

Supporting Information

Linear Bimetallic Alkynylplatinum(II) Terpyridyl Complexes Bearing *para*-Phenylene Ethynylene Oligomers: Synthesis, Characterization, Aggregation and Photophysical Properties

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1. Additional photophysical data

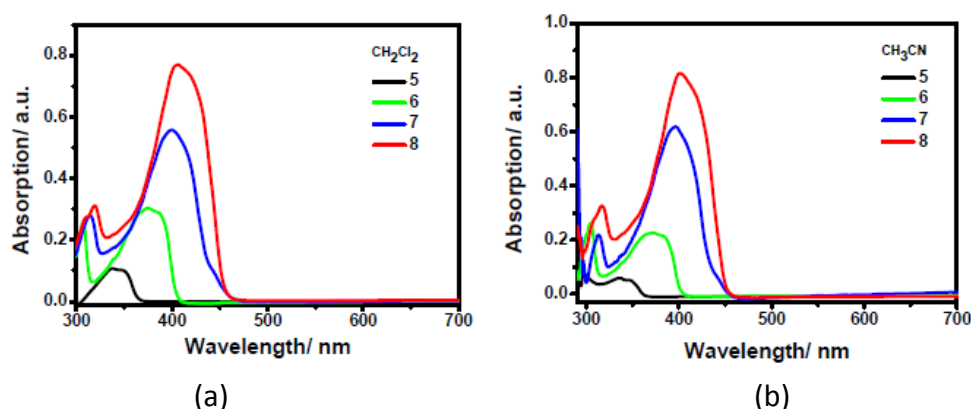


Figure S1. Absorption spectra of compounds **5-8** at 298 K (concentration = 1×10^{-5} M) (a) in CH_2Cl_2 ; (b) in CH_3CN .

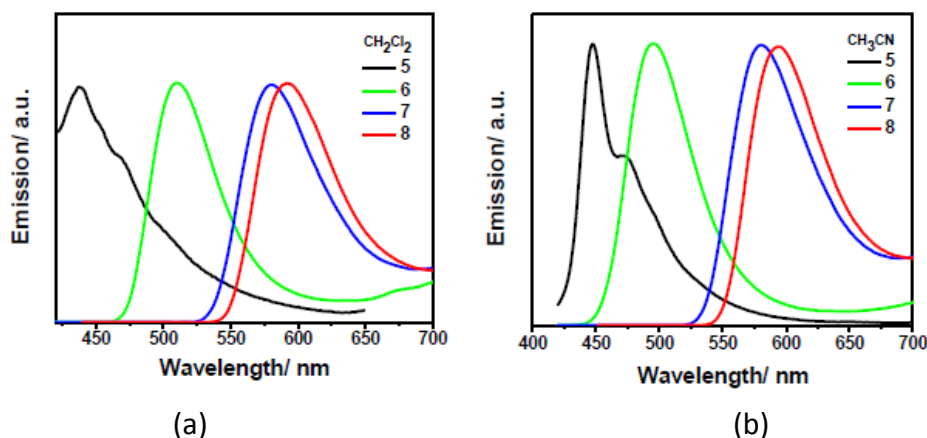


Figure S2. Normalized emission spectra of compounds **5-8** at 298 K ($\lambda_{\text{ex}} = 400$ nm, concentration = 1×10^{-5} M) (a) in CH_2Cl_2 ; (b) in CH_3CN .

Table S1. Electronic absorption and emission data for compounds **5-8**

	medium	$\lambda_{\text{abs}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	$\lambda_{\text{em}}/\text{nm}$
5	CH_2Cl_2	336 (11667)	437
	CH_3CN	336 (6658)	448
6	CH_2Cl_2	375 (31224)	510
	CH_3CN	372 (23634)	495
7	CH_2Cl_2	400 (56557)	580
	CH_3CN	395 (62627)	580
8	CH_2Cl_2	406 (78075)	592
	CH_3CN	401 (82423)	594

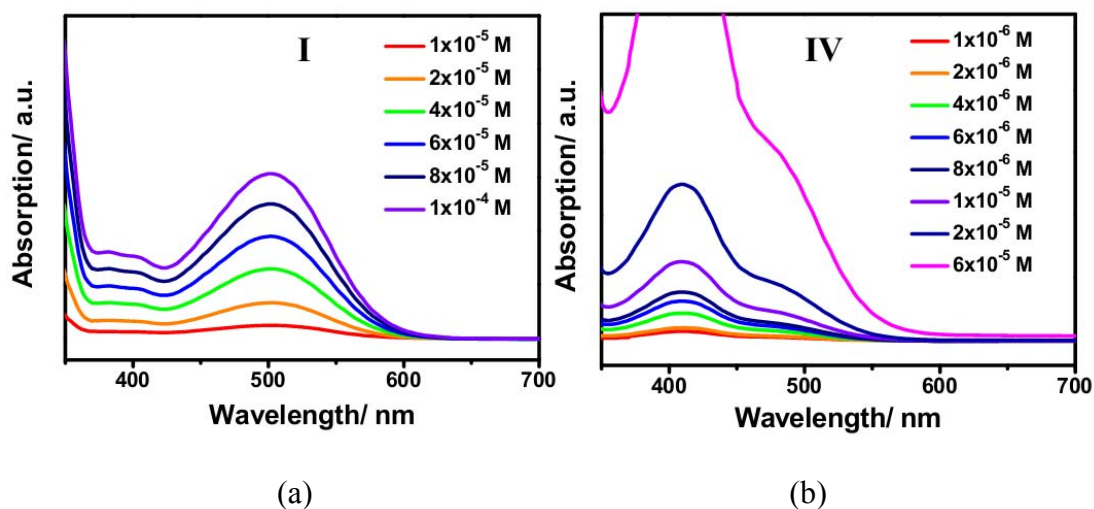


Figure S3. Absorption spectra of complex **I** (a) and **IV** (b) in CH_3CN under different concentrations at 298 K.

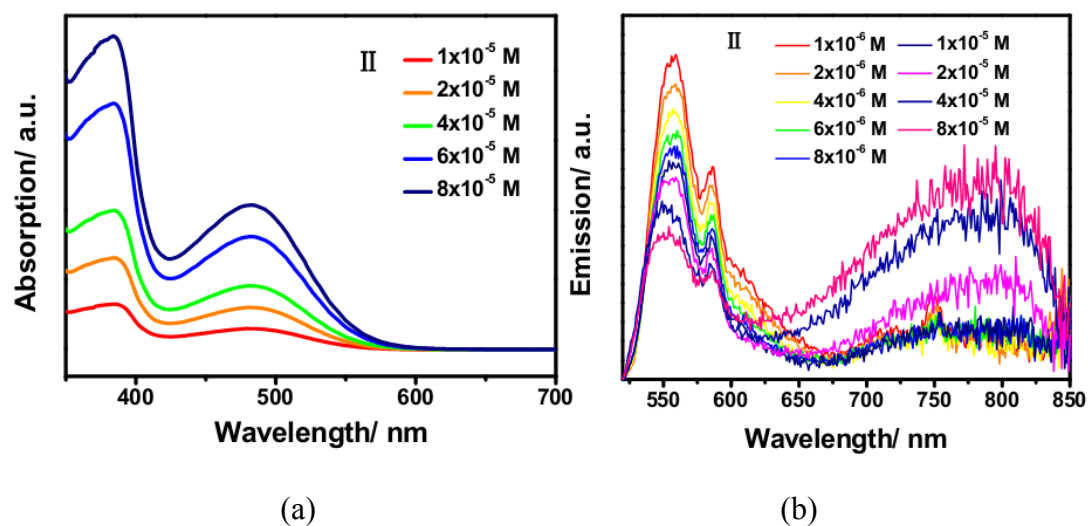


Figure S4. (a) Absorption spectra of complex **II** in CH_3CN under different concentrations at 298 K; (b) Normalized emission spectra of complex **II** in CH_3CN under different concentrations at 298 K ($\lambda_{\text{ex}} = 500$ nm).

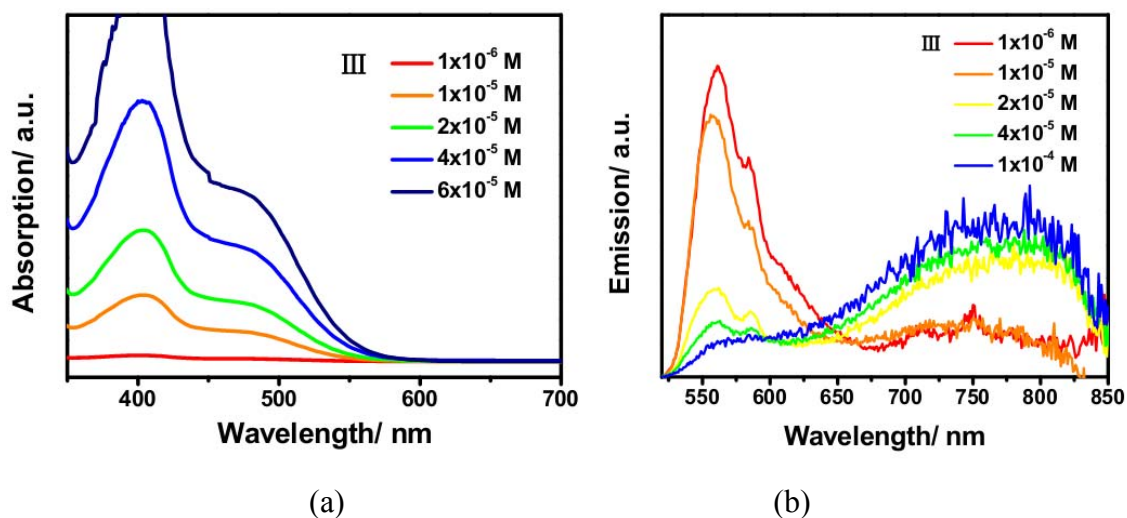


Figure S5. (a) Absorption spectra of complex **III** in CH_3CN and at different concentrations at 298 K; (b) Normalized emission spectra of complex **III** in CH_3CN at different concentrations at 298 K ($\lambda_{\text{ex}} = 500 \text{ nm}$).

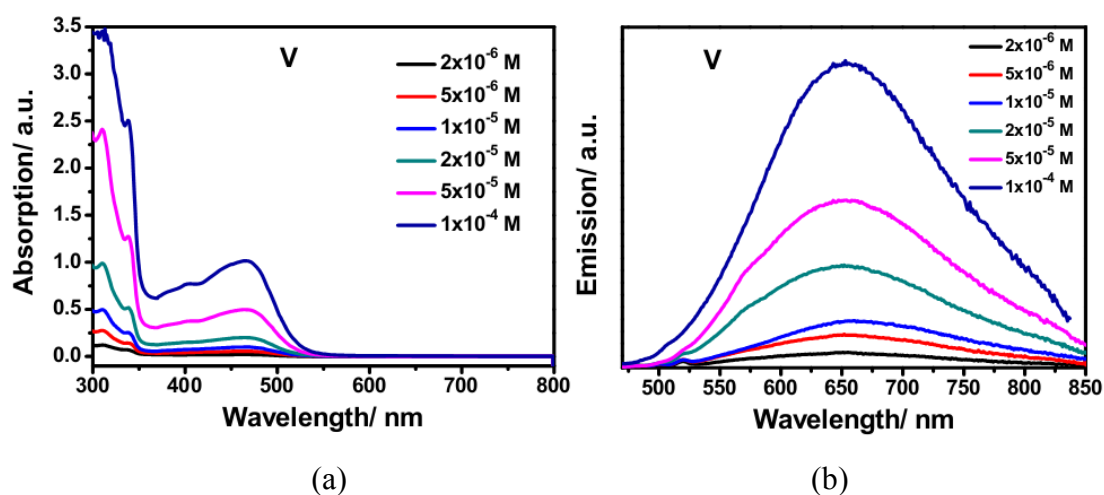


Figure S6. (a) Absorption spectra of complex **V** in CH_3CN and at different concentrations at 298 K; (b) Normalized emission spectra of complex **V** in CH_3CN at different concentrations excited at 450 nm at 298 K.

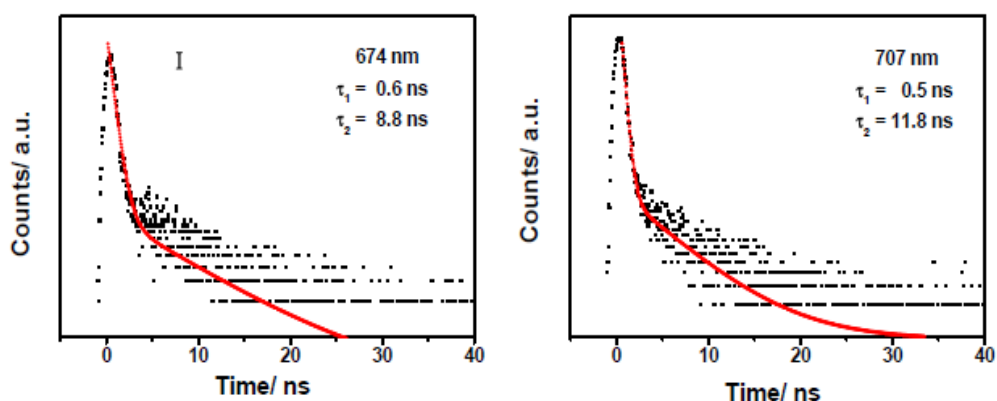


Figure S7. The luminescent lifetimes of complex **I** in CH_2Cl_2 solution at 298 K. The red lines are the fitting curves (concentration = $1 \times 10^{-6} \text{ M}$).

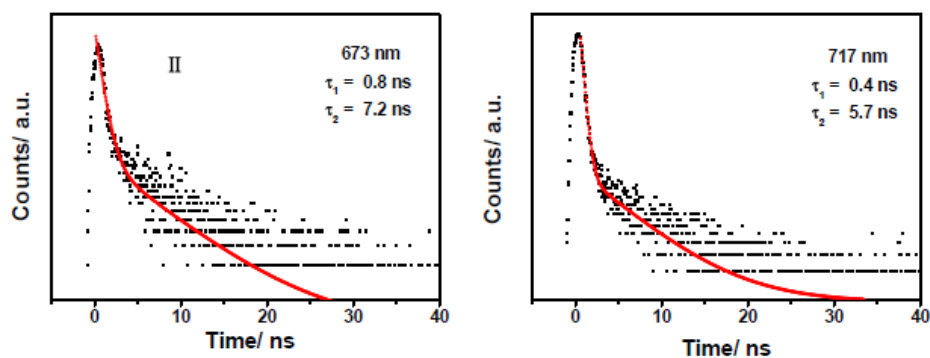


Figure S8. The luminescent lifetimes of complex **II** in CH_2Cl_2 solution at 298 K (concentration = $1 \times 10^{-6} \text{ M}$).

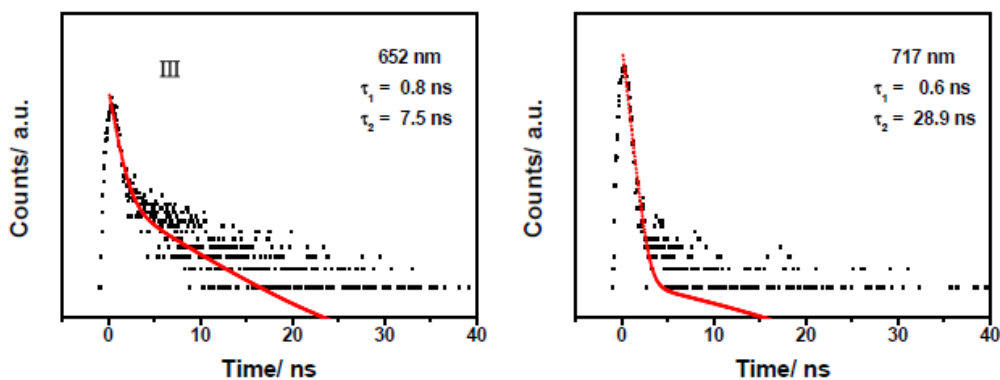


Figure S9. The luminescent lifetimes of complex **III** in CH_2Cl_2 solution at 298 K (concentration = $1 \times 10^{-6} \text{ M}$).

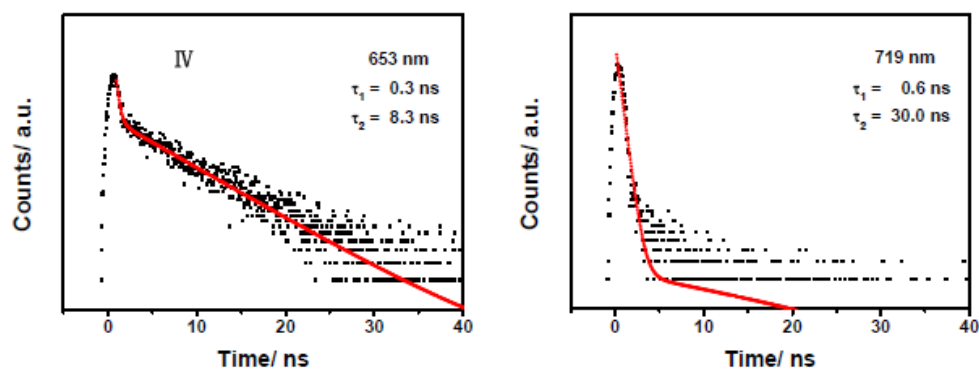


Figure S10. The luminescent lifetimes of complex **IV** in CH_2Cl_2 solution at 298 K (concentration = $1 \times 10^{-6} \text{ M}$).

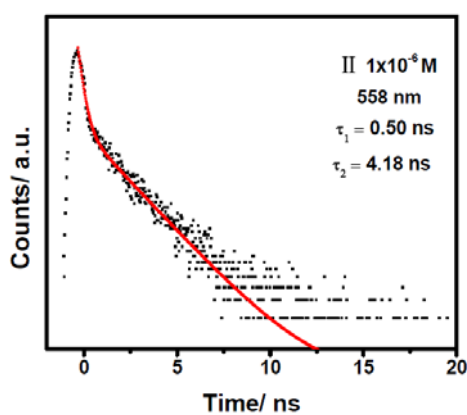


Figure S11. The luminescent lifetimes of complex **II** in CH_3CN collected at 558 nm at 298 K (concentration = $1 \times 10^{-6} \text{ M}$).

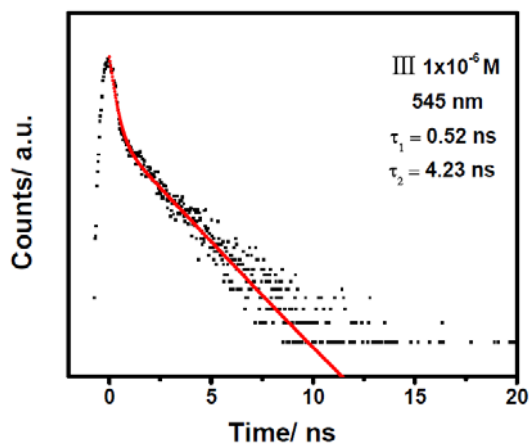


Figure S12. The luminescent lifetimes of complex **III** in CH_3CN collected at 545 nm at 298 K (concentration = $1 \times 10^{-6} \text{ M}$).

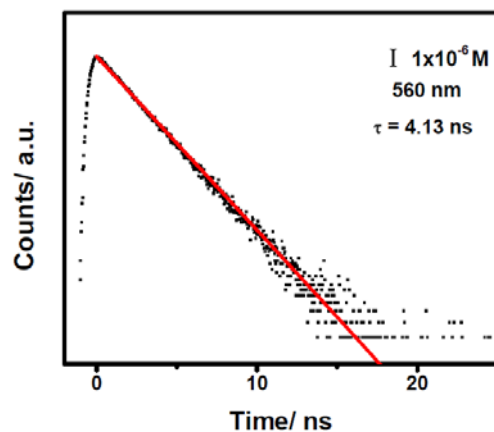


Figure S13 The luminescent lifetimes of complex I in CH₃CN collected at 560 nm at 298 K (concentration = 1×10^{-6} M).

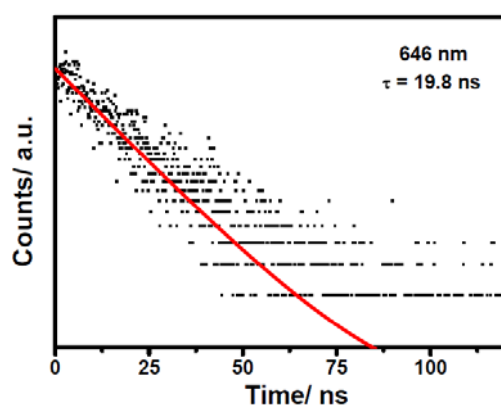


Figure S14. The luminescent lifetimes of complex V in CH₃CN at 298 K (concentration = 1×10^{-5} M).

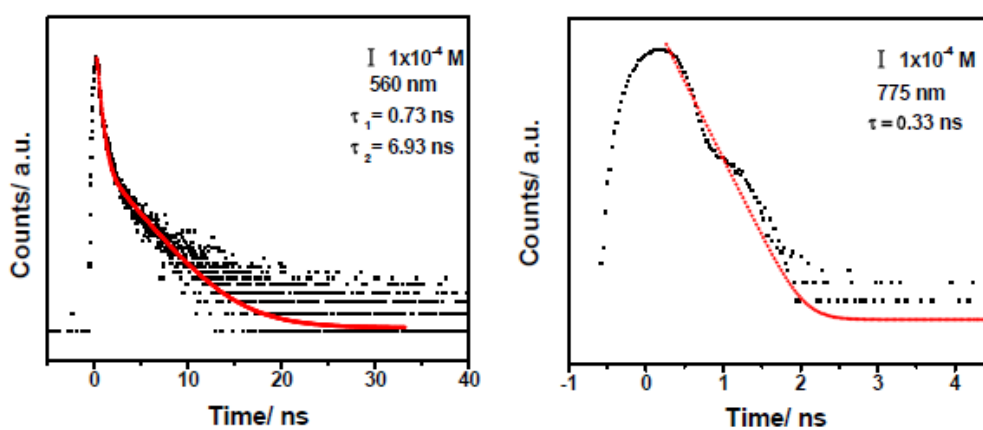
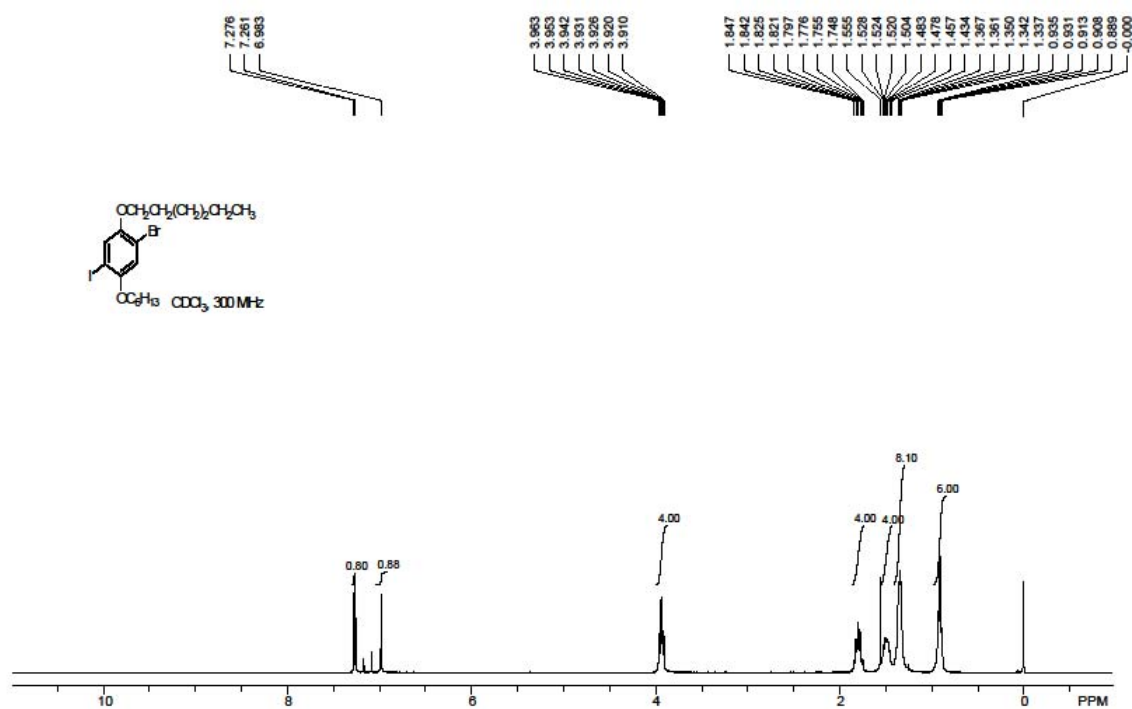
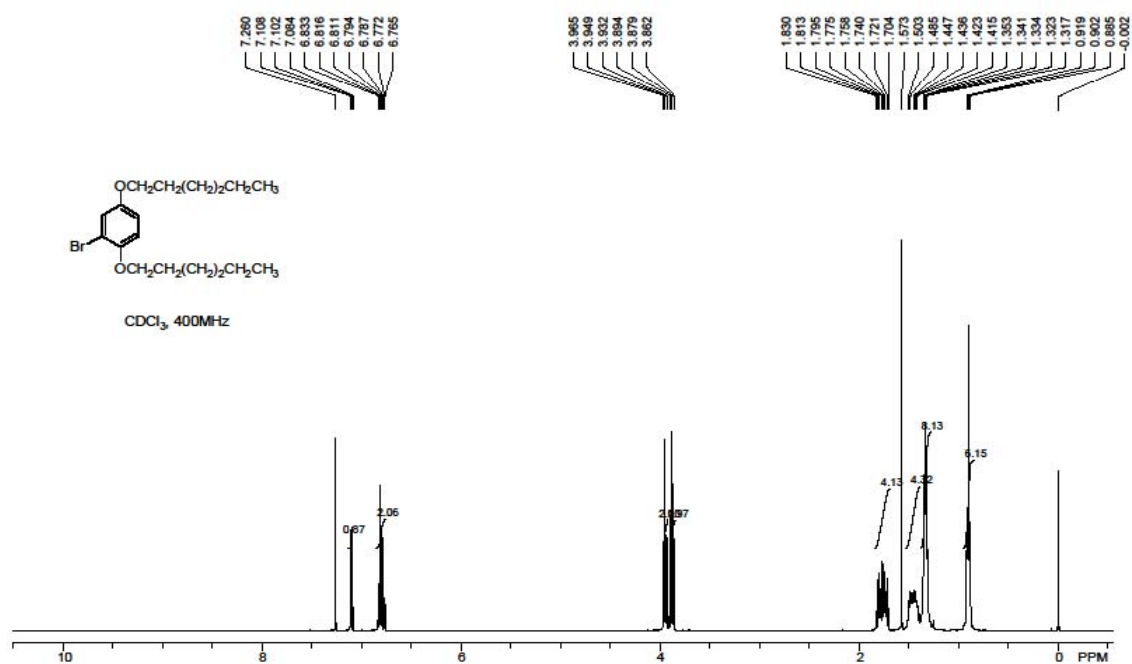
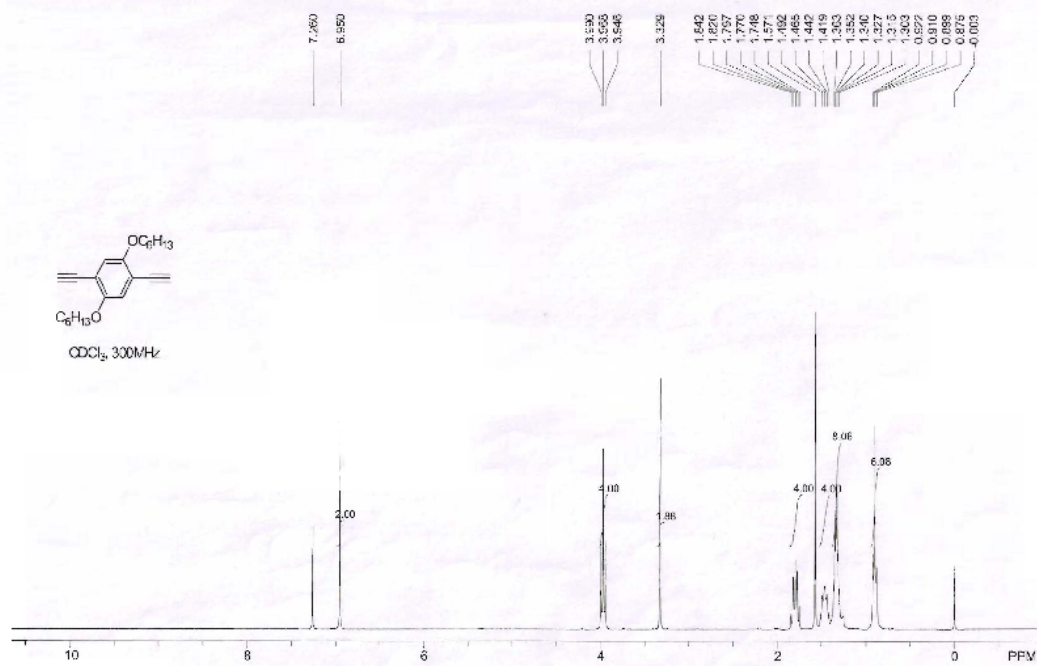
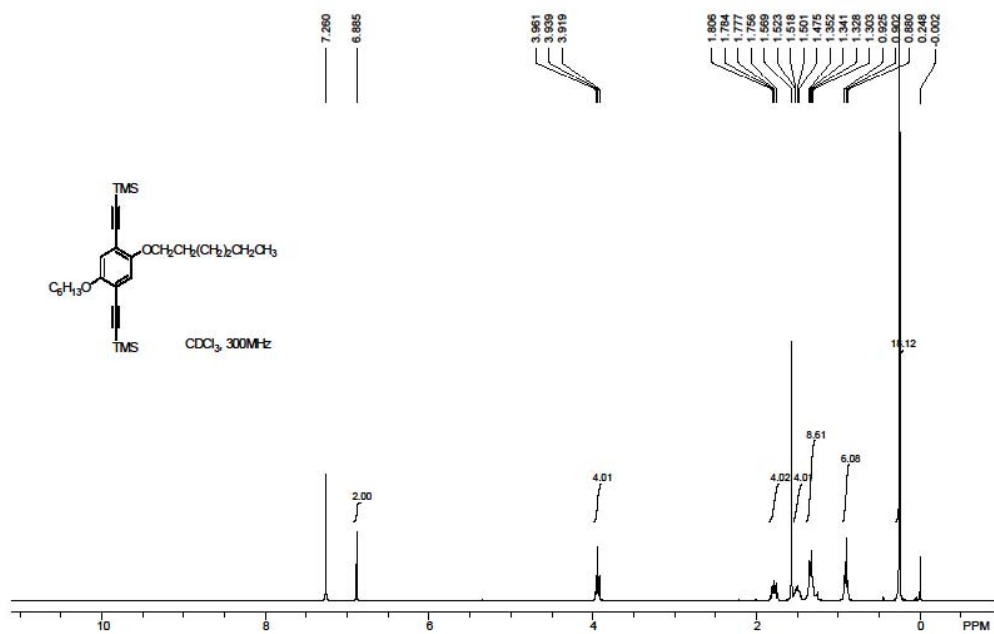
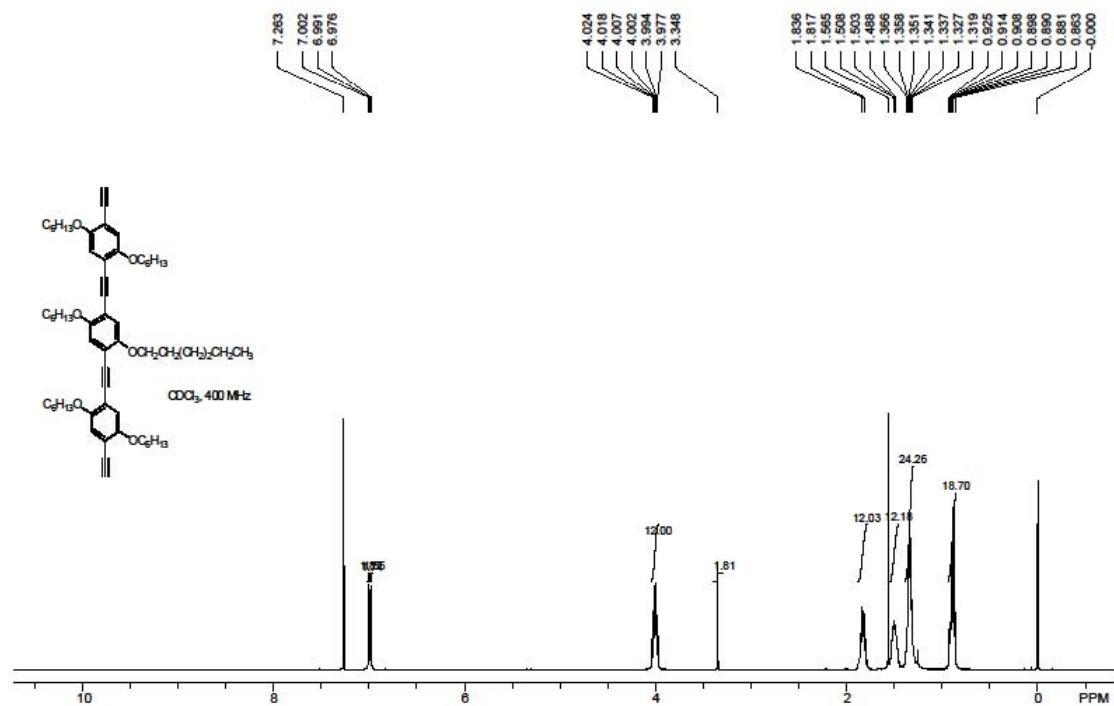
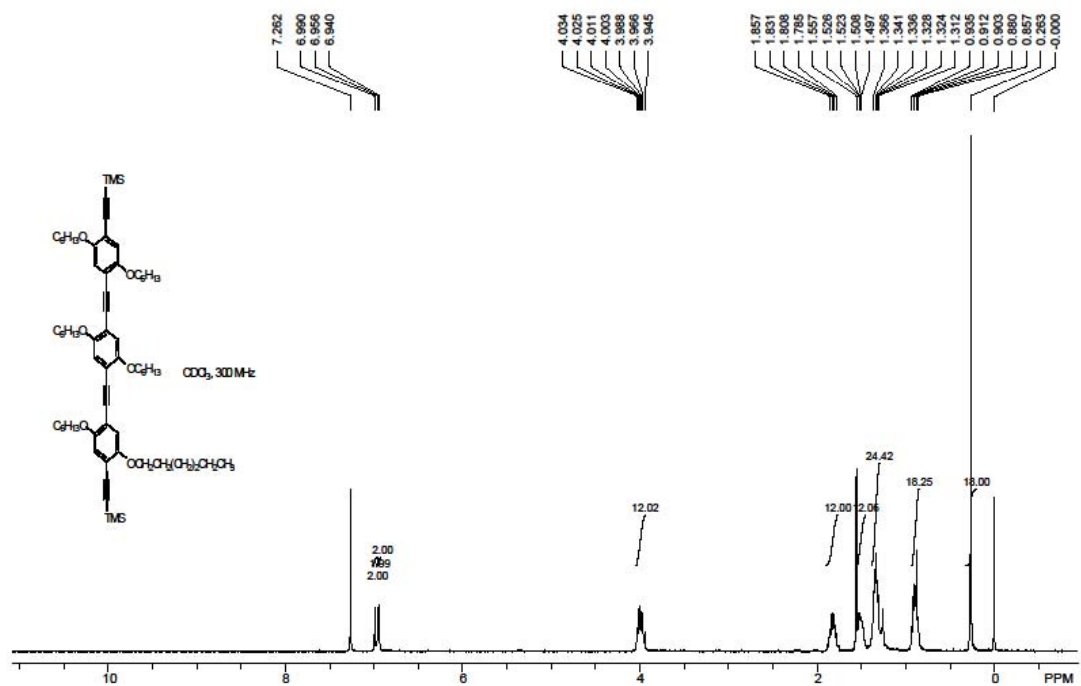


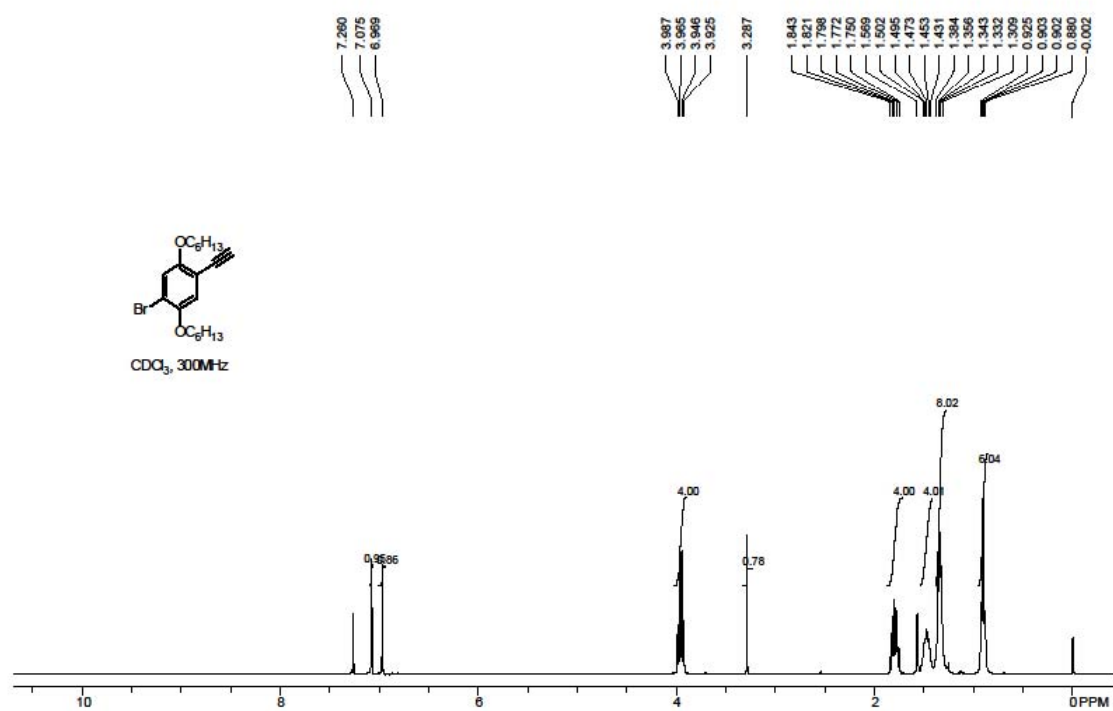
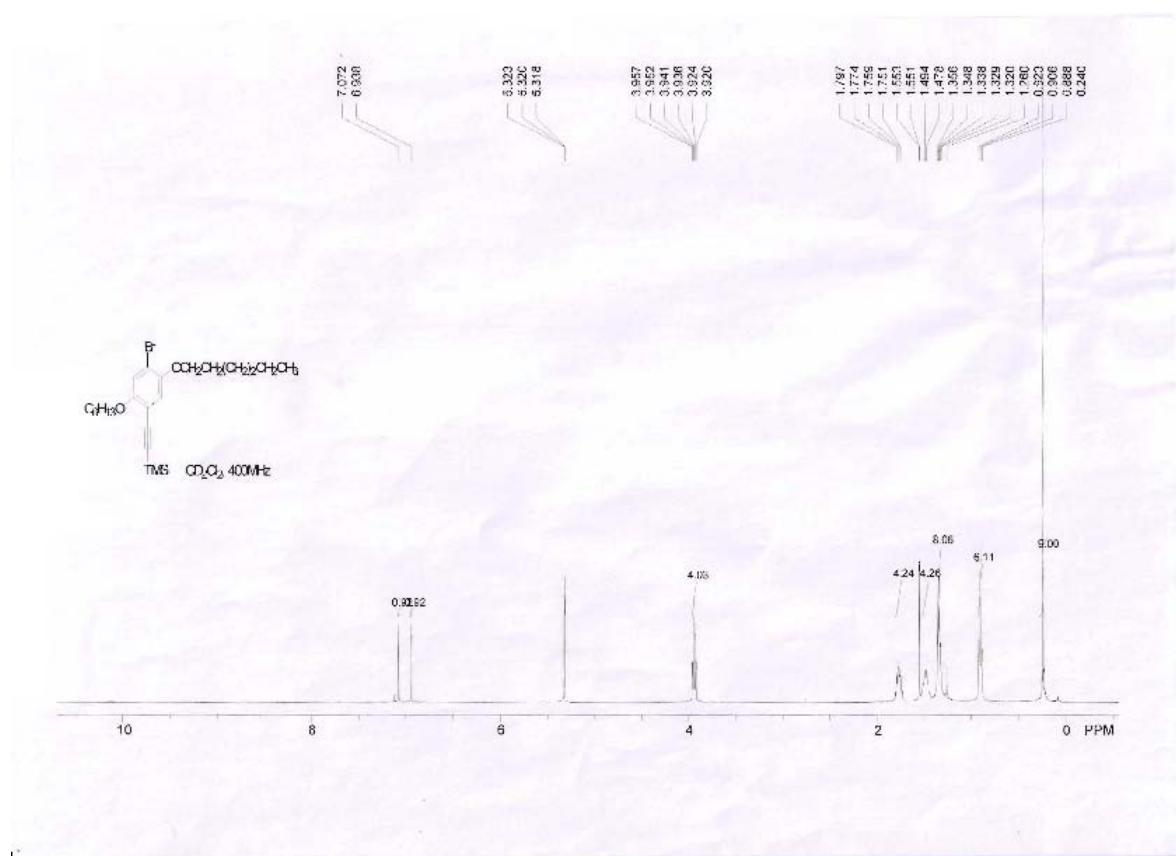
Figure S15. The luminescent lifetimes of complex I in CH₃CN at 298 K (concentration = 1×10^{-4} M).

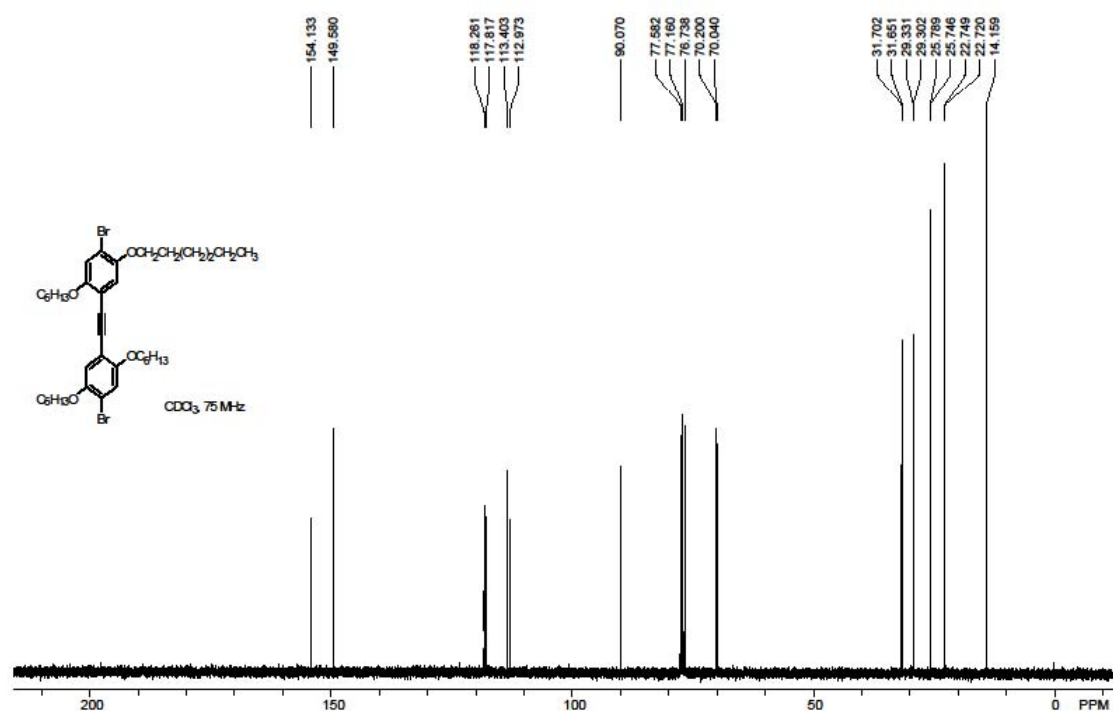
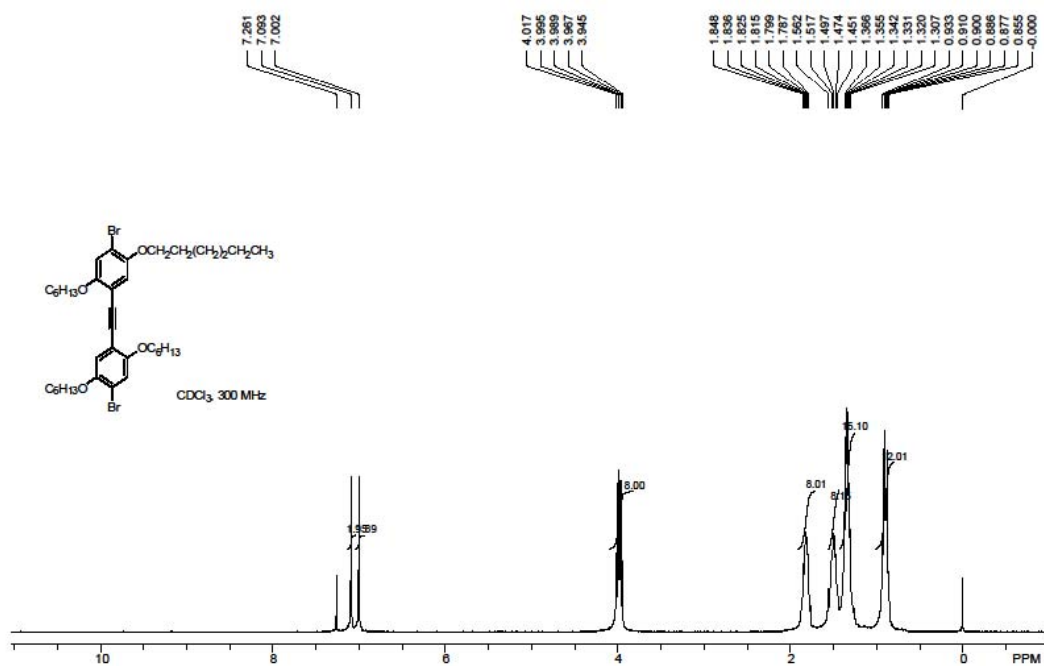
2. ^1H NMR and ^{13}C NMR spectra copies

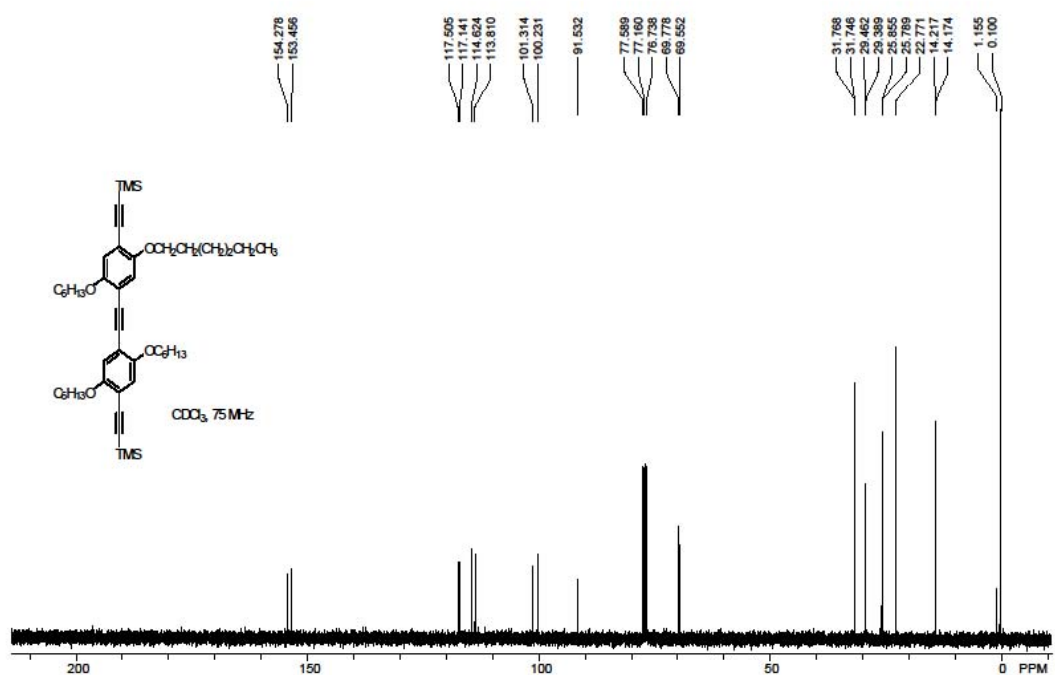
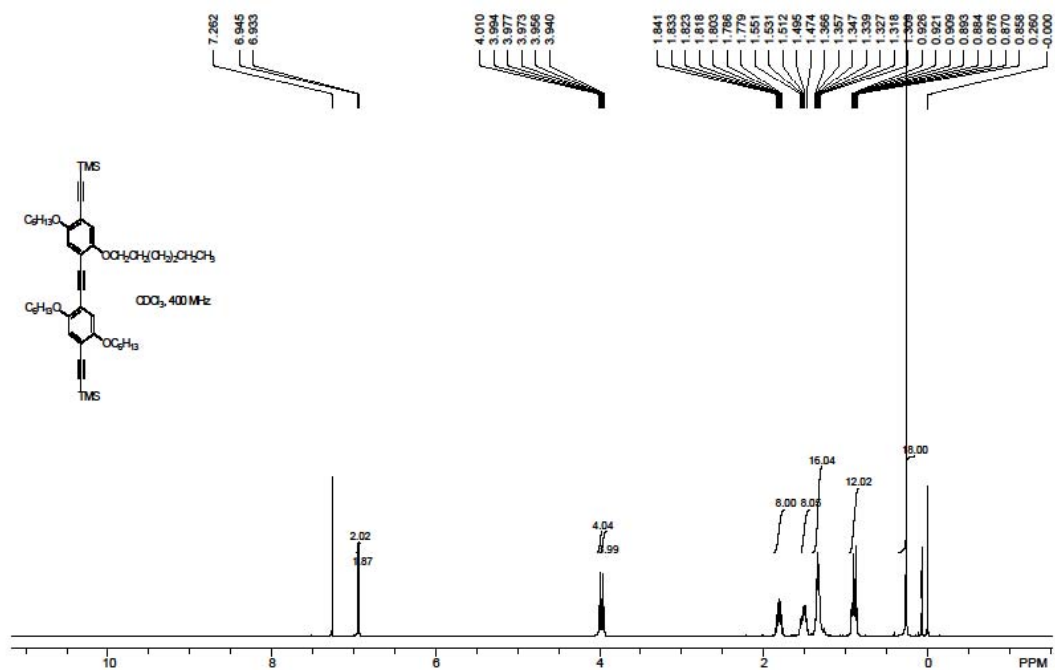


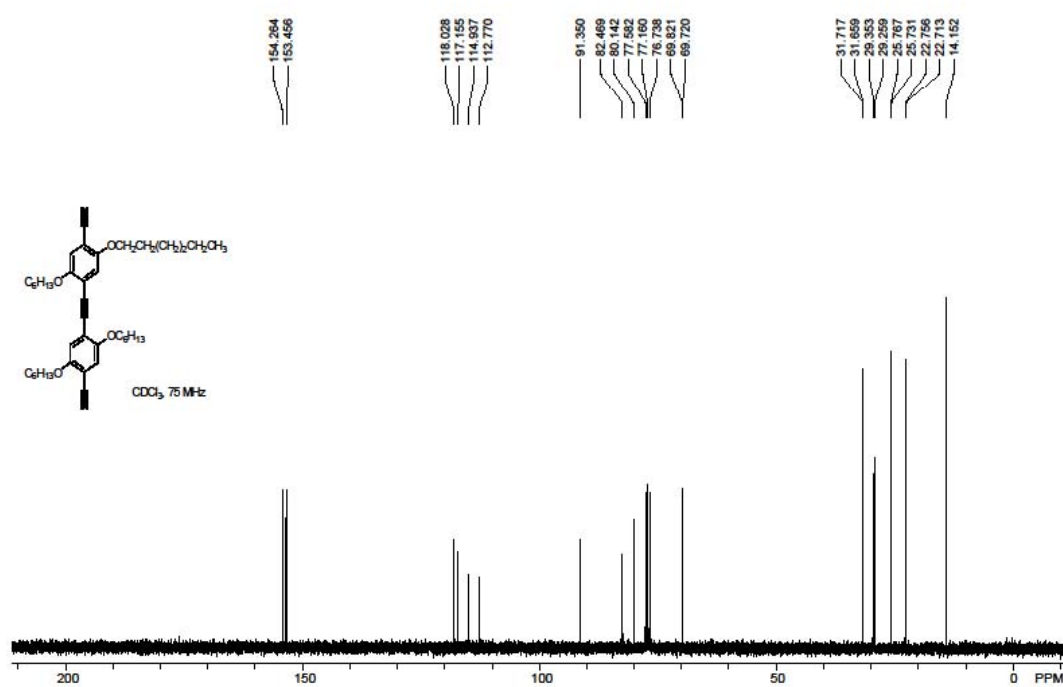
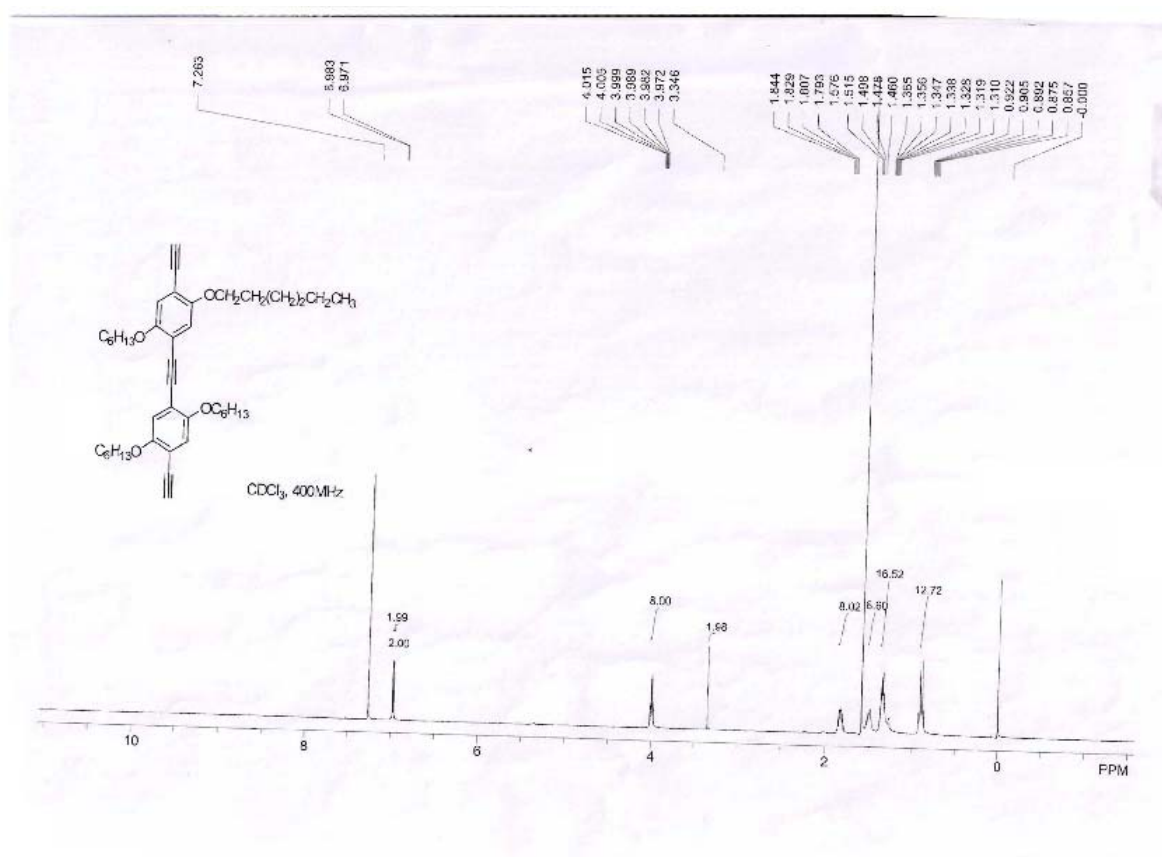


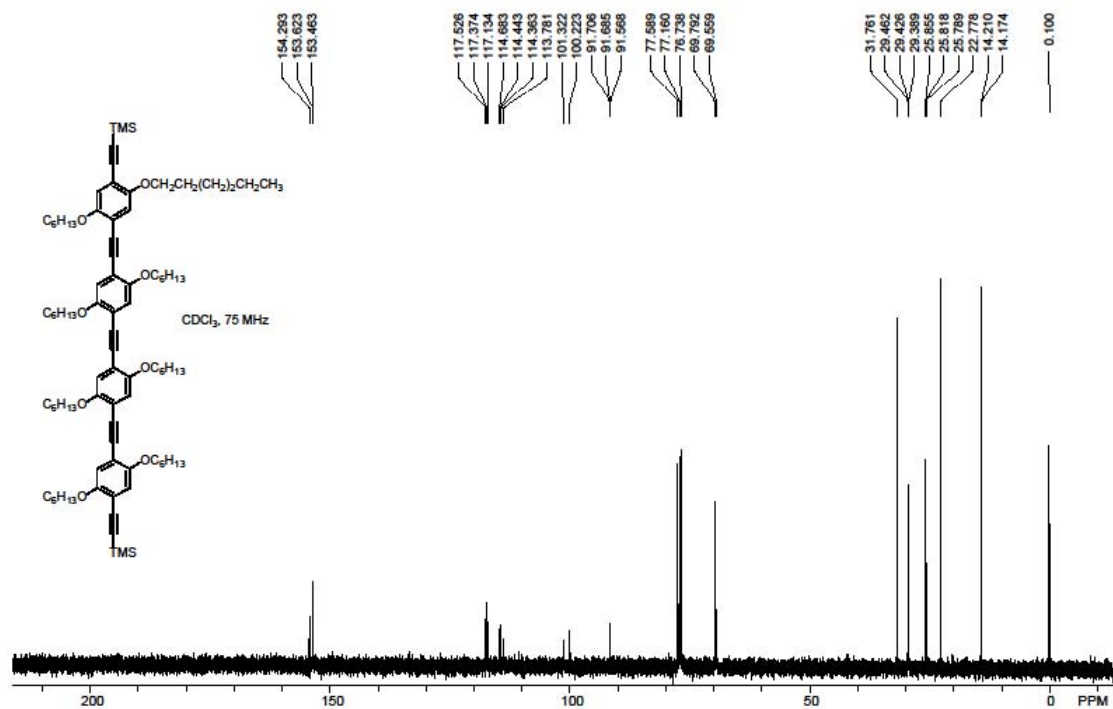
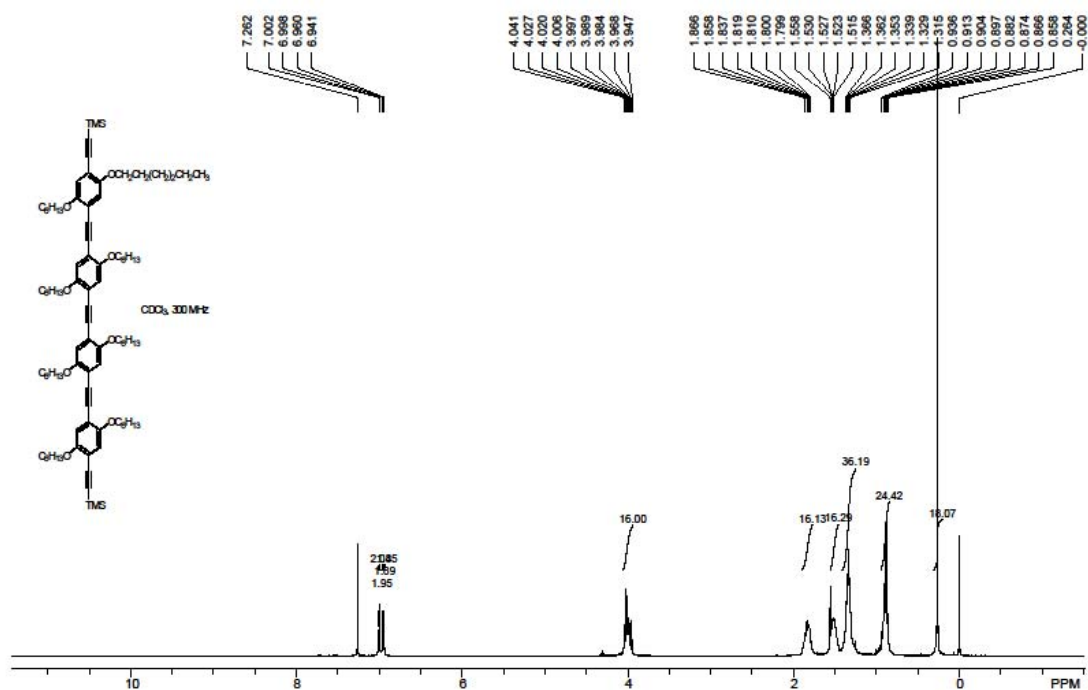


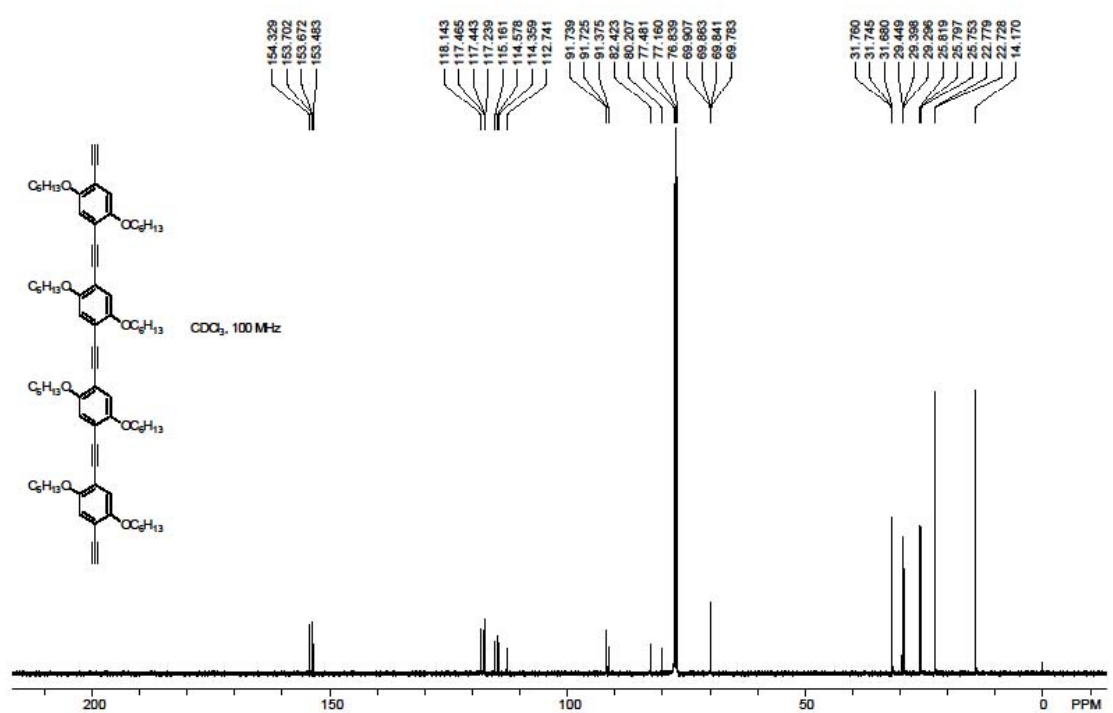
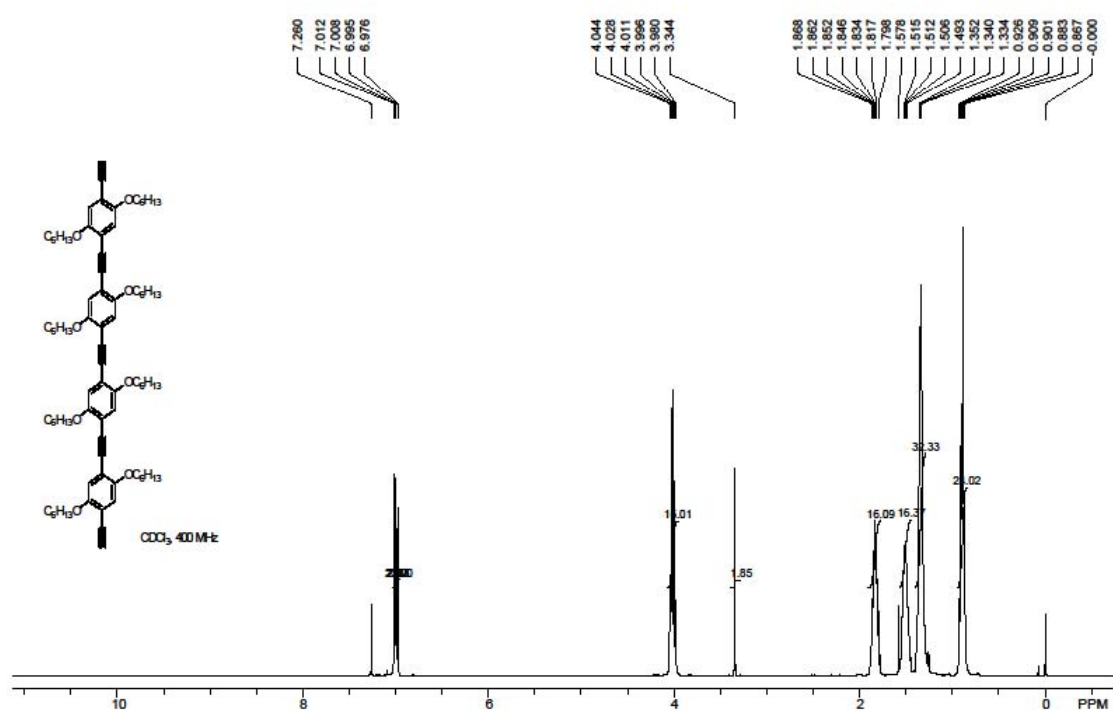


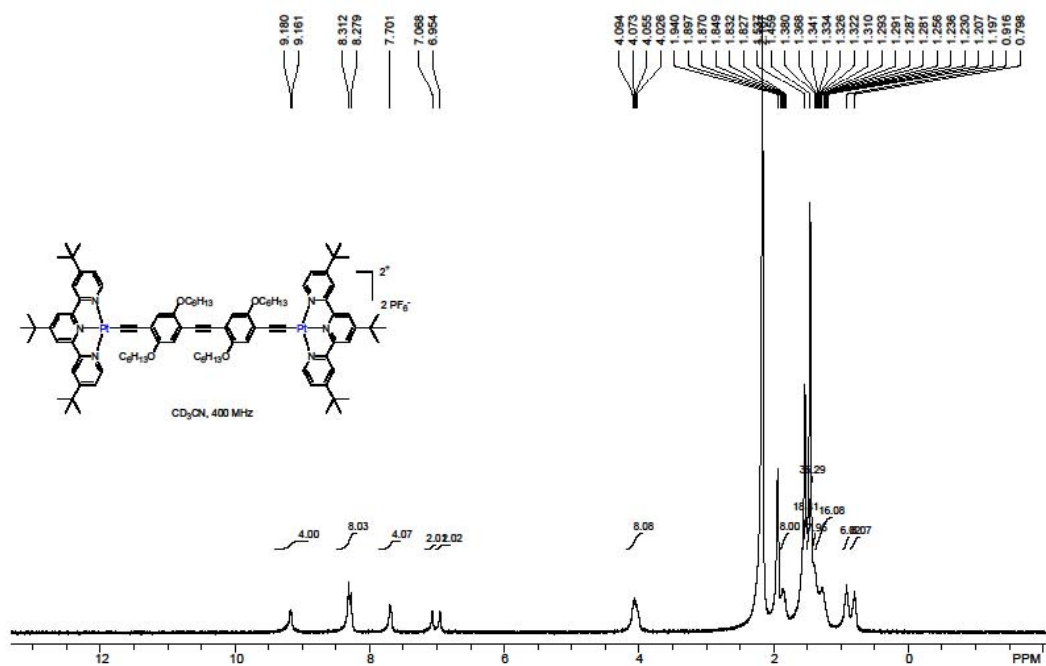
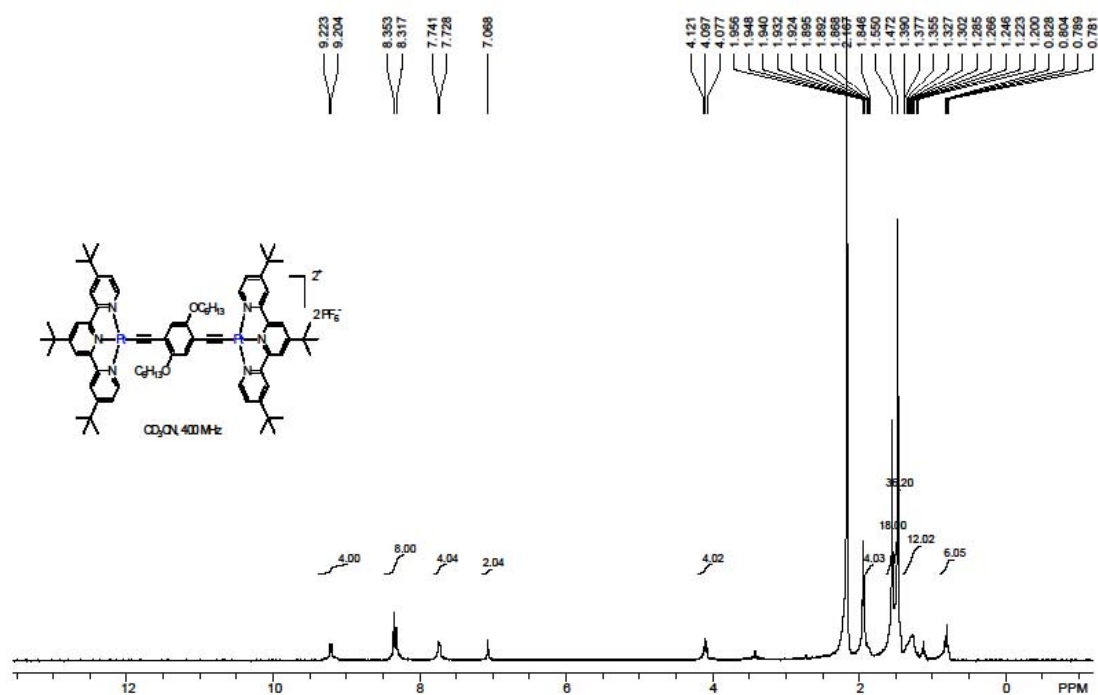


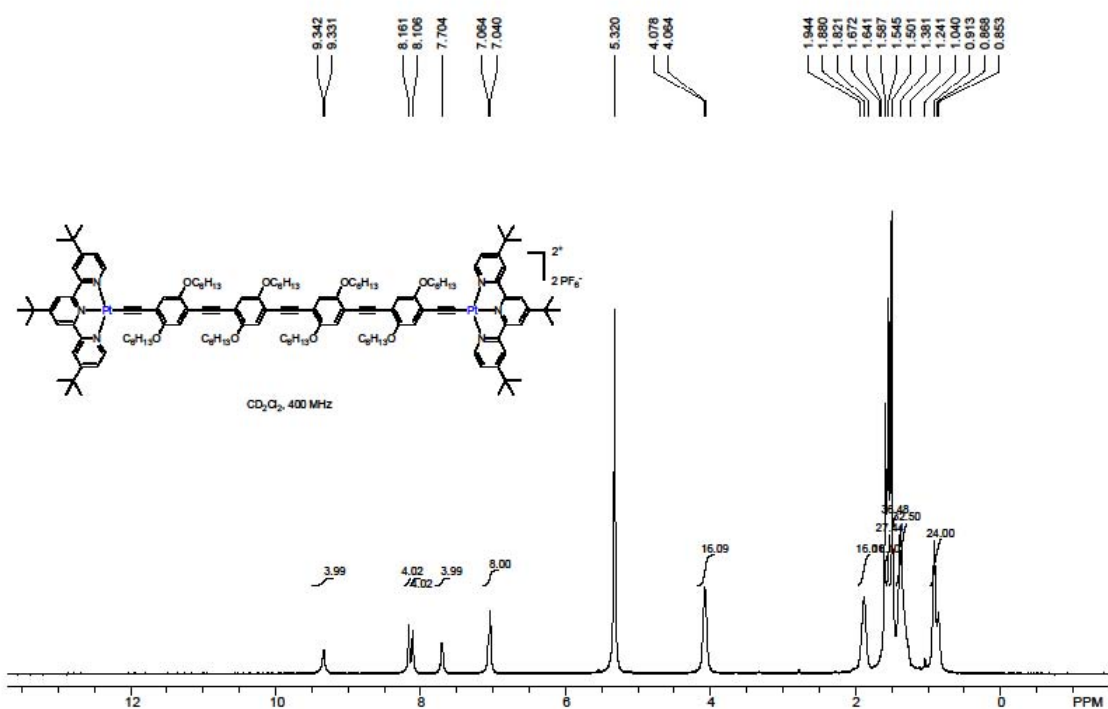


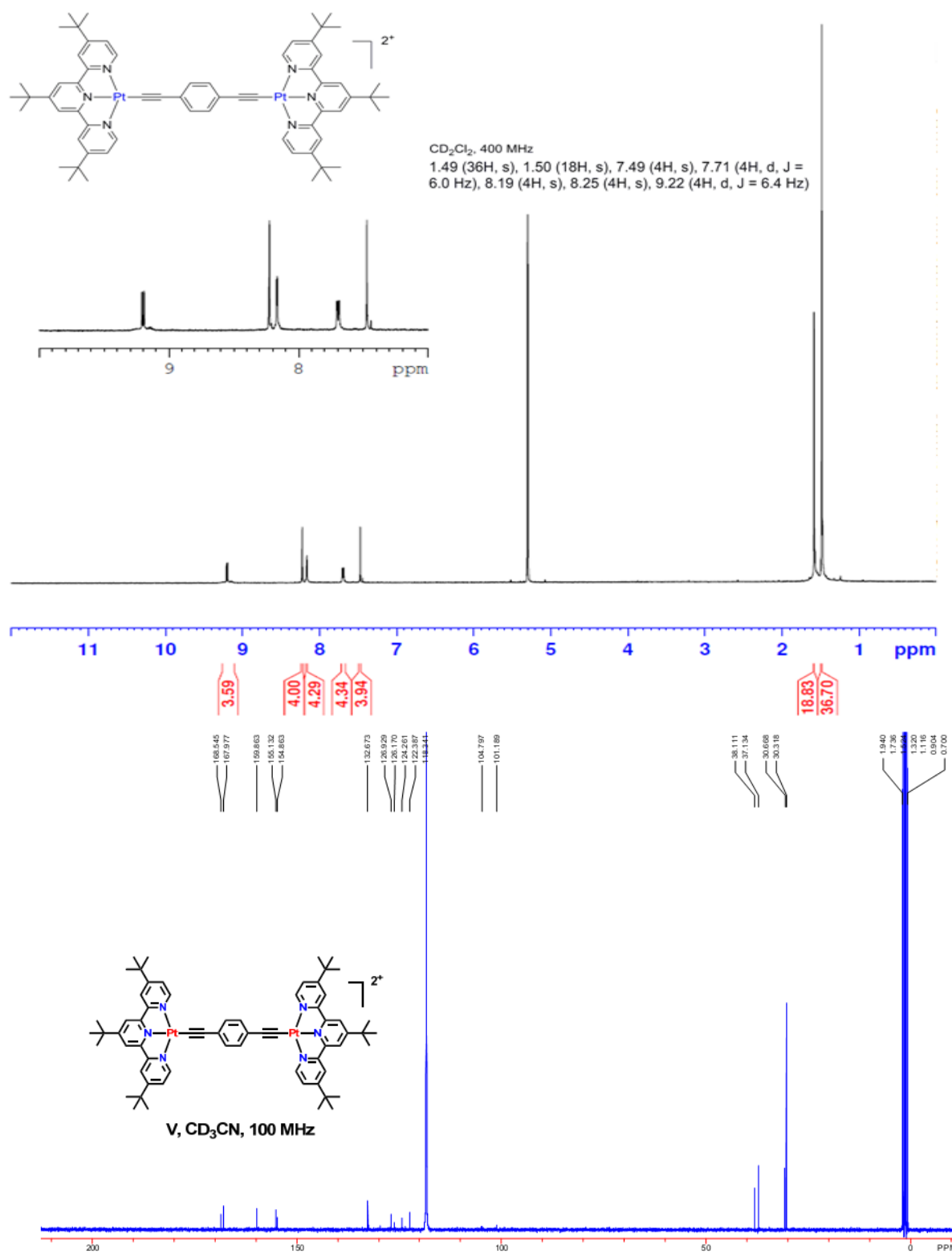


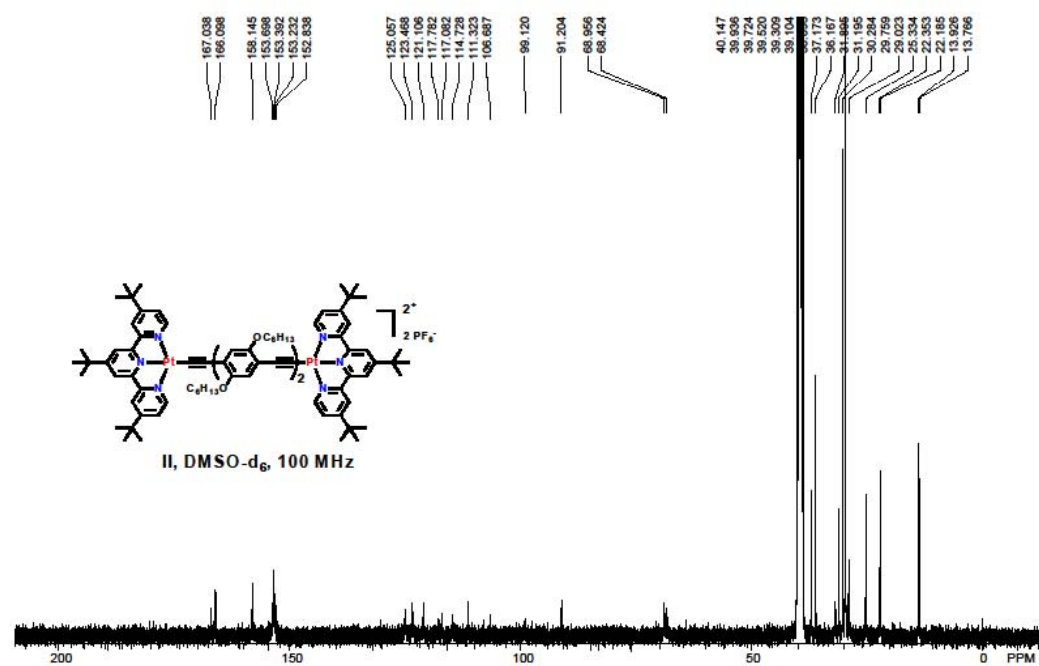
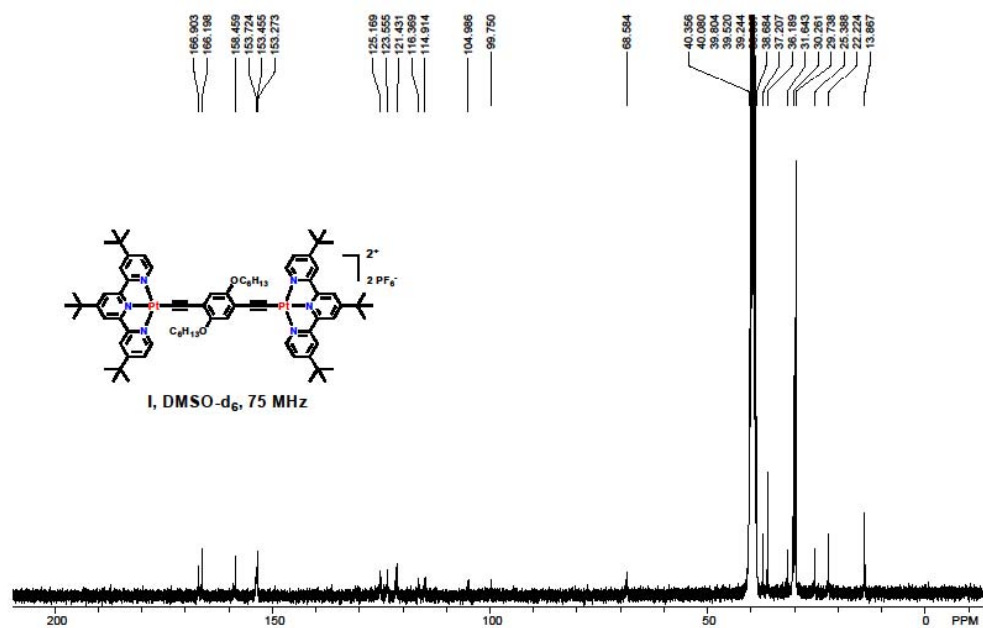




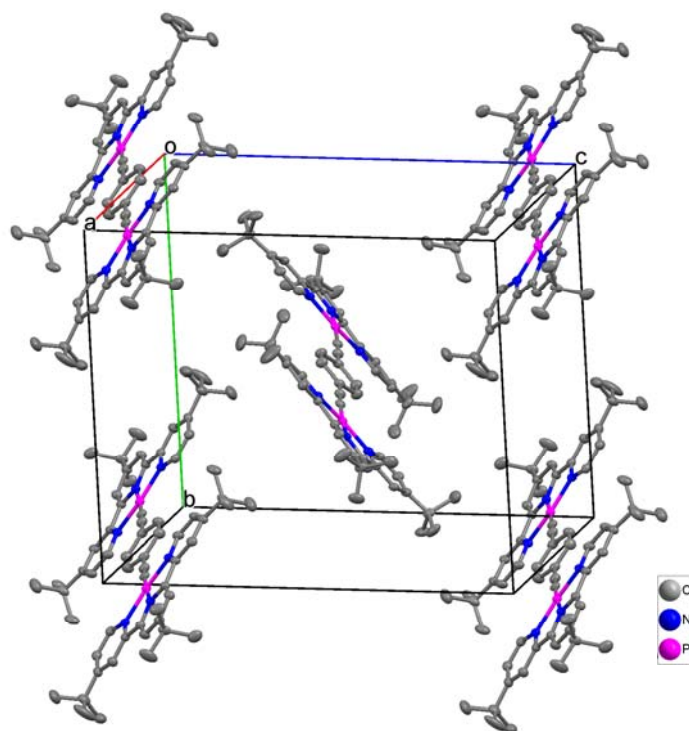








3. Crystal data and structure refinement for complex V



Scheme S1. Crystal packing diagram of compound **V**. Anions and hydrogen atoms have been omitted for clarity. Thermal ellipsoids were shown at the 50% probability level.

Table S2. Crystal data and structure refinement for V.

Empirical formula	C ₆₈ H ₇₆ Cl ₁₄ N ₆ O ₈ Pt ₂	
Formula weight	1991.83	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.4183(4) Å	α = 90°.
	b = 18.7275(6) Å	β = 101.3560(10)°.
	c = 20.6091(8) Å	γ = 90°.
Volume	3942.3(2) Å ³	
Z	2	
Density (calculated)	1.678 Mg/m ³	
Absorption coefficient	4.074 mm ⁻¹	
F(000)	1968	
Crystal size	0.25 x 0.22 x 0.20 mm ³	
Theta range for data collection	2.27 to 26.43°.	
Index ranges	-11 ≤ h ≤ 13, -23 ≤ k ≤ 23, -25 ≤ l ≤ 25	
Reflections collected	23777	
Independent reflections	8006 [R(int) = 0.0197]	
Completeness to theta = 26.43°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4963 and 0.4291	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8006 / 0 / 474	
Goodness-of-fit on F ²	1.086	
Final R indices [I > 2σ(I)]	R1 = 0.0297, wR2 = 0.0701	
R indices (all data)	R1 = 0.0382, wR2 = 0.0756	
Largest diff. peak and hole	1.932 and -1.051 e.Å ⁻³	

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

	x	y	z	U(eq)
C(1)	833(4)	11193(2)	294(2)	26(1)
C(2)	1428(4)	11765(2)	53(2)	29(1)
C(3)	2721(4)	11945(2)	323(2)	29(1)
C(4)	3377(4)	11506(2)	827(2)	28(1)
C(5)	2747(4)	10931(2)	1046(2)	23(1)
C(6)	3398(4)	10423(2)	1561(2)	23(1)
C(7)	4671(4)	10429(2)	1912(2)	26(1)
C(8)	5100(4)	9890(2)	2376(2)	25(1)
C(9)	4206(4)	9359(2)	2473(2)	25(1)
C(10)	2937(4)	9376(2)	2114(2)	22(1)
C(11)	1824(4)	8901(2)	2175(2)	23(1)
C(12)	1907(4)	8341(2)	2616(2)	25(1)
C(13)	795(4)	7953(2)	2681(2)	27(1)
C(14)	-375(4)	8143(2)	2257(2)	29(1)
C(15)	-413(4)	8698(2)	1818(2)	27(1)
C(16)	-1121(4)	10015(2)	792(2)	24(1)
C(17)	-2276(4)	10041(2)	562(2)	27(1)
C(18)	-3652(4)	10025(2)	282(2)	26(1)
C(19)	-4488(4)	9552(2)	517(2)	32(1)
C(20)	-5803(4)	9523(2)	239(2)	32(1)
C(21)	3338(5)	12607(2)	79(2)	39(1)
C(22)	2625(7)	13267(3)	289(3)	58(2)
C(23)	3122(7)	12597(3)	-675(3)	63(2)
C(24)	4778(6)	12655(4)	372(4)	85(3)
C(25)	6501(4)	9878(2)	2781(2)	28(1)
C(26)	7373(5)	10423(3)	2534(3)	56(2)
C(27)	7088(4)	9131(3)	2751(3)	44(1)
C(28)	6424(5)	10043(3)	3501(3)	42(1)
C(29)	789(4)	7379(2)	3204(2)	33(1)
C(30)	2166(5)	7200(3)	3573(3)	47(1)
C(31)	129(5)	6700(2)	2885(3)	42(1)
C(32)	-10(6)	7676(3)	3697(3)	54(1)
C(1S)	7751(5)	2894(3)	9107(3)	45(1)

C(2S)	8029(15)	5173(8)	1183(8)	158(5)
Cl(1)	5357(1)	7365(1)	2306(1)	40(1)
Cl(2)	9109(2)	3104(1)	8776(1)	84(1)
Cl(3)	7875(2)	2014(1)	9404(1)	70(1)
Cl(4)	7639(2)	3498(1)	9741(1)	78(1)
Cl(4S)	7436(5)	5747(2)	1721(2)	81(1)
Cl(5S)	6609(7)	4949(3)	600(4)	124(2)
Cl(6S)	9356(5)	5013(3)	816(5)	181(3)
Cl(7S)	6778(5)	4547(3)	886(3)	116(2)
Cl(8S)	9229(6)	4743(4)	1409(5)	93(2)
Cl(9S)	8501(11)	5481(6)	1818(4)	133(5)
N(1)	1458(3)	10788(2)	787(2)	22(1)
N(2)	2579(3)	9902(2)	1669(2)	20(1)
N(3)	658(3)	9087(2)	1779(2)	22(1)
O(1)	4981(4)	7914(2)	1834(2)	56(1)
O(2)	6728(4)	7247(2)	2423(2)	65(1)
O(3)	4995(5)	7576(3)	2911(2)	86(2)
O(4)	4700(5)	6729(2)	2056(4)	128(3)
Pt(1)	749(1)	9947(1)	1207(1)	19(1)

Table S4. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **V**.

C(1)-N(1)	1.330(5)
C(1)-C(2)	1.380(6)
C(1)-H(1)	0.9500
C(2)-C(3)	1.393(6)
C(2)-H(2)	0.9500
C(3)-C(4)	1.395(6)
C(3)-C(21)	1.525(6)
C(4)-C(5)	1.381(5)
C(4)-H(4)	0.9500
C(5)-N(1)	1.370(5)
C(5)-C(6)	1.487(5)
C(6)-N(2)	1.342(5)
C(6)-C(7)	1.380(5)
C(7)-C(8)	1.400(6)
C(7)-H(7)	0.9500
C(8)-C(9)	1.405(5)
C(8)-C(25)	1.532(5)
C(9)-C(10)	1.382(5)
C(9)-H(9)	0.9500
C(10)-N(2)	1.348(5)
C(10)-C(11)	1.486(5)
C(11)-N(3)	1.368(5)
C(11)-C(12)	1.381(5)
C(12)-C(13)	1.395(5)
C(12)-H(12)	0.9500
C(13)-C(14)	1.397(6)
C(13)-C(29)	1.524(5)
C(14)-C(15)	1.374(6)
C(14)-H(14)	0.9500
C(15)-N(3)	1.348(5)
C(15)-H(15)	0.9500
C(16)-C(17)	1.205(6)
C(16)-Pt(1)	1.972(4)
C(17)-C(18)	1.436(6)
C(18)-C(19)	1.393(6)
C(18)-C(20)#1	1.397(6)

C(19)-C(20)	1.379(6)
C(19)-H(19)	0.9500
C(20)-C(18)#1	1.397(6)
C(20)-H(20)	0.9500
C(21)-C(24)	1.506(7)
C(21)-C(23)	1.525(7)
C(21)-C(22)	1.548(7)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-C(26)	1.520(6)
C(25)-C(27)	1.532(6)
C(25)-C(28)	1.534(7)
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-C(30)	1.524(6)
C(29)-C(31)	1.531(6)
C(29)-C(32)	1.539(7)
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800

C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(1S)-Cl(2)	1.733(6)
C(1S)-Cl(4)	1.750(5)
C(1S)-Cl(3)	1.754(5)
C(1S)-H(1S)	1.0000
C(2S)-Cl(9S)	1.426(16)
C(2S)-Cl(8S)	1.483(16)
C(2S)-Cl(6S)	1.727(16)
C(2S)-Cl(4S)	1.743(15)
C(2S)-Cl(5S)	1.762(16)
C(2S)-Cl(7S)	1.770(16)
Cl(1)-O(1)	1.417(4)
Cl(1)-O(2)	1.418(4)
Cl(1)-O(4)	1.419(4)
Cl(1)-O(3)	1.427(5)
Cl(4S)-Cl(9S)	1.196(13)
Cl(5S)-Cl(7S)	0.951(7)
Cl(6S)-Cl(8S)	1.352(10)
Cl(8S)-Cl(9S)	1.857(15)
N(1)-Pt(1)	2.007(3)
N(2)-Pt(1)	1.958(3)
N(3)-Pt(1)	2.009(3)

N(1)-C(1)-C(2)	122.1(4)
N(1)-C(1)-H(1)	119.0
C(2)-C(1)-H(1)	119.0
C(1)-C(2)-C(3)	120.8(4)
C(1)-C(2)-H(2)	119.6
C(3)-C(2)-H(2)	119.6
C(2)-C(3)-C(4)	116.6(4)
C(2)-C(3)-C(21)	120.1(4)
C(4)-C(3)-C(21)	123.2(4)
C(5)-C(4)-C(3)	120.5(4)
C(5)-C(4)-H(4)	119.7
C(3)-C(4)-H(4)	119.7
N(1)-C(5)-C(4)	121.2(4)
N(1)-C(5)-C(6)	115.2(3)

C(4)-C(5)-C(6)	123.6(4)
N(2)-C(6)-C(7)	119.7(4)
N(2)-C(6)-C(5)	111.6(3)
C(7)-C(6)-C(5)	128.7(4)
C(6)-C(7)-C(8)	119.8(4)
C(6)-C(7)-H(7)	120.1
C(8)-C(7)-H(7)	120.1
C(7)-C(8)-C(9)	118.4(4)
C(7)-C(8)-C(25)	121.7(4)
C(9)-C(8)-C(25)	119.9(4)
C(10)-C(9)-C(8)	119.9(4)
C(10)-C(9)-H(9)	120.0
C(8)-C(9)-H(9)	120.0
N(2)-C(10)-C(9)	119.2(3)
N(2)-C(10)-C(11)	112.3(3)
C(9)-C(10)-C(11)	128.4(4)
N(3)-C(11)-C(12)	121.3(4)
N(3)-C(11)-C(10)	114.5(3)
C(12)-C(11)-C(10)	124.2(4)
C(11)-C(12)-C(13)	120.8(4)
C(11)-C(12)-H(12)	119.6
C(13)-C(12)-H(12)	119.6
C(12)-C(13)-C(14)	116.6(4)
C(12)-C(13)-C(29)	123.6(4)
C(14)-C(13)-C(29)	119.7(4)
C(15)-C(14)-C(13)	120.7(4)
C(15)-C(14)-H(14)	119.6
C(13)-C(14)-H(14)	119.6
N(3)-C(15)-C(14)	122.1(4)
N(3)-C(15)-H(15)	119.0
C(14)-C(15)-H(15)	119.0
C(17)-C(16)-Pt(1)	177.2(4)
C(16)-C(17)-C(18)	176.4(4)
C(19)-C(18)-C(20)#1	117.7(4)
C(19)-C(18)-C(17)	121.1(4)
C(20)#1-C(18)-C(17)	121.2(4)
C(20)-C(19)-C(18)	121.2(4)
C(20)-C(19)-H(19)	119.4

C(18)-C(19)-H(19)	119.4
C(19)-C(20)-C(18)#1	121.1(4)
C(19)-C(20)-H(20)	119.5
C(18)#1-C(20)-H(20)	119.5
C(24)-C(21)-C(3)	111.6(4)
C(24)-C(21)-C(23)	110.2(5)
C(3)-C(21)-C(23)	109.8(4)
C(24)-C(21)-C(22)	109.5(5)
C(3)-C(21)-C(22)	107.5(4)
C(23)-C(21)-C(22)	108.2(4)
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(21)-C(23)-H(23A)	109.5
C(21)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(21)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(21)-C(24)-H(24A)	109.5
C(21)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(21)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(26)-C(25)-C(8)	112.1(4)
C(26)-C(25)-C(27)	109.3(4)
C(8)-C(25)-C(27)	109.7(3)
C(26)-C(25)-C(28)	109.6(4)
C(8)-C(25)-C(28)	107.3(3)
C(27)-C(25)-C(28)	108.7(4)
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5

H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(25)-C(28)-H(28A)	109.5
C(25)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(25)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(30)-C(29)-C(13)	112.0(3)
C(30)-C(29)-C(31)	109.2(4)
C(13)-C(29)-C(31)	110.3(4)
C(30)-C(29)-C(32)	109.2(4)
C(13)-C(29)-C(32)	106.9(4)
C(31)-C(29)-C(32)	109.2(4)
C(29)-C(30)-H(30A)	109.5
C(29)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(29)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(29)-C(31)-H(31A)	109.5
C(29)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(29)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(29)-C(32)-H(32A)	109.5
C(29)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(29)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5

Cl(2)-C(1S)-Cl(4)	109.1(3)
Cl(2)-C(1S)-Cl(3)	109.9(3)
Cl(4)-C(1S)-Cl(3)	111.0(3)
Cl(2)-C(1S)-H(1S)	108.9
Cl(4)-C(1S)-H(1S)	108.9
Cl(3)-C(1S)-H(1S)	108.9
Cl(9S)-C(2S)-Cl(8S)	79.3(11)
Cl(9S)-C(2S)-Cl(6S)	108.0(11)
Cl(8S)-C(2S)-Cl(6S)	49.1(6)
Cl(9S)-C(2S)-Cl(4S)	42.9(7)
Cl(8S)-C(2S)-Cl(4S)	121.2(11)
Cl(6S)-C(2S)-Cl(4S)	143.1(10)
Cl(9S)-C(2S)-Cl(5S)	144.4(12)
Cl(8S)-C(2S)-Cl(5S)	128.9(10)
Cl(6S)-C(2S)-Cl(5S)	107.4(9)
Cl(4S)-C(2S)-Cl(5S)	103.0(8)
Cl(9S)-C(2S)-Cl(7S)	133.1(11)
Cl(8S)-C(2S)-Cl(7S)	105.4(9)
Cl(6S)-C(2S)-Cl(7S)	109.4(8)
Cl(4S)-C(2S)-Cl(7S)	107.4(8)
Cl(5S)-C(2S)-Cl(7S)	31.2(4)
O(1)-Cl(1)-O(2)	111.2(3)
O(1)-Cl(1)-O(4)	108.2(3)
O(2)-Cl(1)-O(4)	109.2(3)
O(1)-Cl(1)-O(3)	108.3(3)
O(2)-Cl(1)-O(3)	109.0(3)
O(4)-Cl(1)-O(3)	111.0(4)
Cl(9S)-Cl(4S)-C(2S)	54.3(6)
Cl(7S)-Cl(5S)-C(2S)	74.8(8)
Cl(8S)-Cl(6S)-C(2S)	56.0(6)
Cl(5S)-Cl(7S)-C(2S)	73.9(7)
Cl(6S)-Cl(8S)-C(2S)	74.9(7)
Cl(6S)-Cl(8S)-Cl(9S)	104.6(5)
C(2S)-Cl(8S)-Cl(9S)	49.0(7)
Cl(4S)-Cl(9S)-C(2S)	82.8(9)
Cl(4S)-Cl(9S)-Cl(8S)	133.0(6)
C(2S)-Cl(9S)-Cl(8S)	51.7(7)
C(1)-N(1)-C(5)	118.7(3)

C(1)-N(1)-Pt(1)	127.6(3)
C(5)-N(1)-Pt(1)	113.7(2)
C(6)-N(2)-C(10)	123.0(3)
C(6)-N(2)-Pt(1)	118.6(3)
C(10)-N(2)-Pt(1)	118.3(3)
C(15)-N(3)-C(11)	118.4(3)
C(15)-N(3)-Pt(1)	127.1(3)
C(11)-N(3)-Pt(1)	114.5(2)
N(2)-Pt(1)-C(16)	176.50(14)
N(2)-Pt(1)-N(1)	80.62(13)
C(16)-Pt(1)-N(1)	100.26(15)
N(2)-Pt(1)-N(3)	80.51(13)
C(16)-Pt(1)-N(3)	98.59(14)
N(1)-Pt(1)-N(3)	161.13(13)

Symmetry transformations used to generate equivalent atoms:

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