Electronic Supplementary Information for

A heteroleptic cyclometalated iridium(III) fluorophenylpyridine complex from partial defluorohydrogenation reaction: synthesis, photophysical properties and mechanistic insights†

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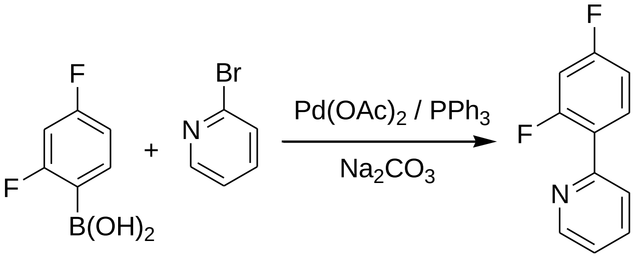
Contents:

(1) Experimental details and characterization data for related complexes

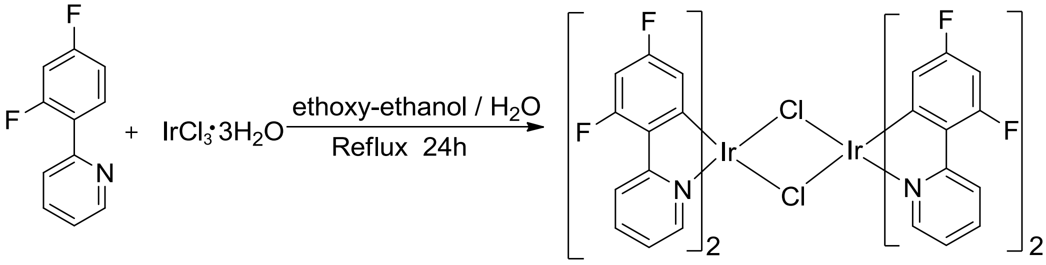
Synthesis of 2-(2,4-difluorophenyl)pyridine (dfppy).



Scheme 1: Formation of dfppy from the reaction of 2,4-difluorophenylboricacid and 2-bromopyridine

2-(2,4-difluorophenyl)pyridine were prepared by using Suzuki coupling reaction (Scheme 1). 0.636g (6.0mmol) Na_2CO_3, 0.569g (3.6mmol) 2,4-difluorophenylboricacid, 0.017g (0.075mmol) $Pd(OAc)_2$ and 0.079g (0.3mmol) PPh_3 were added into a 100mL three necks flask. After vacuumized by a vacuum pump and refilled with dry nitrogen for three times, 0.474g (3.0mmol) 2-bromopyridine, toluene (10 mL), ethanol (10 mL), deionized water (5 mL) was then added to the mixture. The resulting mixture was stirred at 373.15K (100ºC) for 24 hours, which was then the organic layer was separated and washed with saturated salt solution and dried with anhydrous magnesium sulfate to afford dfppy as a red-brown crude liquid, which was further distilled under reduced pressure and a desired colorless transparent liquid was obtained in 92.0% yield (3.479 g). IR: 3057 m, 3013 m, 1619 s, 1466 s, 1440 s, 1417 s, 1296 s, 1263 s, 850 m, 781 s. ^{1}H NMR (400MHz, $CDCl_3$, 25ºC): δ 6.91 (m, 1H), 7.00 (m, 1H), 7.25 (dd, J = 8.7, 4.3 Hz, 1H), 7.75 (d, J = 3.9 Hz, 2H), 8.00 (dd, J = 15.6, 8.8 Hz, 1H), 8.71 (d, J = 4.7 Hz, 1H). ^{19}F NMR (377MHz, $CDCl_3$, 25°C): δ -109.33 (d, J = 8.6 Hz), -112.95 (d, J = 8.7 Hz).

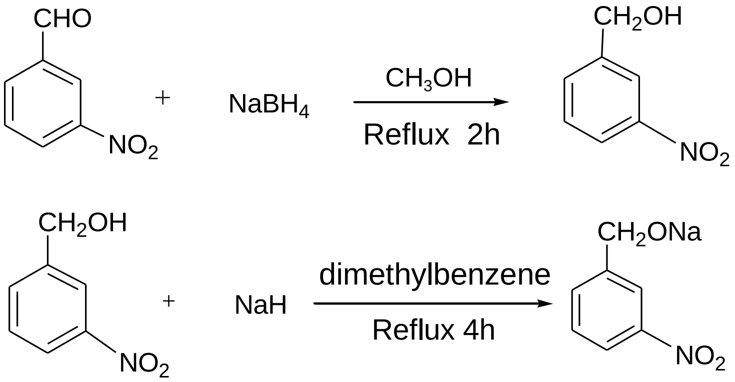
Synthesis of μ-chloro-bridged dimer $(dfppy)_2Ir(\mu\text{-}Cl)_2Ir(dfppy)_2$ (1).



Scheme 2: Formation of **1** from the reaction of dfppy and $IrCl_3$•$3H_2O$

$(dfppy)_2Ir(\mu\text{-}Cl)_2Ir(dfppy)_2$ was obtained by reaction of dfppy ligand with $IrCl_3$•$3H_2O$ via a general procedure described in the literature (Scheme 2).[S1] 0.8g (4.19mmol) dfppy and 0.5g (1.67mmol) $IrCl_3$ were added into a 100mL three necks flask. After vacuumized by a vacuum pump and refilled with dry nitrogen for three times, ethoxy-ethanol (15 mL) and deionized water (5 mL) was then added to the mixture. The resulting mixture was stirred at 393.15K (120ºC) for 24 hours, which was then filtered and the residue was washed with deionized water, hexane and ethanol to afford **1** as a yellow crude powder, which was further recrystallized in hexane/toluene and a desired yellow crystal product **1** was obtained in a 78.14% yield (0.797 g). IR (KBr): 3080 m, 1602 s, 1478 m, 1428 m, 1403 m, 1293 m, 1247 m, 846 m, 830 m, 755 m. ^{1}H NMR (400MHz, $CDCl_3$, 25ºC): δ 5.29 (m, 2H), 6.34 (t, *J* = 9.7 Hz, 2H), 6.83 (t, *J* = 6.4 Hz, 2H), 7.83 (t, *J* = 7.5 Hz, 2H), 8.31 (d, *J* = 8.5 Hz, 2H), 9.12 (d, *J* = 5.4 Hz, 2H).

Synthesis of sodium *m*-nitrobenzenemethoxide.



Scheme 3: Formation of Sodium *m*-nitrobenzenemethoxide from *m*-nitrobenzaldehyde

Sodium *m*-nitrobenzenemethoxide was prepared via the procedure (Scheme 3) described as follows: *m*-nitrobenzaldehyde (2.131g , 14.11 mmol) was dissolved in methanol (10 mL) in a 100mL three necks flask, then the mixture was heated to reflux in an oil bath. A solution of sodium borohydride (0.593 g, 15.61 mmol) in methanol (20 mL) was added by drops to it. The resulting mixture was heated to 353.15K(80ºC) and stirred for 2 hours, which solvent was removed by reduced pressure when it cooled to room temperature. The residue was then washed with water and diethyl ether to afford the yellowish-brown oiliness liquid. The desired light yellow crystal product *m*-nitrobenzenemethol was obtained in 97.49% yield (2.105 g). IR (KBr): 3358 s, 3088 m, 2933 m, 2868 m, 1619 m, 1525 s, 1479 s, 1345 s, 889 s, 794 s, 689 s.

0.304g（1.98mmol）*m*-nitrobenzenemethol and 0.15g（6.25mmol）sodium hydride was added into a 100mL three necks flask, 10mL dimethylbenzene was also added into it after it was vacuumized by a vacuum pump and refilled with dry nitrogen for three times. The mixture was heated to reflux and stirred for 4 hours. The resulting mixture was filtered under reduced pressure after it was cooled to room temperature to afford black crude product, which was washed with diethyl ether and a desired brown powder product sodium *m*-nitrobenzenemethoxide was obtained in 84.57% yield (0.296 g).

(2) S-reference:

[S1] N. Matsuo, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 767.

(3) X-ray crystallographic analysis data

Table S1. Crystal data and structure refinement for complex **2**.

Empirical formula	$C_{33}H_{29}F_5IrN_3$
Formula weight	744.71
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system, space group	Cubic, I 41/acd : 2
Unit cell dimensions	a = 17.643(3) Å α = 90°
	b = 17.643(3) Å β = 90°
	c = 34.487(7) Å γ = 90°
Volume	10735(3) A^3
Z, Calculated density	16, 1.843 Mg/m^3
Absorption coefficient	5.039 mm^{-1}
F(000)	5760
Crystal size	0.1000 x 0.4000 x 0.1000 mm
Theta range for data collection	3.13 to 26°
Limiting indices	$-21 \leqq h \leqq 19, -21 \leqq k \leqq 17, -42 \leqq l \leqq 29$
Reflections collected / unique	16939/ 2634 [R(int) = 0.0650]
Completeness to θ = 25.10	99.5 %
Max. and min. transmission	1.0000 and 0.5133
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7669 / 0 / 422
Goodness-of-fit on F2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0697, wR2 = 0.1576
R indices (all data)	R1 = 0.0810, wR2 = 0.1644
Largest diff. peak and hole	1.123 and -0.859 e. A^{-3}

(4) Characterization data and photophysical properties for complex **2**

Figure S1. ^{1}H-NMR spectrum of complex **2**.

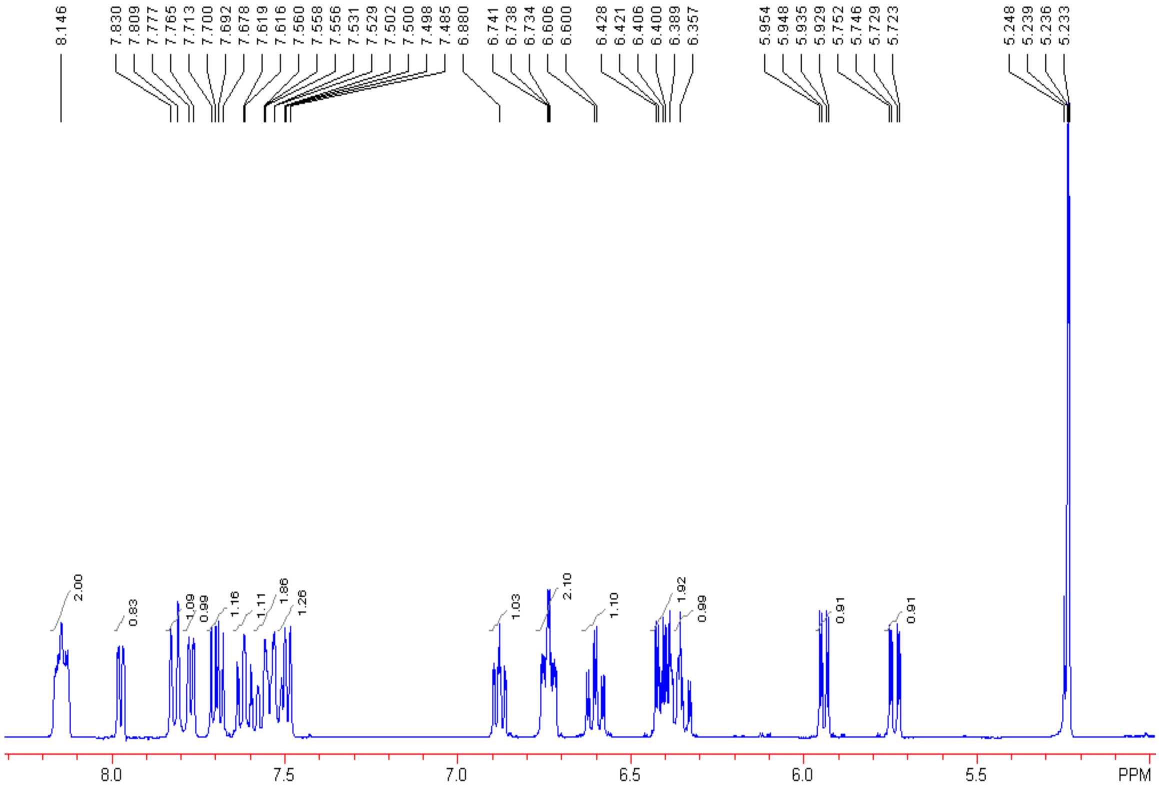


Figure S2. ^{19}F-NMR spectrum of complex **2**.

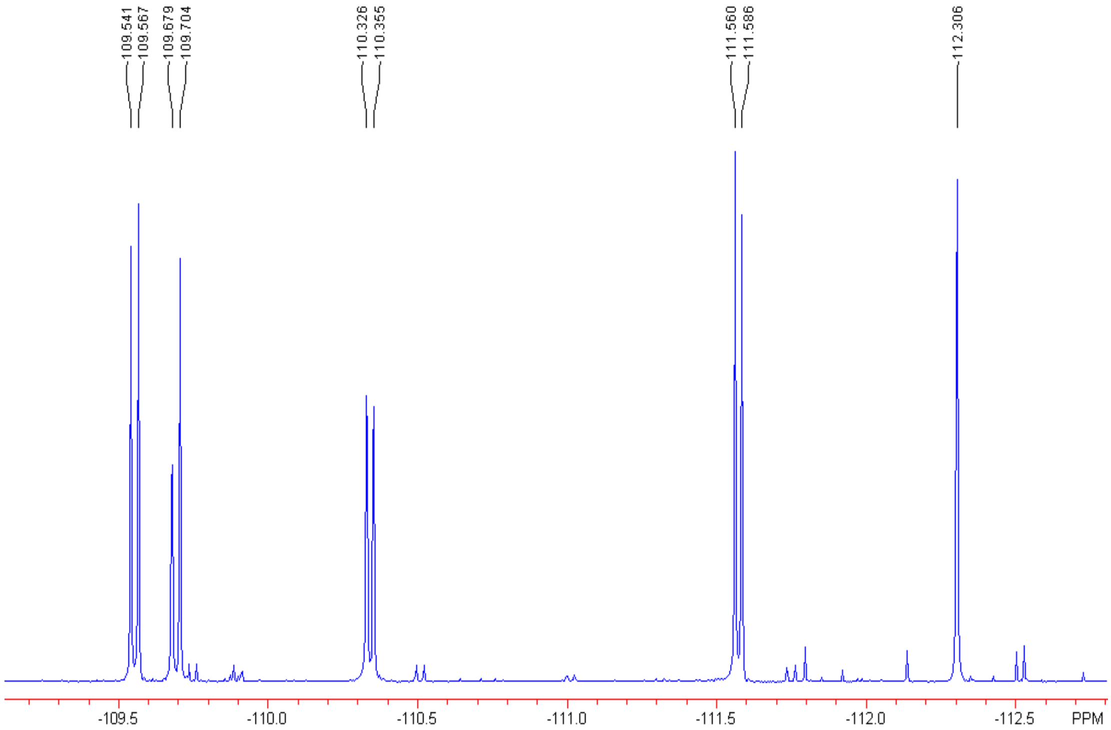


Figure S3. UV-Vis absorption spectrum of complex **2** at a concentration of 10^{-5} mol/L in CH_2Cl_2 solution at 298 K.

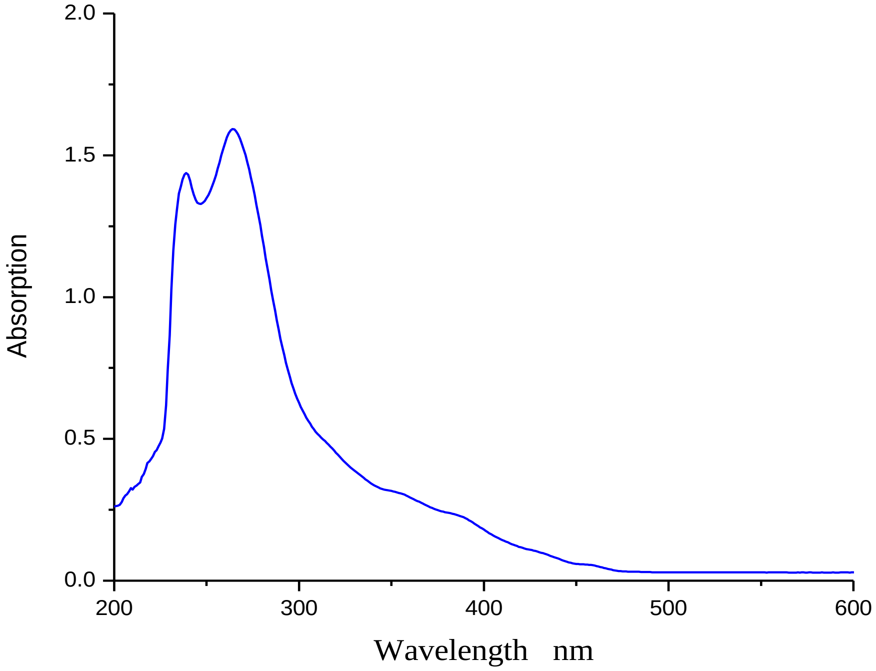
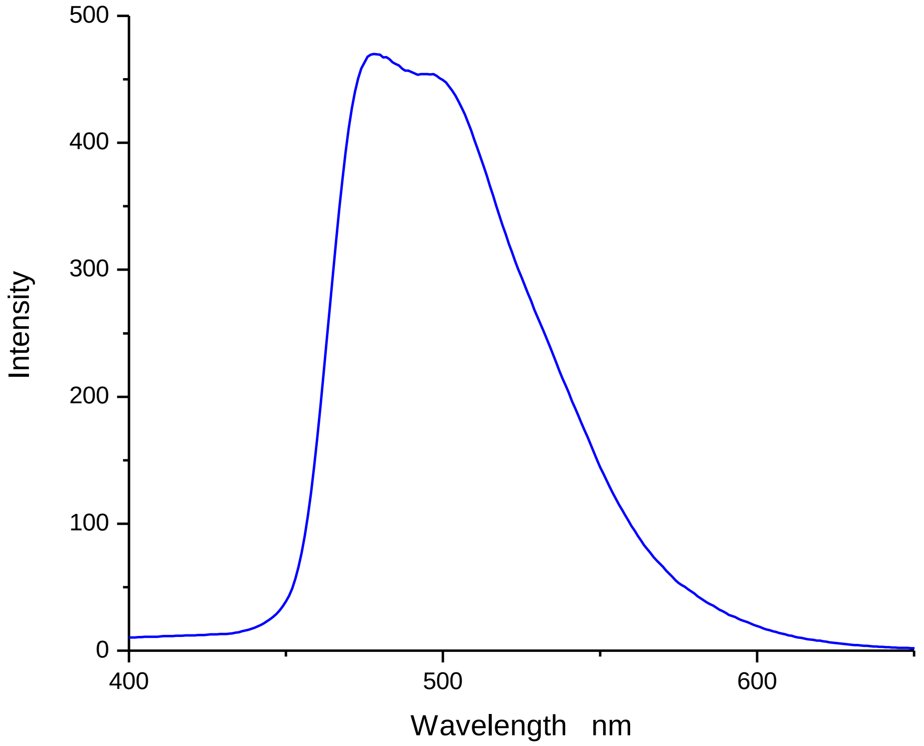


Figure S4. Normalized photoluminescent emission spectrum of complex **2** at a concentration of 10^{-5} mol/L in CH_2Cl_2 solution at 298 K.



(5) Additional spectroscopic spectra

Figure S5. ^{1}H NMR of the mixture containing *m*-nitrobenzaldehyde.

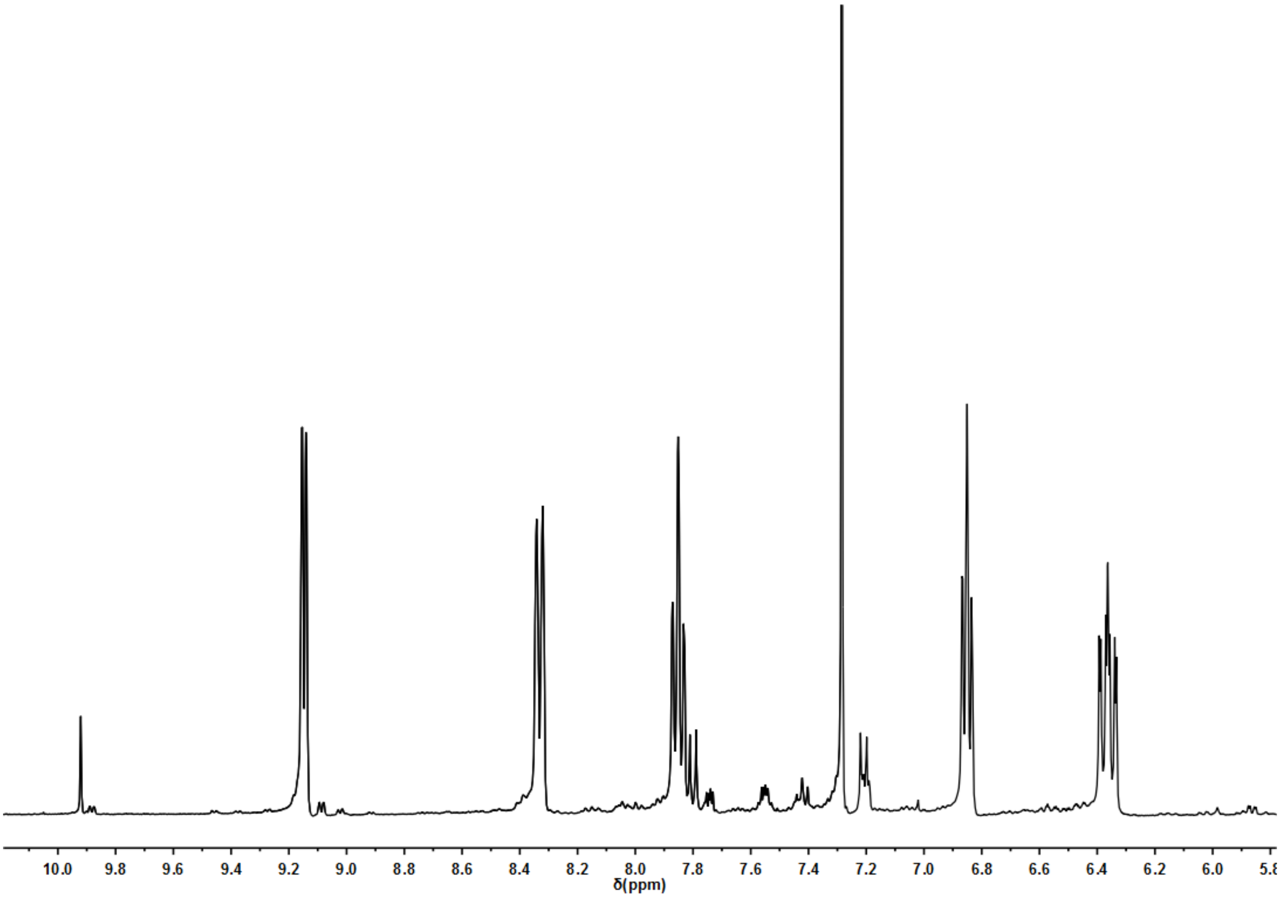


Figure S6. ^{1}H NMR spectrum of mixture containing **4** and **8**.

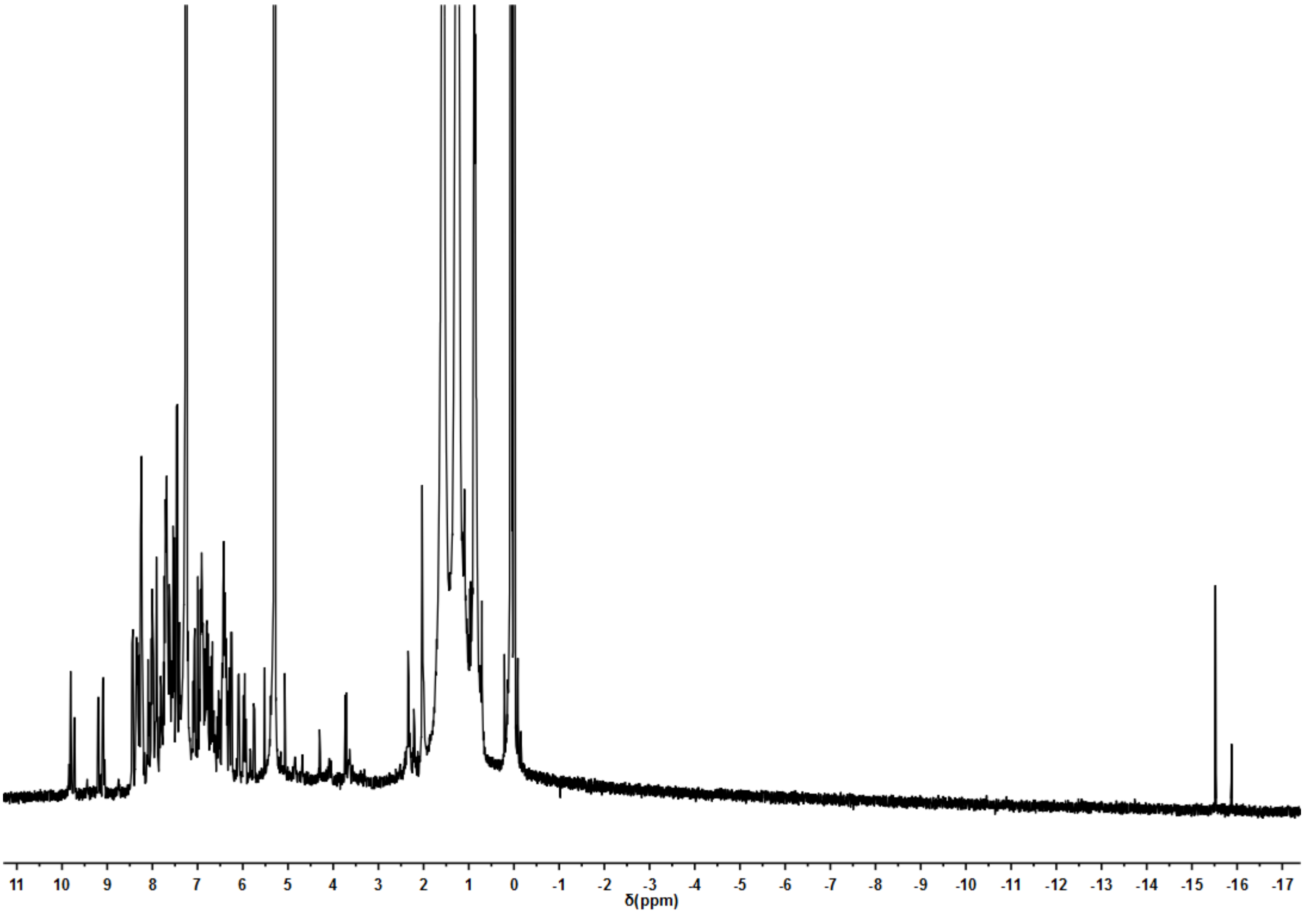


Figure S7. ^{19}F NMR spectrum of mixture containing **7** and **8**.

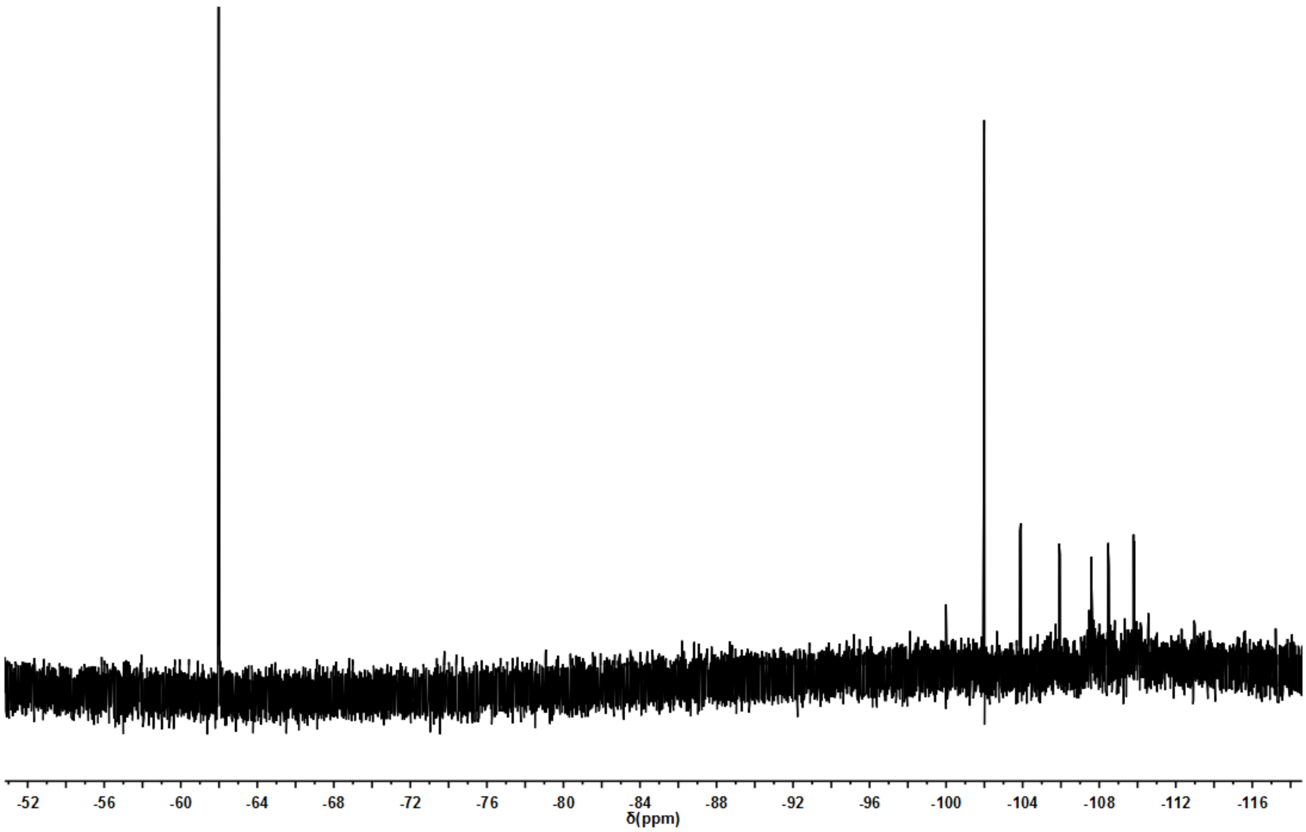


Figure S8. Mass spectrum of 2-(2,4-difluorophenyl)pyridine.

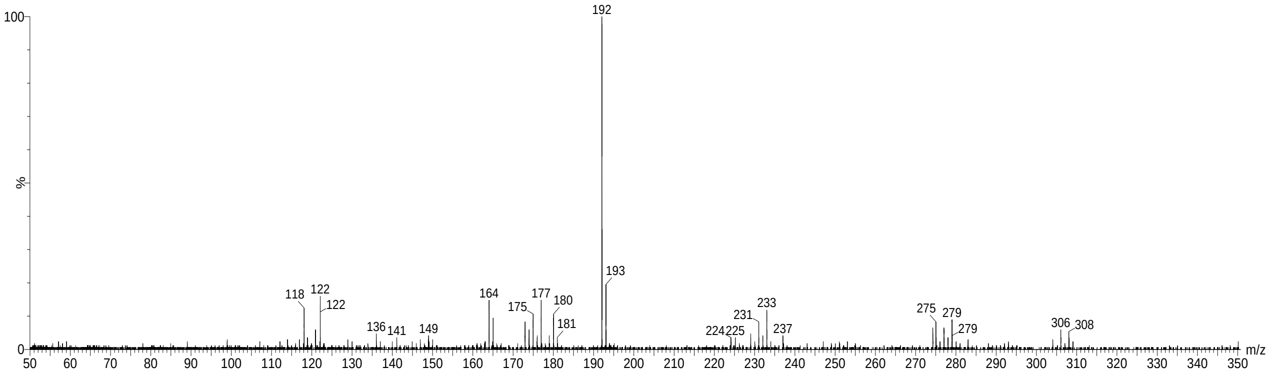


Figure S9. Mass spectrum of 2-(4-difluorophenyl)pyridine.

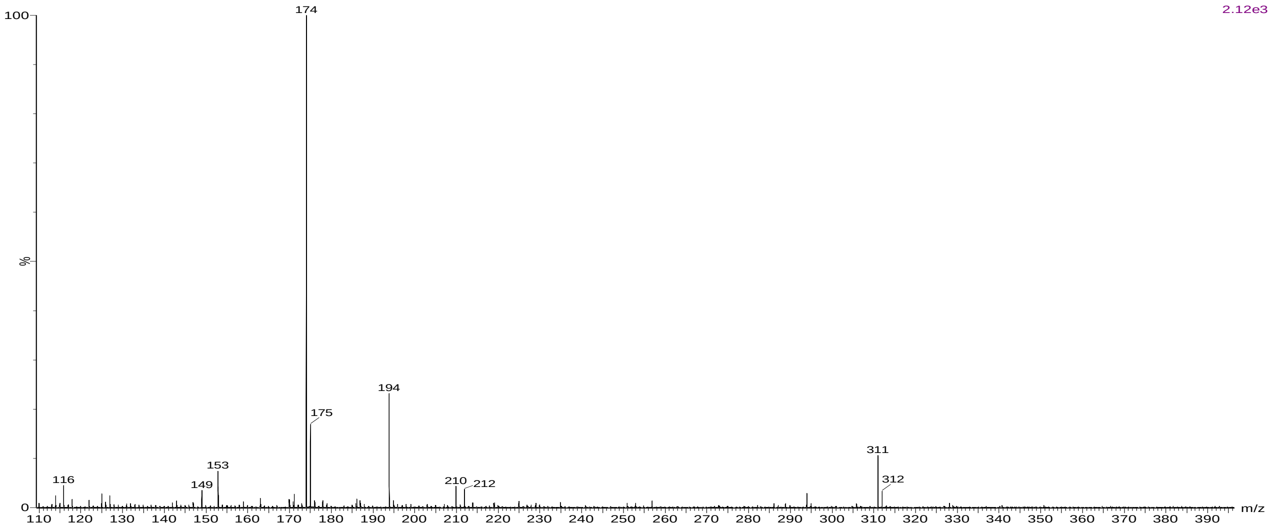


Figure S10. Mass spectrum of $[(dfppy)_2Ir]^+$.

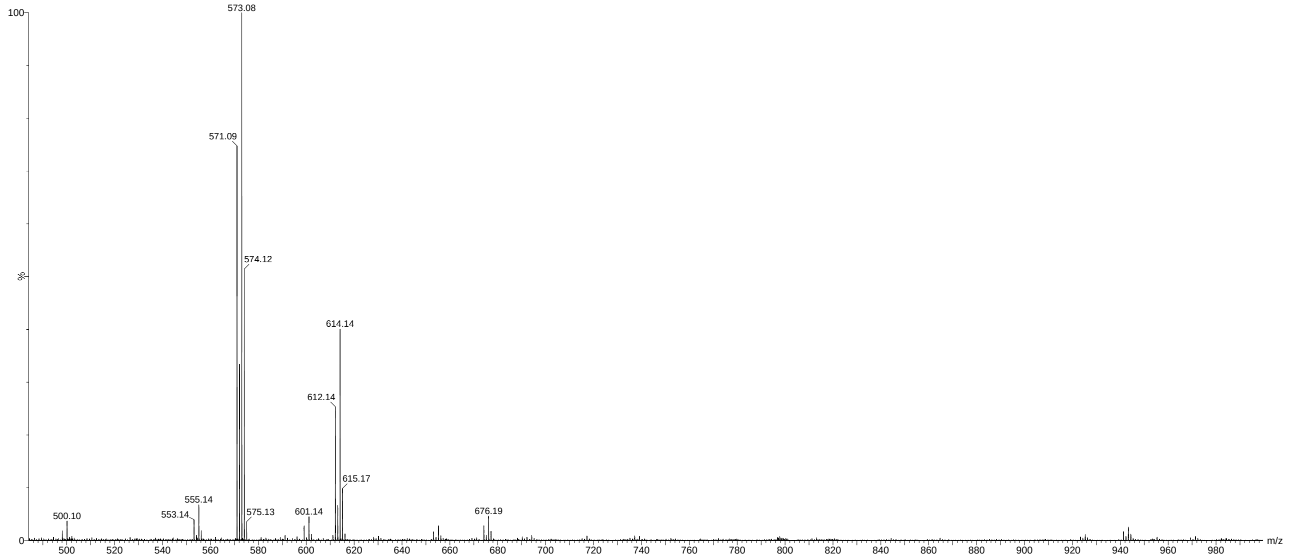
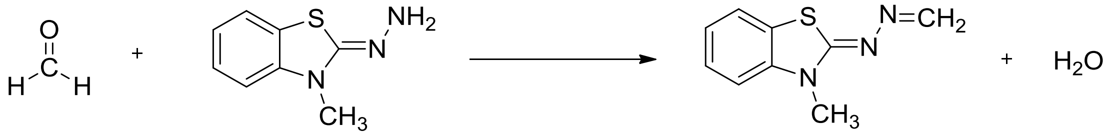


Figure S11. Mass spectrum of [(dfppy)Ir(fppy)]$^+$.

(6) Method for the determination of formaldehyde



Molecular weight: 191

Figure S12. Calculated Mass spectrum of formaldehyde-2-(3-methyl-2-benzothiazolylidene)hydrazone.

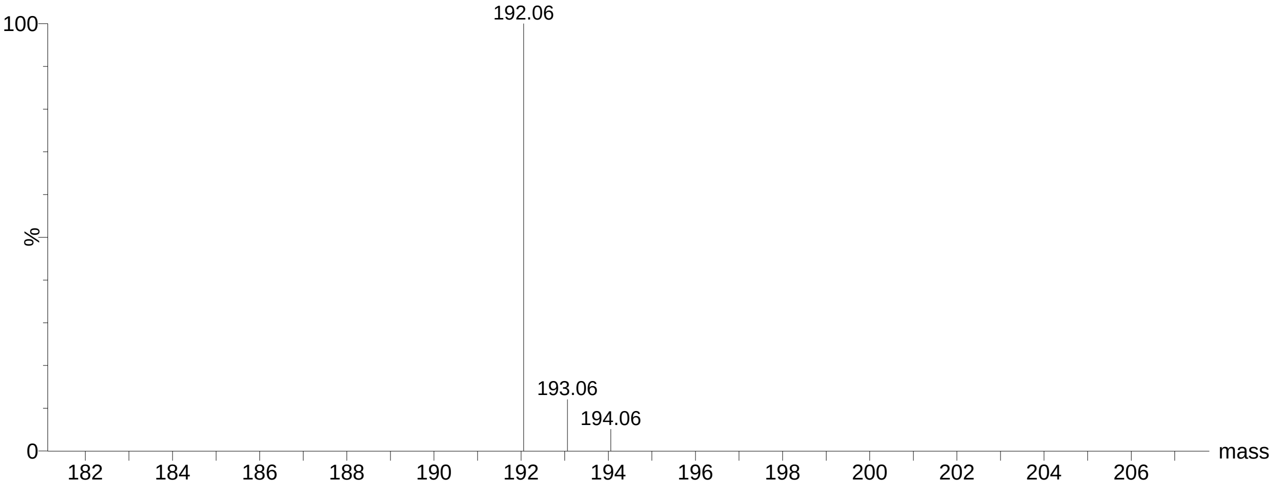


Figure S13. The mass spectrum obtained from HPLC-Mass analysis.