

## Electronic Supplementary Information (ESI)

### Oxygen-bridged triarylamine polycyclic unit based tris-cyclometalated heteroleptic iridium(III) complex: correlation between structure and photophysical property

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#### Contents:

<b>General information.....</b>	<b>S2</b>
<b>X-ray crystal structure analysis.....</b>	<b>S2</b>
<b>Electrochemical determination.....</b>	<b>S5</b>
<b>DFT calculation.....</b>	<b>S6</b>
<b>NMR spectra.....</b>	<b>S8</b>
<b>References.....</b>	<b>S15</b>

## General information

Unless noted, all reagents or solvents were obtained from commercial suppliers and used without further purification. All air sensitive experiments were performed in N<sub>2</sub> atmosphere through schlenck technology. Intermediate **1-a** was synthesized according to literature procedures<sup>1</sup>. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured by using a Bruker 500 MHz spectrometer at room temperature. Mass spectra were conducted at Micromass Q-ToF instrument (ESI) and Agilent Technologies 5973N (EI). A Hitachi F-4600 fluorescence spectrophotometer was used to measure phosphorescence spectral. An Edinburgh FLS-920 spectrometer was used to determine phosphorescence quantum efficiency and lifetimes of the molecules in solution.

## X-ray crystal structure analysis

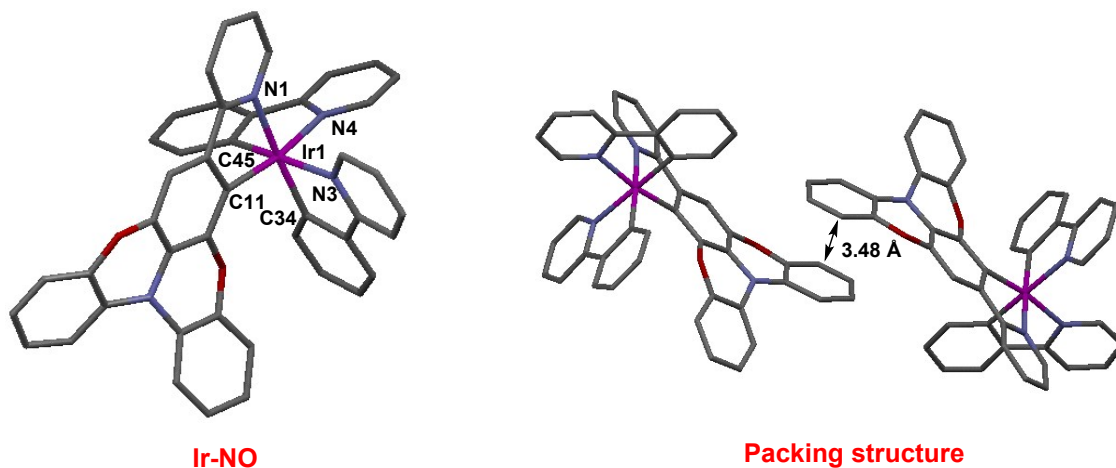
Single-crystals of **Ir-NO** and **Ir-O** were both obtained by slow diffusion of ethanol to their CH<sub>2</sub>Cl<sub>2</sub> solutions, respectively. The X-ray diffraction data were collected on a Bruker Smart CCD Apex DUO diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using the  $\omega$ -2 $\theta$  scan mode. Both crystal data are deposited in The Cambridge Crystallographic Data Centre (CCDC: 1864843 for **Ir-NO** and 1864844 for **Ir-O**).

**Table S1.** Crystallographic Data for **Ir-NO** and **Ir-O**.

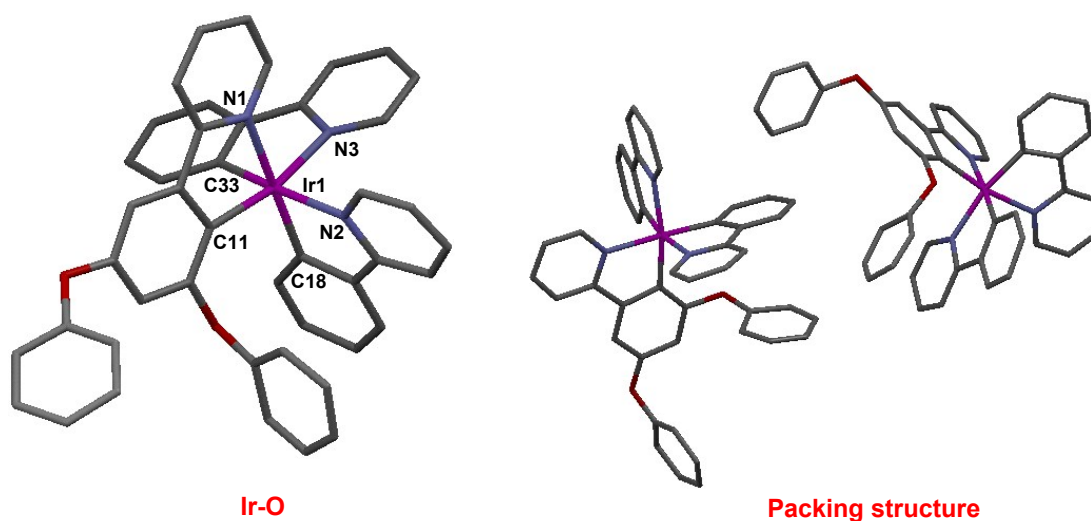
Complex	Ir-NO	Ir-O
chemical formula	4(C <sub>45</sub> H <sub>29</sub> IrN <sub>4</sub> O <sub>2</sub> )·2H <sub>2</sub> O	C <sub>45</sub> H <sub>32</sub> IrN <sub>3</sub> O <sub>2</sub>
formula weight	3435.71	838.96
crystal size (mm)	0.22 × 0.24 × 0.26	0.23 × 0.27 × 0.28
temperature (K)	291	296

radiation	0.71073	0.71073
crystal system	Monoclinic	Tetragonal
space group	C2/c	I-4
a(Å)	37.650(3)	27.492(3)
b(Å)	9.272(2)	27.492(3)
c(Å)	20.135(3)	9.296(3)
$\alpha$ (°)	90	90
$\beta$ (°)	96.852	90
$\gamma$ (°)	90	90
V(Å <sup>3</sup> )	6978.7(19)	7026(3)
Z	2	8
$\rho$ (calc) (g/cm <sup>3</sup> )	1.635	1.586
F (000)	3400	3328
absorp.coeff. (mm <sup>-1</sup> )	3.874	3.844
$\theta$ range (deg)	1.1 to 25.0	1.0 to 26.0
reflns collected	24457(R <sub>int</sub> = 0.074)	49759 (R <sub>int</sub> = 0.110)
indep. reflns	5890	6913
Refns obs.[I > 2 $\sigma$ (I)]	4553	5550
data/restr/paras	5890/0/475	6913/0/460
GOF	1.04	1.07
R <sub>1</sub> /wR <sub>2</sub> [I > 2 $\sigma$ (I)]	0.0389/0.0867	0.0545/0.1231
R <sub>1</sub> /wR <sub>2</sub> (all data)	0.0603/0.0924	0.0758/0.1310
larg peak and hole(e/Å <sup>3</sup> )	1.89/-1.24	1.29/-1.35

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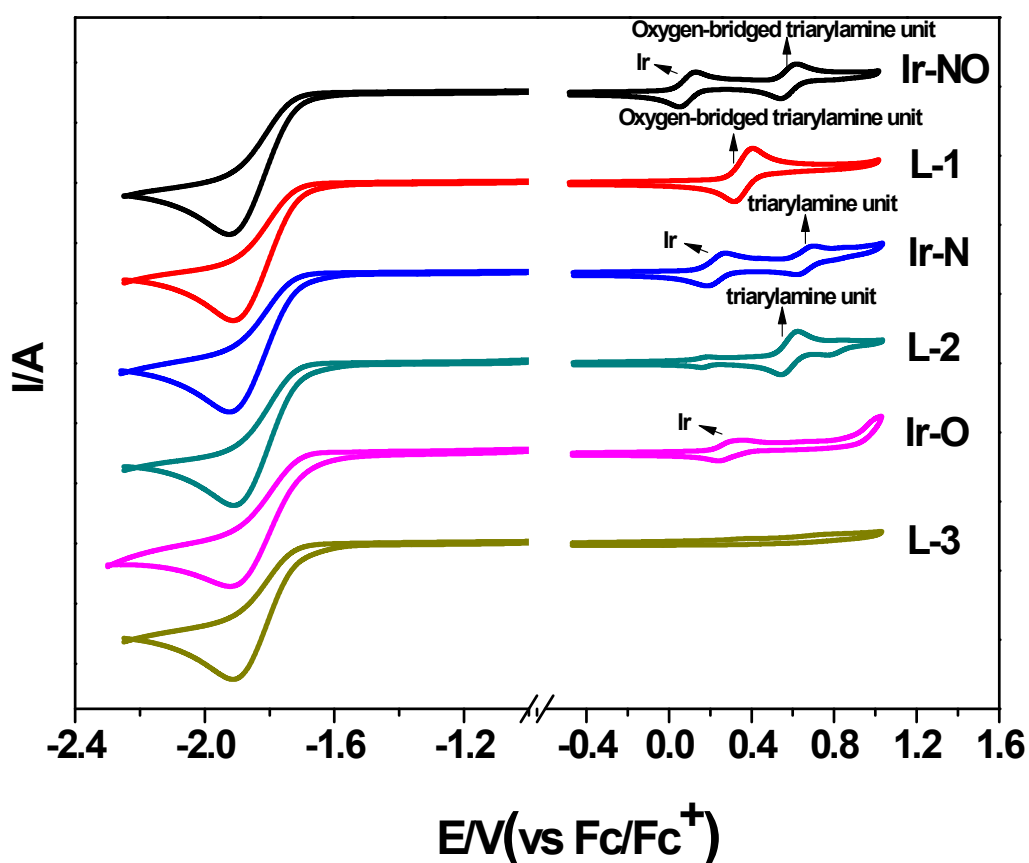
**Fig. S1.** Crystal and packing structure of **Ir-NO**, the hydrogen atoms have been omitted for clarity, selected bond lengths (Å) and angles (°): Ir1–N1 2.118(4), Ir1–N3 2.143(5), Ir1–N4 2.115(5), Ir1–C11 2.040(6), Ir1–C34 2.009(6), Ir1–C45 2.003(6); N1–Ir1–C11 79.4(2), N1–Ir1–N4 94.28(18), N1–Ir1–N3 93.93(17), N1–Ir1–C34 174.0(2), N1–Ir1–C45 91.7(2), C11–Ir1–C34 100.6(2), C11–Ir1–C45 95.5(2), C34–Ir1–C45 94.3(3).



**Fig. S2.** Crystal and packing structure of **Ir-O**, the hydrogen atoms have been omitted for clarity, selected bond lengths (Å) and angles (°): Ir1–N1 2.135(8), Ir1–N3 2.138(9), Ir1–N2 2.122(11), Ir1–C11 2.041(12), Ir1–C33 2.003(11), Ir1–C18 2.000(11); N1–Ir1–C11 80.0(4), N1–Ir1–N3 91.6(3), N1–Ir1–N2 97.7(4), N1–Ir1–C18 176.9(4), N1–Ir1–C33 90.2(4), C11–Ir1–C18 176.9(4), C11–Ir1–C33 93.1(4), C18–Ir1–C33 92.7(4).

## Electrochemical determination

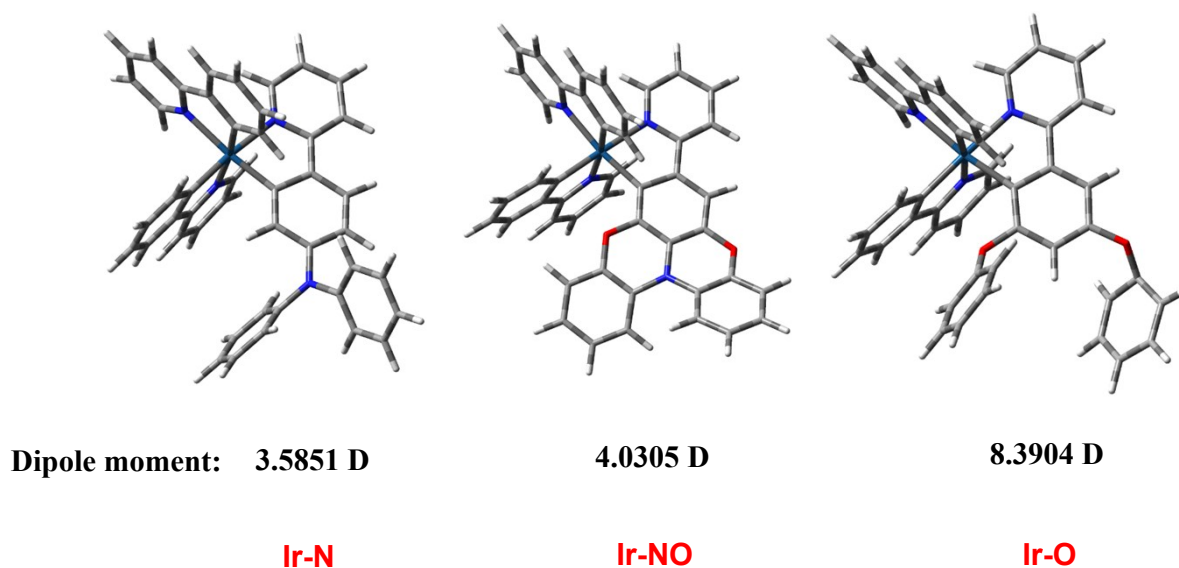
Cyclic Volta metric experiments were carried out with an IM6ex (Zahner) using three electrode cell assemblies. All measurements were carried out in a one-compartment cell under Argon, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and a Ag/Ag<sup>+</sup> reference electrode with a scan rate of 100 mV s<sup>-1</sup>. The supporting electrolyte was a 0.10 mol L<sup>-1</sup> CH<sub>2</sub>Cl<sub>2</sub> solution of tetrabutyl-ammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>). Each oxidation and reduction potential was calibrated with ferrocene as a reference.



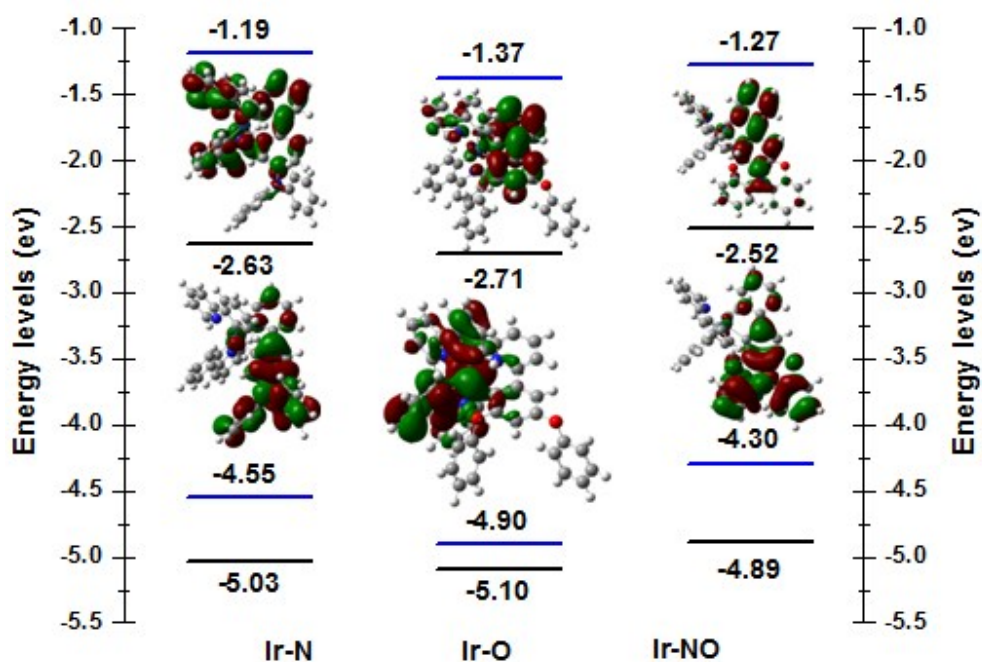
**Fig. S3.** Cyclic voltammograms of all complexes (Ir-NO, Ir-O and Ir-N) and all free ligands (L-1, L-2 and L-3) in degassed CH<sub>2</sub>Cl<sub>2</sub> solution (5\*10<sup>-4</sup> mol/L) with tetrabutyl-ammonium hexafluorophosphate (0.1 mol/L) as supporting electrolyte under the scan rate of 100 mV s<sup>-1</sup>.

## DFT calculation

DFT method was used to optimize the geometries all the complexes. The electronic transition energies and electron correlation effects were also calculated by (TD)-DFT method with the B3LYP functional (TD-B3LYP). The LANL2DZ basis set was used to treat with the iridium atom, and the 6-31G(d) basis set was used to treat with all other atoms. All calculations were carried out according to the Gaussian 09 program.<sup>2</sup>



**Fig. S4.** Calculated structure and dipole moment of excited state for **Ir-N**, **Ir-NO** and **Ir-O**.



**Fig. S5.** Comparison between calculated values and experimental values of Energy Levels of HOMO and LUMO.

**Table S2.** Calculated dipole moment of complexes in both ground state and excited state

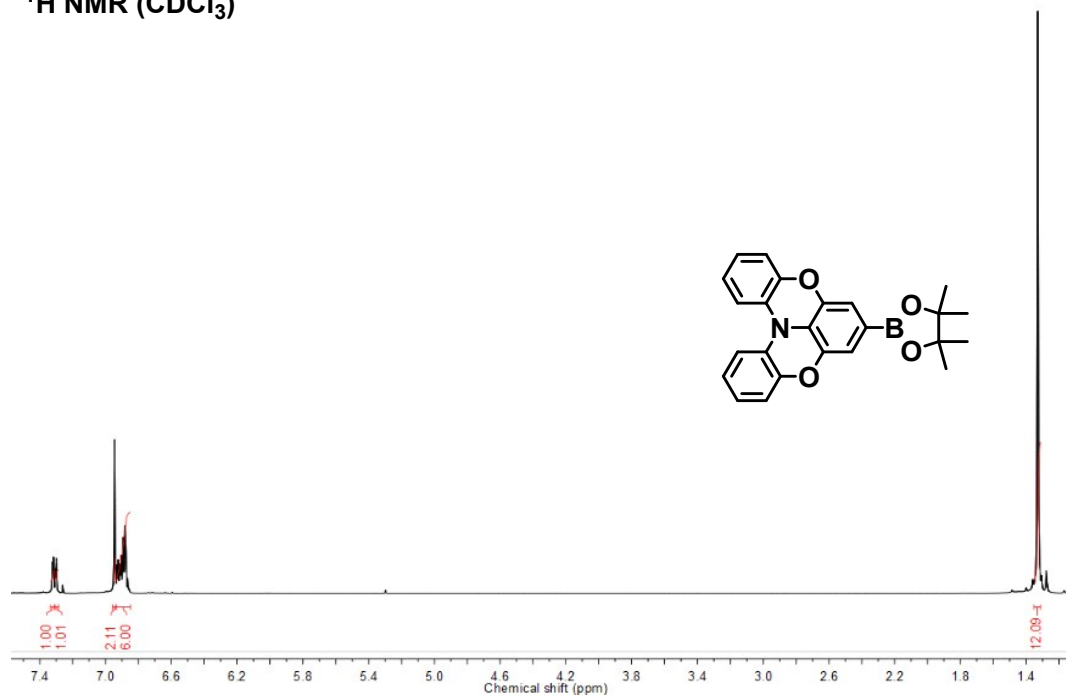
Compounds	Dipole moment (ground state) (D)	Dipole moment (excited state) (D)
<b>Ir-NO</b>	6.8178	4.0305
<b>Ir-N</b>	8.1733	3.5851
<b>Ir-O</b>	6.0813	8.3904

**Table S3.** Calculated energies and oscillator strengths for lowest-energy singlet (S<sub>1</sub>) and triplet (T<sub>1</sub>) transitions.

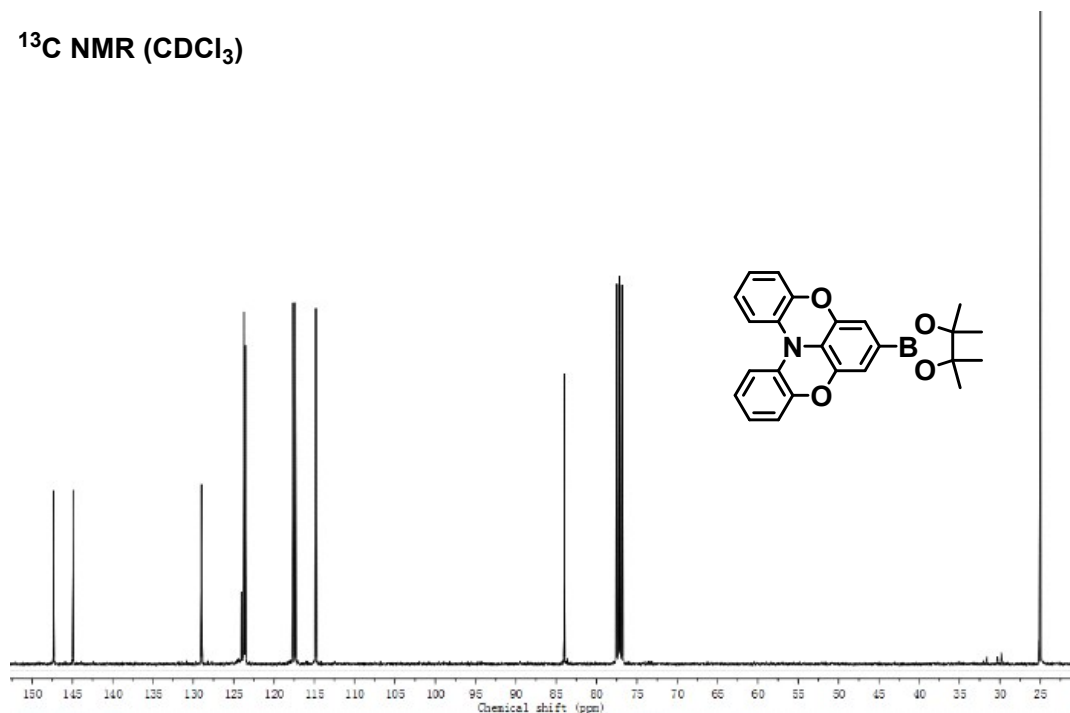
complexes	states	E (eV)	Oscillator strength	main configurations (CI coeff)	Character
<b>Ir-N</b>	S <sub>1</sub>	2.84	0.0596	HOMO→LUMO (0.56)	MLCT/ILCT/LLCT
	T <sub>1</sub>	2.01	0	HOMO→LUMO (0.65)	<sup>3</sup> ILCT/ <sup>3</sup> MLCT
<b>Ir-O</b>	S <sub>1</sub>	2.80	0.0023	HOMO→LUMO (0.64)	MLCT/LLCT/ILCT
	T <sub>1</sub>	1.90	0	HOMO→LUMO (0.68)	<sup>3</sup> ILCT/ <sup>3</sup> MLCT
<b>Ir-NO</b>	S <sub>1</sub>	2.58	0.1442	HOMO→LUMO (0.66)	ILCT/LLCT
	T <sub>1</sub>	1.68	0	HOMO→LUMO (0.67)	<sup>3</sup> ILCT

## NMR spectra

### $^1\text{H}$ NMR ( $\text{CDCl}_3$ )



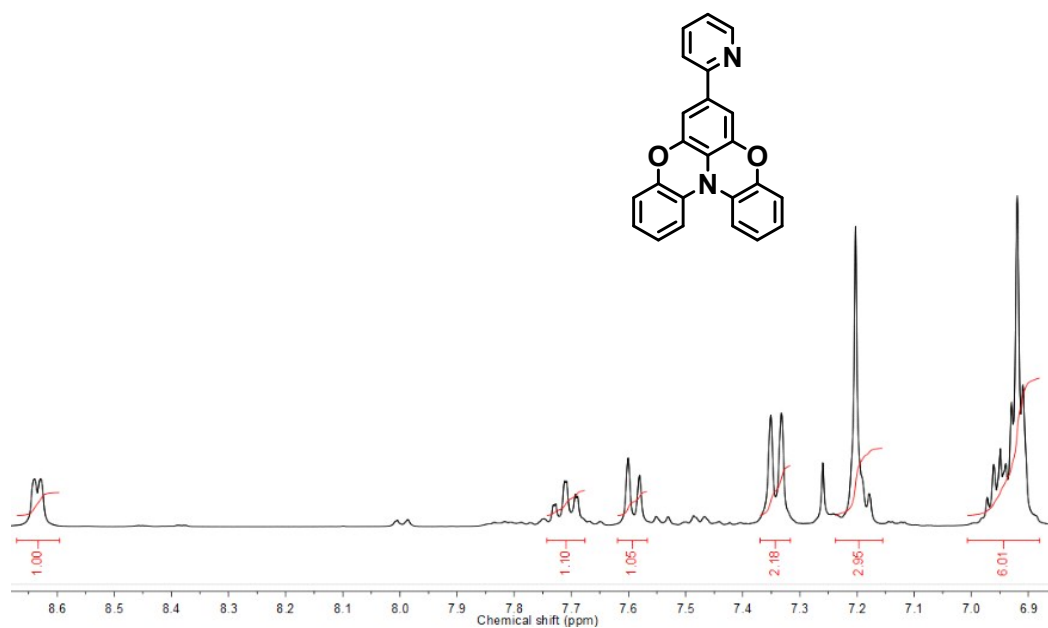
### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ )



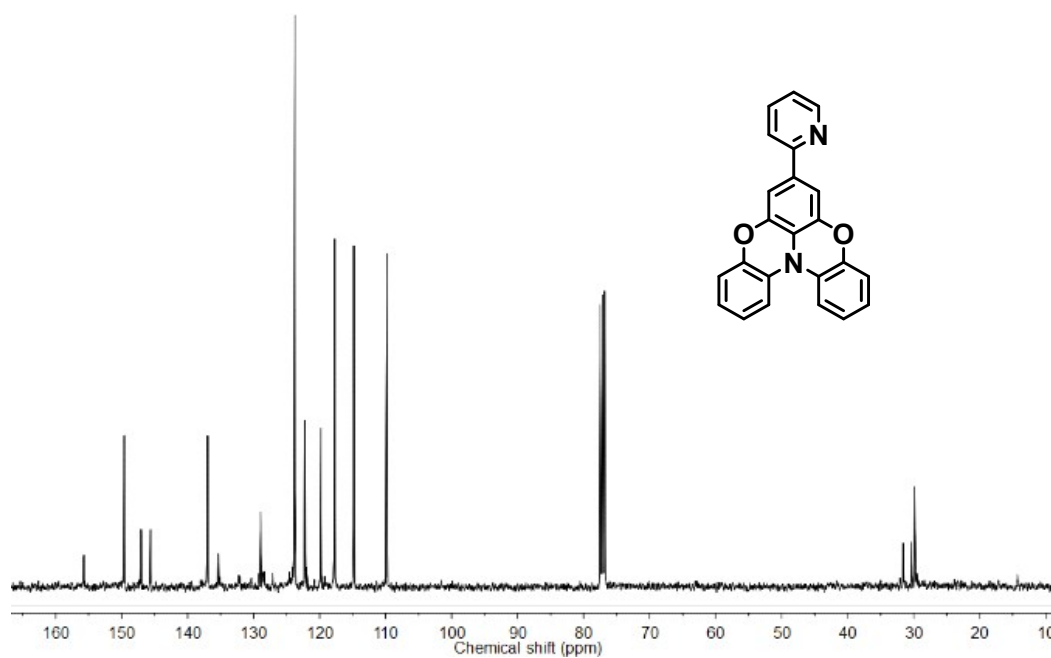
**Fig. S6.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **1-b**.



**$^1\text{H}$  NMR ( $\text{CDCl}_3$ )**

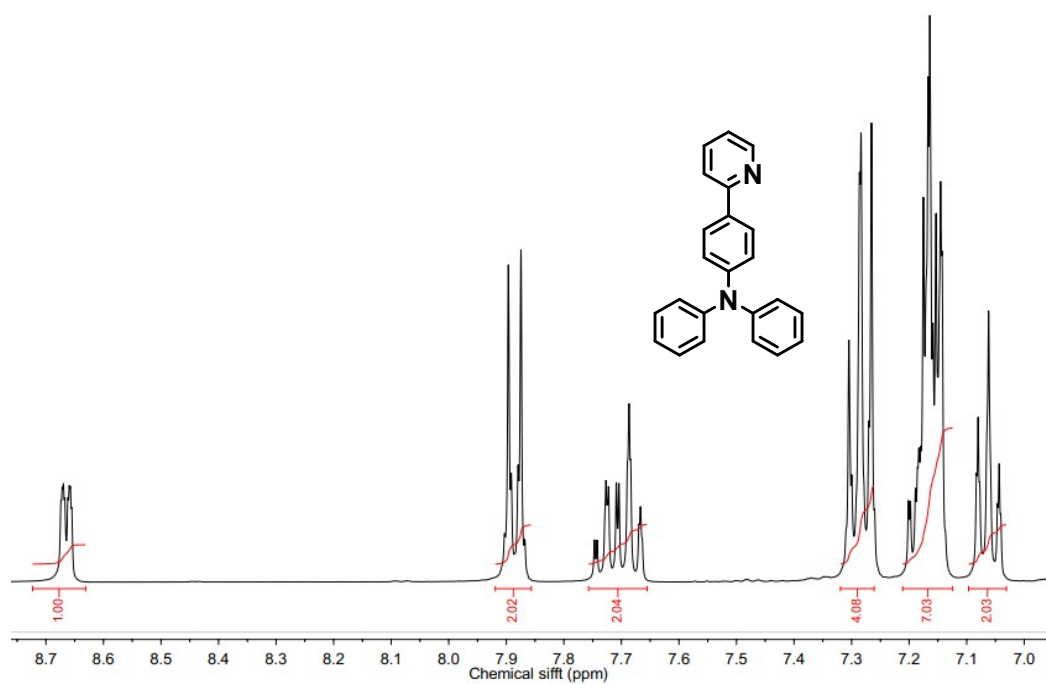


**$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )**

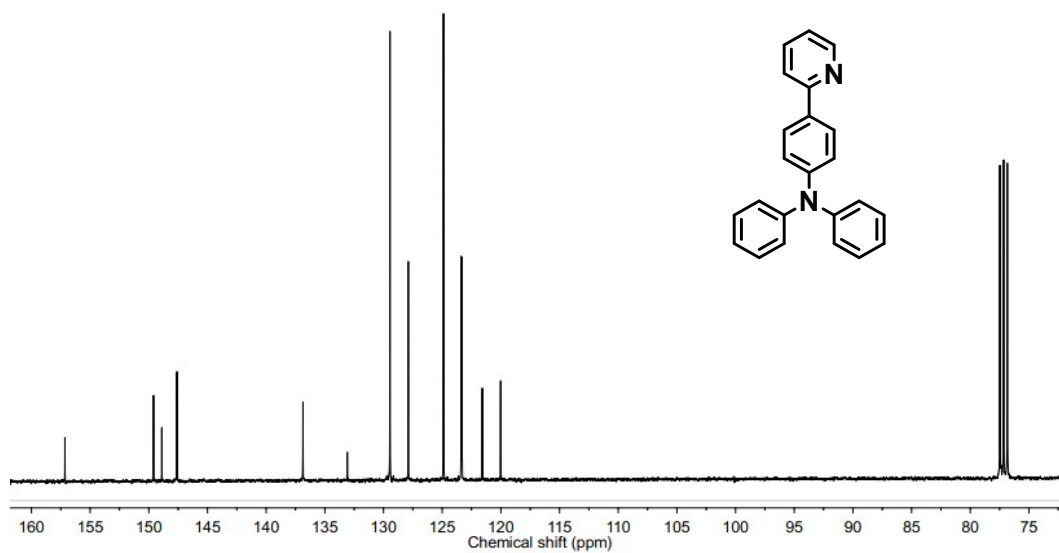


**Fig. S7.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of L-1.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>)**

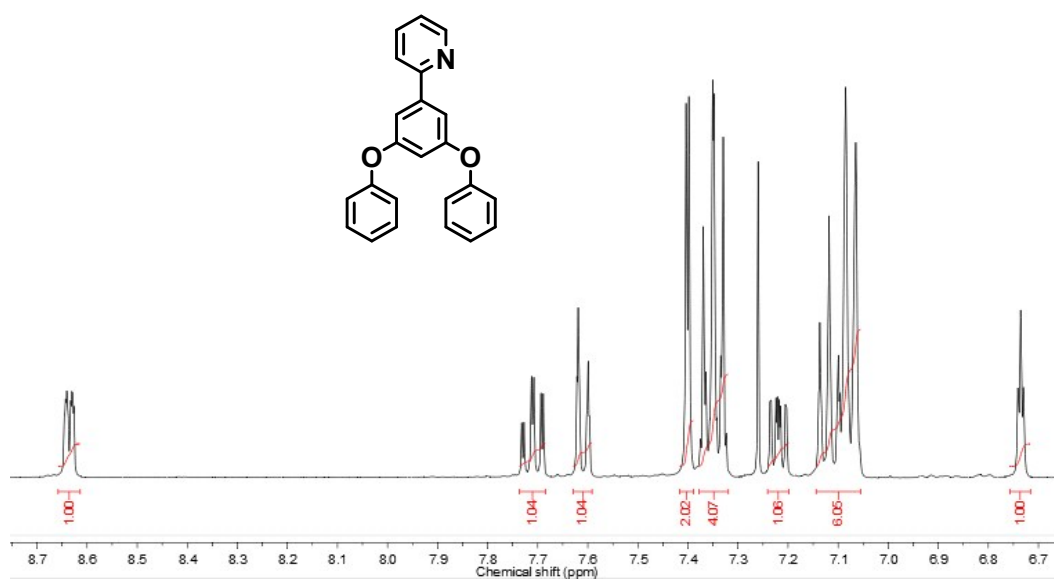


**<sup>13</sup>C NMR (CDCl<sub>3</sub>)**

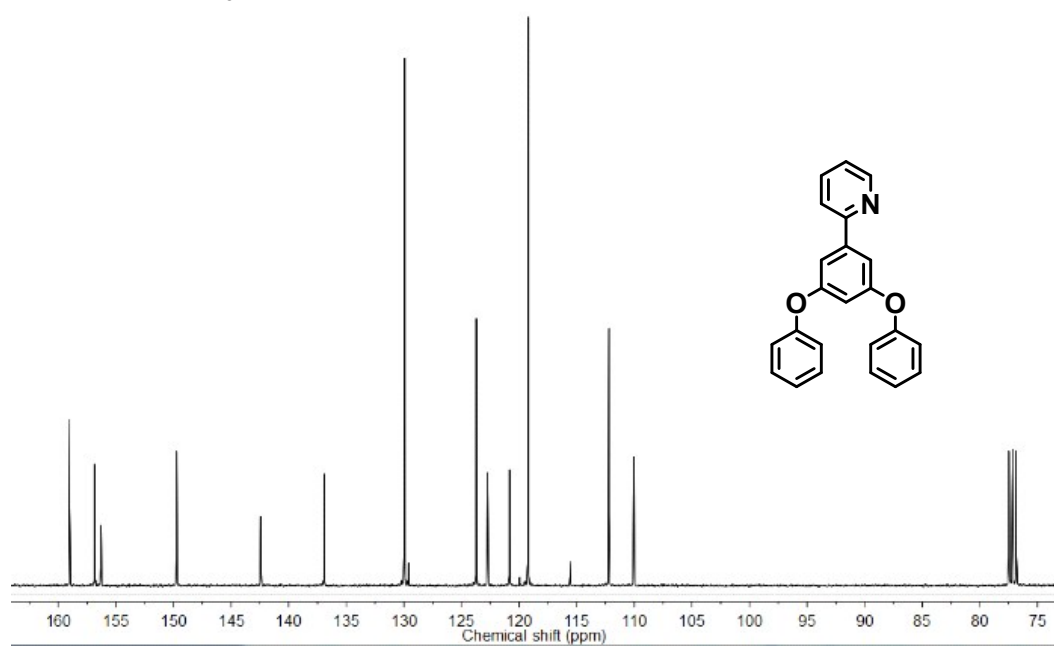


**Fig. S8.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of L-2.

**$^1\text{H}$  NMR ( $\text{CDCl}_3$ )**

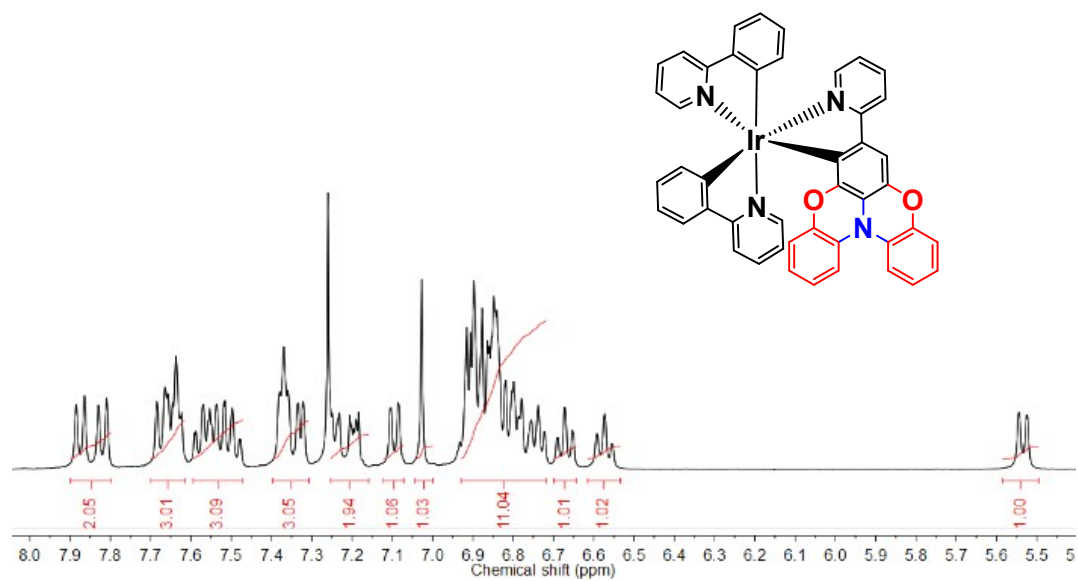


**$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )**



**Fig. S9.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **L-3**.

<sup>1</sup>H NMR (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (CDCl<sub>3</sub>)

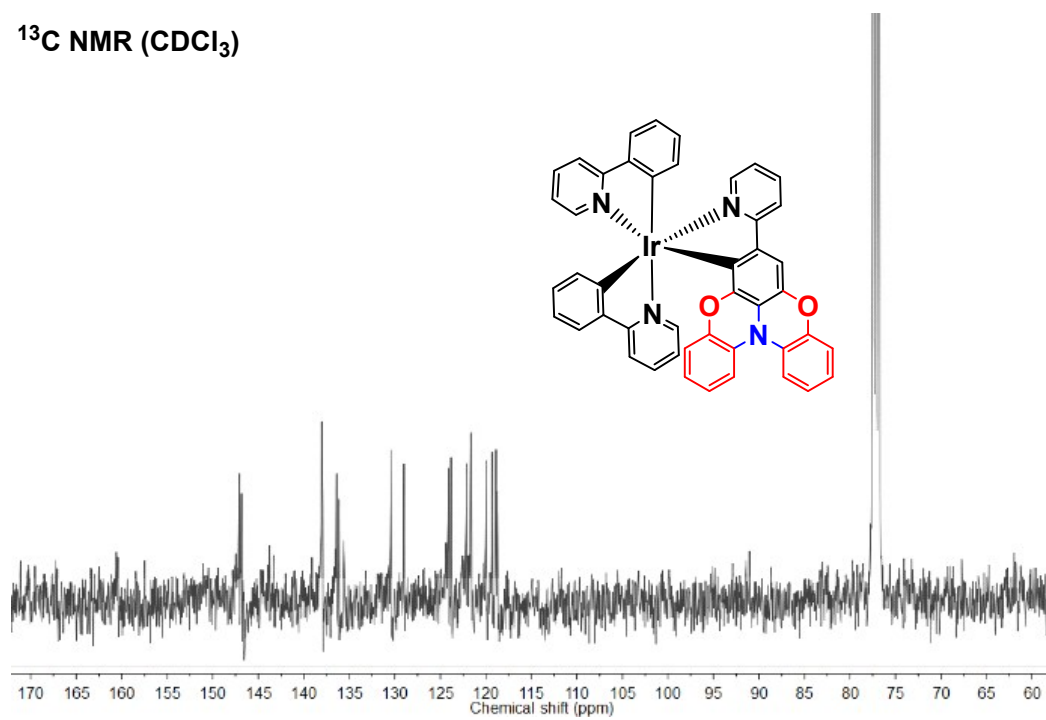
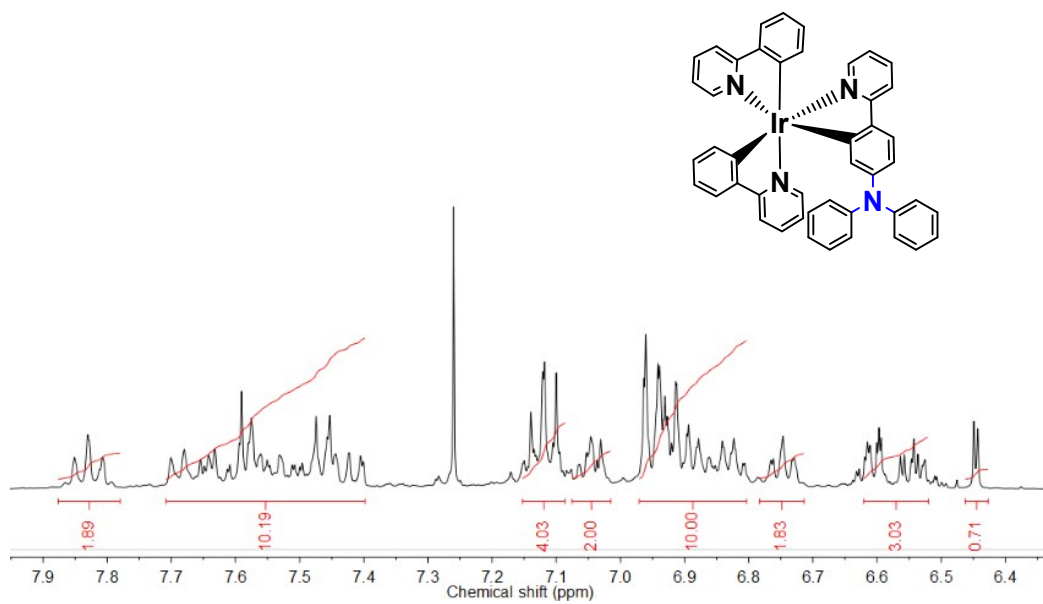
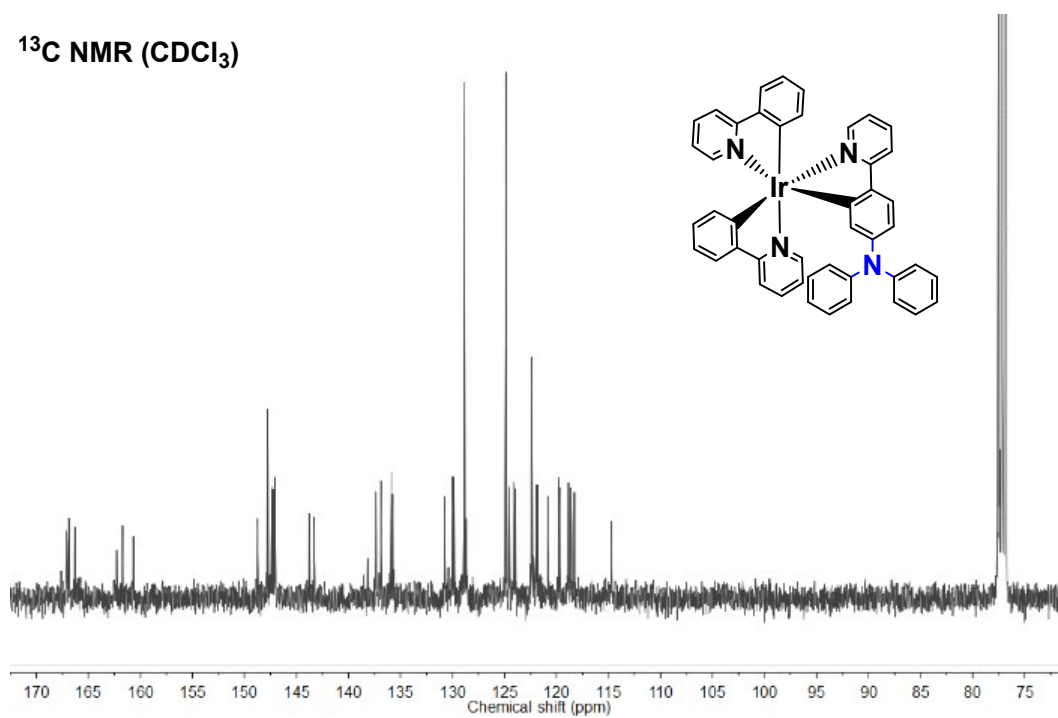


Fig. S10. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of Ir-NO.

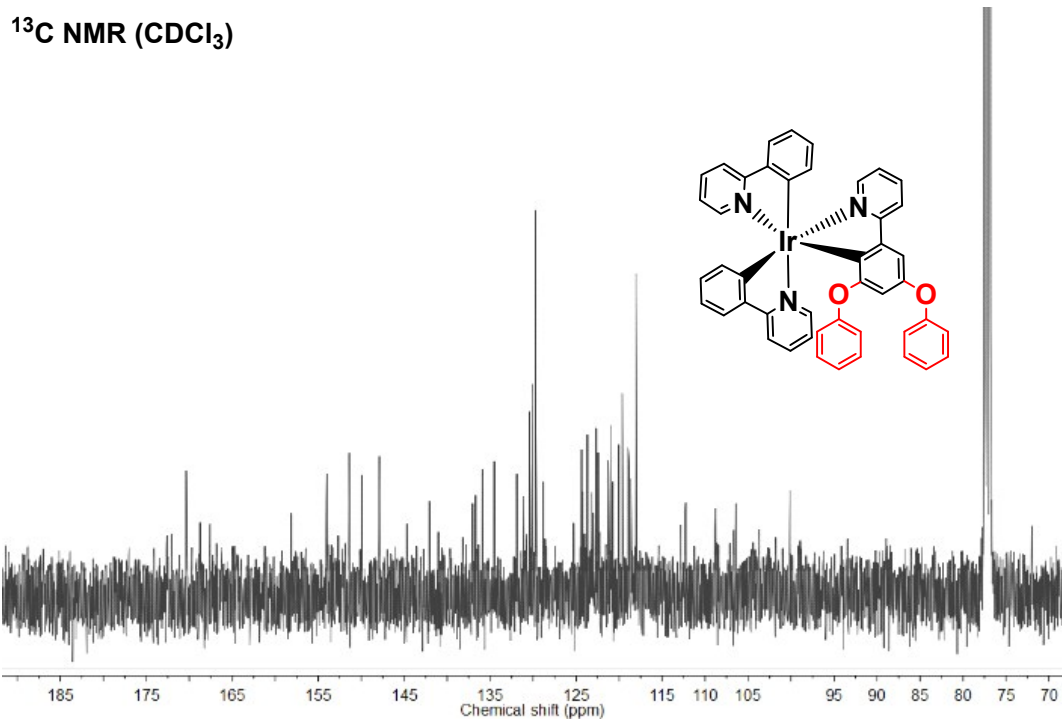
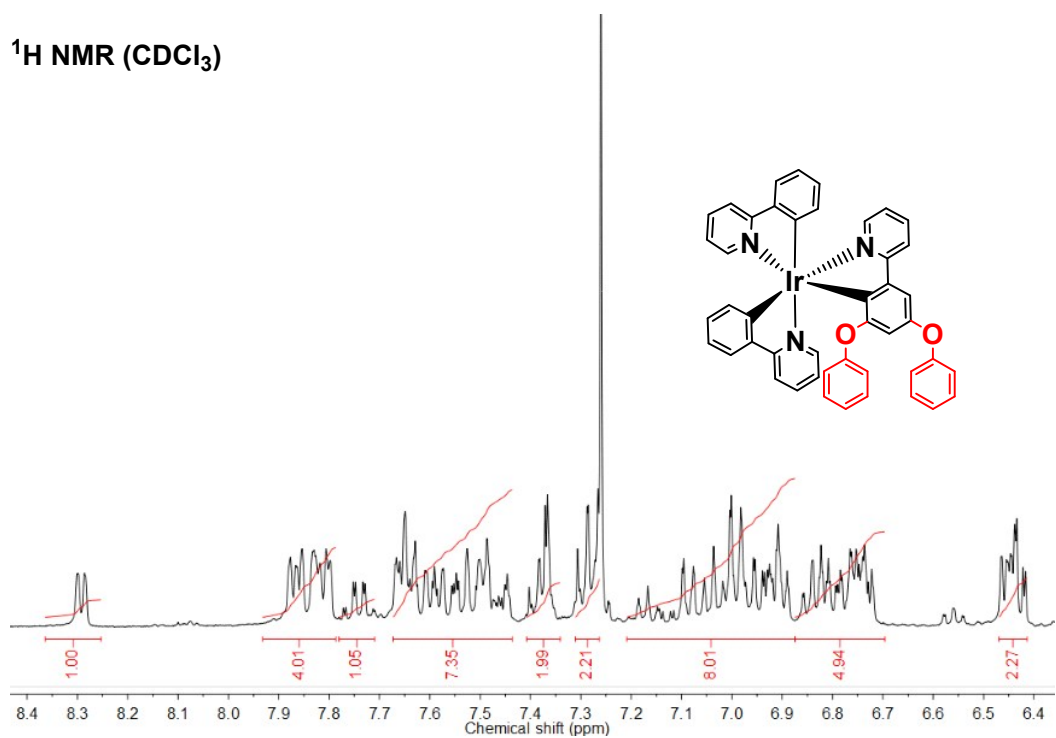
**<sup>1</sup>H NMR (CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (CDCl<sub>3</sub>)**



**Fig. S11.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of Ir-N.



**Fig. S12.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of Ir-O.

## References

1. A. Wakamiya, H. Nishimura, T. Fukushima, F. Suzuki, A. Saeki, S. Seki, I. Osaka, T. Sasamori, M. Murata, Y. Murata, H. Kaji, *Angew. Chem. Int. Ed.* 2014, **53**, 5800.
2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision B.01*, Gaussian, Inc., Wallingford CT, **2010**.