Supporting Information

for

Fluorine-free Blue Phosphorescent Emitters for Efficient Phosphorescent Organic Light Emitting Diodes

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- **Table S6.** Intermolecular C-H···π for **2** [Å and °]. *Cg*1, *Cg*2, *Cg*3, *Cg*4, *Cg*5, *Cg*6, and *Cg*7 are the centroids of the N2/C6-C10, N3/C14-C16, N5/C27-C31, N6/C33-C37, N7/C38-C42, N9/C51-C55, and N10/C59-C63 pyridine rings, respectively.

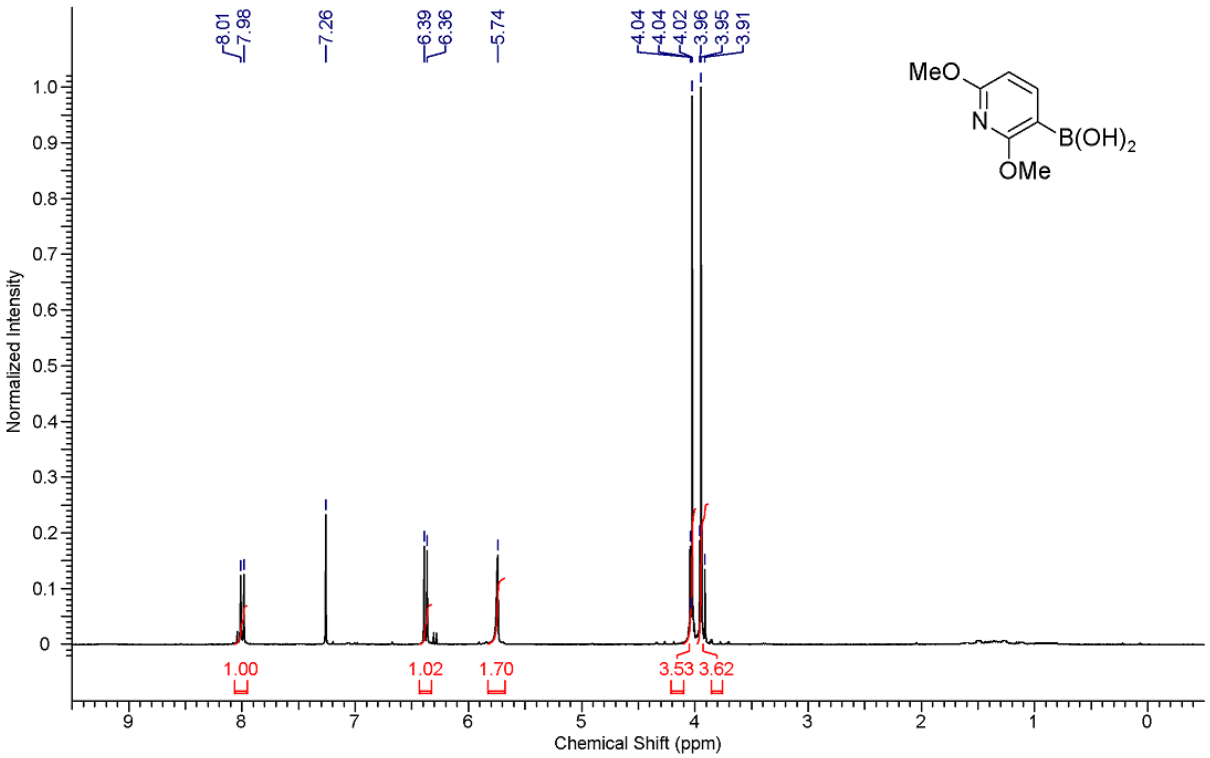

Figure S1. ^{1}H NMR of *2,5-dimethoxypyridine-3-boronic acid.* in $CDCl_3$.

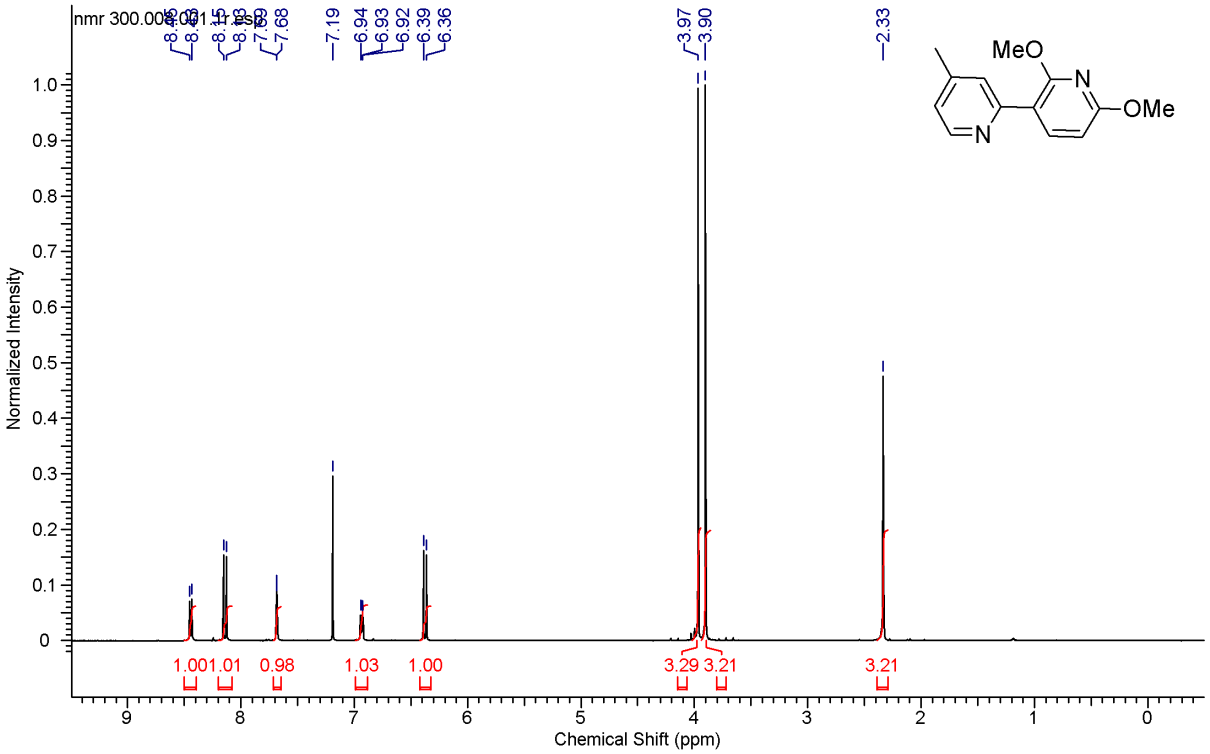

Figure S2. ^{1}H NMR of *2',6'-dimethoxy-4-methyl-2,3'-bipyridine* in $CDCl_3$.

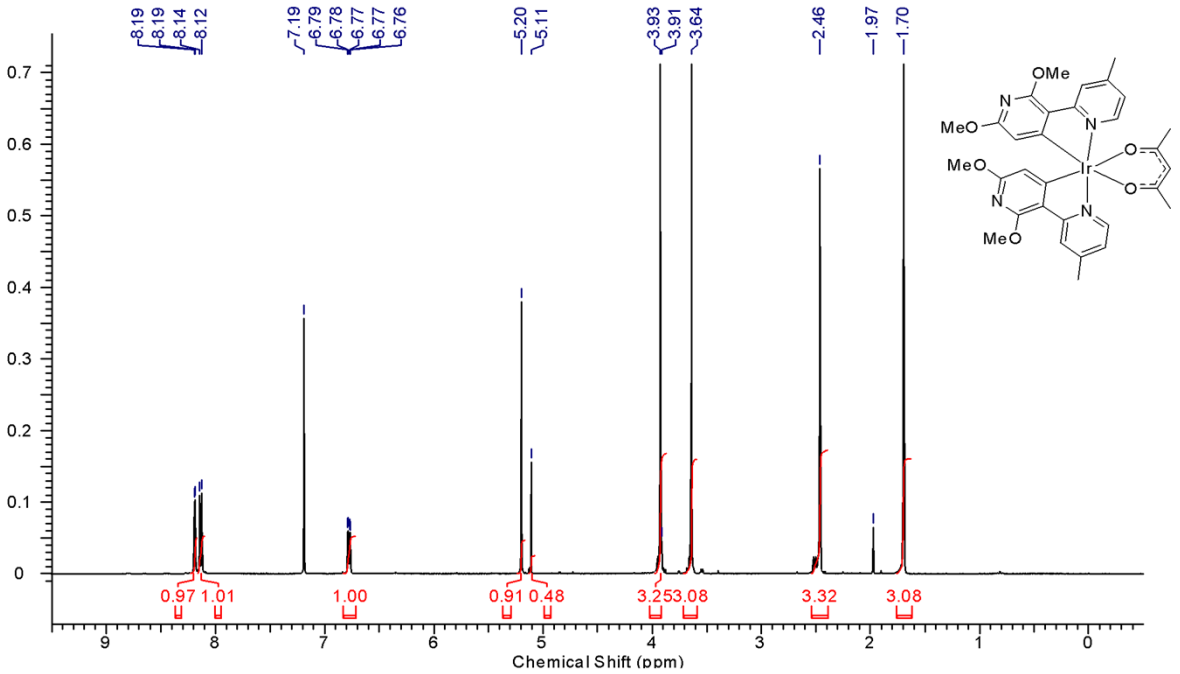

Figure S3. ^{1}H NMR of **1** in $CDCl_3$.

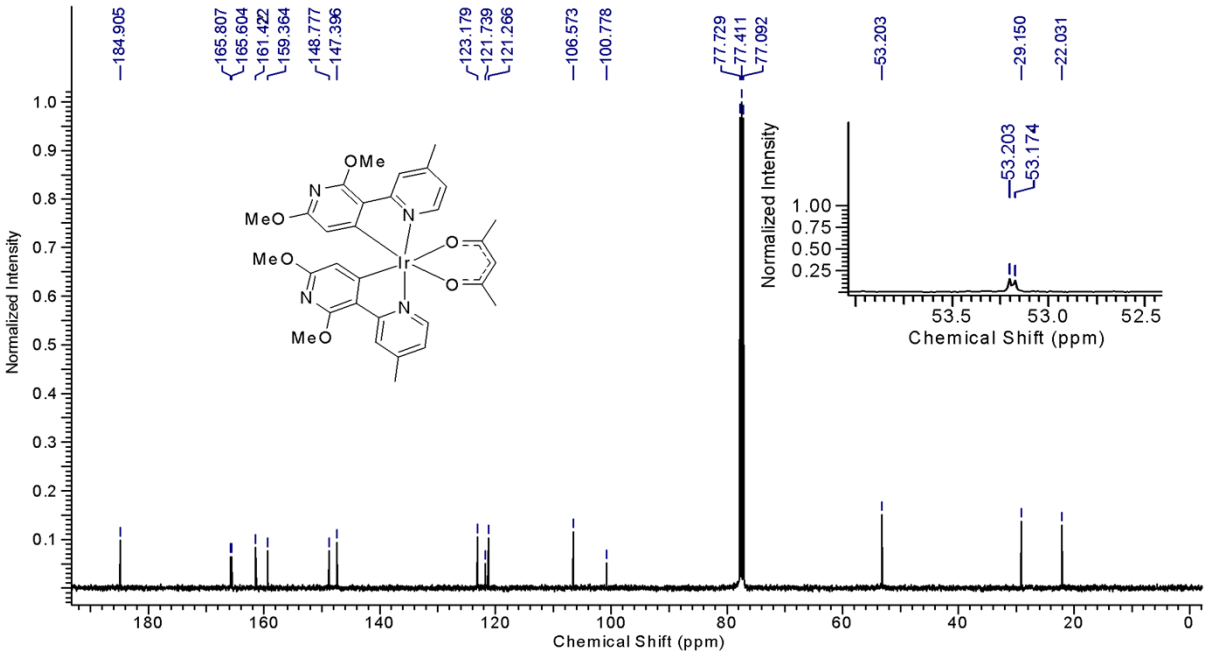

Figure S4. ^{13}C NMR of **1** in $CDCl_3$.

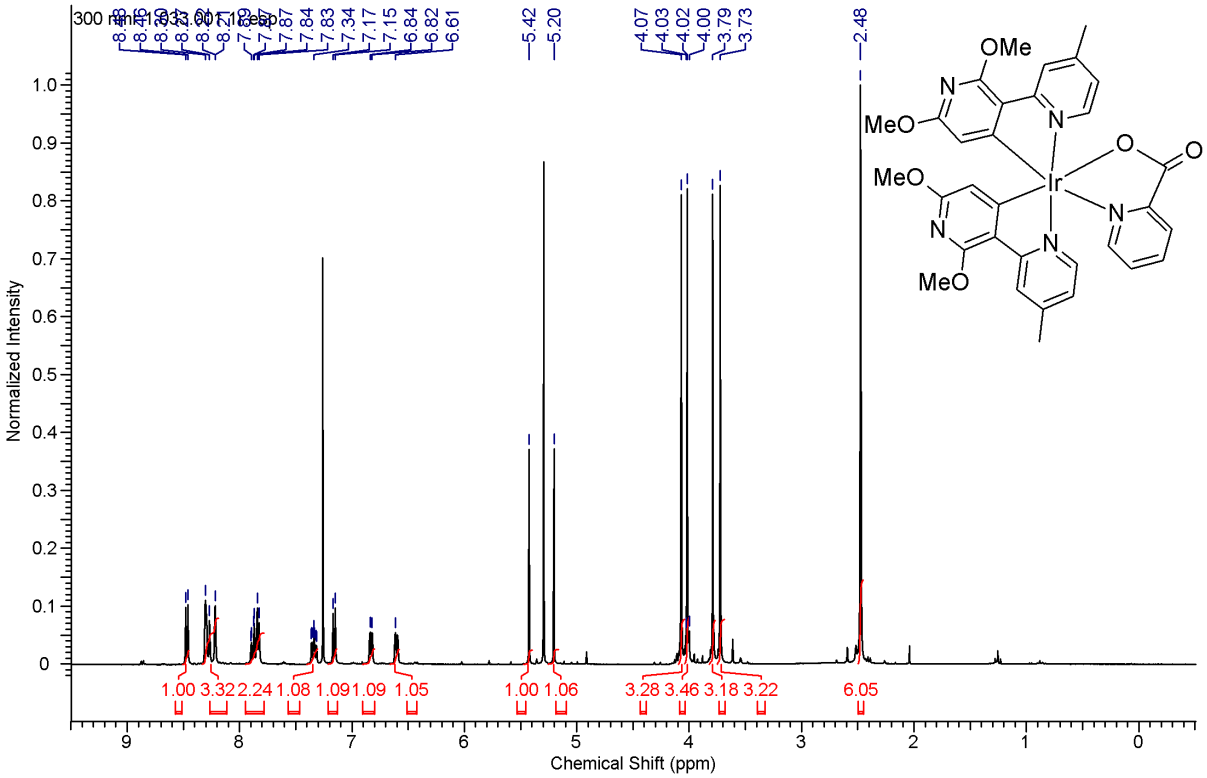

Figure S5. ^{1}H NMR of **2** in $CDCl_3$.

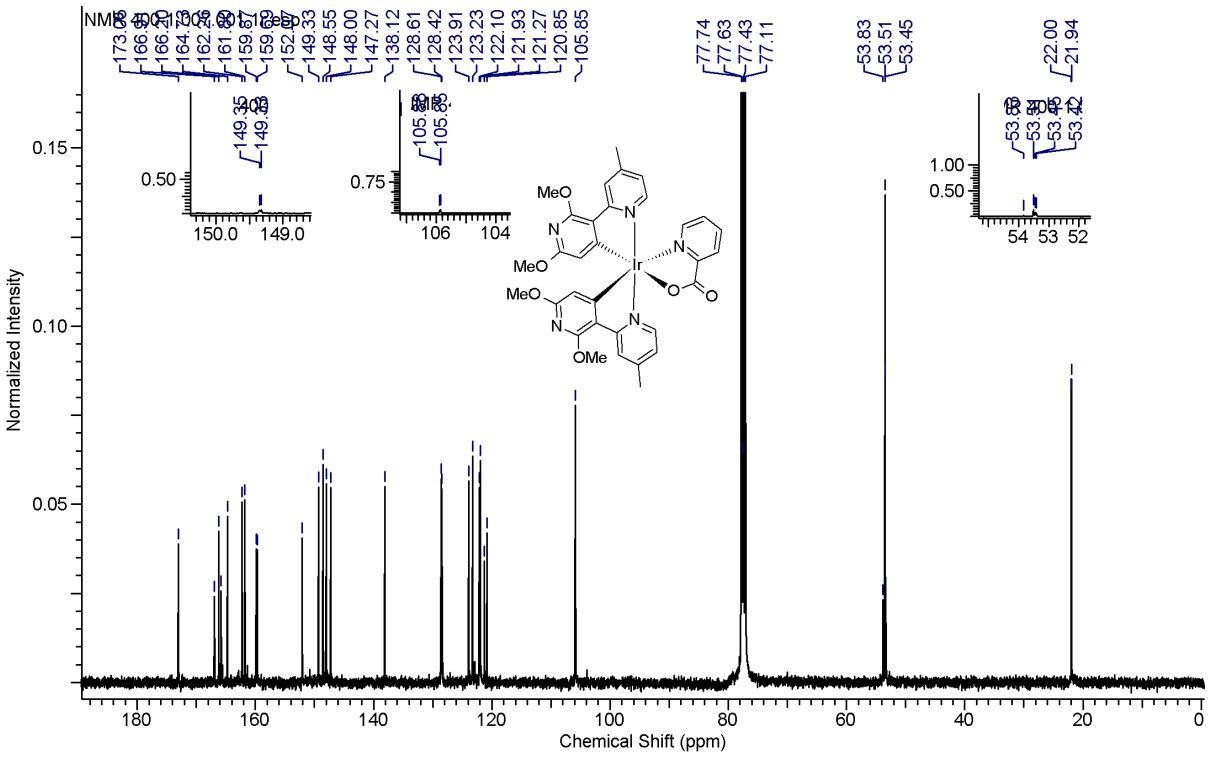

Figure S6. ^{13}C NMR of **2** in $CDCl_3$.

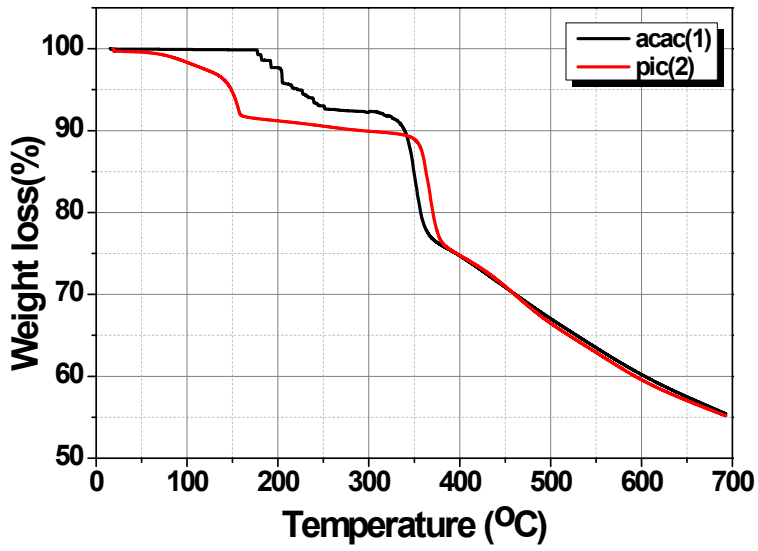

Figure S7. TGA curves of **1** and **2**.

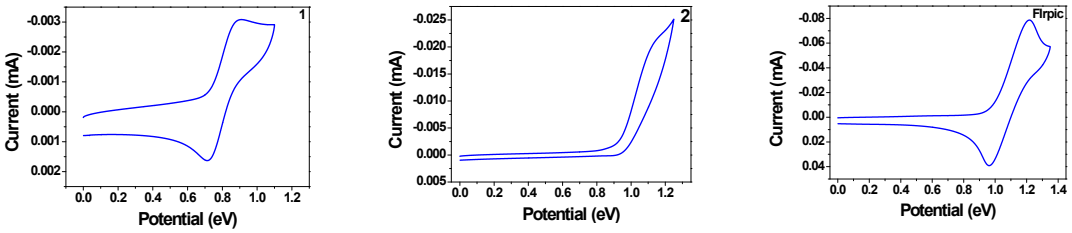

Figure S8. Oxidation potentials of **1**, **2** and **Firpic**.

Table S1. Crystal Data and Structure Refinement for **1** and **2**.

Identification code	**1**	**2**
Empirical formula	$C_{31}H_{33}IrN_4O_6$	$C_{36}H_{38}IrN_5O_8$
Formula weight	749.81	860.91
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	*Aba*2	*P*-1
a (Å)	15.1324(5)	14.8259(15)
b (Å)	19.6891(7)	15.4270(15)
c (Å)	9.9117(3)	16.4898(16)
α (°)	90	87.206(5)
β (°)	90	77.253(4)
γ (°)	90	71.403(4)
Volume (Å^3)	2953.12(17)	3485.6(6)
Z	4	4
Density (calculated) (Mg/m^3)	1.686	1.641
Absorption coefficient (mm^{-1})	4.571	3.890
F(000)	1488	1720
Crystal size (mm^3)	0.10 × 0.20 × 0.32	0.06 × 0.10 × 0.15
Theta range for data collection	2.07 to 28.37°	0.86 to 27.00°
Index ranges	-19<=*h*<=20	-16<=*h*<=18
	-18<=*k*<=26	-19<=*k*<=19
	-13<=*l*<=12	-21<=*l*<=21

Reflections collected	14188	60581
Independent reflections	3636 [R(int) = 0.0422]	15098 [R(int) = 0.0438]
Completeness to theta = 26.00°	99.8 %	99.3 %
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6578 and 0.3225	0.8001 and 0.5930
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3636 / 1 / 191	15098 / 0 / 901
Goodness-of-fit on F^2	1.055	1.007
Final R indices [I>2σ(I)]	R_1 = 0.0203, wR_2 = 0.0504	R_1 = 0.0327, wR_2 = 0.0651
R indices (all data)	R_1 = 0.0278, wR_2 = 0.0547	R_1 = 0.0515, wR_2 = 0.0728
Largest diff. peak and hole (e.Å^{-3})	0.940 and -0.359	1.536 and -1.144

Table S2. Selected bond lengths (Å) and bond angles (°) for **1**.

Ir1-C1	1.981(4)	Ir1-N1	2.035(2)
Ir1-O3	2.125(3)		
C1-Ir1-C1^{i}	92.8(2)	C1-Ir1-N1	80.78(13)
C1-Ir1-O3	89.27(10)	C1-Ir1-O3^{i}	175.90(14)
N1-Ir1-C1^{i}	94.25(13)	N1-Ir1-O3	89.56(10)
N1-Ir1-N1^{i}	172.84(17)	N1-Ir1-O3^{i}	95.56(10)
O3-Ir1-O3^{i}	88.86(14)		

Symmetry transformation used to generate equivalent atoms: i) -x, -y, z.

Table S3. Selected bond lengths (Å) and bond angles (°) for **2**.

Ir1-C10	1.978(4)	Ir1-C23	1.989(4)
Ir1-N1	2.036(3)	Ir1-N3	2.040(3)
Ir1-N5	2.142(3)	Ir1-O5	2.148(3)
Ir2-C42	2.001(4)	Ir2-C55	1.995(4)
Ir2-N6	2.047(3)	Ir2-N8	2.026(3)
Ir2-N10	2.139(3)	Ir2-O11	2.159(3)
C10-Ir1-C23	89.61(15)	C10-Ir1-N1	80.30(14)
C10-Ir1-N3	95.85(14)	C10-Ir1-N5	98.22(14)
C10-Ir1-O5	173.14(12)	C23-Ir1-N1	96.18(14)
C23-Ir1-N3	80.50(14)	C23-Ir1-N5	171.59(13)
C23-Ir1-O5	95.71(13)	N1-Ir1-N3	174.99(12)
N1-Ir1-N5	88.21(12)	N1-Ir1-O5	94.77(11)
N3-Ir1-N5	95.56(12)	N3-Ir1-O5	89.32(11)
N5-Ir1-O5	76.74(11)	C42-Ir2-C55	88.41(16)
C42-Ir2-N6	80.21(15)	C42-Ir2-N8	94.60(15)
C42-Ir2-N10	173.50(14)	C42-Ir2-O11	96.73(13)
C55-Ir2-N6	100.44(15)	C55-Ir2-N8	80.03(16)
C55-Ir2-N10	97.95(14)	C55-Ir2-O11	173.10(13)
N6-Ir2-N10	97.22(12)	N6-Ir2-O11	85.02(12)
N8-Ir2-N6	174.75(13)	N8-Ir2-N10	87.87(13)
N8-Ir2-O11	94.92(12)	N10-Ir2-O11	77.04(11)

Table S4. Intermolecular C-H···O Hydrogen Bonds for **1** and **2** [Å and °]

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
Complex **1**				
C12-H12A···O3^{i}	0.98	2.59	3.395(5)	140.0
[Symmetry transformations used to generate equivalent atoms: i) -*x*, -*y*+1/2, *z*+1/2.]				
Complex **2**				
C2-H2···O12	0.95	2.41	3.266(5)	150.6
C46-H46···O12^{i}	0.95	2.56	3.133(5)	118.7
C61-H61···O2^{ii}	0.95	2.44	3.291(5)	148.9
C65-H65C···O6^{iii}	0.98	2.37	3.270(7)	151.9
C67-H67B···O10^{iv}	0.99	2.43	3.253(7)	139.6
C69-H69B···O13^{v}	0.98	2.45	3.329(9)	149.2
[Symmetry transformations used to generate equivalent atoms: i) -*x*+1, -*y*, -*z*+1; ii) *x*, *y*-1, *z*; iii) *x*, *y*+1, *z*; iv) -*x*+1, -*y*+1, -*z*; v) *x*-1, *y*, *z*.]				

Table S5. Intermolecular C-H···π for **1** [Å and °]. *Cg*1, and *Cg*2 are the centroids of the N1/C6-C10, and N2/C1-C5 pyridine rings, respectively.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C11-H11A···*Cg*2^{i}	0.98	3.23	4.07(5)	145
C12-H12B···*Cg*1^{ii}	0.98	3.32	3.90(4)	119

Symmetry transformations used to generate equivalent atoms: i) -*x*+1/2, *y*, *z*+1/2;

ii) -*x*, -*y*+1/2, *z*+1/2.

Table S6. Intermolecular C-H···π for **2** [Å and °]. *Cg*1, *Cg*2, *Cg*3, *Cg*4, *Cg*5, *Cg*6, and *Cg*7 are the centroids of the N2/C6-C10, N3/C14-C16, N5/C27-C31, N6/C33-C37, N7/C38-C42, N9/C51-C55, and N10/C59-C63 pyridine rings, respectively.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C11-H11A···*Cg*7^{i}	0.98	3.13	3.66(4)	115
C11-H11B···*Cg*1^{ii}	0.98	2.99	3.82(5)	143
C13-H13B···*Cg*5^{ii}	0.98	2.96	3.64(5)	127
C24-H24A···*Cg*4^{iii}	0.98	3.25	3.89(5)	124
C25-H25B···*Cg*6^{iv}	0.98	3.18	4.08(5)	153
C28-H28···*Cg*5^{v}	0.95	2.67	3.56(5)	156
C45-H45B···*Cg*1^{vi}	0.98	3.04	3.77(5)	132
C56-H56A···*Cg*3^{i}	0.98	3.13	3.77(4)	124
C69-H69A···*Cg*2^{vi}	0.98	3.26	4.11(5)	146
C72-H72B···*Cg*2^{iii}	0.98	3.11	3.92(4)	141

Symmetry transformations used to generate equivalent atoms: i) -*x*+1, -*y*, -*z*+1; ii) -*x*+1, -*y*+1, -*z*+1; iii) -*x*+1, -*y*+1, -*z*; iv) *x*, *y*+1, *z*; v) *x*+1, *y*, *z*; vi) *x*-1, *y*, *z*.