Electronic Supplementary Information

Photophysical and Electrochemical Properties of 1,3-bis(2-pyridylimino)isoindolate Platinum(II) Derivatives

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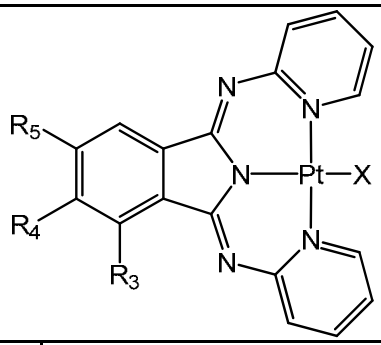
Chart 1



Complex	X	R_3	R_4	R_5
1	Cl	H	H	H
2	F	H	H	H
3	CN	H	H	H
4	$OOCCH_3$	H	H	H
5	Ph	H	H	H
6	$PhNMe_2$	H	H	H
7	Cl	H	t-Bu	H
8	Cl	NO_2	H	H
9	Cl	H	NO_2	H
10	Cl	H	OC_5H_{11}	H
11	Cl	H	I	H
12	Cl	H	Cl	Cl

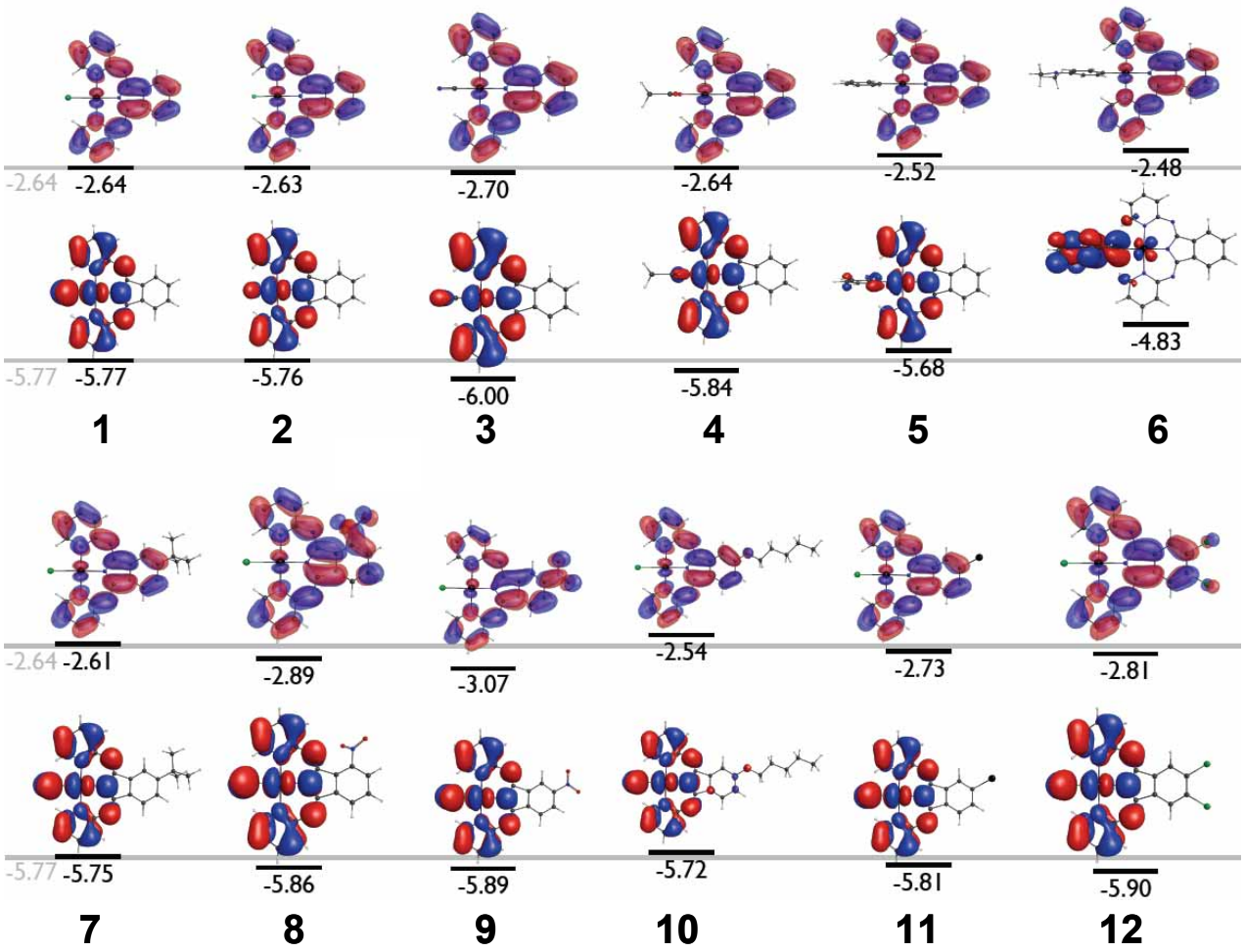


Figure S1. HOMO and LUMO orbitals and energies for complexes **1-12**. The HOMO (solid) and LUMO (transparent) surfaces are displayed as viewed above the π-symmetric orbitals, with opposite phases above and below the plane of the molecule. The gray lines are a reference to the parent complex **1**.

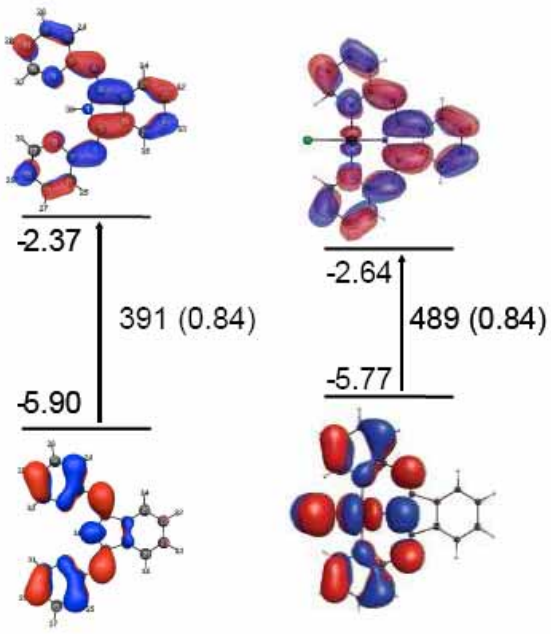


Figure S2. Orbitals, energies and lowest energy vertical excitation of BPI and **1.**

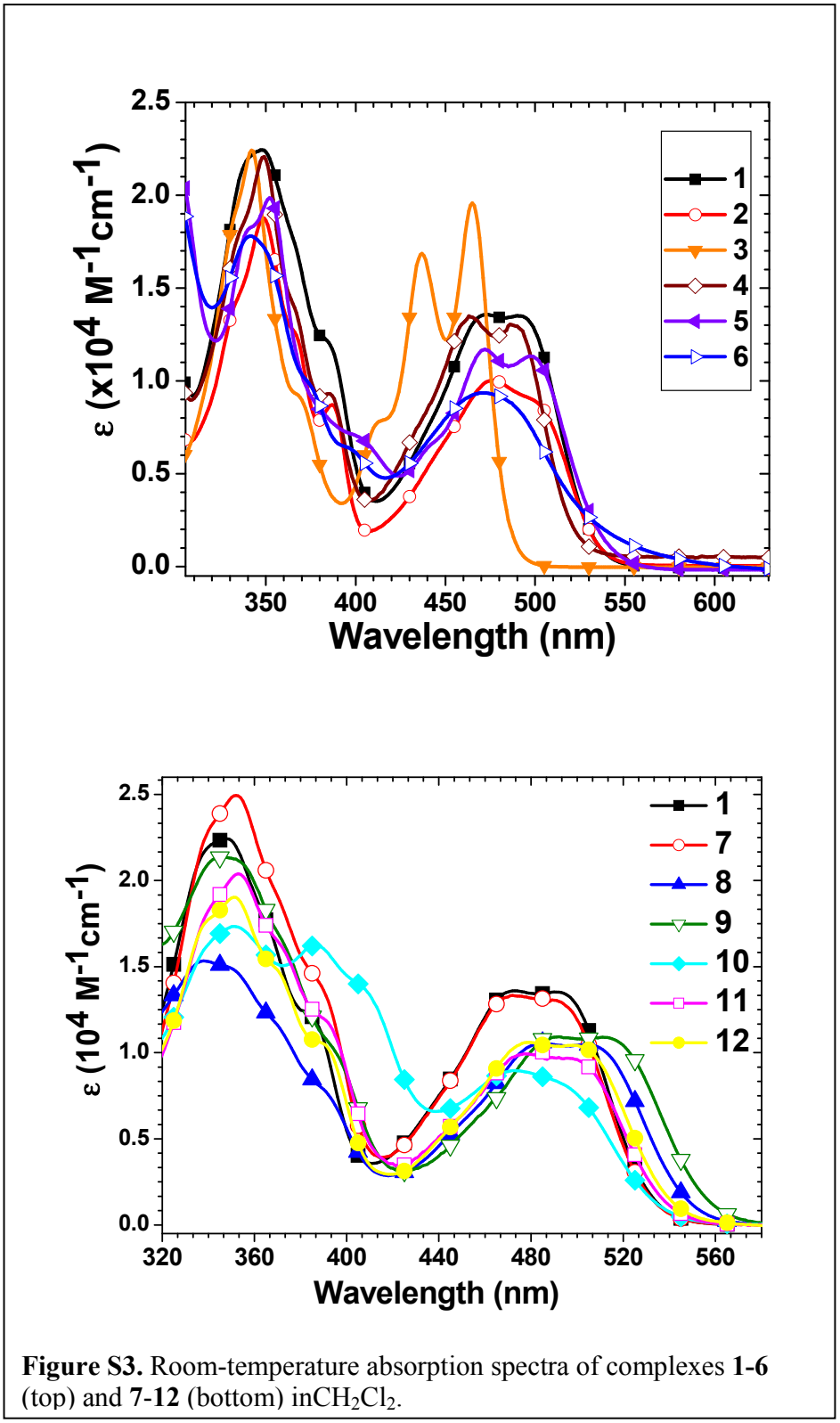


Figure S3. Room-temperature absorption spectra of complexes **1-6** (top) and **7-12** (bottom) inCH_2Cl_2.

Table S1. The relative intensities and the orbitals involved in the 20 lowest energy transitions of **6** found by TDDFT**.**

Transition	Energy (nm)	Dominent Contributor (square of the amplitude)	Relative intensity
1	661	HOMO → LUMO (1.00)	7.31E-04
2	476	HOMO-1 → LUMO (0.81)	0.23364
3	431	HOMO-2 → LUMO (0.99)	2.10E-05
4	419	HOMO → LUMO+1 (0.99)	4.50E-04
5	374	HOMO → LUMO+2 (0.53) HOMO-4 → LUMO (0.39)	0.10901
6	372	HOMO-4 → LUMO (0.45) HOMO → LUMO+2 (0.45)	0.17091
7	371	HOMO-3 → LUMO (0.74)	0.124
8	352	HOMO-5 → LUMO (0.82)	0.00487
9	351	HOMO-7 → LUMO (0.79)	0.00137
10	350	HOMO → LUMO+3 (0.95)	0.00458
11	335	HOMO-1 → LUMO+1 (0.89)	0.05926
12	329	HOMO-6 → LUMO (0.87)	0.29268
13	315	HOMO → LUMO+6 (0.82)	0.00791
14	311	HOMO-8 → LUMO (0.67)	7.22E-04
15	308	HOMO-2 → LUMO+1 (0.98)	9.61E-04
16	306	HOMO-1 → LUMO+2 (0.83)	0.01336
17	305	HOMO-9 → LUMO (0.64)	0.00284
18	300	HOMO → LUMO+4 (0.96)	1.60E-05
19	297	HOMO-10 → LUMO (0.87)	7.68E-04
20	295	HOMO → LUMO+5 (0.77)	0.02447

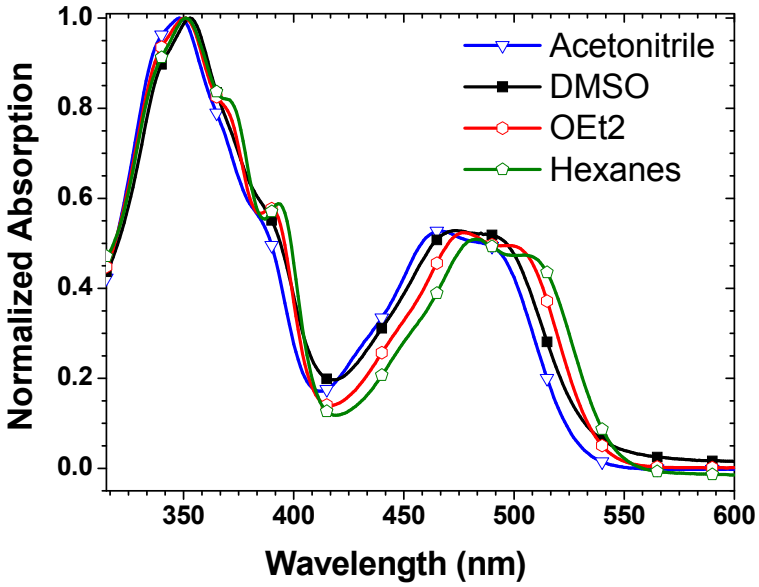


Figure S4. Room-temperature absorption spectra of complex **7** in various solvents.

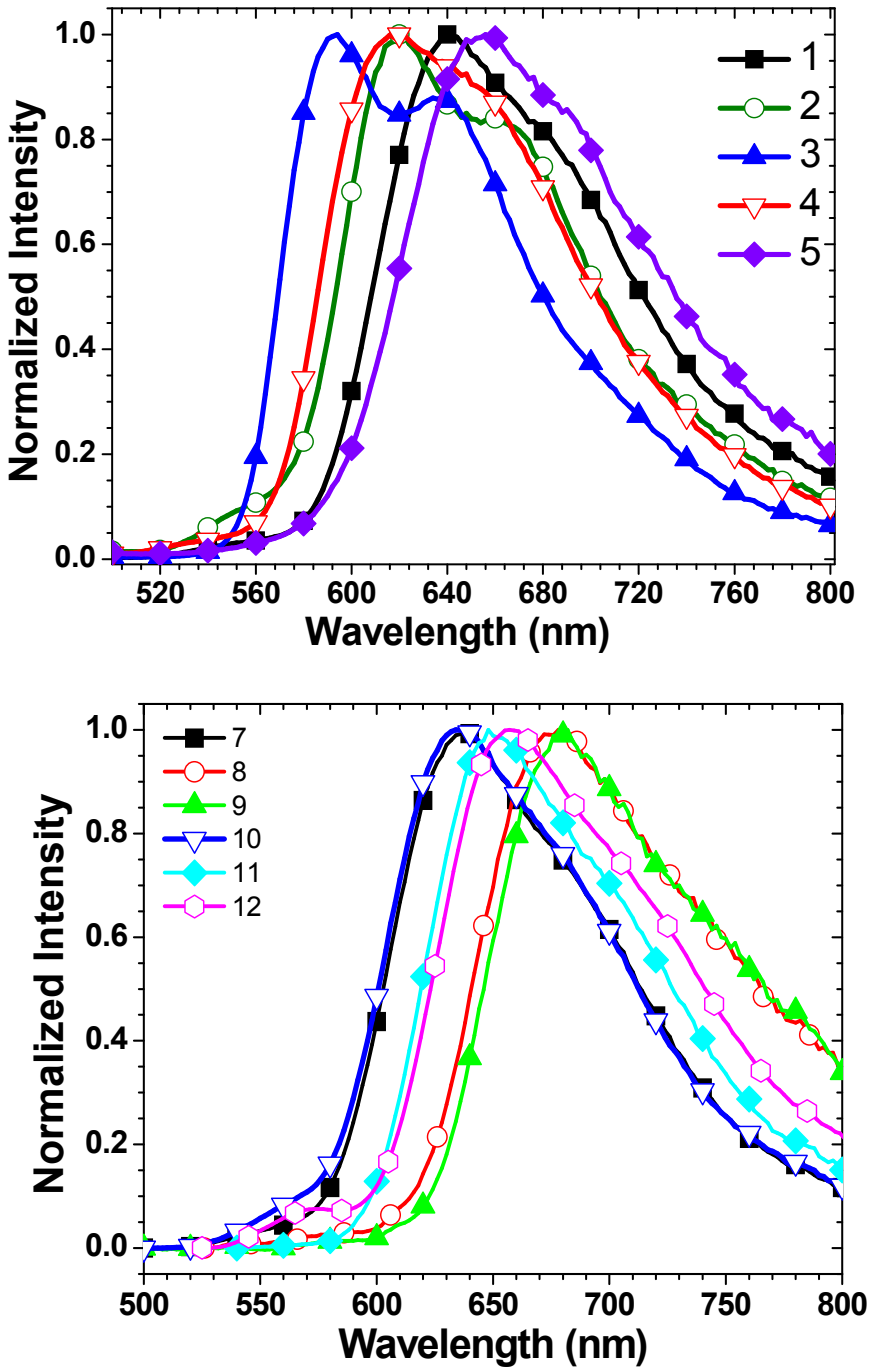


Figure S5. Room-temperature emission spectra of complexes **1-5** (top) and **7-12** (bottom) in CH_2Cl_2.

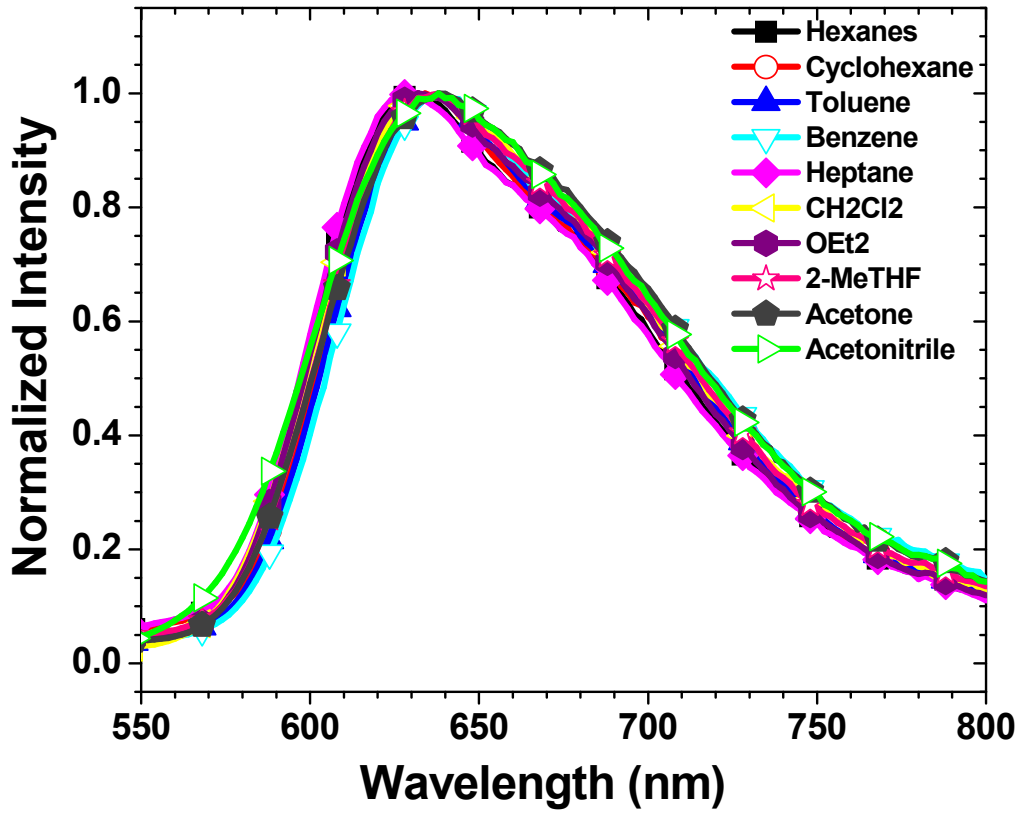


Figure S6. Room-temperature emission spectra of complex **7** in various solvents.

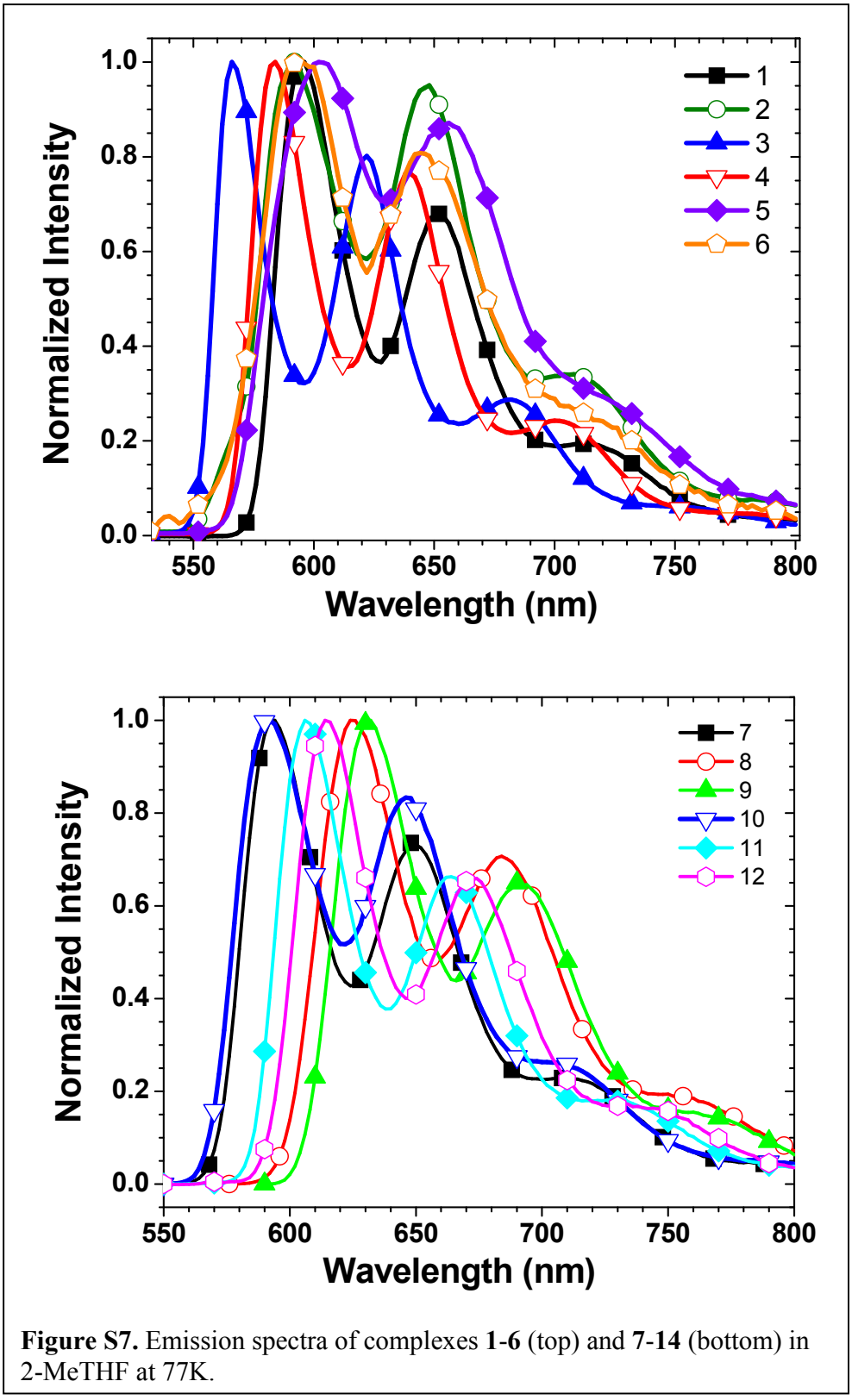


Figure S7. Emission spectra of complexes **1-6** (top) and **7-14** (bottom) in 2-MeTHF at 77K.

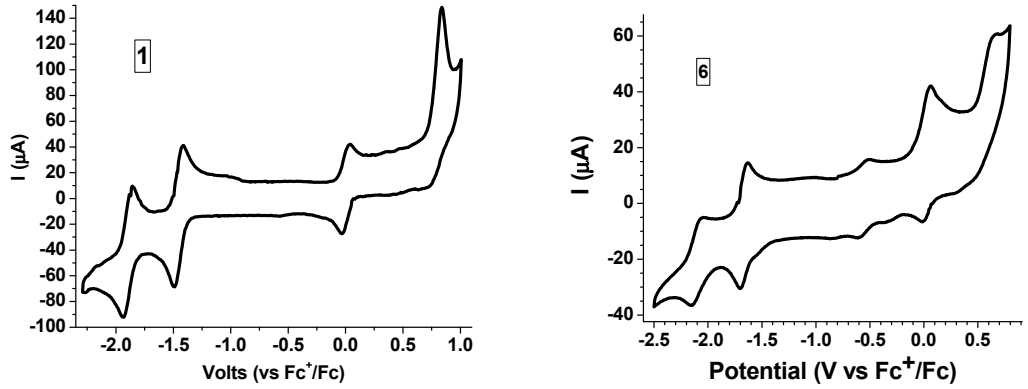


Figure S8. CV traces for **1** and **6** in CH_2Cl_2.

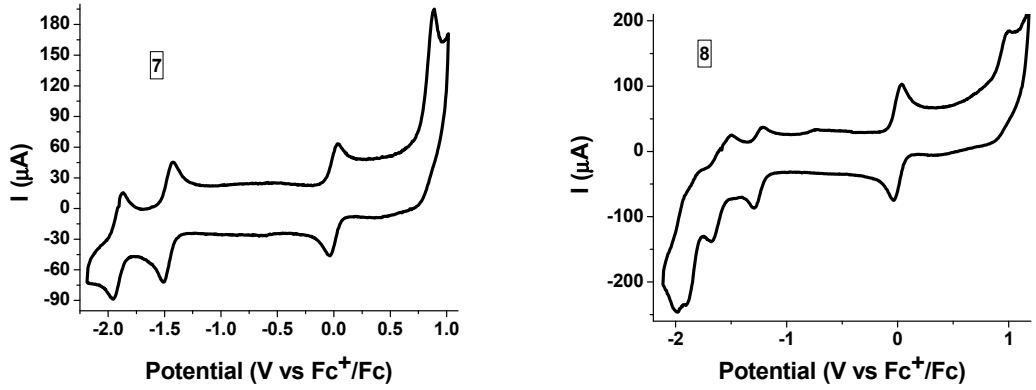


Figure S9. CV traces for **7** and **8** in CH_2Cl_2.

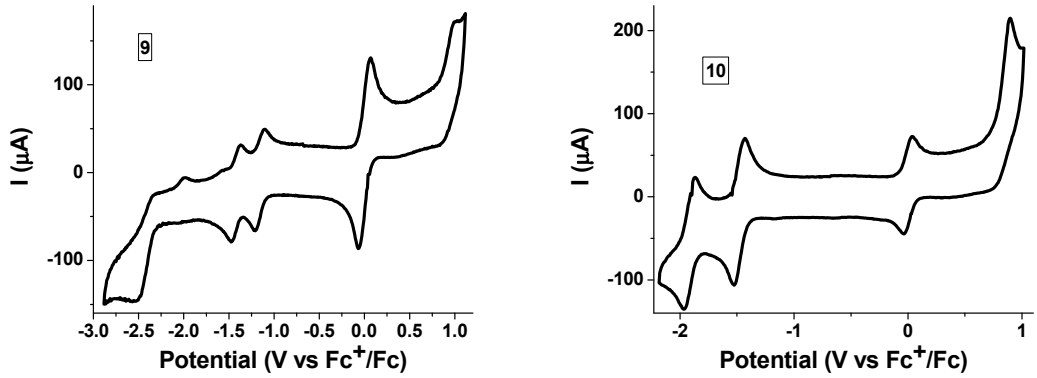


Figure S10. CV traces for **9** and **10** in CH_2Cl_2.

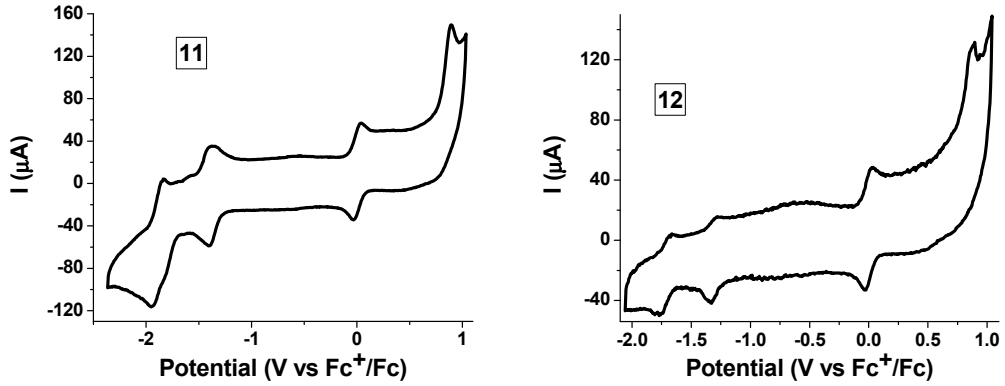


Figure S11. CV traces for **11** and **12** in CH_2Cl_2.

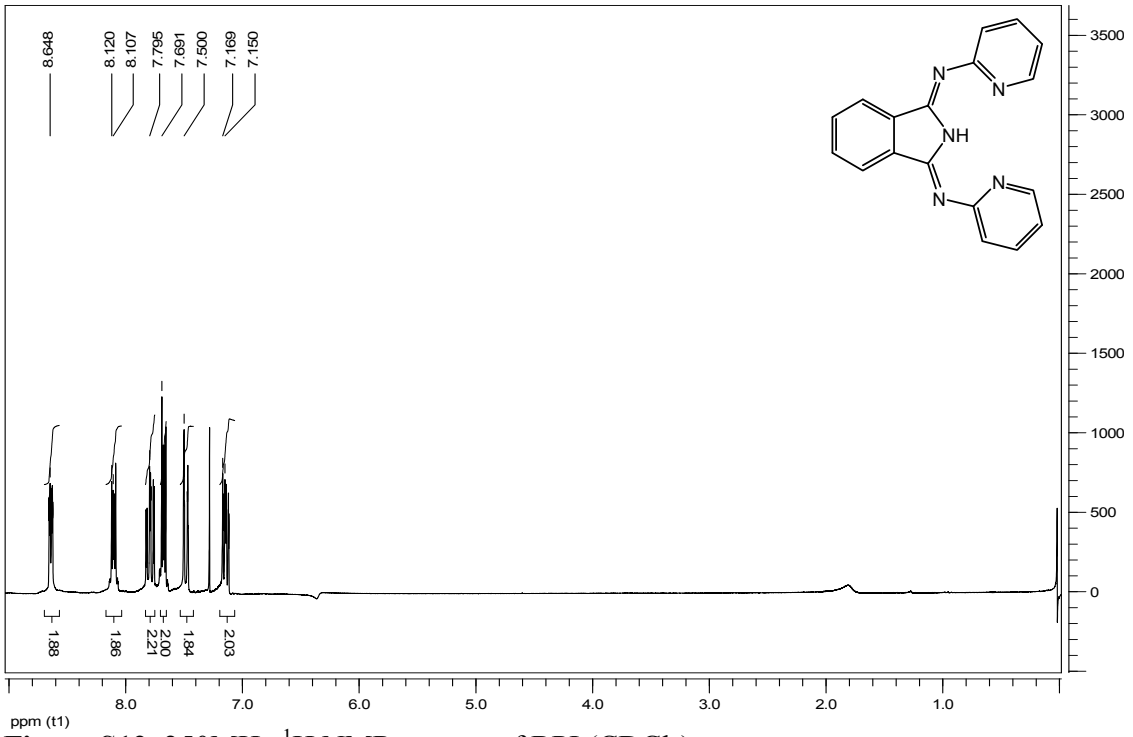


Figure S12. 250MHz ^{1}H NMR spectra of BPI ($CDCl_3$).

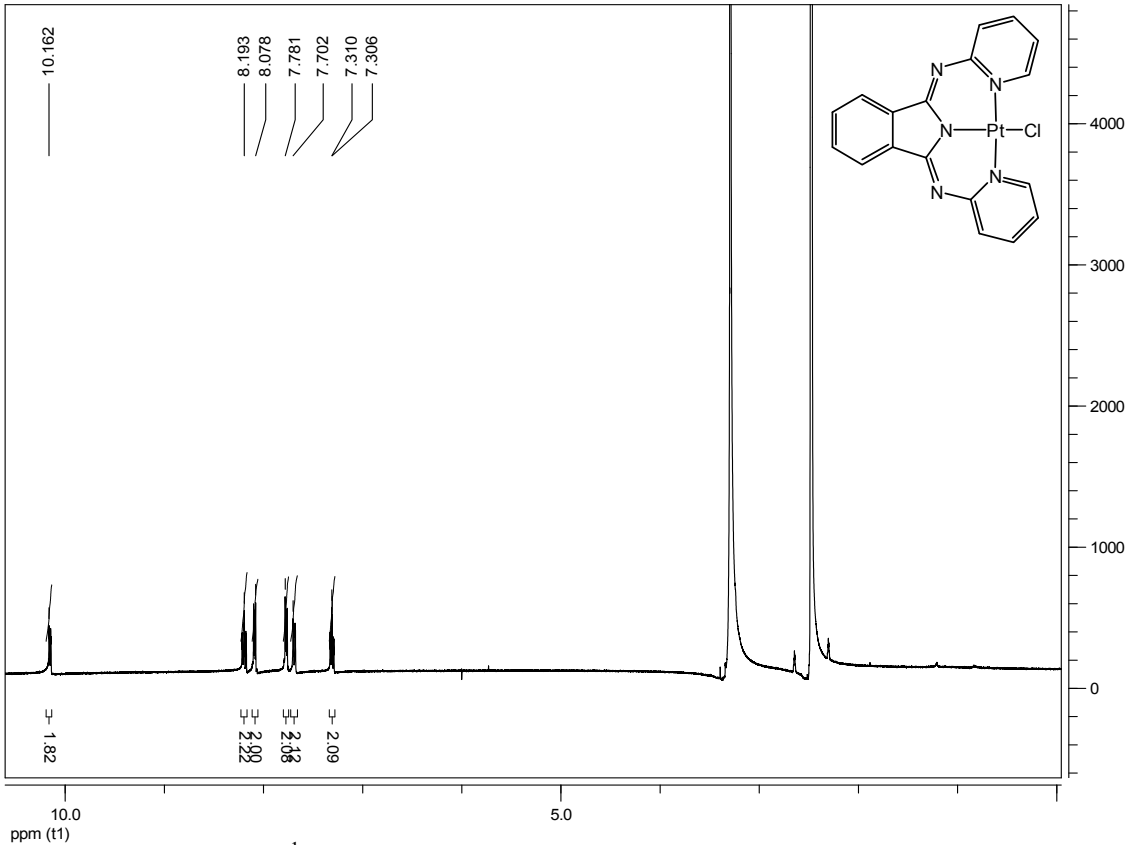


Figure S13. 400 MHz ^{1}H NMR spectra of complex **1** ($CDCl_3$).

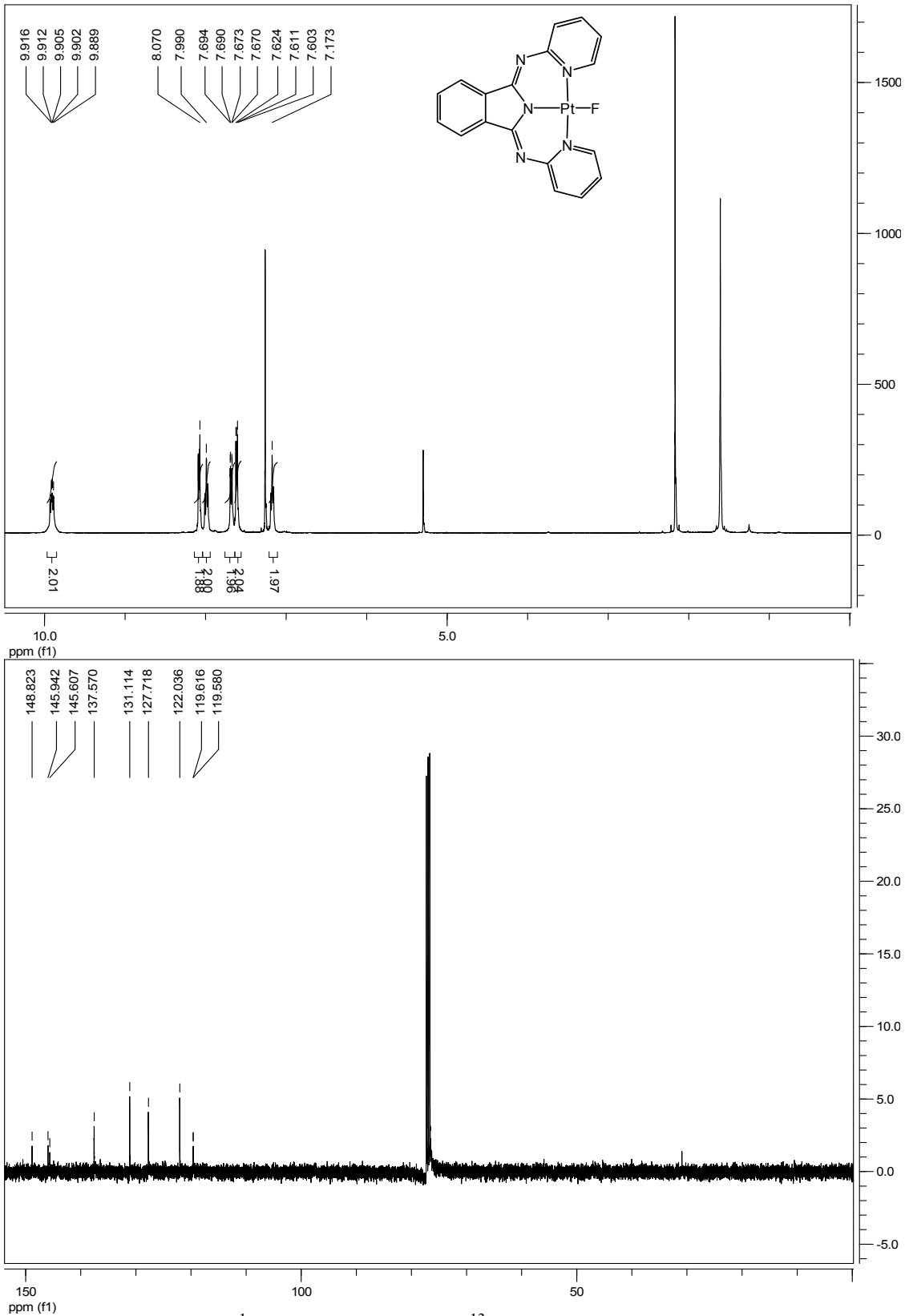


Figure S14. 400 MHz ^{1}H (top) and 100 MHz ^{13}C (bottom) NMR spectra of **2** ($CDCl_3$).

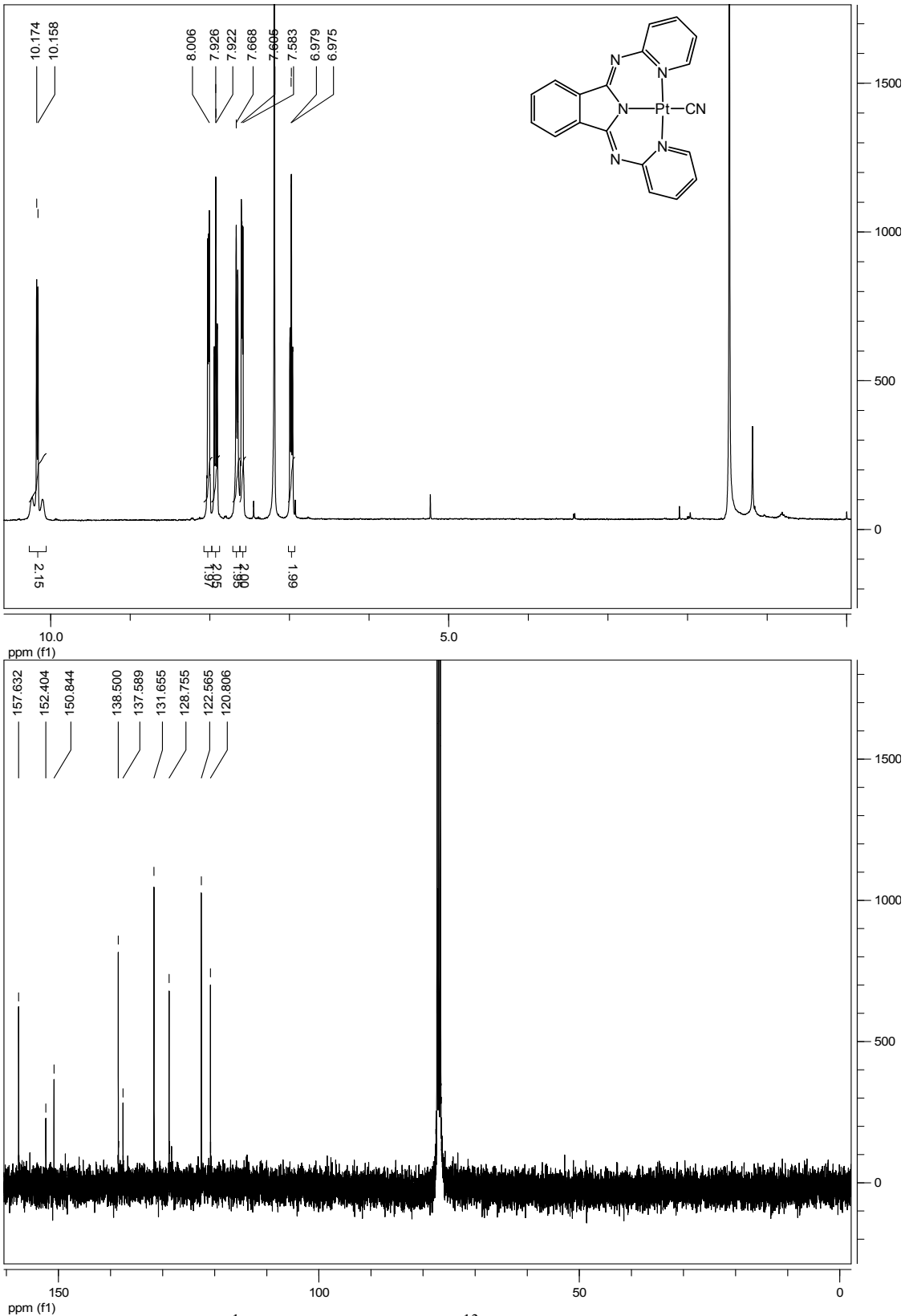


Figure S15. 400 MHz ^{1}H (top) and 100 MHz ^{13}C (bottom) NMR spectra of **3** ($CDCl_3$).

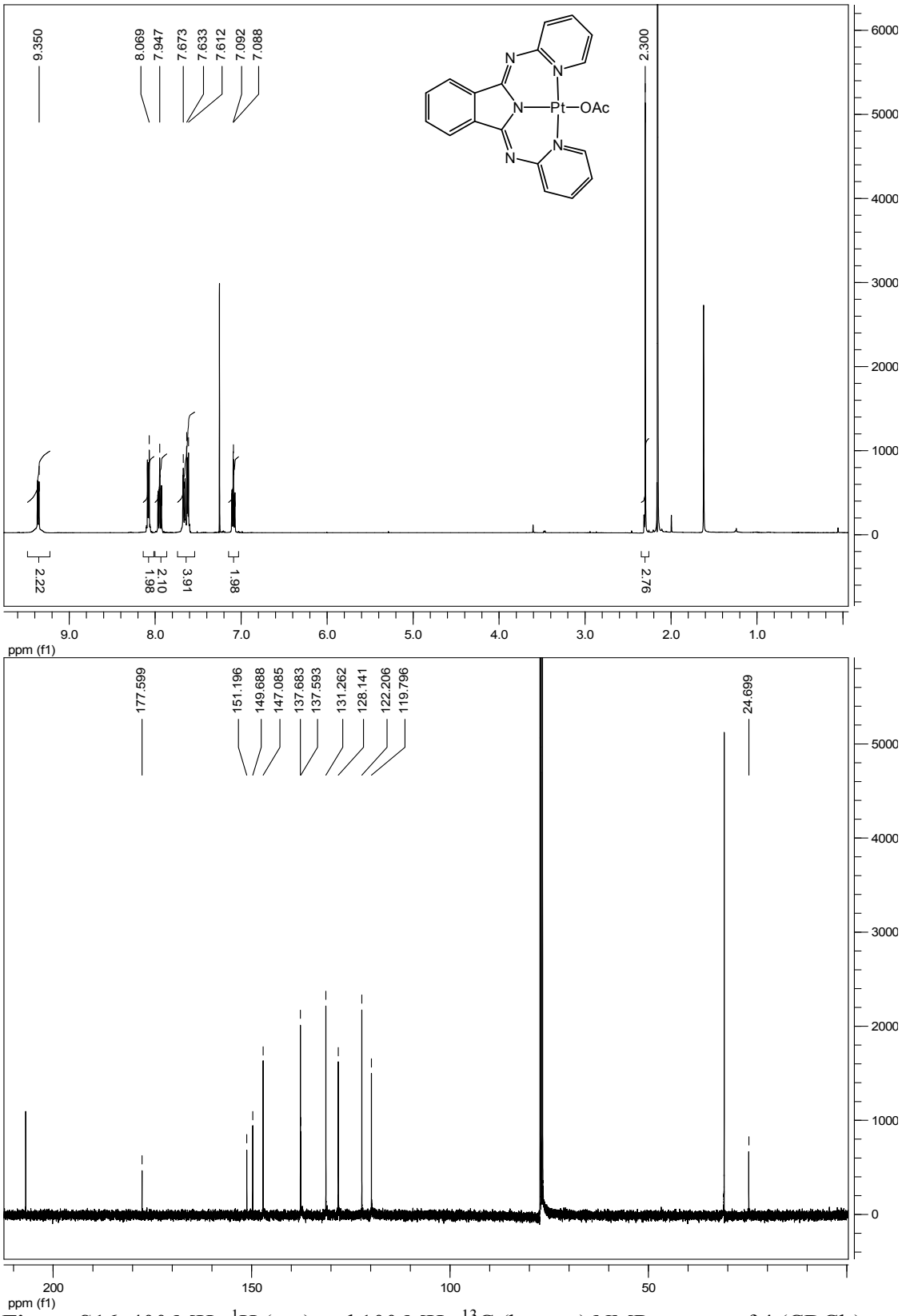


Figure S16. 400 MHz ^{1}H (top) and 100 MHz ^{13}C (bottom) NMR spectra of **4** ($CDCl_3$).

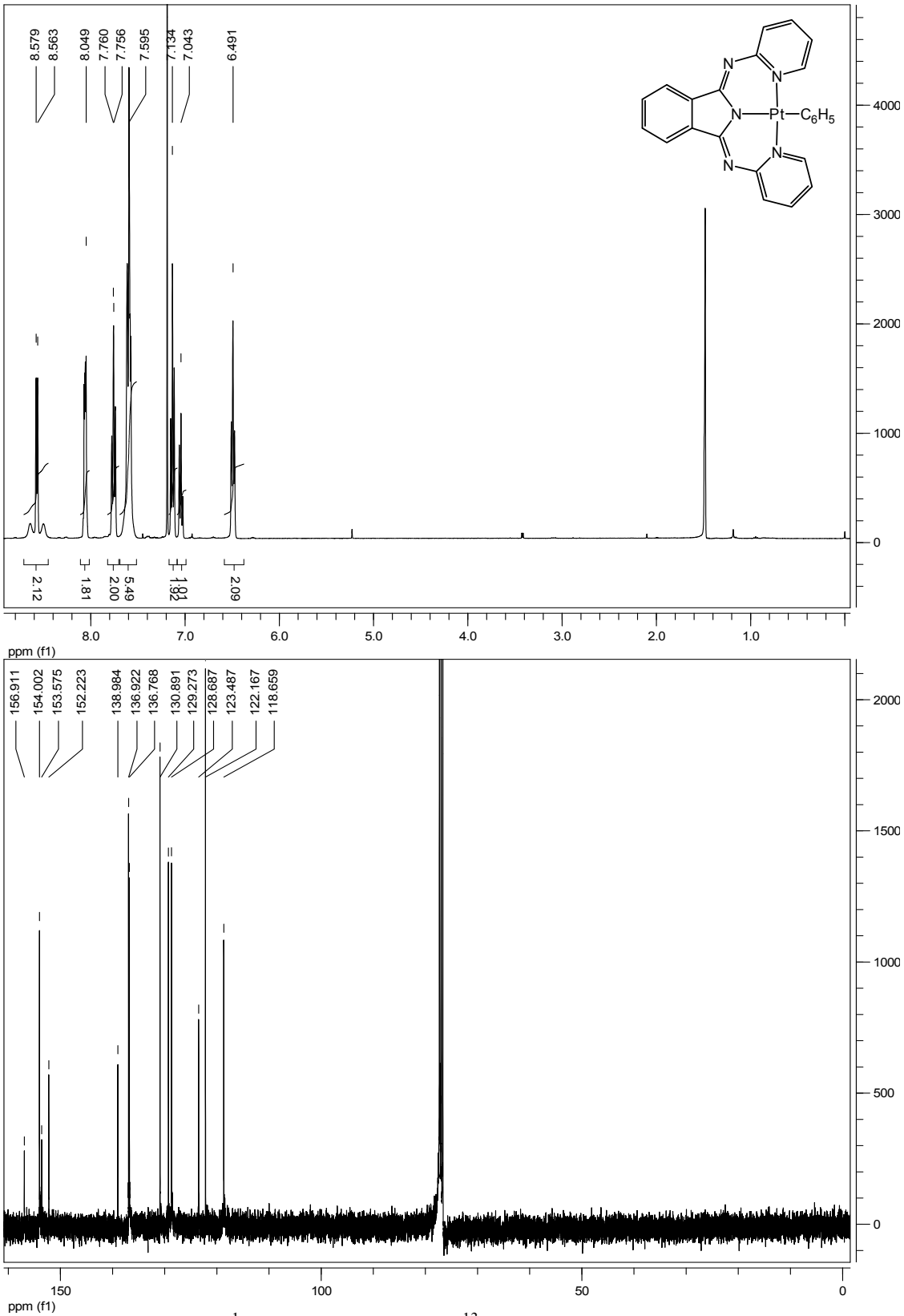


Figure S17. 400 MHz ^{1}H (top) and 100 MHz ^{13}C (bottom) NMR spectra of **5** ($CDCl_3$).

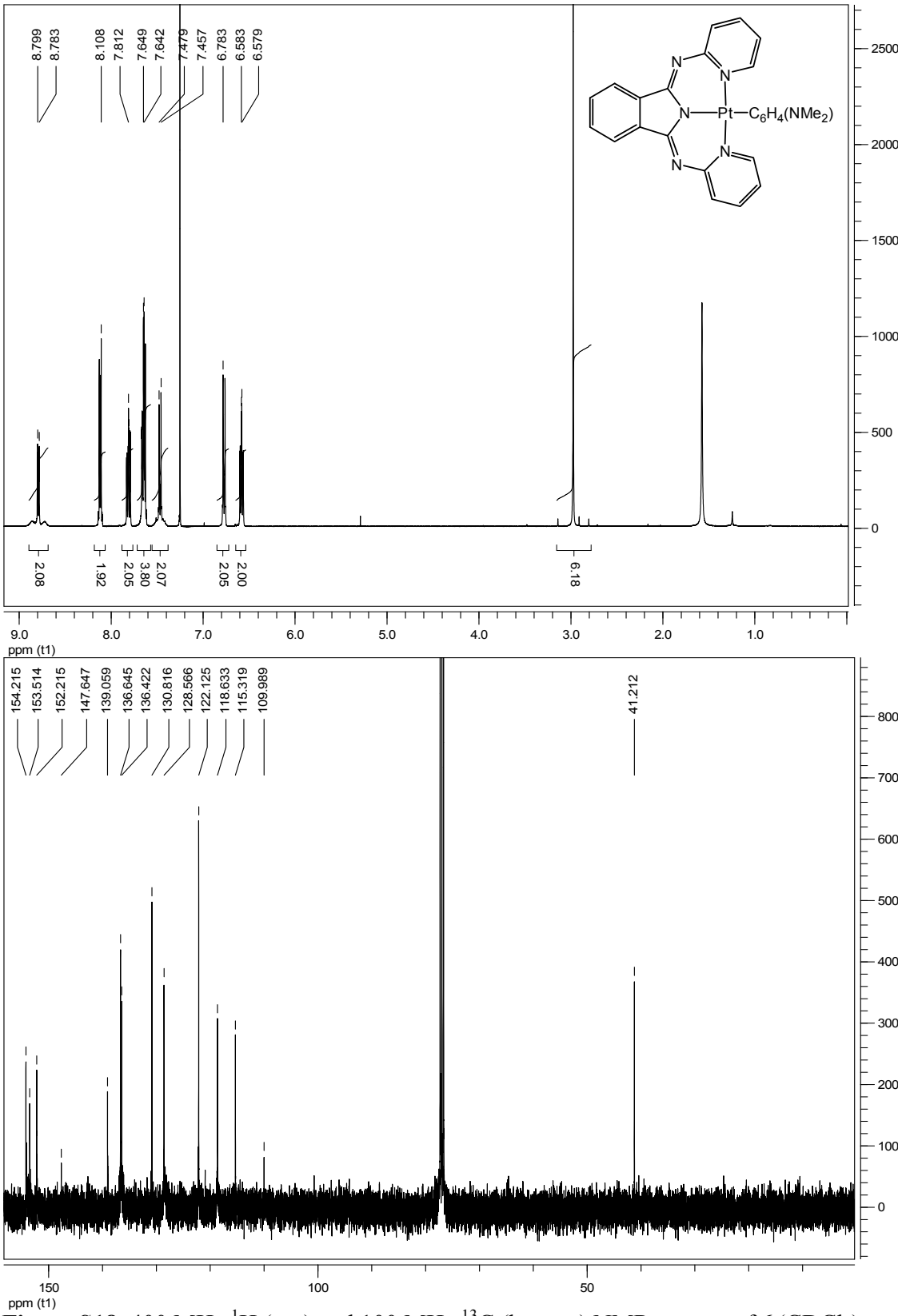


Figure S18. 400 MHz ^{1}H (top) and 100 MHz ^{13}C (bottom) NMR spectra of **6** ($CDCl_3$).

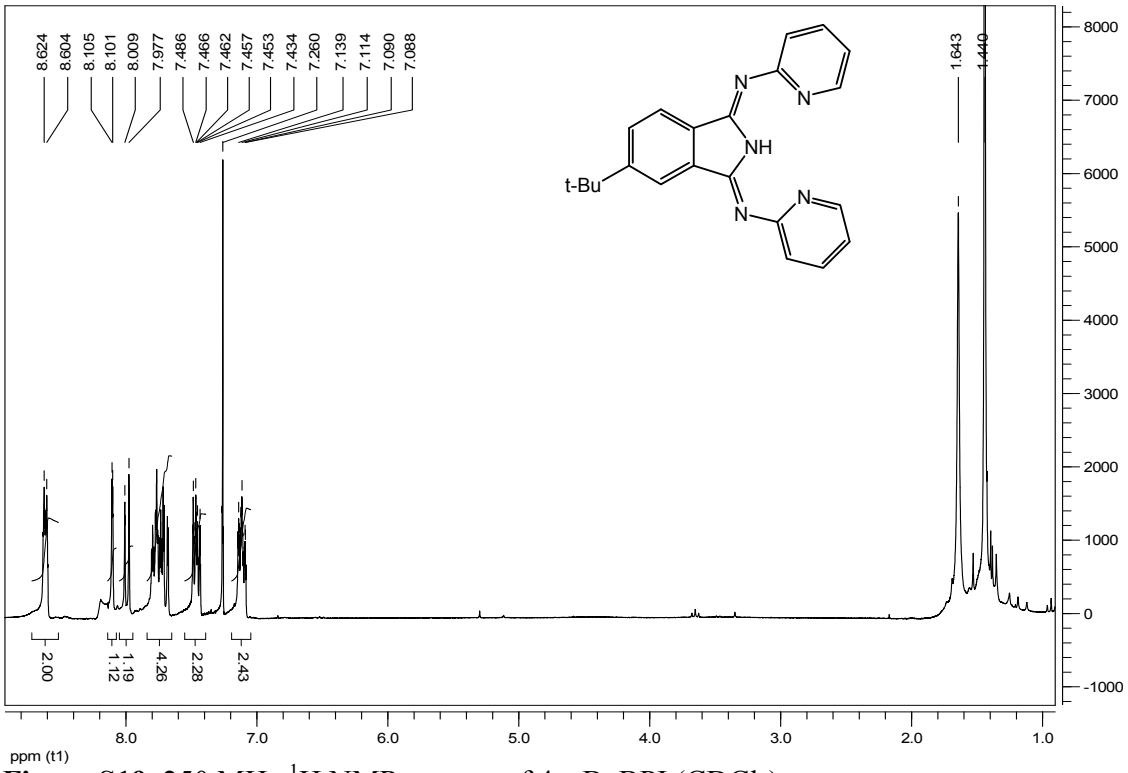


Figure S19. 250 MHz ^{1}H NMR spectra of 4-t-BuBPI ($CDCl_3$).

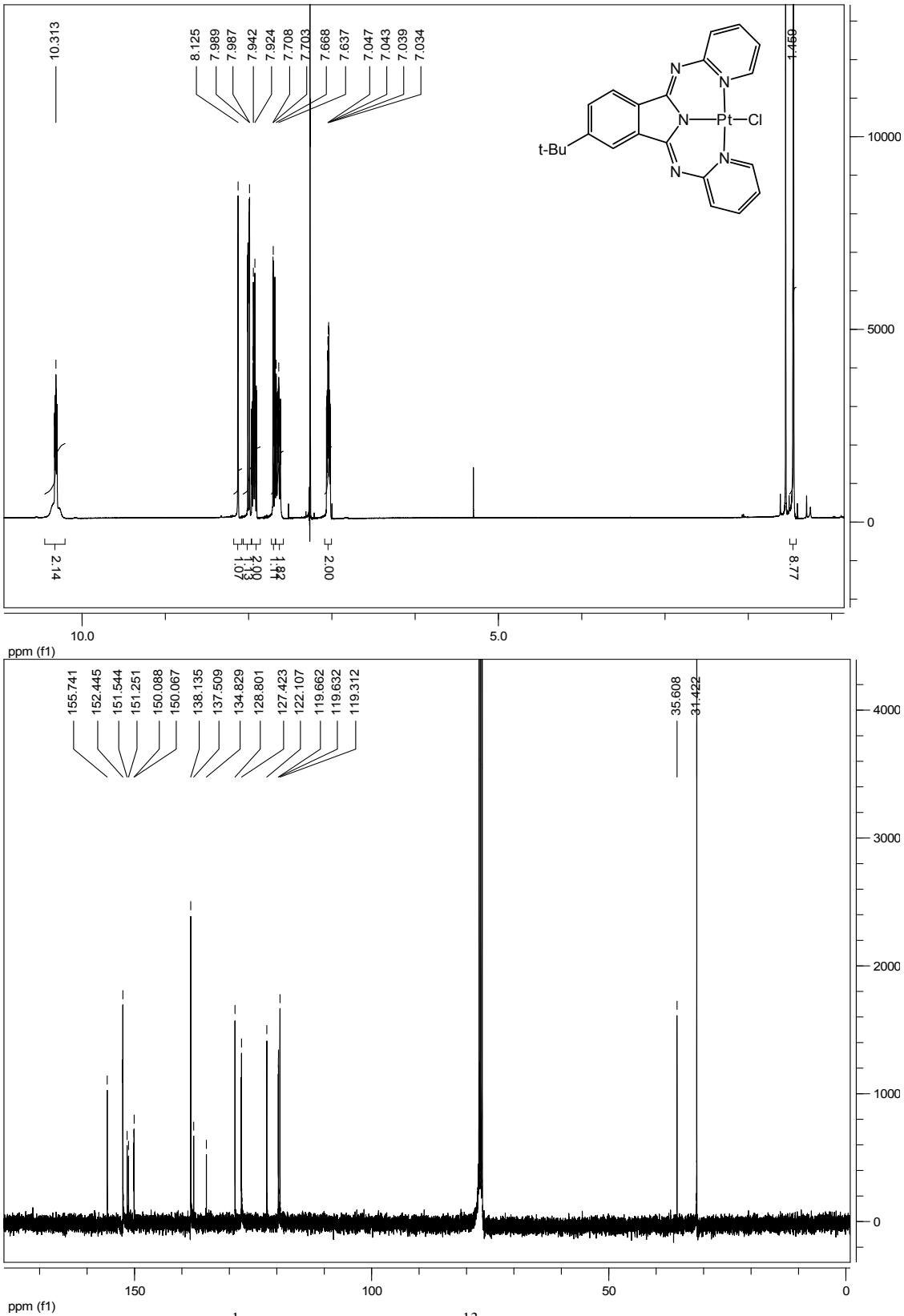


Figure S20. 400 MHz ^{1}H (top) and 100 MHz ^{13}C (bottom) NMR spectra of **7** ($CDCl_3$).

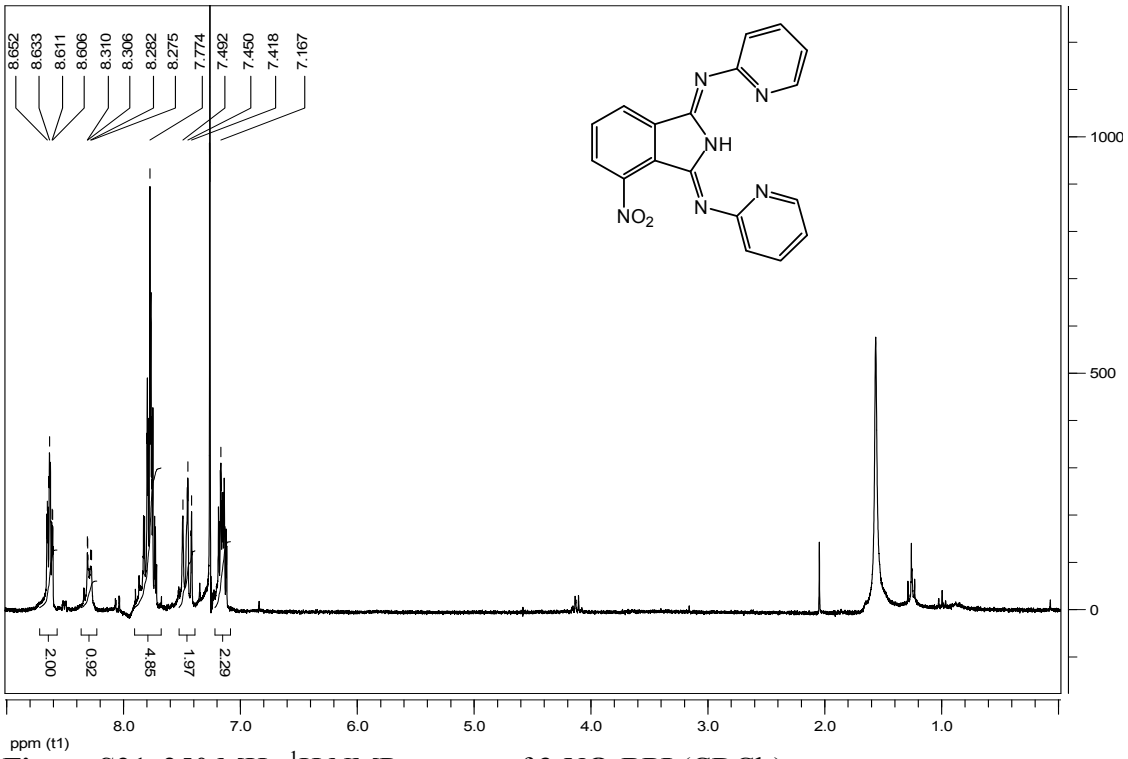


Figure S21. 250 MHz ^{1}H NMR spectra of **3-NO_2BPI** ($CDCl_3$).

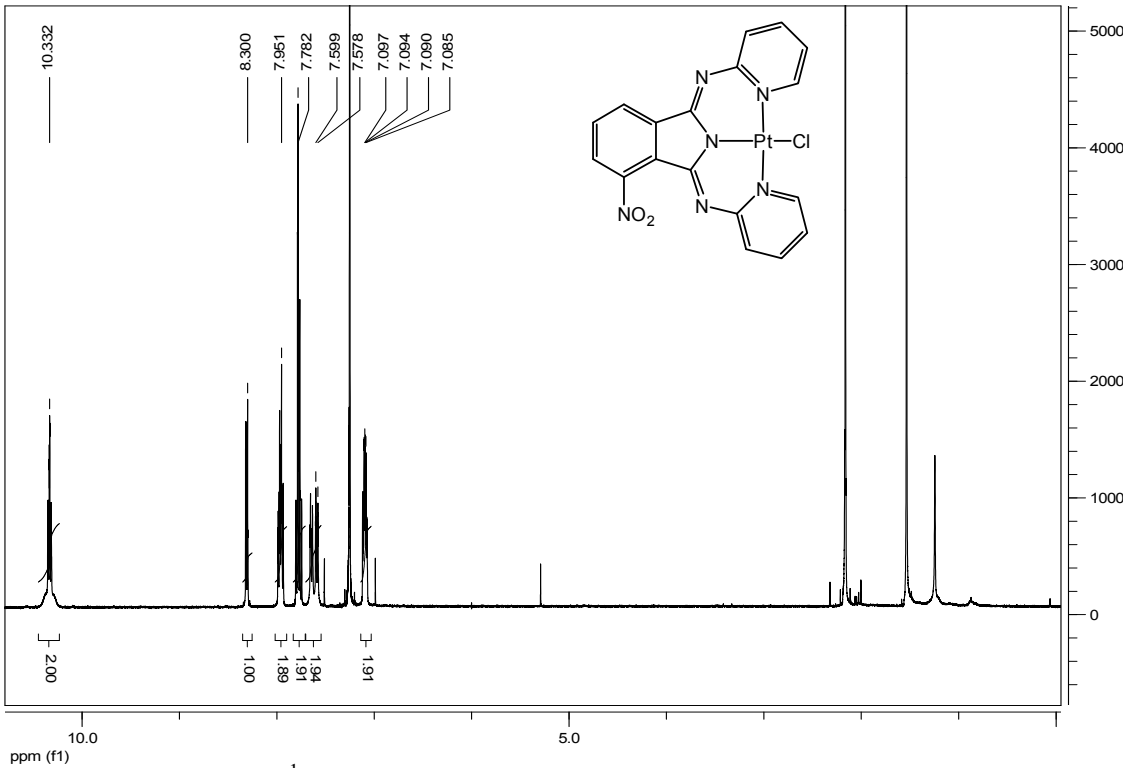


Figure S22. 400 MHz ^{1}H NMR spectra of **8** ($CDCl_3$).

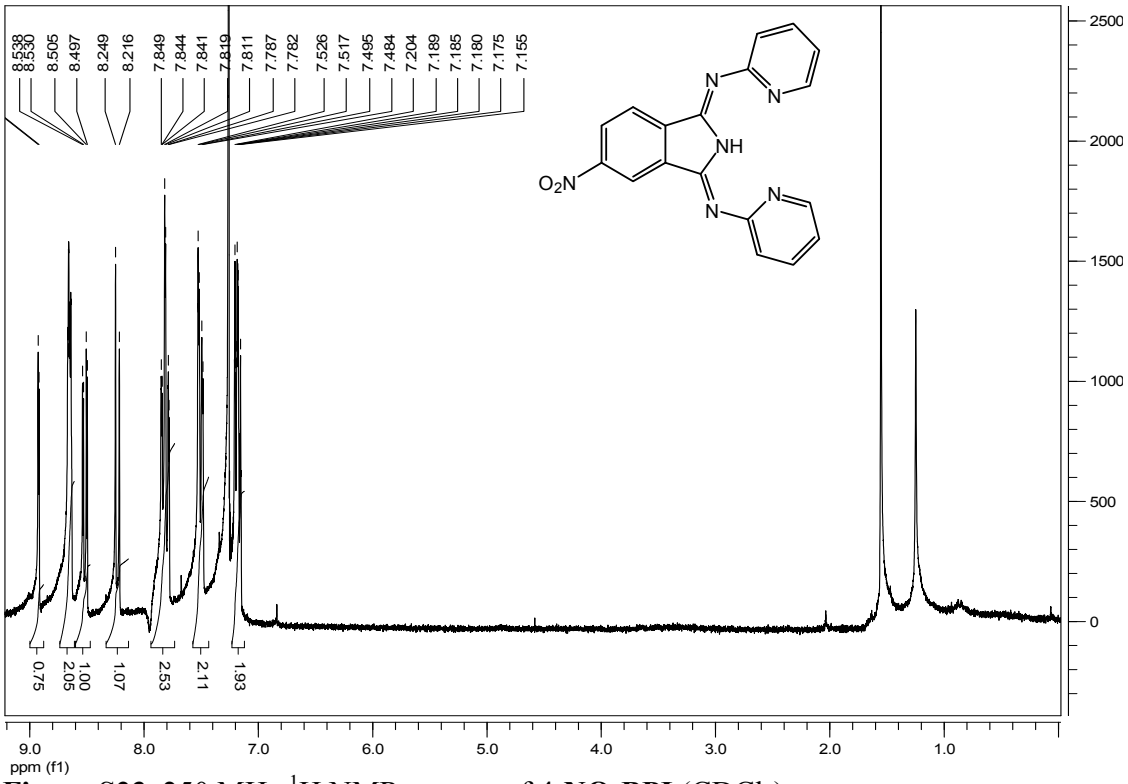


Figure S23. 250 MHz ^{1}H NMR spectra of **4-NO_2BPI** ($CDCl_3$).

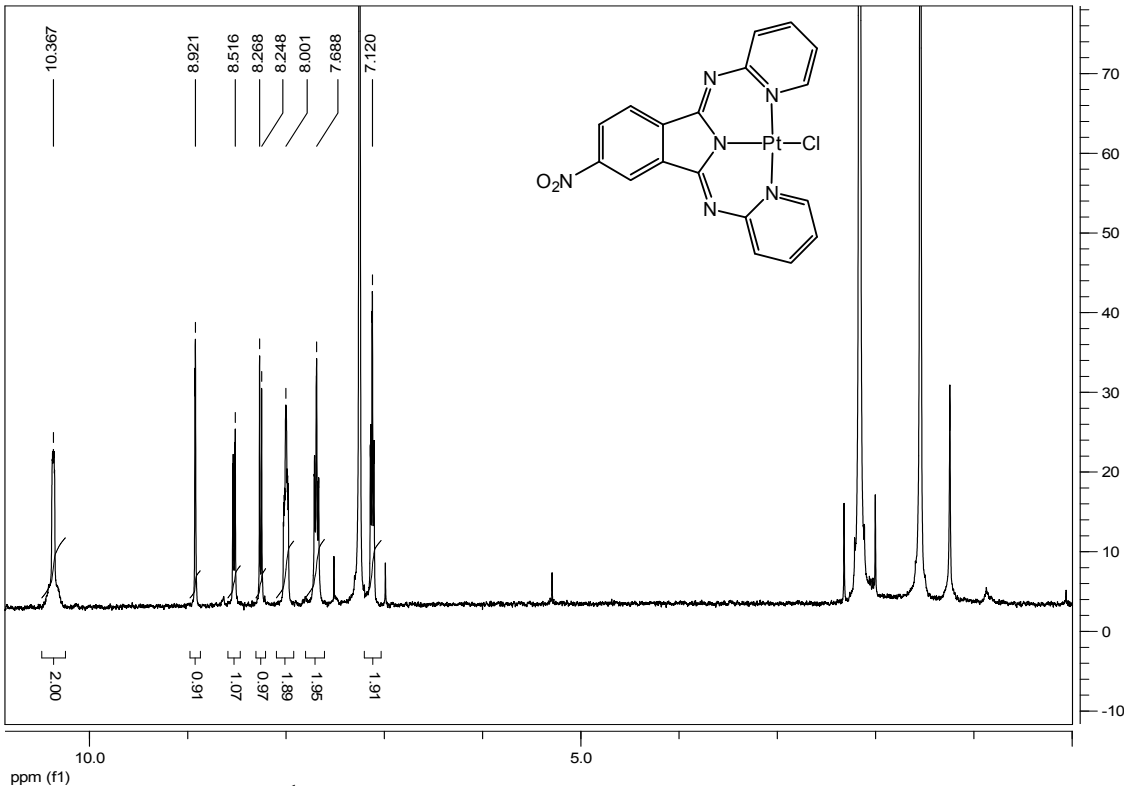


Figure S24. 400 MHz ^{1}H NMR spectra of **9** ($CDCl_3$).

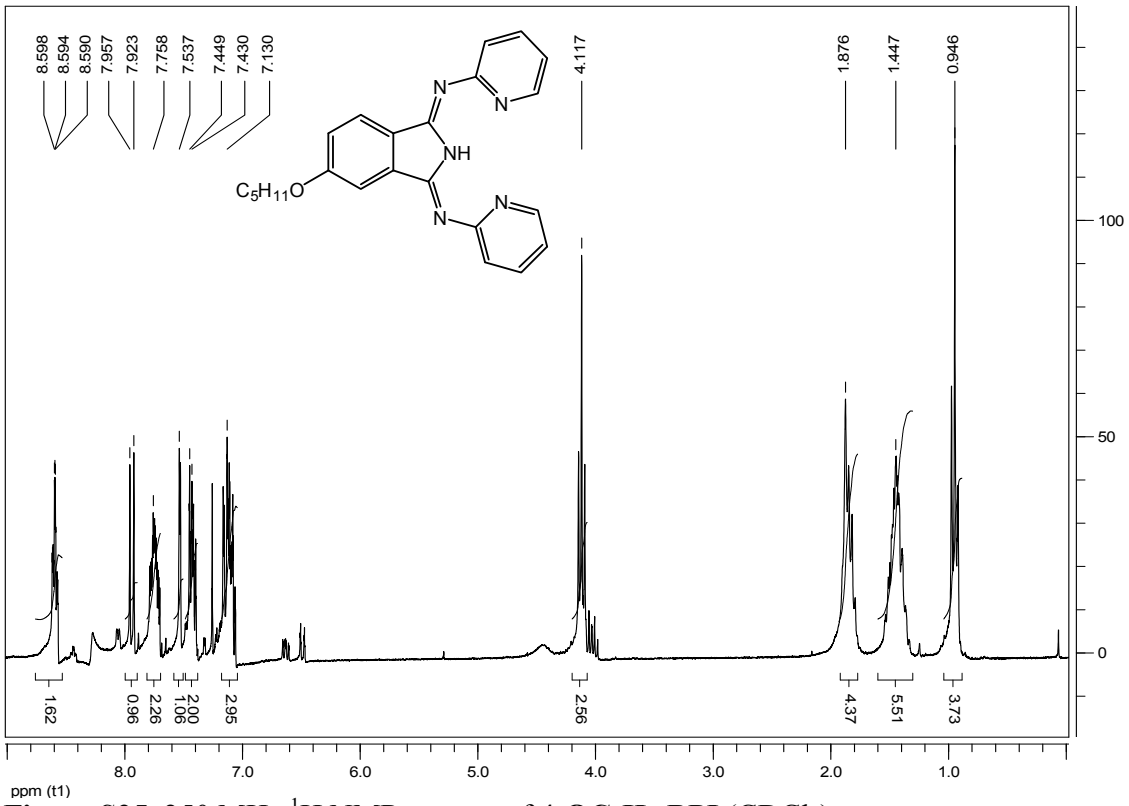


Figure S25. 250 MHz ^{1}H NMR spectra of **4-OC$_5$H$_{11}$BPI** ($CDCl_3$).

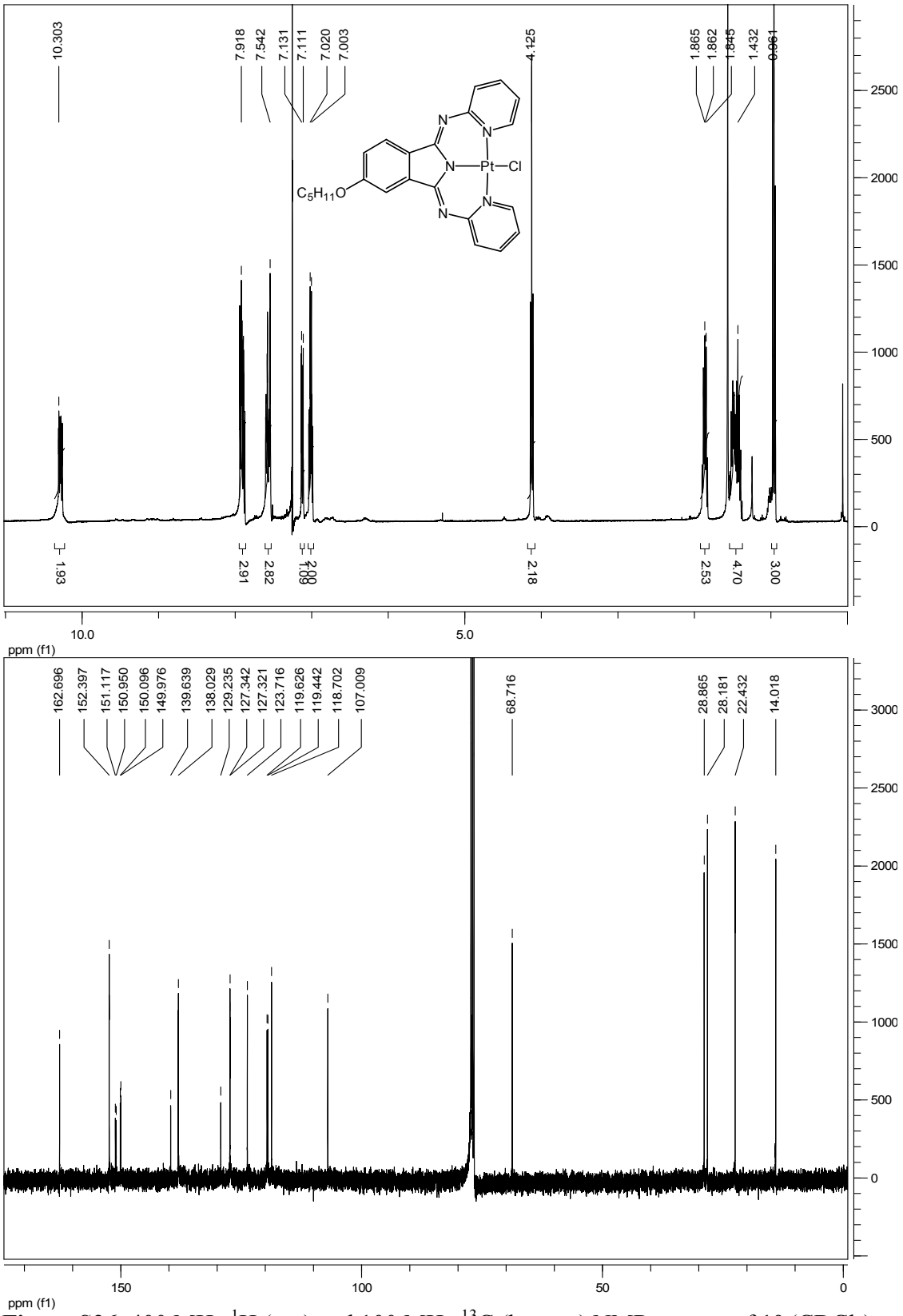


Figure S26. 400 MHz ^{1}H (top) and 100 MHz ^{13}C (bottom) NMR spectra of **10** ($CDCl_3$).

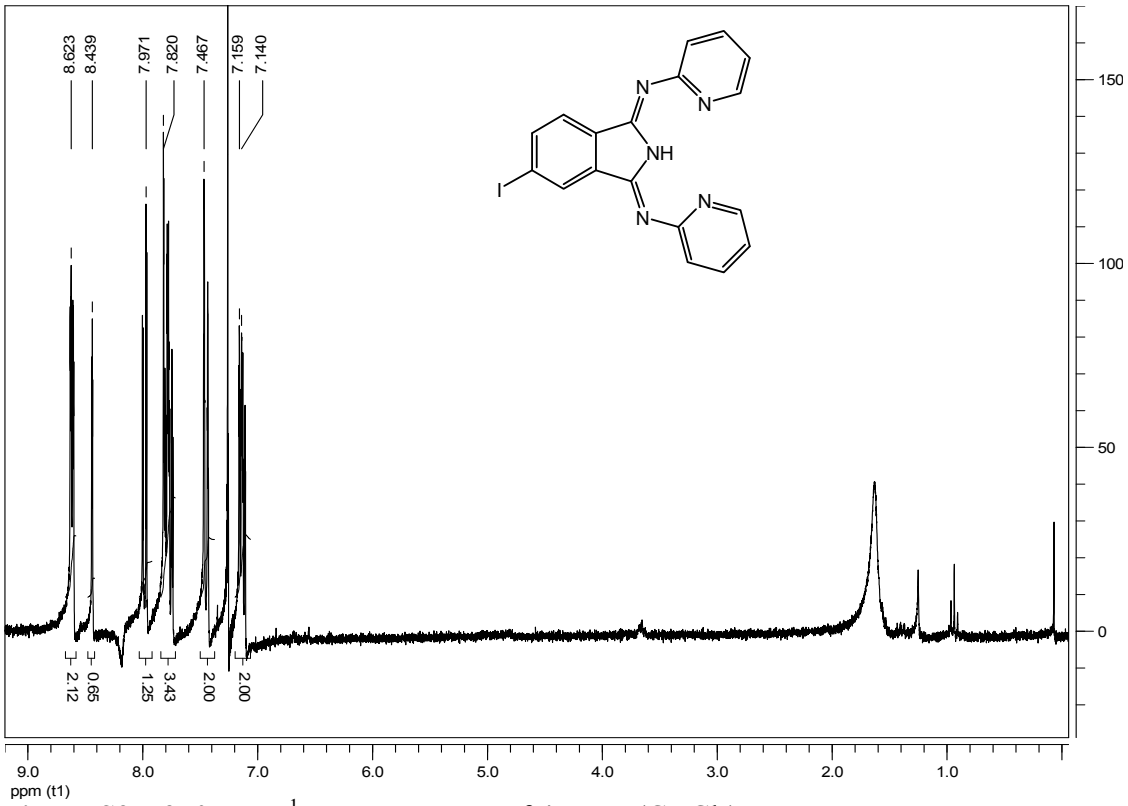


Figure S27. 250 MHz ^{1}H NMR spectra of **4-IBPI** ($CDCl_3$).

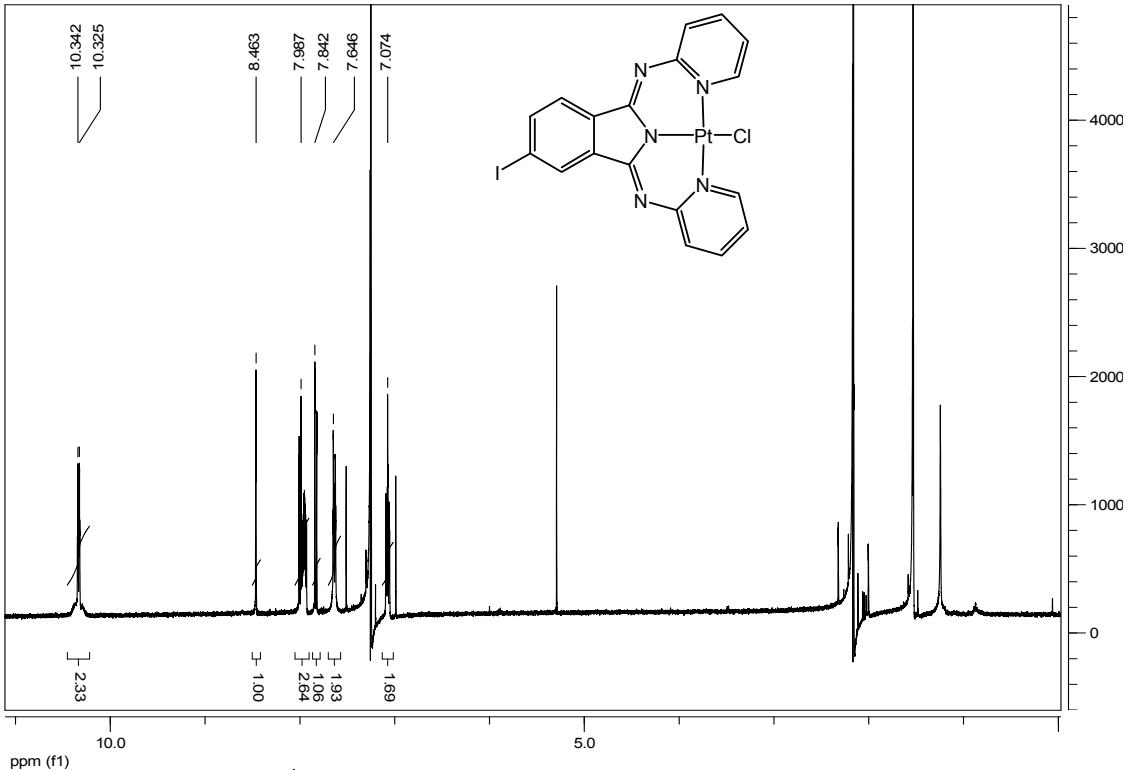


Figure S28. 400 MHz ^{1}H NMR spectra of **11** ($CDCl_3$).

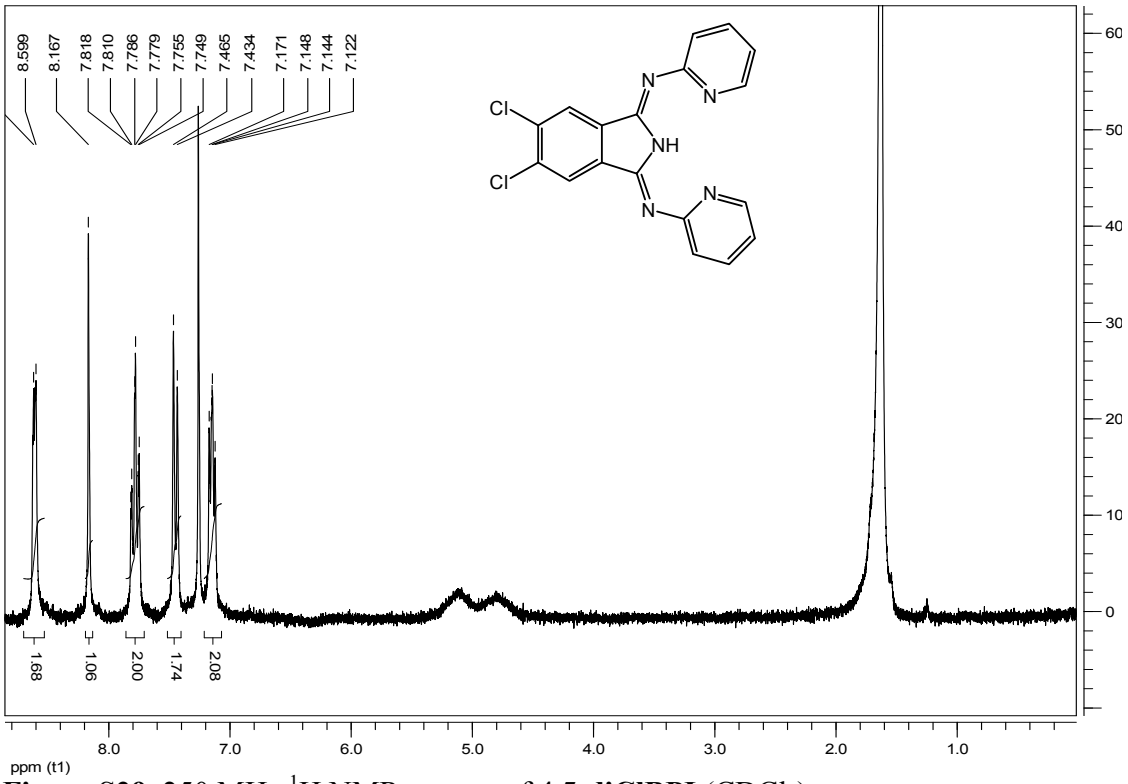


Figure S29. 250 MHz ^{1}H NMR spectra of **4,5-diClBPI** ($CDCl_3$).

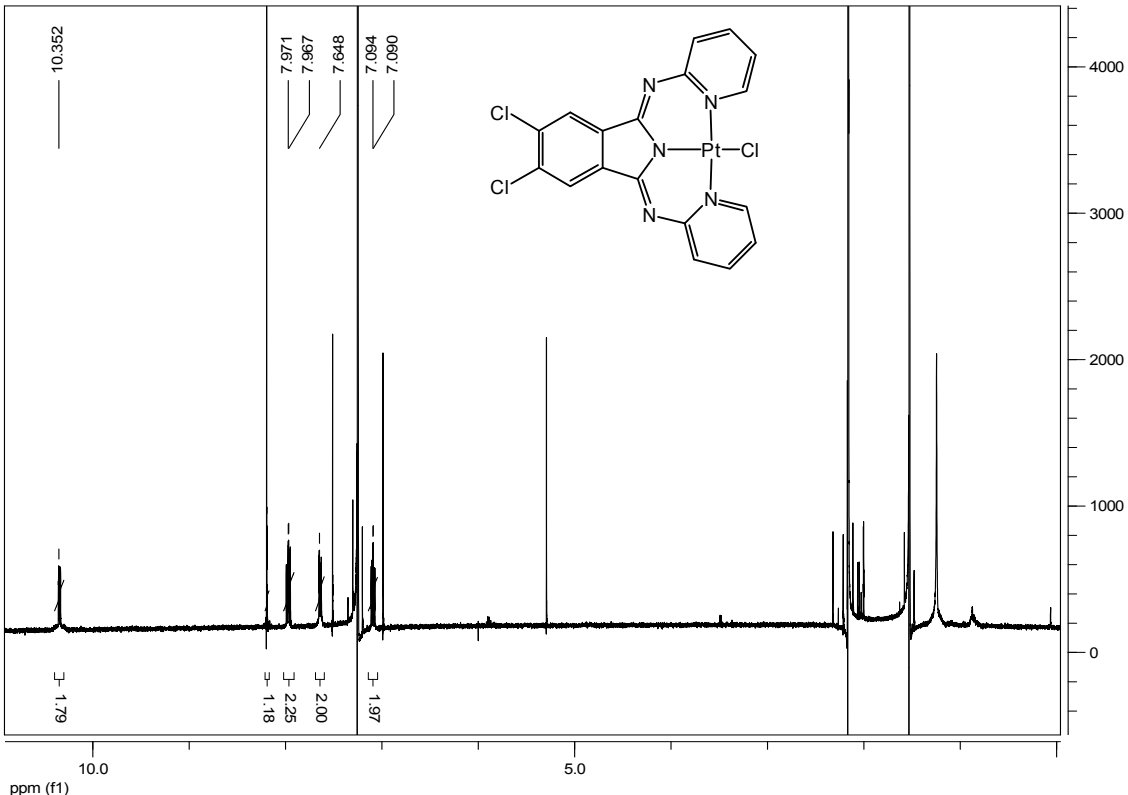


Figure S30. 400 MHz ^{1}H NMR spectra of **12** ($CDCl_3$).

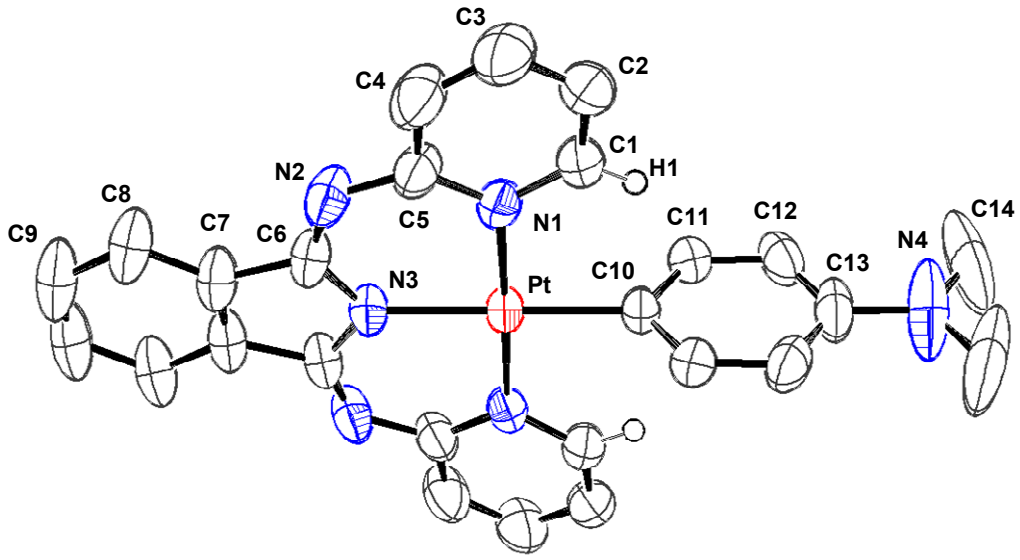


Figure S31. ORTEP diagram of **6** with atom labels. Selected hydrogen atoms omitted for clarity.

Table S2. Crystal data and structure refinement for **6**.

Empirical formula	$C_{26}H_{22}N_6Pt$	
Formula weight	613.59	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 11.1436(7) Å	α = 90°.
	b = 23.4283(13) Å	β = 115.0110(10)°.
	c = 9.3583(6) Å	γ = 90°.
Volume	2214.1(2) $Å^3$	
Z	4	
Density (calculated)	1.841 Mg/m^3	
Absorption coefficient	6.365 mm^{-1}	
F(000)	1192	
Crystal size	0.29 x 0.17 x 0.10 mm^3	
Theta range for data collection	2.20 to 30.53°.	
Index ranges	-15<=h<=15, -32<=k<=33, -13<=l<=13	
Reflections collected	26464	
Independent reflections	3363 [R(int) = 0.0251]	
Completeness to theta = 30.53°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.54 and 0.46	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3363 / 0 / 153	
Goodness-of-fit on F^2	1.143	
Final R indices [I>2σ(I)]	R1 = 0.0186, wR2 = 0.0427	
R indices (all data)	R1 = 0.0221, wR2 = 0.0452	
Largest diff. peak and hole	1.301 and -1.003 $e.Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7150(3)	6858(1)	1778(3)	57(1)
C(2)	8125(3)	6904(1)	1268(4)	65(1)
C(3)	8550(4)	6422(1)	777(5)	79(1)
C(4)	7998(4)	5912(1)	877(5)	77(1)
C(5)	7021(3)	5872(1)	1458(3)	56(1)
C(6)	5780(3)	5167(1)	2045(3)	54(1)
C(7)	5470(3)	4562(1)	2202(3)	60(1)
C(8)	5956(4)	4057(1)	1874(4)	75(1)
C(9)	5460(5)	3550(1)	2193(4)	85(1)
C(10)	5000	7231(1)	2500	45(1)
C(11)	4269(2)	7553(1)	1150(3)	51(1)
C(12)	4249(3)	8146(1)	1144(4)	62(1)
C(13)	5000	8457(2)	2500	69(1)
C(14)	4308(7)	9362(2)	1067(8)	165(3)
N(1)	6555(2)	6358(1)	1870(3)	48(1)
N(2)	6653(3)	5318(1)	1558(3)	63(1)
N(3)	5000	5497(1)	2500	48(1)
N(4)	5000	9052(2)	2500	139(3)
Pt(1)	5000	6368(1)	2500	43(1)

Table S4. Bond lengths [Å] and angles [°] for **6**.

C(1)-C(2)	1.364(4)
C(1)-N(1)	1.367(3)
C(1)-H(1)	0.9300
C(2)-C(3)	1.378(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.365(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.410(4)
C(4)-H(4)	0.9300
C(5)-N(1)	1.372(3)
C(5)-N(2)	1.376(3)
C(6)-N(2)	1.286(3)
C(6)-N(3)	1.360(3)
C(6)-C(7)	1.480(3)
C(7)-C(7)#1	1.381(6)
C(7)-C(8)	1.388(4)
C(8)-C(9)	1.395(5)
C(8)-H(8)	0.9300
C(9)-C(9)#1	1.370(9)
C(9)-H(9)	0.9300
C(10)-C(11)	1.400(3)
C(10)-C(11)#1	1.400(3)
C(10)-Pt(1)	2.022(3)
C(11)-C(12)	1.388(4)
C(11)-H(11)	0.9300
C(12)-C(13)	1.394(4)
C(12)-H(12)	0.9300
C(13)-C(12)#1	1.394(4)
C(13)-N(4)	1.395(5)
C(14)-N(4)	1.430(6)
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
N(1)-Pt(1)	2.053(2)

N(3)-C(6)#1	1.360(3)
N(3)-Pt(1)	2.038(3)
N(4)-C(14)#1	1.430(6)
Pt(1)-N(1)#1	2.053(2)

C(2)-C(1)-N(1)	124.8(3)
C(2)-C(1)-H(1)	117.6
N(1)-C(1)-H(1)	117.6
C(1)-C(2)-C(3)	119.2(3)
C(1)-C(2)-H(2)	120.4
C(3)-C(2)-H(2)	120.4
C(4)-C(3)-C(2)	117.8(3)
C(4)-C(3)-H(3)	121.1
C(2)-C(3)-H(3)	121.1
C(3)-C(4)-C(5)	121.9(3)
C(3)-C(4)-H(4)	119.0
C(5)-C(4)-H(4)	119.0
N(1)-C(5)-N(2)	127.1(2)
N(1)-C(5)-C(4)	120.0(2)
N(2)-C(5)-C(4)	112.9(2)
N(2)-C(6)-N(3)	129.3(2)
N(2)-C(6)-C(7)	122.8(2)
N(3)-C(6)-C(7)	107.9(2)
C(7)#1-C(7)-C(8)	121.53(19)
C(7)#1-C(7)-C(6)	106.78(15)
C(8)-C(7)-C(6)	131.7(3)
C(7)-C(8)-C(9)	116.9(3)
C(7)-C(8)-H(8)	121.6
C(9)-C(8)-H(8)	121.6
C(9)#1-C(9)-C(8)	121.6(2)
C(9)#1-C(9)-H(9)	119.2
C(8)-C(9)-H(9)	119.2
C(11)-C(10)-C(11)#1	114.7(3)
C(11)-C(10)-Pt(1)	122.67(15)
C(11)#1-C(10)-Pt(1)	122.67(15)
C(12)-C(11)-C(10)	123.1(3)

C(12)-C(11)-H(11)	118.5
C(10)-C(11)-H(11)	118.5
C(11)-C(12)-C(13)	121.1(3)
C(11)-C(12)-H(12)	119.4
C(13)-C(12)-H(12)	119.4
C(12)#1-C(13)-C(12)	116.9(3)
C(12)#1-C(13)-N(4)	121.53(17)
C(12)-C(13)-N(4)	121.53(17)
N(4)-C(14)-H(14A)	109.5
N(4)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
N(4)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(1)-N(1)-C(5)	116.2(2)
C(1)-N(1)-Pt(1)	119.94(16)
C(5)-N(1)-Pt(1)	123.82(17)
C(6)-N(2)-C(5)	125.1(2)
C(6)-N(3)-C(6)#1	110.5(3)
C(6)-N(3)-Pt(1)	124.73(14)
C(6)#1-N(3)-Pt(1)	124.73(14)
C(13)-N(4)-C(14)	120.5(3)
C(13)-N(4)-C(14)#1	120.5(3)
C(14)-N(4)-C(14)#1	119.0(6)
C(10)-Pt(1)-N(3)	180.0
C(10)-Pt(1)-N(1)	90.66(5)
N(3)-Pt(1)-N(1)	89.34(5)
C(10)-Pt(1)-N(1)#1	90.66(5)
N(3)-Pt(1)-N(1)#1	89.34(5)
N(1)-Pt(1)-N(1)#1	178.68(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

Table S5. Anisotropic displacement parameters ($Å^2$ x 10^3) for **6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	53(1)	45(1)	76(2)	1(1)	30(1)	-1(1)
C(2)	56(1)	58(2)	86(2)	8(1)	34(1)	-2(1)
C(3)	73(2)	73(2)	113(3)	13(2)	61(2)	11(2)
C(4)	83(2)	59(2)	112(3)	10(2)	63(2)	18(2)
C(5)	60(1)	45(1)	69(2)	11(1)	32(1)	12(1)
C(6)	73(2)	34(1)	56(1)	5(1)	30(1)	8(1)
C(7)	92(2)	34(1)	54(1)	4(1)	32(1)	5(1)
C(8)	120(3)	40(1)	72(2)	5(1)	49(2)	17(2)
C(9)	151(4)	36(1)	71(2)	1(1)	48(2)	13(2)
C(10)	47(2)	32(1)	57(2)	0	23(1)	0
C(11)	50(1)	44(1)	58(1)	3(1)	20(1)	1(1)
C(12)	67(2)	46(1)	80(2)	20(1)	38(1)	14(1)
C(13)	89(3)	32(2)	112(4)	0	68(3)	0
C(14)	252(8)	51(2)	268(8)	60(3)	184(7)	60(3)
N(1)	49(1)	39(1)	56(1)	5(1)	22(1)	5(1)
N(2)	81(2)	40(1)	79(2)	10(1)	45(1)	16(1)
N(3)	59(2)	31(1)	55(2)	0	26(1)	0
N(4)	226(8)	35(2)	173(6)	0	102(6)	0
Pt(1)	47(1)	31(1)	51(1)	0	20(1)	0

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **6**.

	x	y	z	U(eq)
H(1)	6869	7190	2086	68
H(2)	8499	7258	1251	78
H(3)	9193	6442	390	95
H(4)	8273	5581	553	93
H(8)	6582	4057	1460	90
H(9)	5760	3204	1984	102
H(11)	3774	7362	214	62
H(12)	3725	8338	221	74
H(14A)	4413	9171	219	247
H(14B)	4663	9741	1179	247
H(14C)	3385	9382	841	247