

Blue and highly emitting [Ir(IV)] complexes by an efficient photoreaction of yellow luminescent [Ir(III)] complexes

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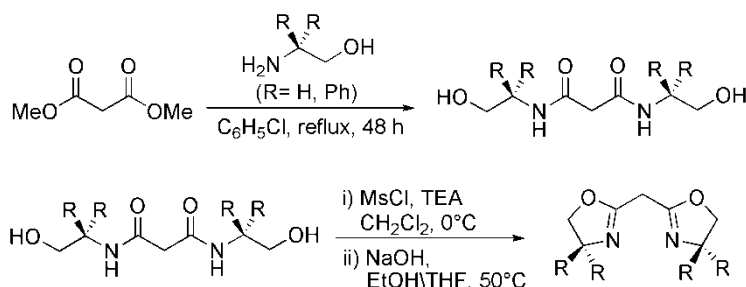
Supporting Information

Materials

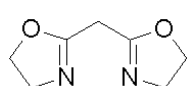
Anhydrous THF was supplied by Fluka in Sureseal® bottles and used as received. All chemicals were utilized as received.

Synthesis

Synthesis of the 2,2'-methylenebis[oxazoline] ligands. Bis-oxazolines **LL**₁ and **LL**₂ were synthesized starting from commercially available β-amino alcohols through known three-steps protocols (un-optimized syntheses).ⁱ



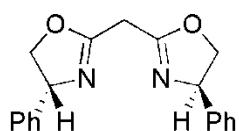
LL₁: Purification via filtration through a pad of silica eluting (CH₂Cl₂:MeOH:TEA 95:4:1). Yield = 18% (three steps).



¹H-NMR (400 MHz, CDCl₃) δ: 4.17- 4.07 (m, 4 H), 3.74-3.64 (m, 4H), 3.14 (d, J = 2.1 Hz, 2 H). ¹³C-NMR (100 MHz, CDCl₃) δ: 162.6, 67.9, 54.5, 28.6. GC-MS (m/z): 56(22), 68(65), 85(100), 96(8), 111(7), 124(15), 154(20). IR (CH₂Cl₂): 3387, 2979, 2911, 2887, 1664, 1228 (cm⁻¹).

ESI-MS: (M+1): 155.

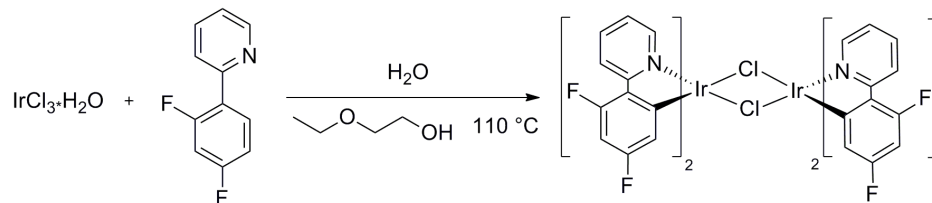
(*R*)-**LL**₂: Purification via flash chromatography (CH₂Cl₂:MeOH 99:1) to give the desired product as a yellow solid. [α]_D = + 90° (*c* = 1 in ethanol). Yield = 25% (three steps).



¹H-NMR (400 MHz, CDCl₃) δ: 7.32-7.29 (m, 10H), 5.21 (t, J = 8.4 Hz, 2H), 4.65 (t, J = 8.8 Hz, 2H), 4.14 (t, J = 8.1 Hz, 2H) 3.55 (s, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ:

162.8, 141.7, 128.5, 128.5, 128.4, 128.3, 127.5, 127.41, 127.6, 126.5, 126.5, 126.4, 126.2, 75.1, 69.4, 28.1.
IR (CH₂Cl₂): 3061, 3029, 2964, 2901, 1660, 1592, 1473 (cm⁻¹) ESI-MS: (M+1): 307.

Synthesis of the dimeric cyclometalated iridium (III) complex.

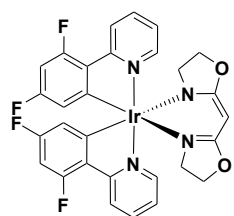


To a degassed ethoxyethanol-water mixture (3:1, 4 mL), 100 mg (0.33 mmol) of IrCl₃·H₂O and 0.66 mmol (2 eq) of the cyclometalating ligand (F₂ppy) were added.ⁱⁱ The mixture was refluxed overnight (24 h, then cooled down. The insoluble bright yellow solid was collected by filtration, washed with water and ethyl ether and dried (200 mg, 88% yield).

¹H-NMR (400 MHz, CDCl₃) δ: 9.12 (d, J = 5.2 Hz, 4H), 8.30 (d, J = 8.2 Hz, 4H), 7.82 (t, J = 7.6, 4H), 6.82 (t, J = 6.1, 4H), 6.36-6.30 (m, 4H), 5.28 (dd, J₁ = 2.1 Hz, J₂ = 2.4 Hz, 4H).

Synthesis of 2,2'-methylenebis[oxazoline]-cyclometalated Ir (III) complex (2)

To a cooled (-55 °C) solution of LL₁ (0.54 mmol in anhydrous THF (10 mL), 340 μL of MeLi (1.6 M, Et₂O, 0.54 mmol) were added dropwise. The pale yellow solution was stirred at the same temperature for 1 h. Then the chloride-bridged iridium dimer (343 mg, 0.30 mmol) was added at once, the solution was allowed to reach rt over 15 min, then the slurry was refluxed for 12 h. After evaporation of the volatiles under vacuum, the crude was directly purified through a plug of silica (CH₂Cl₂:MeOH 95:5).

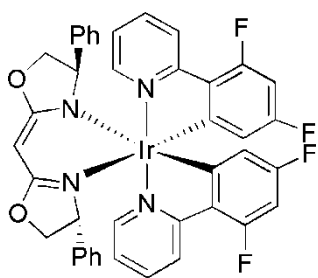


Yellow-orange solid. Yield = 80%. Mp = 199 °C. ¹H-NMR (300 MHz, CD₃COCD₃): δ 2.74-2.80 (m, 1H), 3.29-3.35 (m, 1H), 2.90-4.02 (m, 1H), 4.03-4.10 (m, 1H), 5.74 (dd, J = 2.1, 8.4 Hz, 2H), 6.48 (t, J = 10.2 Hz, 2H), 7.44 (t, J = 10.4 Hz, 2H), 8.02 (t, J = 7.8 Hz, 2H), 8.29 (d, J = 8.4 Hz, 2H), 8.71 (d, J = 5.4 Hz, 2H). ¹³C-NMR (75 MHz, CD₃COCD₃): δ 54.1, 67.3, 97.4, 114.5, 114.7, 123.2, 123.5, 123.9, 129.5, 138.9, 150.9, 166.1, 167.5. IR (CH₂Cl₂): 3389, 3075, 2922, 1620, 1600, 1537 (cm⁻¹). ESI-MS: (M+1): 728. Anal. calcd for (C₂₉H₂₁F₄IrN₄O₂: 725.71): C, 48.00; H, 2.92; N, 7.72. Found: C, 48.05; H, 2.89; N, 7.69.

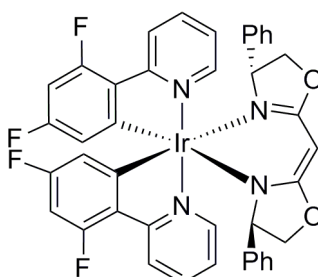
Synthesis of the cyclometalated iridium (III) complexes with 2,2'-methylenebis[(4R)-4-phenyl-2-oxazoline] (1)

To a round-bottom two-necked flask, conned to the nitrogen line 5 mL of THF anhydrous and 50 mg of 2,2'-methylenebis[(4R)-4-phenyl-2-oxazoline] (0.16 mmol) were added in sequence and the solution cooled down at -55 °C. Then 100 μL of MeLi 1.6 M (0.16 mmol) were added drop-wise and the mixture stirred for 1 h at -55 °C. Finally, 100 mg of the dimeric chloro bridged [Ir(III)] complex [(F₂ppy)₂Ir(μ-Cl)₂Ir(F₂ppy)₂] were added at once and the mixture was brought to refluxed overnight. After cooling the mixture to room temperature, the solvent was removed by low pressure distillation and the resulting purified by flash

chromatography to afford $[\text{Ir}(\text{F}_2\text{ppy})_2((R)\text{-4ph-box})]$ as a 1:1 diastereomeric ratio (yield = 79%). Flash chromatography ($\text{CH}_2\text{Cl}_2:\text{MeOH}$ 95:5).



Δ -1. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 8.70 (d, $J = 5.2$ Hz, 2H), 7.50 (m, 4H), 7.17 (t, $J = 5.6$ Hz, 2H), 6.87 (t, $J = 7.2$ Hz, 2H), 6.69 (t, $J = 7.6$ Hz, 4H), 6.19-6.13 (m, 6H), 5.39 (dd, $J_1 = 2.1$ Hz, $J_2 = 8.4$ Hz, 2H), 4.58 (d, $J = 6.4$ Hz, 2H), 4.42 (t, $J = 8.1$ Hz, 2H), 4.20 (s, 1H), 3.80 (dd, $J_1 = 2.1$ Hz, $J_2 = 7.6$ Hz, 2H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 167.2, 167.2, 164.4, 162, 161.8, 159.2, 159.1, 147.9, 138.3, 136.4, 129, 128.7, 128.7, 128.5, 128.4, 128.2, 128, 127.9, 127.5, 127.7, 126.2, 124.7, 123.1, 122.9, 112.5, 112.3, 96.7, 75.3, 69, 54.5, 47.2, 42.6. ESI-MS: (M+1): 880.



A-1. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 8.67 (d, $J = 4.4$ Hz, 2H), 8.15 (d, $J = 8.0$ Hz, 2H), 7.69 (t, $J = 6.8$ Hz, 2H), 7.09-7.04 (m, 6H), 6.93 (dd, $J_1 = 6.0$ Hz, $J_2 = 12$ Hz, 2H), 6.70 (dd, $J_1 = 1.2$ Hz, $J_2 = 6.8$ Hz, 4H), 6.26-6.20 (m, 2H), 4.91 (dd, $J_1 = 2.1$ Hz, $J_2 = 8.4$ Hz, 2H), 4.15-4.11 (m, 2H), 4.01-3.95 (m, 4H), 3.77 (q, $J = 5.6$ Hz), 3.71 (s, 1H). $^{13}\text{C-NMR}$ (100 MHz, CD_3CN) δ : 169.1, 152.8, 144.9, 138.6, 128.6, 127.9, 127.7, 123, 122.8, 122.6, 115.8, 115.7, 115.6, 97.5, 97.2, 96.9, 75.7, 69.2, 54.4. ESI-MS: (M+1): 880.

Photoreaction of cyclometalated iridium (III) complex Δ -1.

A 5×10^{-5} M air-equilibrated solution of complex Δ -1 in CH_3CN , was irradiated at 365 nm with *Helios Italquartz* high pressure immersion mercury lamp. An efficient photoreaction takes place and photoproduct was purified by flash chromatography (acetone + NH_4PF_6), followed by extraction with water to remove any impurities. The paramagnetic properties of the product make it difficult to determine the structure, however, it is assumed a reorganization of the octahedral structure due to oxidation of the metal center.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) diagnostic peaks δ : 9.04 (d, $J = 5.2$ Hz, 2H), 8.31 (d, $J = 8.4$ Hz, 2H), 7.99 (t, $J = 8.1$ Hz, 2H), 7.47 (t, $J = 1.2$ Hz, 2H), 5.50 (dd, $J_1 = 2.4$ Hz, $J_2 = 8.8$ Hz, 2H).

IR (CH_2Cl_2): 3327, 2924, 1701, 1605, 1379, 1149 (cm^{-1}). ESI-MS: (M+1): 912.

X-ray crystallography: The diffraction experiments for **1** and **2** were carried out at RT by using a Bruker SMART Apex II CCD-based diffractometer with graphite-monochromated MoK α radiation ($\lambda=0.71073$ nm). Intensity data were measured over the full diffraction sphere by using ω scans with a width of 0.3° . The software SMARTⁱⁱⁱ was used for collecting frames of data, indexing reflections, and determining the lattice parameters. The collected frames were then processed for integration by using the software SAINT,⁸ and an empirical absorption correction was applied by using SADABS.^{iv} The structures were solved by direct methods (SIR97)^v and subsequent Fourier syntheses, and were refined by full-matrix least-squares calculations on F^2 (SHELXTL),^{vi} which attributed anisotropic thermal parameters to all non-hydrogen atoms. The hydrogen atoms that were located in the Fourier difference map were placed in calculated positions and

refined with idealized geometry by using $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$. Complex **2** crystallizes with one CH_2Cl_2 solvent molecule in the asymmetric unit. Crystal data and experimental details are reported in Table S1.

CCDC-955144 (for **1**) and CCDC-692212 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and experimental details for **1** and **2**. CH_2Cl_2

Compound	1	2 . CH_2Cl_2
Formula	$\text{C}_{41}\text{H}_{29}\text{F}_4\text{IrN}_4\text{O}_2$	$\text{C}_{29}\text{H}_{21}\text{F}_4\text{IrN}_4\text{O}_2 \cdot \text{CH}_2\text{Cl}_2$
<i>M</i>	877.88	810.62
T, K	296(2)	296(2)
Crystal symmetry	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/c$
<i>a</i> , Å	13.338(11)	9.9118(4)
<i>b</i> , Å	9.590(8)	18.8734(9)
<i>c</i> , Å	13.460(11)	15.8937(7)
α , °	90	90
β , °	95.853(9)	102.641(1)
γ , °	90	90
<i>V</i> , Å ³	1713(3)	2901.2(2)
<i>Z</i>	2	4
D_c , Mg m ⁻³	1.702	1.856
$\mu(\text{Mo-K}\alpha)$, mm ⁻¹	3.963	4.848
F(000)	864	1576
Crystal size, mm	0.23 x 0.25 x 0.30	0.10 x 0.20 x 0.30
θ limits, °	2.05 - 25.50	2.53 - 27.87
Reflections collected	12407	32157
Unique obs. reflections [$F_o > 4\sigma(F_o)$]	5936 [R(int) = 0.0952]	6838 [R(int) = 0.0411]
Goodness-of-fit-on F^2	1.174	1.019
$R_1(F)^a$, $wR_2(F^2)^b$, $I > 2\sigma(I)$	0.0908, 0.2074	0.0250, 0.0587
Absolute structure parameter	0.04(3)	-
Largest diff. peak and hole, e. Å ⁻³	2.995 and 2.598	-0.628 and 1.244

^a $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. ^b $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2) / 3$.

NMR spectra

Figure S1: ^1H _NMR (CDCl_3) 2,2'-methylene-[bis-oxazoline]

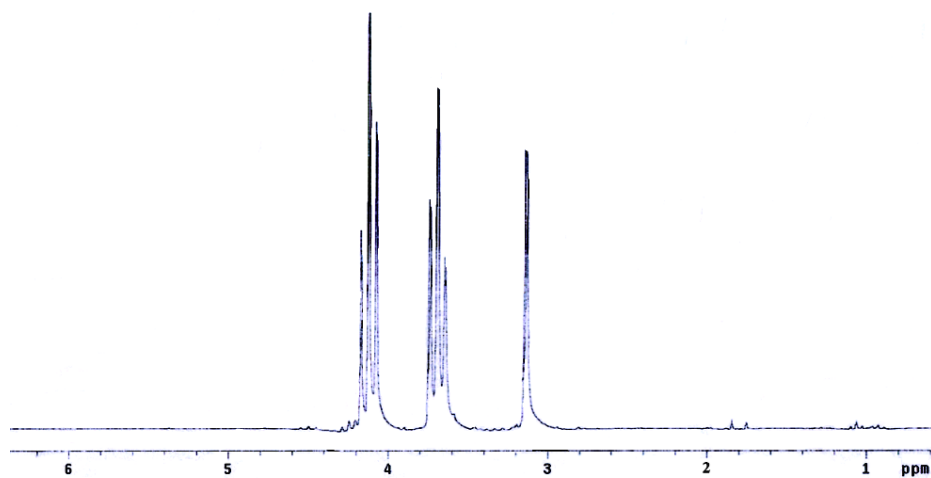


Figure S2: ^{13}C _NMR (CDCl_3): 2,2'-methylene-[bis-oxazoline]

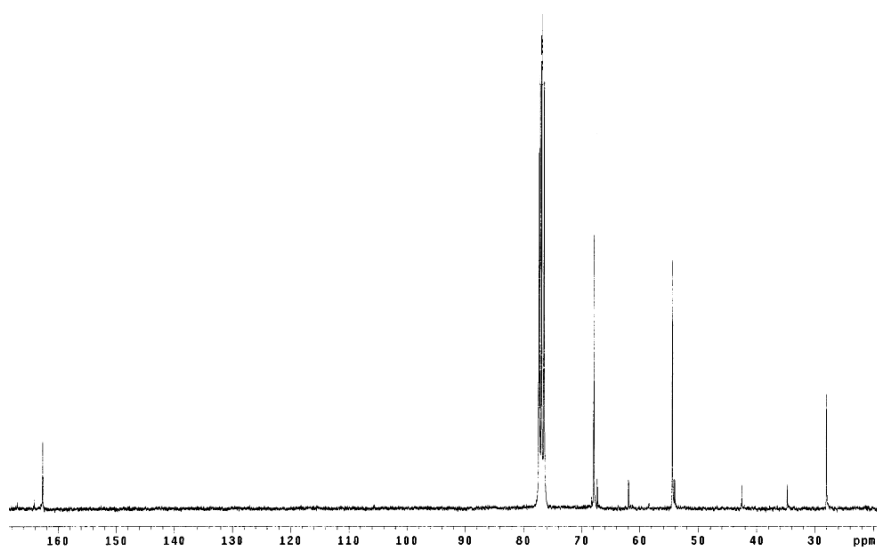


Figure S3: ^1H _NMR (CDCl_3): 2,2'-methylenebis[(4R)-4-phenyl-2-oxazoline]

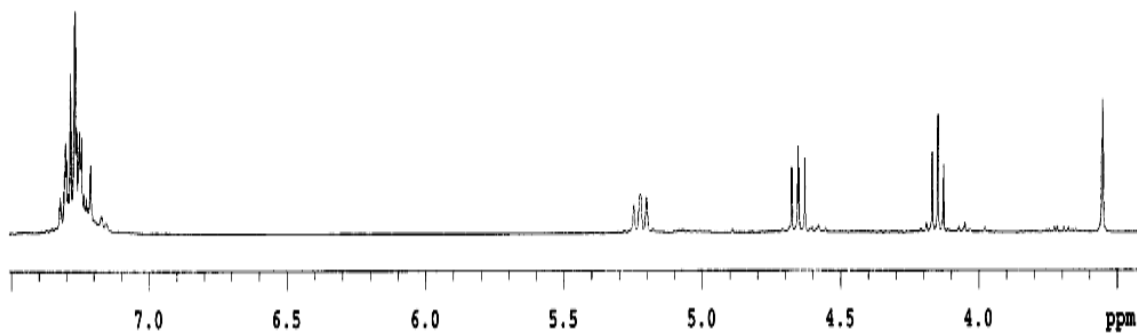


Figure S4: ^{13}C _NMR (CDCl_3): 2,2'-methylenebis[(4R)-4-phenyl-2-oxazoline]

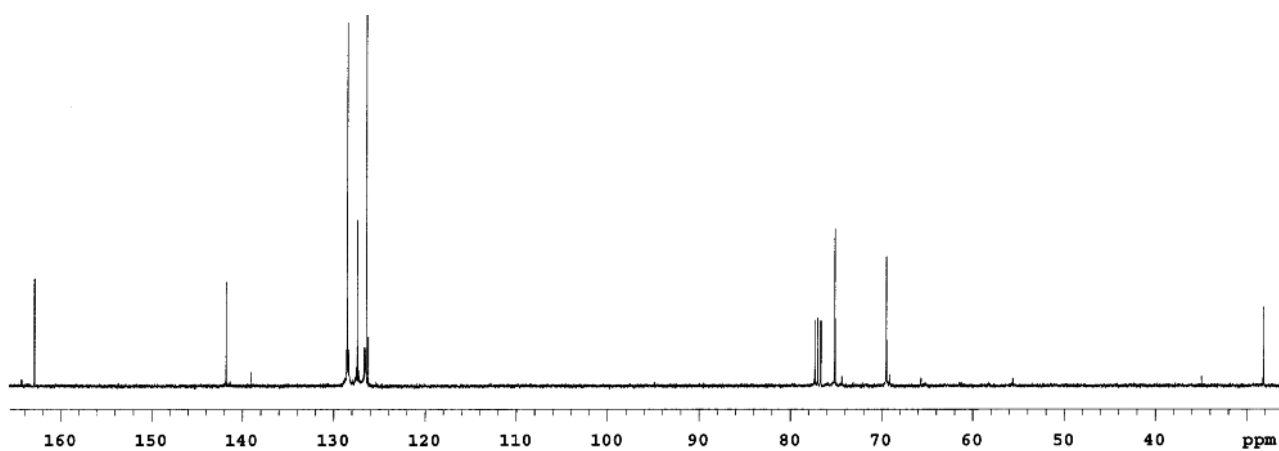


Figure S5: ^1H _NMR (CDCl_3): $[(\text{F}_2\text{ppy})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{F}_2\text{ppy})]$

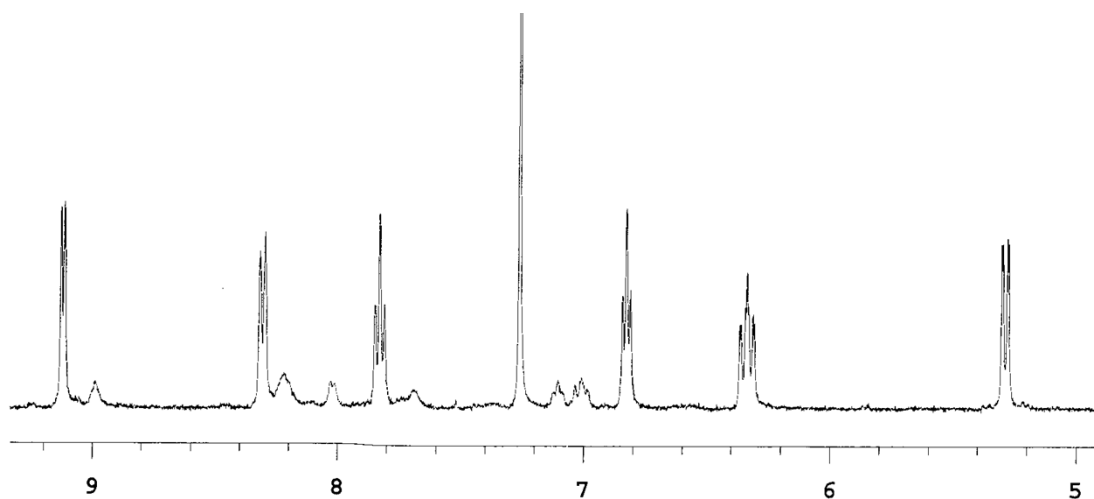


Figure S6: ^1H -NMR (CDCl_3): **2** [$\text{Ir}(\text{F}_2\text{ppy})_2(\text{CH}_2\text{-box})$]

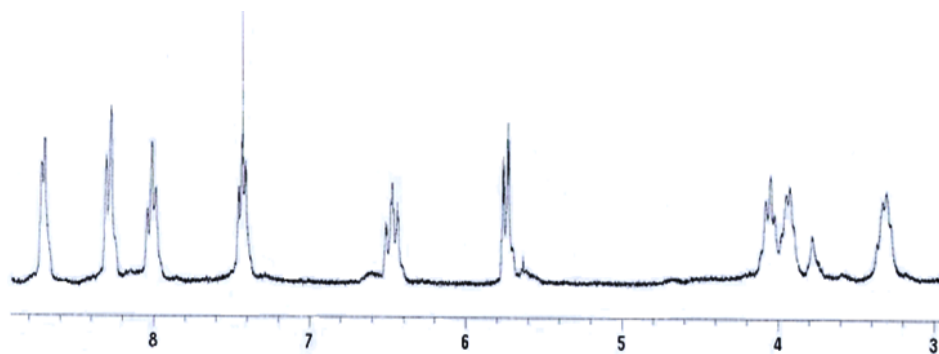


Figure S7: ^{13}C NMR(CD_3COCD_3): **2** [$\text{Ir}(\text{F}_2\text{ppy})_2(\text{CH}_2\text{-box})$]

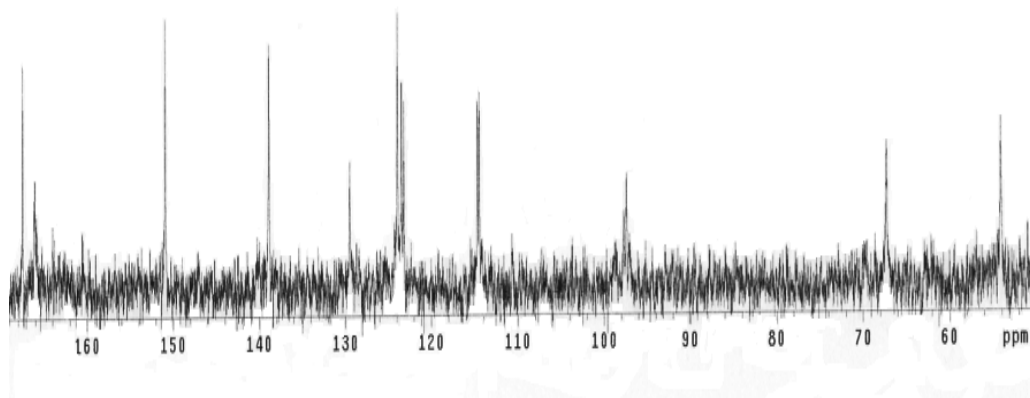


Figure S8: ^1H -NMR (CDCl_3): **Δ -1** [$\text{Ir}(\text{F}_2\text{ppy})_2((R)\text{-4ph-box})$]

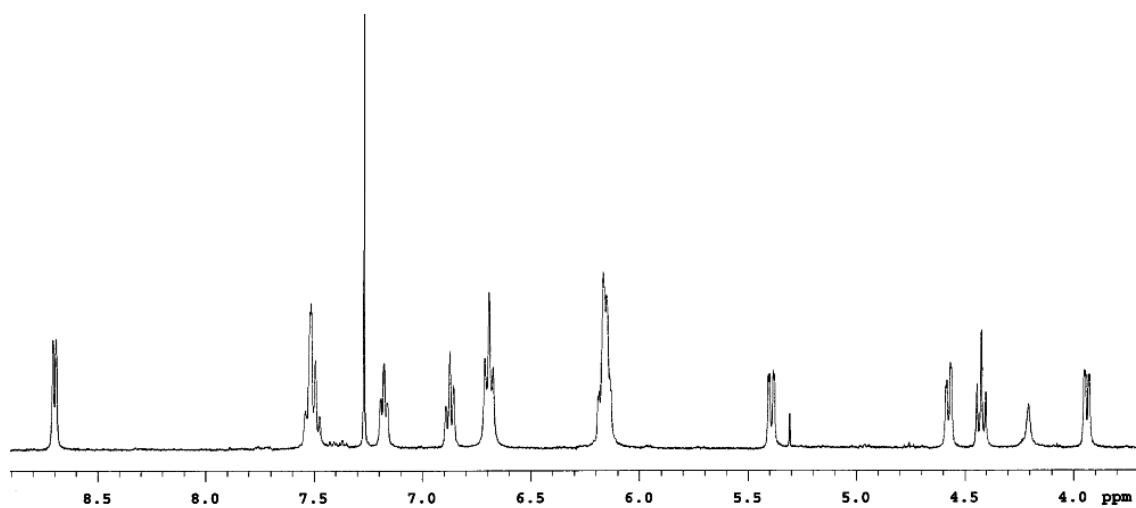


Figure S9: ^{13}C _NMR(CDCl_3): Δ -1 [$\text{Ir}(\text{F}_2\text{ppy})_2((R)\text{-4ph-box})$]

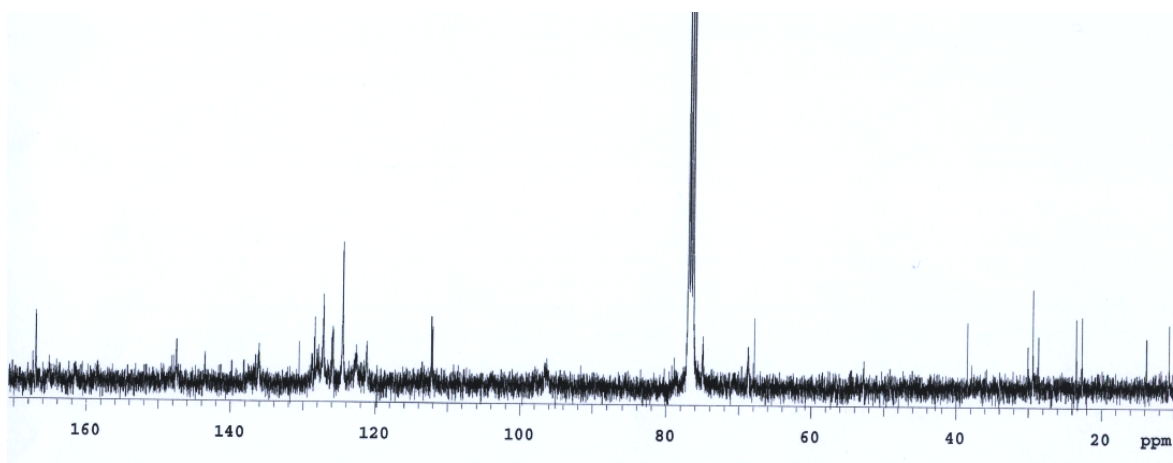


Figure S10: ^1H - ^1H COSY (CDCl_3): Δ -1 [$\text{Ir}(\text{F}_2\text{ppy})_2((R)\text{-4ph-box})$]

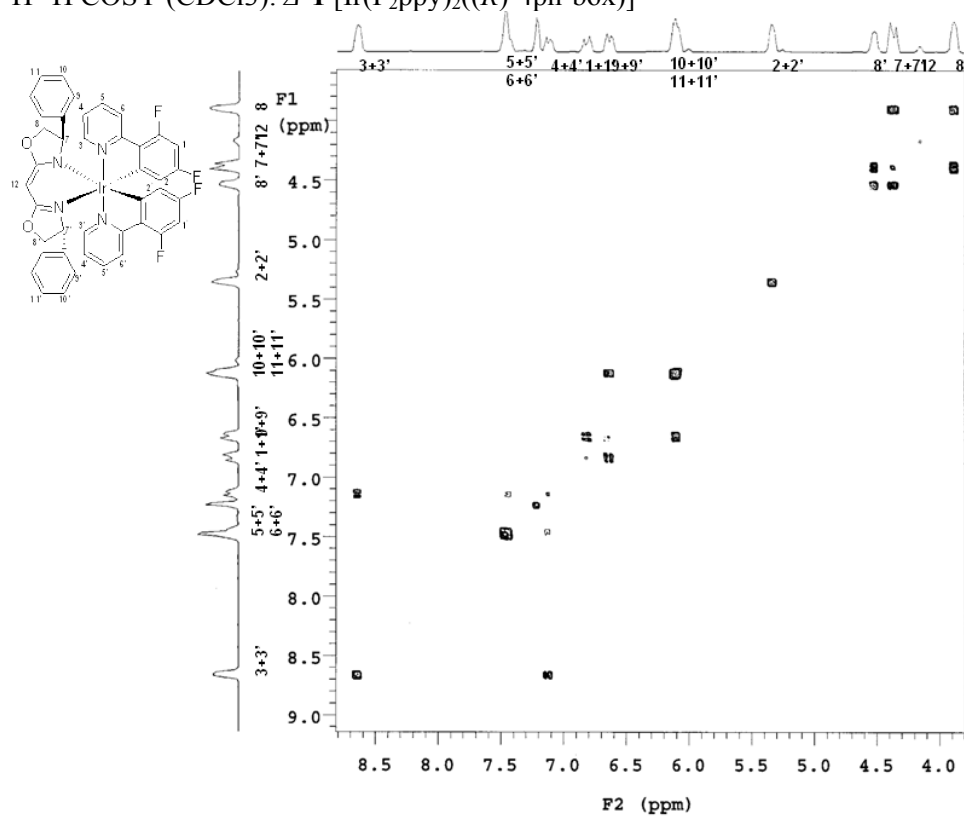


Figure S11: ^1H _NMR (CDCl_3): *A-1* [$\text{Ir}(\text{F}_2\text{ppy})_2((R)\text{-4ph-box})$]

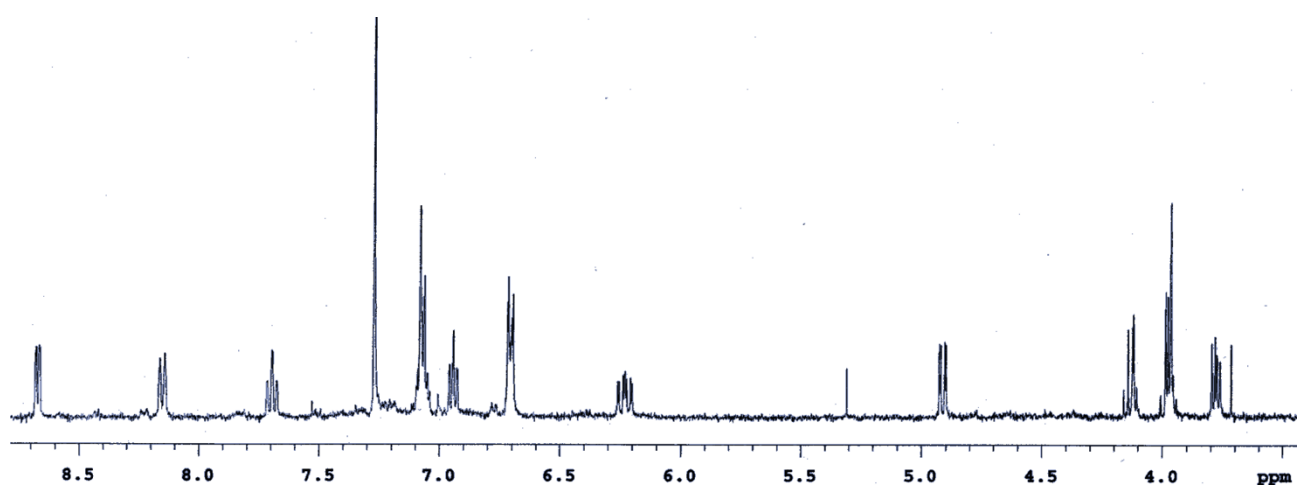


Figure S12: ^{13}C _NMR (CDCl_3): *A-1* [$\text{Ir}(\text{F}_2\text{ppy})_2((R)\text{-4ph-box})$]

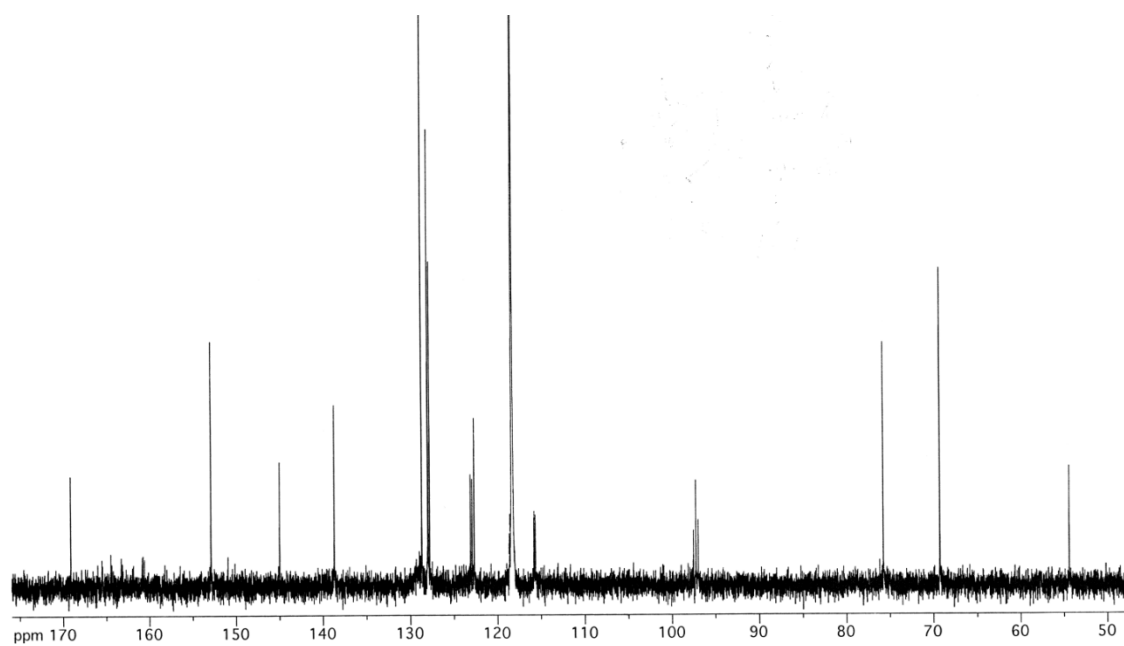


Figure S13: ^1H - ^1H COSY (CDCl_3): Δ -1 $[\text{Ir}(\text{F}_2\text{ppy})_2((R)\text{-4ph-box})]$

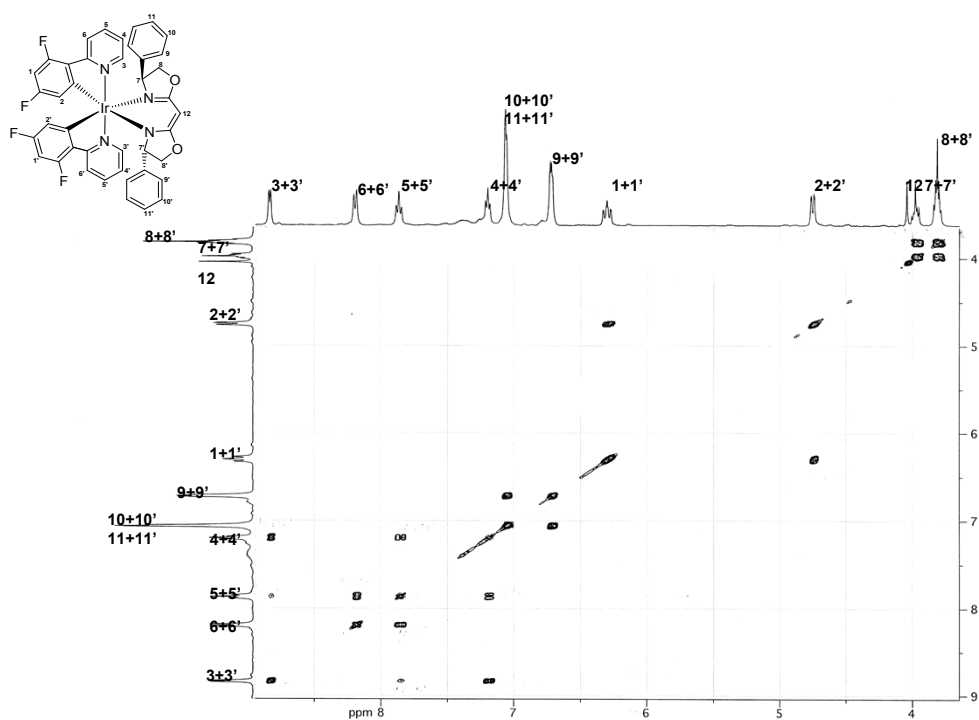
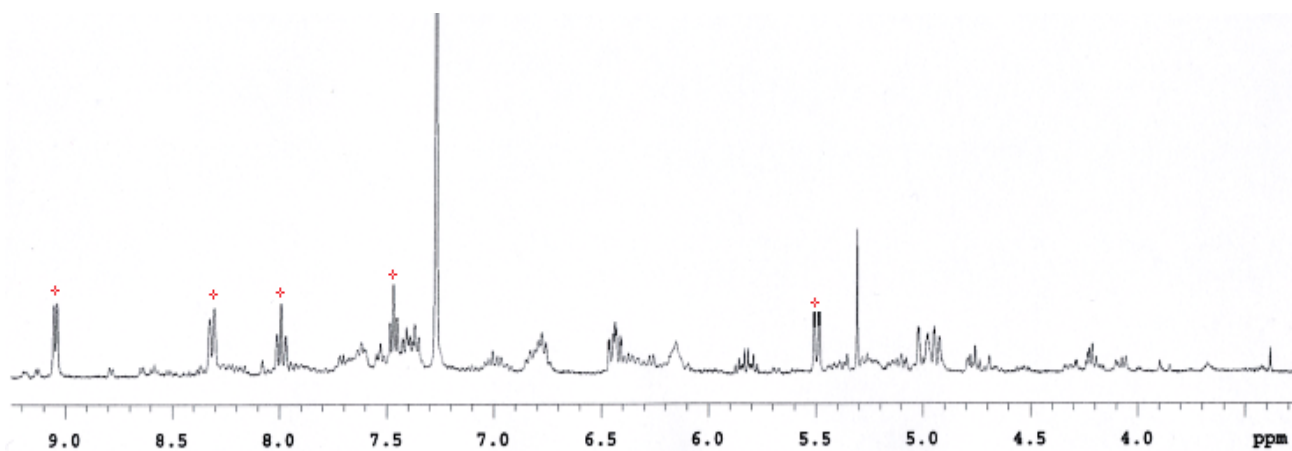


Figure S14: ^1H -NMR (CDCl_3): photoproduct of Δ -1 $[\text{Ir}(\text{F}_2\text{ppy})_2((R)\text{-4ph-box})]$ (P1)



Electrochemistry of *box* free ligand

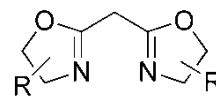
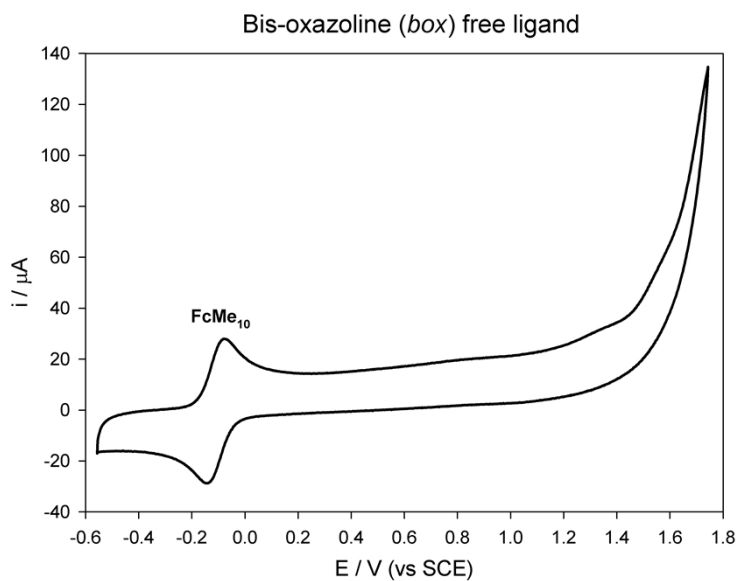


Figure S15: Cyclic voltammogram of a 1.0 mM solution of the *box* free ligand in CH₃CN/TEAPF₆. T= 298 K; $\nu=1$ V/s; working electrode: glassy carbon. Decamethylferrocene (FcMe₁₀) has been added as internal standard.

Photochemistry of *box* and *F₂ppy* free ligands

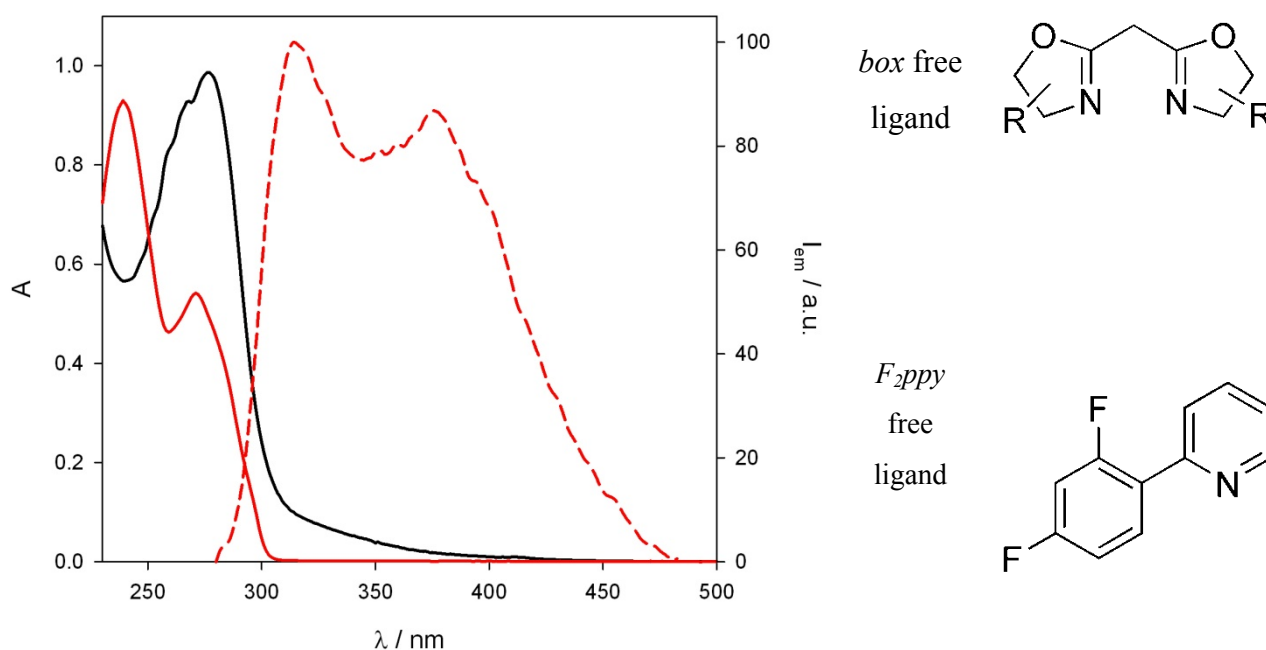


Figure S16: Absorption (full line) and emission (dashed line) of the *box* (black) and *F₂ppy* (red) free ligands in air-equilibrated CH₃CN solution at 298 K. The *box* free ligand is not emitting. Emission of *F₂ppy* free ligand: $\lambda_{ex} = 255$ nm.

IR spectra

Figure S17: 2,2'-methylenebis[(4*R*)-4-phenyl-2-oxazoline]

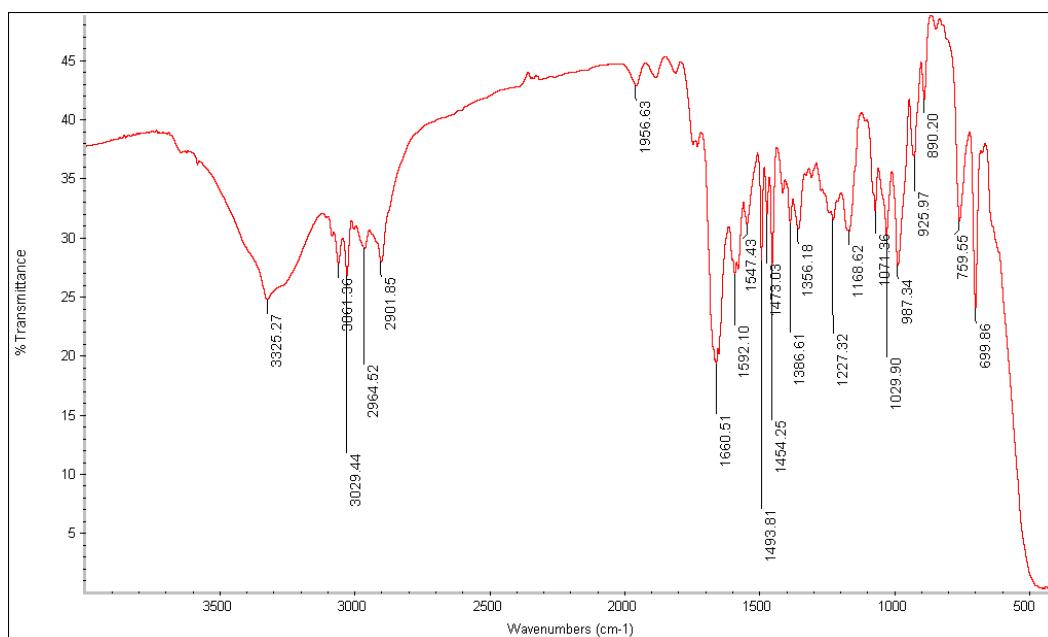


Figure S18: Δ -1 [Ir(F₂ppy)₂](*R*)-4ph-box]

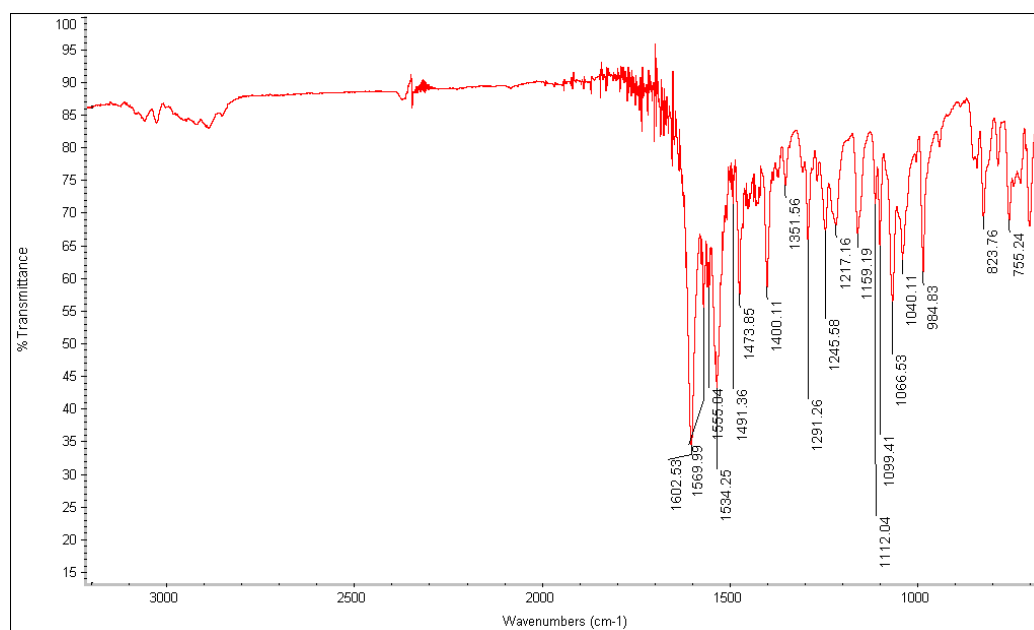
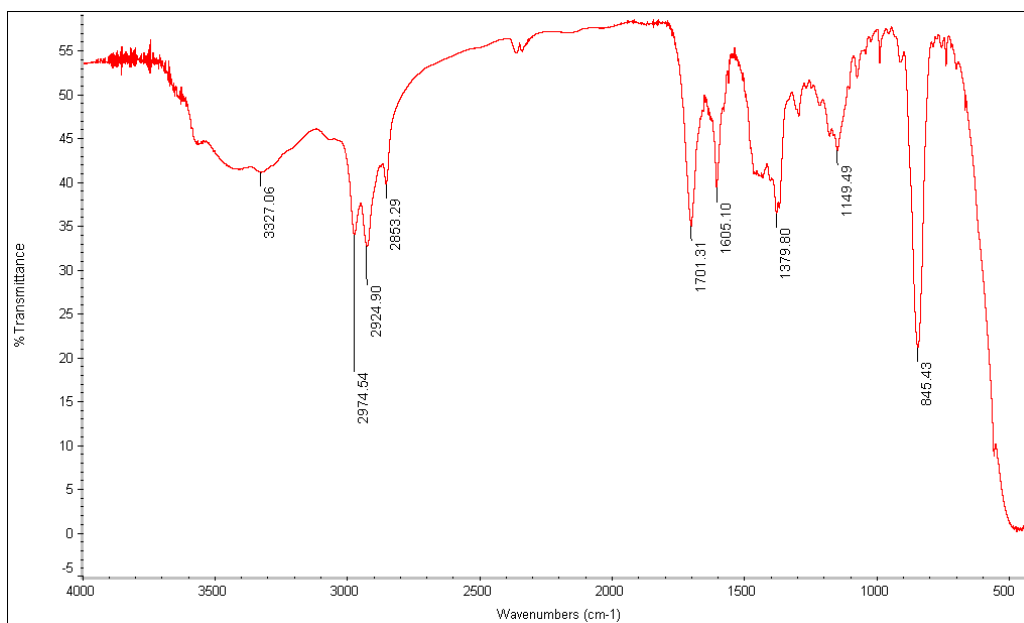


Figure S19: Photoproduct of **A-1** [Ir(F₂ppy)₂((*R*)-4ph-box)] (**P1**)



Evans balance calculations

The magnetic susceptibility (X_g) is defined as:

$$X_g = \frac{C * l * (R - R_0)}{1 \times 10^9 * m} \left[\text{erg G}^{-2} \text{g}^{-1} \right]$$

where: C is the calibration constant of the instrument, 1.28 in our case; l is the length of the sample inside the tube in cm; R is the value read by the instrument with the sample inside the tube; R_0 is the value read by the instrument for the empty tube; m is the mass of the sample in grams.

The molar magnetic susceptibility (X_m) is defined as:

$$X_m = X_g * MW \left[\text{erg G}^{-2} \text{mol}^{-1} \right]$$

The magnetic moment (μ_s) is defined as:

$$\mu_s = 2.828(X_m * T) \left[\text{BM} \right]$$

where T is the absolute temperature of the sample.

Knowing that $\mu_s = g[S(S+1)]^{1/2}$ (where g is the gyromagnetic ratio of the electron and S is the total spin angular momentum of the unpaired electrons) one can calculate the magnetic moment due to a number of unpaired electrons, then we can compare this number with the one obtained from the Evans balance.

For complex **1**:

$$m = 54.2 * 10^{-3} \text{ g}$$

$$l = 2.7 \text{ cm}$$

$$R_0 = -58$$

$$R = -57$$

$$MW = 879$$

$$T = 298 \text{ K}$$

$$\mu_s = 0.365 \text{ BM}$$

This value corresponds, within experimental error, to the absence of unpaired electrons (0 BM).

For the photoproduct **P1**:

$$m = 39.9 \cdot 10^{-3} \text{ g}$$

$$l = 1.6 \text{ cm}$$

$$R_0 = -59$$

$$R = -37$$

$$MW = 911$$

$$T = 298 \text{ K}$$

$$\mu_s = 1.538 \text{ BM}$$

This value corresponds, within experimental error, to one unpaired electrons (1.73 BM).

ⁱ G. De Simoni, G. Faita and K. A. Jørgensen, *Chem. Rev.* 2006, **106**, 3561, and references therein.

ⁱⁱ M. Nonoyama, *Bull. Chem. Soc. Jpn* **1974**, *47*, 767-768.

ⁱⁱⁱ SMART&SAINT Software Reference Manuals (Windows NT Version), Version 5.051, Bruker Analytical X-ray Instruments Inc., Madison, 1998.

^{iv} G. M. Sheldrick, SADABS, Program for empirical absorption correction, University of Göttingen, Göttingen, 1996.

^v A. Altomare, M. C. Burla, M. Cavalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.

^{vi} G. M. Sheldrick, SHELXTLplus (Windows NT version) Structure Determination Package, Version 5.1, Bruker Analytical X-ray Instruments Inc., Madison, 1998.