Supplementary Material

Selective hydrogen generation from formic acid catalyzed by an iridium-azocarboxamide complex under neat conditions

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Table of Contents

TON and TOF Calculations

To calculate TON and TOF, the sum of H_2 and CO_2 volumes considered to be equals to the total volume. Total volume was calculated as the product between the number of moles and the molar volume of the species.

$$\mathrm{V}_{H_2} + \mathrm{V}_{CO_2} = \mathrm{V}$$

$$\mathrm{n}_{H_2}\mathrm{V}_{m,H_2} + \mathrm{n}_{CO_2}\mathrm{V}_{m,CO_2} = \mathrm{V}$$

$$n(\mathrm{V}_{m,H_2} + \mathrm{V}_{m,CO_2}) = \mathrm{V}$$

$$n = \frac{\mathrm{V}}{(\mathrm{V}_{m,H_2} + \mathrm{V}_{m,CO_2})}$$

$TON = \frac{\mathrm{n}}{n_{cat}}$ where n_{cat} is the number of moles of the catalyst

$TOF = \frac{\mathrm{TON}}{T}$ where the T is time in hours (h)

In Table 1, the TOF is calculated at the initial 10 min (T = 0.1667 h) therefore the TOF will be calculated as following

$$TOF_{10\ min} = \frac{\mathrm{TON}_{10\ min}}{0.1667\ h}$$

The conversion was calculated based on the following equation:

$$Conversion = \frac{\mathrm{V}}{\mathrm{V}_{theoritical}} \times 100$$

$$\mathrm{V}_{theoritical} = n_{Formic\ acid}\left(\mathrm{V}_{m,H_2} + \mathrm{V}_{m,CO_2}\right)$$

In our case, we used 30 mmol of formic acid (Table 1) and the molar volume values is explained below. Therefore, the theoretical volume was calculated as following:

$$\mathrm{V}_{theoritical} = 0.0265\ mol\ (24.48\ L\ mol^{-1} + 24.36\ L\ mol^{-1}) = 1.2942\ L$$

To calculate the molar volume for both H_2 and CO_2, the following equations was used:

$$\mathrm{V}_{m,H_2} = \frac{RT}{p} + b - \frac{a}{RT} = 24.48\ L\ mol^{-1}$$

Where:

$R = 8.31447\ m^3 Pa\ mol^{-1}K^{-1}$

$T = 298.15\ K$

$p = 101325\ Pa$

$b = 26.7 \times 10^{-6}\ m^3 mol^{-1}$

$a = 2.49 \times 10^{-10}\ Pa\ m^3 mol^{-2}$

$$\mathrm{V}_{m,CO_2} = \frac{RT}{p} + b - \frac{a}{RT} = 24.36\ L\ mol^{-1}$$

Where:

$R = 8.31447\ m^3 Pa\ mol^{-1} K^{-1}$

$T = 298.15\ K$

$p = 101325\ Pa$

$b = 42.7 \times 10^{-6}\ m^3 mol^{-1}$

$a = 36.5 \times 10^{-10}\ Pa\ m^3 mol^{-2}$

$\mathrm{n}_{H_2} = \mathrm{n}_{CO_2} = \mathrm{n}$

Table S1. TOF in the dehydrogenation of formic acid at different temperature[a]

Temperature(°C)	TOF (h^{-1})
100	12500
90	10600
80	5300
70	3400
60	2500

[a] Reaction conditions: Complex **Ir-2** (10.0 µmol), FA solution (1.0 mL, 26.5 mmol), Sodium Formate (0.85g, 13.25mmol), 90 °C. TOF was calculated for the first 3 min.

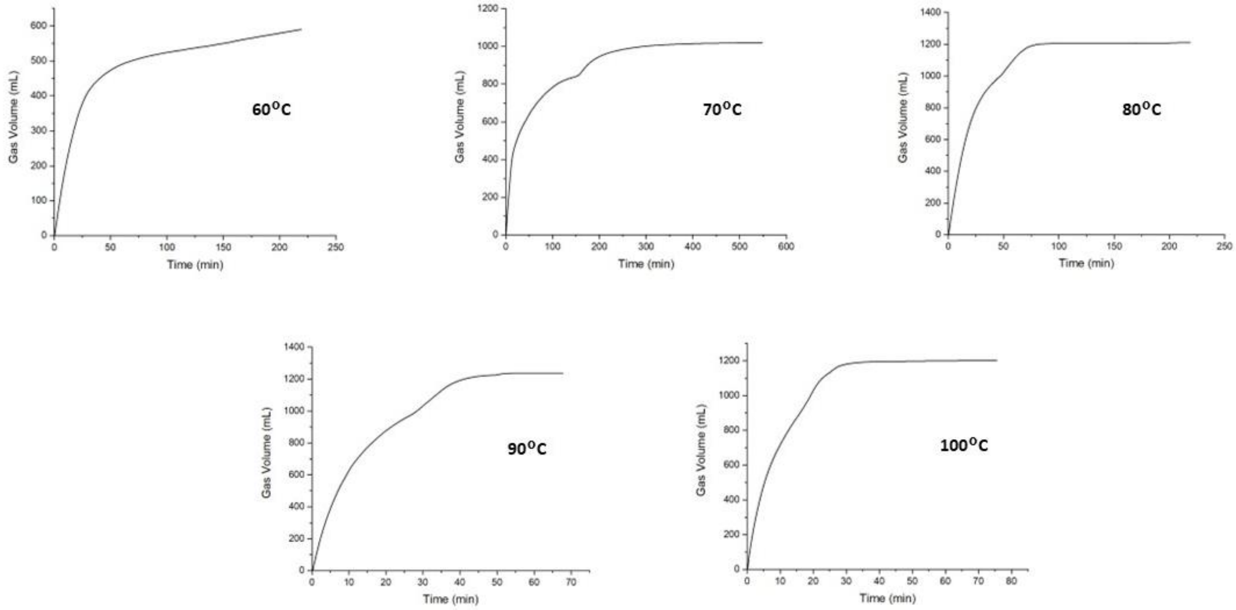


Figure S1. Time vs gas evolution plots of the formic acid dehydrogenation reaction for **Ir-2** (10 mmol), FA solution (1.0 mL, 26.5 mmol), Sodium Formate (0.85g, 13.25mmol) at different temperature.

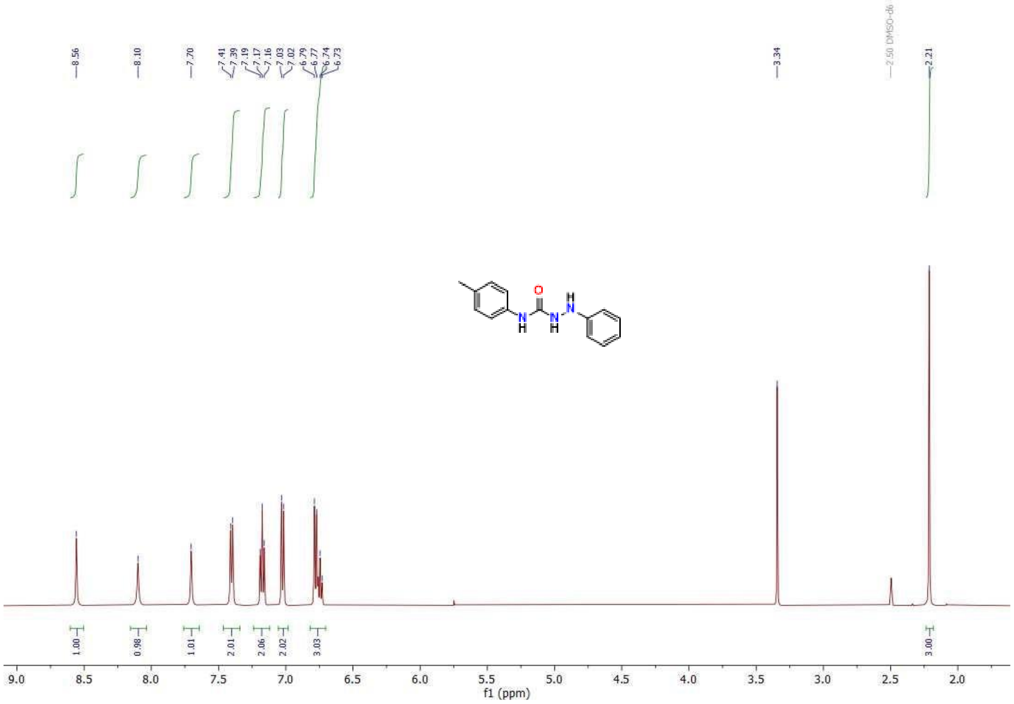


Figure S2. ^{1}H NMR spectrum of Ligand **L1** in DMSO-d$_6$ (600 MHz, 25 °C).

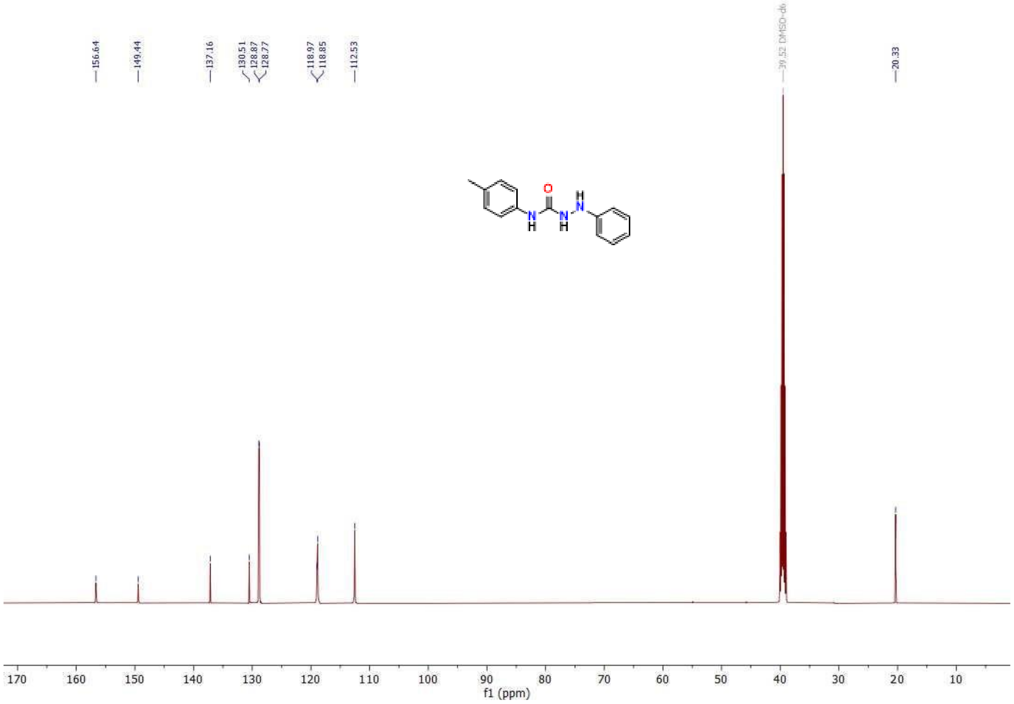


Figure S3. ^{13}C NMR spectrum of Ligand **L1** in DMSO-d$_6$ (600 MHz, 25 °C).

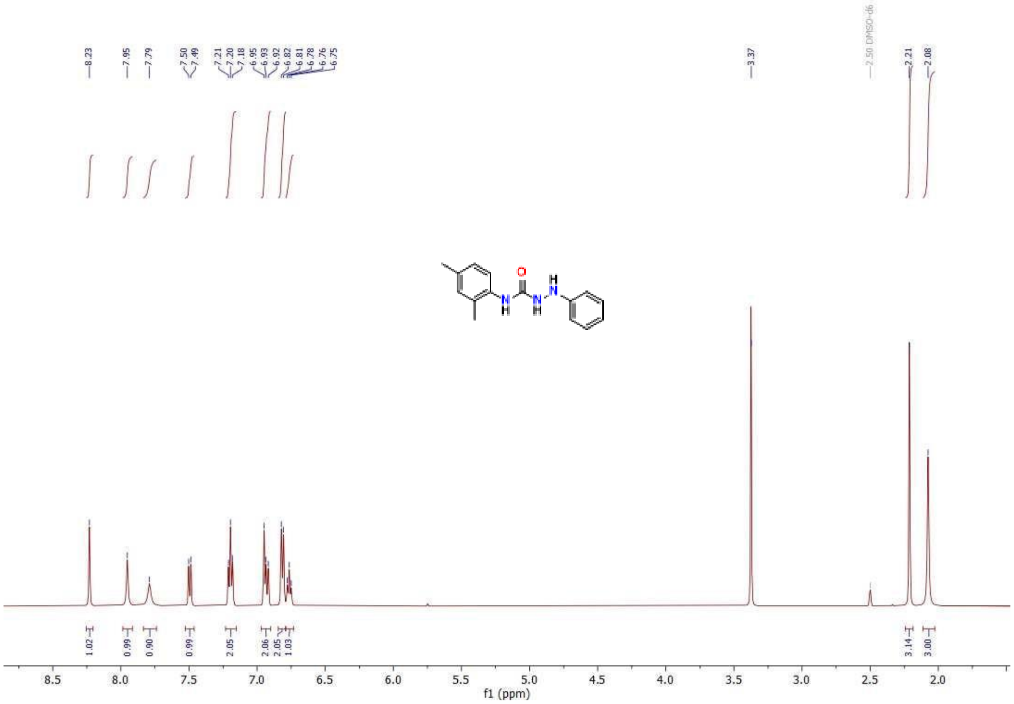


Figure S4. ^{1}H NMR spectrum of Ligand **L2** in DMSO-d_6 (600 MHz, 25 °C).

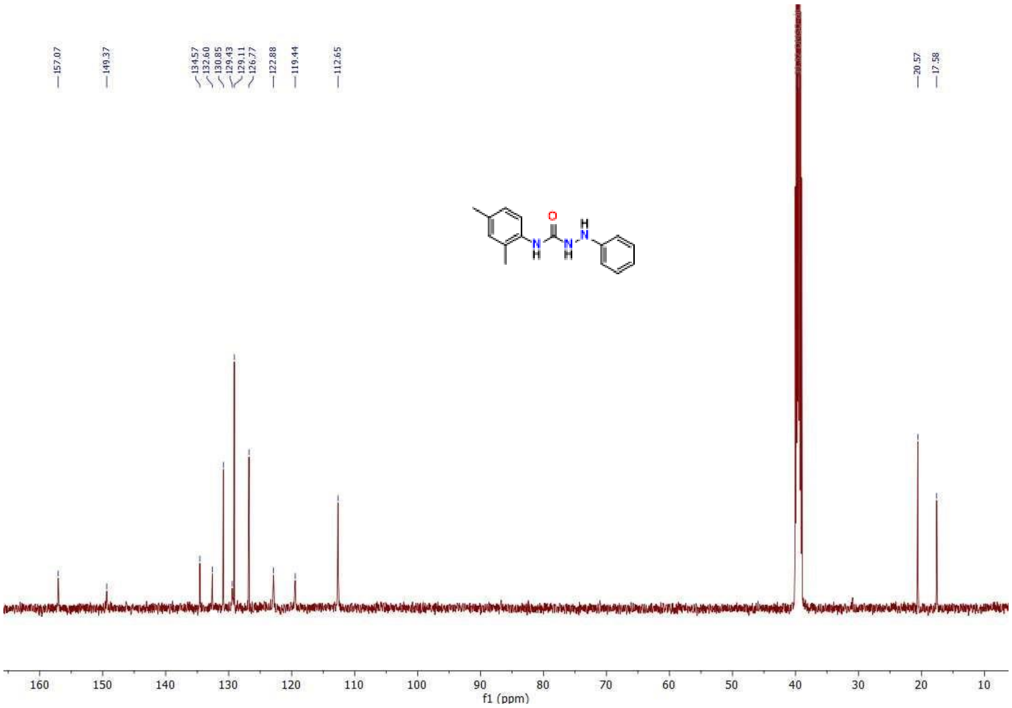


Figure S5. ^{13}C NMR spectrum of Ligand **L2** in DMSO-d_6 (600 MHz, 25 °C).

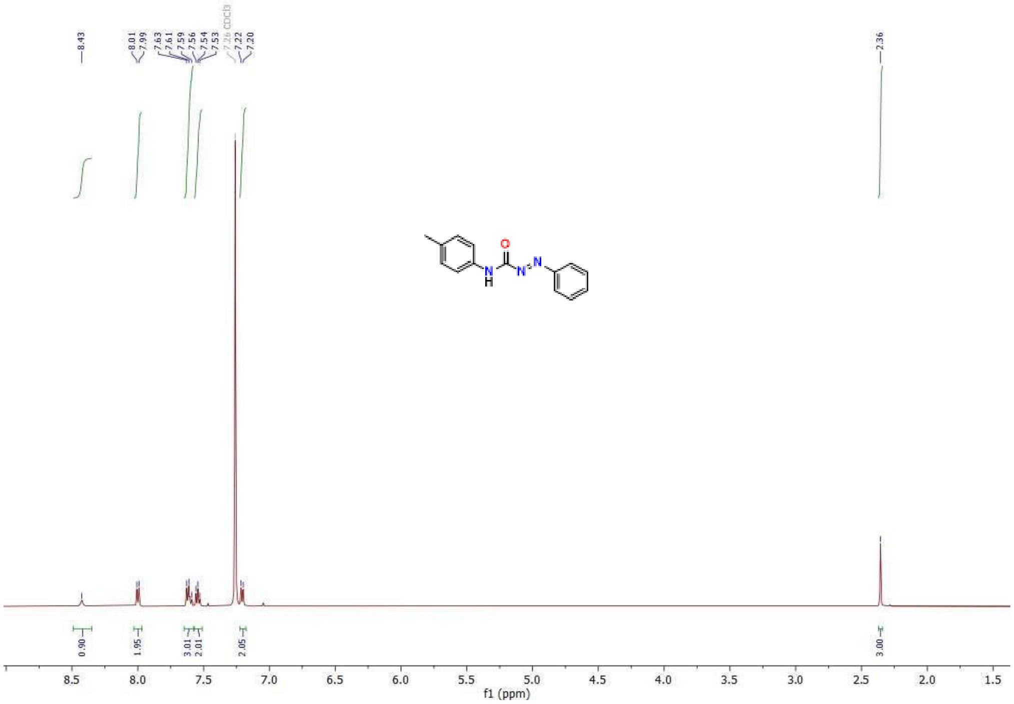


Figure S6. ^{1}H NMR spectrum of Ligand **L3** in CDCl$_3$ (600 MHz, 25 °C).

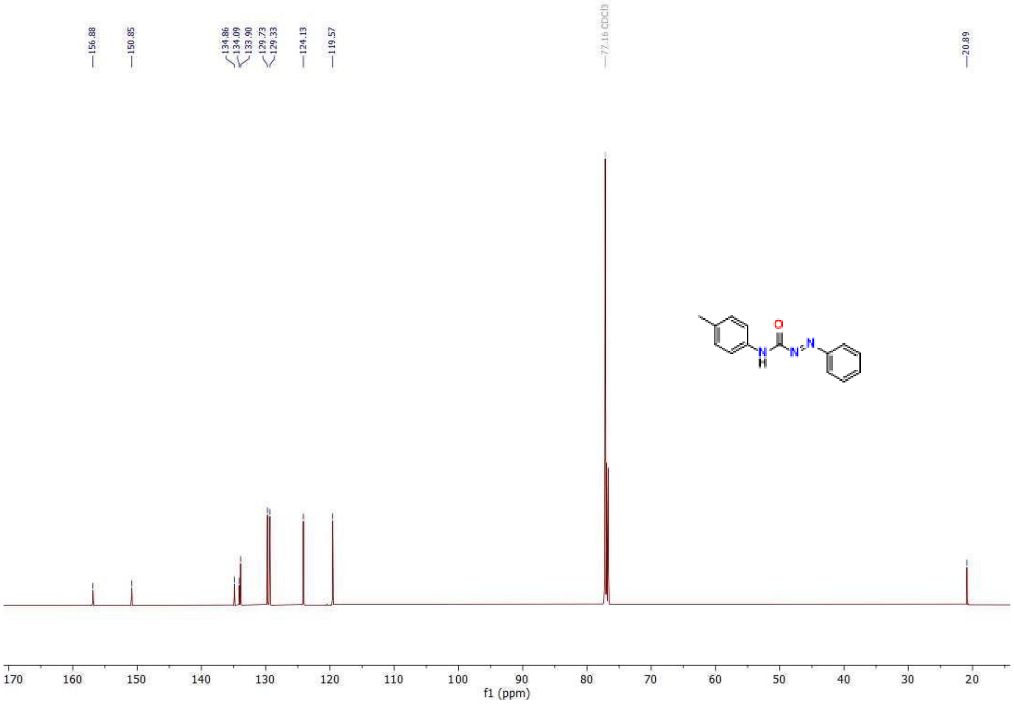


Figure S7. ^{13}C NMR spectrum of Ligand **L3** in CDCl$_3$ (600 MHz, 25 °C).

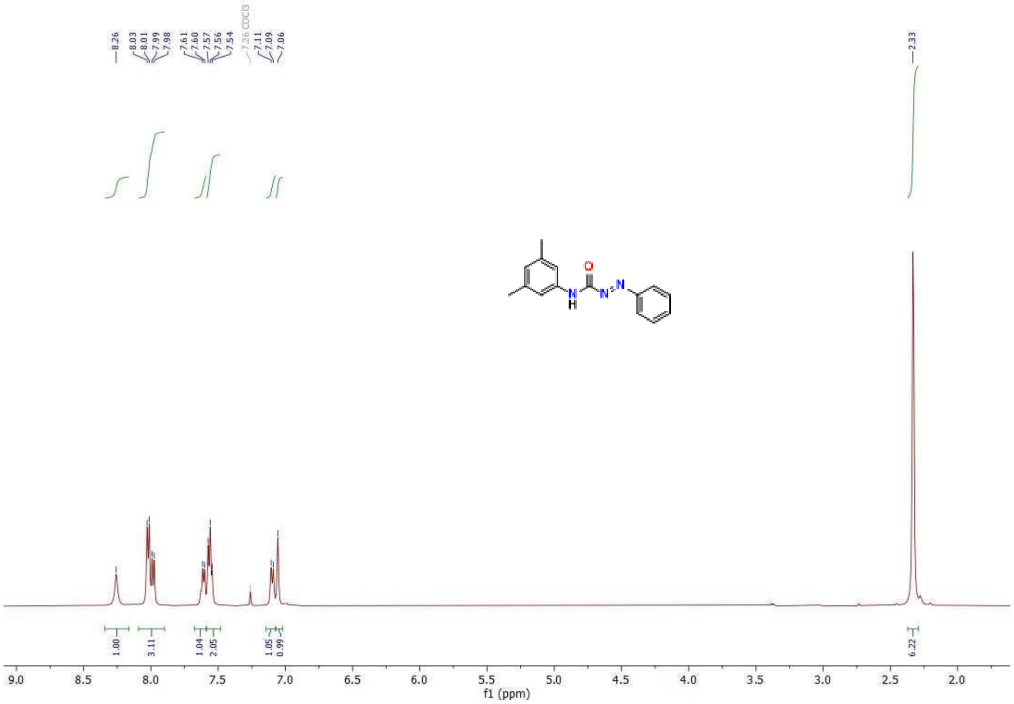


Figure S8. ^{1}H NMR spectrum of Ligand **L4** in $CDCl_3$ (600 MHz, 25 °C).

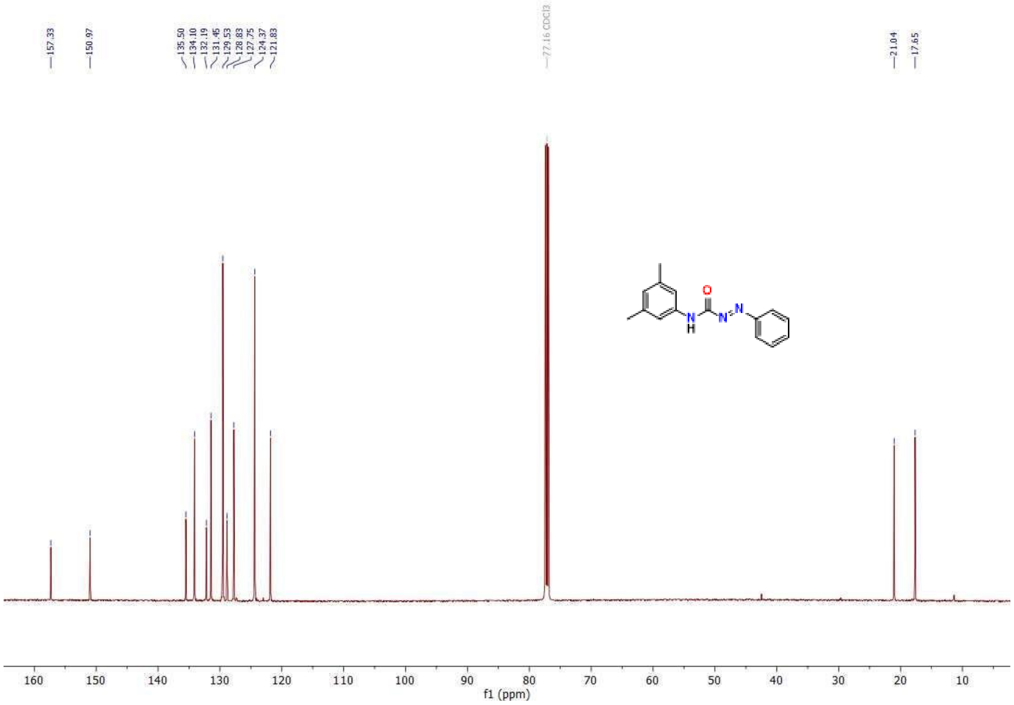


Figure S9. ^{13}C NMR spectrum of Ligand **L4** in $CDCl_3$ (600 MHz, 25 °C).

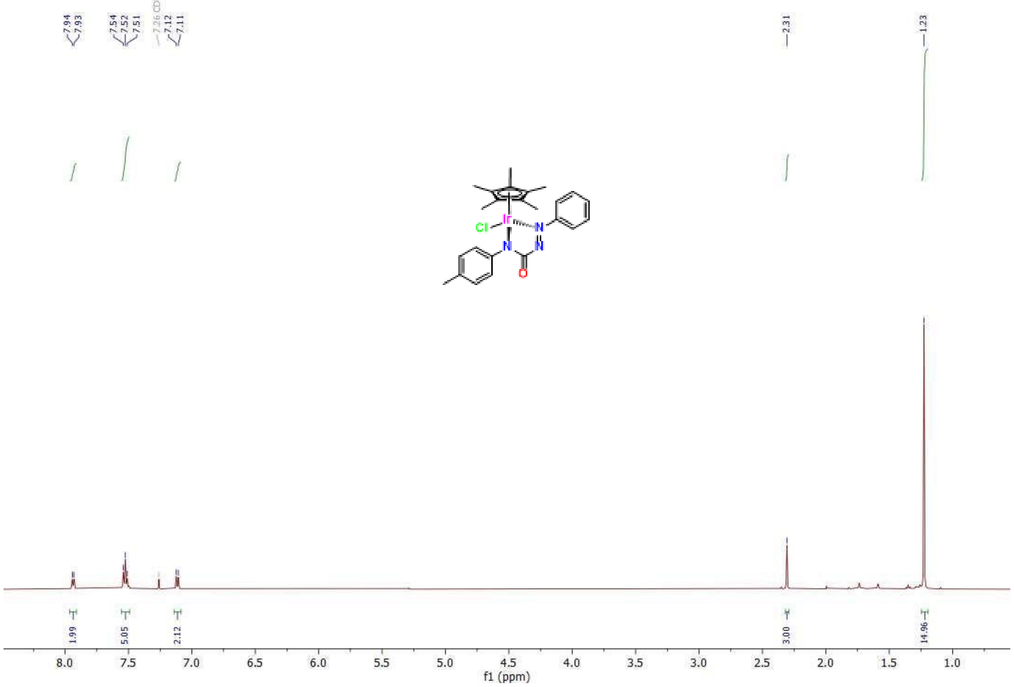


Figure S10. ^{1}H NMR spectrum of complex **Ir-1** in CDCl$_3$ (600 MHz, 25 °C).

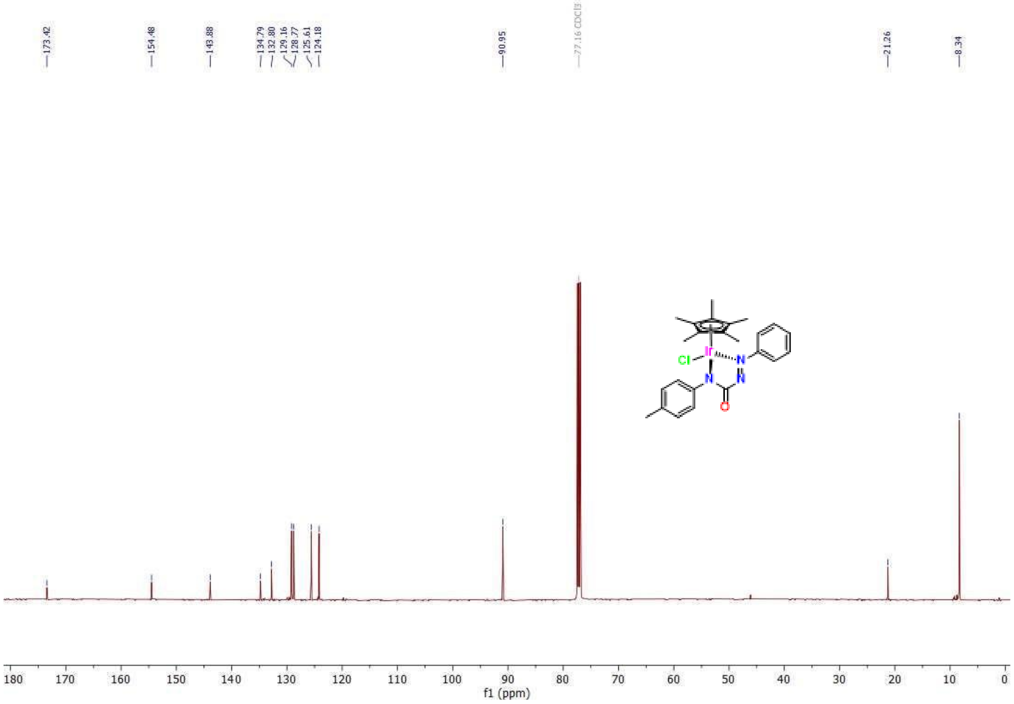


Figure S11. ^{13}C NMR spectrum of complex **Ir-1** in CDCl$_3$ (600 MHz, 25 °C).

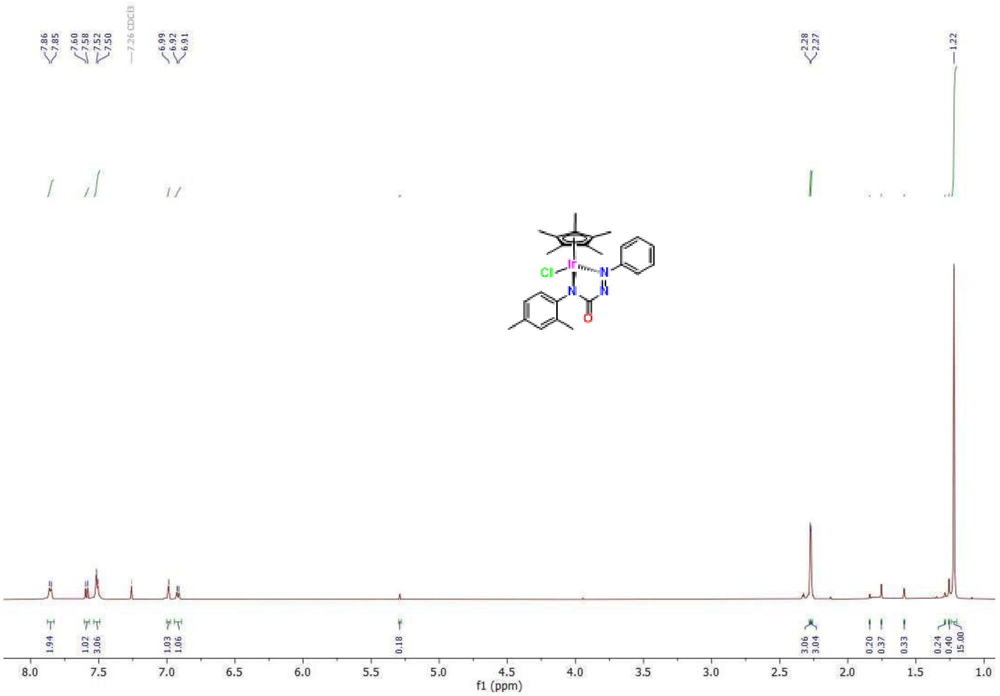


Figure S12. ^{1}H NMR spectrum of complex **Ir-2** in $CDCl_3$ (600 MHz, 25 °C).

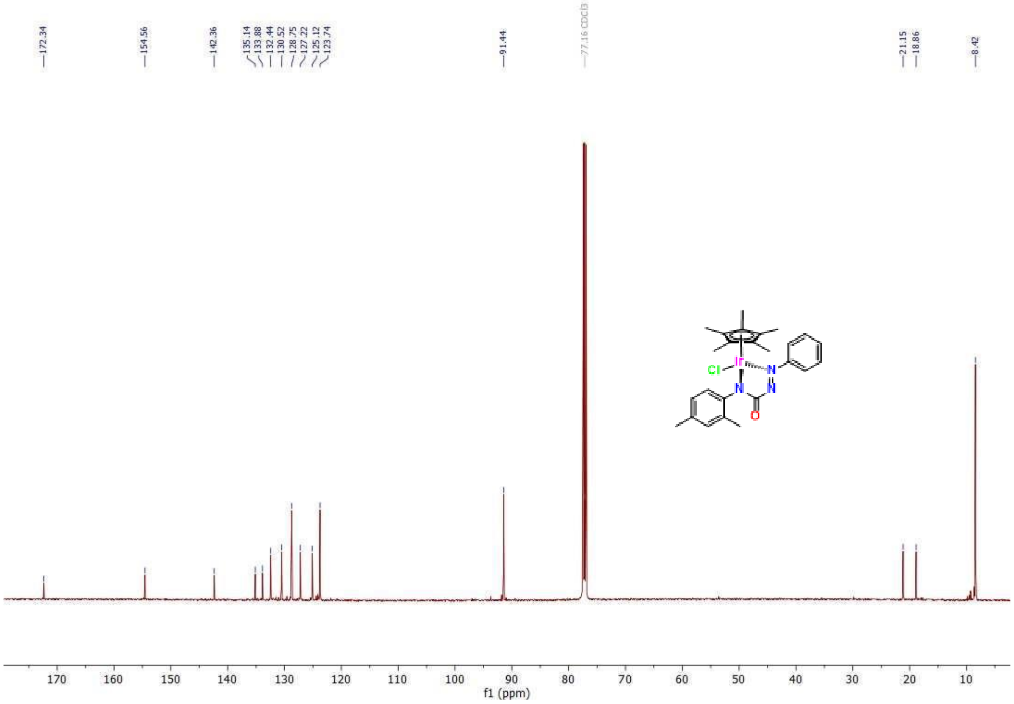
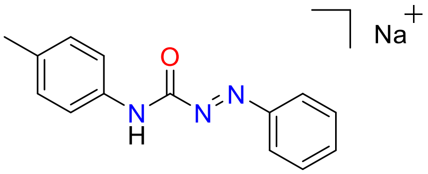
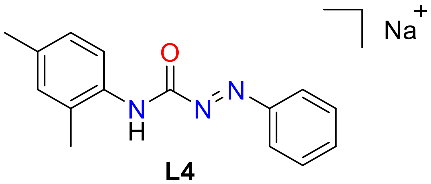
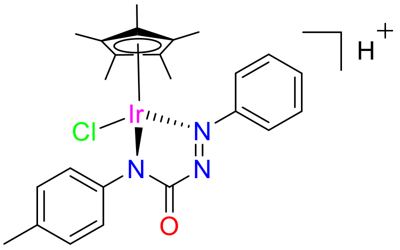
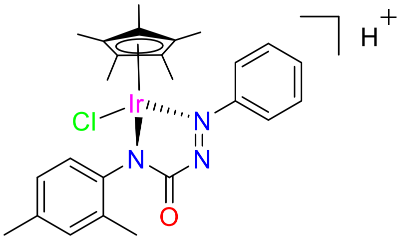


Figure S13. ^{13}C NMR spectrum of complex **Ir-2** in $CDCl_3$ (600 MHz, 25 °C).

Table S2. The composition, empirical formula and peak position of the species in the ESI-MS positive spectra in MeCN.

 **L3** {[**L3**]+Na$^+$}; $C_{14}H_{13}N_3ONa$ {[**L3**]+Na$^+$};m/z = 262.0967	 **L4** {[**L4**]+Na$^+$}; $C_{15}H_{15}N_3ONa$] {[**L4**]+Na$^+$}; m/z = 276.1117
 **Ir-1** {[**Ir-1**]+H$^+$}; $C_{24}H_{27}Cl\ IrN_3O$] {[**Ir-1**]+H$^+$}; m/z = 602.1469	 **Ir-2** [{[**Ir-2**]+H$^+$}; $C_{25}H_{29}Cl\ IrN_3O$] {[**Ir-2**]+H$^+$}; m/z = 616.1594

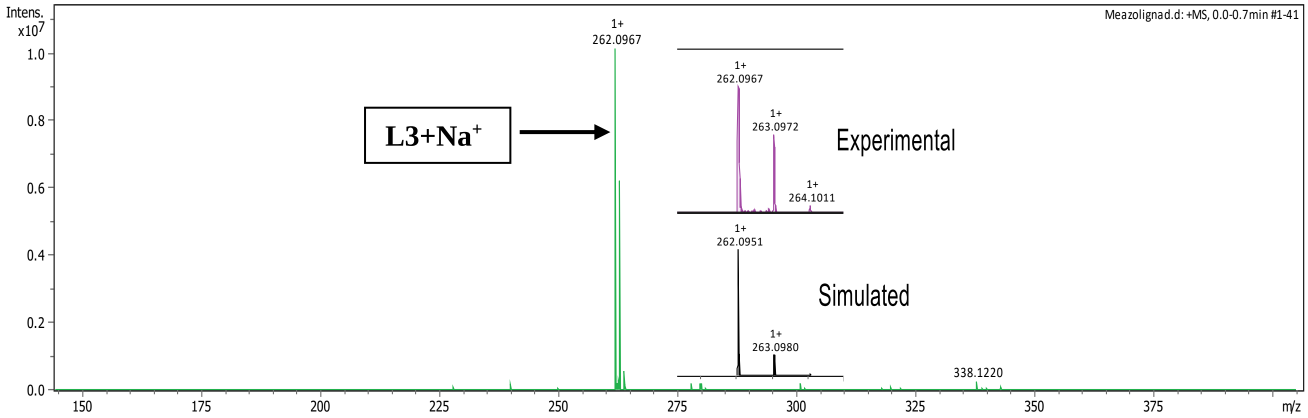


Figure S14. Electron Spray Ionisation-Mass Spectroscopy (positive mode) for L3. {[**L3**]+Na$^+$}; $C_{14}H_{13}N_3ONa$; m/z = 262.0967

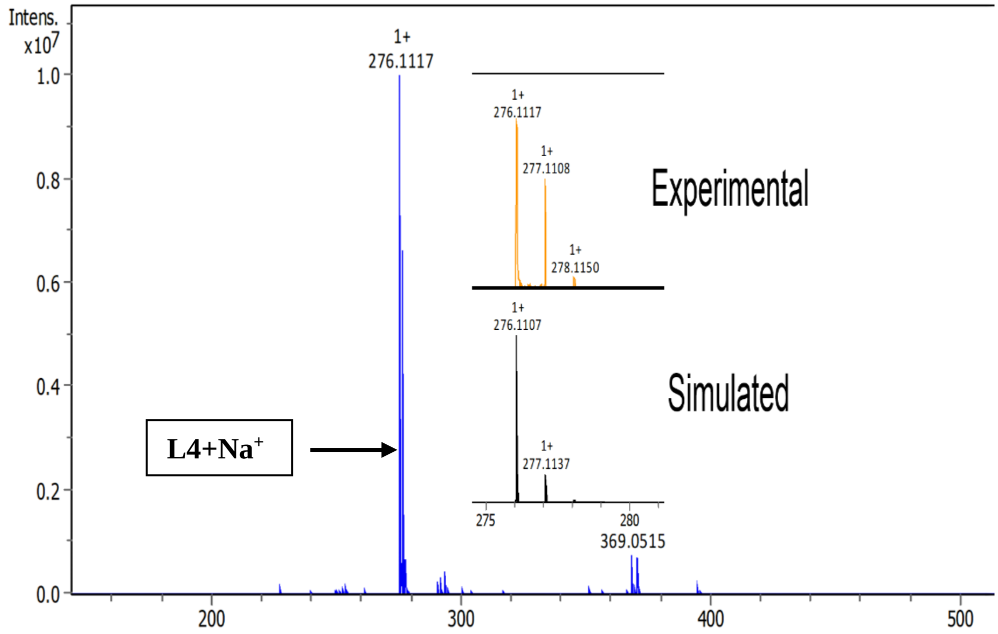


Figure S15. Electron Spray Ionisation-Mass Spectroscopy (positive mode) of L4.{[**L4]**+Na$^+$}; $C_{15}H_{15}N_3ONa$]; m/z = 276.1117

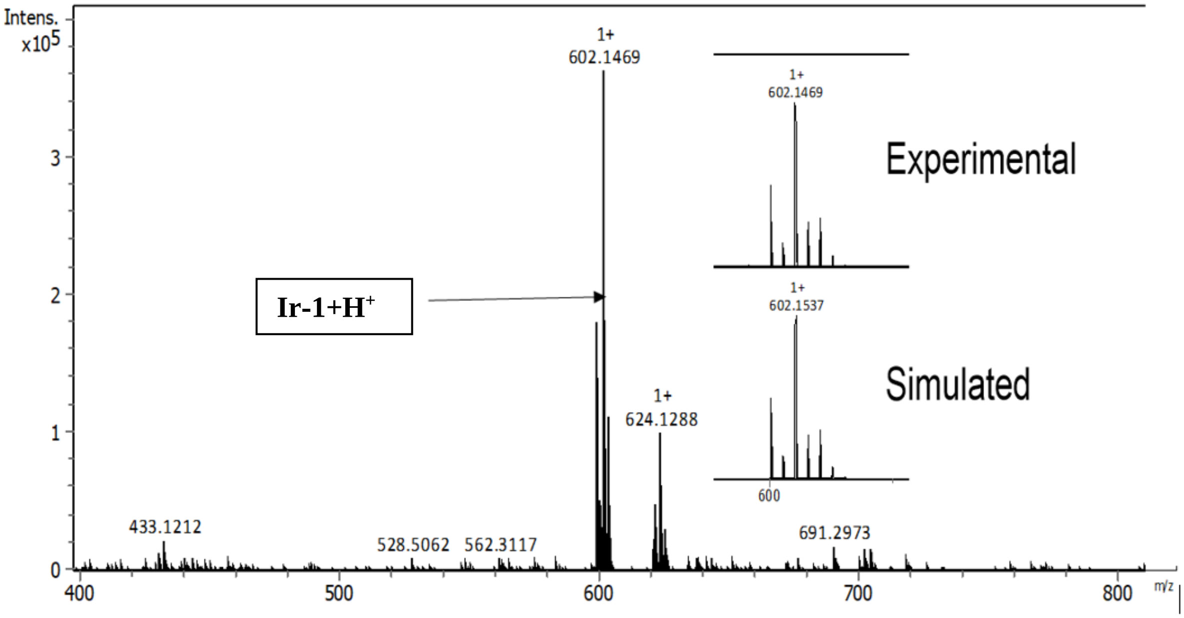


Figure S16. Electron Spray Ionisation-Mass Spectroscopy (positive mode) of Ir-1. {[**Ir-1**]+H$^+$}; $C_{24}H_{27}Cl\ IrN_3OH$]; m/z = 602.1469

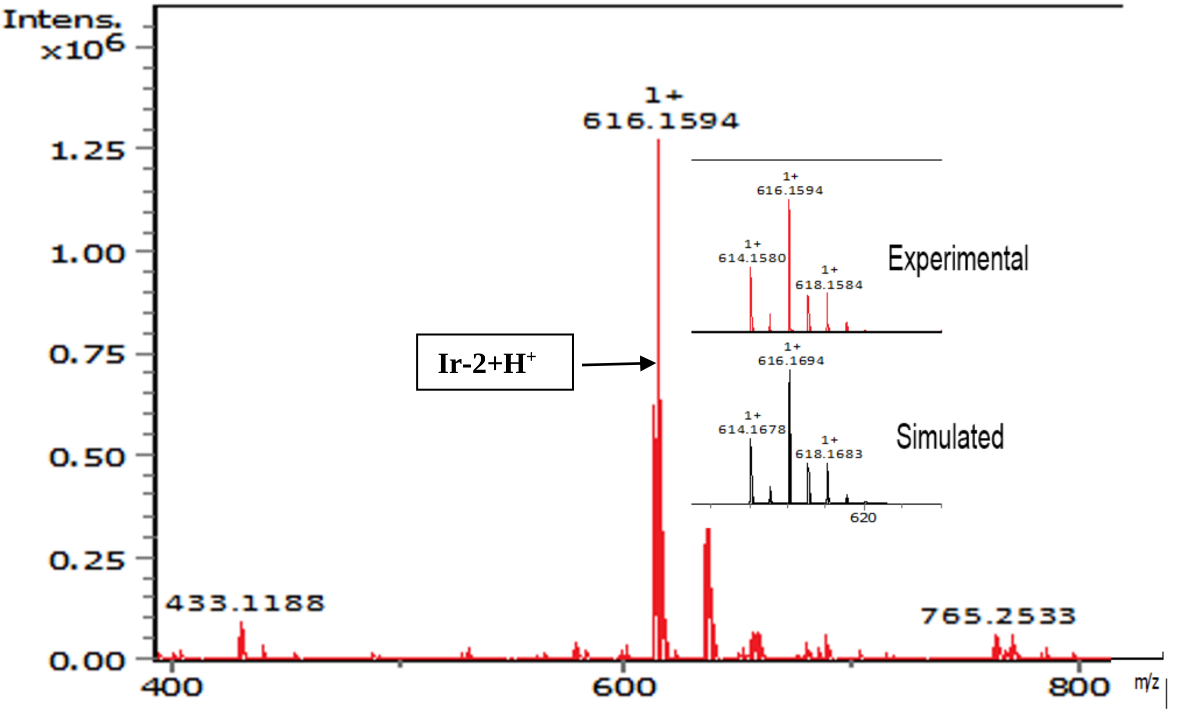


Figure S17. Electron Spray Ionisation-Mass Spectroscopy (positive mode) of Ir-2. [{[**Ir-2**]+H$^+$}; $C_{25}H_{29}Cl\ IrN_3OH$]; m/z = 616.1594

Table S3. Crystallographic data for complexes **Ir-1** and **Ir-2**

Empirical formula	$C_{24}H_{27}ClIrN_3O$	$C_{25}H_{29}ClIrN_3O$
Formula weight	601.13	615.16
Temperature/K	120.0	150.0
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	7.5017(5)	7.7439(3)
b/Å	18.1132(14)	18.8099(7)
c/Å	16.4172(13)	16.2456(5)
α/°	90	90
β/°	95.869(3)	96.6250(10)
γ/°	90	90
Volume/Å^3	2219.1(3)	2350.56(15)
Z	4	4
ρ_{calc}g/cm^3	1.799	1.738
μ/mm^{-1}	6.158	5.816
F(000)	1176.0	1208.0
Crystal size/mm^3	0.22 × 0.2 × 0.18	0.22 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.498 to 65.85	4.33 to 83.5
Index ranges	$-11 \le h \le 11$ $-27 \le k \le 27$ $-25 \le l \le 25$	$-14 \le h \le 13$ $-32 \le k \le 30$ $-30 \le l \le 27$
Reflections collected	108646	88349
Independent reflections	8292 [R_{int} = 0.0741, R_{sigma} = 0.0293]	13756 [R_{int} = 0.0459, R_{sigma} = 0.0411]
Data/restraints/parameters	8292/0/286	13756/0/287
Goodness-of-fit on F^2	1.140	1.123
Final R indexes [I>=2σ (I)]	R_1 = 0.0366, wR_2 = 0.0838	R_1 = 0.0333, wR_2 = 0.0607
Final R indexes [all data]	R_1 = 0.0433, wR_2 = 0.0894	R_1 = 0.0589, wR_2 = 0.0748
CCDC Number	2270633	2270634

Crystal structure determination:

X-ray diffraction data were collected on a Bruker D8 VENTURE/PHOTON100 CMOS diffractometer at 120 K for the complex **Ir-1** 150 K for the complex **Ir-2**. Mirror-monochromated Mo Kα radiation (λ = 0.71073 Å) source was used for data collection. For data processing, the SAINT[1] packages were used. Multi-scan absorption corrections were made for all the cases using the program SADABS2.[1, 2] Structures were solved by direct and Fourier methods and refined by full-matrix least squares based on F^2 using olex-2.[3]

For complex **Ir-1**, it was found that the Ir-Cl moiety is disordered over two positions, with occupancy factors of 0.9603(6) and 0.0397(6). EADP restraint needs to be used to the Ir1A/Ir1B couple to fix their ADP well.

All other hydrogen atoms in the two compounds were inserted on geometrical calculated positions with fixed thermal parameters and were refined isotropically, while all the nonhydrogen atoms were refined anisotropically. The final least-squares refinements (R1) based on I > 2r(I) converged to 0.0366 and 0.0333for **Ir-1** and **Ir-2**, respectively.

(1) Bruker, S.; SAINT, S. Bruker AXS Inc. *Madison, Wisconsin, USA* **2002**.
(2) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. C Struct. Chem.* **2015**, *71* (1), 3-8.
(3) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42* (2), 339-341.