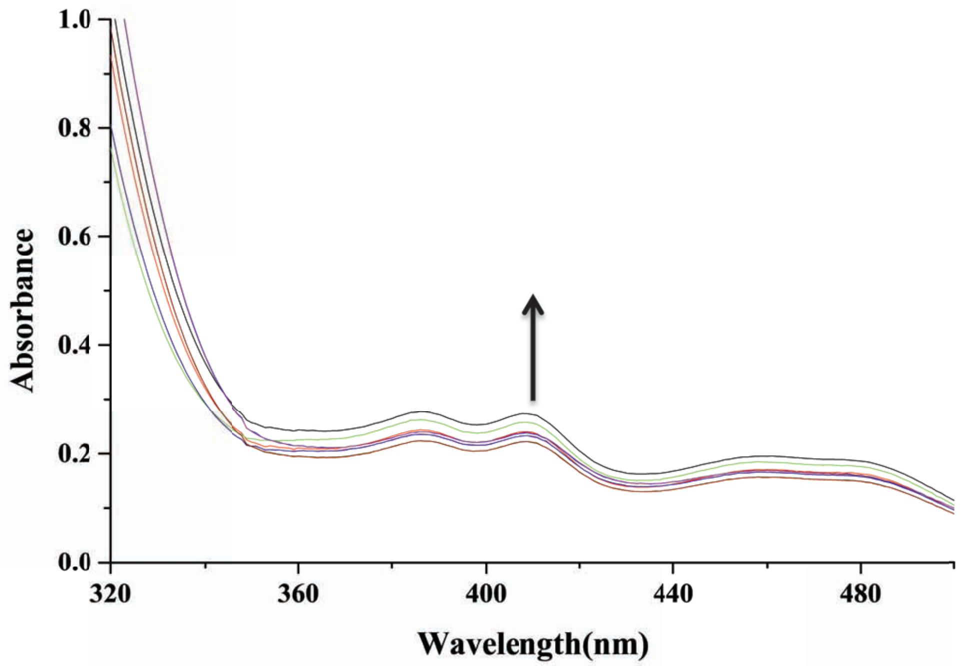


Figure S1 18 UV/Visible overlay kinetic spectra of **Pt3** and **Tmtu** at 298K