Rigid Biimidazole Ancillary Ligands as an Avenue to Bright Deep Blue Cationic Iridium (III) Complexes

Adam Henwood[a], *Sloane Evariste*[b,c], *Alexandra M.Z. Slawin*[a] *and Eli Zysman-Colman*[a]*

[a] EaStCHEM School of Chemistry, University of St Andrews, St Andrews, Fife, UK, KY16 9ST, Fax: +44-1334 463808; Tel: +44-1334 463826; E-mail: eli.zysman-colman@st-andrews.ac.uk;
[b] *Département de Chimie, Université de Sherbrooke, 2500 Boul. de l'Université, Sherbrooke, QC, Canada, J1K 2R1*
[c] *Sciences Chimiques, UMR 6226 CNRS - Université de Rennes 1, Campus de Beaulieu, Rennes Cedex, France 35042*
URL: http://www.zysman-colman.com

SUPPORTING INFORMATION

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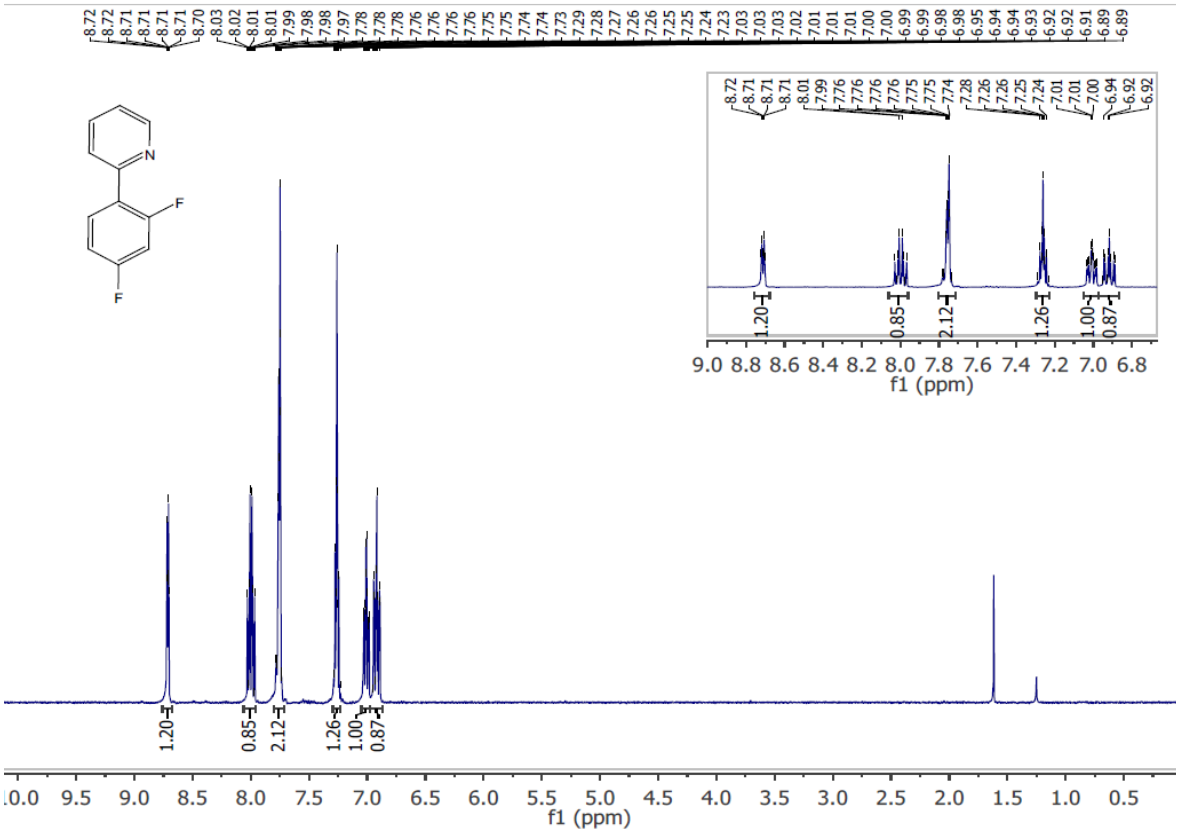

Figure **S1**. ^{1}H NMR spectrum of **2-(2,4-Difluorophenyl)pyridine (dFppy)** in $CDCl_3$.

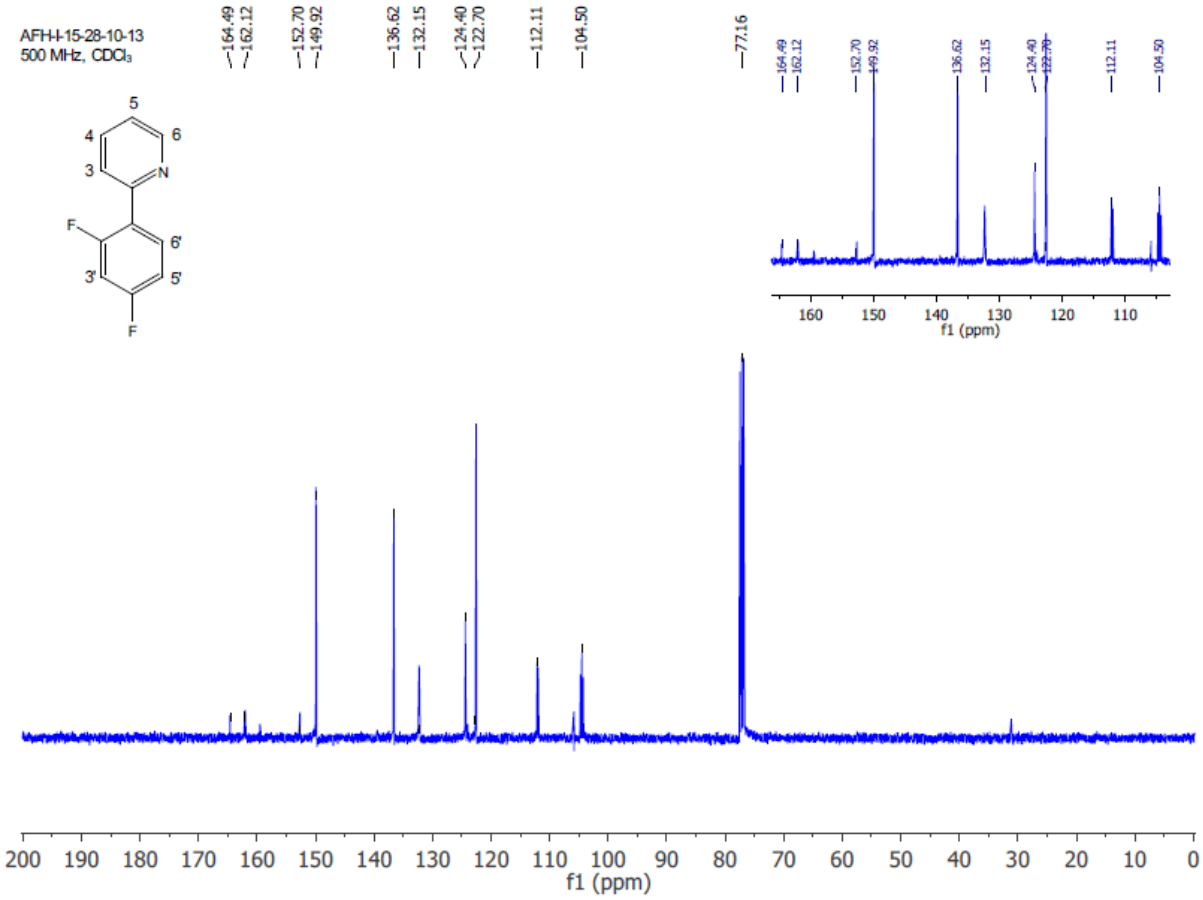

Figure **S2**. ^{13}C NMR spectrum of **2-(2,4-Difluorophenyl)pyridine (dFppy)** in $CDCl_3$.

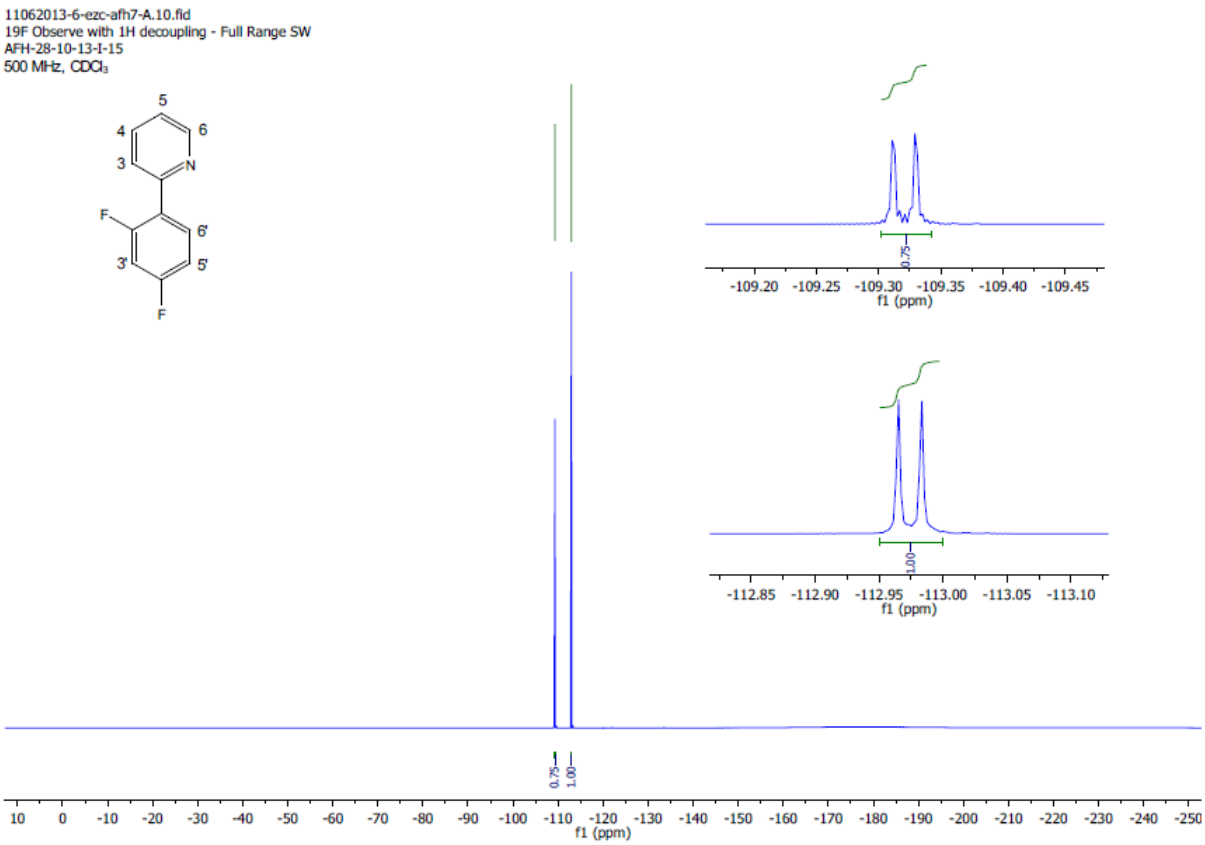

Figure **S3**. ^{19}F $\{^{1}H\}$ NMR spectrum of **2-(2,4-Difluorophenyl)pyridine (dFppy)** in $CDCl_3$.

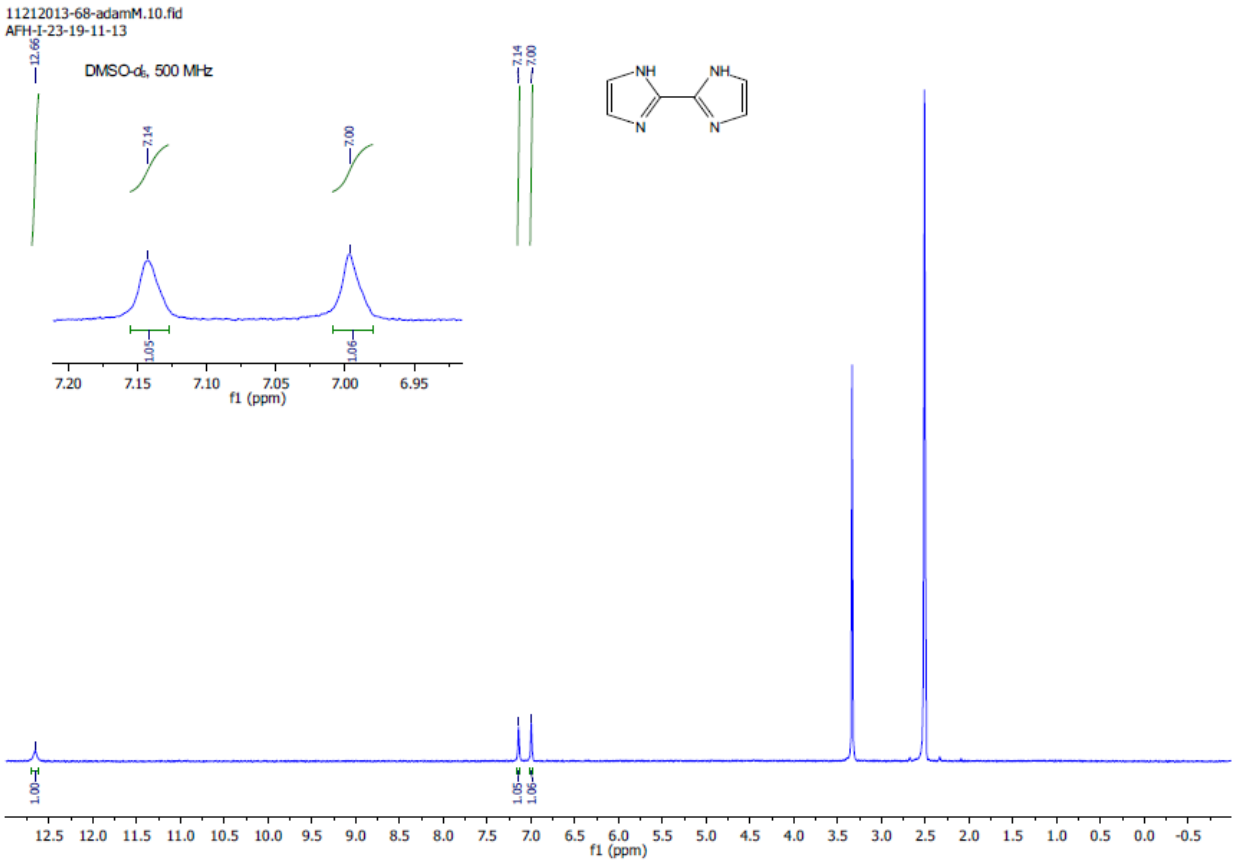

Figure **S4**. ^{1}H NMR spectrum of **1*H*,1'*H*-2,2'-biimidazole (biim)** in DMSO-d_6.

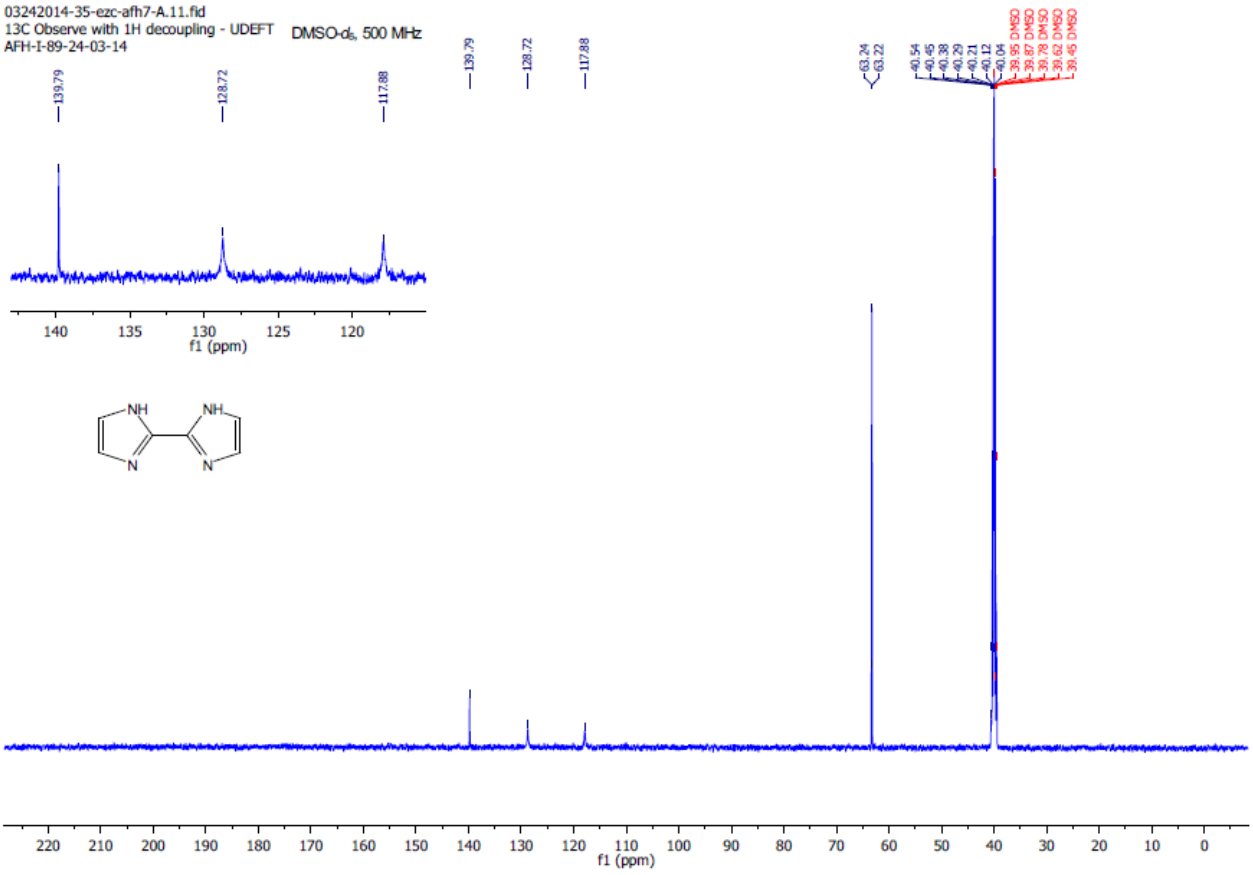

Figure **S5**. ^{13}C NMR spectrum of **1*H*,1'*H*-2,2'-biimidazole (biim)** in DMSO-d_6.

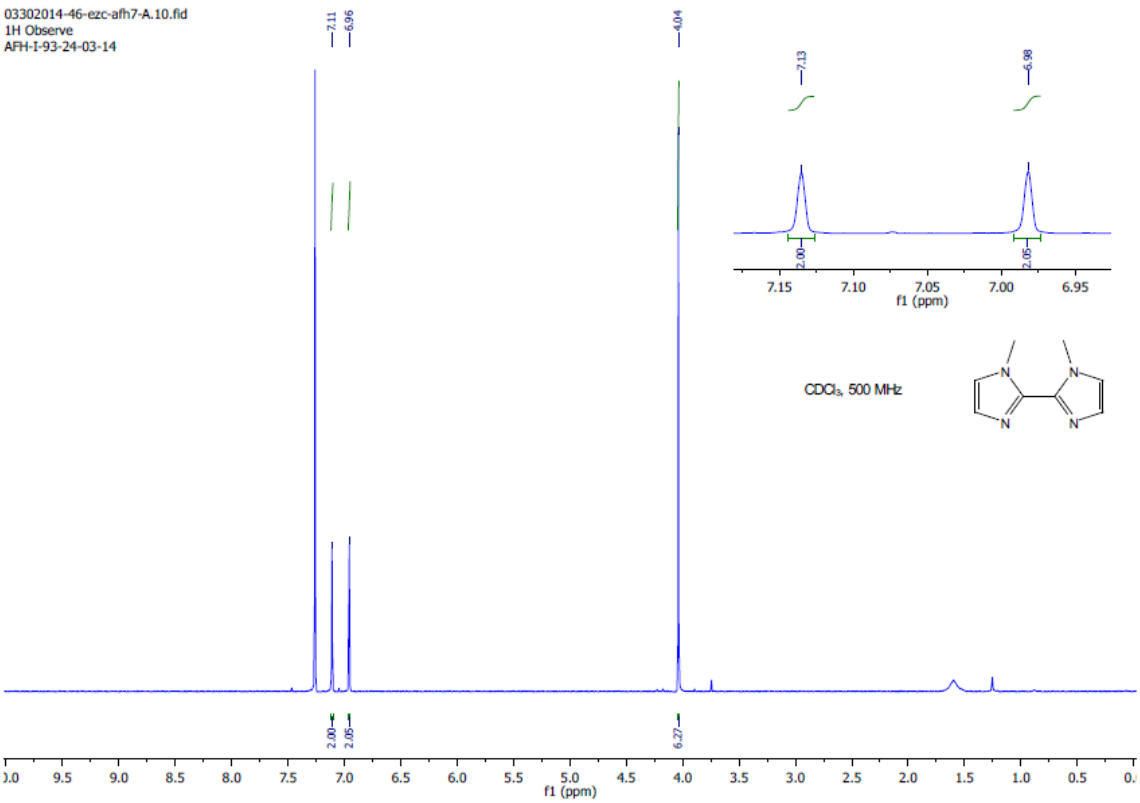

Figure **S6**. ^{1}H NMR spectrum of **1,1'-Dimethyl-2,2'-biimidazole (dMebiim)** in $CDCl_3$.

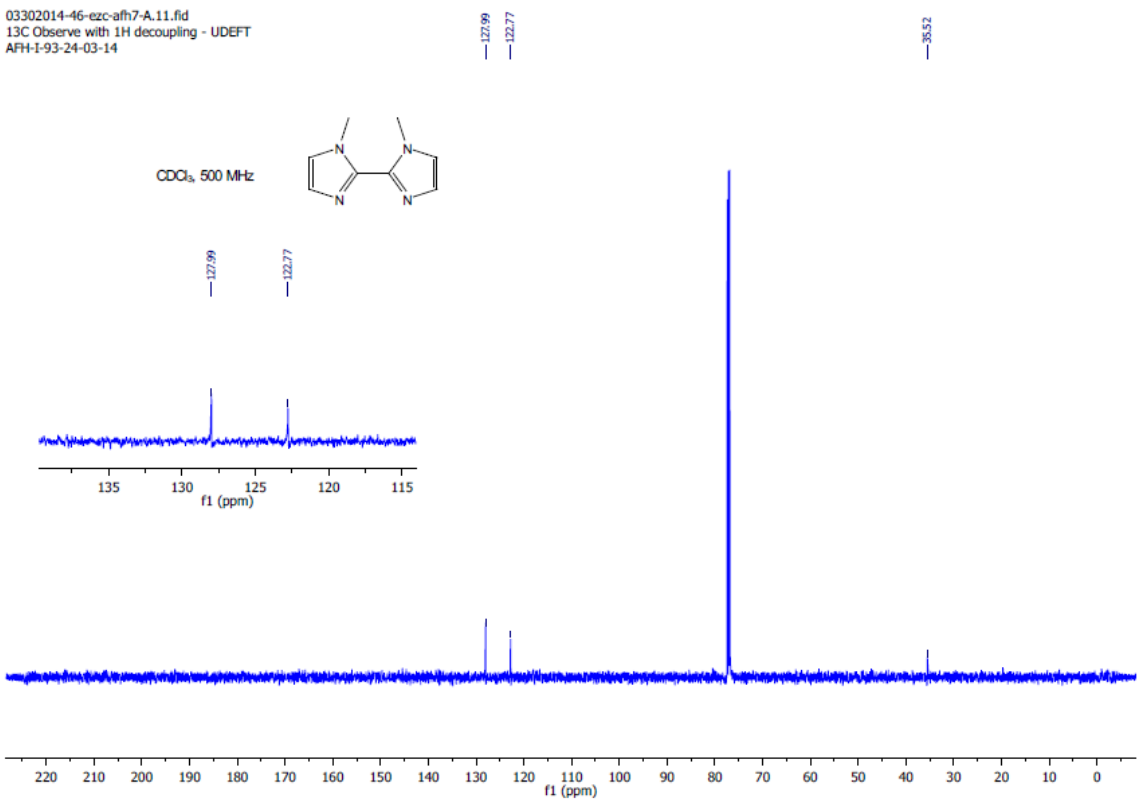

Figure **S7**. ^{13}C NMR spectrum of **1,1'-Dimethyl-2,2'-biimidazole (dMebiim)** in $CDCl_3$.

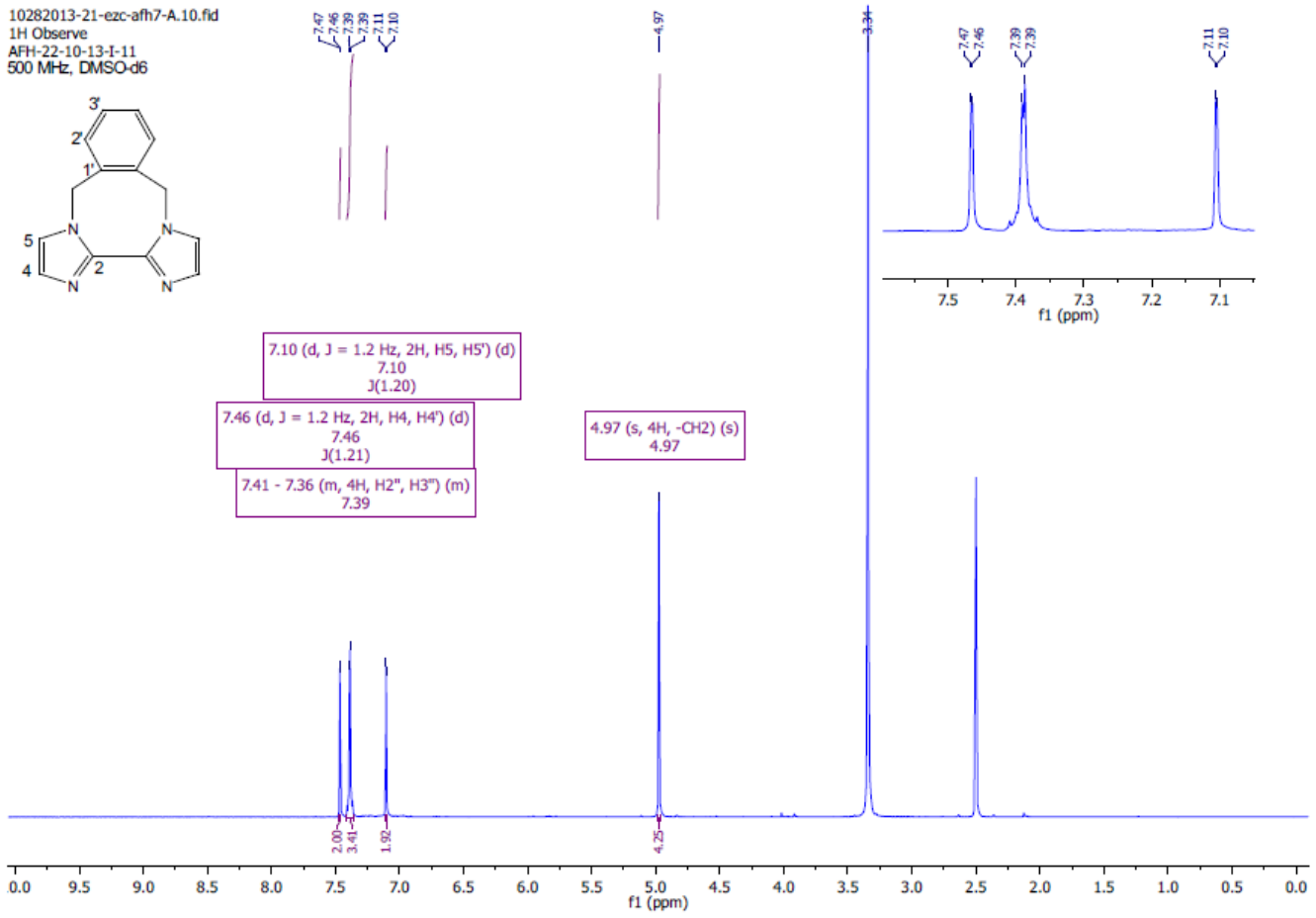

Figure **S8**. ^{1}H NMR spectrum of **1,1'-(α,α'-*o*-Xylylene)-2,2'-biimidazole (*o*Xylbiim)** in DMSO-d_6.

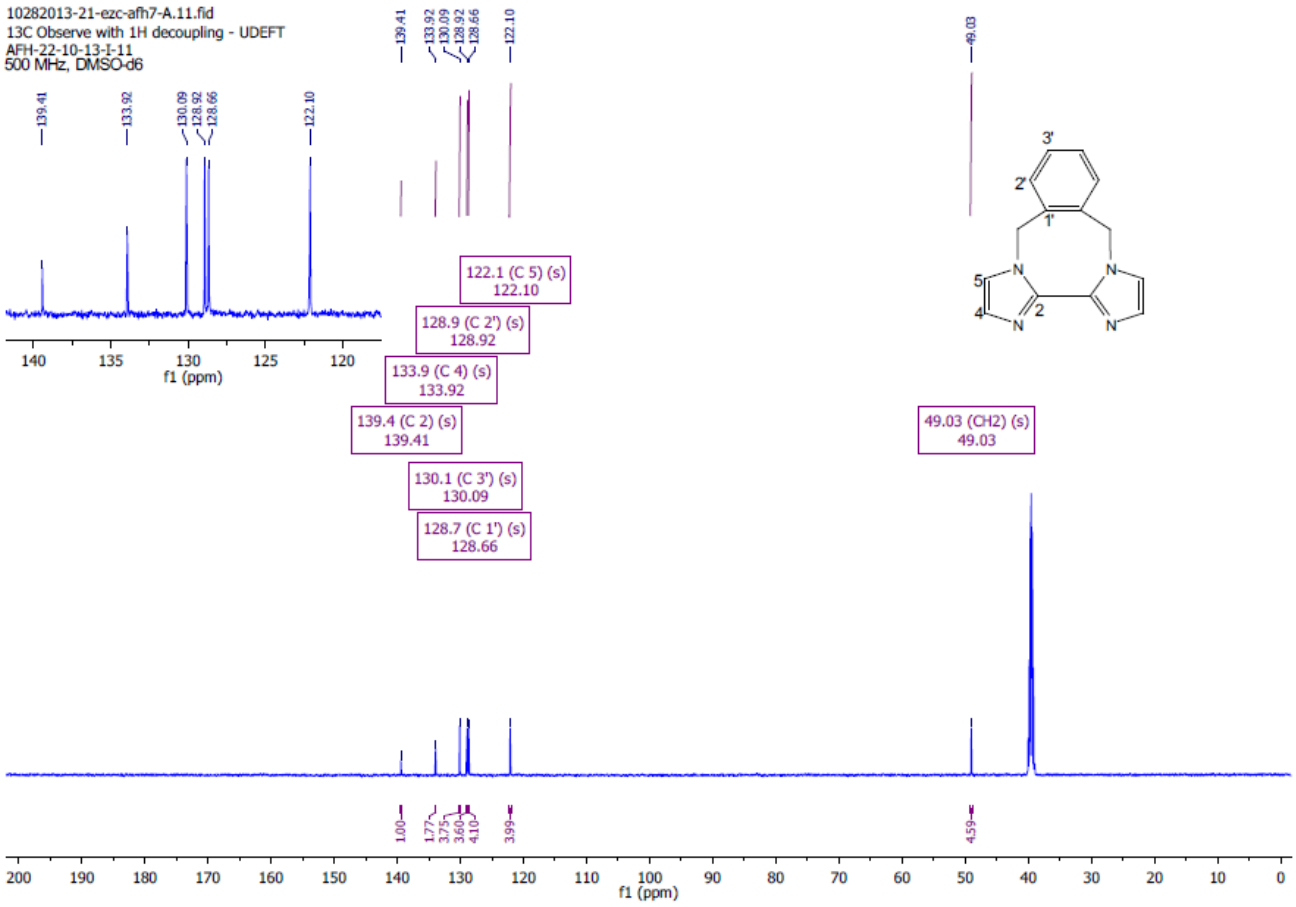

Figure **S9**. ^{13}C NMR spectrum of **1,1'-(α,α'-*o*-Xylylene)-2,2'-biimidazole (*o*Xylbiim)** in DMSO-d_6.

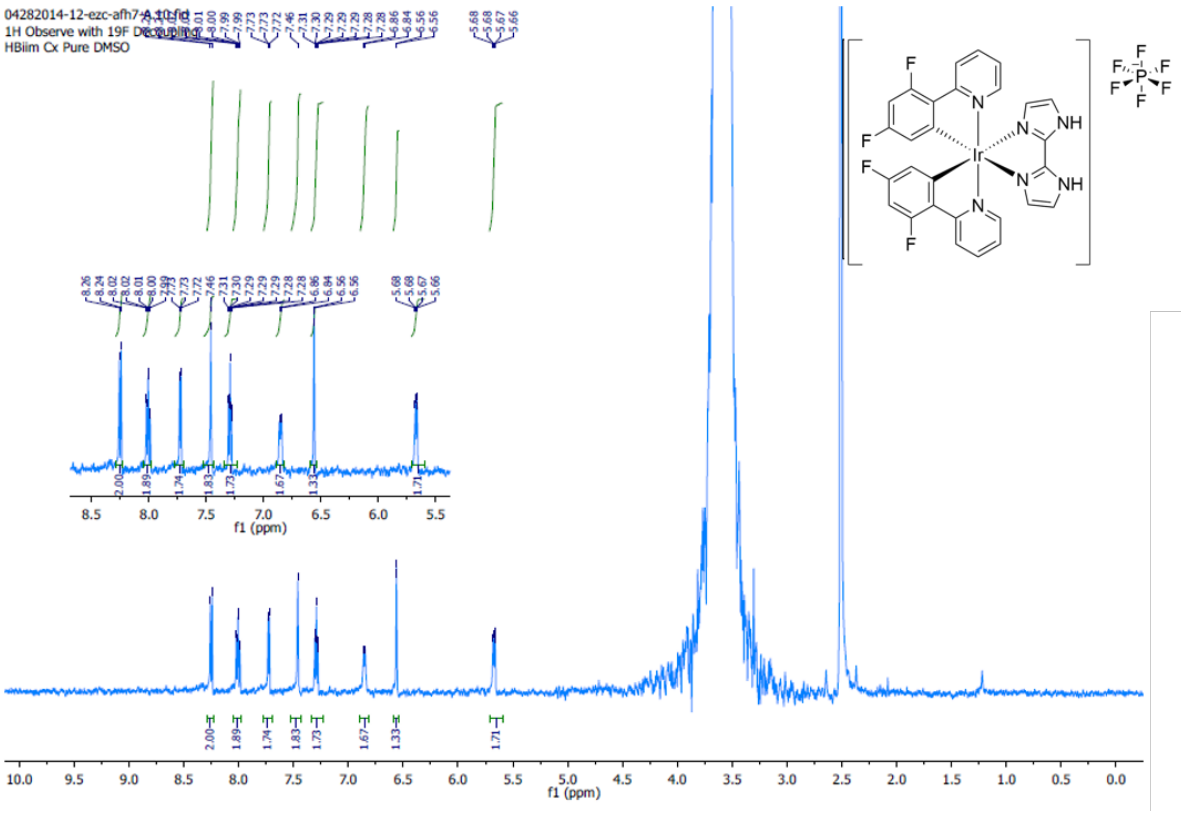

Figure **S10**. ^{1}H $\{^{19}F\}$ NMR spectrum of **[(dFppy)$_2$Ir(biim)](PF$_6$)**, **1**, in DMSO-d_6.

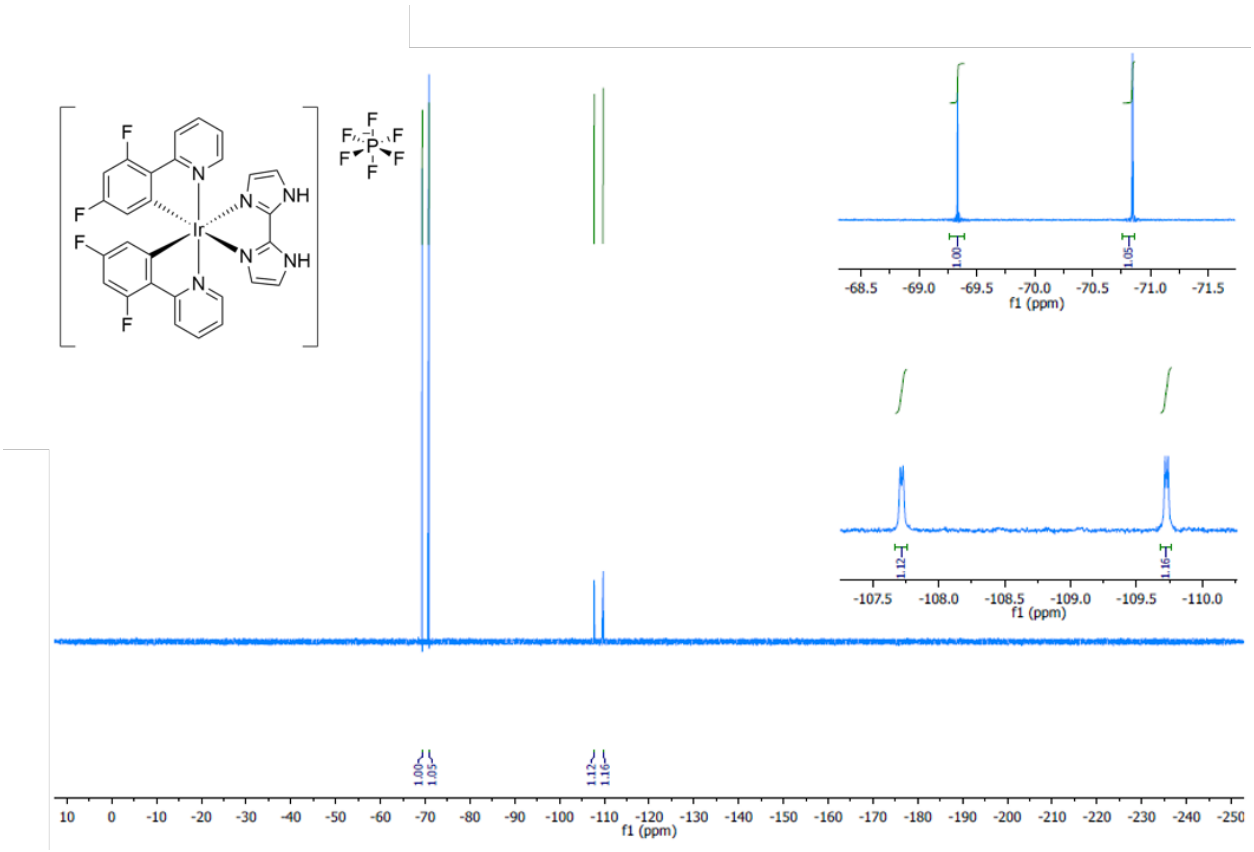

Figure **S11**. ^{19}F $\{^{1}H\}$ NMR spectrum of **[(dFppy)$_2$Ir(biim)](PF$_6$)**, **1**, in DMSO-d_6.

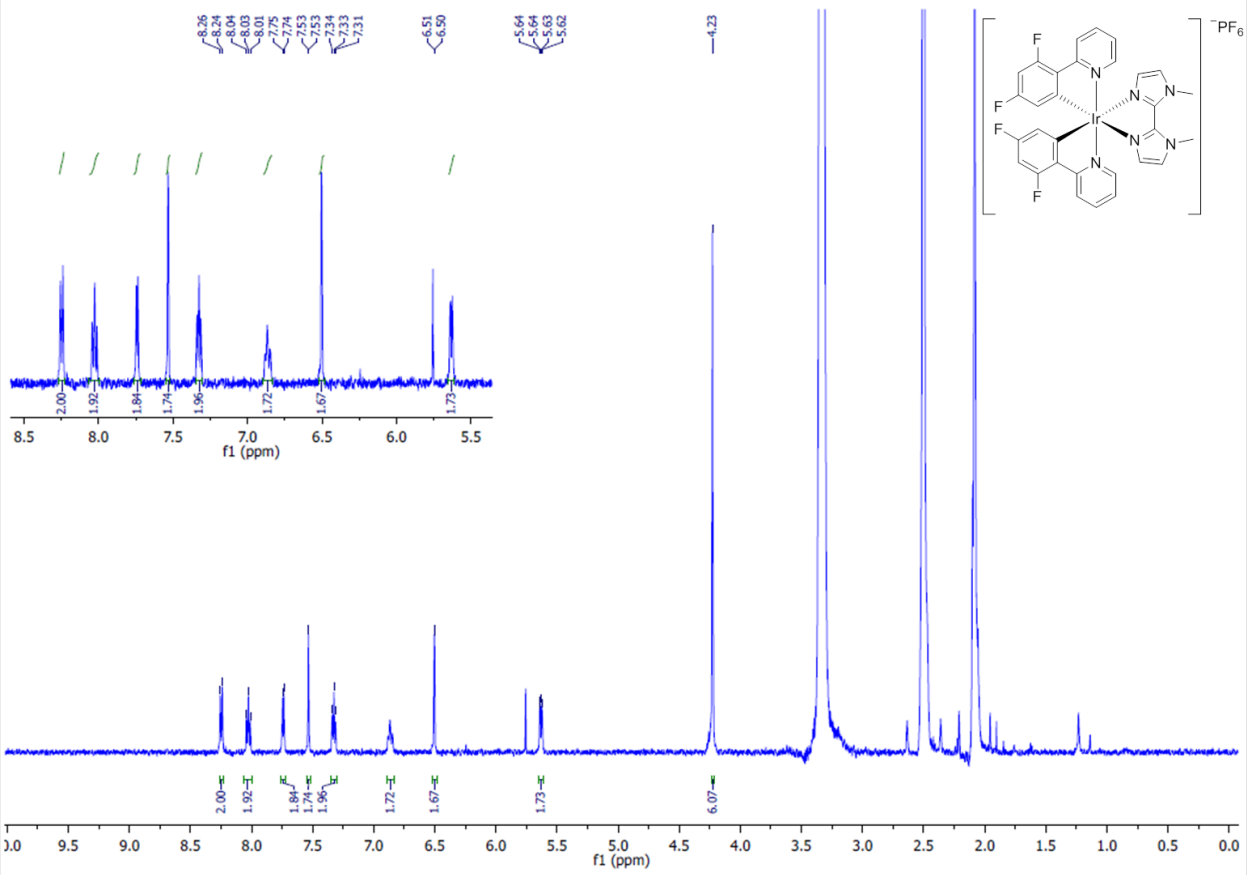

Figure **S12**. ^{1}H $\{^{19}$F$\}$ NMR spectrum of **[(dFppy)$_2$Ir(dMebiim)](PF$_6$)**, **2**, in DMSO-d_6.

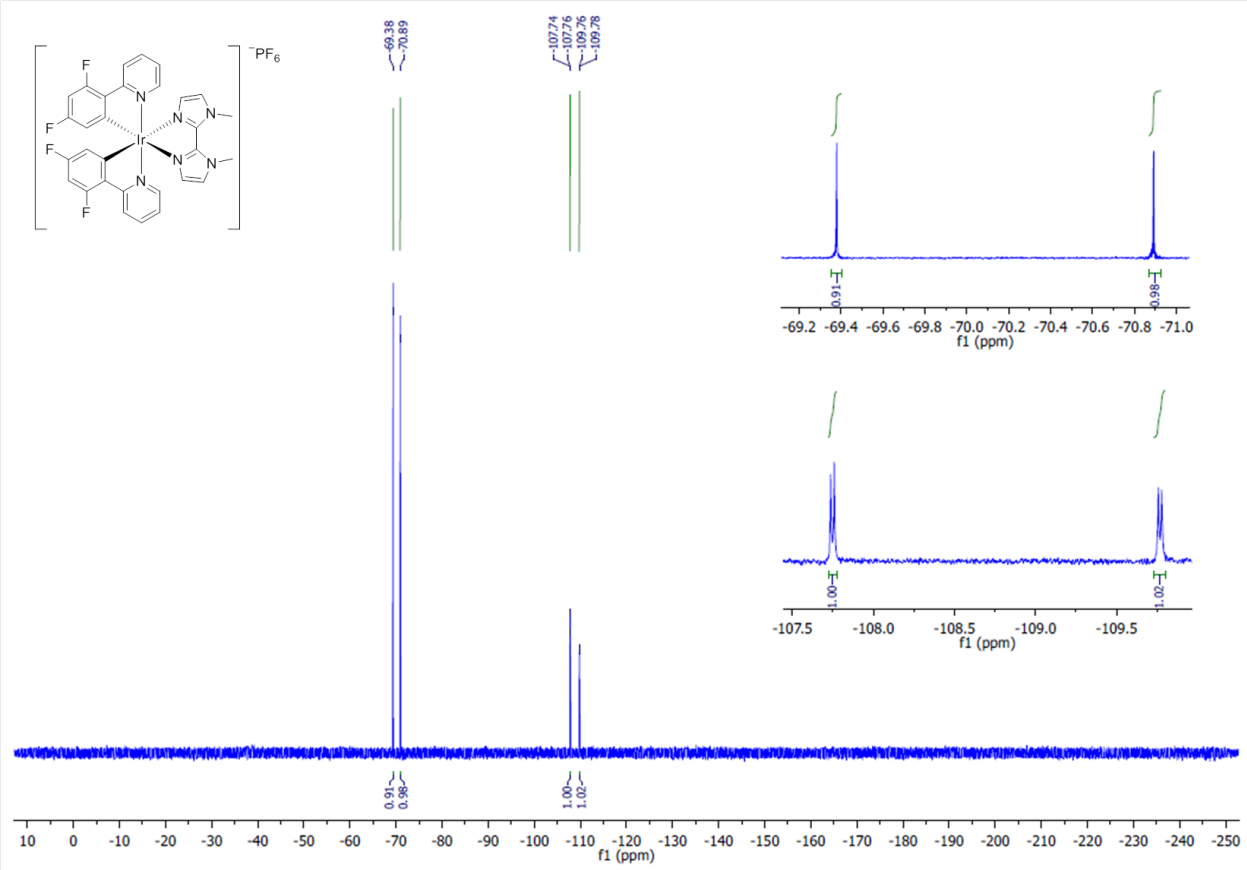

Figure **S13**. ^{19}F $\{^{1}H\}$ NMR spectrum of **[(dFppy)$_2$Ir(dMebiim)](PF$_6$)**, **2**, in DMSO-d_6.

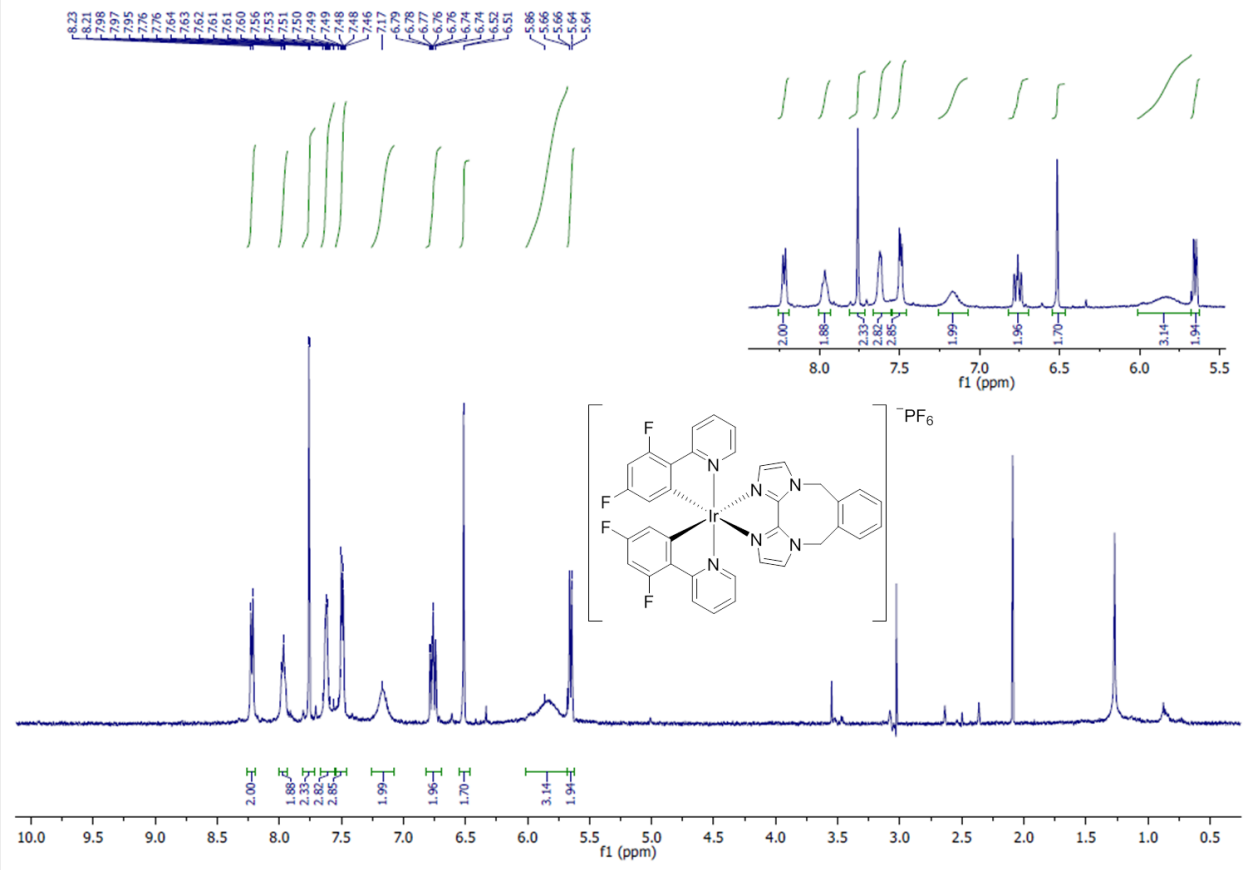

Figure **S14**. ^{1}H $\{^{19}F\}$ NMR spectrum of **[(dFppy)$_2$Ir(Xylbiim)](PF$_6$), 3**, in DMSO-d_6 at 364 K.

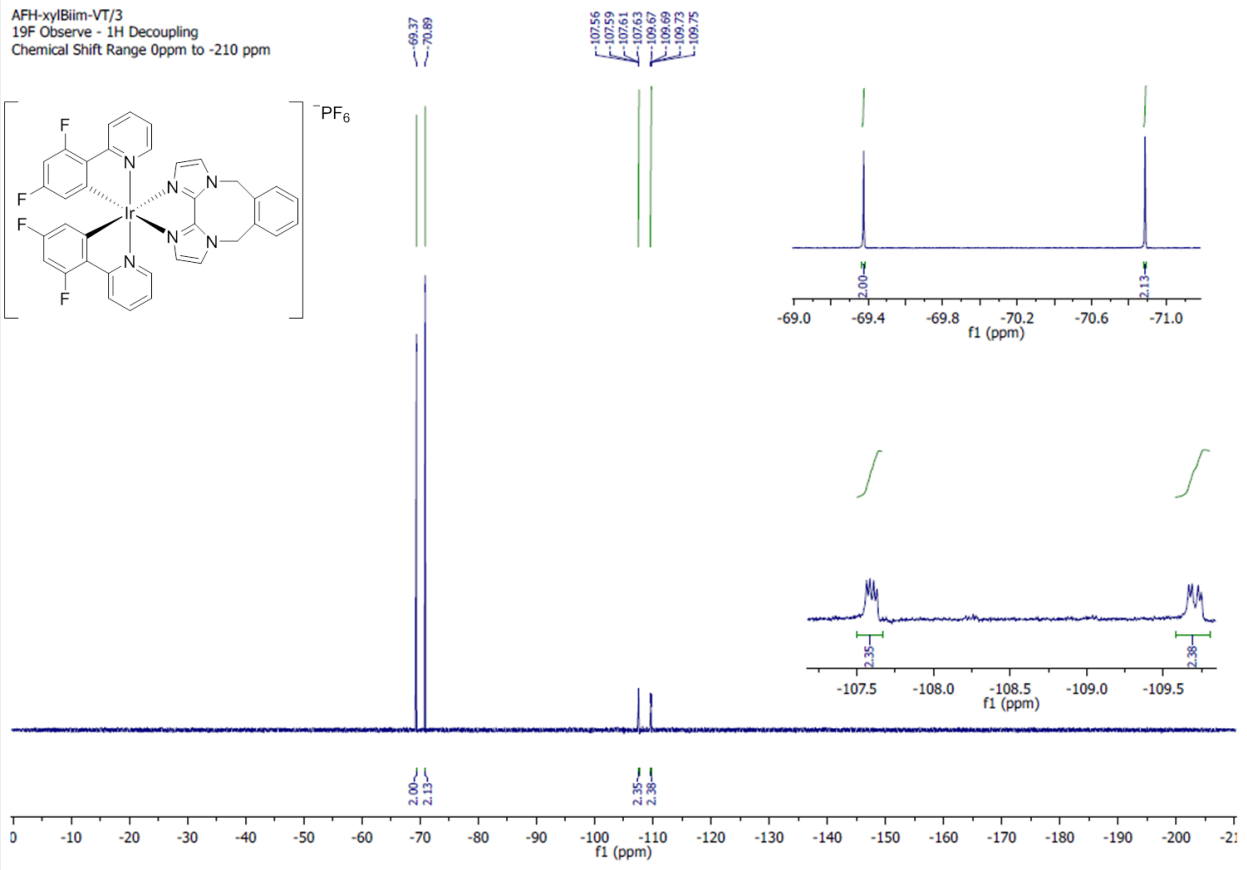

Figure **S15**. ^{19}F $\{^{1}H\}$ NMR spectrum of **[(dFppy)$_2$Ir(Xylbiim)](PF$_6$), 3**, in DMSO-d_6.

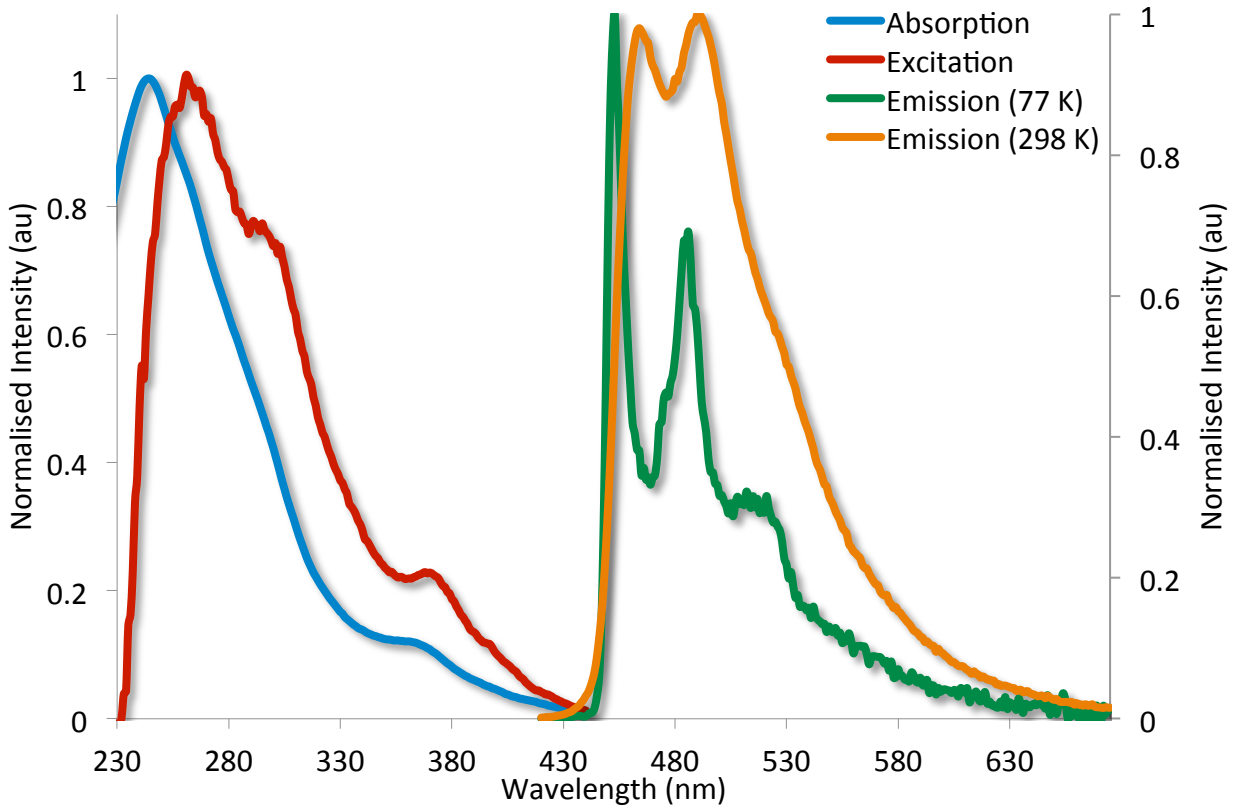

Figure **S16**. Summary of photophysical data for complex **1**, **[(dFppy)$_2$Ir(biim)](PF$_6$)**. Normalised absorption spectra in HPLC grade MeOH. Normalised excitation and 298 K emission spectra in HPLC grade MeOH. Normalised 77 K emission spectra, in 1:1 MeOH/EtOH glass.

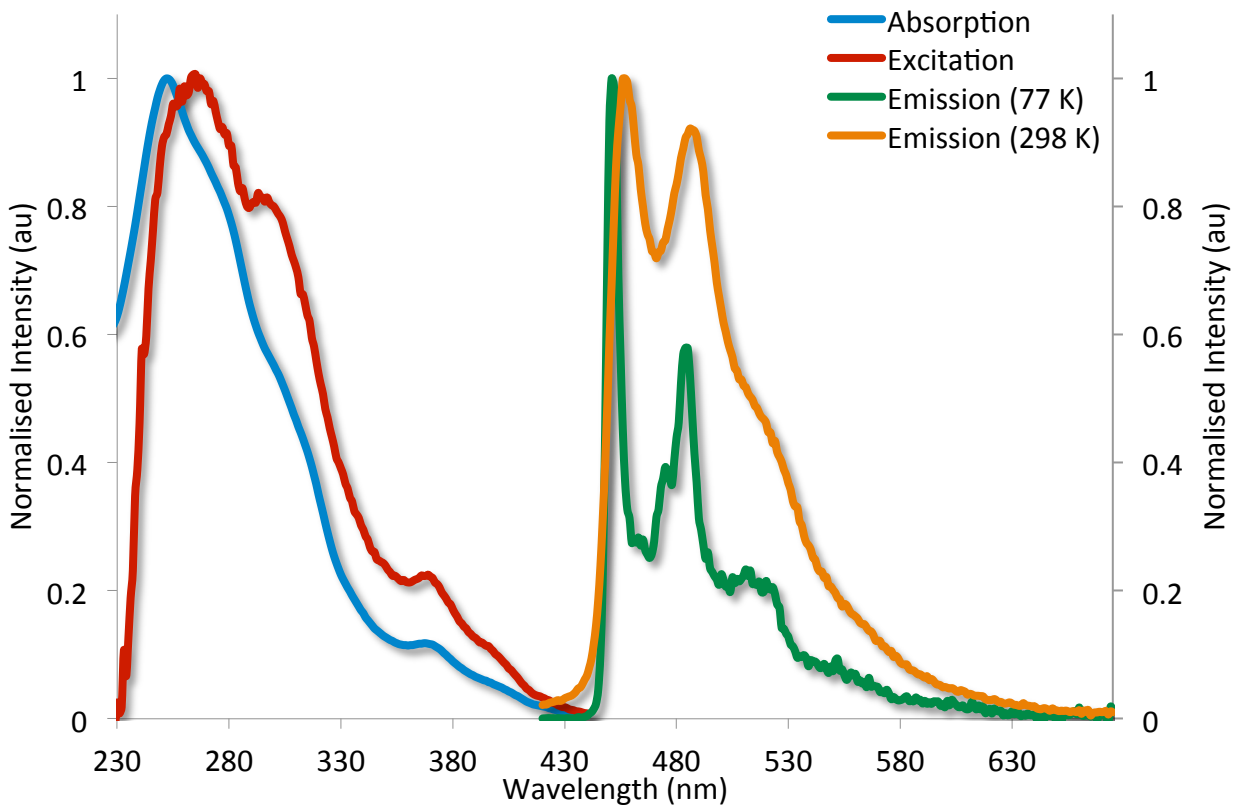

Figure **S17**. Summary of photophysical data for complex **2**, **[(dFppy)$_2$Ir(dMebiim)](PF$_6$)**. Normalised absorption spectra in HPLC grade MeOH. Normalised excitation and 298 K emission spectra in HPLC grade MeOH. Normalised 77 K emission spectra, in 1:1 MeOH/EtOH glass.

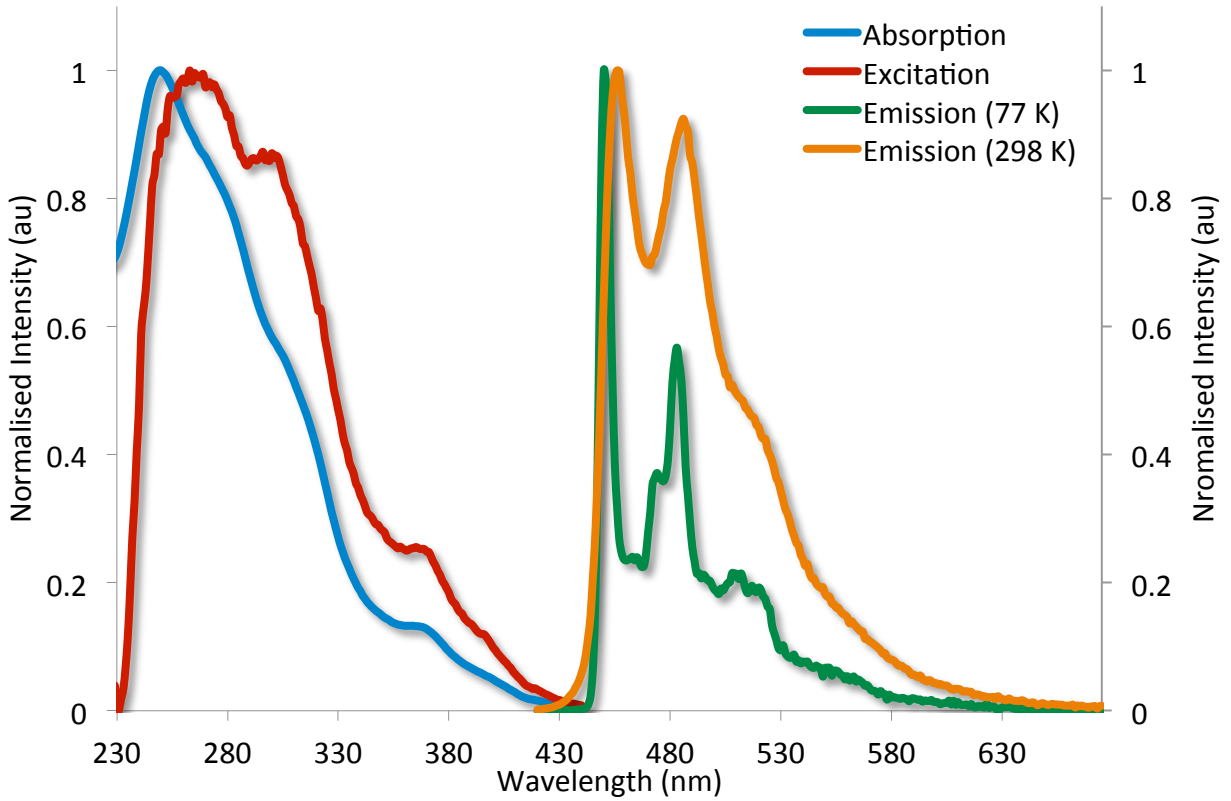

Figure **S18**. Summary of photophysical data for complex **3**, **[(dFppy)$_2$Ir(Xylbiim)](PF$_6$)**. Normalised absorption spectra in HPLC grade MeOH. Normalised excitation and 298 K emission spectra in HPLC grade MeOH. Normalised 77 K emission spectra, in 1:1 MeOH/EtOH glass.

Table **S1**: Summary of molar absorptivities for complexes **1** – **3**. [a]

Compound	Absorption at 298 K [Molar Absorptivities ($\times 10^4$ M^{-1} cm^{-1})] [a]
1	245 [3.5], 264 [2.7], 300 [1.4], 365 [0.3], 420 [0.05], 445 [0.01]
2	253 [3.1], 279* [2.6], 303* [1.7], 316* [1.3], 370 [0.4], 422* [0.07], 450 [0.02]
3	251 [4.0], 279* [3.2], 314* [1.8], 368* [0.5], 420 [0.07], 450 [0.02]

[a] All measurements performed in HPLC grade MeOH

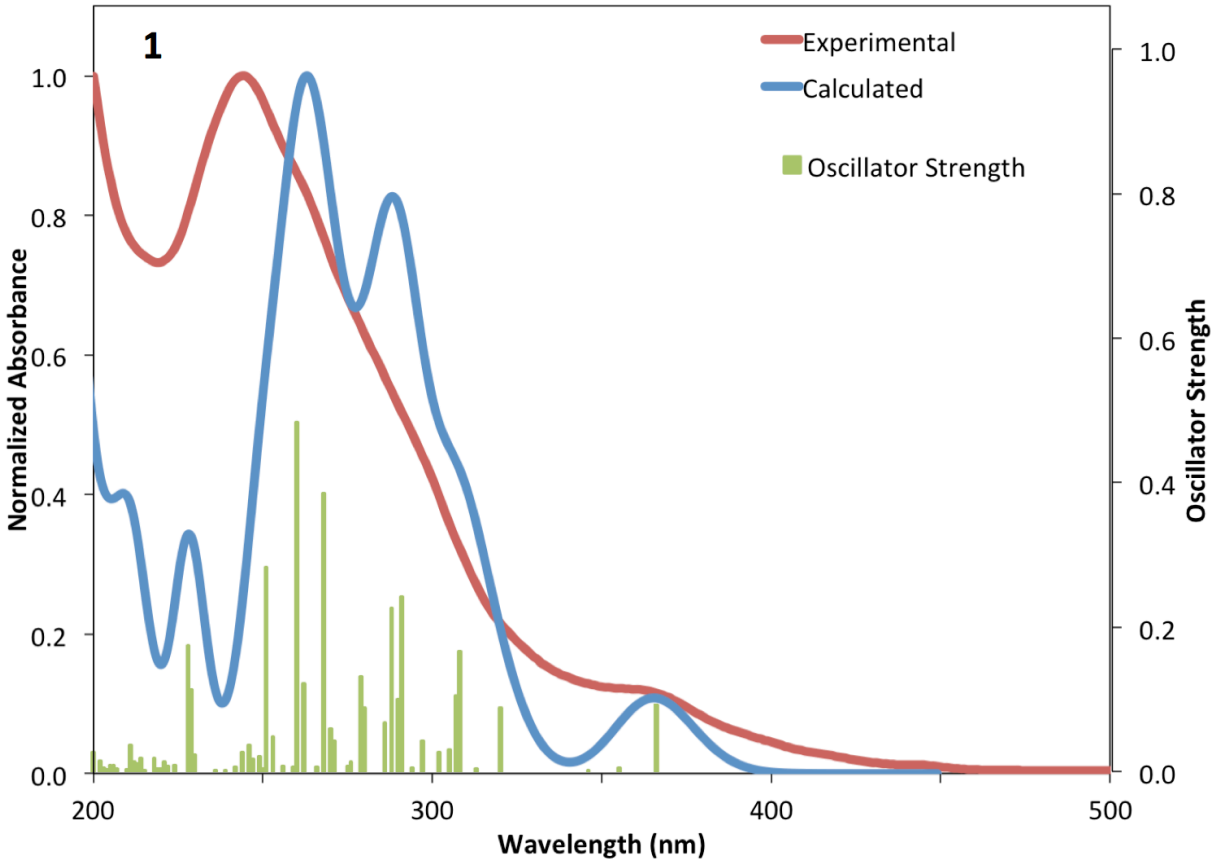

Figure **S19**. Experimental (red) and calculated UV-Vis spectrum (blue – fwhm = 1000 cm^{-1}) obtained from TDDFT calculations with the corresponding vertical excitations (green) for **1**.

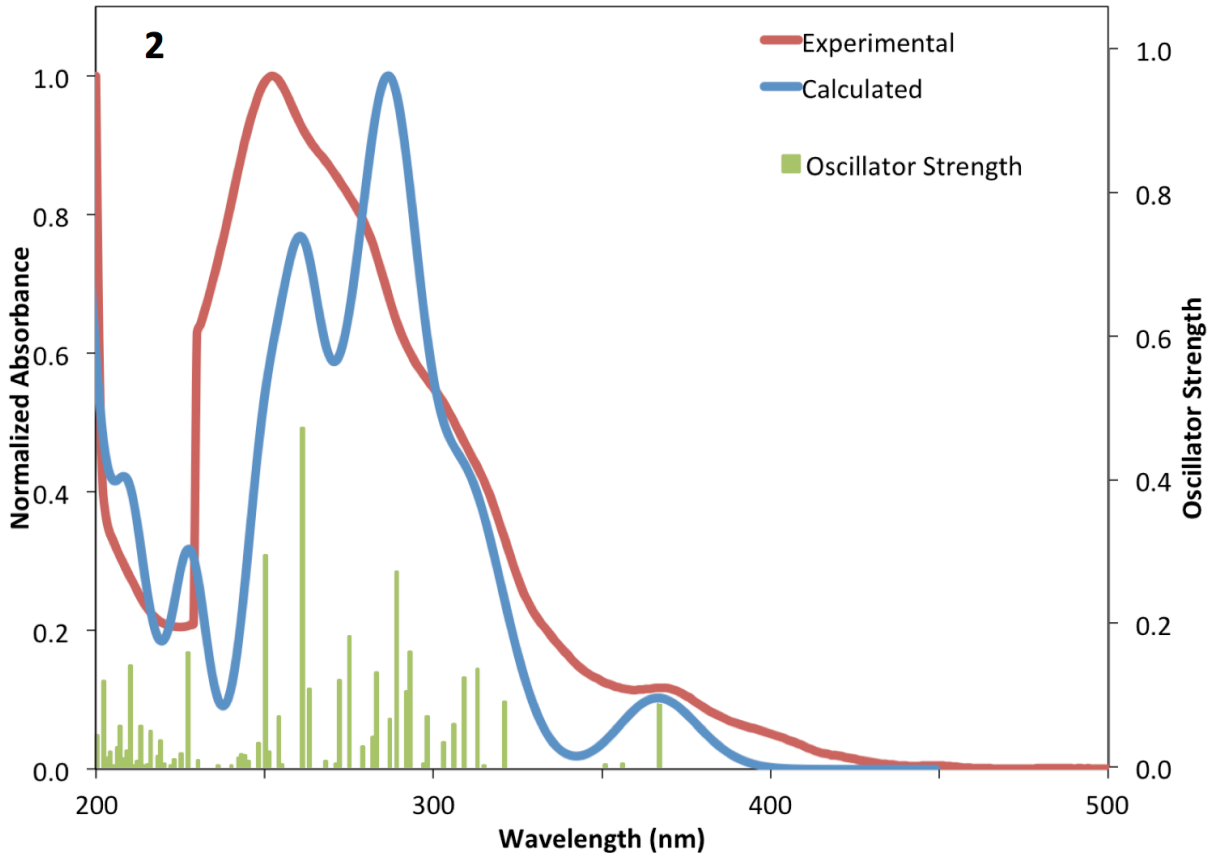

Figure **S20**. Experimental (red) and calculated UV-Vis spectrum (blue – fwhm = 1000 cm^{-1}) obtained from TDDFT calculations with the corresponding vertical excitations (green) for **1**.

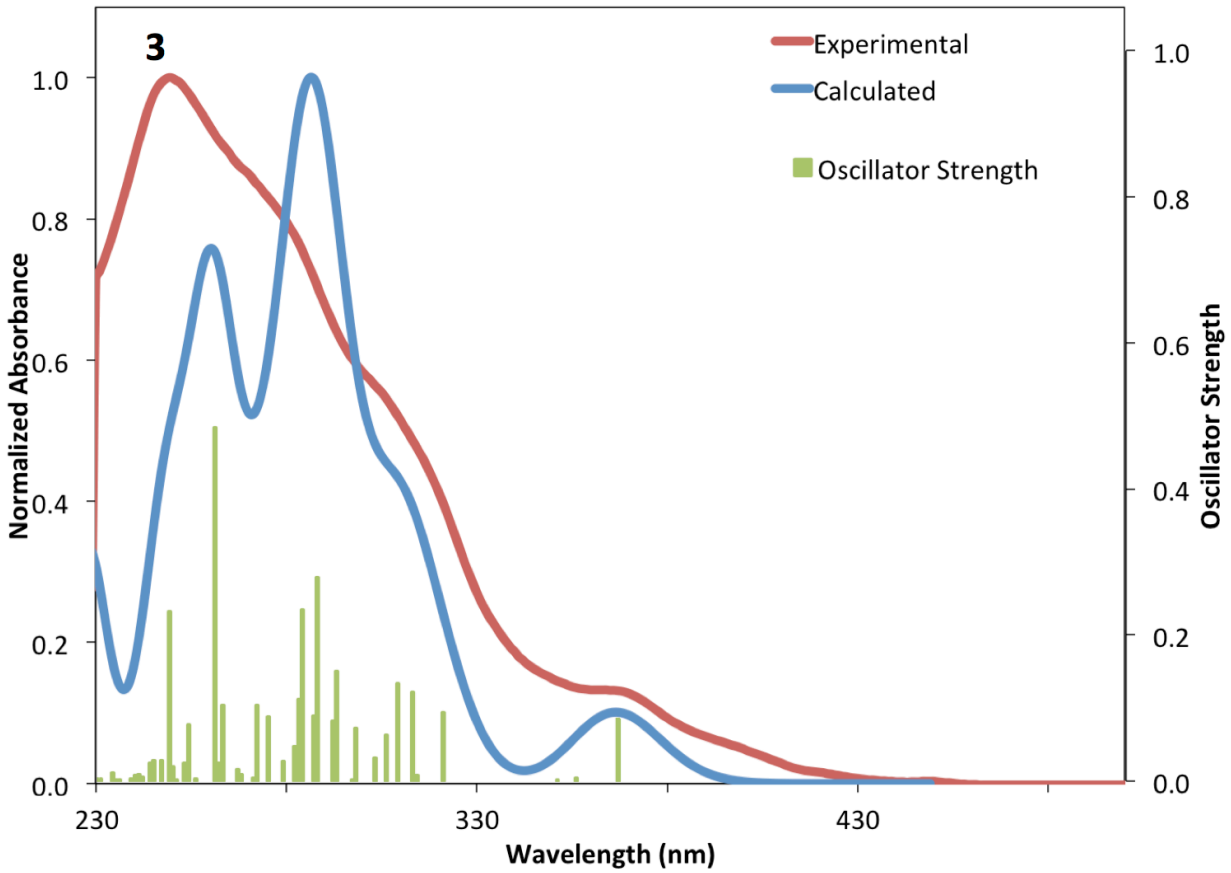

Figure **S21**. Experimental (red) and calculated UV-Vis spectrum (blue – fwhm = 1000 cm^{-1}) obtained from TDDFT calculations with the corresponding vertical excitations (green) for **1**.