

## Two-photon spectroscopy of cyclometalated iridium complexes

### Electronic Supporting Information

Robert M. Edkins, Sylvia L. Bettington, Andrés E. Goeta and Andrew Beeby\*

Department of Chemistry, Durham University, South Road, Durham, UK, DH1 3LE; E-mail:

[andrew.beeby@durham.ac.uk](mailto:andrew.beeby@durham.ac.uk); Tel. +44 (0) 191 33 42023.

## Experimental

For all photophysical measurements of iridium compounds, toluene (GPR grade) was used as the solvent, as it had been observed in fluorimetry and NMR spectroscopy experiments that some of these compounds can be photolytically degraded in chlorinated solvents. All samples were additionally checked for purity by thin layer chromatography (TLC) using 254 nm fluorescent silica plates (Polygram Sil G/UV254 0.2 mm silica) visualised under UV light or by I<sub>2</sub> staining.

### UV-visible absorption spectroscopy

Absorption spectra of solutions in quartz cuvettes of path length  $l = 1$  cm with an absorbance,  $A$ ,  $< 0.2$  at 400 nm were measured on a Unicam UV2-100 spectrometer operated with the Unicam Vision software. Baseline correction was achieved by reference to pure solvent. Extinction coefficients ( $\epsilon$ ,  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) were calculated using the Beer-Lambert law,  $A = \epsilon cl$ , ( $c$  is the concentration,  $\text{mol dm}^{-3}$ ) by recording the absorption spectrum for samples weighed on an analytical balance.

### One-photon photoluminescence spectroscopy

Excitation and emission photoluminescence spectra were recorded on an Horiba Jobin Yvon SPEX Fluorolog 3-22 spectrofluorometer. Samples were held in quartz fluorescence cuvettes,  $l = 1$  cm x 1 cm, degassed by repeated freeze-pump-thaw cycles using a turbomolecular pump until the pressure gauge showed no further movement upon a new pump phase, typically at  $5 \times 10^{-5}$  mbar, and sealed by way of a Teflon Young's tap. Solutions had  $A = 0.10$ - $0.15$  at 400 nm to minimise inner filter effects. PLQYs were measured using the Fluorolog 3-22 and an integrating sphere using a published method.<sup>1</sup> DataMax software was used throughout.

### Two-photon absorption (TPA) spectroscopy

Two-photon cross-sections were measured using the femtosecond TPA induced fluorescence method. A mode-locked, cavity dumped (APE Pulse switch) Ti:sapphire laser (Coherent MIRA) was pumped by the 2nd harmonic (532 nm) of a CW Nd:YAG laser (Coherent Verdi V6) at a power of 4.5 W to create a pulsed excitation source. The pulse characteristics were: a temporal full width at half maximum (FWHM) of  $\sim 150$  fs, average power 5-35 mW at a repetition rate of  $\sim 2.5$  MHz, giving average energies of 2-38 nJ pulse<sup>-1</sup>. A variable ND filter (Edmund Optics) mounted on a translation stage was used to control the light intensity incident on the sample, with the power monitored by splitting the beam to a photodiode of known response, calibrated against a

free standing power meter. Gold mirrors, highly reflective of NIR radiation, were used with a 20x objective (Olympus LWD C A20) to focus the source onto the sample. Samples were prepared with  $A = 0.2-0.3$  at 400 nm (concentrations: Ir(4-pe-2-ppy)<sub>2</sub>(acac) 11.5  $\mu\text{M}$ , Ir(ppy)<sub>3</sub> 13.9  $\mu\text{M}$ , Ir(ppy)<sub>2</sub>(acac) 37.3  $\mu\text{M}$ , Ir(ppy)<sub>2</sub>(fppy) 40.4  $\mu\text{M}$  and Ir(ppm)<sub>3</sub> 22.0  $\mu\text{M}$ ) in quartz cuvettes of path length,  $l = 1$  cm and degassed by the same method as for one-photon PL. Two photon PL was collected with a dichroic mirror (Semrock FF735) and detected with a 100  $\mu\text{m}$  core fibre optic cable coupled CCD spectrograph (Avantes Avaspec 2048FT) fitted with a 670 nm shortpass filter to remove extraneous laser light. TPA cross sections ( $\sigma_2$ ) were measured relative to a reference, as per the standard methodology of Webb *et al.*,<sup>2</sup> using the equation:

$$\sigma_2^S = \frac{\sigma_2^R \Phi_p^R c^R n^S F^S(\lambda)}{\Phi_p^S c^S n^R F^R(\lambda)}$$

The superscripts  $R$  and  $S$  refer to the reference and sample respectively,  $\Phi_p$  is the one photon photoluminescence quantum yield,  $c$  is the concentration,  $n$  is the solvent refractive index and  $F(\lambda)$  is the integrated two-photon emission spectrum. The sample and reference were recorded under identical pulse conditions. The concentration of the reference fluorescein was measured by UV-visible spectroscopy using  $\epsilon_{492 \text{ nm}} = 88,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  and interpolated literature values<sup>2</sup> of  $\sigma_2$  for fluorescein in 0.1 M NaOH with  $\Phi_p = 0.9$  were used. The laser's wavelength was tuned step-wise to allow the full TPA spectrum to be obtained in 10 nm steps in the range 770 to 870 nm. The system was calibrated to correct for the dark noise of the detector and the photoluminescence spectrum was averaged over 100 measurements of 100 ms integration time. In-house software was used for data collection and analysis. Estimated error  $\pm 20\%$ .

### One-photon emission lifetime measurement

The 3<sup>rd</sup> harmonic (355 nm) of a Q-switched Nd:YAG laser (Spectra Physics GCR-150-10), pulsed at a frequency of 10 Hz with a FWHM of 15 ns and a typical pulse energy of  $\sim 1-2$  mJ was employed as an excitation source in a home-made fluorimeter. The laser was filtered for the residual fundamental (1064 nm) and 2<sup>nd</sup> harmonic (532 nm). Emission was collected at 90° to the excitation by a photomultiplier tube (Hamamatsu R928) as a function of time selecting an observed wavelength close to the peak emission by way of a monochromator (Horiba Jobin Yvon Triax 320) with a 0.1-2.0 nm bandpass. The signal was averaged over a

minimum of 64 pulses and converted to a digital signal by a digital storage oscilloscope (Tetronix TDS 340). The decay data were fitted to exponential functions of the form  $I(t) = I_0 \exp(-t/\tau)$ . Estimated error  $\pm 5\%$ .

### Single crystal X-ray diffraction

Single crystal structure determination was carried out at 120 K using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Bruker SMART-CCD detector diffractometer equipped with a Cryostream N<sub>2</sub> flow cooling device.<sup>3</sup> A series of narrow  $\omega$ -scans ( $0.3^\circ$ ) were performed at several  $\phi$ -settings in such a way as to cover a sphere of data to a maximum resolution of  $0.70 \text{ \AA}$ . Cell parameters were determined and refined using the SMART software,<sup>4</sup> and raw frame data were integrated using the SAINT program.<sup>5</sup> The structure was solved using Direct Methods and refined by full-matrix least squares on  $F^2$  using SHELXTL.<sup>6</sup> Crystal data and structure refinement parameters are shown in footnote 29. The reflection intensities were corrected for absorption effects by the multi-scan method, based on multiple scans of identical and Laue equivalent reflections (using the SADABS software).<sup>7</sup> Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and refined using a riding model.

### Computational

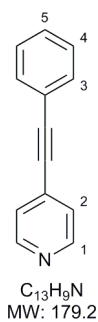
Calculations were carried out using the Gaussian-09 package.<sup>8</sup> DFT ground-state optimised structures were calculated using Becke's 3 parameter Lee-Yang-Parr (B3LYP) exchange-correlation functional with a mixed basis set of 6-31+G for light atoms (C, H, O, N) and the Los Alamos National Laboratories 2nd double zeta (LANL2DZ) basis set for both the valence and effective core potential functions of heavy atoms (Ir). Orbital surfaces generated from the DFT calculations were visualised in GaussView 4.1. TD-DFT calculations were performed on the B3LYP/6-31+G optimised ground-state geometries over 10 states (singlets and triplets) using the Coulomb-attenuating method B3LYP (CAM-B3LYP)/6-31G/LANL2DZ level of theory. Solvent effects were omitted. The initial geometry input for optimisation was based on the crystallographic coordinates to maximise the probability of locating the global minimum on the potential energy surface.

### Synthesis

Where required, anhydrous conditions were maintained using standard Schlenk-line apparatus and techniques using SPS dried solvents under an inert atmosphere of dry nitrogen. De-ionised water was used where appropriate. All reagents were used as received without further purification. Column chromatography was performed on silica gel and monitored by TLC. All enantiomeric iridium complexes were isolated as their

racemic mixtures.  $\text{Ir}(\text{ppy})_3$ ,<sup>9</sup>  $\text{Ir}(\text{ppy})_2(\text{acac})$ <sup>10</sup> and  $\text{Ir}(\text{ppy})_2(\text{fppy})$ <sup>11</sup> were prepared as previously reported. Care was taken to minimise the exposure of the complexes to UV light while in chlorinated solvents during preparative, purification and analytical stages. NMR spectra were recorded on a Varian Mercury-200, Varian Mercury-400, Bruker Avance-400, Varian Inova-500 or Varian VNMRS-700.  $J$  coupling (1H–1H) values are given in Hz and chemical shifts,  $\delta$ , in ppm, internally referenced to the residual protonated solvent or the solvent  $^{13}\text{C}$  resonance. Assignment was aided, where necessary, by  $^1\text{H}$ – $^1\text{H}$  correlation spectroscopy (COSY) 2D-NMR. Mass spectrometry (MS) was performed using a Micromass LCT electrospray ionisation (ESI) MS (in positive mode) in a flow of methanol or by GC-MS. GCMS was performed using an Agilent Technologies 6890 N chromatograph equipped with a 5983 inert mass selective detector and a 10 m fused silica capillary column (5 % cross-linked phenylmethylsilicone) using UHP helium as the carrier gas with the following conditions: injector temperature 250 °C, detector temperature 300 °C, the oven temperature was ramped from 70 °C to 280 °C at 20 °C  $\text{min}^{-1}$ . Dichloromethane (DCM) was used as the sample solvent in all cases. In the case of iridium complexes, samples were prepared immediately before use and kept in the dark to minimise photodegradation. Raman spectra were measured with a Horiba Jobin Yvon LabRAM HR Raman microscope using a diode laser of wavelength 785 nm on solid samples mounted atop glass microscope slides.

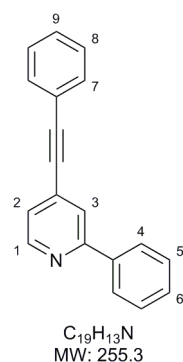
#### 4-(Phenylethynyl)pyridine



Using a modified version of the method of Nishikawa *et al.*,<sup>12</sup> 4-bromopyridine HCl (3.53 g, 18 mmol) was suspended in a 3:1 mixture of acetonitrile and triethylamine (36 ml) and degassed using 2 freeze-pump-thaw cycles and back-filled with nitrogen. Phenylacetylene (2.4 ml, 22 mmol) was added and degassed one further time.  $\text{PdCl}_2(\text{PPh}_3)_2$  (127 mg, 1 mol%) and CuI (34 mg, 1 mol%) were added and the solution stirred at RT for h. The solution was reduced *in vacuo* and separated by column chromatography on silica gel (9:1 hexane:EtOAc) as the fore-running fraction to yield the title compound (2.75 g, 85%) as a yellow-white solid.  $\delta_{\text{H}}$ (400 MHz;

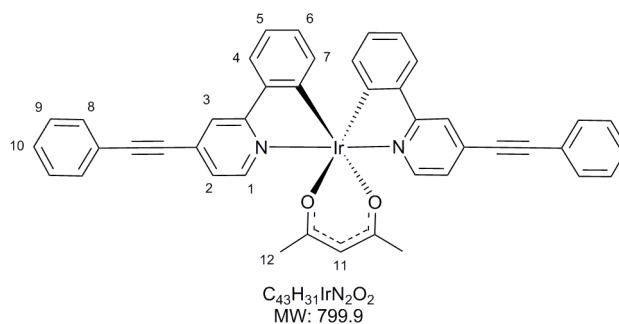
acetone- $d_6$ ) 8.60 (2 H, d,  $J$  5.2,  $H_1$ ), 7.56 (2 H, m), 7.38 (5 H, m);  $\delta_C$ (101 MHz; acetone- $d_6$ ) 150.1, 132.0, 131.0, 129.6, 129.0, 125.8, 122.3, 93.5, 86.7;  $m/z$  (GC-MS) (1 peak) 179 ( $M^+$ ).

### 2-Phenyl-4-(phenylethynyl)pyridine (4-pe-2-ppyH)



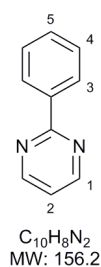
4-(Phenylethynyl)pyridine (0.77 g, 4.6 mmol) was dissolved in dry toluene (15 ml) under nitrogen and stirred for 10 min. The solution was cooled to 0°C and phenyl lithium (1.8 M in  $Bu_2O$ , 2.6 ml, 4.7 mmol) was added slowly and stirred for 30 min. The reaction was quenched with water (25 ml), the toluene layer was separated and the aqueous layer extracted with DCM (3 x 20 ml). The combined organics were dried over  $K_2CO_3$ , reduced *in vacuo* to an oily brown solid. The crude product was purified by column chromatography on silica gel (DCM) to yield 4-pe-2-ppy (304 mg, 26%) as a brown solid.  $\delta_H$ (700 MHz;  $CDCl_3$ ) 8.68 (1 H, d,  $J$  5.6,  $H_1$ ), 8.04 (2 H, d,  $J$  7.0,  $H_4$ ), 7.85 (1 H, s,  $H_3$ ), 7.61 (2 H, dd,  $H_7$ ), 7.50 (2 H, t,  $J$  7.7,  $H_5$ ), 7.44 (1 H, t,  $J$  7.7,  $H_6$ ), 7.39 (3H, m,  $H_{14}$  and  $H_{15}$ ), 7.31 (1 H, dd,  $J$  5.6 and 1.2,  $H_2$ );  $\delta_C$ (176 MHz;  $CDCl_3$ ) 157.9, 149.9, 139.0, 132.4, 132.3, 129.5, 129.1, 128.8, 127.2, 124.1, 122.8, 122.5, 94.0, 87.4;  $m/z$  (GC-MS) (1 peak) 255 ( $M^+$ );  $m/z$  (ESI<sup>+</sup> HRMS) 256.1121 ( $[M+H]^+$ ,  $C_{19}H_{14}N$  requires 256.1126).

### Ir(4-pe-2-ppy)<sub>2</sub>(acac)



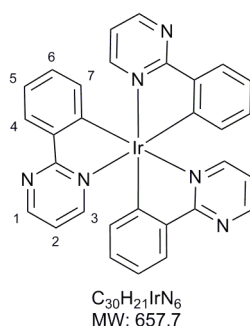
4-Pe-2-ppy (105 mg, 0.41 mmol) was suspended in a 2:1 mixture of 2-ethoxyethanol and water (15 ml) with IrCl<sub>3</sub>·3H<sub>2</sub>O (72 mg, 0.20 mmol) and heated to reflux for 4 h at 110°C to give a dark red-brown solution. The solution was allowed to cool to r.t. and upon the addition of water (30 ml) an orange solid precipitated, which was filtered and washed with water (10 ml), dissolved in DCM, dried over MgSO<sub>4</sub>, filtered and reduced *in vacuo* to an orange solid. The solid, K<sub>2</sub>CO<sub>3</sub> (100 mg) and acetylacetone (1 ml, excess) were dissolved in 1:1 ethanol:acetone (10 ml). The solution was heated to reflux for 10 min and subsequently stirred for 16 h at r.t. The addition of water (15 ml) afforded an orange solid which was filtered and washed with water (2 x 5 ml) and hexane (2 x 5 ml). Purification by column chromatography on silica gel (DCM) gave (12 mg, 8%) as a bright orange solid.  $\nu_{\max, \text{Raman}}(\text{solid})/\text{cm}^{-1}$  3380, 3352, 2217 and 2234 (C≡C stretches), 1917, 1610, 1598;  $\delta_{\text{H}}(600 \text{ MHz}; \text{CD}_2\text{Cl}_2)$  8.49 (2 H, dd, *J* 6 and 0.8, H<sub>1</sub>), 8.01 (2 H, d, *J* 1.2, H<sub>3</sub>), 7.66 (4 H, m, H), 7.62 (2 H, dd, *J* 8 and 1.2), 7.46 (6 H, m), 7.29 (2 H, dd, *J* 6 and 2), 6.90 (2 H, td, *J* 7.6 and 1.2), 6.75 (2 H, td, *J* 7.6 and 1.6), 6.31 (2 H, dd, *J* 7.6 and 1.2, H<sub>7</sub>), 5.24 (1 H, s, H<sub>11</sub>), 1.84 (6 H, s, H<sub>12</sub>);  $\delta_{\text{C}}(151 \text{ MHz}; \text{CD}_2\text{Cl}_2)$  185.4, 168.5, 148.2, 147.9, 144.8, 133.6, 132.8, 132.5, 130.0, 129.5, 129.0, 124.5, 124.1, 122.3, 121.5, 120.1, 100.8, 96.2, 86.8, 28.7; *m/z* (ESI<sup>+</sup> HRMS) 798.1988 (M<sup>+</sup>, <sup>191</sup>IrC<sub>43</sub>H<sub>31</sub>O<sub>2</sub>N<sub>2</sub> requires 798.1986).

### 2-Phenylpyrimidine (ppmH)



2-Chloropyrimidine (0.50 g, 4.4 mmol), benzenboronic acid (0.59 g, 4.8 mmol), potassium carbonate (0.79 g, 4.8 mmol), dimethoxyethane (20 ml) and water (10 ml) were placed in a Schlenk tube and purged with nitrogen. Palladium acetate (0.025 g, 2.5 mol%) and triphenylphosphine (0.12 g, 10 ml%) were added and the solution was heated to 100°C for 18 h. The mixture was cooled to r.t. and the dimethoxyethane removed under vacuum. The aqueous residue was extracted with dichloromethane, dried over MgSO<sub>4</sub> and reduced *in vacuo* to an oil. The crude material was purified by column chromatography on silica gel (DCM) to afford the title compound as a yellow oil (0.48 g, 70%).  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 8.84 (2 H, m), 8.58 (2 H, m), 7.57 (3 H, m), 7.18 (1 H, t, *J* 7.2), 6.96 (1 H, m); *m/z* (ESI<sup>+</sup> MS) 156 (M<sup>+</sup>).

### Ir(ppm)<sub>3</sub>



IrCl<sub>3</sub>·3H<sub>2</sub>O (0.075 g, 0.21 mmol), 2-phenylpyrimidine (0.33 g, 2.1 mmol) and AgCF<sub>3</sub>CO<sub>2</sub> were added heated at 190°C for 10 h under nitrogen. The solution was cooled to r.t. and water (10 ml) added. The aqueous solution was extracted with DCM (10 ml), dried over MgSO<sub>4</sub> and reduced *in vacuo* to a solid. The crude material was purified by column chromatography (DCM) to afford the title compound as a bright yellow solid.  $\delta_{\text{H}}$ (200 MHz; CDCl<sub>3</sub>) 8.70 (3 H, m), 8.10 (3 H, m), 7.78 (3 H, dd, *J* 5.5), 6.91 (12 H, m);  $\delta_{\text{C}}$ (50 MHz; CDCl<sub>3</sub>) 159.7, 157.3, 154.5, 147.3, 141.0, 137.0, 132.4, 128.2, 121.2, 118.2; *m/z* (EI<sup>+</sup> HRMS) 658.1442 (M<sup>+</sup>, <sup>193</sup>IrC<sub>30</sub>H<sub>21</sub>N<sub>6</sub> requires 658.1457).



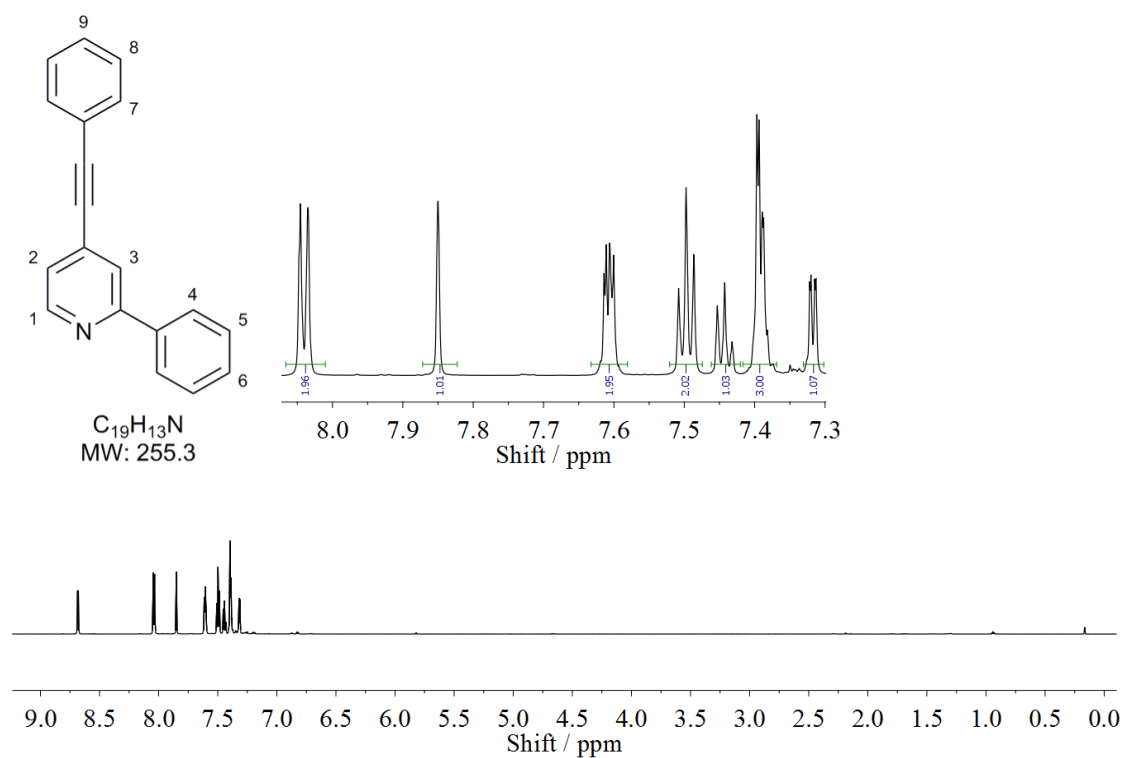


Figure 1 700 MHz <sup>1</sup>H NMR of 4-pe-2-ppyH in CDCl<sub>3</sub>

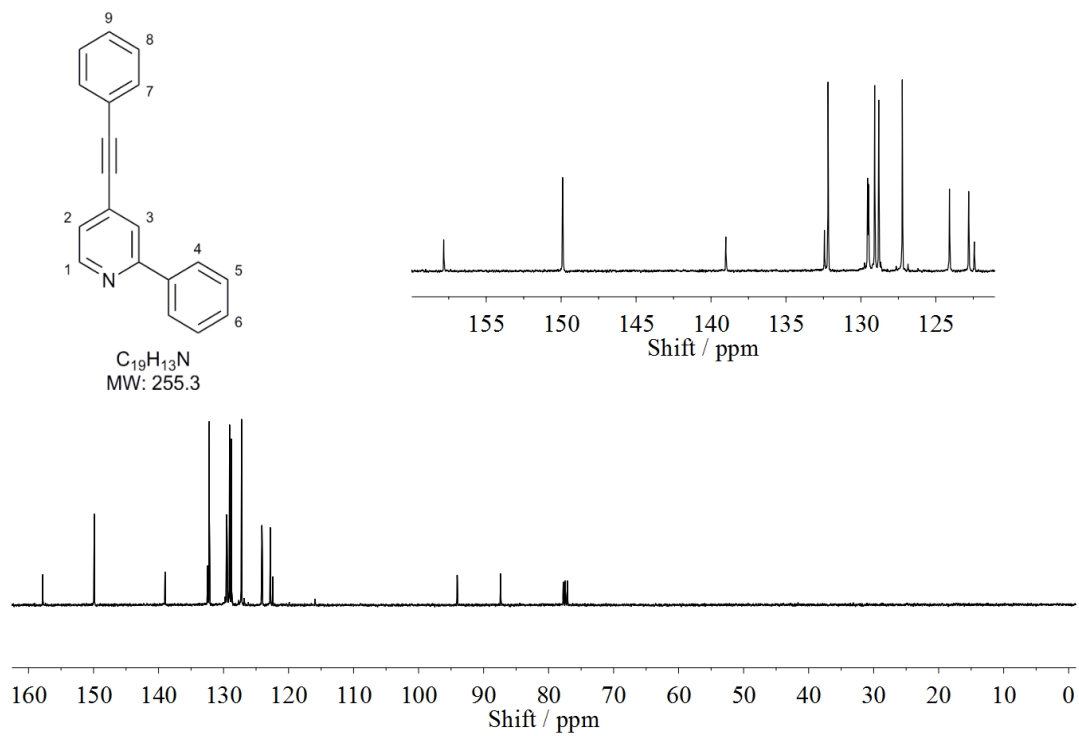
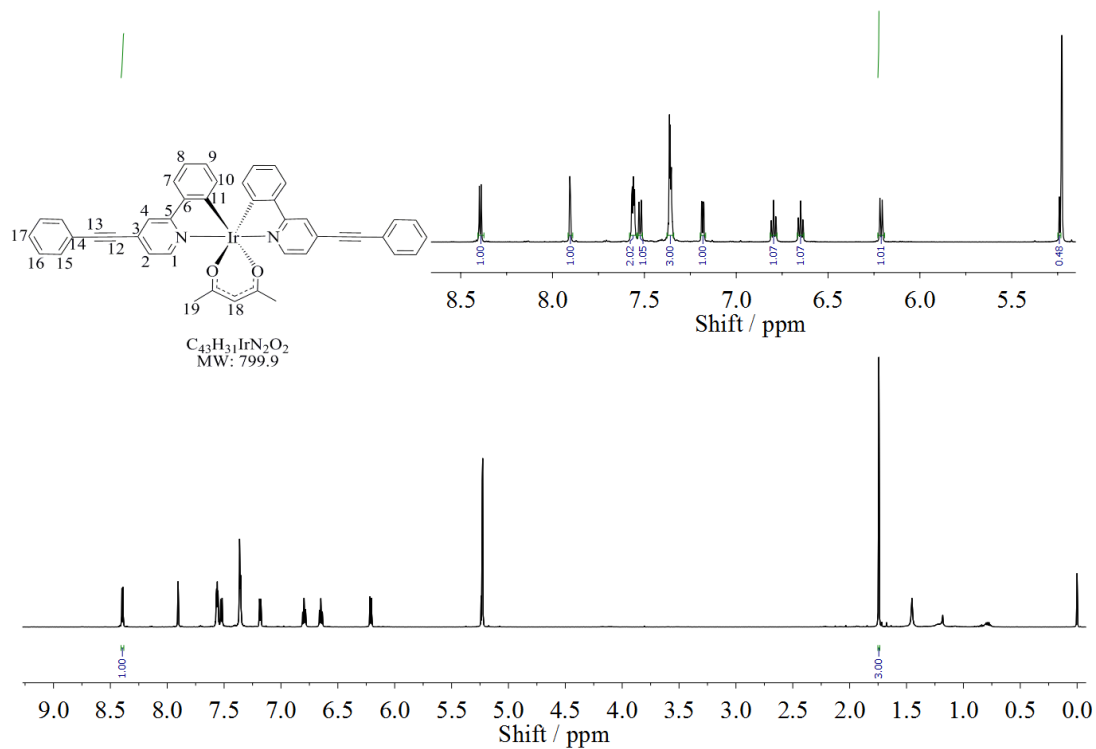
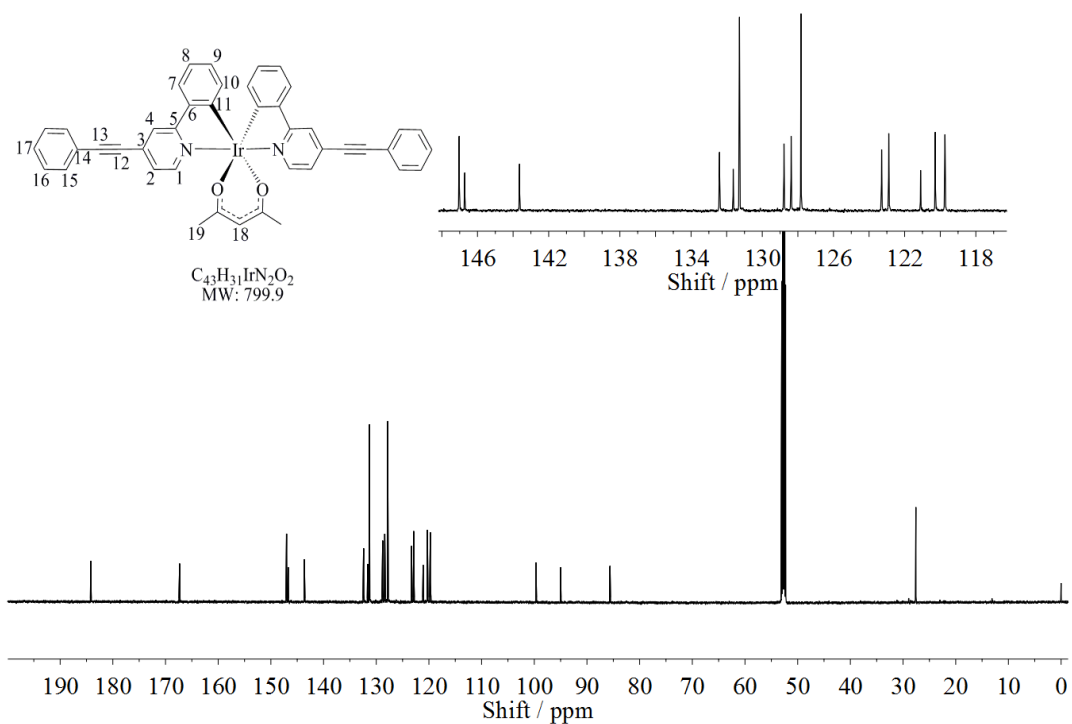


Figure 2 176 MHz <sup>13</sup>C NMR of 4-pe-2-ppyH in CDCl<sub>3</sub>



**Figure 3** 600 MHz  $^1H$  NMR of  $Ir(4-pe-2-ppy)_2(acac)$  in  $CD_2Cl_2$



**Figure 4** 151 MHz  $^{13}C$  NMR of  $Ir(4-pe-2-ppy)_2(acac)$  in  $CD_2Cl_2$

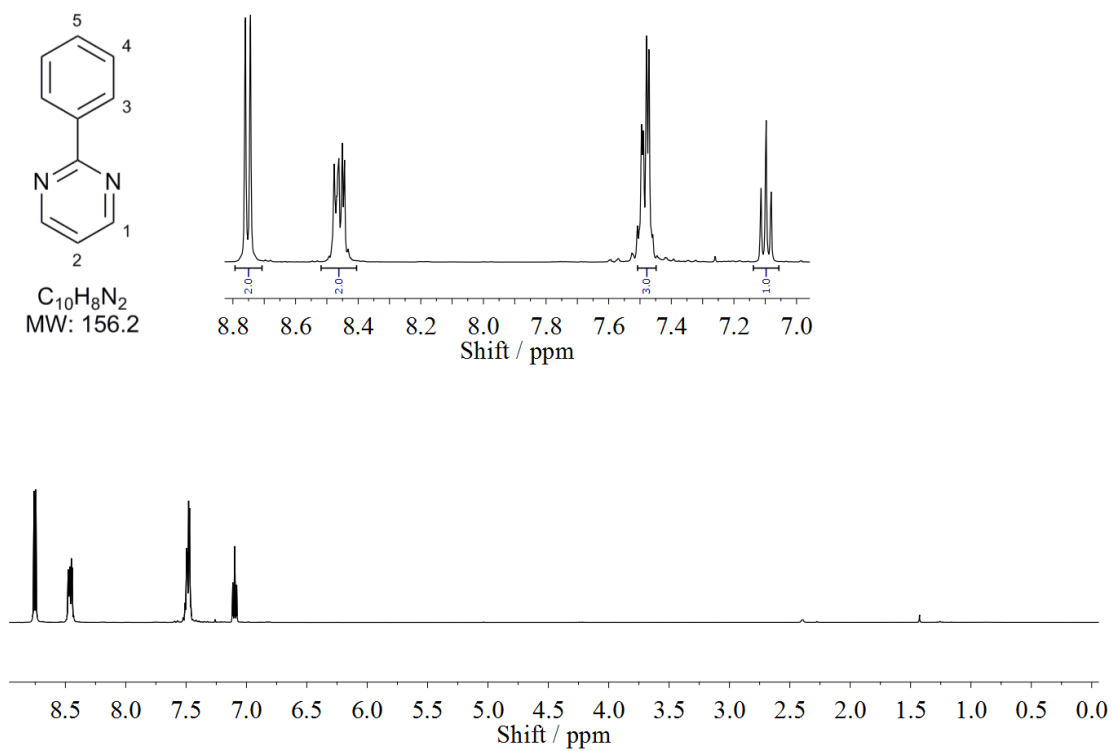


Figure 5 300 MHz  $^1\text{H}$  NMR of ppmH in  $\text{CDCl}_3$

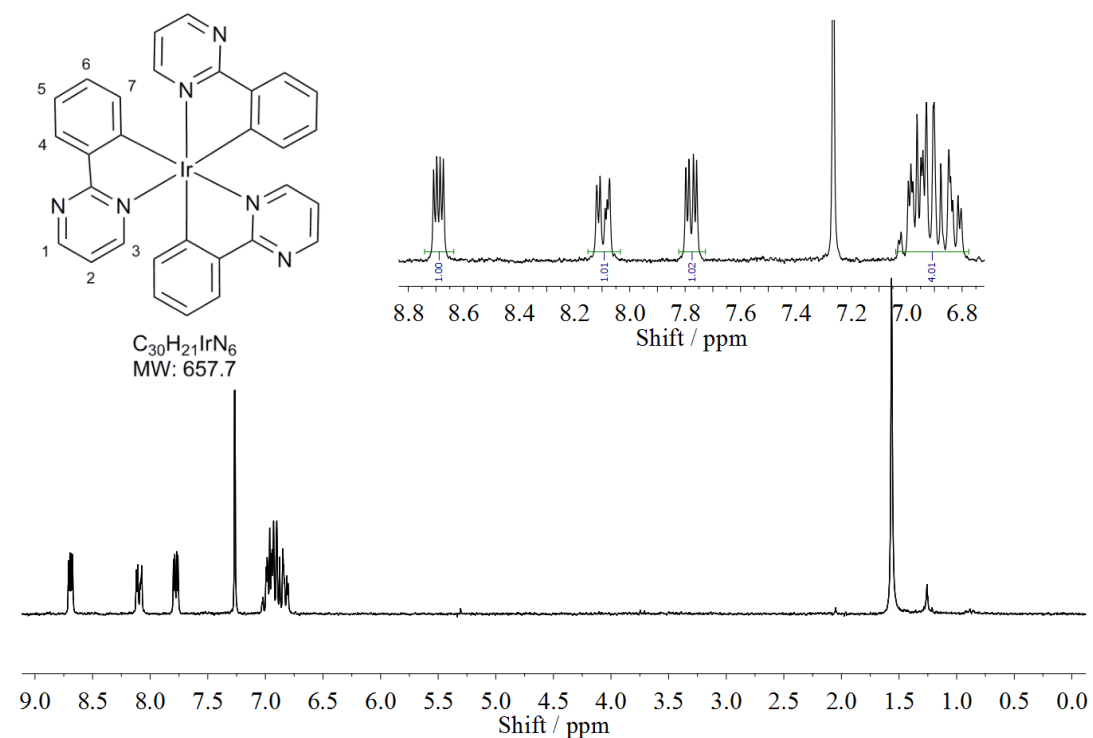
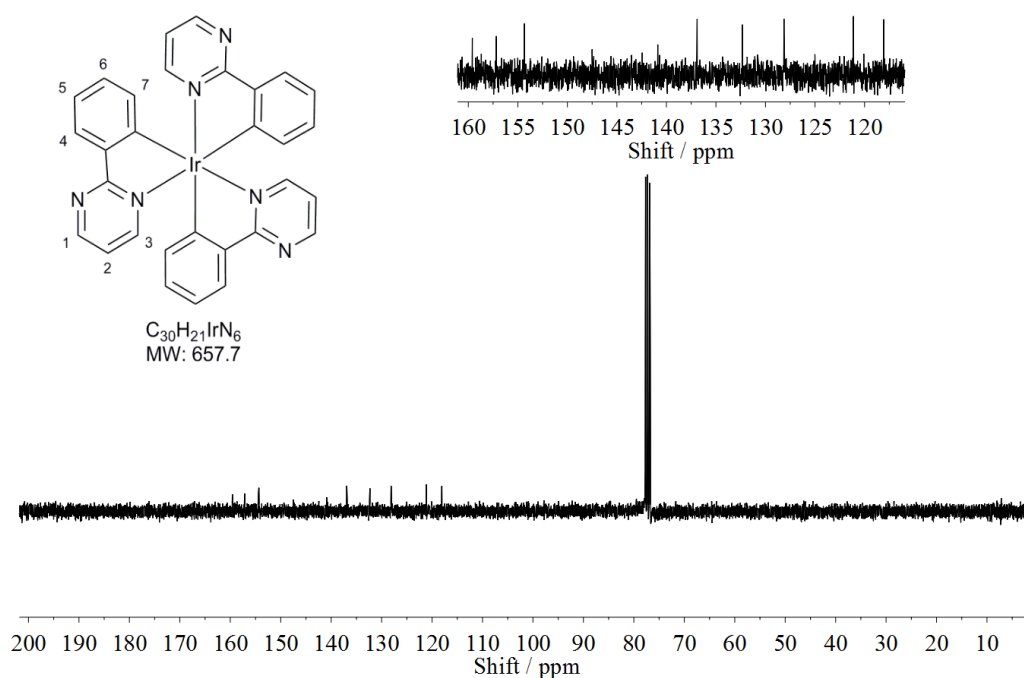


Figure 6 200 MHz  $^1\text{H}$  NMR of  $\text{Ir}(\text{ppm})_3$  in  $\text{CDCl}_3$



**Figure 7** 50 MHz  $^{13}C$  NMR of  $Ir(ppm)_3$  in  $CDCl_3$ . Low signal to noise ratio is a result of poor solubility.

- 1 L. Porres, A. Holland, L. -O. Palsson, A. P. Monkman, C. Kemp and A. Beeby, *J. Fluoresc.*, 2006, **16**, 267.
- 2 M. A. Albota, C. Xu and W. W. Webb, *Appl. Opt.*, 1998, **37**, 7352; C. Xu and W. W. Webb, *J. Opt. Soc. Am. B*, 1996, **13**, 481.
- 3 J. Cosier and A. M. Glazer, *J. Appl. Cryst.*, 1986, **19**, 105.
- 4 SMART V5.63, Bruker AXS Inc., Madison, Wisconsin, USA, 2003.
- 5 SAINT V6.45A, Bruker AXS Inc., Madison, Wisconsin, USA, 2003.
- 6 G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
- 7 SADABS 2006/1, Bruker AXS area detector scaling and absorption correction, Bruker AXS Inc., Madison, Wisconsin, USA, 2006.
- 8 Gaussian 09, Revision A.02, 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, 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, Inc., Wallingford CT, 2009.
- 9 M. C. Colombo, T. C. Brunold, T. Riedener, H. U. Güdel, M. Förtsch and H. Bürgi, *Inorg. Chem.*, 1994, **33**, 545.
- 10 S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2001, **40**, 1704.
- 11 A. Beeby, S. Bettington, I. D. W. Samuel and Z. Wang, *J. Mater. Chem.*, 2003, **13**, 80.
- 12 S. Nishikawa, M. Sato, H. Kojima, C. Suzuki, N. Yamada, M. Inagaki, N. Kashimura and H. Mizuno, *J. Agric. Food Chem.*, 1996, **44**, 1337.