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Supplementary Information

High-Yielding Synthesis of Cyclometallated Iridium Complexes with Hydrogen Bond-Rich Ligands

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S0. Materials and Techniques

Materials. All starting materials were purchased from commercial sources (Sigma Aldrich, Fisher Scientific and TCI) and used without further purification. Analytical thin layer chromatography (TLC) was carried out on precoated TLC plates Alugram Sil G/ UV254. Column chromatography purifications were done with silica gel (ultrapure, 60-200 µm (60 Å)). Experiments were performed as follows:

(i) A conventional hotplate (IKA™ RCT Basic magnetic hot plate stirrer (Stirring range: 50 to 1500 rpm; Size: 5.3 in. dia; Supplier: IKA™ 3810001) - fumehood), under a dry N_2 atmosphere using standard Schlenk Line techniques when specified.

(ii) Microwave reactor – Anton Paar-Monowave 400 (max. temp. 300°C, power 850 W and pressure of 30 bar) with 10- and 30-mL borosilicate glass vials with a cap material of PEEK. The seal material is made from Teflon-coated silicone. Supplier: Anton Paar.

(iii) Mixer Mill MM 400 (RETSCH). Vibrational frequency up to 30 Hz and grinding time up to 99 min. Equipped with 2 grinding stations. Grinding jars with a nominal volume of the screw-top between 5-25 mL and two grinding balls made of stainless steel were used. Supplier: RETSCH.

Nuclear Magnetic Resonance (NMR). ^{1}H (400 MHz) and ^{13}C (201 MHz) NMR spectra were recorded on an Agilent 400 MR and a Bruker Avance III HD 800 MHz spectrometers in deuterated solvents, namely chloroform-*d* ($CDCl_3$) and dimethyl sulfoxide-d_6 (DMSO-d_6), which were purchased from Fisher Scientific. All chemical shifts are reported in δ (ppm) referenced to tetramethylsilane ($Si(CH_3)_4$) and the peak multiplicities are referred to as singlet (s), doublet (d), triplet(t), quartet (q), multiplet (m). Spin-spin coupling effect is quantified with the coupling constants, which is abbreviated with the capital letter J.

Mass Spectrometry. High-resolution mass spectral data measurements were performed by Xiao Feng at the Mass Spectrometry Laboratory (Dalhousie University, Halifax, Canada). High-resolution mass spectra were recorded on Bruker Daltonics MicrOTOF instrument. The ionization method used for low/high-resolution analysis was positive electrospray ionization (ESI+). The sample was introduced by a syringe pump at a flow rate of 2 μL/min and the spray voltage applied to the ESI needle was 4.5 kV. The dry gas flow rate was 4 L/min with a pressure of 1 Bar and a temperature of 180°C. For the analysis, samples sizes were between 1.0-2.5 mg and the experiment was replicated 2-3 times to ensure the viability of the results (sample sizes of 5-7 mg were sent).

Elemental Analysis. Elemental analysis was performed by Patricia Granados at the Centre for Environmental Analysis and Remediation (Saint Mary's University, Halifax, Canada). Carbon, hydrogen, and nitrogen analyses were conducted on a PerKin Elmer 2400 Series II CHN Analyser. CHN results were processed as a percentage by weight of each element and were measured as a function of thermal conductivity. For the analysis, samples sizes were between 2.5-3.5 mg and the experiment was replicated 2-3 times to ensure the viability of the results (sample sizes of 15-20 mg were sent).

UV-Vis Spectroscopy. UV-Vis spectra for the cyclometalated Ir(III) complexes **5-11** were recorded with a Cary Series UV-Vis Spectrophotometer (Agilent Technologies). Chloroform – HPLC grade (C606-1, LOT 214513) was used as the blank solution and the solvent to prepare the solutions of the several Ir(III) complexes **5-11**. Two standard Q macro cuvettes with an optical path length of 10 millimetres which are made of fused quartz glass were used to measure the absorbance of these compounds. UV-Vis spectra were collected with a concentration of the cyclometalated Ir(III) complexes **5-11** of $1.1 \cdot 10^{-5} – 2.8 \cdot 10^{-6}$ M (**Table S1**).

Table S1. Ir(III) complexes' concentrations.

Compound	**Concentration (M^{-1})**
5	$9.5 \cdot 10^{-6}$
6	$1.1 \cdot 10^{-5}$
7	$2.8 \cdot 10^{-6}$
8	$9.3 \cdot 10^{-6}$
9	$9.4 \cdot 10^{-6}$
10	$9.0 \cdot 10^{-6}$
11	$7.2 \cdot 10^{-6}$

Photoluminescence Emission Spectroscopy. Emission and excitation spectra, PLQY, and decay lifetime measurements were recorded with a FS5 Spectrofluorometer (Edinburgh Instruments).

- Excitation and emission spectra for the cyclometalated Ir(III) complexes **5-11** were recorded with a FS5 Spectrofluorometer (Edinburgh Instruments) and a SC-05 (Standard Cuvette Holder) at 298 K. A Hellma Fluorescence Cuvette (Suprasil 6 Quartz, spectral range 200-2,500 nm, pathlength 10x4 mm and chamber volume 3,500 µL) was used to measure the excitation and emission spectra of **5-11**. The sample solutions were prepared in chloroform – HPLC grade (C606-1, LOT 214513), which was used as a blank solution and the solvent to prepare the solutions of **5-11** (concentration of $1.1 \cdot 10^{-5}$ – $2.8 \cdot 10^{-6}$ M (**Table S1**)). All solutions were degassed in the cuvette for one minute (N_2) before each measurement.

- Photoluminescence quantum yields were calculated using the relative method. A solution of quinine sulphate in 0.1 M sulfuric acid was used as a reference sample and Ir(III) compounds **5-11** were measured at a concentration depicted in **Table S2**. Absorbance spectra were recorded in triplicate for both the reference and Ir(III) complexes **5-11** at a fixed absorbance value below 0.1, ranging from 0.075 to 0.080. All solutions were degassed in the cuvette for 20 minutes (Ar) before each measurement. (absorbance value recommended by Edinburgh Instruments). An average of these absorbances was used as the standard value for both the reference and the Ir(III) complexes **5-11**. Emission spectra were then recorded in triplicate for both the reference and Ir(III) complexes **5-11** with all samples being excited at 350 nm. The area under the curve of the emission scan was then calculated. An average of these integration values was used as the standard value for both the reference and the Ir(III) complexes **5-11**. Photoluminescence quantum yields for each Ir(III) complex **5-11** were then calculated using **eq. 1**, and the values reported in **Table S5**.

Equation 1:

$$\boldsymbol{QY}\ of\ Ir(III)\ complexes = \boldsymbol{QY}_{ref} \times \frac{I_{sample}}{I_{ref}} \times \frac{A_{ref}}{A_{sample}} \times \frac{\eta^2_{sample}}{\eta^2_{ref}}$$

I = Integrated area under the emission curve

A = Absorbance at the wavelength of excitation maxima

$\boldsymbol{\eta}$ = Refractive index

Citation: Brouwer, A. M. (2011). Standards for photoluminescence quantum yield measurements in solution (IUPAC technical report). Pure and Applied Chemistry, 83(12), 2213–2228

Table S2. Quinine sulphate and Ir(III) complexes' concentrations.

Compound	**Concentration (M^{-1})**
5	$9.5•10^{-6}$
6	$1.1•10^{-5}$
7	$2.8•10^{-6}$
8	$9.3•10^{-6}$
9	$9.4•10^{-6}$
10	$9.0•10^{-6}$
11	$7.2•10^{-6}$
QS	$1.25•10^{-5}$

- Decay lifetime measurements were recorded with a FS5 Spectrofluorometer (Edinburgh Instruments) and a SC-05 (Standard Cuvette Holder). All solutions of **5-11** were prepared to a concentration of ~$1·10^{-6}$ M using chloroform – HPLC grade (C606-1, LOT 214513) that was degassed in a cuvette for 20 minutes (Ar) before each measurement at 298 K. A QF2001 – 10 mm Lightpath Spectrophotometer Screw Cap Cuvette (Threaded – Quartz 3.5 mL) was used to measure the excitation spectra of each Ir(III) complexes (**5-11**). The excited state lifetimes were measured by the time correlated single photon counting spectra (TCSPC) technique using an EPLED-365 (Edinburgh Instruments) laser with emission detection at 520 nm for all complexes. Each lifetime measurement was calculated through an Exponential Fit Time Scan that follows the formula:

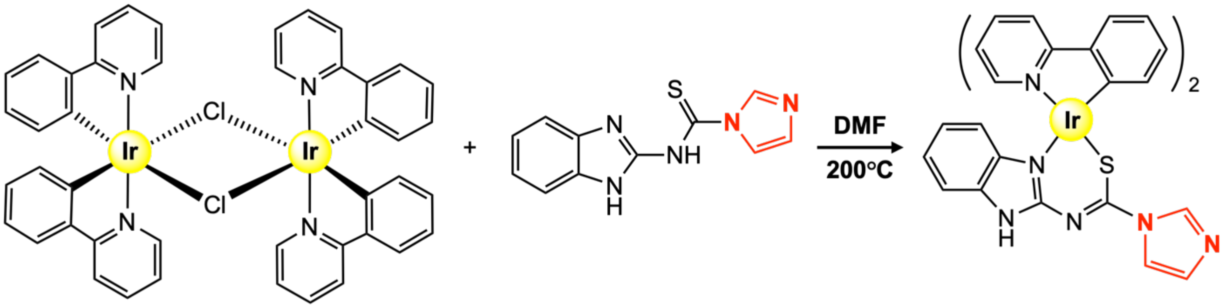
$$\text{Fit: } B_1 e^{(-t/\tau_1)} + B_2 e^{(-t/\tau_2)} + B_3 e^{(-t/\tau_3)} + B_4 e^{(-t/\tau_4)}$$

A chi-squared (χ^2) of values between 1-1.3 were found suitable. These complexes showed either monoexponential decay or biexponential decay.

S1: Synthesis of Ir(PPy)$_2$(N^S) 4 using alternative methodologies

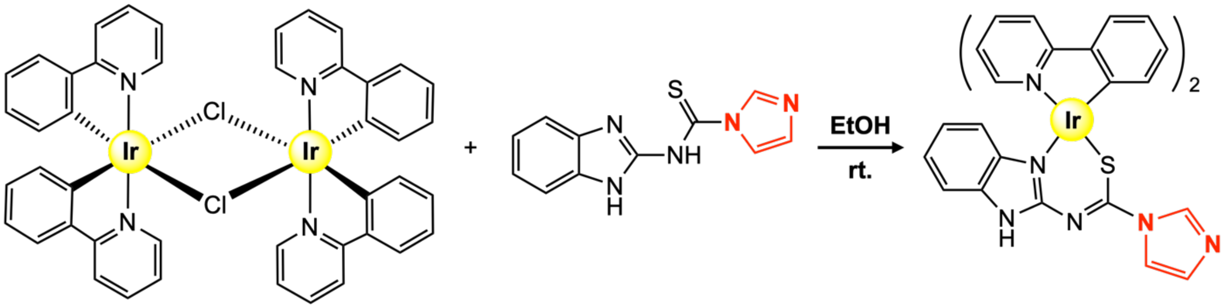
The synthesis of Ir(PPy)$_2$(N^S) **4** (Scheme 2) was also explored using two other methodologies. **Table S3** and **S4** outlines microwave (Anton Paar-monowave 400) and mechanochemistry-based (RETSCH MM 400 Mixer Mill) approaches towards **4**, respectively.

Table S3. Optimizing the synthesis of **4** with an Anton Par-Monowave 400 reactor.



Entry	Ir dimer (mg)	Base	Time (min)	Yield (%)
1	50	K_2CO_3	40	43
2	50	Cs_2CO_3	40	40
3	50	Na_2CO_3	40	34
4	50	$NaHCO_3$	40	27
5	100	Cs_2CO_3	60	58
6	100	K_2CO_3	60	62

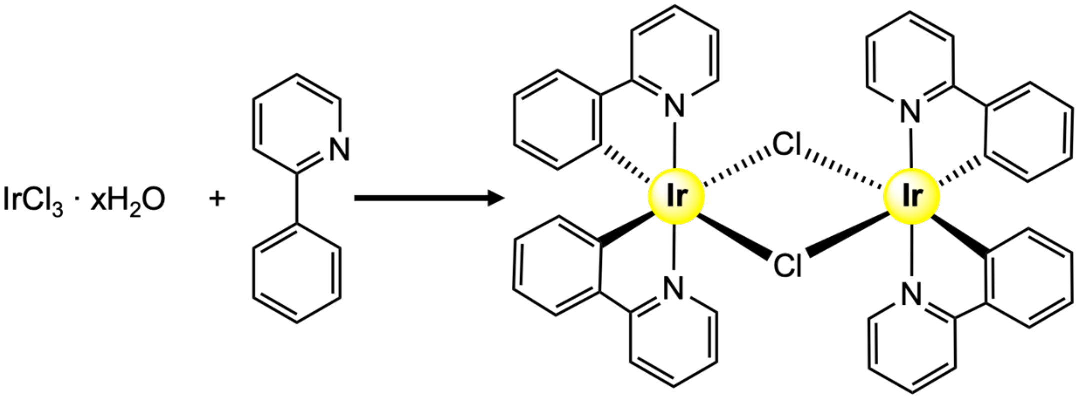
Table S4. Optimizing the formation of compound **4** using a RETSCH Mixer Mill MM 400.



Entry	Ir dimer (mg)	Base	Time (min)	Yield (%)
1	30	K_2CO_3	40	31
2	30	Cs_2CO_3	40	33
3	30	Na_2CO_3	40	27
4	100	K_2CO_3	40	44
5	100	Cs_2CO_3	40	24
6	150	K_2CO_3	60	83
7	150	Cs_2CO_3	60	47
8	50	K_2CO_3	90	54
9	50	Cs_2CO_3	90	47

SII: Synthetic Procedures and Characterization Data

Synthesis of Cyclometalated Ir(III) dimer **[Ir(ppy)$_2$Cl]$_2$**:

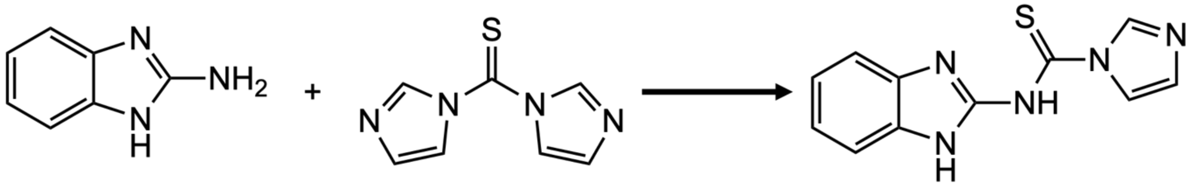


A mixture of iridium(III) chloride trihydrate (0.4 g, 1.13 mmol, 1.0 eq) and 2-phenylpyridine (0.34 mL, 2.38 mmol, 2.1 eq) was dissolved in 2-ethoxyethanol/water (3:1) mixture (30 mL). The reaction was refluxed under N_2 and stirred for 24 hours. The crude mixture was slowly cooled to room temperature and filtered to afford **[Ir(ppy)$_2$Cl]$_2$** (0.46 g, 76%) as a yellow solid. The characterization matches that reported in literature.[18]

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.28 – 9.19 (m, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.80 – 7.68 (m, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 6.84 – 6.68 (m, 2H), 6.56 (ddd, *J* = 7.8, 1.2, 0.7 Hz, 1H), 5.93 (d, *J* = 7.8 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 168.69, 151.84, 145.48, 143.84, 136.28, 130.72, 129.23, 123.78, 122.24, 121.45, 118.52.

Synthesis of *N*-(benzoimidazol-2-yl)imidazole-1-carbothioamide (**3**):

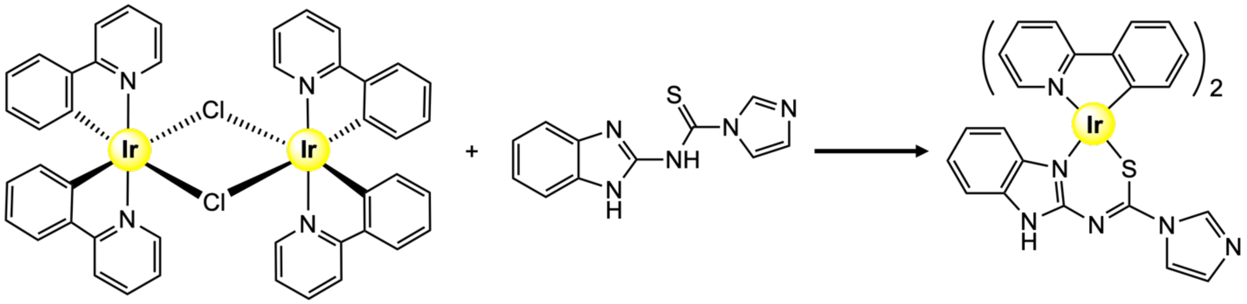


A mixture of 2-aminobenzimidazole (2.00 g, 15 mmol, 1.0 eq) and thiocarbonyldiimidazole (3.48 g, 19.5 mmol, 1.3 eq) was dissolved in acetonitrile (30 mL) and heated to 50°C. Then, the reaction was stirred at this temperature for 18 hours. The crude mixture was slowly cooled to room temperature and filtered to afford **3** (3.65 g, 63%) as a pale orange solid. The characterization matches that reported in literature.[18]

^{1}H NMR (400 MHz, DMSO-d_6): δ 13.26 (s, 2H), 8.55 (s, 1H), 7.93 (s, 1H), 7.61 (dd, J = 5.9, 3.1 Hz, 2H), 7.34 (dd, J = 5.9, 3.1 Hz, 2H), 7.00 (s, 1H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 178.87, 152.17, 135.98, 129.30, 128.84, 123.87, 117.81, 112.49.

Iridium(III) primer complex (**4**):



A mixture of iridium complex **[Ir(ppy)$_2$Cl]$_2$** (0.1 g, 0.093 mmol, 1.0 eq), *N*-(benzoimidazol-2-yl)imidazole-1-carbothioamide (**3**) (0.047 g, 0.20 mmol, 2.1 eq) and K_2CO_3 (0.13 g, 0.93 mmol, 10 eq) was dissolved in toluene (10 mL). The reaction was heated to 110°C and stirred for 24 hours. Then, the reaction was slowly cooled down to room temperature. The mixture was quenched with water (20 mL) and diluted with EtOAc (15 mL). The aqueous phase was washed further with EtOAc (2 x 15 mL), before the organic phases were combined, dried over with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica eluting with EtOAc to afford **4** (0.082 g, 75%) as a yellow solid.

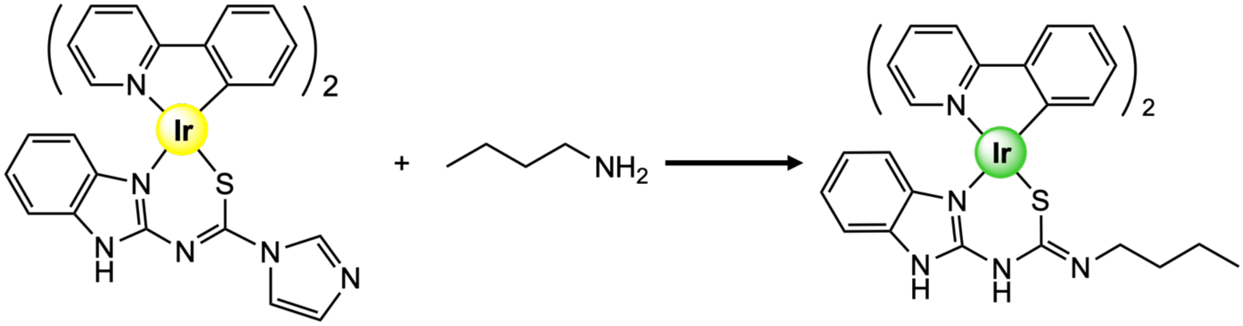
^{1}H NMR (400 MHz, DMSO-*d$_6$*) δ 12.53 (s, 1H), 9.35 – 9.29 (m, 1H), 8.48 – 8.44 (m, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 8.15 – 8.10 (m, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.95 – 7.88 (m, 1H), 7.87 – 7.74 (m, 4H), 7.29 (ddd, *J* = 13.1, 9.5, 4.6 Hz, 2H), 7.23 – 7.16 (m, 1H), 7.01 – 6.89 (m, 3H), 6.87 – 6.79 (m, 2H), 6.68 (td, *J* = 7.4, 1.2 Hz, 1H), 6.57 – 6.49 (m, 1H), 6.28 – 6.22 (m, 2H), 6.10 - 6.05 (m, 1H).

^{13}C NMR (101 MHz, DMSO-*d$_6$*) δ 167.90, 167.14, 161.38, 156.66, 150.09, 149.75, 149.30, 148.10, 144.19, 144.08, 142.00, 137.79, 137.48, 135.33, 132.35, 131.37, 131.08, 129.38, 129.17, 129.05, 124.75, 124.13, 123.05, 122.88, 122.31, 121.43, 121.07, 121.03, 119.68, 119.20, 117.72, 117.55, 110.37.

Anal. Calcd. for $C_{34}H_{24}IrN_7S$: C, 53.35; H, 3.26; N, 13.20%. Found: C, 53.75; H, 3.49; N, 12.48 %.

$C_{33}H_{25}IrN_7S$ [M^+] Exact Mass: 743.1438. Expected HRMS $[M+H]^+$: 744.1515; Found HRMS $[M+H]^+$: 744.1508.

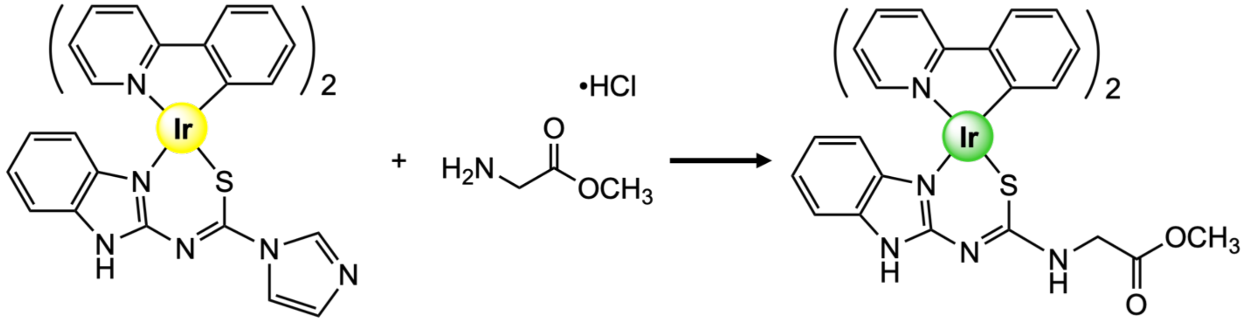
Cyclometalated Ir(III) complex **2**:



A mixture of iridium primer complex (**4**) (60.1 mg, 0.080 mmol, 1.0 eq), *n*-butylamine (0.01 mL, 0.104 mmol, 1.3 eq) and Et_3N (0.11 mL, 0.802 mmol, 10 eq) was dissolved in DMF (10 mL). The reaction was heated to 153°C and stirred for 48 hours. Then, the reaction was slowly cooled down to room temperature. The mixture was quenched with water (20 mL) and diluted with EtOAc (15 mL). The aqueous phase was washed further with EtOAc (2 x 15 mL), before the organic phases were combined, dried over with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica eluting with EtOAc to afford **2** (56.8 mg, 94%) as a yellow solid. The characterization matches that reported in literature.[18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 6.0 Hz, 1H), 8.43 (br. s, 1H), 8.16 (d, *J* = 5.4 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.73 – 7.67 (m, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.16 – 7.10 (m, 1H), 7.05 – 6.99 (m, 2H), 6.98 – 6.89 (m, 2H), 6.88 – 6.83 (m, 1H), 6.80 – 6.75 (m, 1H), 6.73 – 6.68 (m, 1H), 6.44 (d, *J* = 8.4 Hz, 1H), 6.37 (d, *J* = 7.4 Hz, 1H), 6.22 (d, *J* = 7.5 Hz, 1H), 3.54 – 3.38 (m, 2H), 1.42 – 1.31 (m, 2H), 1.23 (dd, *J* = 12.7, 5.7 Hz, 2H), 0.92 – 0.87 (m, 3H).

Cyclometalated Ir(III) complex **5**:



A mixture of iridium primer complex (**4**) (0.03 g, 0.040 mmol, 1.0 eq), glycine methyl ester hydrochloride (0.0066 g, 0.052 mmol, 1.3 eq) and Et_3N (0.056 mL, 0.403 mmol, 10 eq) was dissolved in DMF (10 mL). The reaction was heated to 153°C and stirred for 48 hours. Then, the reaction was slowly cooled down to room temperature. The mixture was quenched with water (20 mL) and diluted with EtOAc (15 mL). The aqueous phase was washed further with EtOAc (2 x 15 mL), before the organic phases were combined, dried over with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica eluting with EtOAc to afford **139** (0.0289 g, 94%) as a yellow solid.

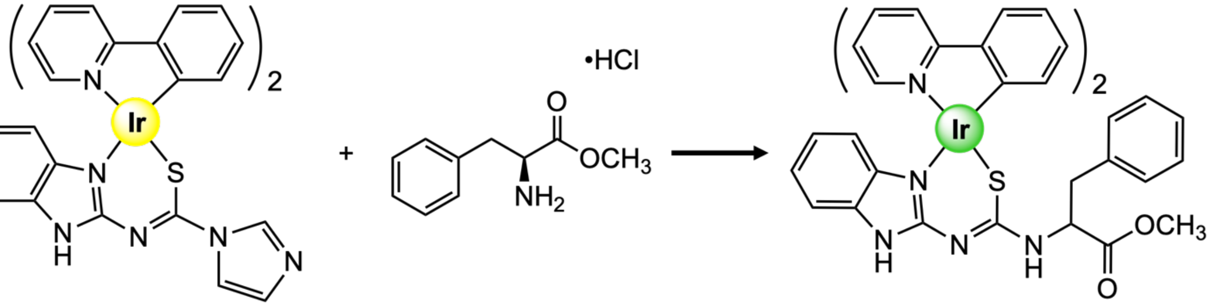
^1H NMR (400 MHz, DMSO-d_6) δ 11.33 (s, 1H), 9.43 – 9.36 (m, 1H), 8.19 (dd, *J* = 7.3, 6.5 Hz, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.83 – 7.76 (m, 1H), 7.75 – 7.67 (m, *J* = 7.9 Hz, 2H), 7.29 – 7.22 (m, 1H), 7.21 – 7.13 (m, 1H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.84 (dd, *J* = 10.8, 4.1 Hz, 1H), 6.80 – 6.69 (m, 3H), 6.65 – 6.57 (m, 1H), 6.38 – 6.32 (m, 1H), 6.28 (d, *J* = 6.9 Hz, 1H), 6.19 (d, *J* = 8.2 Hz, 1H), 6.02 (d, *J* = 6.9 Hz, 1H), 3.17 – 3.12 (m, 5H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 169.52, 168.35, 167.42, 158.78, 153.69, 151.59, 150.38, 149.56, 144.12, 144.08, 142.33, 137.09, 136.72, 132.37, 131.28, 131.17, 128.89,

128.66, 124.43, 123.83, 122.31, 122.11, 120.58, 120.24, 120.01, 119.54, 119.12, 118.73, 116.16, 108.52, 59.72, 20.74, 14.07.

$C_{33}H_{27}IrN_6O_2S$ [M^+] Exact Mass: 764.1545. Expected HRMS [$M-CH_3$]$^+$: 749.1198; Found HRMS [$M-CH_3$]$^+$: 749.2. Expected HRMS [$M-C(O)OCH_3$]$^+$:705.1407; Found HRMS [$M-C(O)OCH_3$]$^+$:705.2.

Cyclometalated Ir(III) complex **6**:



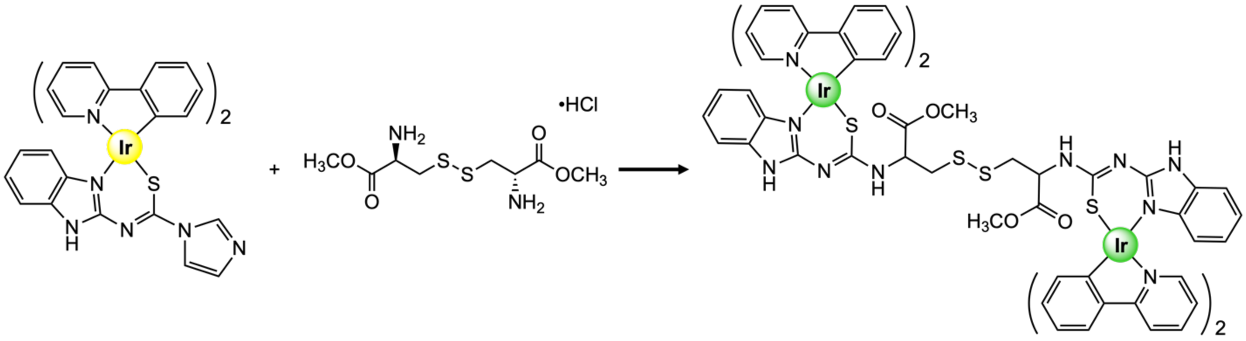
A mixture of iridium primer complex (**4**) (0.1 g, 0.134 mmol, 1.0 eq), L-phenylalanine methyl ester hydrochloride (0.037 g, 0.175 mmol, 1.3 eq) and Et_3N (0.187 mL, 1.344 mmol, 10 eq) was dissolved in DMF (10 mL). The reaction was heated to 153°C and stirred for 48 hours. Then, the reaction was slowly cooled down to room temperature. The mixture was quenched with water (20 mL) and diluted with EtOAc (15 mL). The aqueous phase was washed further with EtOAc (2 x 15 mL), before the organic phases were combined, dried over with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica eluting with EtOAc to afford **6** (0.1044 g, 91%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 – 9.43 (m, 1H), 9.00 (s, 1H), 8.51 – 8.24 (m, 1H), 7.99 – 7.80 (m, J = 16.2 Hz, 1H), 7.73 – 7.47 (m, 6H), 7.41 – 7.12 (m, J = 3.0 Hz, 2H), 7.09 – 6.77 (m, 9H), 6.78 – 6.66 (m, J = 6.4 Hz, 1H), 6.64 – 6.53 (m, 1H), 6.53 – 6.38 (m, J = 2.9 Hz, 2H), 6.32 – 6.19 (m, J = 7.0 Hz, 1H), 3.44 – 3.17 (m, 6H).

^{13}C NMR (201 MHz, DMSO-*d₆*) δ 172.78, 171.39, 169.63, 168.32, 167.39, 160.85, 158.66, 153.68, 151.48, 150.32, 149.51, 144.04, 142.26, 136.96, 136.76, 136.58, 132.30, 131.21, 131.06, 128.92, 128.76, 128.53, 128.13, 126.48, 124.30, 123.69, 122.14, 121.94, 120.46, 120.11, 119.88, 119.43, 118.96, 118.59, 116.07, 108.41, 51.78, 39.52, 36.63, 28.86.$C_{40}H_{33}IrN_6O_2S$ [M$^+$] Exact Mass: 854.2015. Expected HRMS [M+Na]$^+$: 877.2015;

Found HRMS $[M+Na]^+$: 877.3. Expected HRMS $[M-\{(CH2-(Ph))+(C(O)OCH_3)\}]^+$: 705.1407; Found HRMS $[M-\{(CH2-(Ph))+(C(O)OCH_3)\}]^+$:705.2. Expected HRMS [M-Ancillary ligand]$^+$: 501.0943; Found HRMS [M-Ancillary ligand]$^+$:501.1.

Cyclometalated Ir(III) complex **7**:



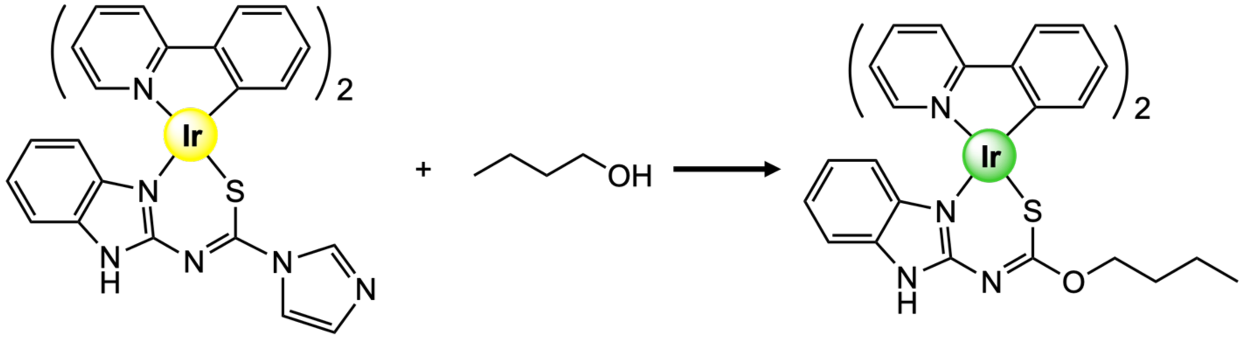
A mixture of iridium primer complex (**4**) (0.1 g, 0.134 mmol, 2.0 eq), L-cystine dimethyl ester hydrochloride (0.023 g, 0.067 mmol, 1.0 eq) and Et_3N (0.094 mL, 0.672 mmol, 10 eq) was dissolved in DMF (10 mL). The reaction was heated to 153°C and stirred for 48 hours. Then, the reaction was slowly cooled down to room temperature. The mixture was quenched with water (20 mL) and diluted with EtOAc (15 mL). The aqueous phase was washed further with EtOAc (2 x 15 mL), before the organic phases were combined, dried over with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica eluting with EtOAc to afford **7** (0.092 g, 85%) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.34 (s, 2H), 9.40 (d, J = 5.8 Hz, 2H), 8.20 (d, J = 5.8 Hz, 2H), 8.15 (d, J = 8.3 Hz, 2H), 8.02 (d, J = 8.3 Hz, 2H), 7.91 – 7.83 (m, 2H), 7.83 – 7.75 (m, 2H), 7.71 (t, J = 8.1 Hz, 4H), 7.29 – 7.22 (m, 2H), 7.21 – 7.14 (m, 2H), 6.99 (d, J = 7.8 Hz, 2H), 6.85 (dd, J = 10.4, 4.4 Hz, 2H), 6.80 – 6.69 (m, 6H), 6.66 – 6.57 (m, 2H), 6.39 – 6.31 (m, 2H), 6.28 (d, J = 7.6 Hz, 2H), 6.19 (d, J = 8.3 Hz, 2H), 6.02 (d, J = 7.6 Hz, 2H), 3.23 – 3.07 (m, J = 10.8, 1.8 Hz, 12H).

^{13}C NMR (201 MHz, DMSO-d_6) δ 206.93, 150.06, 137.59, 137.22, 131.77, 131.66, 131.39, 130.74, 130.56, 130.18, 129.38, 129.15, 128.57, 124.93, 124.32, 123.51, 122.81, 122.60, 122.42, 121.87, 121.32, 121.07, 120.88, 120.73, 120.50, 120.03, 119.61, 119.23, 116.64, 114.97, 109.01, 69.76, 29.48, 29.16.

$C_{68}H_{56}Ir_2N_{12}O_4S_4$ [M$^+$] Exact Mass: 1618.2689. Expected HRMS [M-PPy ligand]$^+$: 1463.2032; Found HRMS [M-1Cyclometalated ligand]$^+$:1463.3. Expected HRMS [M-{1Ancillary ligand + Ir(III) + 2 Cyclometalated ligands}]$^+$: 501.0943; Found HRMS [M-{1Ancillary ligand + Ir(III) + 2 Cyclometalated ligands}]$^+$: 501.1.

Cyclometalated Ir(III) complex **8**:



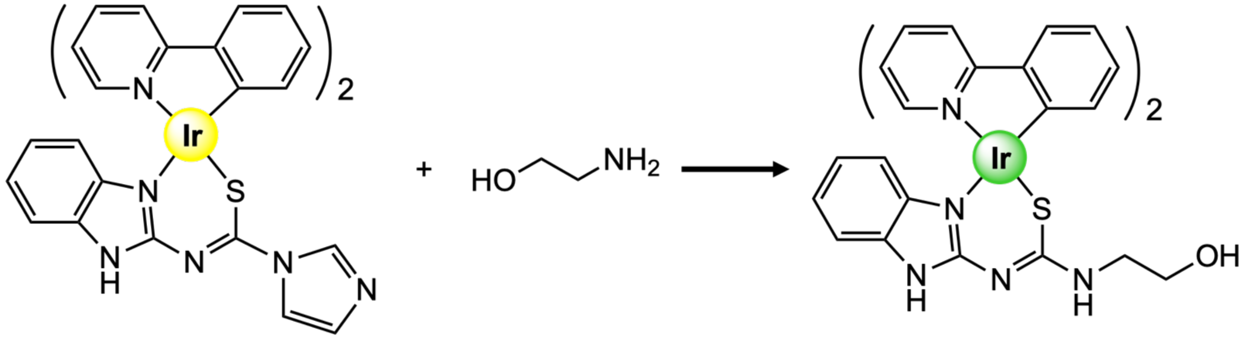
A mixture of iridium primer complex (**4**) (0.1 g, 0.134 mmol, 1.0 eq), 1-butanol (0.016 mL, 0.175 mmol, 1.3 eq) and KHMDS (0.225 g, 1.344 mmol, 10 eq) was dissolved in DMF (10 mL). The reaction was heated to 153°C and stirred for 48 hours. Then, the reaction was slowly cooled down to room temperature. The mixture was quenched with water (20 mL) and diluted with EtOAc (15 mL). The aqueous phase was washed further with EtOAc (2 x 15 mL), before the organic phases were combined, dried over with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica eluting with EtOAc to afford **8** (0.0876 g, 87%) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.33 (s, 1H), 9.39 (d, J = 2.2 Hz, 1H), 8.18 (t, J = 5.2 Hz, 1H), 8.15 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.89 – 7.82 (m, 1H), 7.83 – 7.75 (m, 1H), 7.70 (dd, J = 11.0, 5.0 Hz, 2H), 7.30 – 7.22 (m, 1H), 7.21 – 7.14 (m, 1H), 6.98 (dd, J = 7.7, 2.1 Hz, 1H), 6.85 (ddd, J = 7.5, 5.5, 2.3 Hz, 1H), 6.81 – 6.69 (m, 3H), 6.65 – 6.57 (m, 1H), 6.38 – 6.31 (m, 1H), 6.28 (dd, J = 7.4, 2.2 Hz, 1H), 6.19 (dd, J = 8.1, 2.4 Hz, 1H), 6.02 (dd, J = 7.5, 2.2 Hz, 1H), 3.17 – 3.11 (m, J = 3.1 Hz, 4H), 1.29 – 1.22 (m, 5H).

^{13}C NMR (201 MHz, DMSO-d_6) δ 169.52, 168.37, 167.43, 158.80, 153.70, 151.62, 150.38, 149.57, 144.15, 144.10, 142.35, 137.11, 136.74, 132.39, 131.30, 131.19, 128.91, 128.68, 124.45, 123.85, 122.34, 122.13, 120.60, 120.25, 120.02, 119.55, 119.14, 118.75, 116.17, 108.53, 59.74, 29.77, 20.76, 14.09.

$C_{34}H_{30}IrN_5OS$ [M^+] Exact Mass: 749.1800. Expected HRMS [$M-CH_2CH_2CH_3$]$^+$: 705.1247; Found HRMS [$M-CH_2CH_2CH_3$]$^+$: 705.2. Expected HRMS [M-Ancillary ligand]$^+$: 501.0943; Found HRMS [M-Ancillary ligand]$^+$:501.1.

Cyclometalated Ir(III) complex **9**:



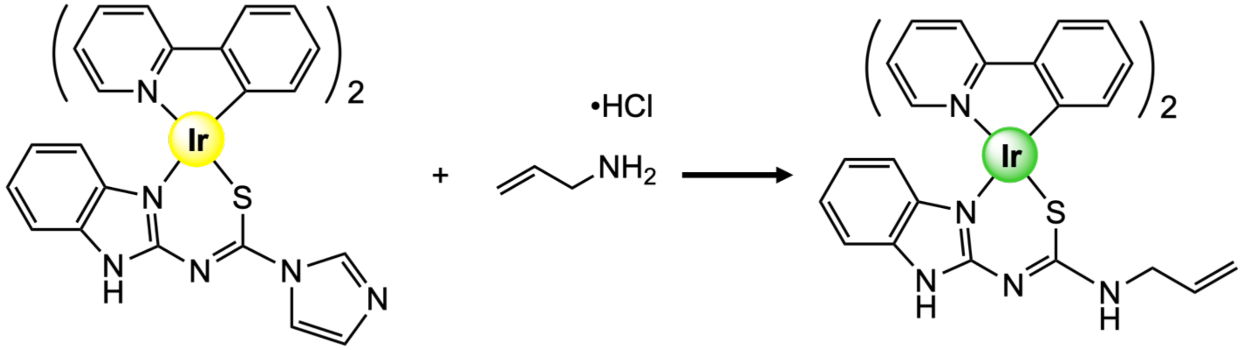
A mixture of iridium primer complex (**4**) (0.05 g, 0.0672 mmol, 1.0 eq), ethanolamine (0.006 mL, 0.0873 mmol, 1.3 eq) and Et_3N (0.094 mL, 0.672 mmol, 10 eq) was dissolved in DMF (10 mL). The reaction was heated to 153°C and stirred for 48 hours. Then, the reaction was slowly cooled down to room temperature. The mixture was quenched with water (20 mL) and diluted with EtOAc (15 mL). The aqueous phase was washed further with EtOAc (2 x 15 mL), before the organic phases were combined, dried over with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica eluting with EtOAc to afford **9** (0.0505 g, 97%) as a yellow solid.

^{1}H NMR (800 MHz, DMSO-*d*$_6$) δ 11.34 (s, 1H), 9.39 (dd, *J* = 5.8, 0.8 Hz, 1H), 8.21 – 8.19 (m, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.80 – 7.77 (m, 1H), 7.73 – 7.71 (m, 1H), 7.71 – 7.69 (m, 1H), 7.25 (ddd, *J* = 7.3, 5.9, 1.4 Hz, 1H), 7.17 (ddd, *J* = 7.3, 5.9, 1.4 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.86 – 6.83 (m, 1H), 6.78 – 6.75 (m, 1H), 6.75 – 6.72 (m, 2H), 6.63 – 6.58 (m, 1H), 6.36 – 6.33 (m, 1H), 6.29 – 6.26 (m, 1H), 6.19 (d, *J* = 8.3 Hz, 1H), 6.01 (dd, *J* = 9.0, 8.2 Hz, 1H), 3.15 – 3.14 (m, 4H).

^{13}C NMR (201 MHz, DMSO-d_6) δ 170.00, 168.86, 167.92, 159.30, 154.18, 152.10, 150.88, 150.07, 144.63, 144.58, 142.83, 137.60, 137.23, 132.87, 131.78, 131.68, 129.40, 129.17, 124.94, 124.34, 122.83, 122.62, 121.09, 120.74, 120.51, 120.04, 119.63, 119.24, 116.66, 109.03, 69.99, 60.69.

$C_{32}H_{27}IrN_6OS$ [M^+] Exact Mass: 736.1596. Expected HRMS $[M+H]^+$: 737.1675; Found HRMS $[M+H]^+$:737.3. Expected HRMS $[M+Na]^+$:759.1494. Found HRMS $[M+Na]^+$:759.1.

Cyclometalated Ir(III) complex **10**:



A mixture of iridium primer complex (**4**) (0.1 g, 0.134 mmol, 1.0 eq), allylamine hydrochloride (0.016 g, 0.175 mmol, 1.3 eq) and KHMDS (0.225 g, 1.344 mmol, 10 eq) was dissolved in DMF (10 mL). The reaction was heated to 153°C and stirred for 48 hours. Then, the reaction was slowly cooled down to room temperature. The mixture was quenched with water (20 mL) and diluted with EtOAc (15 mL). The aqueous phase was washed further with EtOAc (2 x 15 mL), before the organic phases were combined, dried over with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica eluting with EtOAc to afford **10** (0.0885 g, 90%) as a yellow solid.

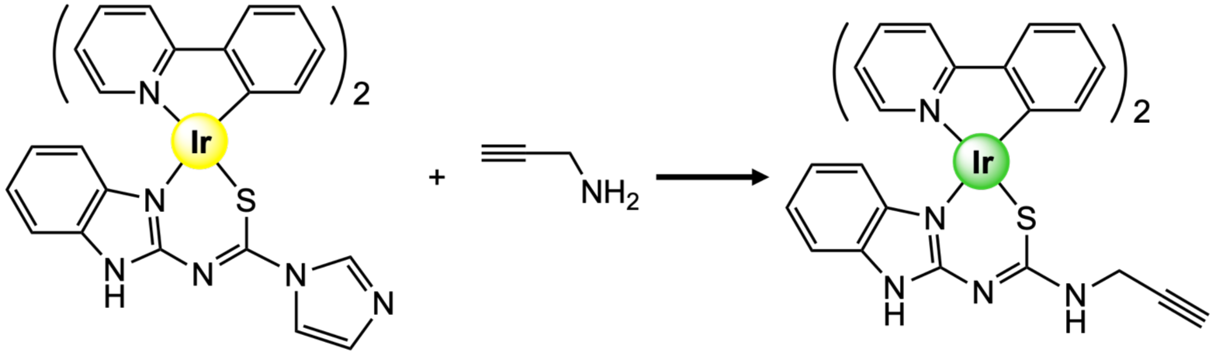
^{1}H NMR (800 MHz, DMSO-*d*$_6$) δ 12.51 (s, 1H), 9.72 (dd, J = 5.7, 0.9 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.99 (dd, J = 5.7, 0.7 Hz, 1H), 7.91 (s, 1H), 7.89 – 7.86 (m, 1H), 7.85 – 7.82 (m, 1H), 7.69 – 7.66 (m, 2H), 7.35 (ddd, J = 7.3, 5.8, 1.4 Hz, 1H), 7.23 (ddd, J = 7.3, 5.8, 1.4 Hz, 1H), 7.11 – 7.09 (m, 1H), 6.82 – 6.80 (m, 1H), 6.74 – 6.71 (m, 2H), 6.71 – 6.68 (m, 1H), 6.62 – 6.59 (m, 1H), 6.16 (dd, J = 7.7, 0.9 Hz, 1H), 6.05 (dd, J = 7.6, 0.9 Hz, 1H), 2.79 – 2.76 (m, 2H).

^{13}C NMR (201 MHz, DMSO-*d*$_6$) δ 168.46, 167.71, 152.40, 150.82, 150.73, 149.46, 145.18, 144.69, 139.68, 137.71, 137.43, 136.79, 132.22, 131.20, 129.83, 129.42, 128.84,

127.17, 125.27, 124.66, 124.12, 123.28, 122.76, 122.72, 122.43, 120.87, 120.52, 119.90, 119.30, 118.99, 117.96, 114.60, 60.23.

$C_{33}H_{27}IrN_6S$ [M^+] Exact Mass: 732.1647. Expected HRMS $[M+H]^+$: 733.1726; Found HRMS $[M+H]^+$: 733.2. Expected HRMS $[M-(=CH_2)]^+$: 719.1563; Found HRMS $[M-(=CH_2)]^+$: 719.2. Expected HRMS [M-Ancillary ligand]$^+$: 501.0943; Found HRMS [M-Ancillary ligand]$^+$:501.1. Expected HRMS $[M-H]^+$: 730.1568; Found HRMS $[M-H]^+$: 731.2.

Cyclometalated Ir(III) complex **11**:



A mixture of iridium primer complex (**4**) (0.15 g, 0.202 mmol, 1.0 eq), propargylamine (0.017 mL, 0.262 mmol, 1.3 eq) and KHMDS (0.337 g, 2.016 mmol, 10 eq) was dissolved in DMF (10 mL). The reaction was heated to 153°C and stirred for 48 hours. Then, the reaction was slowly cooled down to room temperature. The mixture was quenched with water (20 mL) and diluted with EtOAc (15 mL). The aqueous phase was washed further with EtOAc (2 x 15 mL), before the organic phases were combined, dried over with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica eluting with EtOAc to afford **11** (0.1353 g, 92%) as a yellow solid.

^1H NMR (400 MHz, DMSO-d_6) δ 11.34 (s, 1H), 9.40 (d, *J* = 5.8 Hz, 1H), 8.20 (d, *J* = 5.7 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.83 (m, 1H), 7.82 – 7.76 (m, 1H), 7.74 – 7.68 (m, 2H), 7.25 (ddd, *J* = 5.9, 3.7, 1.2 Hz, 1H), 7.21 – 7.15 (m, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.88 – 6.82 (m, 1H), 6.79 – 6.70 (m, 3H), 6.64 – 6.58 (m, 1H), 6.38 – 6.32 (m, 1H), 6.28 (d, *J* = 7.6 Hz, 1H), 6.19 (d, *J* = 8.3 Hz, 1H), 6.05 – 6.00 (m, 1H), 3.15 (s, 2H), 1.99 (s, 1H).

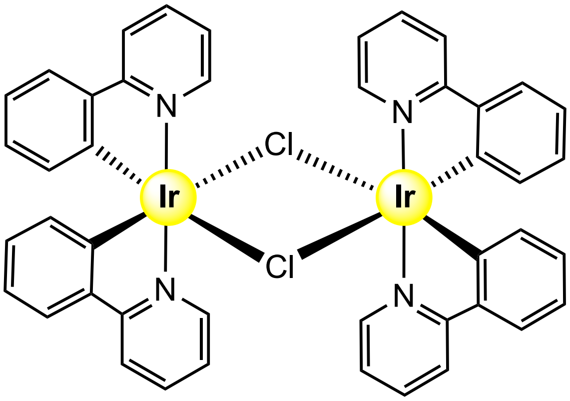
^{13}C NMR (201 MHz, DMSO-d_6) δ 168.38, 167.62, 161.84, 150.22, 149.77, 138.29, 137.98, 132.84, 131.86, 131.57, 129.88, 129.66, 129.55, 129.40, 129.31, 129.16, 127.52,

125.24, 124.62, 123.54, 123.37, 121.91, 121.51, 120.17, 119.76, 119.68, 118.20, 118.02, 113.34, 110.85, 60.23, 60.21, 30.23.

$C_{33}H_{25}IrN_6S$ [M^+] Exact Mass: 730.1491. Expected HRMS [M-(CCH)]$^+$: 719.1563; Found HRMS [M-(CCH)]$^+$: 719.2. Expected HRMS [M-H]$^+$: 729.1412; Found HRMS [M-H]$^+$: 729.2. Expected HRMS [M+H]$^+$: 731.157; Found HRMS [M+H]$^+$: 731.2.

SIII: ^{1}H and ^{13}C NMR Spectra, Mass Spectra and Elemental Analysis

Cyclometalated Ir(III) dimer complex **$[Ir(ppy)_2Cl]_2$**:



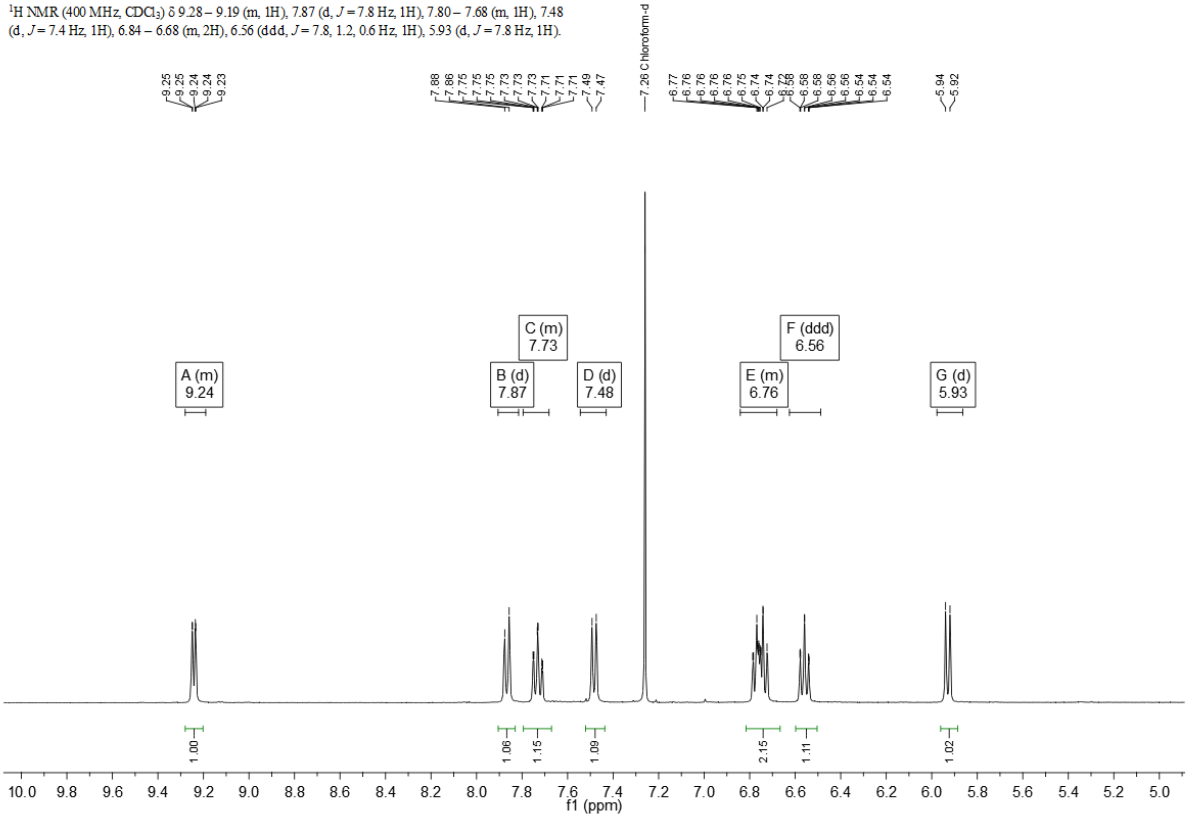
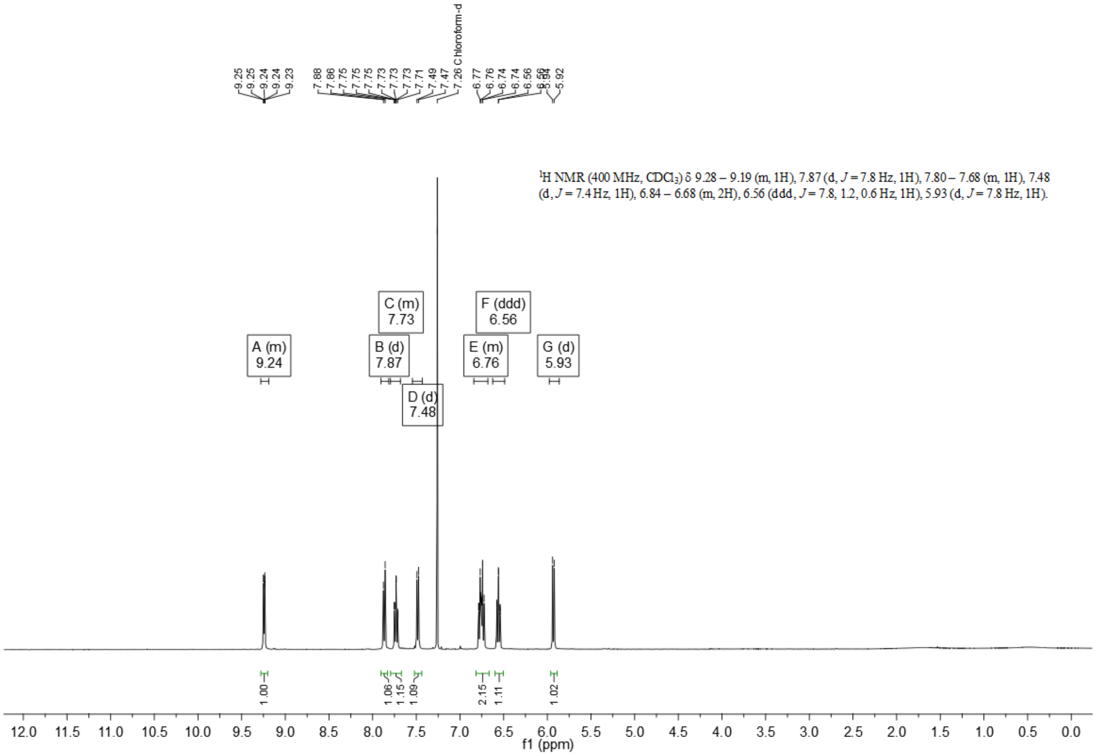
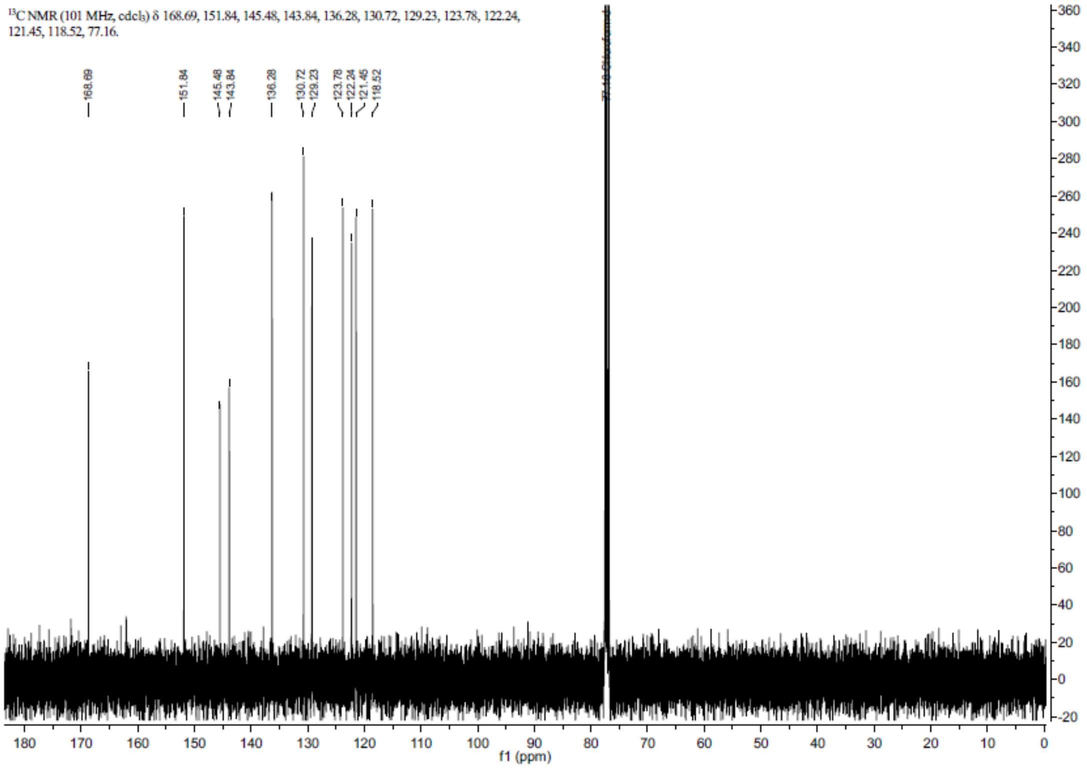

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.28 – 9.19 (m, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.80 – 7.68 (m, 1H), 7.48 (d, J = 7.4 Hz, 1H), 6.84 – 6.68 (m, 2H), 6.56 (ddd, J = 7.8, 1.2, 0.6 Hz, 1H), 5.93 (d, J = 7.8 Hz, 1H).

Figure S1. Zoomed ^{1}H-NMR spectra of **$[Ir(ppy)_2Cl]_2$** (400 MHz, DMSO-d_6) at 298K.



^{1}H NMR (400 MHz, CDCl$_3$) δ 9.28 – 9.19 (m, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.80 – 7.68 (m, 1H), 7.48 (d, J = 7.4 Hz, 1H), 6.84 – 6.68 (m, 2H), 6.56 (ddd, J = 7.8, 1.2, 0.6 Hz, 1H), 5.93 (d, J = 7.8 Hz, 1H).

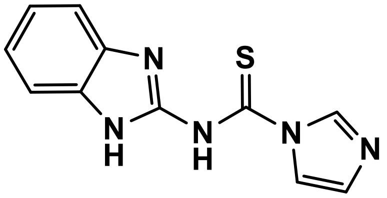
Figure S2. ^{1}H-NMR spectra of **[Ir(ppy)$_2$Cl]$_2$** (400 MHz, DMSO-d_6) at 298K.

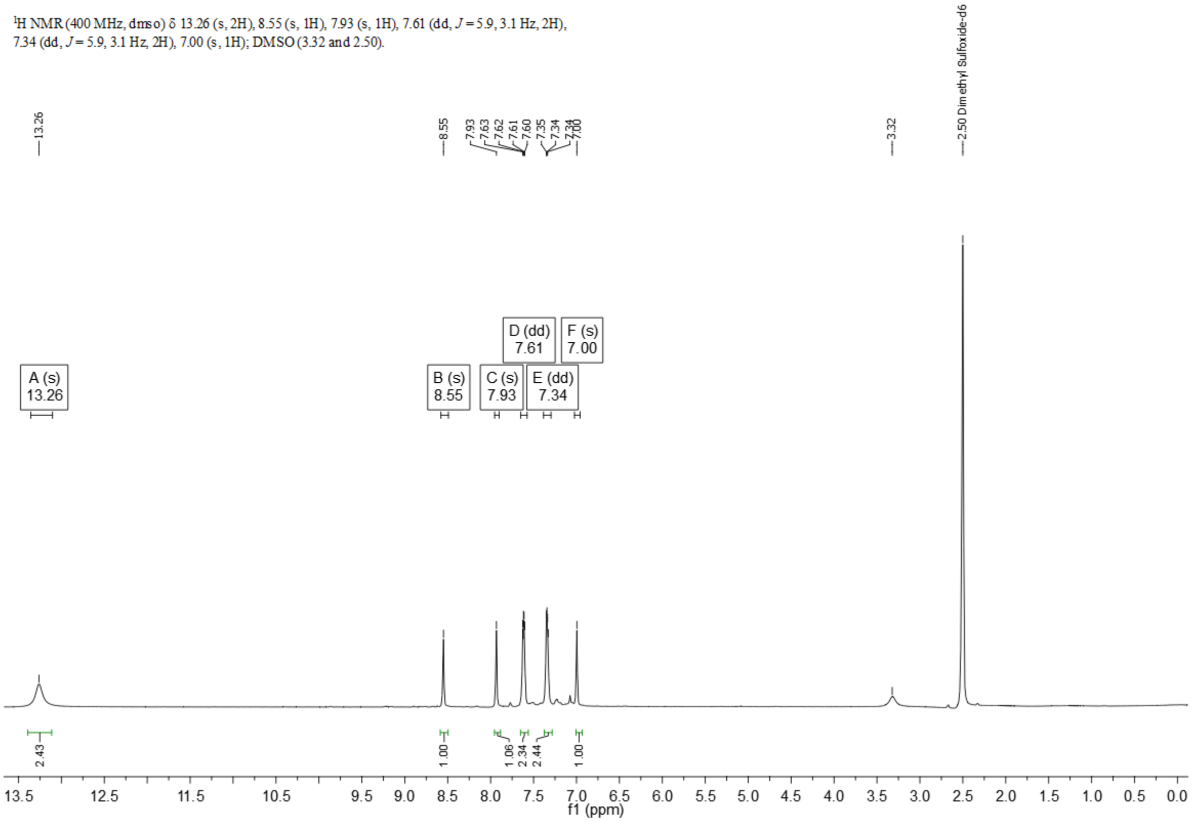


^{13}C NMR (101 MHz, cdcl$_3$) δ 168.69, 151.84, 145.48, 143.84, 136.28, 130.72, 129.23, 123.78, 122.24, 121.45, 118.52, 77.16.

Figure S3. ^{13}C-NMR spectra of compound **[Ir(ppy)$_2$Cl]$_2$** (101MHz, DMSO-d_6) at 298K.

N-(benzoimidazol-2-yl)imidazole-1-carbothioamide (**3**):





^{1}H NMR (400 MHz, dmso) δ 13.26 (s, 2H), 8.55 (s, 1H), 7.93 (s, 1H), 7.61 (dd, *J* = 5.9, 3.1 Hz, 2H), 7.34 (dd, *J* = 5.9, 3.1 Hz, 2H), 7.00 (s, 1H); DMSO (3.32 and 2.50).

Figure S4. ^{1}H-NMR spectra of compound **3** (400 MHz, DMSO-d_6) at 298K.

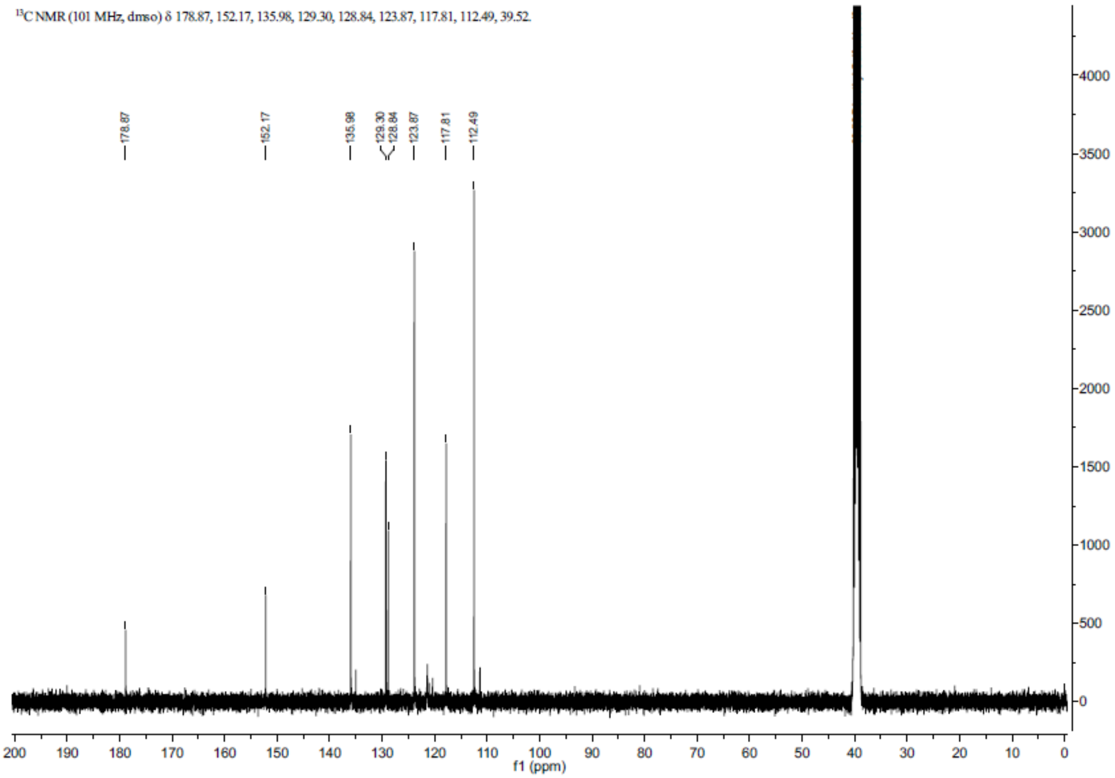
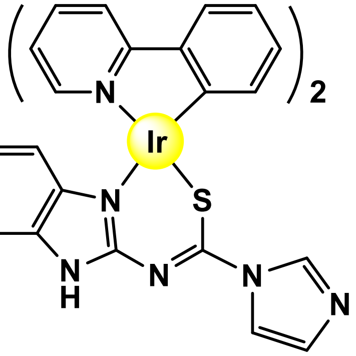


Figure S5. ^{13}C-NMR spectra of compound **3** (101 MHz, DMSO-d_6) at 298K.

Iridium primer complex **4**:



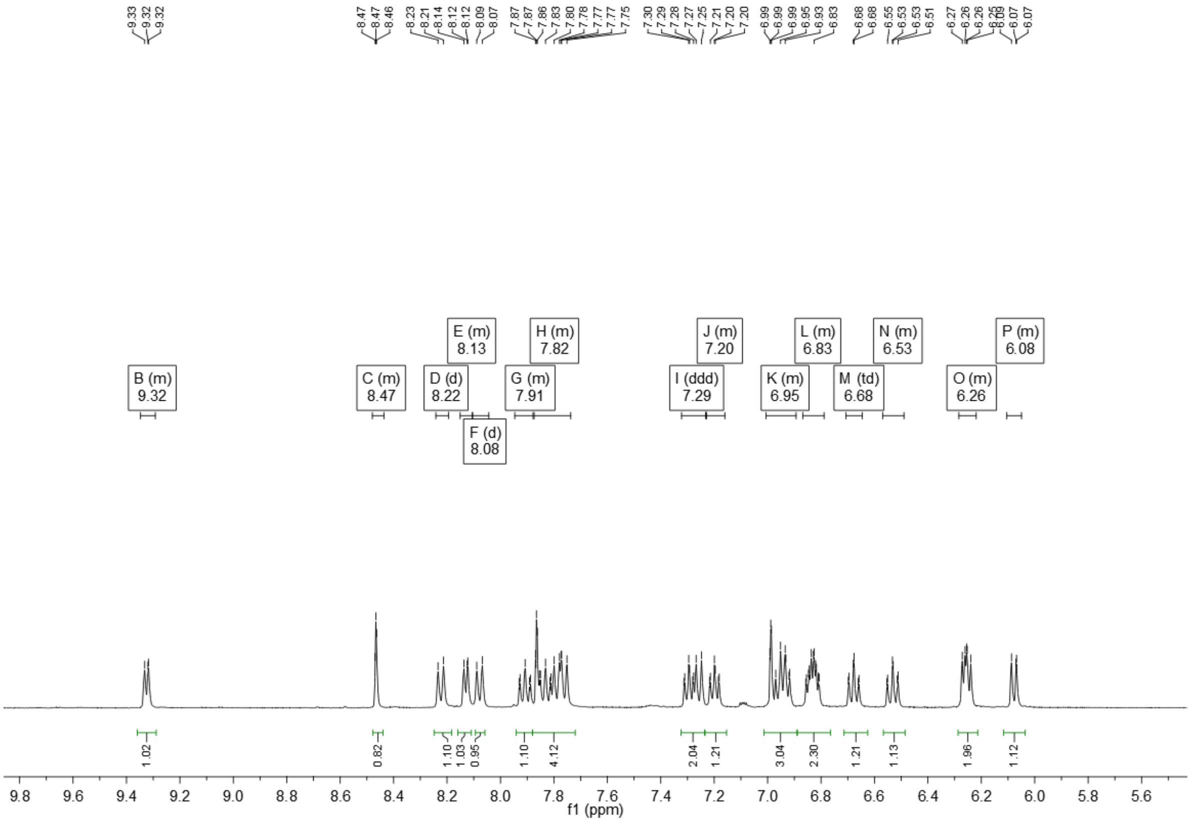
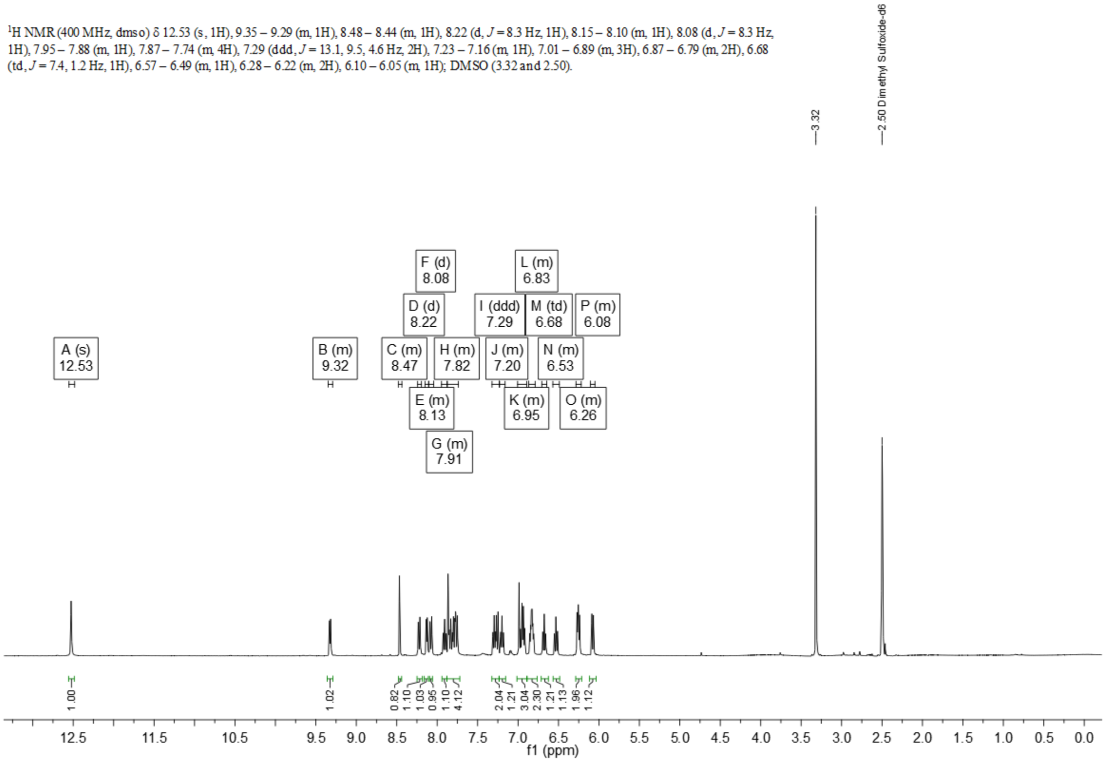


Figure S6. Zoomed ^{1}H-NMR spectra of compound **4** (400 MHz, DMSO-d_6) at 298K.



^{1}H NMR (400 MHz, dmso) δ 12.53 (s, 1H), 9.35 – 9.29 (m, 1H), 8.48 – 8.44 (m, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 8.15 – 8.10 (m, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.95 – 7.88 (m, 1H), 7.87 – 7.74 (m, 4H), 7.29 (ddd, *J* = 13.1, 9.5, 4.6 Hz, 2H), 7.23 – 7.16 (m, 1H), 7.01 – 6.89 (m, 3H), 6.87 – 6.79 (m, 2H), 6.68 (td, *J* = 7.4, 1.2 Hz, 1H), 6.57 – 6.49 (m, 1H), 6.28 – 6.22 (m, 2H), 6.10 – 6.05 (m, 1H); DMSO (3.32 and 2.50).

Figure S7. ^{1}H-NMR spectra of compound **4** (400 MHz, DMSO-*d*$_6$) at 298K.

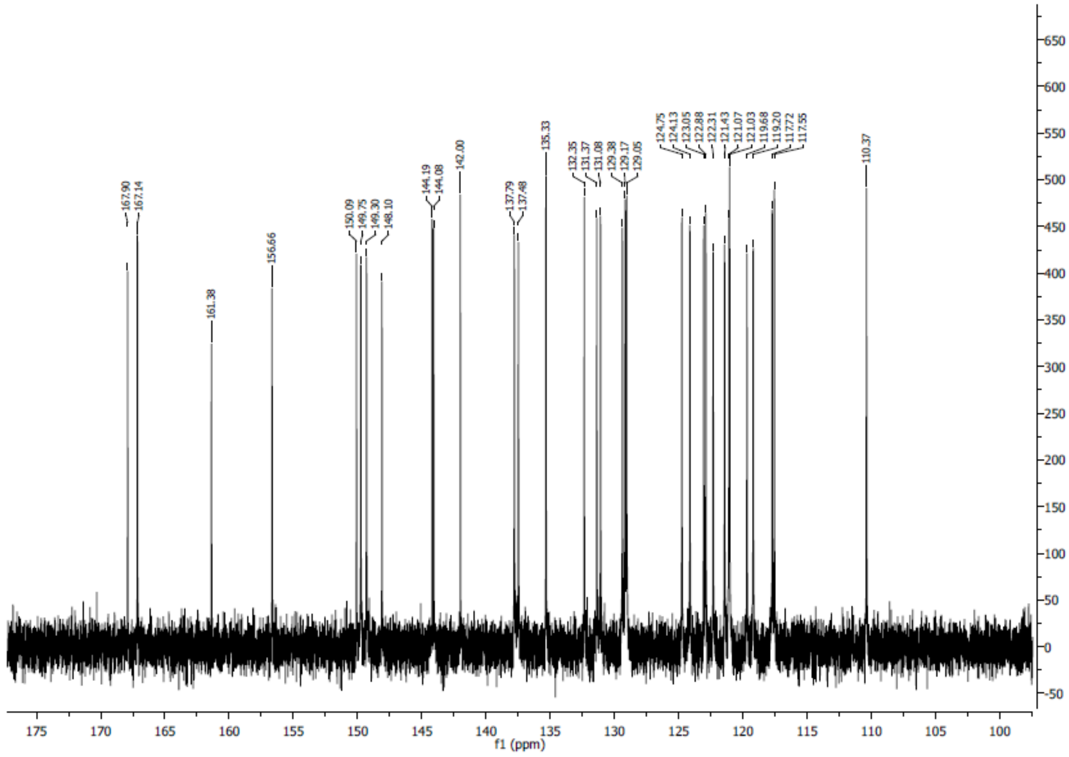
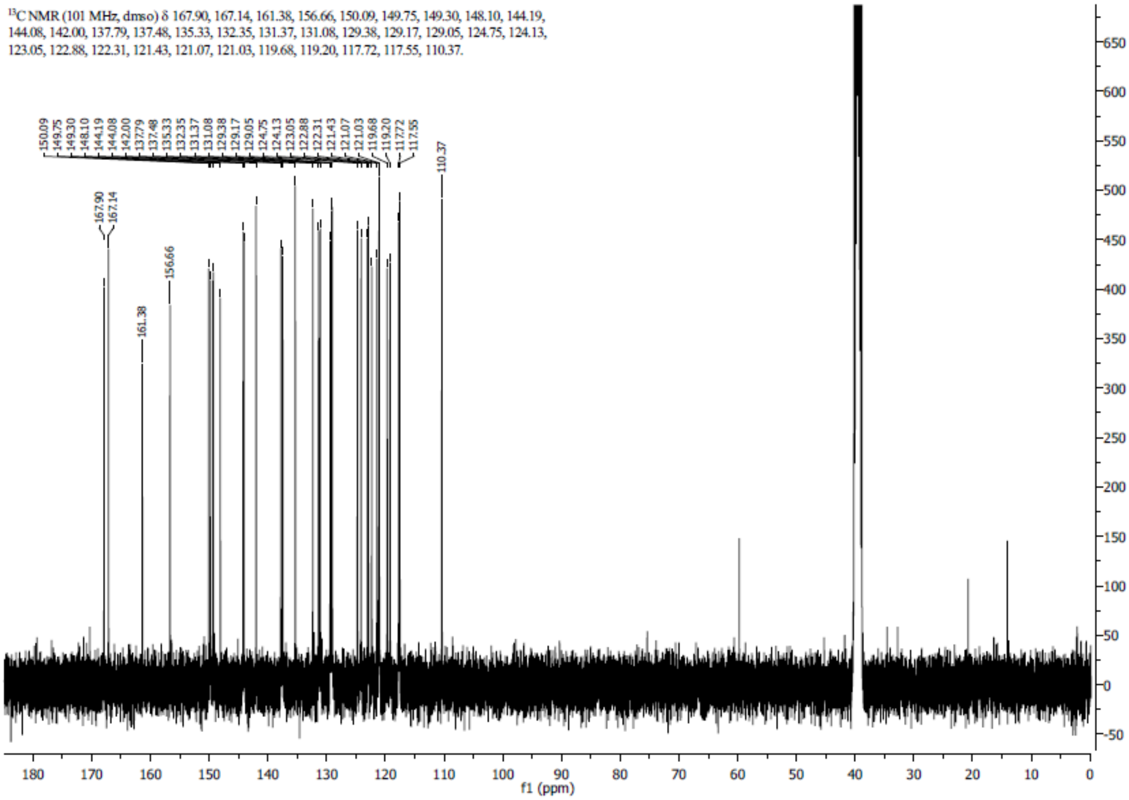
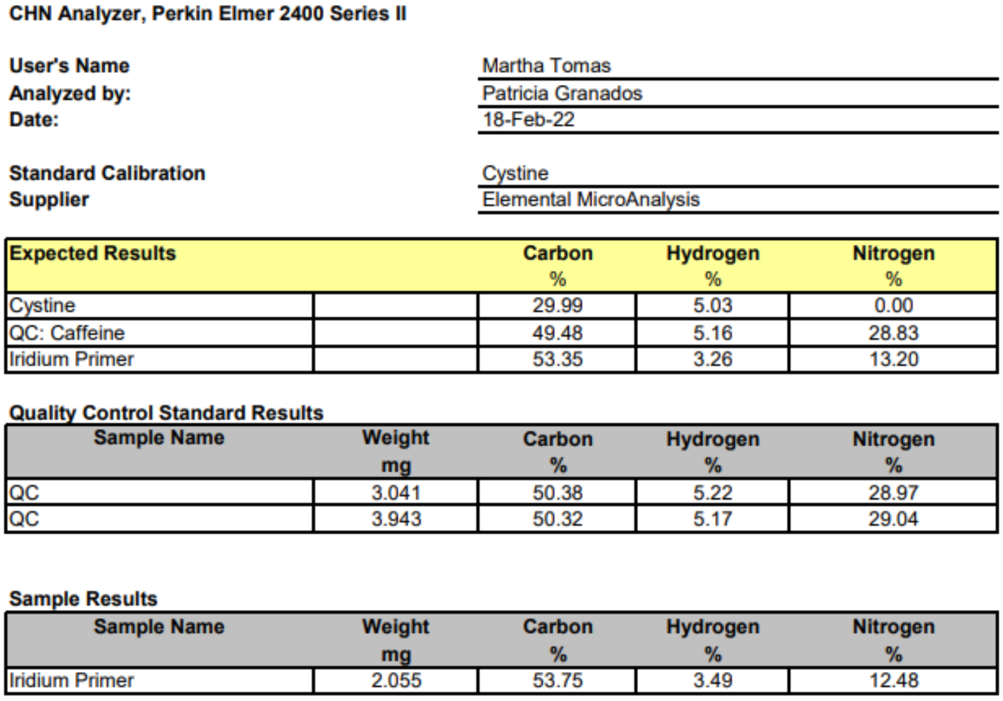


Figure S8. Zoomed ^{13}C-NMR spectra of compound **4** (101 MHz, DMSO-*d*$_6$) at 298K.



¹³C NMR (101 MHz, dmso) δ 167.90, 167.14, 161.38, 156.66, 150.09, 149.75, 149.30, 148.10, 144.19, 144.08, 142.00, 137.79, 137.48, 135.33, 132.35, 131.37, 131.08, 129.38, 129.17, 129.05, 124.75, 124.13, 123.05, 122.88, 122.31, 121.43, 121.07, 121.03, 119.68, 119.20, 117.72, 117.55, 110.37.

Figure S9. ^{13}C-NMR spectra of compound **4** (101 MHz, DMSO-d_6) at 298K.



CHN Analyzer, Perkin Elmer 2400 Series II

User's Name	Martha Tomas
Analyzed by:	Patricia Granados
Date:	18-Feb-22
Standard Calibration	Cystine
Supplier	Elemental MicroAnalysis

Expected Results		**Carbon** **%**	**Hydrogen** **%**	**Nitrogen** **%**
Cystine		29.99	5.03	0.00
QC: Caffeine		49.48	5.16	28.83
Iridium Primer		53.35	3.26	13.20

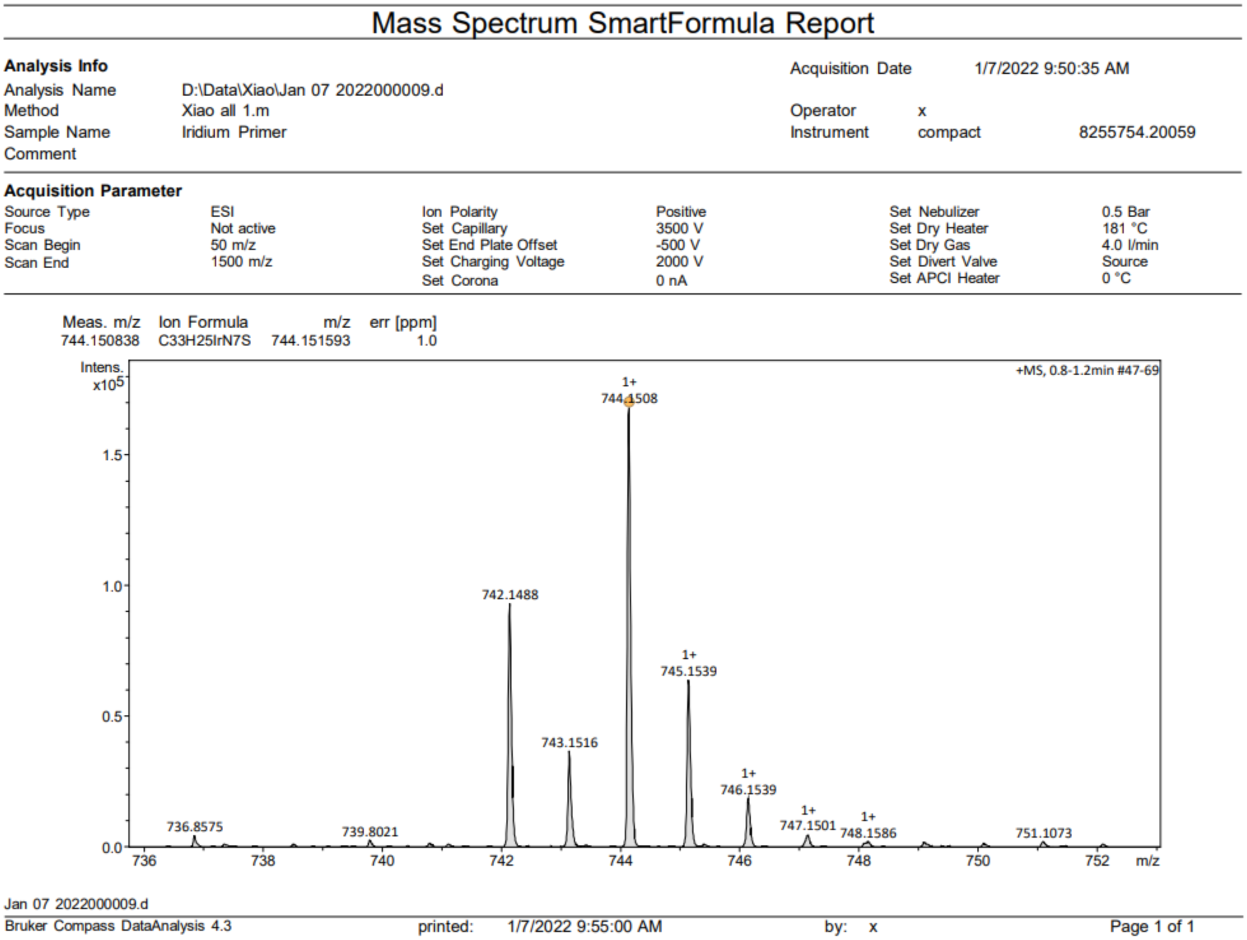
Quality Control Standard Results

Sample Name	**Weight mg**	**Carbon %**	**Hydrogen %**	**Nitrogen %**
QC	3.041	50.38	5.22	28.97
QC	3.943	50.32	5.17	29.04

Sample Results

Sample Name	**Weight mg**	**Carbon %**	**Hydrogen %**	**Nitrogen %**
Iridium Primer	2.055	53.75	3.49	12.48

Figure S10. CHN results of compound **4**.



Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Xiao\Jan 07 2022000009.d	Acquisition Date	1/7/2022 9:50:35 AM	
Method	Xiao all 1.m	Operator	x	
Sample Name	Iridium Primer	Instrument	compact	8255754.20059
Comment				

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Not active	Set Capillary	3500 V	Set Dry Heater	181 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

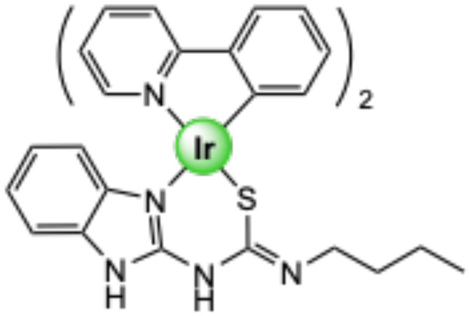
Meas. m/z	Ion Formula	m/z	err [ppm]
744.150838	C33H25IrN7S	744.151593	1.0

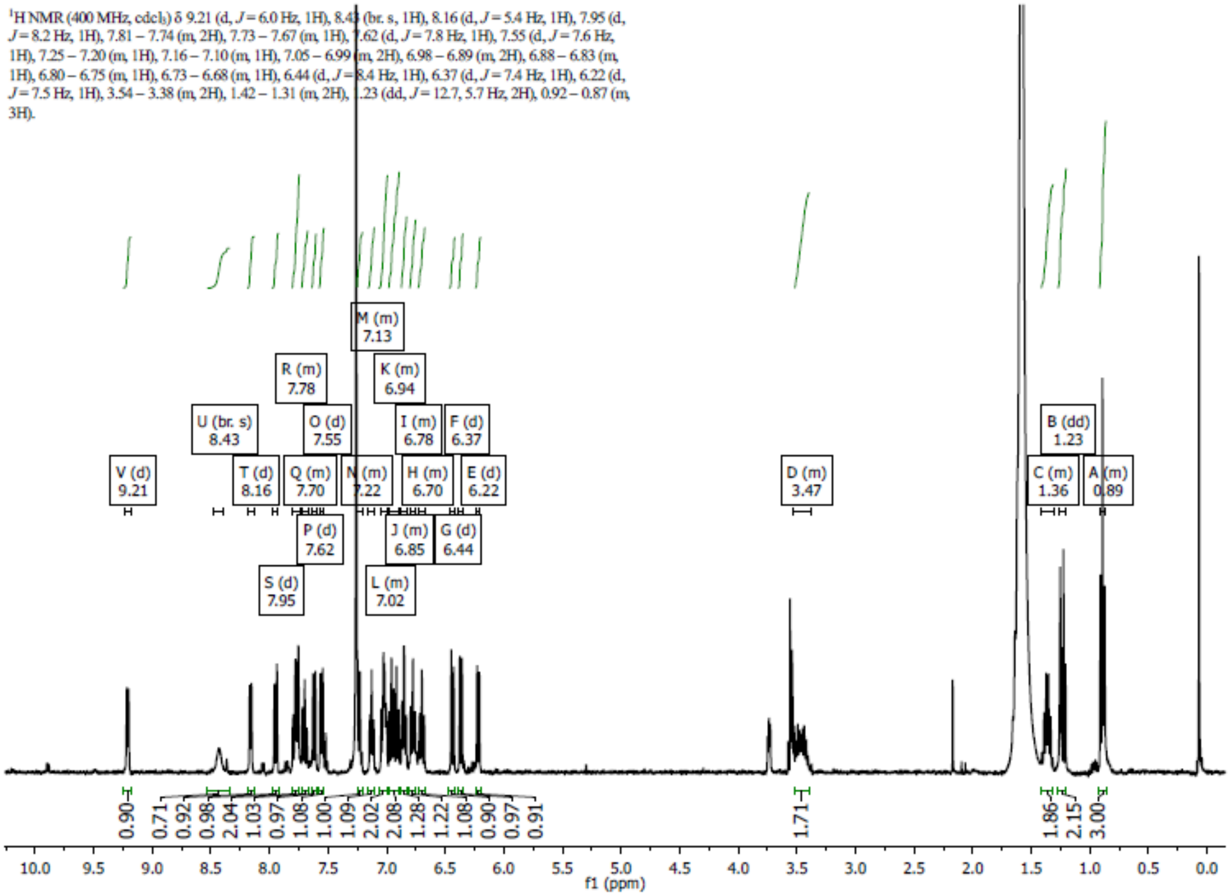
Jan 07 2022000009.d

Bruker Compass DataAnalysis 4.3 printed: 1/7/2022 9:55:00 AM by: x Page 1 of 1

Figure S11. Mass Spectroscopy results of compound **4**.

Cyclometalated Ir(III) complex **2**:

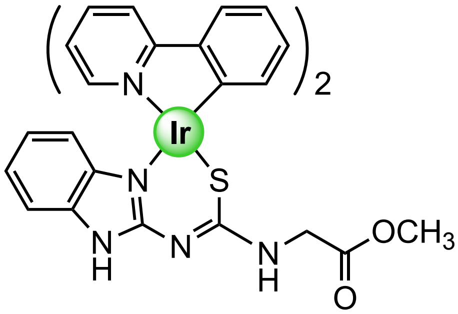




^{1}H NMR (400 MHz, cdcl$_3$) δ 9.21 (d, *J* = 6.0 Hz, 1H), 8.43 (br. s, 1H), 8.16 (d, *J* = 5.4 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.73 – 7.67 (m, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.16 – 7.10 (m, 1H), 7.05 – 6.99 (m, 2H), 6.98 – 6.89 (m, 2H), 6.88 – 6.83 (m, 1H), 6.80 – 6.75 (m, 1H), 6.73 – 6.68 (m, 1H), 6.44 (d, *J* = 8.4 Hz, 1H), 6.37 (d, *J* = 7.4 Hz, 1H), 6.22 (d, *J* = 7.5 Hz, 1H), 3.54 – 3.38 (m, 2H), 1.42 – 1.31 (m, 2H), 1.23 (dd, *J* = 12.7, 5.7 Hz, 2H), 0.92 – 0.87 (m, 3H).

Figure S12. ^{1}H-NMR spectra of compound **2** (400 MHz, CDCl$_3$) at 298K.

Cyclometalated Ir(III) complex **5**:



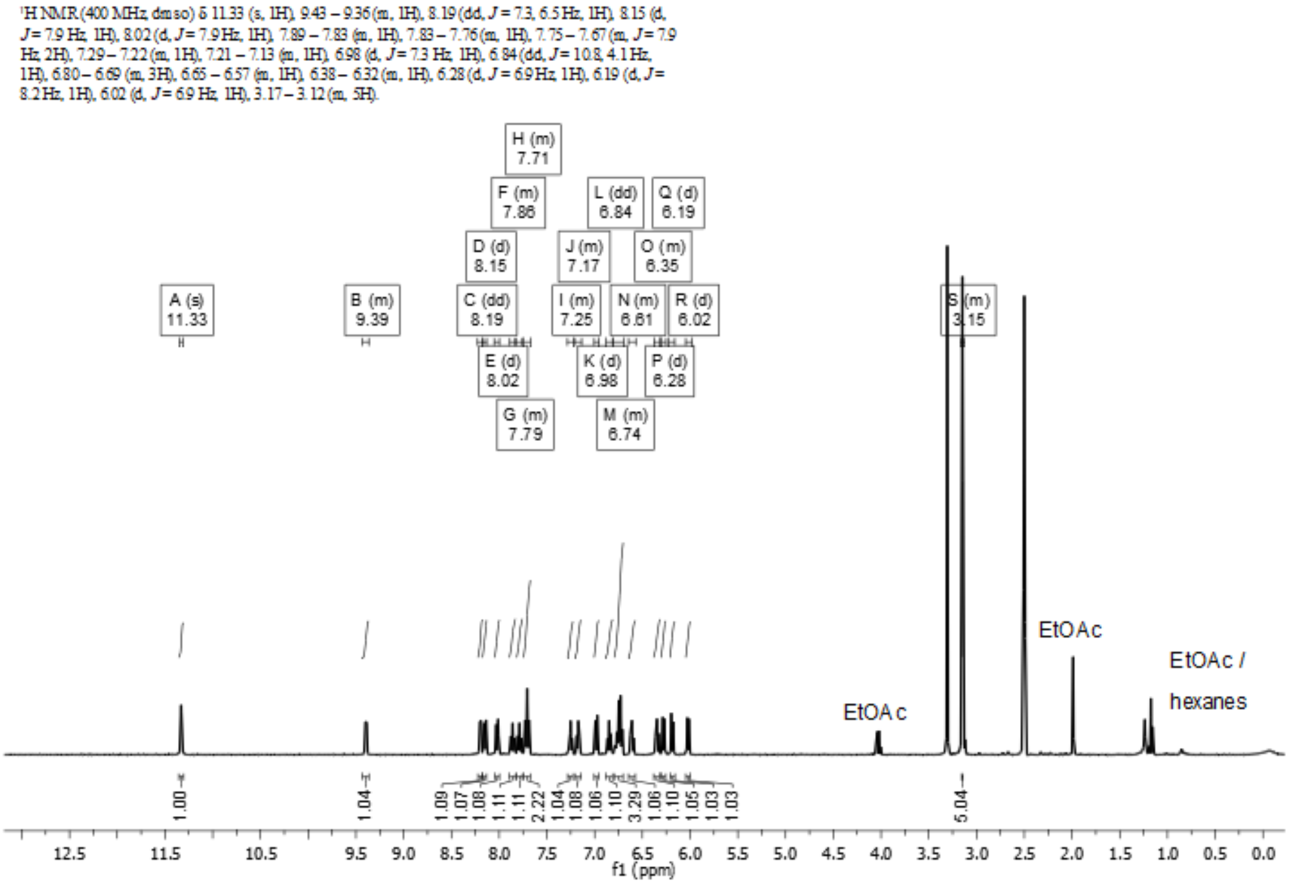
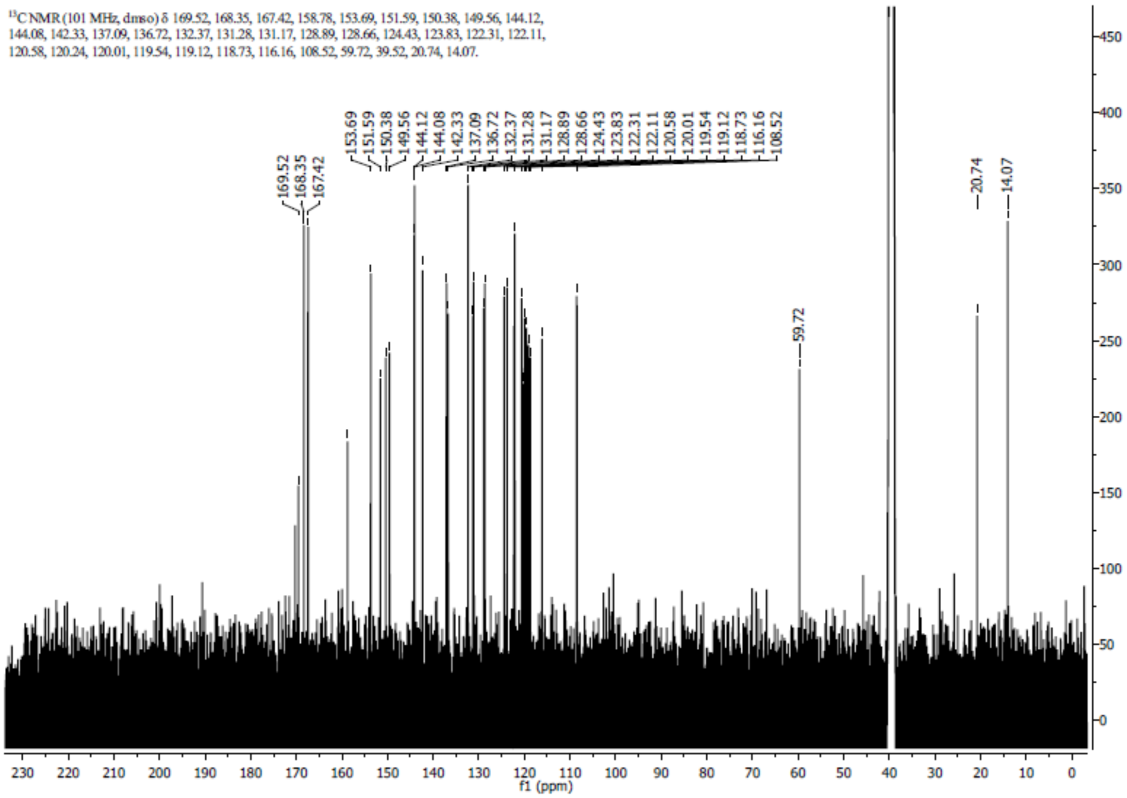
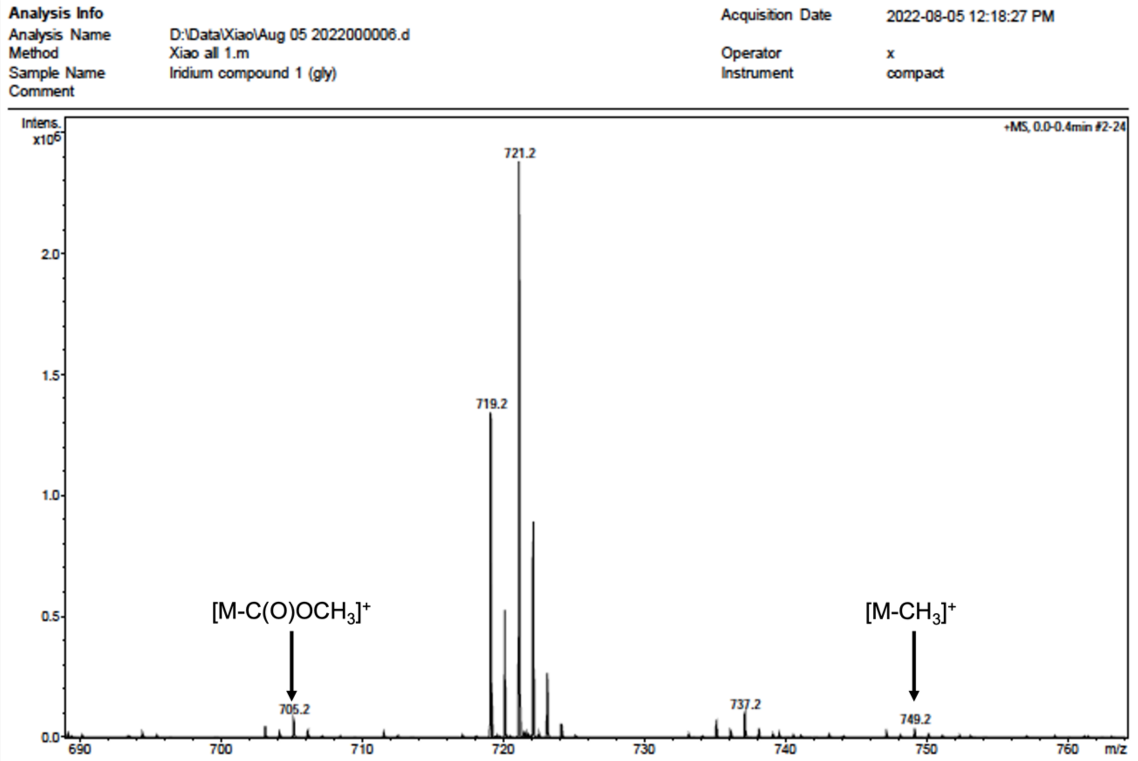

^{1}H NMR (400 MHz, dmso) δ 11.33 (s, 1H), 9.43 – 9.36 (m, 1H), 8.19 (dd, *J* = 7.3, 6.5 Hz, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.83 – 7.76 (m, 1H), 7.75 – 7.67 (m, *J* = 7.9 Hz, 2H), 7.29 – 7.22 (m, 1H), 7.21 – 7.13 (m, 1H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.84 (dd, *J* = 10.8, 4.1 Hz, 1H), 6.80 – 6.69 (m, 3H), 6.65 – 6.57 (m, 1H), 6.38 – 6.32 (m, 1H), 6.28 (d, *J* = 6.9 Hz, 1H), 6.19 (d, *J* = 8.2 Hz, 1H), 6.02 (d, *J* = 6.9 Hz, 1H), 3.17 – 3.12 (m, 5H).

Figure S13. ^{1}H-NMR spectra of compound **5** (400 MHz, DMSO-d_6) at 298K.



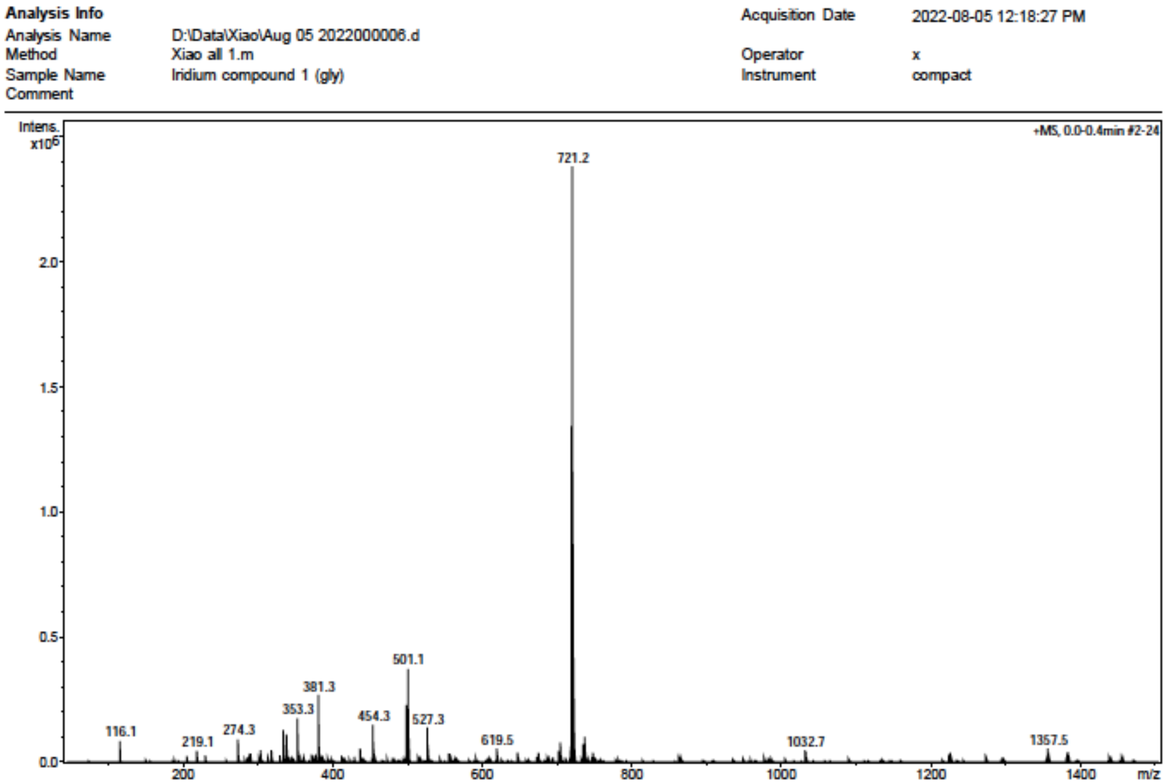
^{13}C NMR (101 MHz, dmso) δ 169.52, 168.35, 167.42, 158.78, 153.69, 151.59, 150.38, 149.56, 144.12, 144.08, 142.33, 137.09, 136.72, 132.37, 131.28, 131.17, 128.89, 128.66, 124.43, 123.83, 122.31, 122.11, 120.58, 120.24, 120.01, 119.54, 119.12, 118.73, 116.16, 108.52, 59.72, 39.52, 20.74, 14.07.

Figure S14. ^{13}C-NMR spectra of compound **5** (101 MHz, DMSO-d_6) at 298K.



Analysis Info
Analysis Name D:\Data\Xiao\Aug 05 2022000006.d
Method Xiao all 1.m
Sample Name Iridium compound 1 (gly)
Comment
Acquisition Date 2022-08-05 12:18:27 PM
Operator x
Instrument compact

Figure S15. Zoomed Mass Spectroscopy spectra of compound **5**.

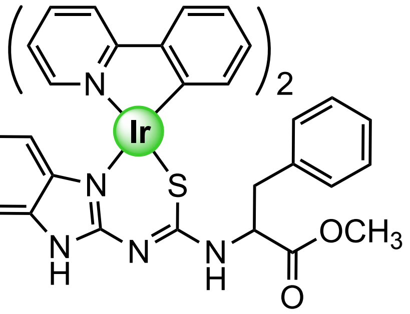


Analysis Info

Analysis Name	D:\Data\Xiao\Aug 05 2022000006.d	Acquisition Date	2022-08-05 12:18:27 PM
Method	Xiao all 1.m	Operator	x
Sample Name	Iridium compound 1 (gly)	Instrument	compact
Comment			

Figure S16. Mass Spectroscopy spectra of compound **5**.

Cyclometalated Ir(III) complex **6**:



^{1}H NMR (400 MHz, cdcl$_3$) δ 9.61 – 9.43 (m, 1H), 9.00 (s, 1H), 8.51 – 8.24 (m, 1H), 7.99 – 7.80 (m, J = 16.2 Hz, 1H), 7.73 – 7.47 (m, 6H), 7.41 – 7.12 (m, J = 3.0 Hz, 2H), 7.09 – 6.77 (m, 9H), 6.78 – 6.66 (m, J = 6.4 Hz, 1H), 6.64 – 6.53 (m, 1H), 6.53 – 6.38 (m, J = 2.9 Hz, 2H), 6.32 – 6.19 (m, J = 7.0 Hz, 1H), 3.44 – 3.17 (m, 6H).

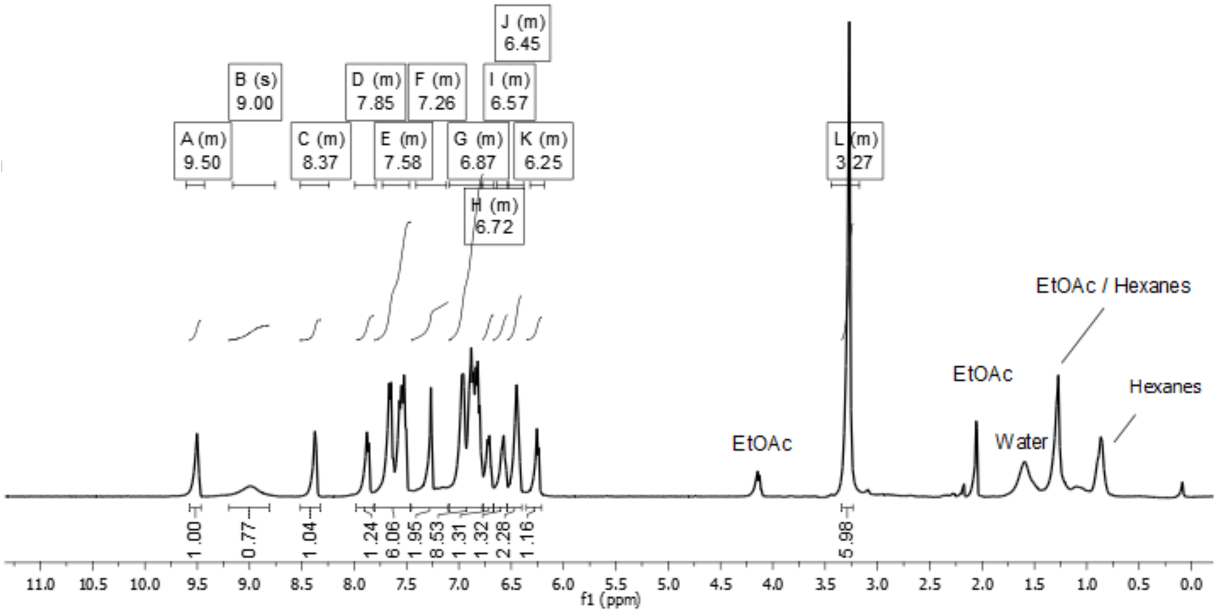
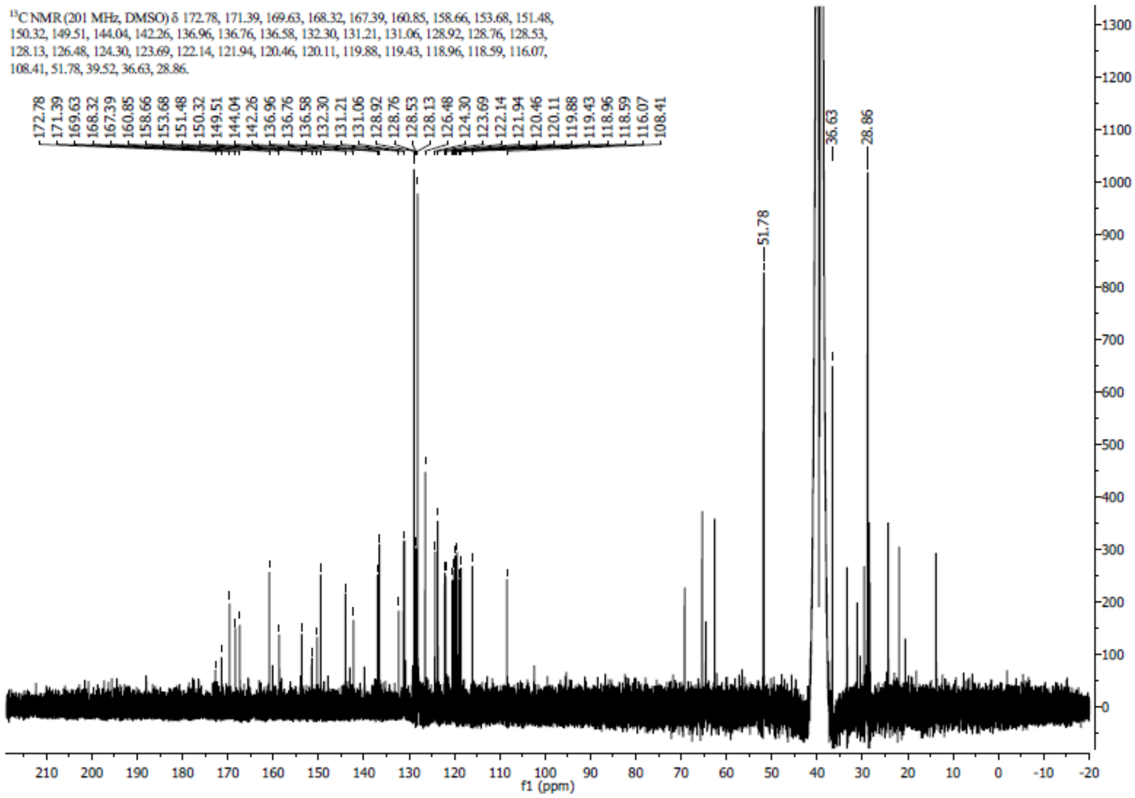
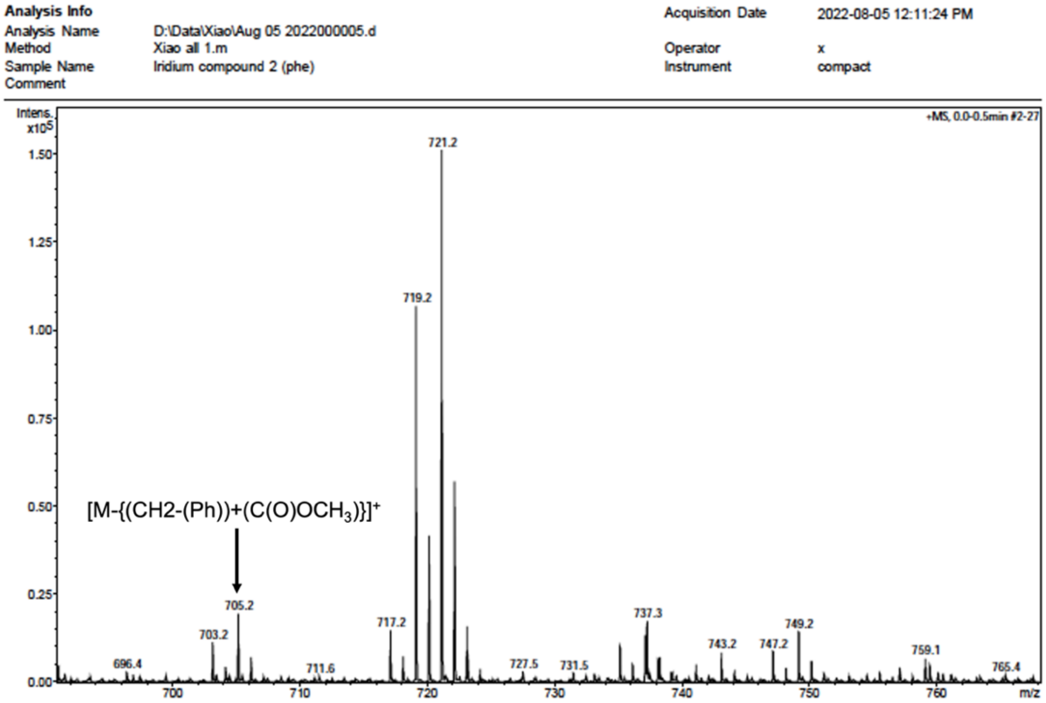


Figure S17. ^{1}H-NMR spectra of compound **6** (400 MHz, DMSO-d_6) at 298K.



^{13}C NMR (201 MHz, DMSO) δ 172.78, 171.39, 169.63, 168.32, 167.39, 160.85, 158.66, 153.68, 151.48, 150.32, 149.51, 144.04, 142.26, 136.96, 136.76, 136.58, 132.30, 131.21, 131.06, 128.92, 128.76, 128.53, 128.13, 126.48, 124.30, 123.69, 122.14, 121.94, 120.46, 120.11, 119.88, 119.43, 118.96, 118.59, 116.07, 108.41, 51.78, 39.52, 36.63, 28.86.

Figure S18. ^{13}C-NMR spectra of compound **6** (201 MHz, DMSO-d_6) at 298K.

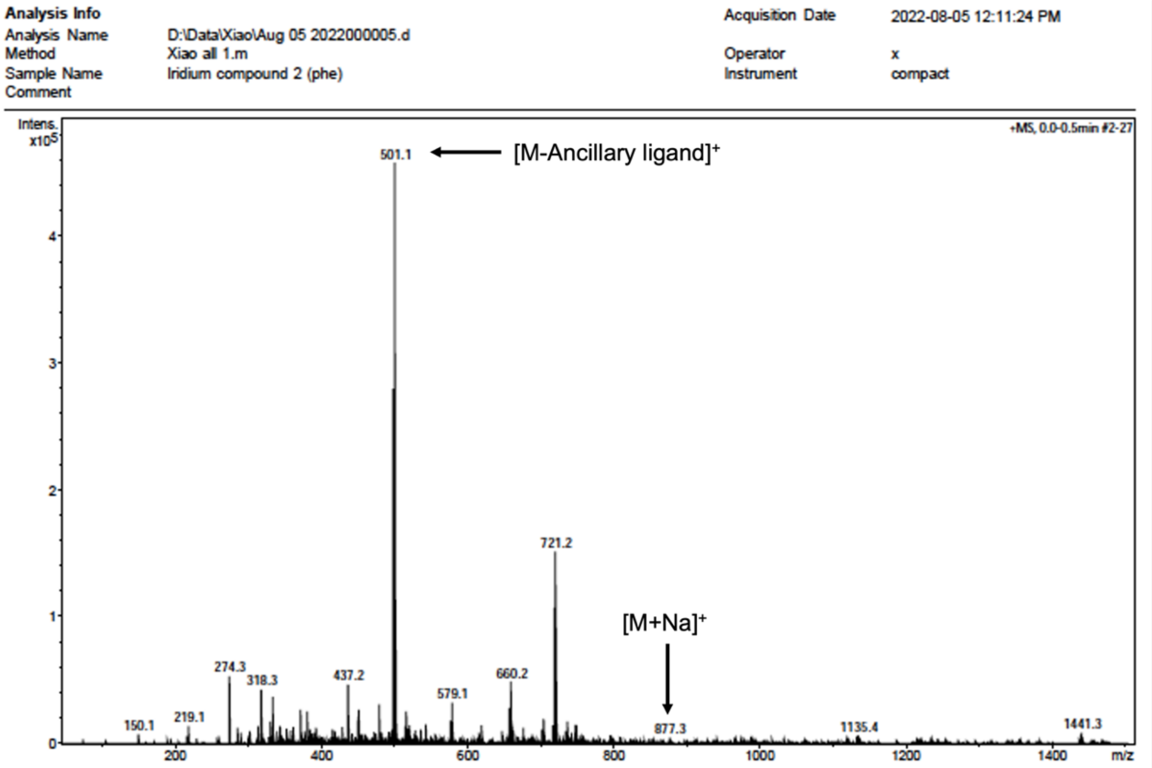


Analysis Info

Analysis Name D:\Data\Xiao\Aug 05 2022000005.d
Method Xiao all 1.m
Sample Name Iridium compound 2 (phe)
Comment

Acquisition Date 2022-08-05 12:11:24 PM
Operator x
Instrument compact

Figure S19. Zoomed Mass Spectroscopy spectra of compound **6**.



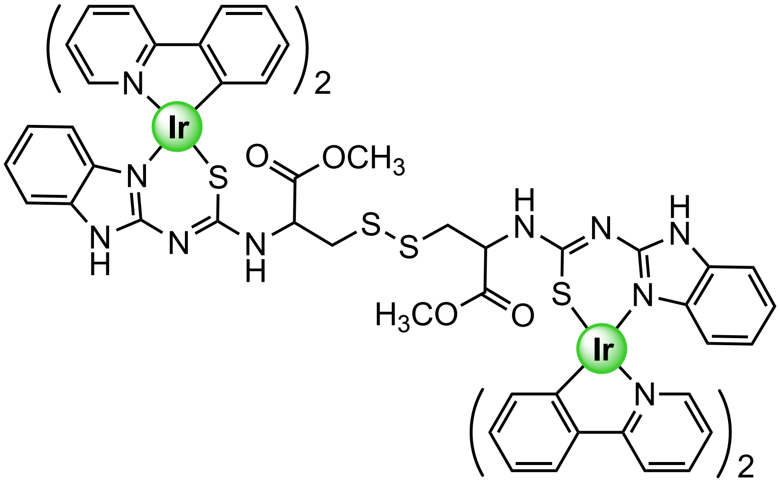
Analysis Info

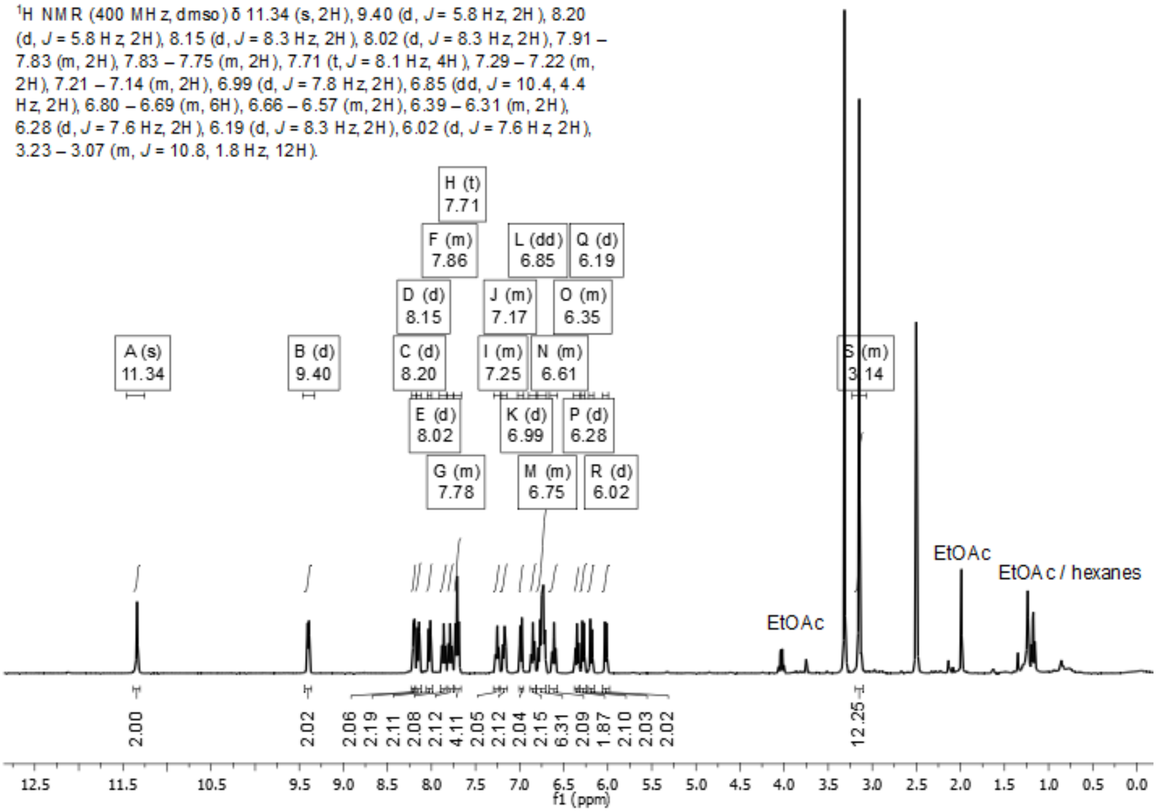
Analysis Name D:\Data\Xiao\Aug 05 2022000005.d
Method Xiao all 1.m
Sample Name Iridium compound 2 (phe)
Comment

Acquisition Date 2022-08-05 12:11:24 PM
Operator x
Instrument compact

Figure S20. Mass Spectroscopy spectra of compound **6**.

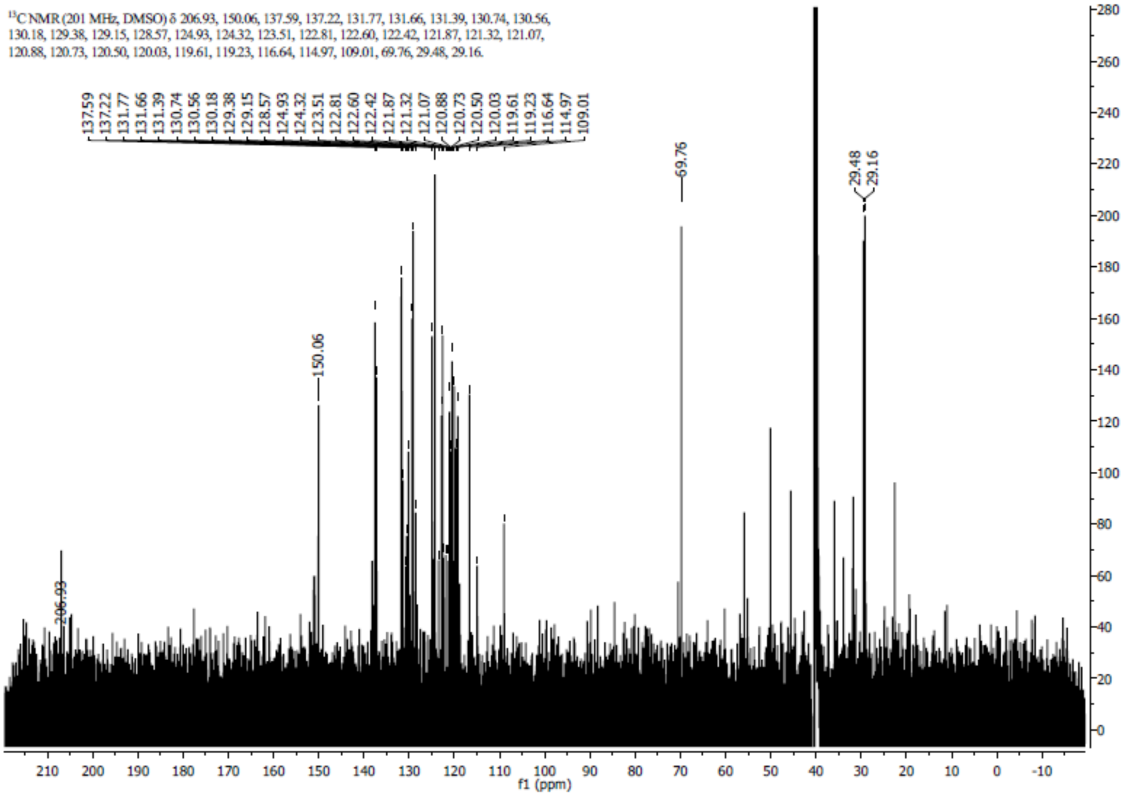
Cyclometalated Ir(III) complex **7**:





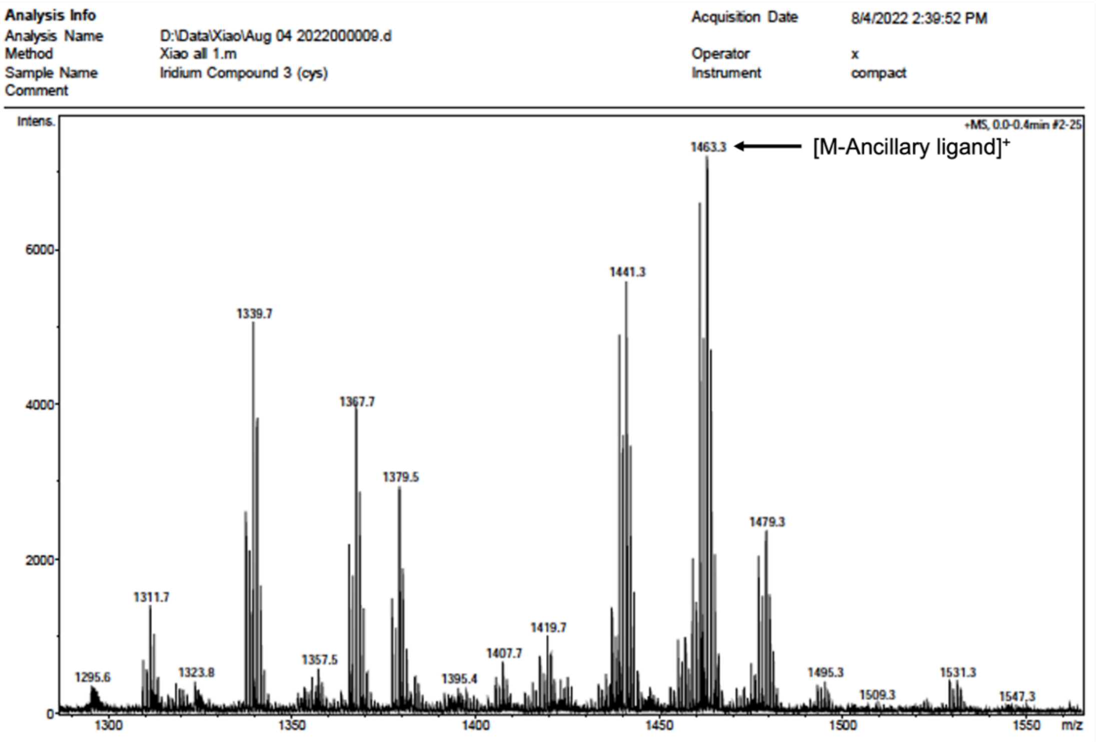
^{1}H NMR (400 MHz, dmso) δ 11.34 (s, 2H), 9.40 (d, *J* = 5.8 Hz, 2H), 8.20 (d, *J* = 5.8 Hz, 2H), 8.15 (d, *J* = 8.3 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.91 – 7.83 (m, 2H), 7.83 – 7.75 (m, 2H), 7.71 (t, *J* = 8.1 Hz, 4H), 7.29 – 7.22 (m, 2H), 7.21 – 7.14 (m, 2H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.85 (dd, *J* = 10.4, 4.4 Hz, 2H), 6.80 – 6.69 (m, 6H), 6.66 – 6.57 (m, 2H), 6.39 – 6.31 (m, 2H), 6.28 (d, *J* = 7.6 Hz, 2H), 6.19 (d, *J* = 8.3 Hz, 2H), 6.02 (d, *J* = 7.6 Hz, 2H), 3.23 – 3.07 (m, *J* = 10.8, 1.8 Hz, 12H).

Figure S21. ^{1}H-NMR spectra of compound **7** (400 MHz, DMSO-d_6) at 298K.



^{13}C NMR (201 MHz, DMSO) δ 206.93, 150.06, 137.59, 137.22, 131.77, 131.66, 131.39, 130.74, 130.56, 130.18, 129.38, 129.15, 128.57, 124.93, 124.32, 123.51, 122.81, 122.60, 122.42, 121.87, 121.32, 121.07, 120.88, 120.73, 120.50, 120.03, 119.61, 119.23, 116.64, 114.97, 109.01, 69.76, 29.48, 29.16.

Figure S22. ^{13}C-NMR spectra of compound **7** (201 MHz, DMSO-d_6) at 298K.



Analysis Info

Analysis Name D:\Data\Xiao\Aug 04 2022000009.d

Method Xiao all 1.m

Sample Name Iridium Compound 3 (cys)

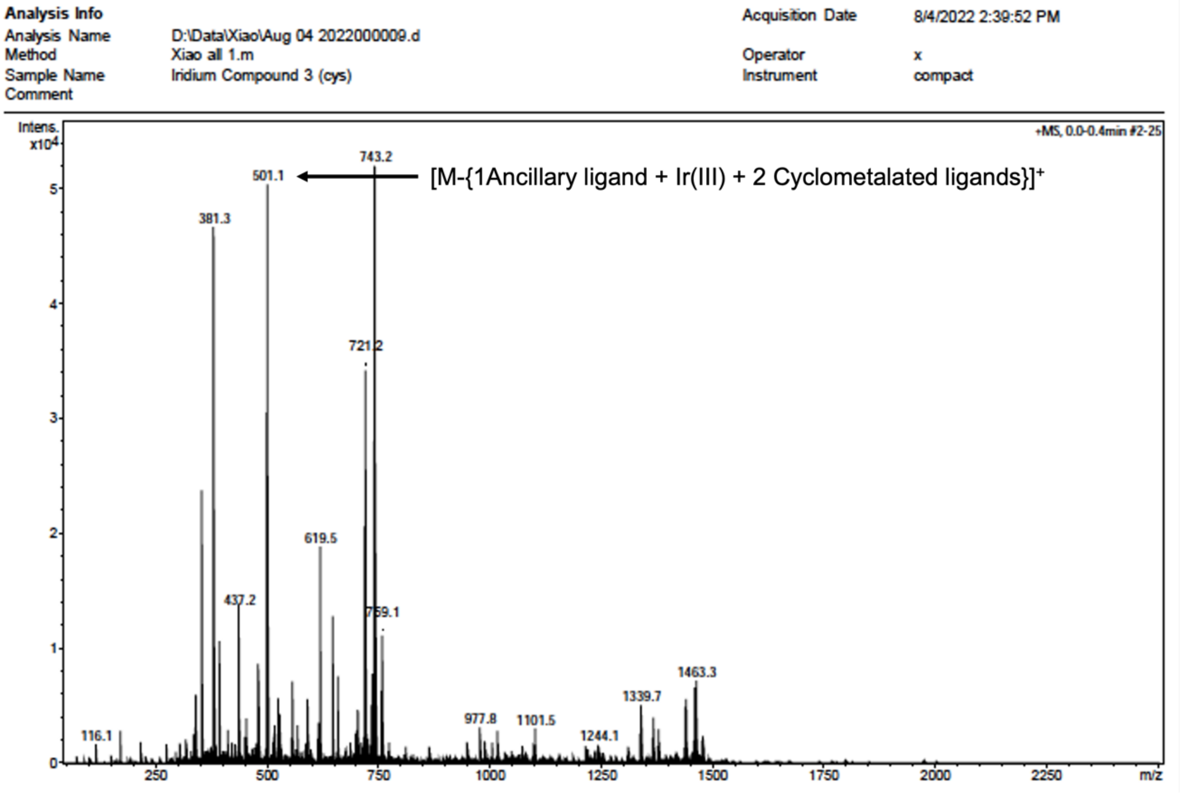
Comment

Acquisition Date 8/4/2022 2:39:52 PM

Operator x

Instrument compact

Figure S23. Zoomed Mass Spectroscopy spectra of compound **7**.



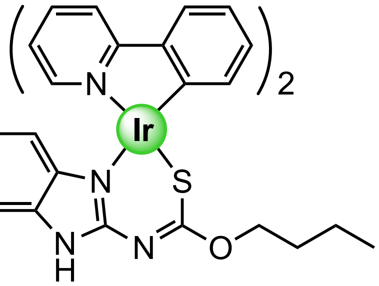
Analysis Info

Analysis Name	D:\Data\Xiao\Aug 04 2022000009.d	Acquisition Date	8/4/2022 2:39:52 PM
Method	Xiao all 1.m	Operator	x
Sample Name	Iridium Compound 3 (cys)	Instrument	compact
Comment			

[M-{1Ancillary ligand + Ir(III) + 2 Cyclometalated ligands}]$^+$

Figure S24. Mass Spectroscopy spectra of compound **7**.

Cyclometalated Ir(III) complex **8**:



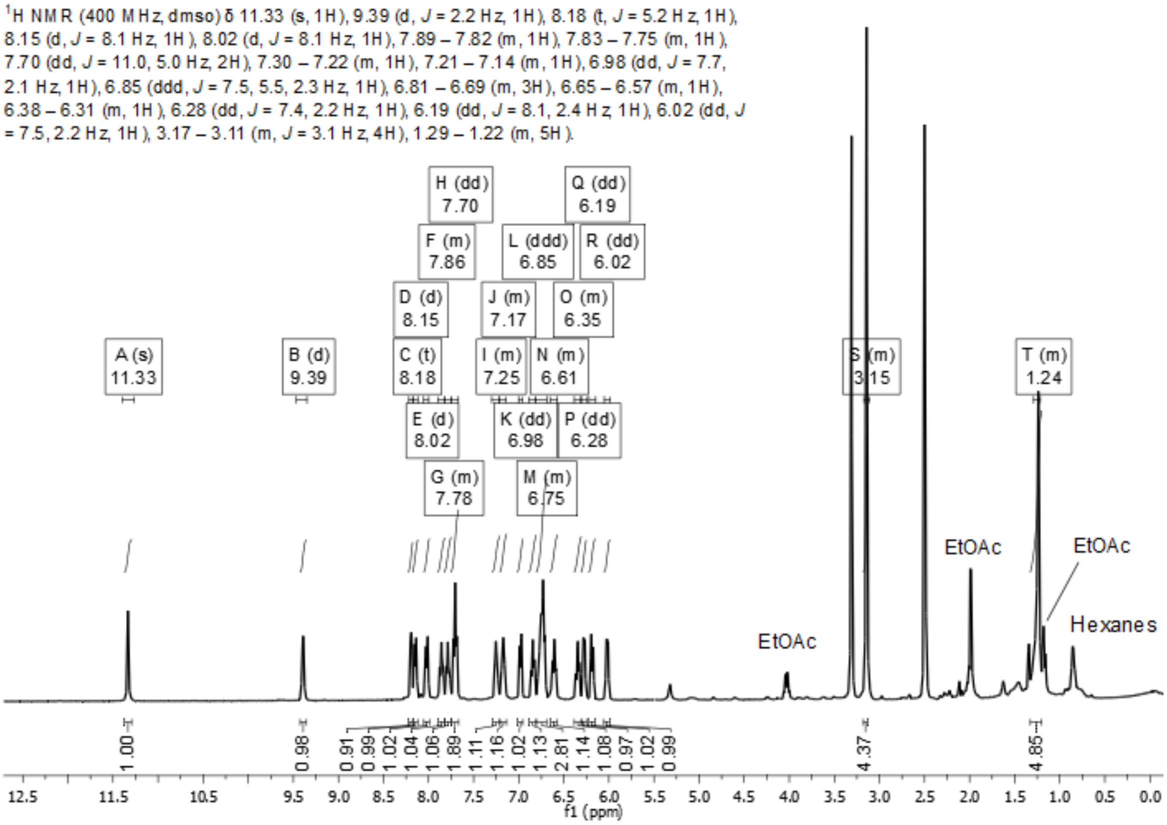
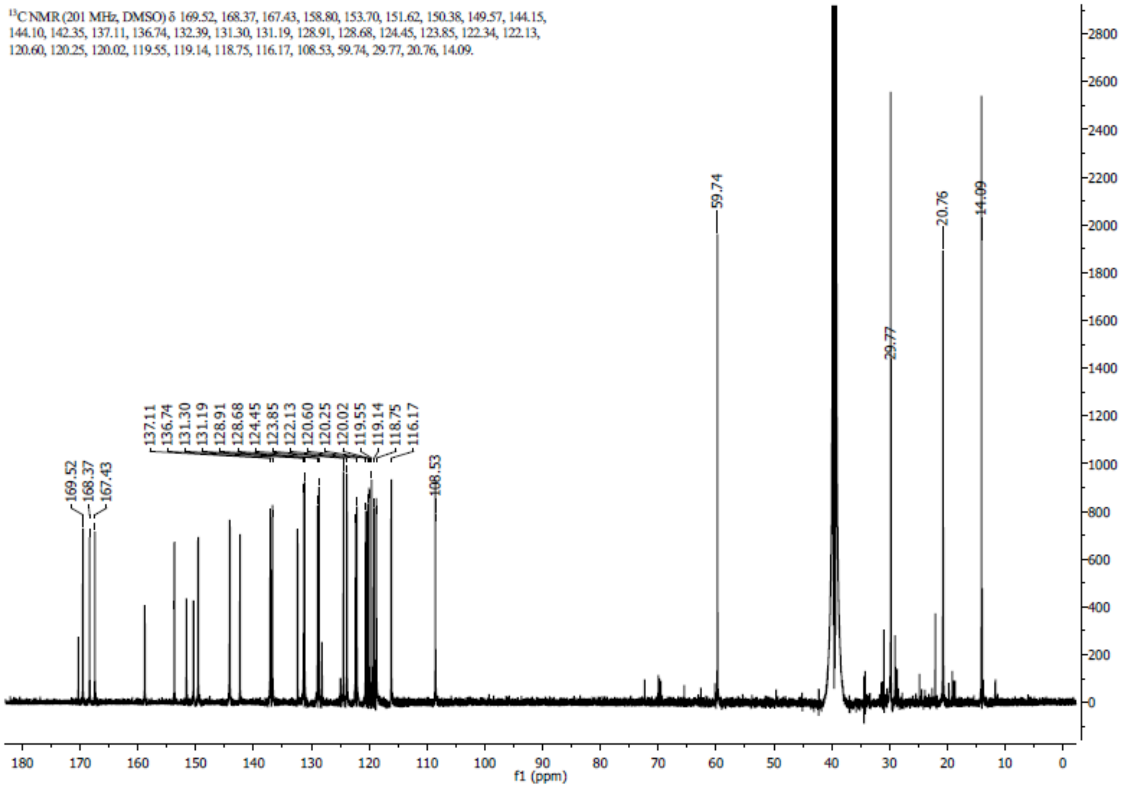
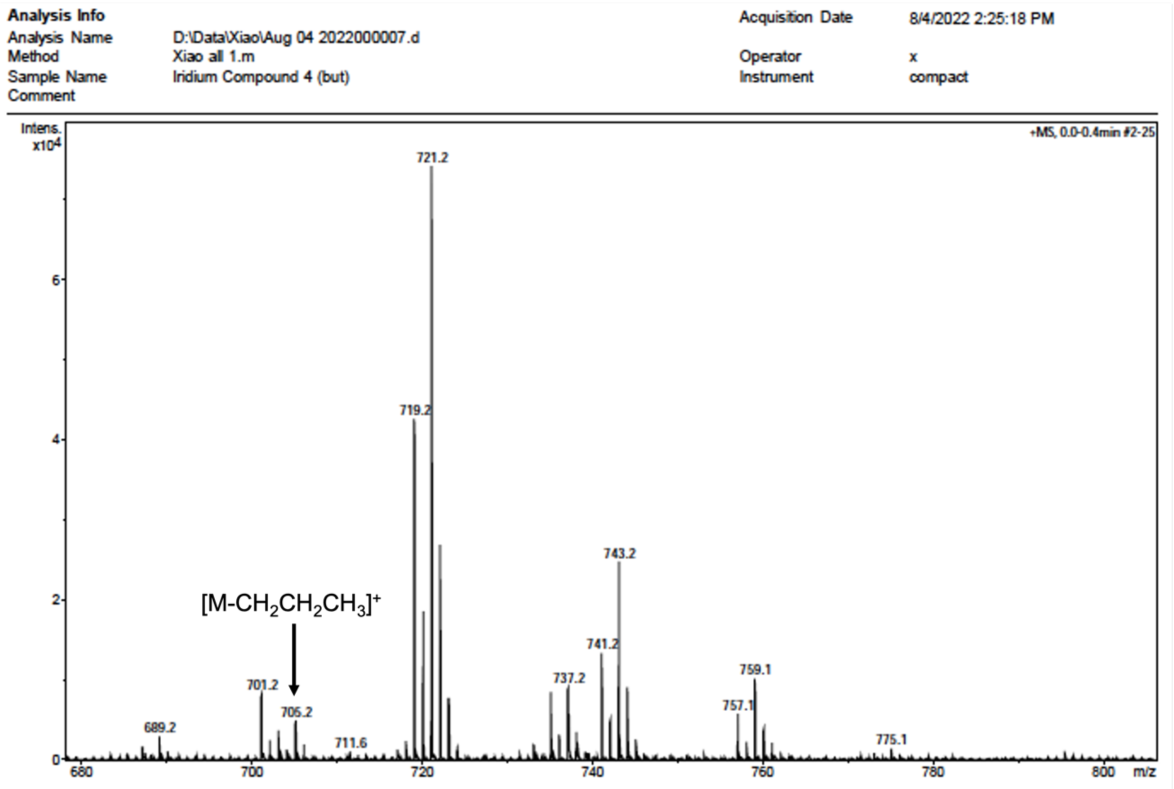

^{1}H NMR (400 MHz, dmso) δ 11.33 (s, 1H), 9.39 (d, J = 2.2 Hz, 1H), 8.18 (t, J = 5.2 Hz, 1H), 8.15 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.89 – 7.82 (m, 1H), 7.83 – 7.75 (m, 1H), 7.70 (dd, J = 11.0, 5.0 Hz, 2H), 7.30 – 7.22 (m, 1H), 7.21 – 7.14 (m, 1H), 6.98 (dd, J = 7.7, 2.1 Hz, 1H), 6.85 (ddd, J = 7.5, 5.5, 2.3 Hz, 1H), 6.81 – 6.69 (m, 3H), 6.65 – 6.57 (m, 1H), 6.38 – 6.31 (m, 1H), 6.28 (dd, J = 7.4, 2.2 Hz, 1H), 6.19 (dd, J = 8.1, 2.4 Hz, 1H), 6.02 (dd, J = 7.5, 2.2 Hz, 1H), 3.17 – 3.11 (m, J = 3.1 Hz, 4H), 1.29 – 1.22 (m, 5H).

Figure S25. ^{1}H-NMR spectra of compound **8** (400 MHz, DMSO-d_6) at 298K.



^{13}C NMR (201 MHz, DMSO) δ 169.52, 168.37, 167.43, 158.80, 153.70, 151.62, 150.38, 149.57, 144.15, 144.10, 142.35, 137.11, 136.74, 132.39, 131.30, 131.19, 128.91, 128.68, 124.45, 123.85, 122.34, 122.13, 120.60, 120.25, 120.02, 119.55, 119.14, 118.75, 116.17, 108.53, 59.74, 29.77, 20.76, 14.09.

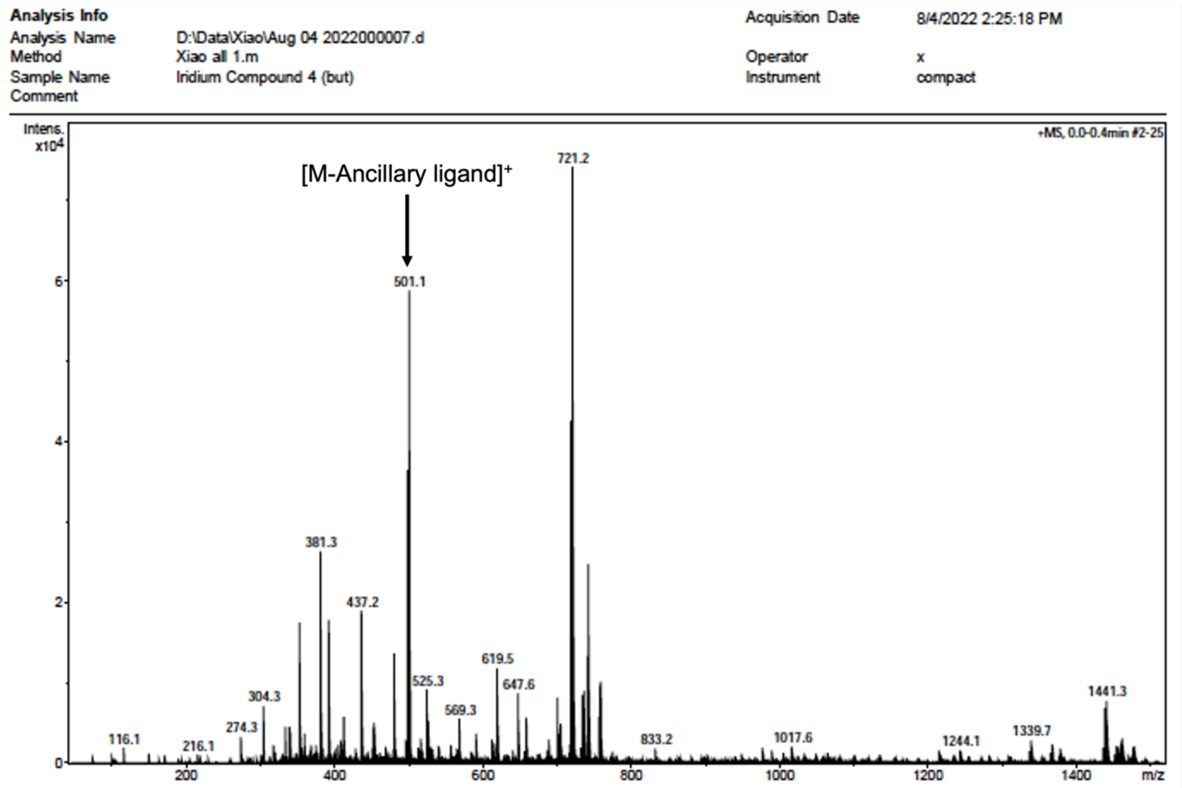
Figure S26. ^{13}C-NMR spectra of compound **8** (201 MHz, DMSO-d_6) at 298K.



Analysis Info

Analysis Name	D:\Data\Xiao\Aug 04 2022000007.d	Acquisition Date	8/4/2022 2:25:18 PM
Method	Xiao all 1.m	Operator	x
Sample Name	Iridium Compound 4 (but)	Instrument	compact
Comment			

Figure S27. Zoomed Mass Spectroscopy spectra of compound **8**.

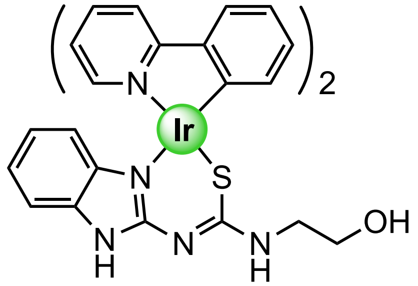


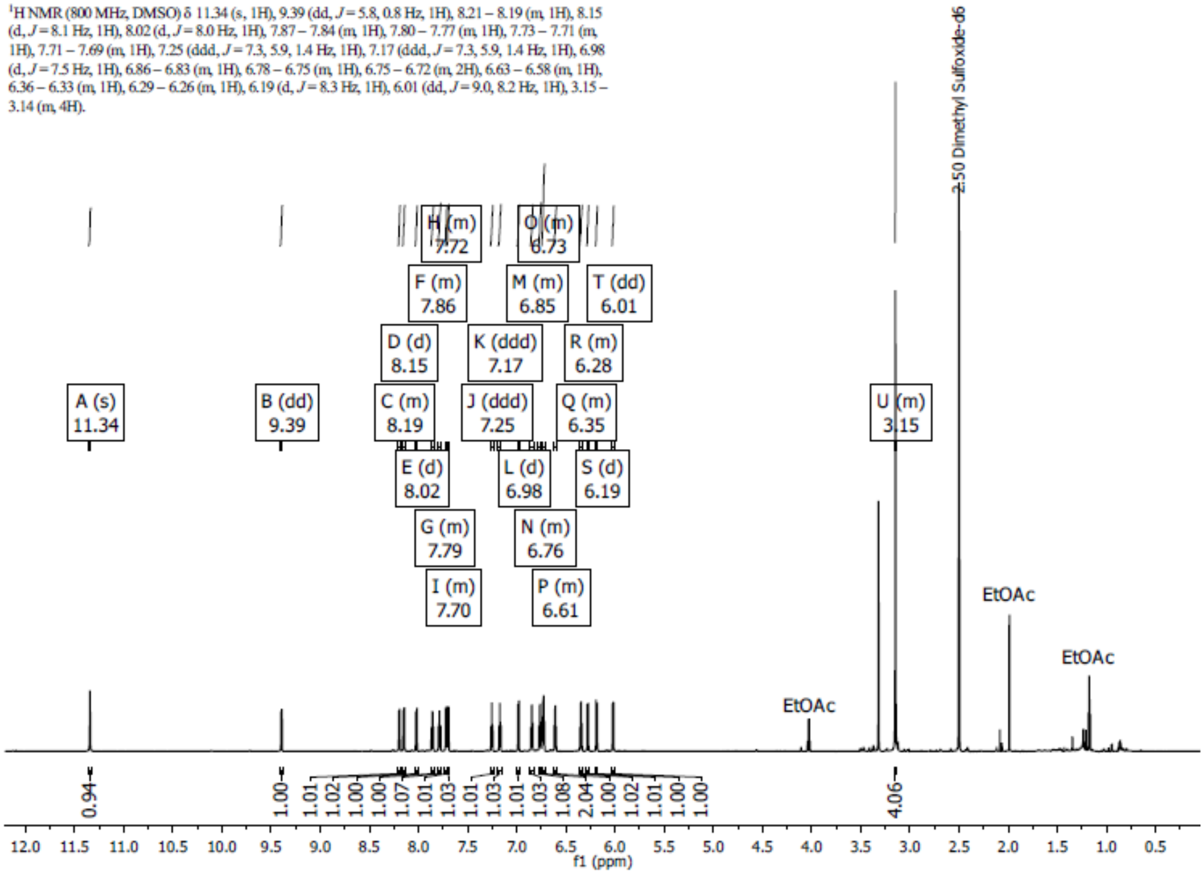
Analysis Info

Analysis Name	D:\Data\Xiao\Aug 04 2022000007.d	Acquisition Date	8/4/2022 2:25:18 PM
Method	Xiao all 1.m	Operator	x
Sample Name	Iridium Compound 4 (but)	Instrument	compact
Comment			

Figure S28. Mass Spectroscopy spectra of compound **8**.

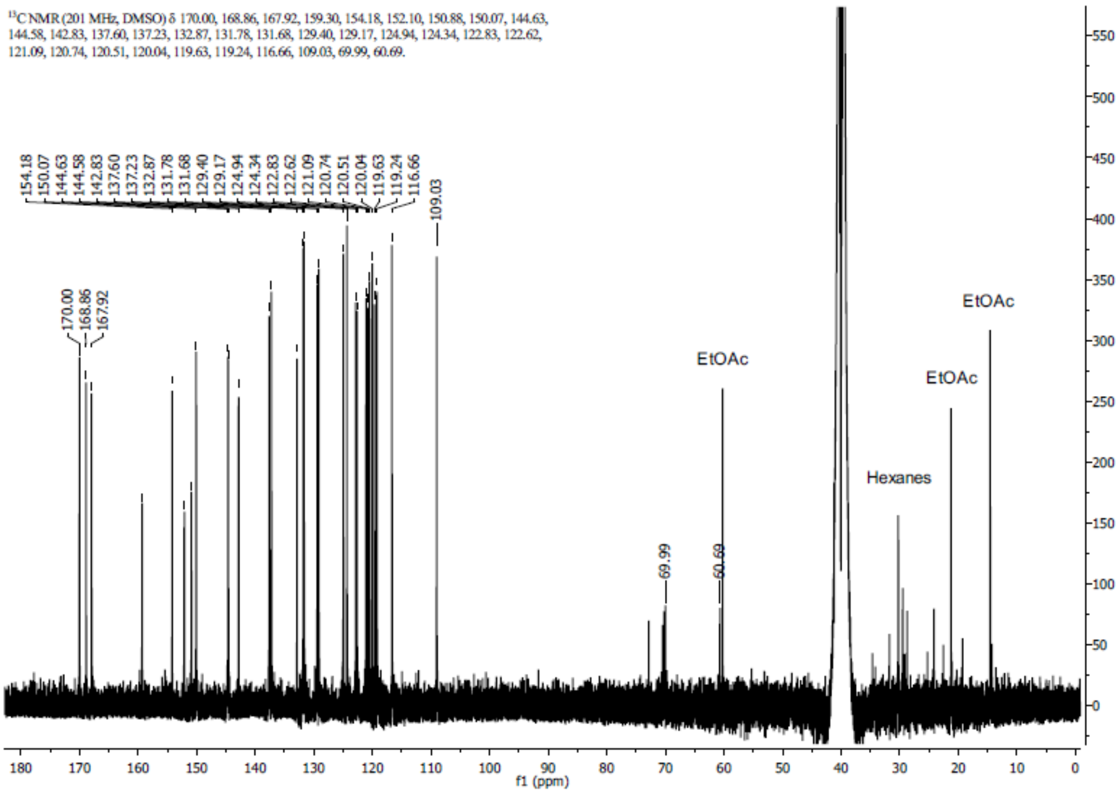
Cyclometalated Ir(III) complex **9**:





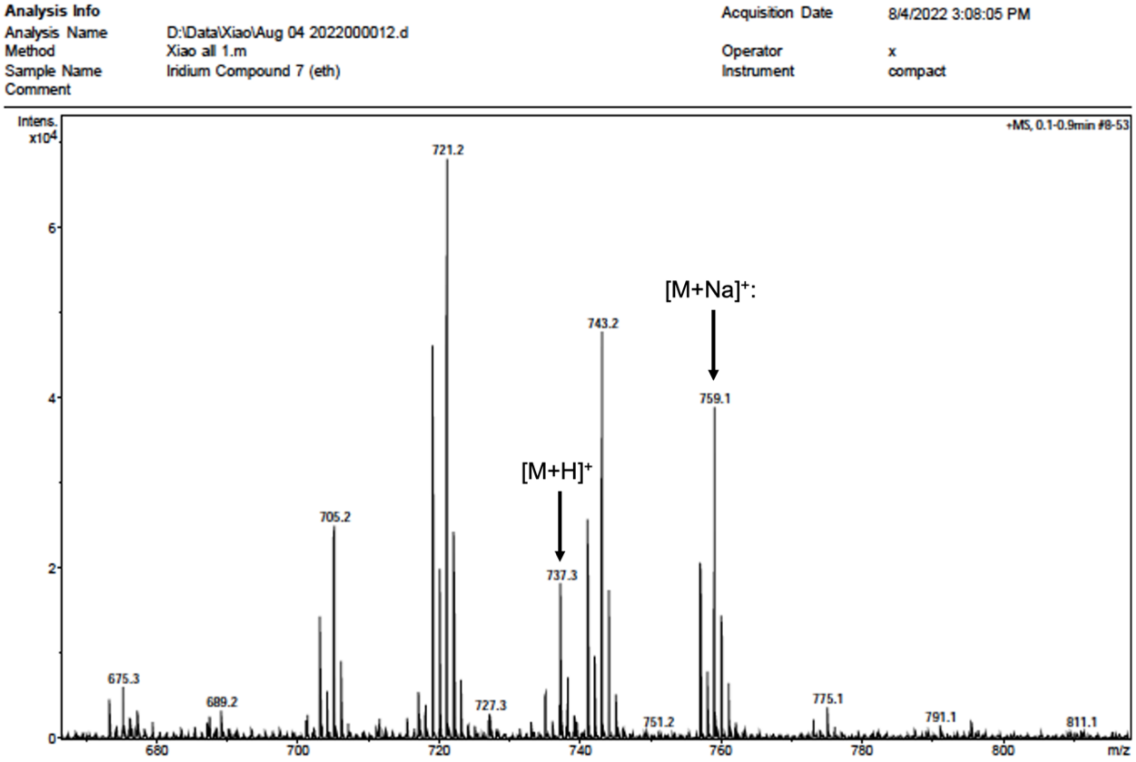
^{1}H NMR (800 MHz, DMSO) δ 11.34 (s, 1H), 9.39 (dd, J = 5.8, 0.8 Hz, 1H), 8.21 – 8.19 (m, 1H), 8.15 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.80 – 7.77 (m, 1H), 7.73 – 7.71 (m, 1H), 7.71 – 7.69 (m, 1H), 7.25 (ddd, J = 7.3, 5.9, 1.4 Hz, 1H), 7.17 (ddd, J = 7.3, 5.9, 1.4 Hz, 1H), 6.98 (d, J = 7.5 Hz, 1H), 6.86 – 6.83 (m, 1H), 6.78 – 6.75 (m, 1H), 6.75 – 6.72 (m, 2H), 6.63 – 6.58 (m, 1H), 6.36 – 6.33 (m, 1H), 6.29 – 6.26 (m, 1H), 6.19 (d, J = 8.3 Hz, 1H), 6.01 (dd, J = 9.0, 8.2 Hz, 1H), 3.15 – 3.14 (m, 4H).

Figure S29. ^{1}H-NMR spectra of compound **9** (400 MHz, DMSO-d_6) at 298K.



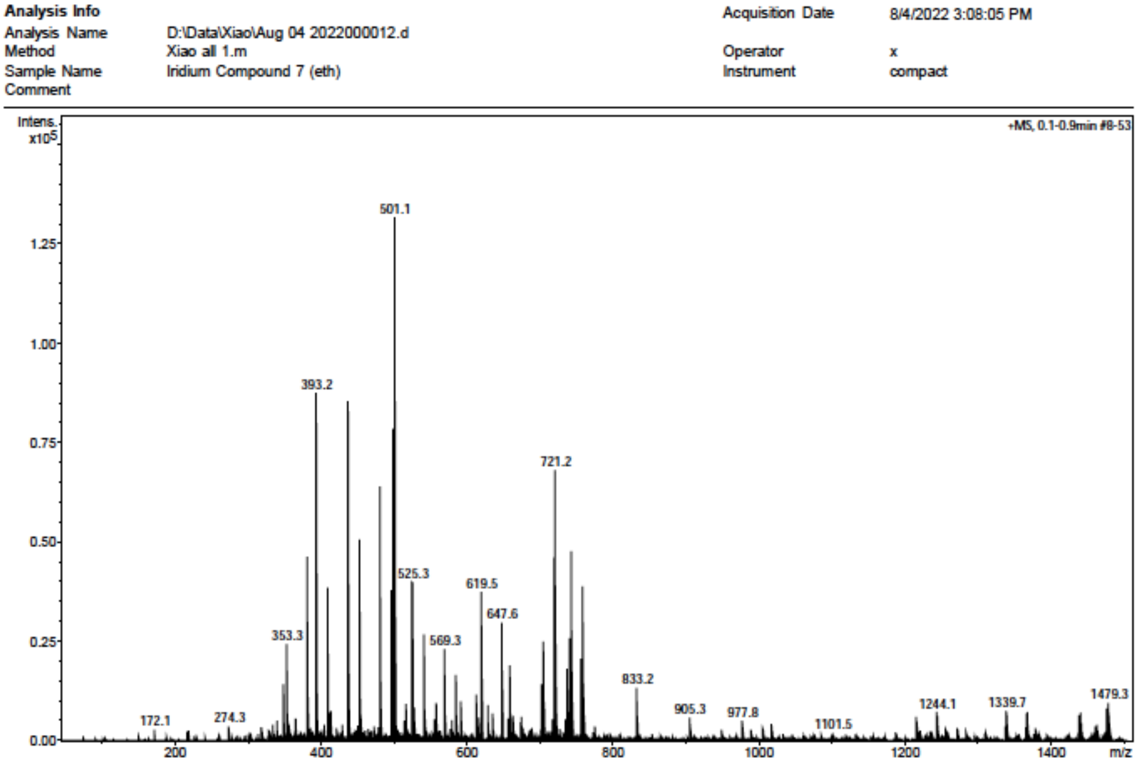
^{13}C NMR (201 MHz, DMSO) δ 170.00, 168.86, 167.92, 159.30, 154.18, 152.10, 150.88, 150.07, 144.63, 144.58, 142.83, 137.60, 137.23, 132.87, 131.78, 131.68, 129.40, 129.17, 124.94, 124.34, 122.83, 122.62, 121.09, 120.74, 120.51, 120.04, 119.63, 119.24, 116.66, 109.03, 69.99, 60.69.

Figure S30. ^{13}C-NMR spectra of compound **9** (201 MHz, DMSO-d_6) at 298K.


Analysis Info

Analysis Name D:\Data\Xiao\Aug 04 2022000012.d
Method Xiao all 1.m
Sample Name Iridium Compound 7 (eth)
Comment
Acquisition Date 8/4/2022 3:08:05 PM
Operator x
Instrument compact

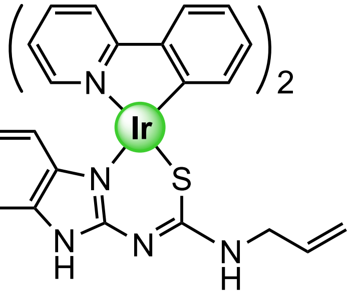
Figure S31. Zoomed Mass Spectroscopy spectra of compound **9**.

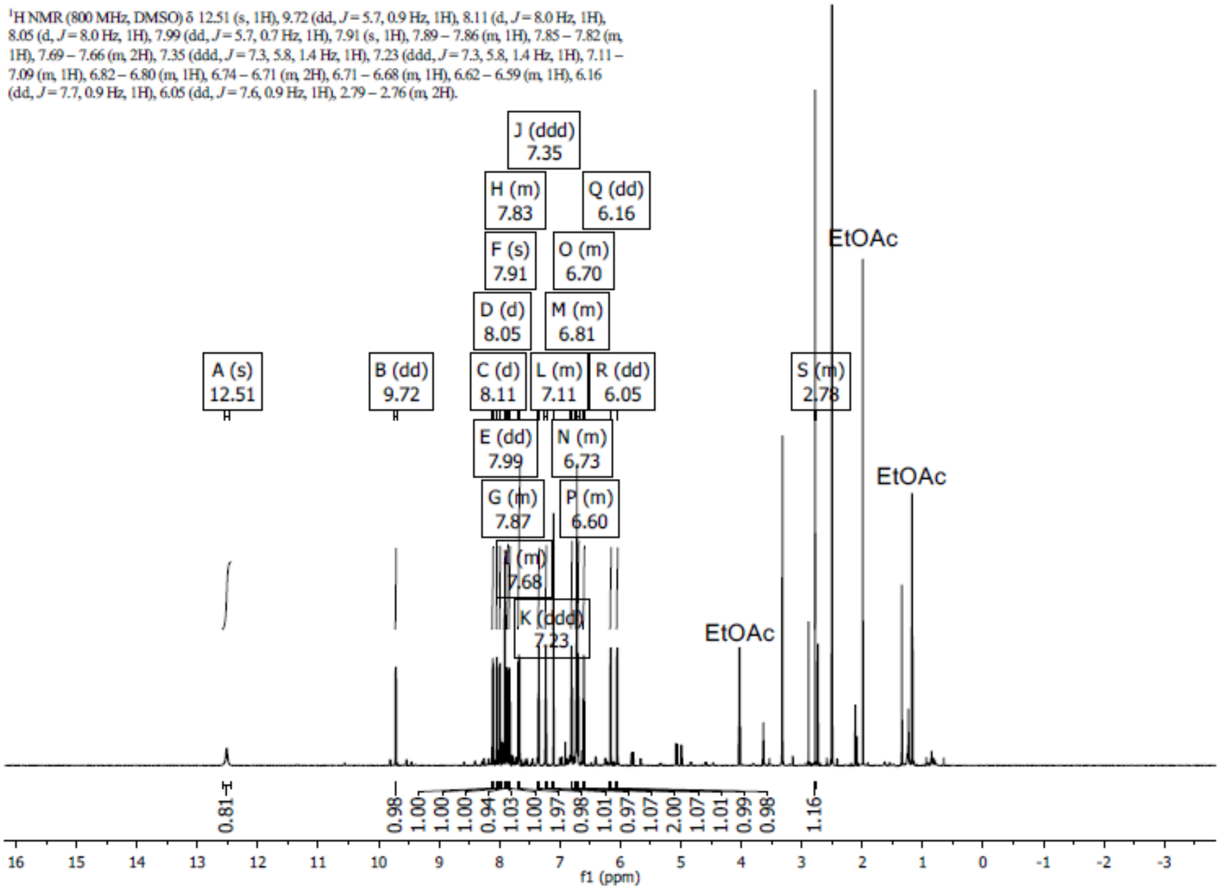

Analysis Info

Analysis Name D:\Data\Xiao\Aug 04 2022000012.d
Method Xiao all 1.m
Sample Name Iridium Compound 7 (eth)
Comment
Acquisition Date 8/4/2022 3:08:05 PM
Operator x
Instrument compact

Figure S32. Mass Spectroscopy spectra of compound **9**.

Cyclometalated Ir(III) complex **10**:





^{1}H NMR (800 MHz, DMSO) δ 12.51 (s, 1H), 9.72 (dd, *J* = 5.7, 0.9 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.99 (dd, *J* = 5.7, 0.7 Hz, 1H), 7.91 (s, 1H), 7.89 – 7.86 (m, 1H), 7.85 – 7.82 (m, 1H), 7.69 – 7.66 (m, 2H), 7.35 (ddd, *J* = 7.3, 5.8, 1.4 Hz, 1H), 7.23 (ddd, *J* = 7.3, 5.8, 1.4 Hz, 1H), 7.11 – 7.09 (m, 1H), 6.82 – 6.80 (m, 1H), 6.74 – 6.71 (m, 2H), 6.71 – 6.68 (m, 1H), 6.62 – 6.59 (m, 1H), 6.16 (dd, *J* = 7.7, 0.9 Hz, 1H), 6.05 (dd, *J* = 7.6, 0.9 Hz, 1H), 2.79 – 2.76 (m, 2H).

Figure S33. ^{1}H-NMR spectra of compound **10** (800 MHz, DMSO-d_6) at 298K.

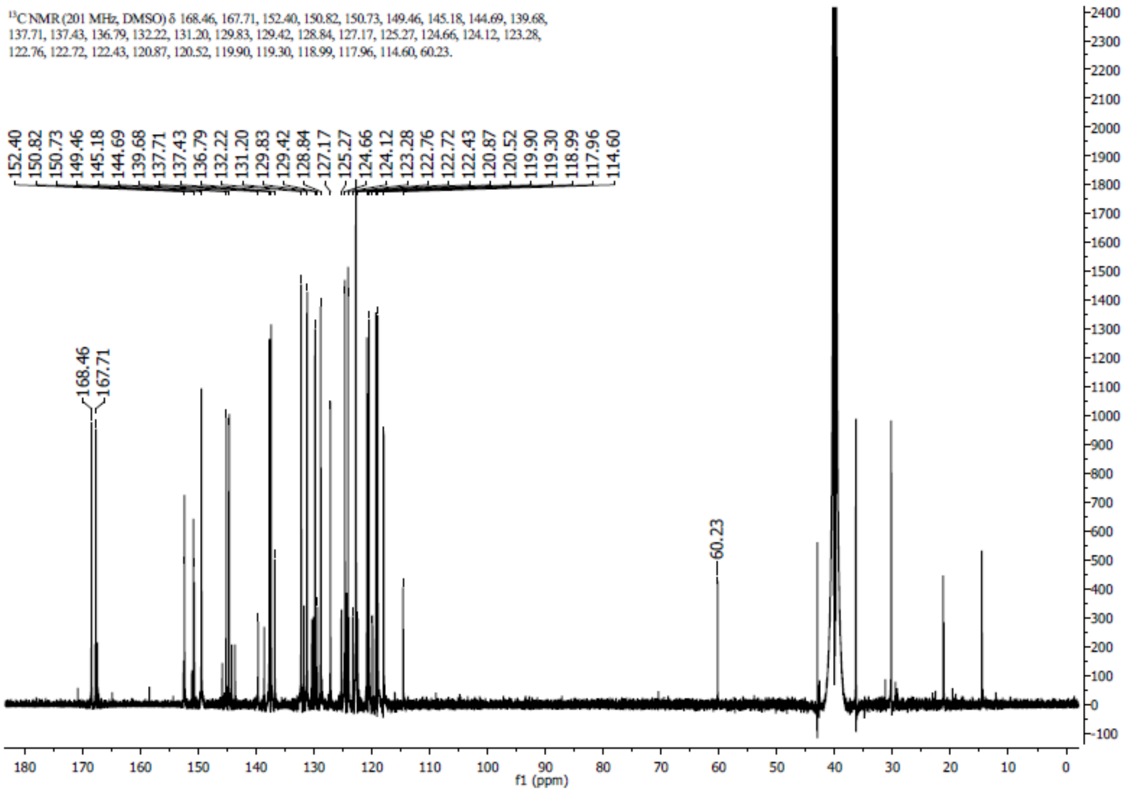
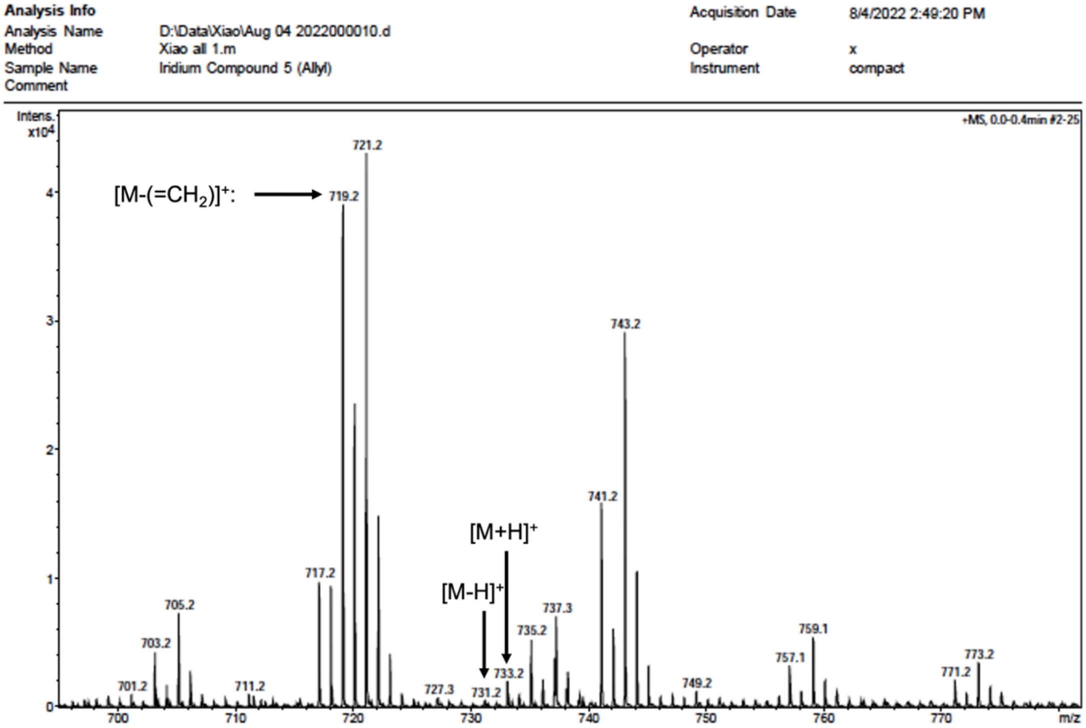

^{13}C NMR (201 MHz, DMSO) δ 168.46, 167.71, 152.40, 150.82, 150.73, 149.46, 145.18, 144.69, 139.68, 137.71, 137.43, 136.79, 132.22, 131.20, 129.83, 129.42, 128.84, 127.17, 125.27, 124.66, 124.12, 123.28, 122.76, 122.72, 122.43, 120.87, 120.52, 119.90, 119.30, 118.99, 117.96, 114.60, 60.23.

Figure S34. ^{13}C-NMR spectra of compound **10** (201 MHz, DMSO-d_6) at 298K.


Analysis Info

Analysis Name D:\Data\Xiao\Aug 04 2022000010.d

Method Xiao all 1.m

Sample Name Iridium Compound 5 (Allyl)

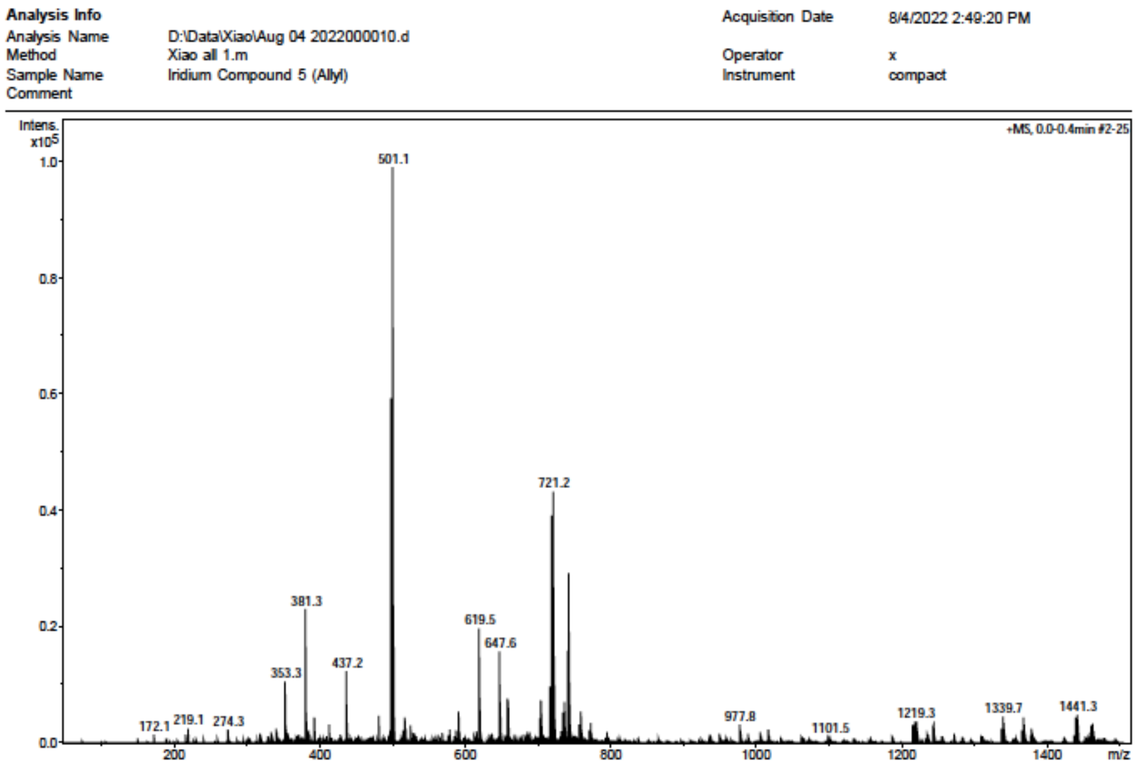
Comment

Acquisition Date 8/4/2022 2:49:20 PM

Operator x

Instrument compact

Figure S35. Zoomed Mass Spectroscopy spectra of compound **10**.

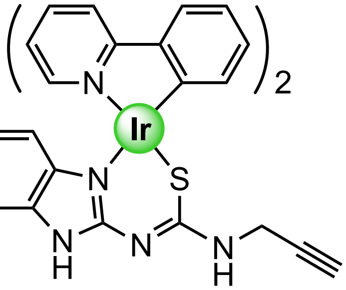


Analysis Info

Analysis Name	D:\Data\Xiao\Aug 04 2022000010.d	Acquisition Date	8/4/2022 2:49:20 PM
Method	Xiao all 1.m	Operator	x
Sample Name	Iridium Compound 5 (Allyl)	Instrument	compact
Comment			

Figure S36. Mass Spectroscopy spectra of compound **10**.

Cyclometalated Ir(III) complex **11**:



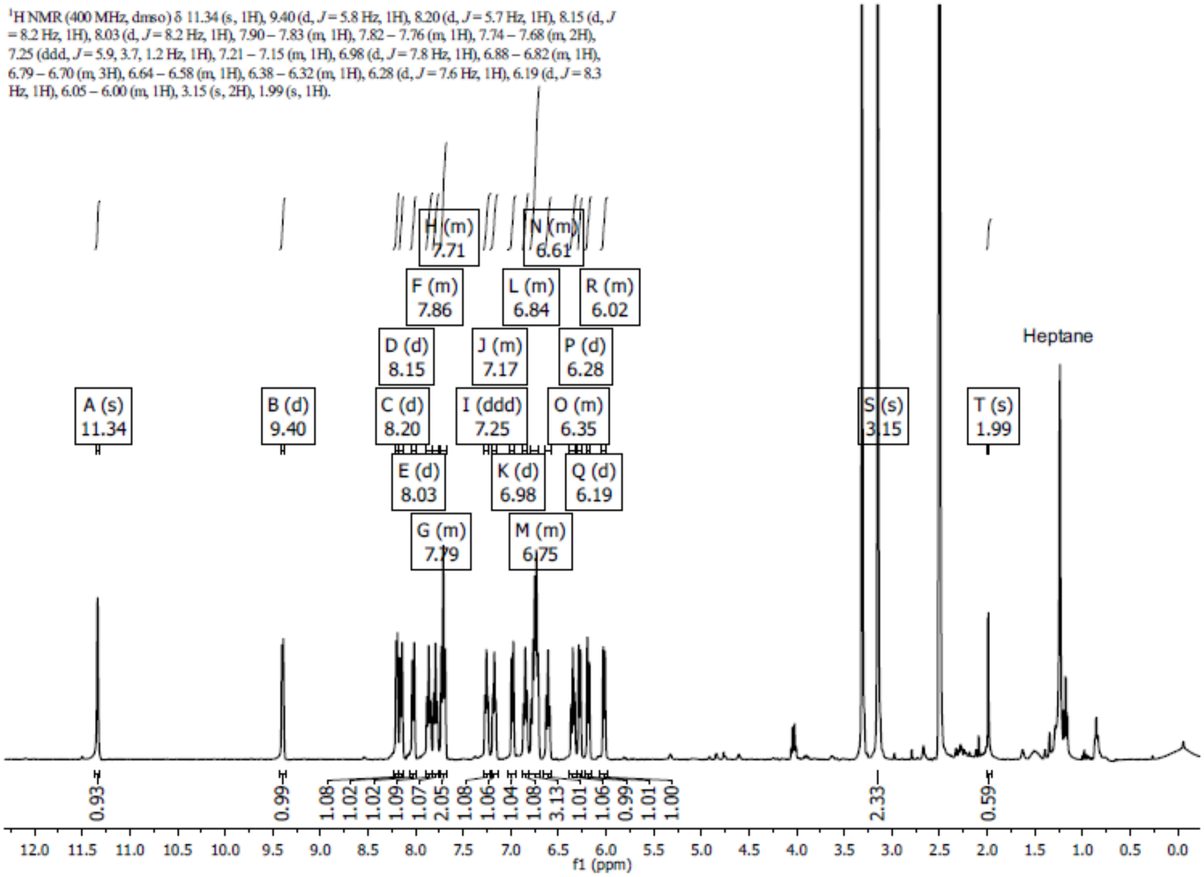
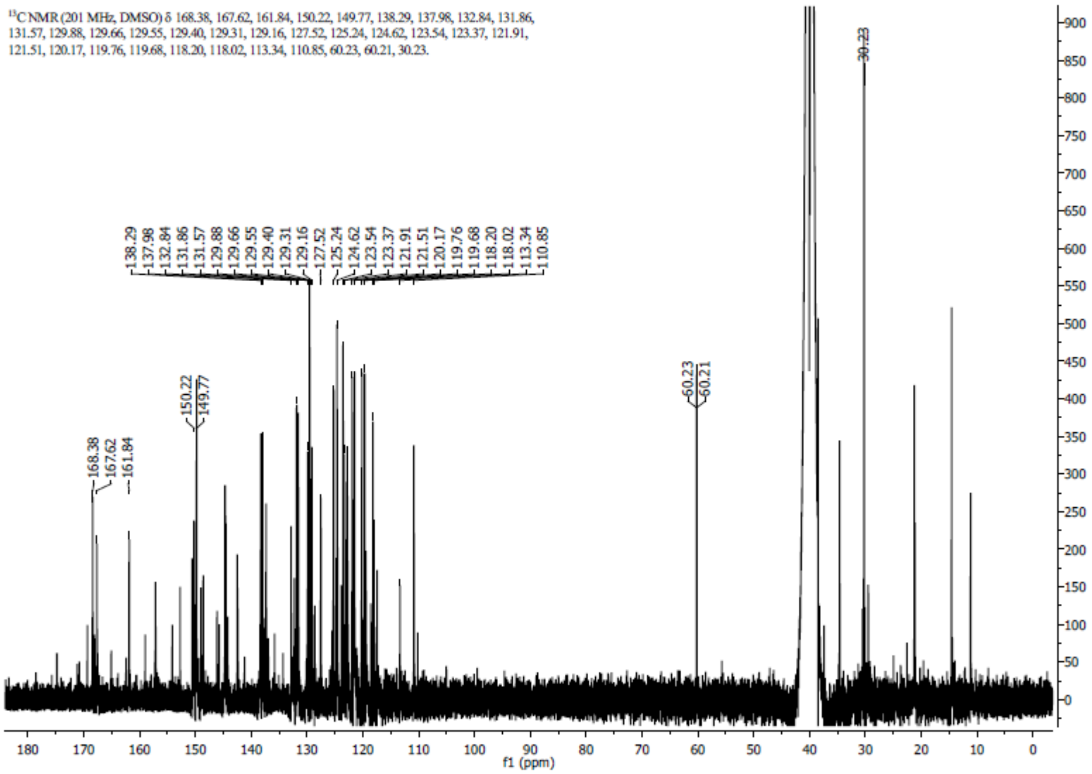
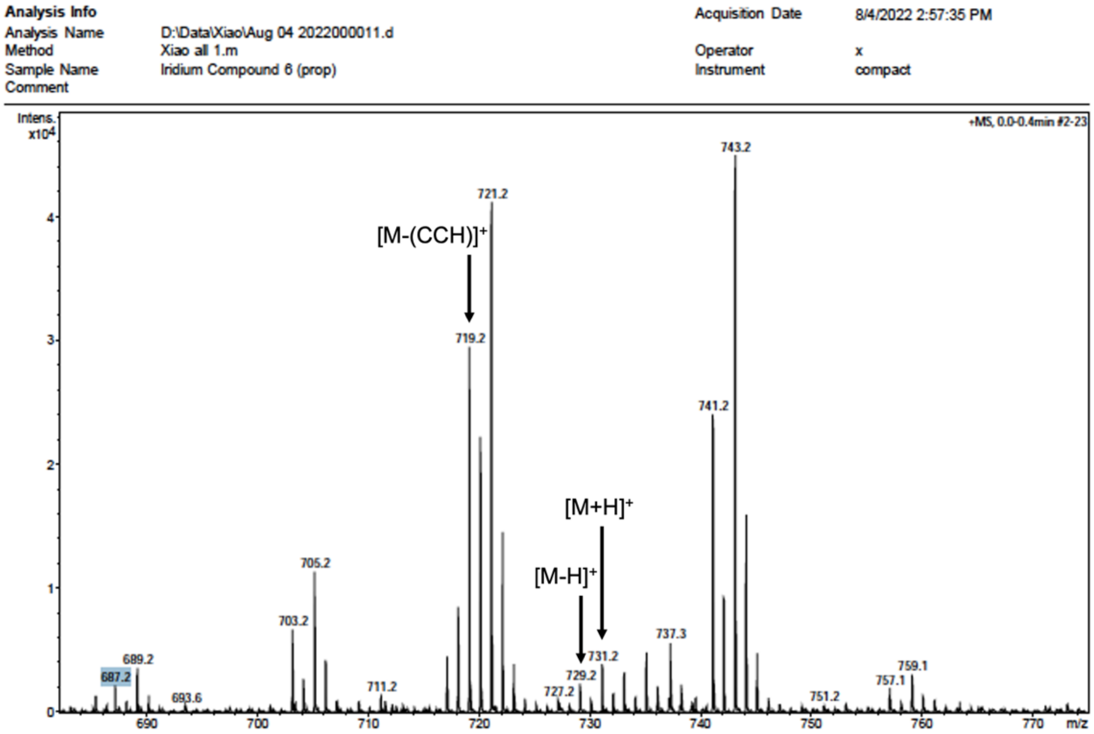

^{1}H NMR (400 MHz, dmso) δ 11.34 (s, 1H), 9.40 (d, *J* = 5.8 Hz, 1H), 8.20 (d, *J* = 5.7 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.83 (m, 1H), 7.82 – 7.76 (m, 1H), 7.74 – 7.68 (m, 2H), 7.25 (ddd, *J* = 5.9, 3.7, 1.2 Hz, 1H), 7.21 – 7.15 (m, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.88 – 6.82 (m, 1H), 6.79 – 6.70 (m, 3H), 6.64 – 6.58 (m, 1H), 6.38 – 6.32 (m, 1H), 6.28 (d, *J* = 7.6 Hz, 1H), 6.19 (d, *J* = 8.3 Hz, 1H), 6.05 – 6.00 (m, 1H), 3.15 (s, 2H), 1.99 (s, 1H).

Figure S37. ^{1}H-NMR spectra of compound **11** (400 MHz, DMSO-d_6) at 298K.



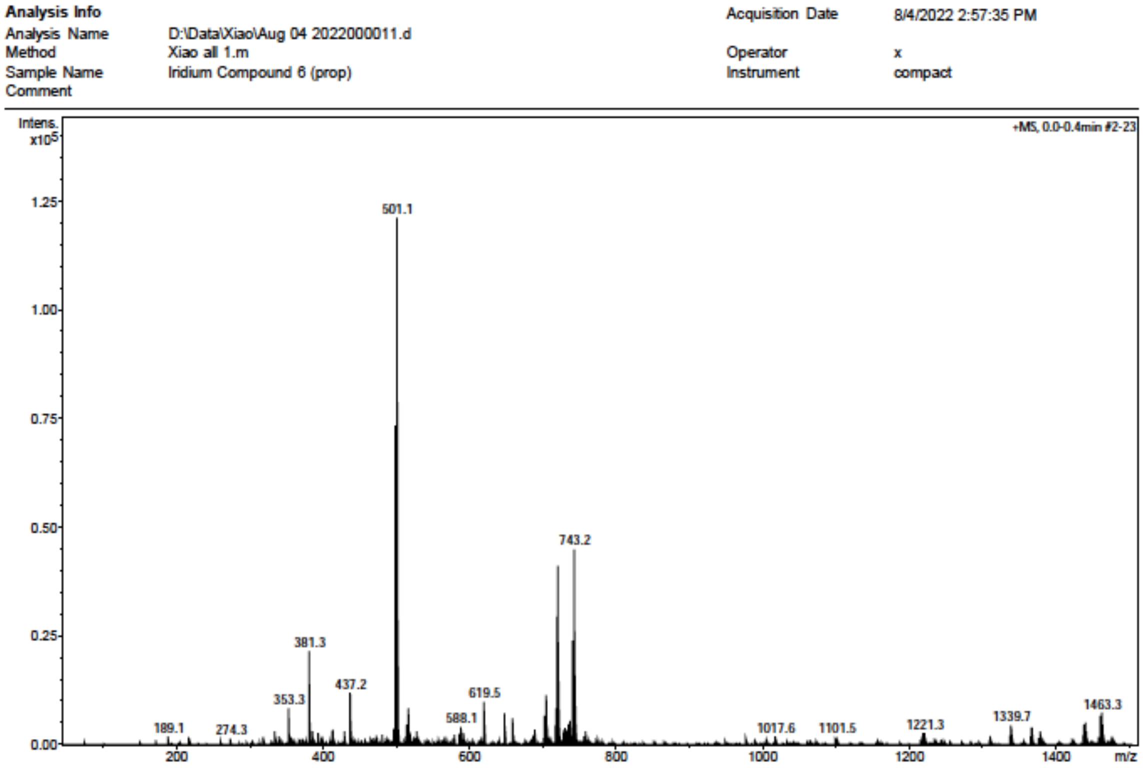
^{13}C NMR (201 MHz, DMSO) δ 168.38, 167.62, 161.84, 150.22, 149.77, 138.29, 137.98, 132.84, 131.86, 131.57, 129.88, 129.66, 129.55, 129.40, 129.31, 129.16, 127.52, 125.24, 124.62, 123.54, 123.37, 121.91, 121.51, 120.17, 119.76, 119.68, 118.20, 118.02, 113.34, 110.85, 60.23, 60.21, 30.23.

Figure S38. ^{13}C-NMR spectra of compound **11** (201 MHz, DMSO-d_6) at 298K.



Analysis Info
Analysis Name D:\Data\Xiao\Aug 04 2022000011.d
Method Xiao all 1.m
Sample Name Iridium Compound 6 (prop)
Comment
Acquisition Date 8/4/2022 2:57:35 PM
Operator x
Instrument compact

Figure S39. Zoomed Mass Spectroscopy spectra of compound **11**.



Analysis Info

Analysis Name	D:\Data\Xiao\Aug 04 2022000011.d	Acquisition Date	8/4/2022 2:57:35 PM
Method	Xiao all 1.m	Operator	x
Sample Name	Iridium Compound 6 (prop)	Instrument	compact
Comment			

Figure S40. Mass Spectroscopy spectra of compound **11**.

SIV. UV-Vis, Excitation and Emission Data

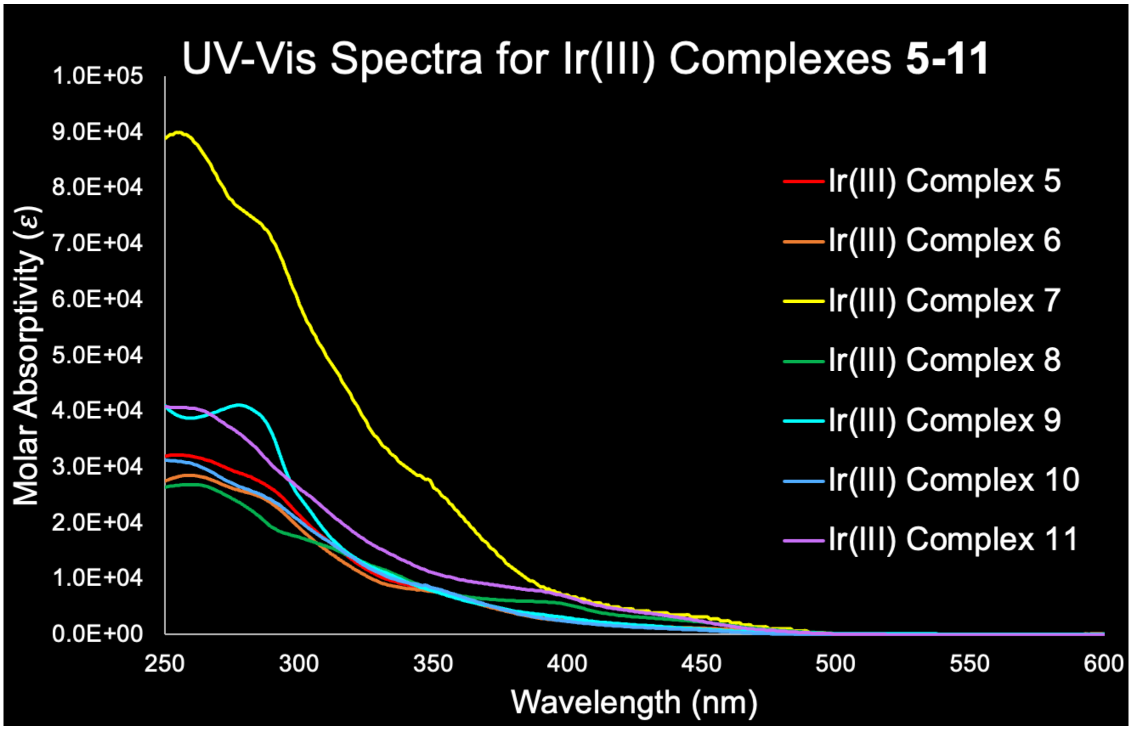


Figure S41. UV-Vis spectra of heteroleptic cyclometalated Ir(III) complexes **5**-**11** (10 μM, $CHCl_3$, 298 K).

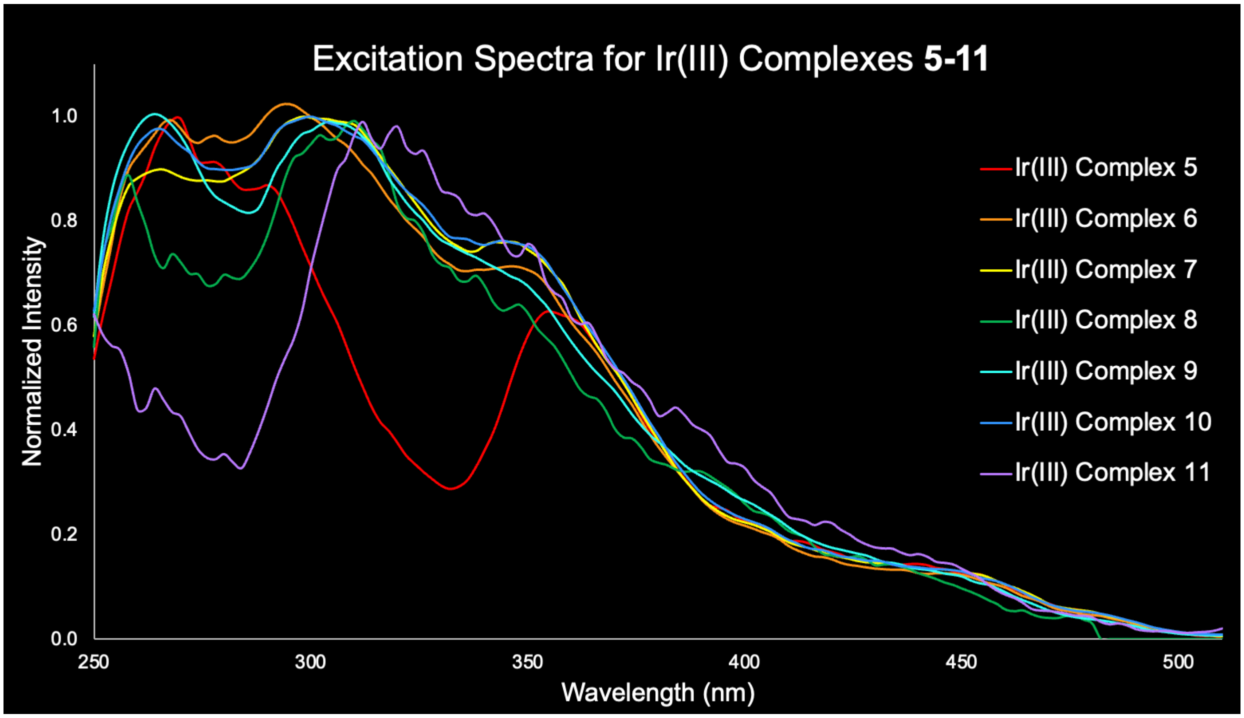


Figure S42. Normalized excitation spectra of heteroleptic cyclometalated Ir(III) complexes **5**-**11**; in $CHCl_3$ degassed for 1 min (N_2) at 298 K.

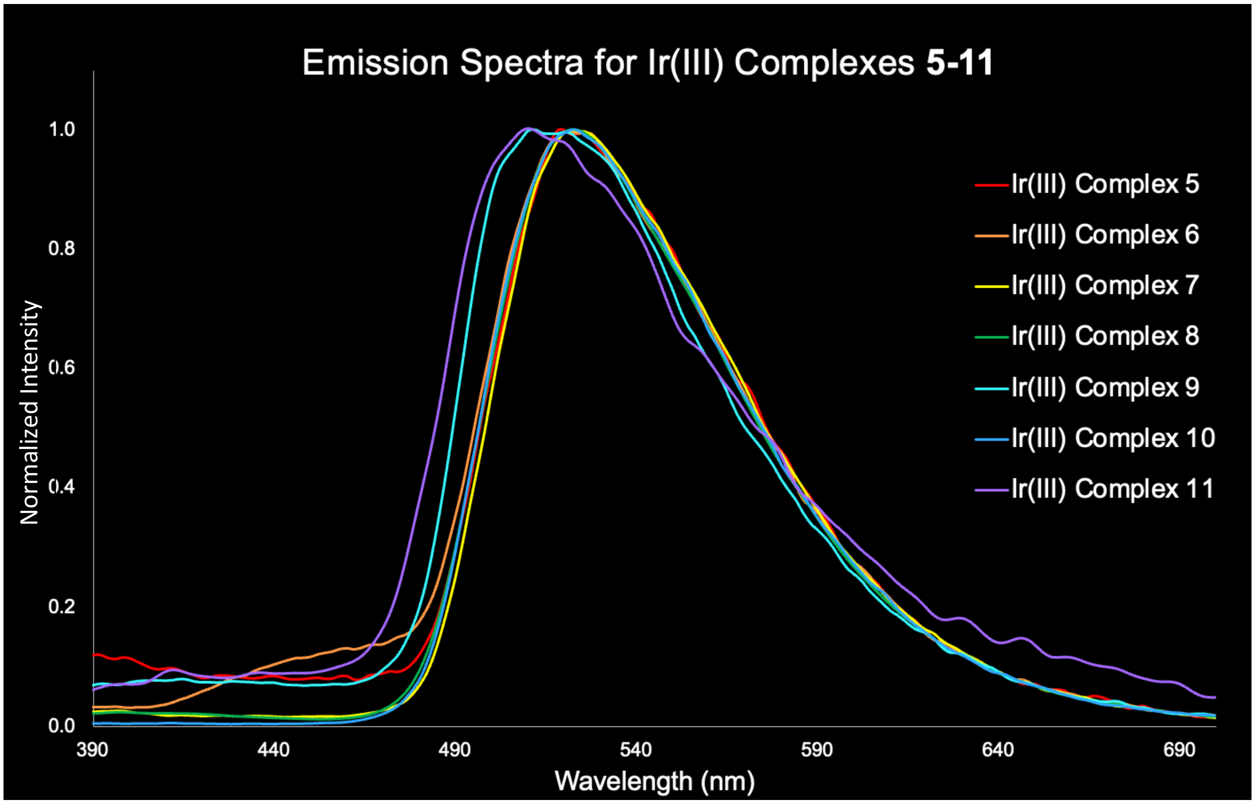


Figure S43. Normalized emission spectra of heteroleptic cyclometallated Ir(III) complexes **5**-**11**; in $CHCl_3$ degassed for 1 min (N_2) at 298 K. Compound **6** exhibits a secondary emission that we attribute to charge transfer interaction from the phenylalanine moiety. Compound **11** shows extended emission out to 700 nm for which we attribute to a contribution from the alkynyl functionality that is present in this structure.

SV. PLQYs and Decay Lifetimes

Table S5. Solution-state photophysical data for iridium(III) compounds **5-11.**

Ir(III) Complex	**Excitation Maxima (nm)**[a]	**Emission Maxima (nm)**[a]	**PLQY (%)**[b]	**Lifetime τ_{PL} (μs), χ^2** [c,d]	**k_r (x 10^5 s^{-1})**[e]	**k_{nr} (x 10^5 s^{-1})**[e]
5	268	524	38	0.90, 1.03 (99%)	4.3	6.8
6	298	524	30	1.0, 1.29	3.0	6.9
7	300	524	39	1.0, 1.05	3.8	5.8
8	312	500	2.0	1.3, 1.13 (94%)	1.7	7.3
9	306	524	22	1.1, 1.02 (99%)	2.0	7.0
10	306	520	24	0.98, 1.02 (97%)	3.5	6.8
11	312	510	6.7	1.1, 1.09 (95%)	6.1	8.5

a) Excitation and emission maxima for Ir(III) complexes **5-11**; in $CHCl_3$ degassed for 1 min (N_2) at 298 K. **b)** PLQYs for Ir(III) complexes **5-11**; in $CHCl_3$ degassed for 20 mins (Ar) at 298 K determined using the relative method with quinine sulfate in 0.1 M H_2SO_4 as a reference (ϕ_{PL}=54.6%). **c)** decay lifetimes using TCSPC excited at 365 nm and their corresponding chi-squared values for Ir(III) complexes **5-11**; in $CHCl_3$ degassed for 20 mins (Ar) at 298 K; **d**) complexes **5**, **8**, **9**, **10**, and **11** decay biexponentially - values with % were major contributor of a biexponential decay - secondary minor components are presented in individual fits below; **e)** the radiative (k_r) and nonradiative (k_{nr}) rate constants were calculated as $k_r = \phi_{PL}/\tau_{PL}$ and $k_{nr} = (1-\phi_{PL})/\tau_{PL}$.

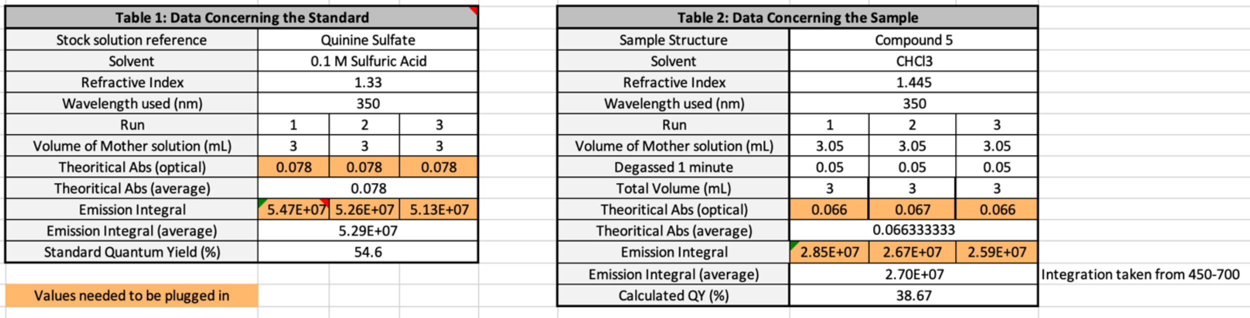


Table 1: Data Concerning the Standard			
Stock solution reference	Quinine Sulfate		
Solvent	0.1 M Sulfuric Acid		
Refractive Index	1.33		
Wavelength used (nm)	350		
Run	1	2	3
Volume of Mother solution (mL)	3	3	3
Theoritical Abs (optical)	0.078	0.078	0.078
Theoritical Abs (average)	0.078		
Emission Integral	5.47E+07	5.26E+07	5.13E+07
Emission Integral (average)	5.29E+07		
Standard Quantum Yield (%)	54.6		

Values needed to be plugged in

Table 2: Data Concerning the Sample			
Sample Structure	Compound 5		
Solvent	CHCl3		
Refractive Index	1.445		
Wavelength used (nm)	350		
Run	1	2	3
Volume of Mother solution (mL)	3.05	3.05	3.05
Degassed 1 minute	0.05	0.05	0.05
Total Volume (mL)	3	3	3
Theoritical Abs (optical)	0.066	0.067	0.066
Theoritical Abs (average)	0.066333333		
Emission Integral	2.85E+07	2.67E+07	2.59E+07
Emission Integral (average)	2.70E+07		
Calculated QY (%)	38.67		

Integration taken from 450-700

Table S6. PLQY of Ir(III) complex **5**; in $CHCl_3$ degassed for 20 mins (Ar) at 298 K, λ_{ex} = 350 nm.

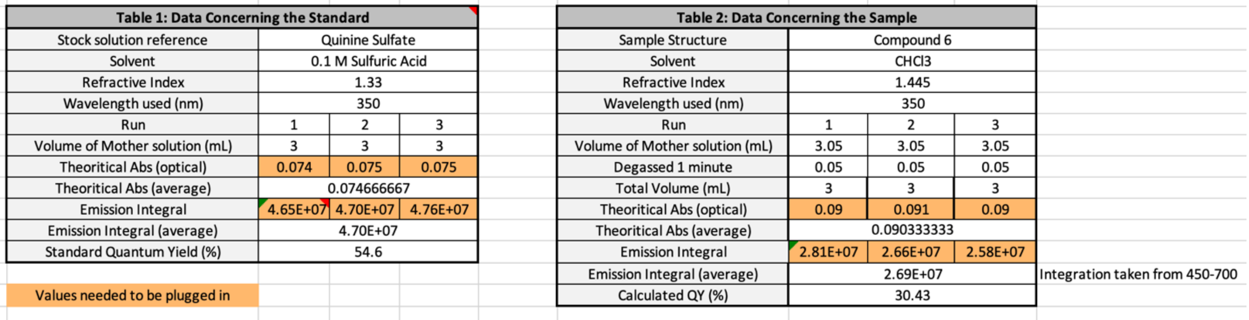


Table 1: Data Concerning the Standard			
Stock solution reference	Quinine Sulfate		
Solvent	0.1 M Sulfuric Acid		
Refractive Index	1.33		
Wavelength used (nm)	350		
Run	1	2	3
Volume of Mother solution (mL)	3	3	3
Theoritical Abs (optical)	0.074	0.075	0.075
Theoritical Abs (average)	0.074666667		
Emission Integral	4.65E+07	4.70E+07	4.76E+07
Emission Integral (average)	4.70E+07		
Standard Quantum Yield (%)	54.6		

Values needed to be plugged in

Table 2: Data Concerning the Sample			
Sample Structure	Compound 6		
Solvent	CHCl3		
Refractive Index	1.445		
Wavelength used (nm)	350		
Run	1	2	3
Volume of Mother solution (mL)	3.05	3.05	3.05
Degassed 1 minute	0.05	0.05	0.05
Total Volume (mL)	3	3	3
Theoritical Abs (optical)	0.09	0.091	0.09
Theoritical Abs (average)	0.090333333		
Emission Integral	2.81E+07	2.66E+07	2.58E+07
Emission Integral (average)	2.69E+07		
Calculated QY (%)	30.43		

Integration taken from 450-700

Table S7. PLQY of Ir(III) complex **6**; in $CHCl_3$ degassed for 20 mins (Ar) at 298 K, λ_{ex} = 350 nm.

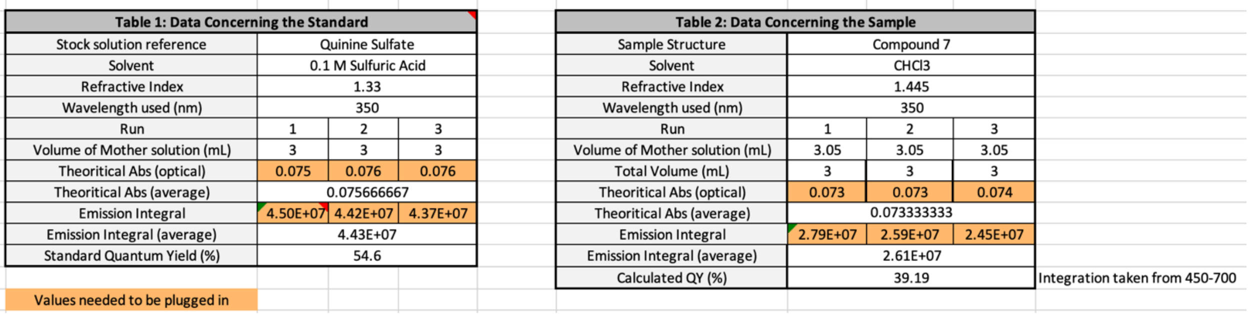


Table 1: Data Concerning the Standard			
Stock solution reference	Quinine Sulfate		
Solvent	0.1 M Sulfuric Acid		
Refractive Index	1.33		
Wavelength used (nm)	350		
Run	1	2	3
Volume of Mother solution (mL)	3	3	3
Theoritical Abs (optical)	0.075	0.076	0.076
Theoritical Abs (average)	0.075666667		
Emission Integral	4.50E+07	4.42E+07	4.37E+07
Emission Integral (average)	4.43E+07		
Standard Quantum Yield (%)	54.6		

Values needed to be plugged in

Table 2: Data Concerning the Sample			
Sample Structure	Compound 7		
Solvent	CHCl3		
Refractive Index	1.445		
Wavelength used (nm)	350		
Run	1	2	3
Volume of Mother solution (mL)	3.05	3.05	3.05
Total Volume (mL)	3	3	3
Theoritical Abs (optical)	0.073	0.073	0.074
Theoritical Abs (average)	0.073333333		
Emission Integral	2.79E+07	2.59E+07	2.45E+07
Emission Integral (average)	2.61E+07		
Calculated QY (%)	39.19		

Integration taken from 450-700

Table S8. PLQY of Ir(III) complex **7**; in $CHCl_3$ degassed for 20 mins (Ar) at 298 K, λ_{ex} = 350 nm.

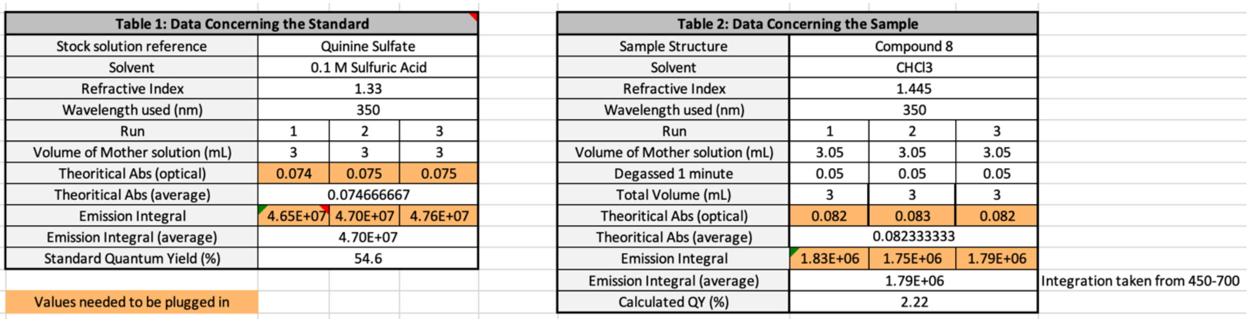


Table 1: Data Concerning the Standard			
Stock solution reference	Quinine Sulfate		
Solvent	0.1 M Sulfuric Acid		
Refractive Index	1.33		
Wavelength used (nm)	350		
Run	1	2	3
Volume of Mother solution (mL)	3	3	3
Theoritical Abs (optical)	0.074	0.075	0.075
Theoritical Abs (average)	0.074666667		
Emission Integral	4.65E+07	4.70E+07	4.76E+07
Emission Integral (average)	4.70E+07		
Standard Quantum Yield (%)	54.6		

Values needed to be plugged in

Table 2: Data Concerning the Sample				
Sample Structure	Compound 8			
Solvent	CHCl3			
Refractive Index	1.445			
Wavelength used (nm)	350			
Run	1	2	3	
Volume of Mother solution (mL)	3.05	3.05	3.05	
Degassed 1 minute	0.05	0.05	0.05	
Total Volume (mL)	3	3	3	
Theoritical Abs (optical)	0.082	0.083	0.082	
Theoritical Abs (average)	0.082333333			
Emission Integral	1.83E+06	1.75E+06	1.79E+06	
Emission Integral (average)	1.79E+06			Integration taken from 450-700
Calculated QY (%)	2.22			

Table S9. PLQY of Ir(III) complex **8**; in $CHCl_3$ degassed for 20 mins (Ar) at 298 K, λ_{ex} = 350 nm.

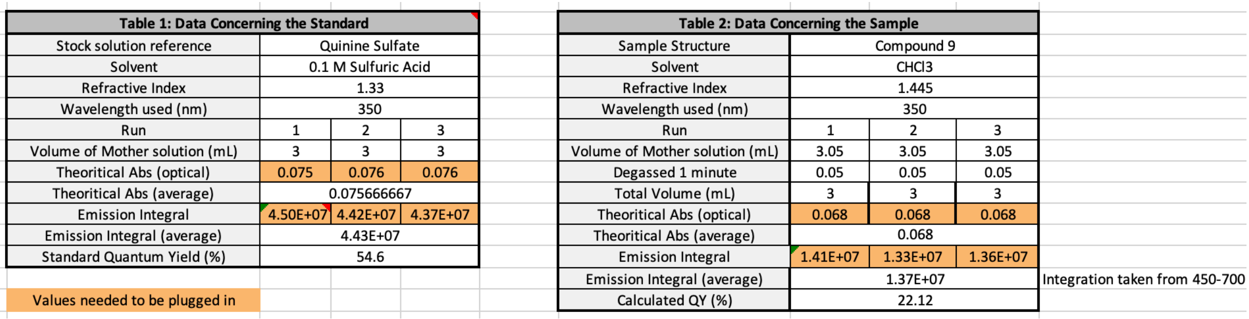


Table 1: Data Concerning the Standard			
Stock solution reference	Quinine Sulfate		
Solvent	0.1 M Sulfuric Acid		
Refractive Index	1.33		
Wavelength used (nm)	350		
Run	1	2	3
Volume of Mother solution (mL)	3	3	3
Theoritical Abs (optical)	0.075	0.076	0.076
Theoritical Abs (average)	0.075666667		
Emission Integral	4.50E+07	4.42E+07	4.37E+07
Emission Integral (average)	4.43E+07		
Standard Quantum Yield (%)	54.6		

Values needed to be plugged in

Table 2: Data Concerning the Sample				
Sample Structure	Compound 9			
Solvent	CHCl3			
Refractive Index	1.445			
Wavelength used (nm)	350			
Run	1	2	3	
Volume of Mother solution (mL)	3.05	3.05	3.05	
Degassed 1 minute	0.05	0.05	0.05	
Total Volume (mL)	3	3	3	
Theoritical Abs (optical)	0.068	0.068	0.068	
Theoritical Abs (average)	0.068			
Emission Integral	1.41E+07	1.33E+07	1.36E+07	
Emission Integral (average)	1.37E+07			Integration taken from 450-700
Calculated QY (%)	22.12			

Table S10. PLQY of Ir(III) complex **9**; in $CHCl_3$ degassed for 20 mins (Ar) at 298 K, λ_{ex} = 350 nm.

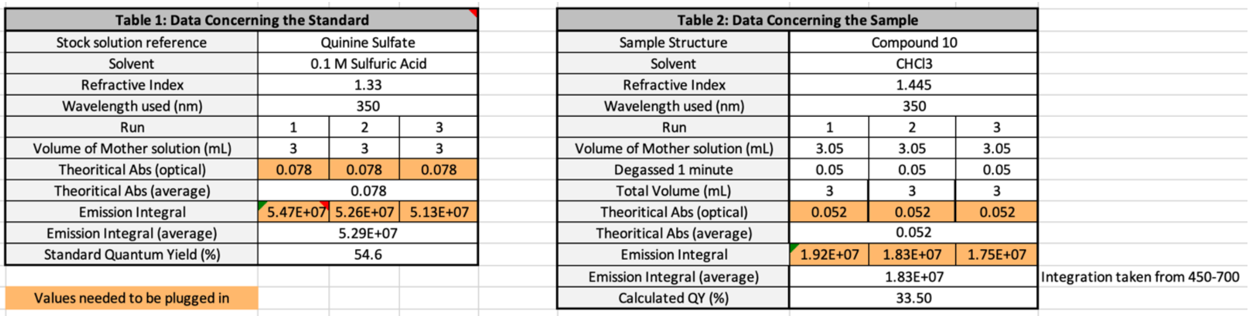


Table 1: Data Concerning the Standard			
Stock solution reference	Quinine Sulfate		
Solvent	0.1 M Sulfuric Acid		
Refractive Index	1.33		
Wavelength used (nm)	350		
Run	1	2	3
Volume of Mother solution (mL)	3	3	3
Theoritical Abs (optical)	0.078	0.078	0.078
Theoritical Abs (average)	0.078		
Emission Integral	5.47E+07	5.26E+07	5.13E+07
Emission Integral (average)	5.29E+07		
Standard Quantum Yield (%)	54.6		

Values needed to be plugged in

Table 2: Data Concerning the Sample				
Sample Structure	Compound 10			
Solvent	CHCl3			
Refractive Index	1.445			
Wavelength used (nm)	350			
Run	1	2	3	
Volume of Mother solution (mL)	3.05	3.05	3.05	
Degassed 1 minute	0.05	0.05	0.05	
Total Volume (mL)	3	3	3	
Theoritical Abs (optical)	0.052	0.052	0.052	
Theoritical Abs (average)	0.052			
Emission Integral	1.92E+07	1.83E+07	1.75E+07	
Emission Integral (average)	1.83E+07			Integration taken from 450-700
Calculated QY (%)	33.50			

Table S11. PLQY of Ir(III) complex **10**; in $CHCl_3$ degassed for 20 mins (Ar) at 298 K, λ_{ex} = 350 nm.

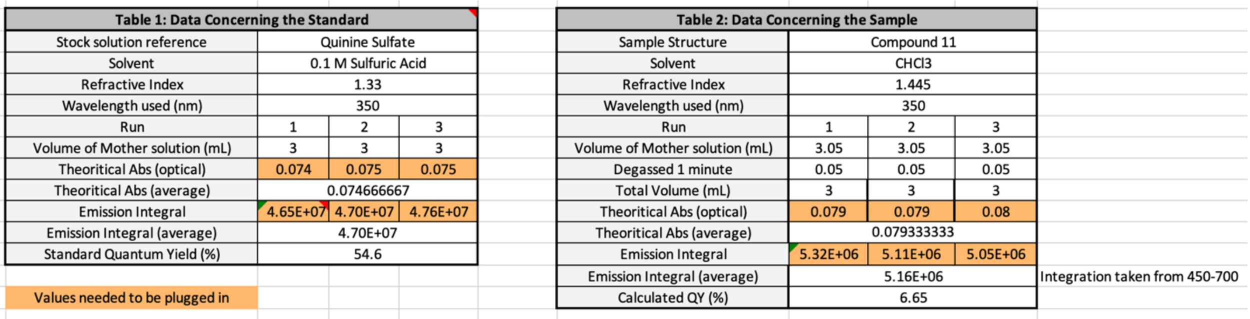


Table 1: Data Concerning the Standard			
Stock solution reference	Quinine Sulfate		
Solvent	0.1 M Sulfuric Acid		
Refractive Index	1.33		
Wavelength used (nm)	350		
Run	1	2	3
Volume of Mother solution (mL)	3	3	3
Theoritical Abs (optical)	0.074	0.075	0.075
Theoritical Abs (average)	0.074666667		
Emission Integral	4.65E+07	4.70E+07	4.76E+07
Emission Integral (average)	4.70E+07		
Standard Quantum Yield (%)	54.6		

Values needed to be plugged in

Table 2: Data Concerning the Sample				
Sample Structure	Compound 11			
Solvent	CHCl3			
Refractive Index	1.445			
Wavelength used (nm)	350			
Run	1	2	3	
Volume of Mother solution (mL)	3.05	3.05	3.05	
Degassed 1 minute	0.05	0.05	0.05	
Total Volume (mL)	3	3	3	
Theoritical Abs (optical)	0.079	0.079	0.08	
Theoritical Abs (average)	0.079333333			
Emission Integral	5.32E+06	5.11E+06	5.05E+06	
Emission Integral (average)	5.16E+06			Integration taken from 450-700
Calculated QY (%)	6.65			

Table S12. PLQY of Ir(III) complex **11**; in $CHCl_3$ degassed for 20 mins (Ar) at 298 K, λ_{ex} = 350 nm.

Decay Lifetime Measurement of Ir(III) complex 5

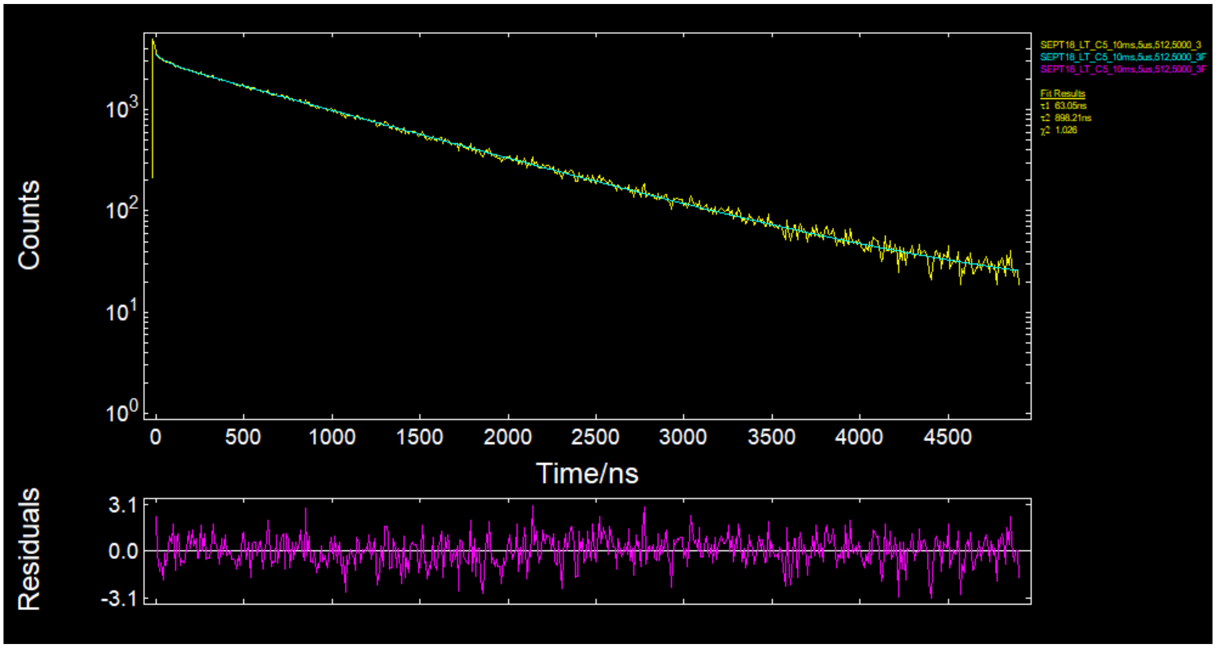
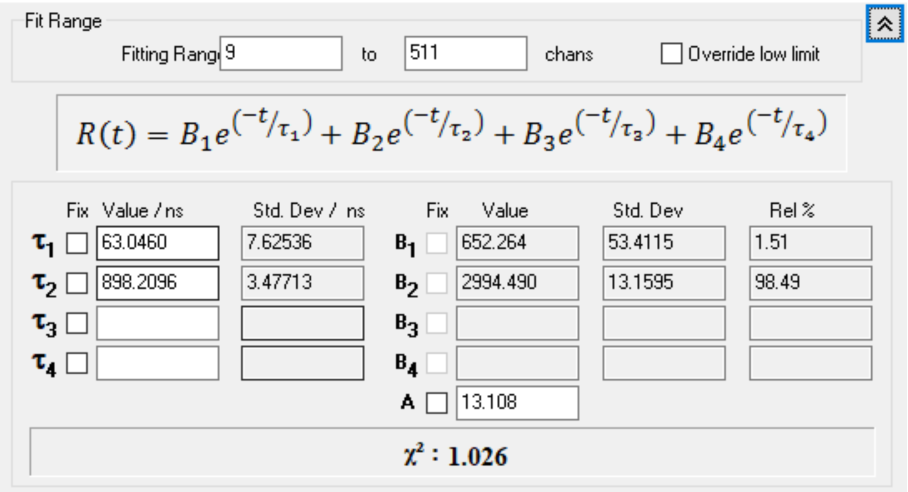


Figure S44. Biexponential lifetime decay of Ir(III) complex **5**, ~1·10^{-6} M (Absorbance of 0.083 from UV-Vis) in $CHCl_3$ degassed for 20 mins (Ar) at 298 K after excitation at 365 nm. Data collected at λ_{max} = 520 nm.



Fit Range

Fitting Rang 9 to 511 chans ☐ Override low limit

$$R(t) = B_1 e^{(-t/\tau_1)} + B_2 e^{(-t/\tau_2)} + B_3 e^{(-t/\tau_3)} + B_4 e^{(-t/\tau_4)}$$

	Fix	Value / ns	Std. Dev / ns		Fix	Value	Std. Dev	Rel %
τ_1	☐	63.0460	7.62536	B_1	☐	652.264	53.4115	1.51
τ_2	☐	898.2096	3.47713	B_2	☐	2994.490	13.1595	98.49
τ_3	☐			B_3	☐			
τ_4	☐			B_4	☐			
				A	☐	13.108		

χ^2 : 1.026

Figure S45. Fit result of Ir(III) complex **5**, ~1·10^{-6} M (Absorbance of 0.083 from UV-Vis) in $CHCl_3$ degassed for 20 mins (Ar) at 298 K after excitation at 365 nm. Data collected at λ_{max} = 520 nm.

Lifetime Measurement of Ir(III) complex 6

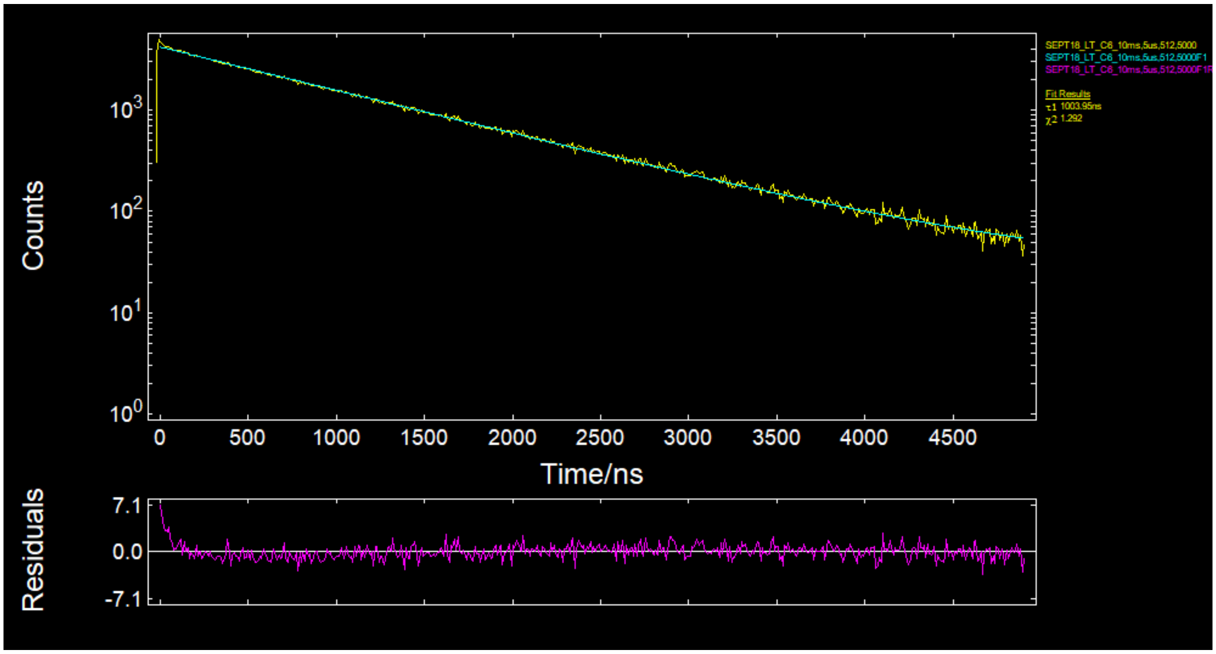
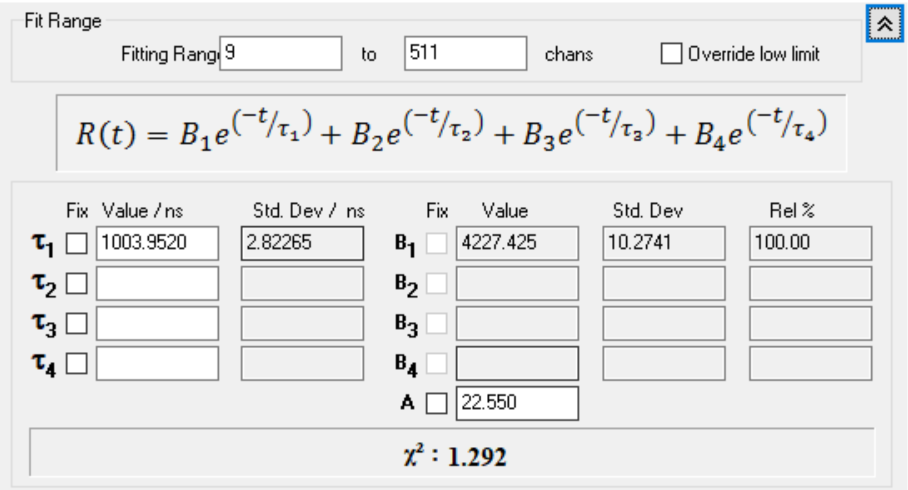


Figure S46. Monoexponential lifetime decay of Ir(III) complex **6**, ~$1\cdot10^{-6}$ M (Absorbance of 0.100 from UV-Vis) in $CHCl_3$ degassed for 20 mins (Ar) at 298 K after excitation at 365 nm. Data collected at λ_{max} = 520 nm.



Fit Range

Fitting Range 9 to 511 chans ☐ Override low limit

$$R(t) = B_1 e^{(-t/\tau_1)} + B_2 e^{(-t/\tau_2)} + B_3 e^{(-t/\tau_3)} + B_4 e^{(-t/\tau_4)}$$

	Fix	Value / ns	Std. Dev / ns		Fix	Value	Std. Dev	Rel %
τ_1	☐	1003.9520	2.82265	B_1	☐	4227.425	10.2741	100.00
τ_2	☐			B_2	☐			
τ_3	☐			B_3	☐			
τ_4	☐			B_4	☐			
				A	☐	22.550		

χ^2 : 1.292

Figure S47. Fit result of Ir(III) complex **6**, ~$1\cdot10^{-6}$ M (Absorbance of 0.100 from UV-Vis) in $CHCl_3$ degassed for 20 mins (Ar) at 298 K after excitation at 365 nm. Data collected at λ_{max} = 520 nm.

Lifetime Measurement of Ir(III) complex 7

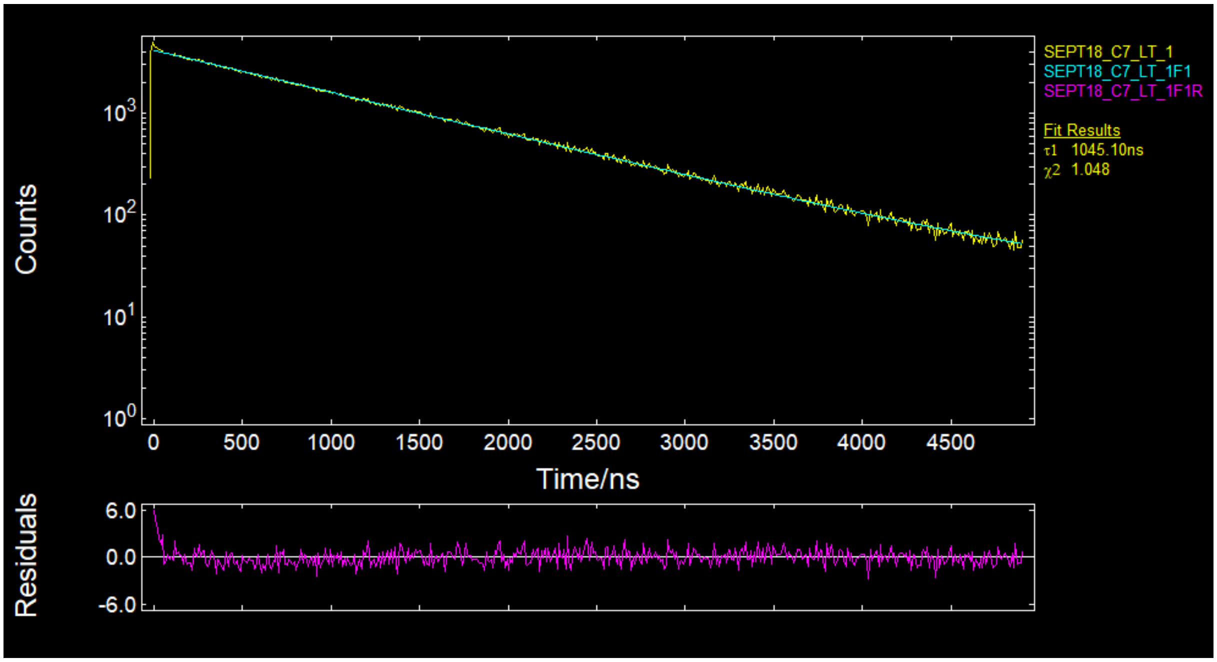
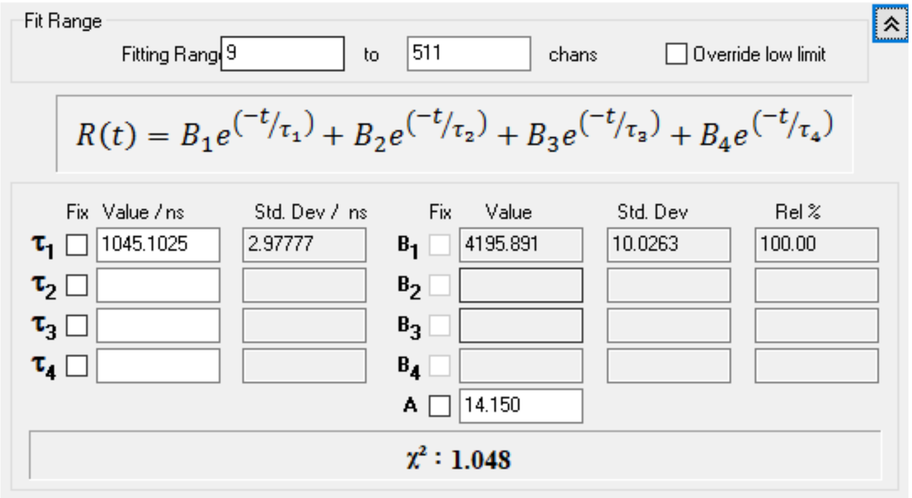


Figure S48. Monoexponential lifetime decay of Ir(III) complex **7**, ~$1\cdot10^{-6}$ M (Absorbance of 0.094 from UV-Vis) in $CHCl_3$ degassed for 20 mins (Ar) at 298 K after excitation at 365 nm. Data collected at λ_{max} = 520 nm.



Fit Range

Fitting Rang 9 to 511 chans ☐ Override low limit

$$R(t) = B_1 e^{(-t/\tau_1)} + B_2 e^{(-t/\tau_2)} + B_3 e^{(-t/\tau_3)} + B_4 e^{(-t/\tau_4)}$$

	Fix	Value / ns	Std. Dev / ns		Fix	Value	Std. Dev	Rel %
τ_1	☐	1045.1025	2.97777	B_1	☐	4195.891	10.0263	100.00
τ_2	☐			B_2	☐			
τ_3	☐			B_3	☐			
τ_4	☐			B_4	☐			
				A	☐	14.150		

χ^2 : 1.048

Figure S49. Fit result of Ir(III) complex **7**, ~$1\cdot10^{-6}$ M (Absorbance of 0.094 from UV-Vis) in $CHCl_3$ degassed for 20 mins (Ar) at 298 K after excitation at 365 nm. Data collected at λ_{max} = 520 nm.

Lifetime Measurement of Ir(III) complex 8

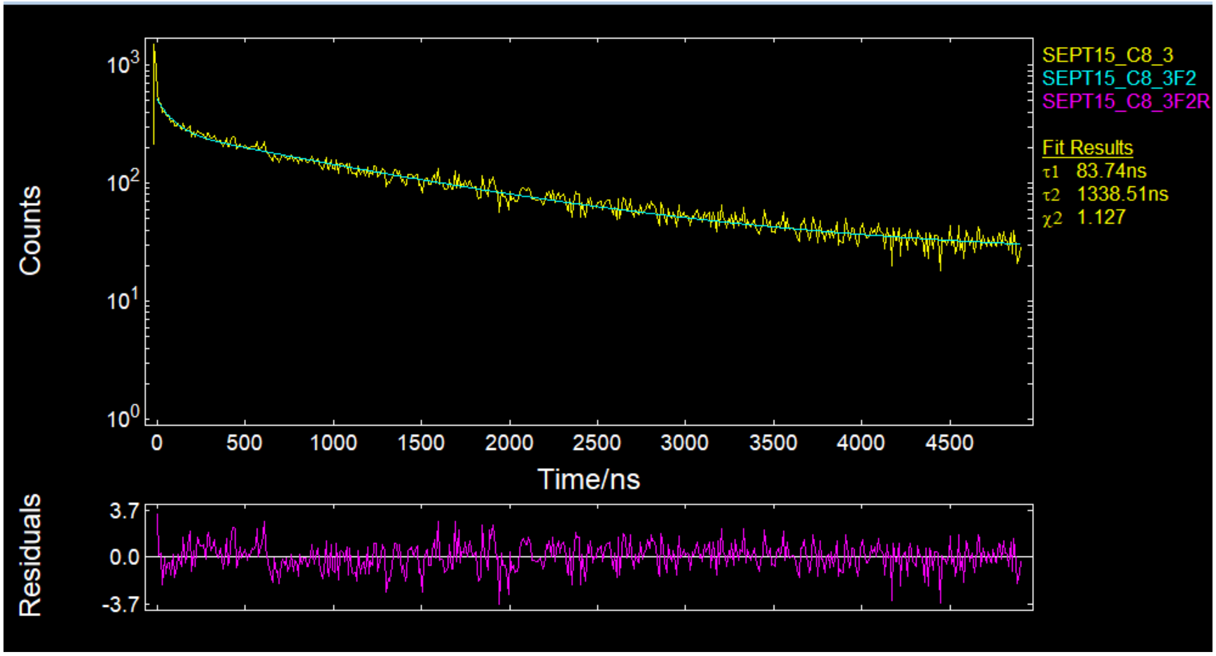
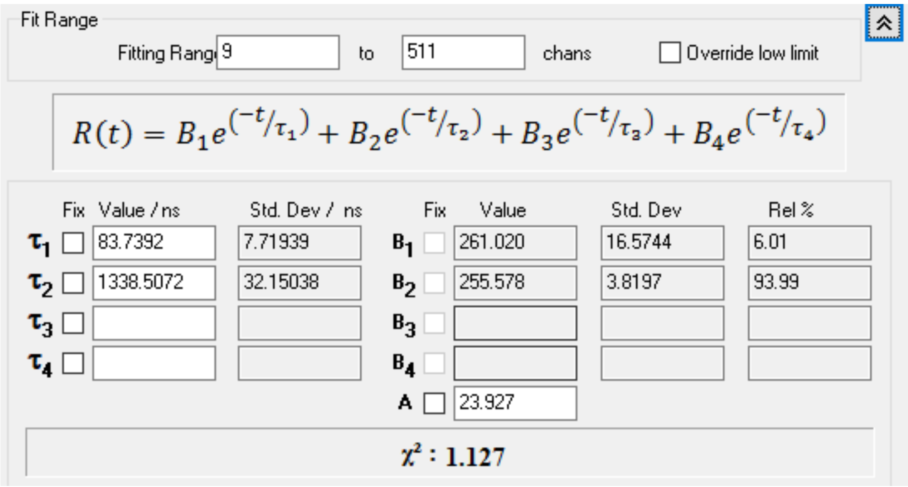


Figure S50. Biexponential lifetime decay of Ir(III) complex **8**, ~$1\cdot10^{-6}$ M (Absorbance of 0.089 from UV-Vis) in $CHCl_3$ degassed for 20 mins (Ar) at 298 K after excitation at 365 nm. Data collected at λ_{max} = 520 nm.



Fit Range

Fitting Rang 9 to 511 chans ☐ Override low limit

$$R(t) = B_1e^{(-t/\tau_1)} + B_2e^{(-t/\tau_2)} + B_3e^{(-t/\tau_3)} + B_4e^{(-t/\tau_4)}$$

	Fix	Value / ns	Std. Dev / ns		Fix	Value	Std. Dev	Rel %
τ_1	☐	83.7392	7.71939	B_1	☐	261.020	16.5744	6.01
τ_2	☐	1338.5072	32.15038	B_2	☐	255.578	3.8197	93.99
τ_3	☐			B_3	☐			
τ_4	☐			B_4	☐			
				A	☐	23.927		

χ^2 : 1.127

Figure S51. Fit result of Ir(III) complex **8**, ~$1\cdot10^{-6}$ M (Absorbance of 0.089 from UV-Vis) in $CHCl_3$ degassed for 20 mins (Ar) at 298 K after excitation at 365 nm. Data collected at λ_{max} = 520 nm.

Lifetime Measurement of Ir(III) complex 9

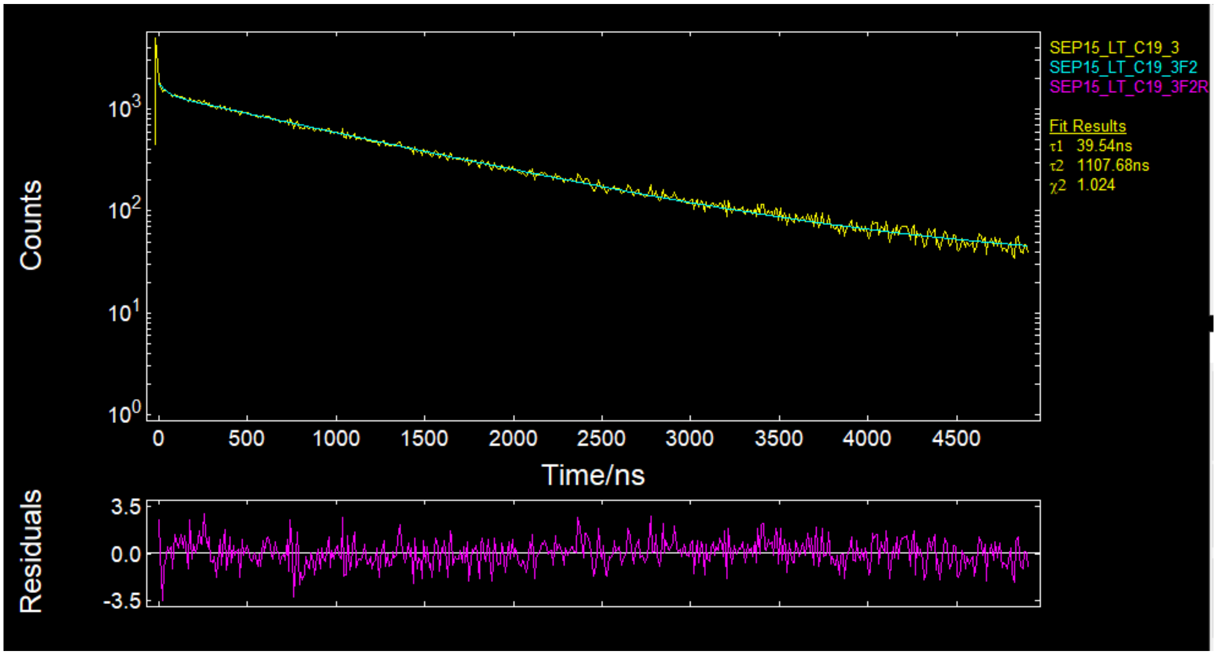
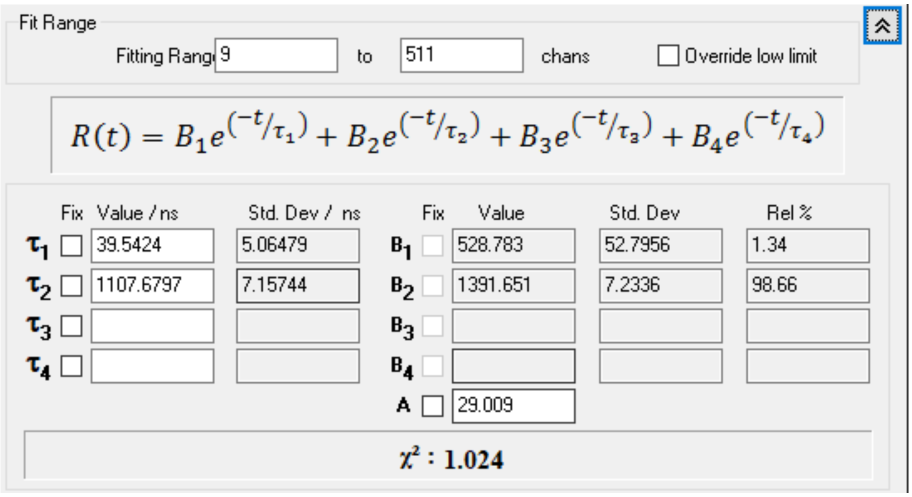


Figure S52. Biexponential lifetime decay of Ir(III) complex **9**, ~1·10^{-6} M (Absorbance of 0.100 from UV-Vis) in CHCl$_3$ degassed for 20 mins (Ar) at 298 K after excitation at 365 nm. Data collected at λ_{max} = 520 nm.



Fit Range

Fitting Rang 9 to 511 chans ☐ Override low limit

$$R(t) = B_1 e^{(-t/\tau_1)} + B_2 e^{(-t/\tau_2)} + B_3 e^{(-t/\tau_3)} + B_4 e^{(-t/\tau_4)}$$

	Fix	Value / ns	Std. Dev / ns		Fix	Value	Std. Dev	Rel %
τ_1	☐	39.5424	5.06479	B_1	☐	528.783	52.7956	1.34
τ_2	☐	1107.6797	7.15744	B_2	☐	1391.651	7.2336	98.66
τ_3	☐			B_3	☐			
τ_4	☐			B_4	☐			
				A	☐	29.009		

χ^2 : 1.024

Figure S53. Fit result of Ir(III) complex **9**, ~1·10^{-6} M (Absorbance of 0.100 from UV-Vis) in CHCl$_3$ degassed for 20 mins (Ar) at 298 K after excitation at 365 nm. Data collected at λ_{max} = 520 nm.

Lifetime Measurement of Ir(III) complex 10

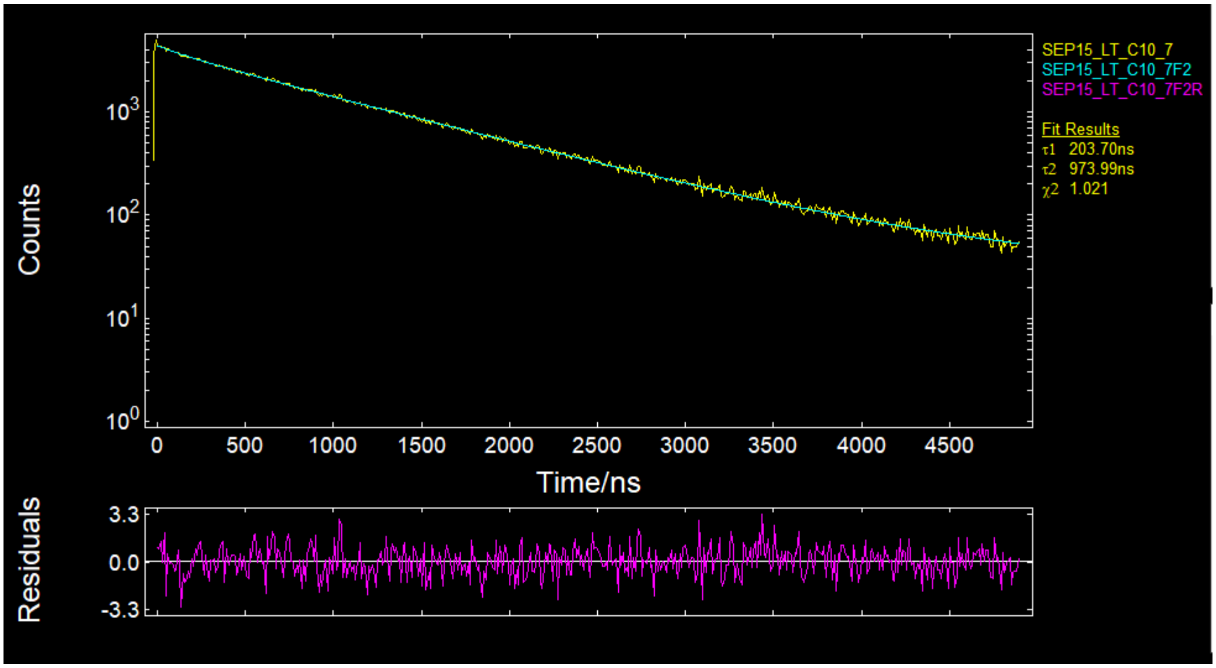
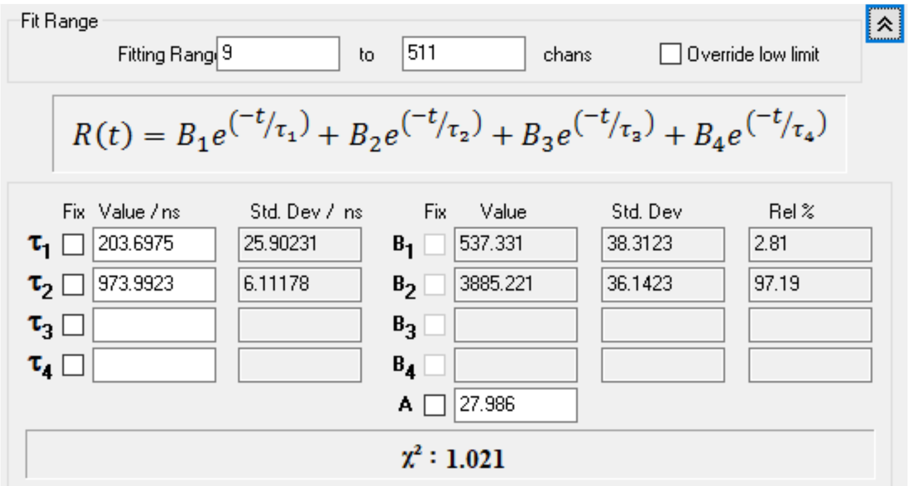


Figure S54. Biexponential lifetime decay of Ir(III) complex **10**, ~1·10^{-6} M (Absorbance of 0.077 from UV-Vis) in CHCl$_3$ degassed for 20 mins (Ar) at 298 K after excitation at 365 nm. Data collected at λ_{max} = 520 nm.



Fit Range

Fitting Rang 9 to 511 chans ☐ Override low limit

$$R(t) = B_1 e^{(-t/\tau_1)} + B_2 e^{(-t/\tau_2)} + B_3 e^{(-t/\tau_3)} + B_4 e^{(-t/\tau_4)}$$

	Fix	Value / ns	Std. Dev / ns		Fix	Value	Std. Dev	Rel %
τ_1	☐	203.6975	25.90231	B_1	☐	537.331	38.3123	2.81
τ_2	☐	973.9923	6.11178	B_2	☐	3885.221	36.1423	97.19
τ_3	☐			B_3	☐			
τ_4	☐			B_4	☐			
				A	☐	27.986		

χ^2 : 1.021

Figure S55. Fit result of Ir(III) complex **10**, ~1·10^{-6} M (Absorbance of 0.077 from UV-Vis) in CHCl$_3$ degassed for 20 mins (Ar) at 298 K after excitation at 365 nm. Data collected at λ_{max} = 520 nm.

Lifetime Measurement of Ir(III) complex 11

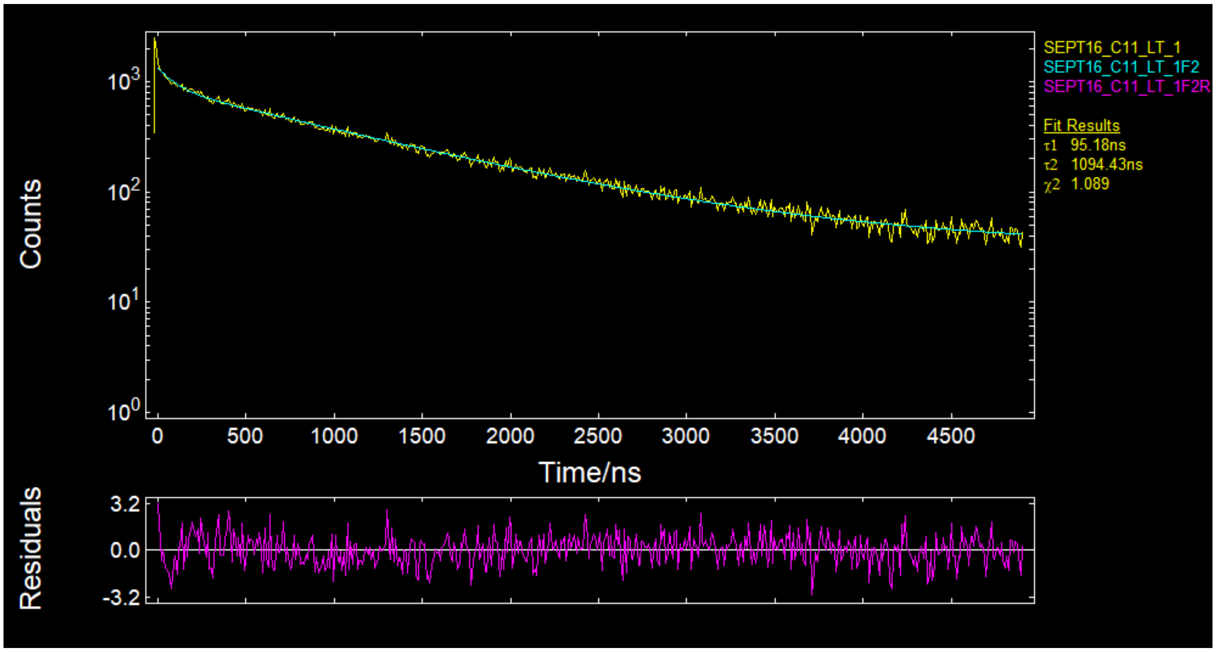
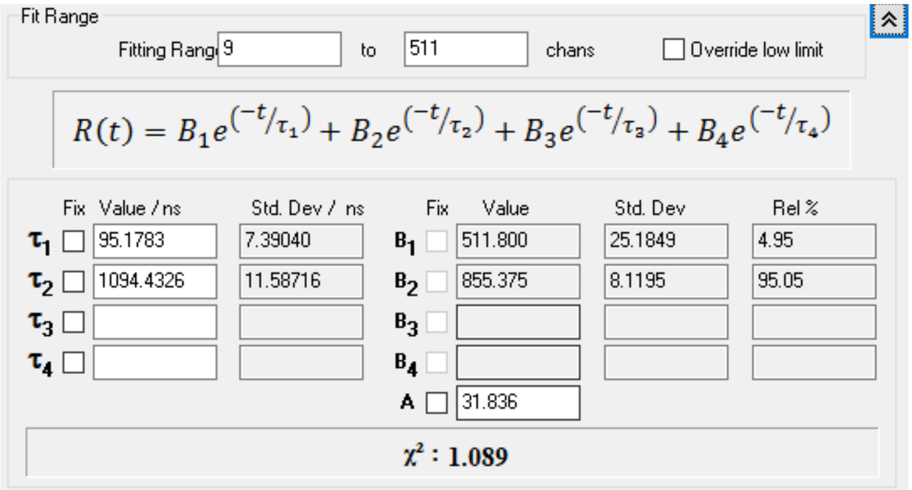


Figure S56. Biexponential lifetime decay of Ir(III) complex **11**, ~$1{\cdot}10^{-6}$ M (Absorbance of 0.078 from UV-Vis) in $CHCl_3$ degassed for 20 mins (Ar) at 298 K after excitation at 365 nm. Data collected at λ_{max} = 520 nm.



Fit Range

Fitting Rang 9 to 511 chans ☐ Override low limit

$$R(t) = B_1 e^{(-t/\tau_1)} + B_2 e^{(-t/\tau_2)} + B_3 e^{(-t/\tau_3)} + B_4 e^{(-t/\tau_4)}$$

	Fix	Value / ns	Std. Dev / ns		Fix	Value	Std. Dev	Rel %
τ_1	☐	95.1783	7.39040	B_1	☐	511.800	25.1849	4.95
τ_2	☐	1094.4326	11.58716	B_2	☐	855.375	8.1195	95.05
τ_3	☐			B_3	☐			
τ_4	☐			B_4	☐			
				A	☐	31.836		

χ^2 : 1.089

Figure S57. Fit result of Ir(III) complex **11**, ~$1{\cdot}10^{-6}$ M (Absorbance of 0.078 from UV-Vis) in $CHCl_3$ degassed for 20 mins (Ar) at 298 K after excitation at 365 nm. Data collected at λ_{max} = 520 nm.