## **Supporting Information**

## Peripherally Cyclometalated Iridium Complexes of Dipyridylporphyrin

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Figure S2. <sup>1</sup>H NMR spectrum of 3 in CDCl<sub>3</sub>.



*Figure S3.* H–H COSY spectrum of **3** in CDCl<sub>3</sub>. The signal at  $\delta = -0.83$  ppm due to the C<sub>8</sub>H<sub>10</sub>O ligand has cross peaks in the circles with a signal around  $\delta = 1.8$  ppm, which is overlapped with *tert*-butyl proton signals.



Table S1. Selected bond lengths (Å) and angles (°)			
2		3	
Ir-C20	1.969(7)	Ir-C20	1.994(7)
Ir-Cl1	2.3333(17)	Ir-C73	2.087(8)
Ir-Cl2	2.3490(17)	Ir-C76	2.351(10)
Ir–O1	2.250(5)	Ir-C77	2.213(10)
Ir–N5	2.045(7)	Ir–C78	2.143(9)
Ir-N6	2.049(6)	Ir-N5	2.134(7)
		Ir-N6	2.145(6)
C20-Ir-N5	92.2(3)	C20-Ir-N5	88.1(3)
C20-Ir-N6	92.4(3)	C20-Ir-N6	88.1(3)
N5-Ir-N6	175.3(2)	N5-Ir-N6	96.6(2)
C20-Ir-O1	176.9(2)	C20-Ir-C73	90.0(3)
N5-Ir-O1	88.0(2)	N5-Ir-C73	87.7(3)
N6-Ir-O1	87.4(2)	N6-Ir-C73	175.3(3)
C20-Ir-Cl2	91.91(18)	C20-Ir-C78	98.9(3)
N5-Ir-Cl2	90.32(17)	N5-Ir-C78	168.2(3)
N6-Ir-Cl2	90.27(16)	N6-Ir-C78	93.2(3)
O1-Ir-Cl2	84.99(14)	C73-Ir-C78	82.8(3)
C20-Ir-Cl1	92.23(18)	C73-Ir-C76	79.8(4)
N5-Ir-Cl1	90.50(17)	N5-Ir-C76	102.1(4)
N6-Ir-Cl1	88.58(16)	N6-Ir-C76	101.2(3)
O1-Ir-Cl1	90.87(14)	C73-Ir-C76	79.8(4)
Cl1-Ir-Cl2	175.78(6)	C76-Ir-C78	69.3(4)



*Figure S4.* Cyclic voltammograms (0.1 V·s<sup>-1</sup>) of (a) **3** and (b) **2** in  $CH_2Cl_2$  (0.1 M TBAPF<sub>6</sub>). working electrode: Pt, counter electrode: Pt, reference electrode: Ag/AgClO<sub>4</sub>.



*Figure S5.* MO diagrams for 1, 2 and 3 calculated at the B3LYP/LANL2DZ level.