

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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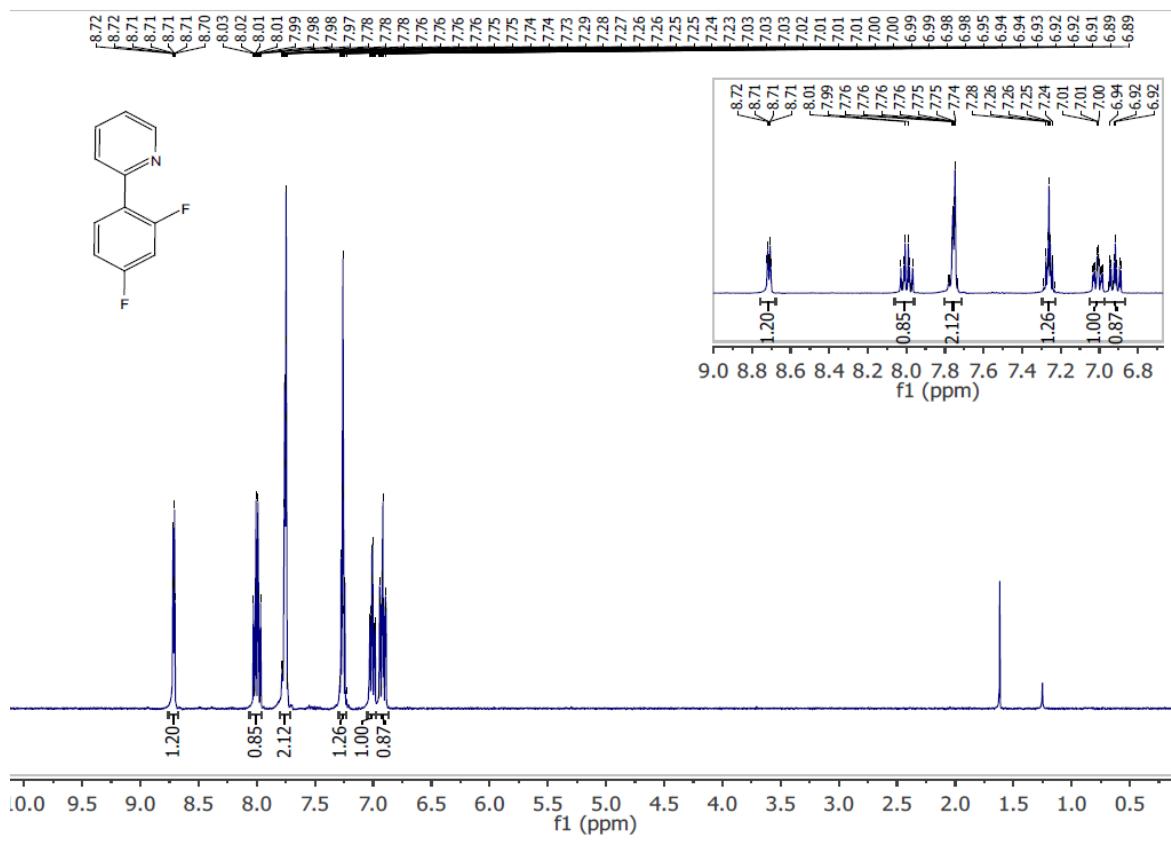


Figure S1. ^1H NMR spectrum of **2-(2,4-Difluorophenyl)pyridine (dFppy)** in CDCl_3 .

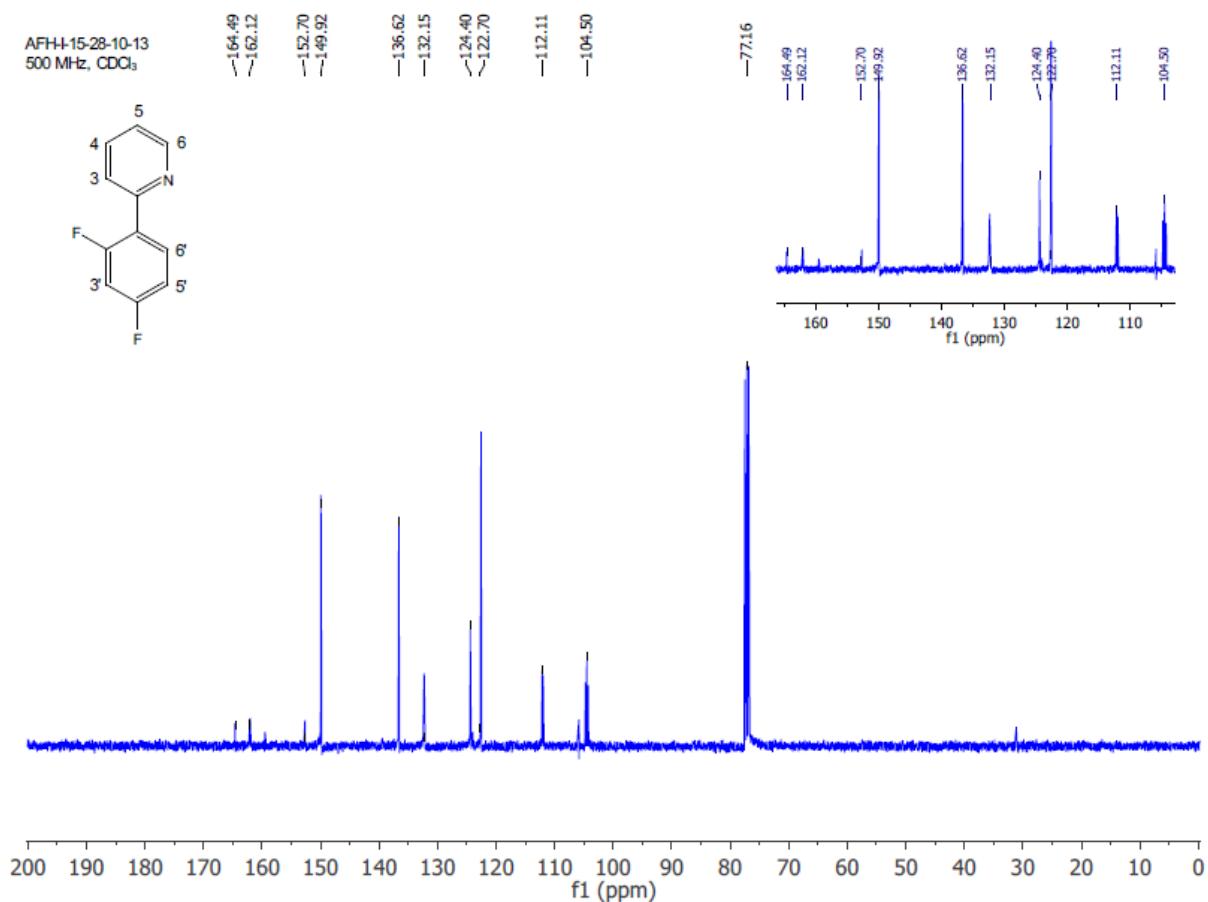


Figure S2. ^{13}C NMR spectrum of 2-(2,4-Difluorophenyl)pyridine (**dFppy**) in CDCl_3 .

11062013-6-ezc-afh7-A.10.fld
19F Observe with 1H decoupling - Full Range SW
AFH-28-10-13-I-15
500 MHz, CDCl₃

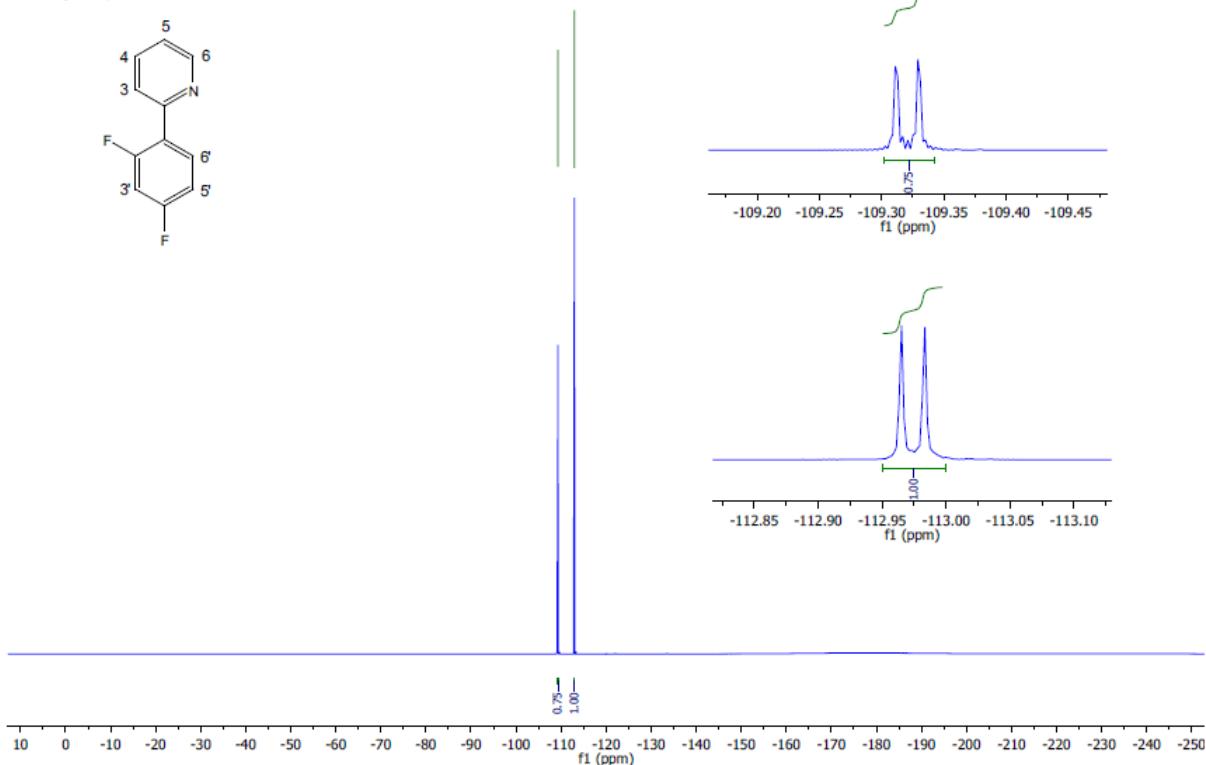


Figure S3. ^{19}F { ^1H } NMR spectrum of 2-(2,4-Difluorophenyl)pyridine (dFppy) in CDCl₃.

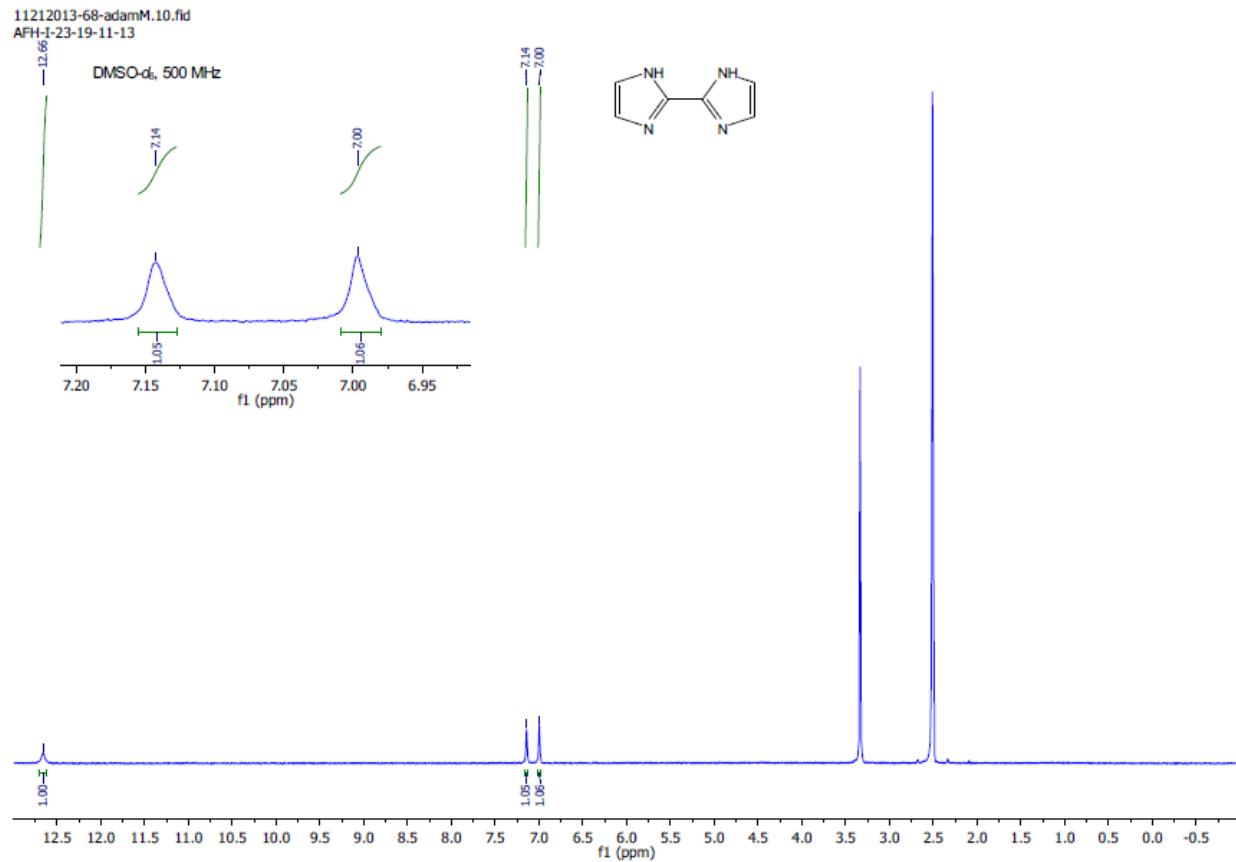


Figure S4. ¹H NMR spectrum of **1H,1'H-2,2'-biimidazole (biim)** in DMSO-*d*₆.

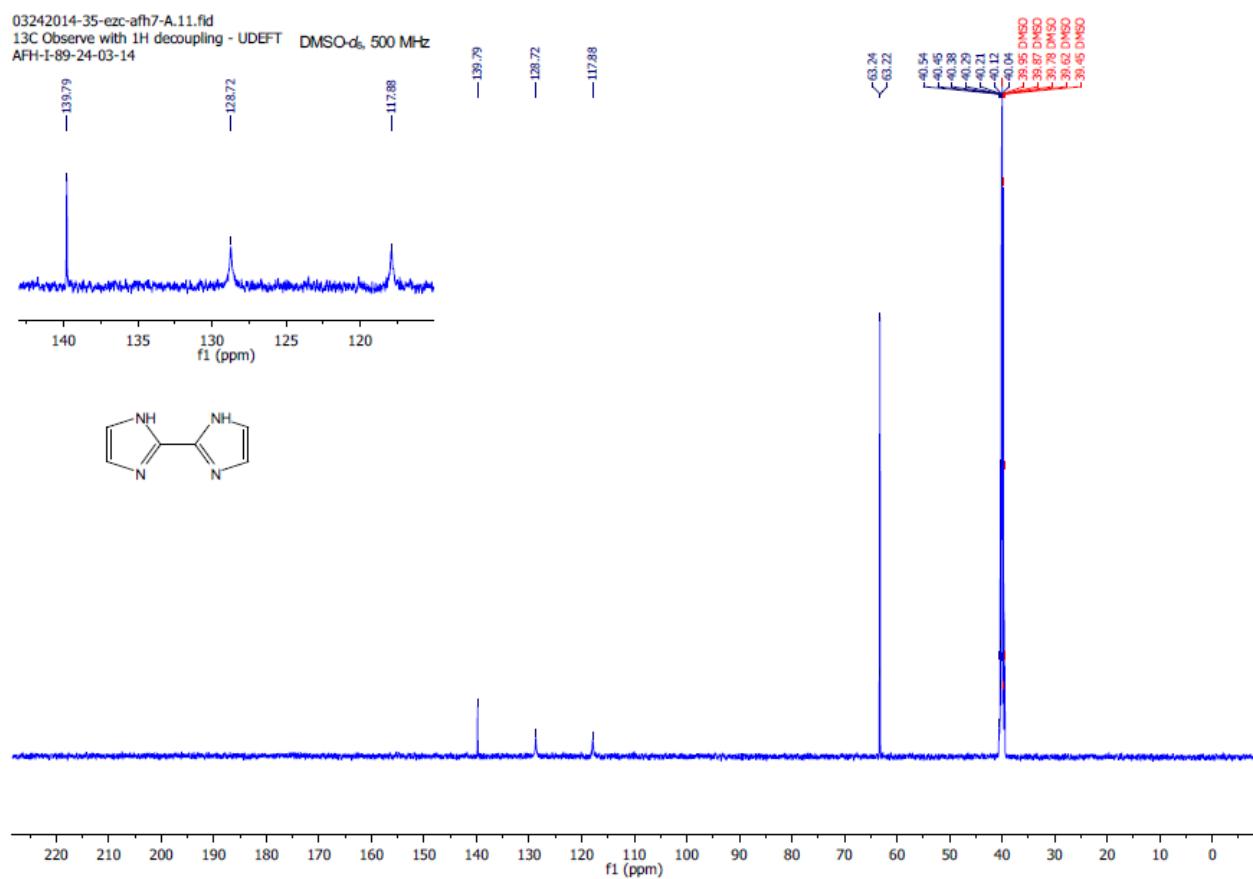


Figure S5. ¹³C NMR spectrum of **1H,1'H-2,2'-biimidazole (biim)** in DMSO-*d*₆.

03302014-46-ezc-afh7-A.10.fid
1H Observe
AFH-I-93-24-03-14

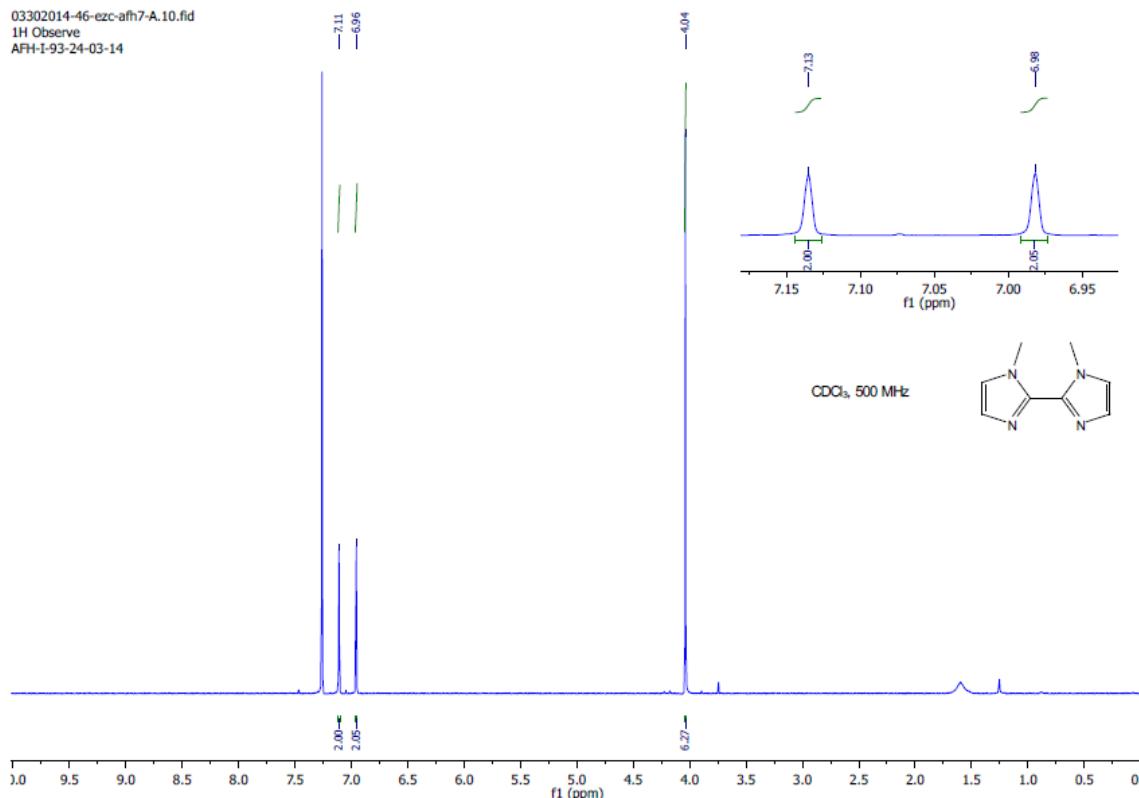


Figure S6. ¹H NMR spectrum of **1,1'-Dimethyl-2,2'-biimidazole (dMebiim)** in CDCl₃.

03302014-46-ezc-afh7-A.11.fid
13C Observe with 1H decoupling - UDEFT
AFH-I-93-24-03-14

— 127.99 —
— 122.77 —
— 35.52 —

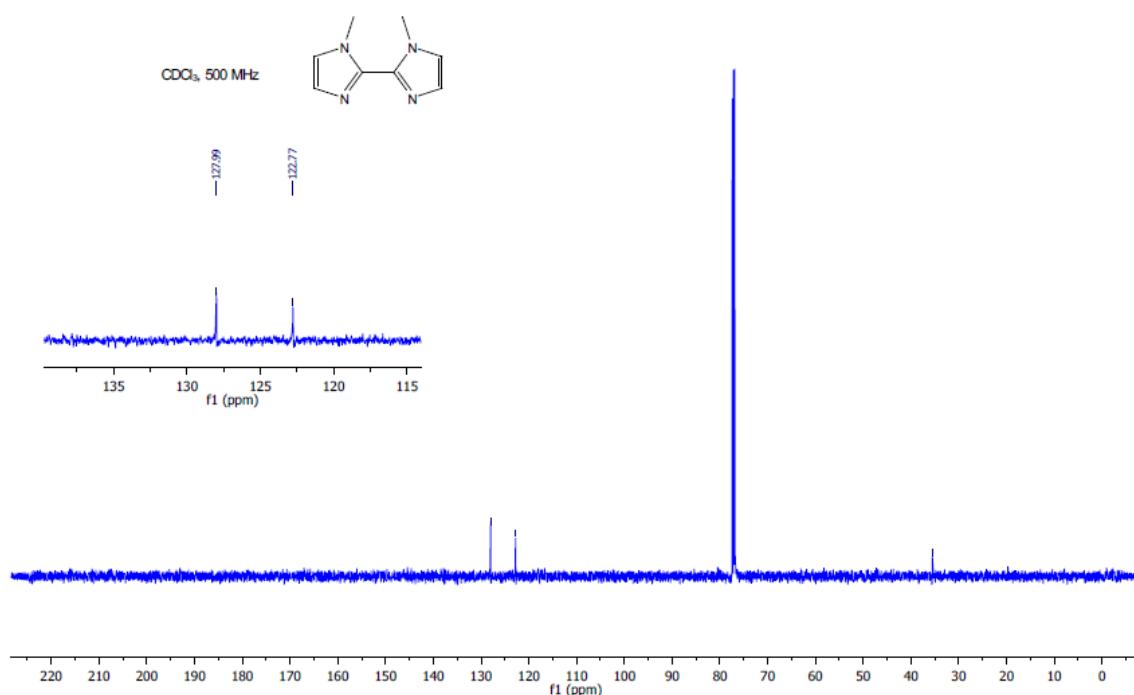


Figure S7. ¹³C NMR spectrum of **1,1'-Dimethyl-2,2'-biimidazole (dMebiim)** in CDCl₃.

10282013-21-ezc-afh7-A.10.fid
1H Observe
AFH-22-10-13-I-11
500 MHz, DMSO-d6

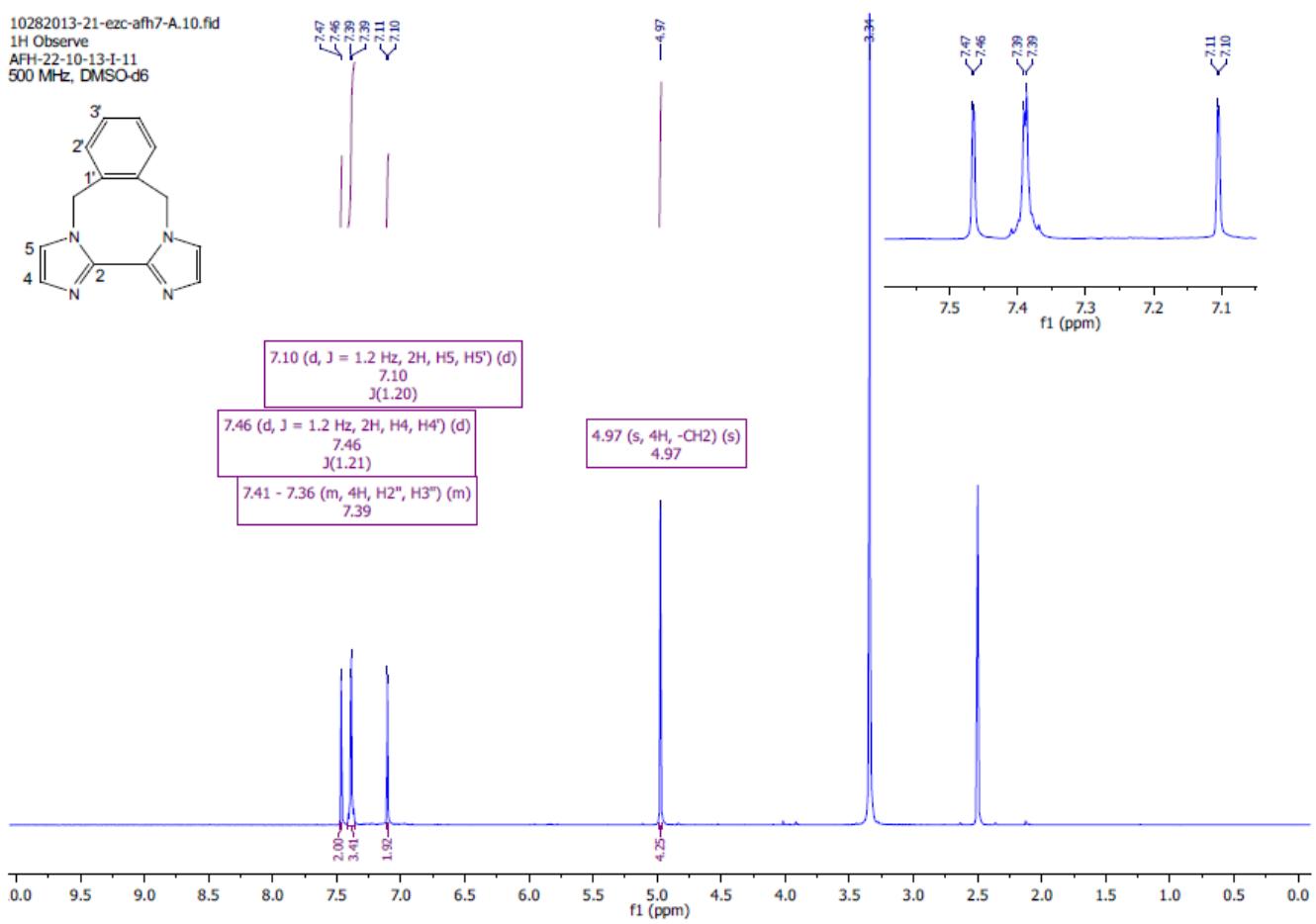
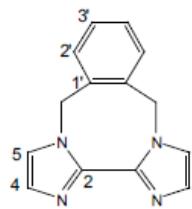


Figure S8. ¹H NMR spectrum of 1,1'-(a,a'-o-Xylylene)-2,2'-biimidazole (*o*Xylbiim) in DMSO-*d*₆.

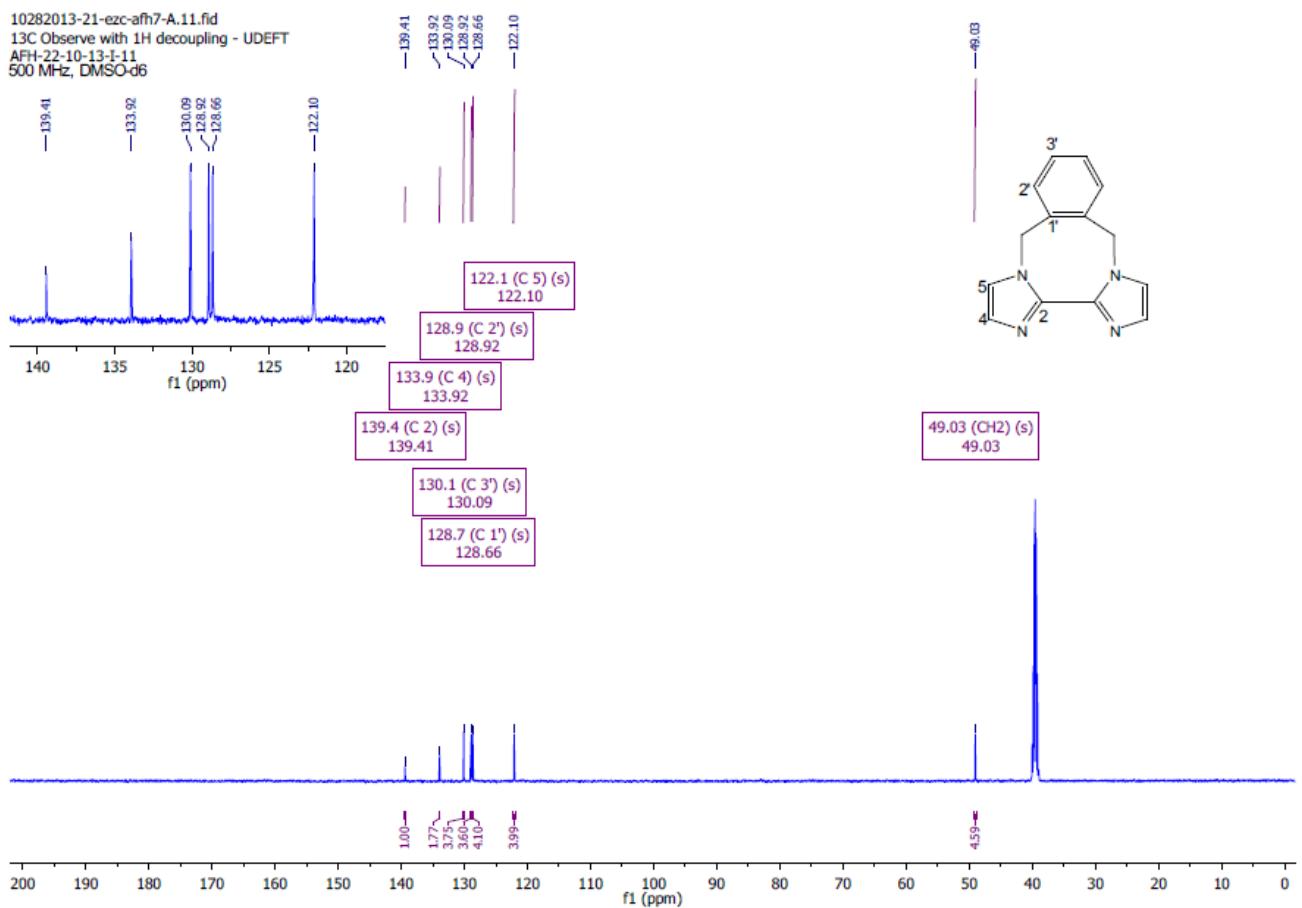


Figure S9. ^{13}C NMR spectrum of 1,1'-(α,α' -*o*-Xylylene)-2,2'-biimidazole (*o*Xylbiim) in DMSO-*d*₆.

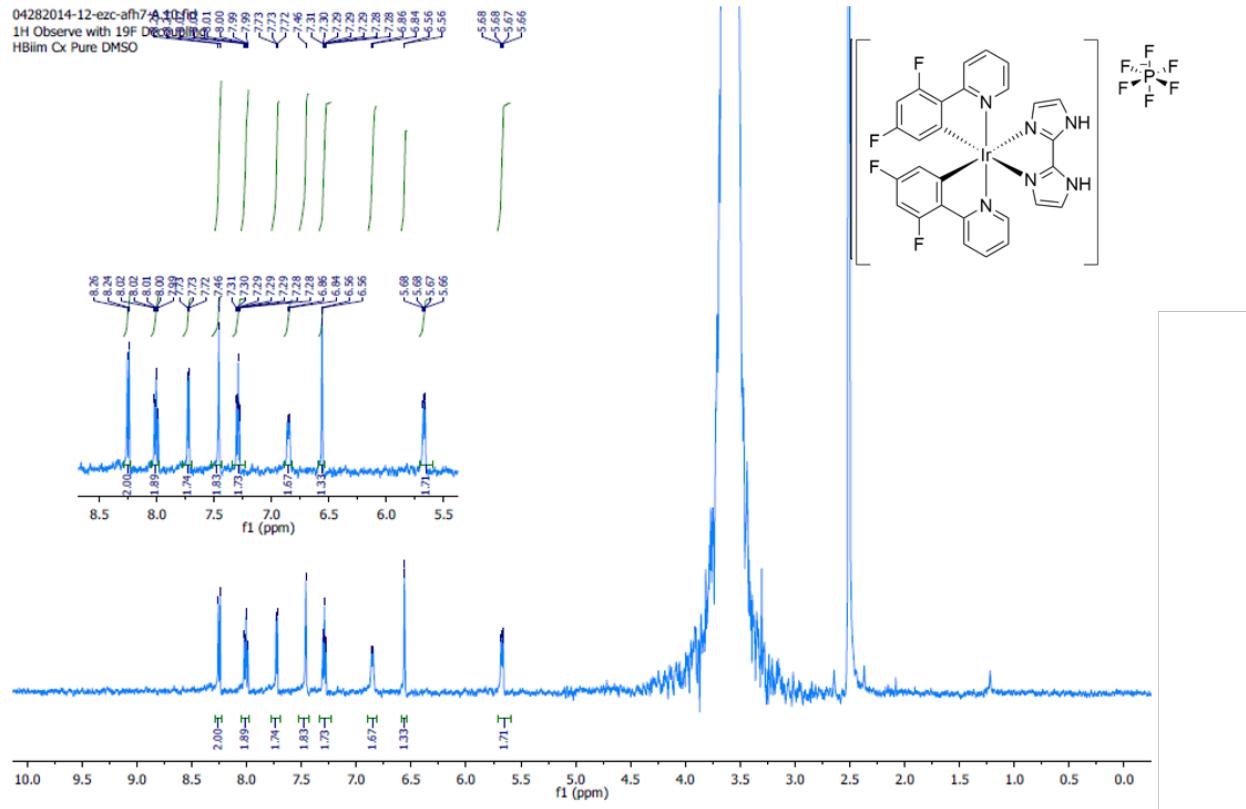


Figure S10. ^1H { ^{19}F } NMR spectrum of $[(\text{dFppy})_2\text{Ir}(\text{biim})](\text{PF}_6)$, 1, in $\text{DMSO}-d_6$.

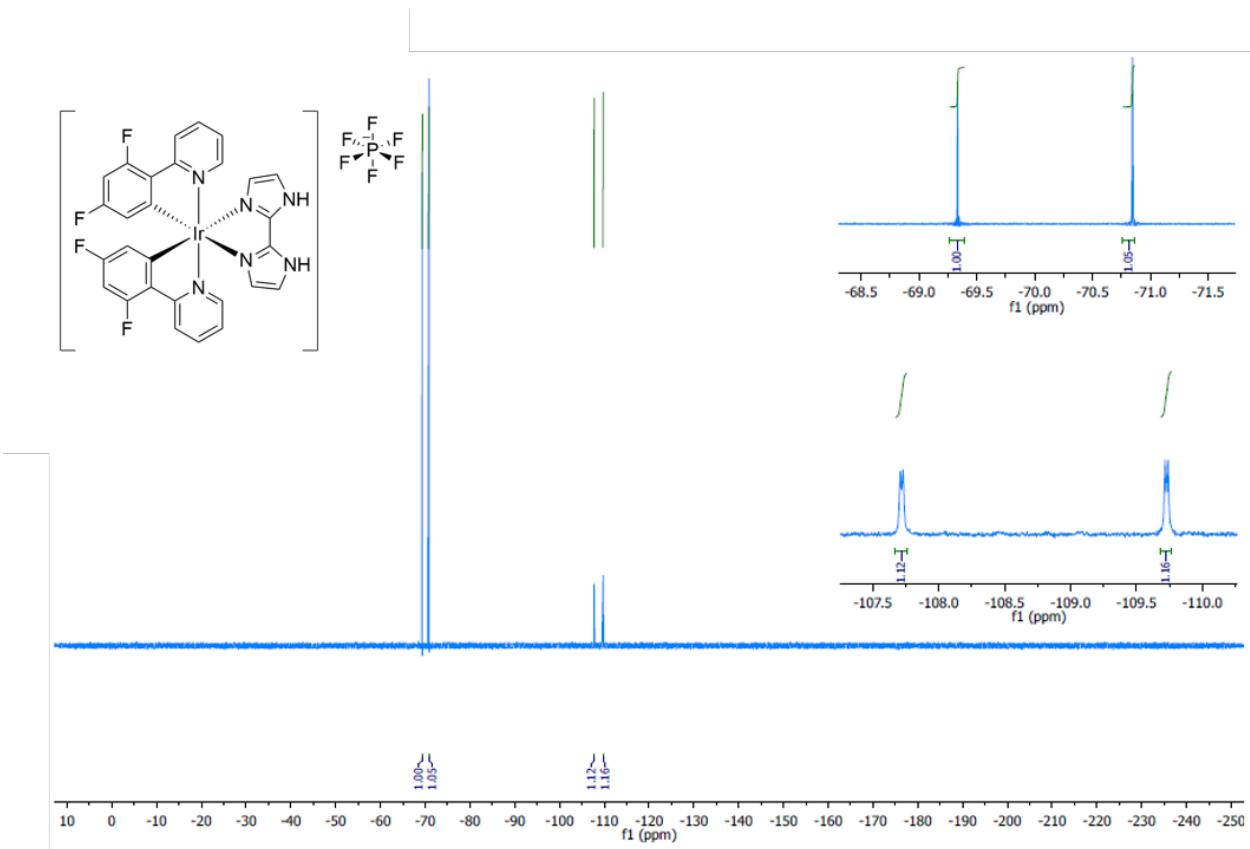


Figure S11. ^{19}F $\{\text{H}\}$ NMR spectrum of $[(\text{dFppy})_2\text{Ir}(\text{biim})](\text{PF}_6)$, **1**, in $\text{DMSO}-d_6$.

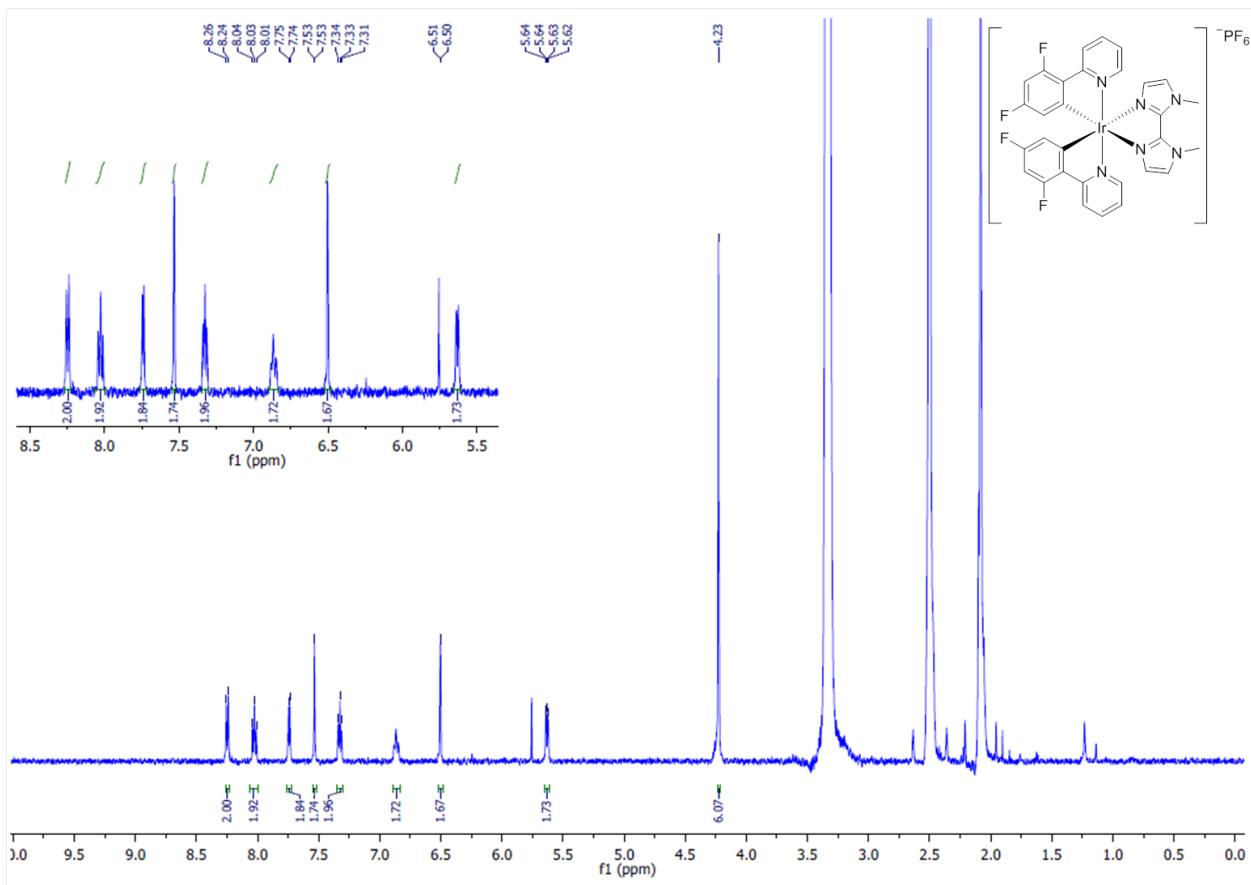


Figure S12. ^1H { ^{19}F } NMR spectrum of $[(\text{dFppy})_2\text{Ir}(\text{dMebiim})](\text{PF}_6)$, 2, in $\text{DMSO}-d_6$.

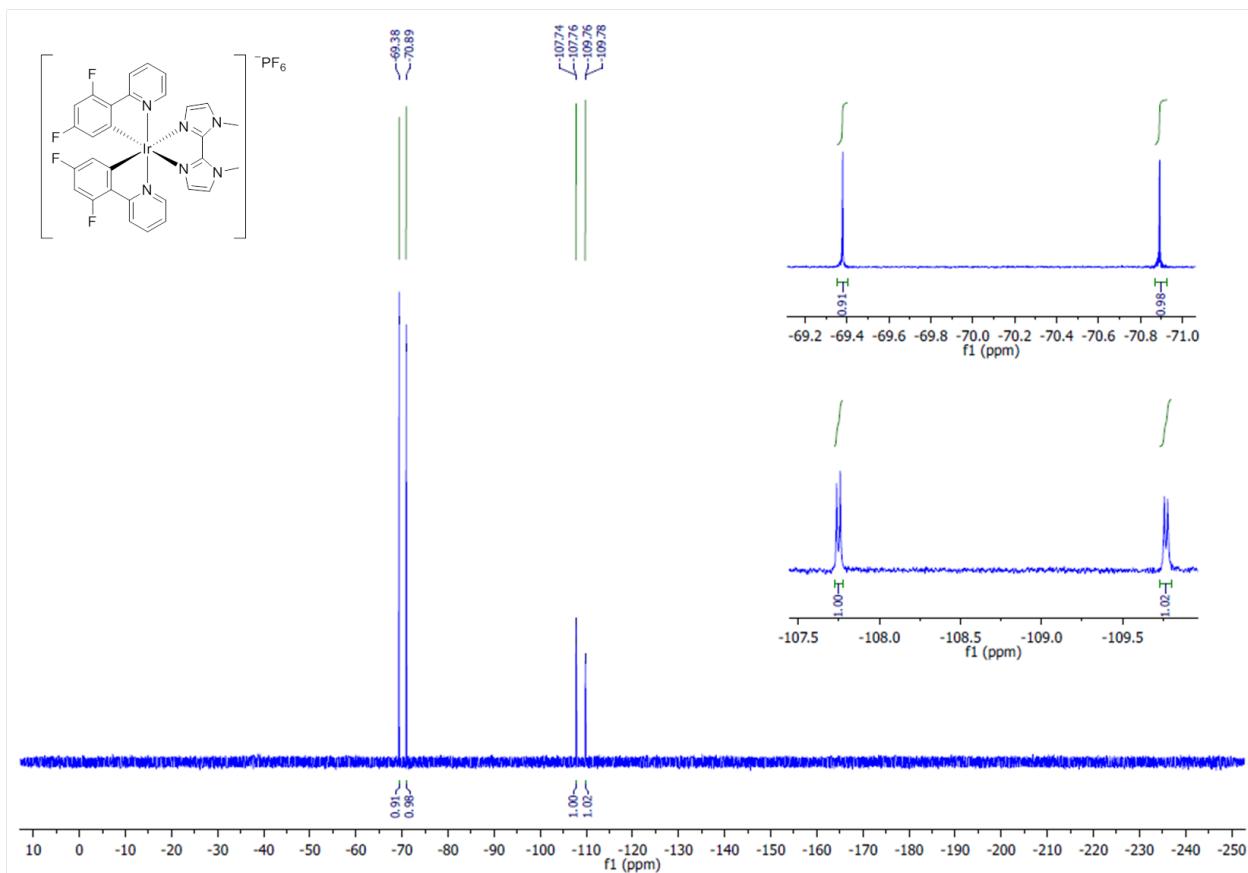


Figure S13. ^{19}F $\{^1\text{H}\}$ NMR spectrum of $[(\text{dFppy})_2\text{Ir}(\text{dMebium})](\text{PF}_6)$, **2**, in $\text{DMSO}-d_6$.

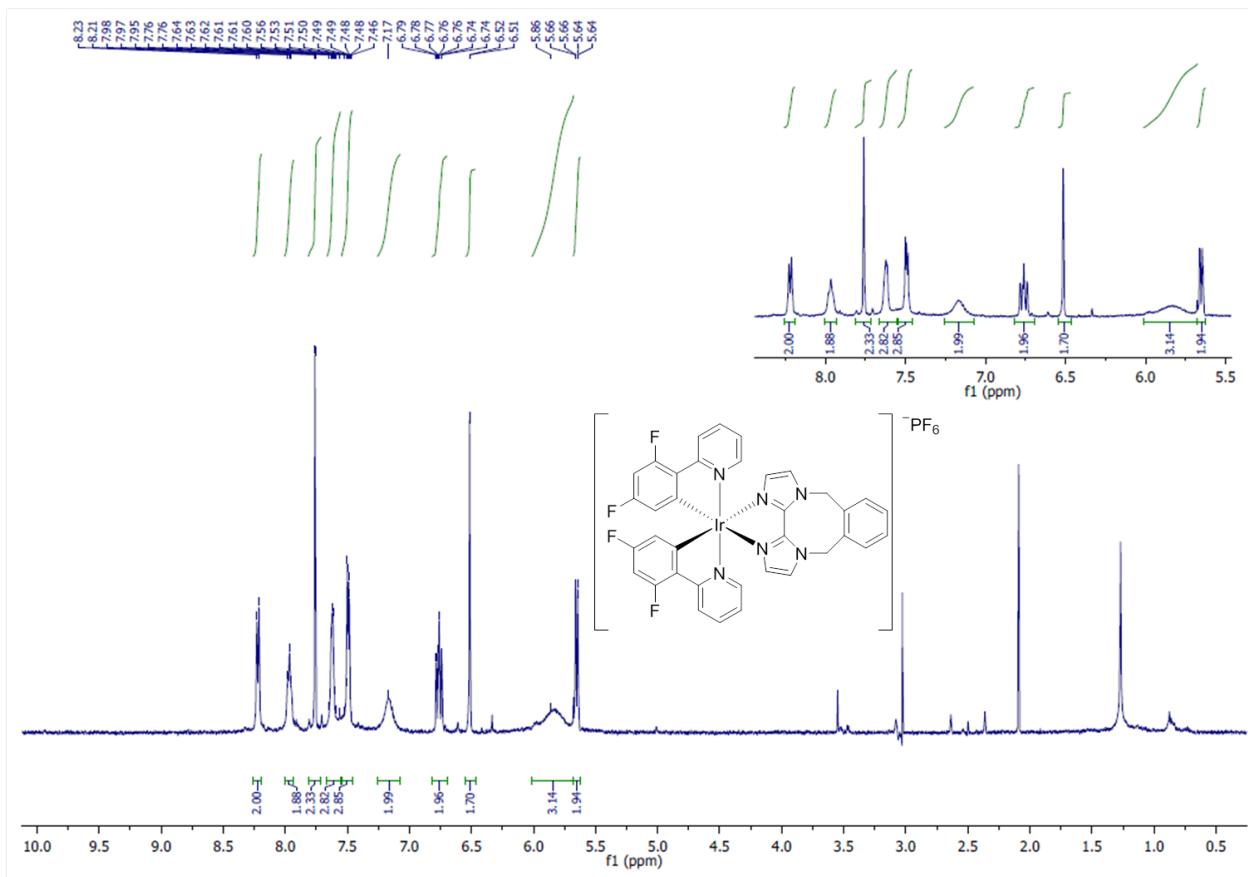


Figure S14. ^1H { ^{19}F } NMR spectrum of $[(\text{dFppy})_2\text{Ir}(\text{Xylbiim})](\text{PF}_6)$, 3, in $\text{DMSO}-d_6$ at 364 K.

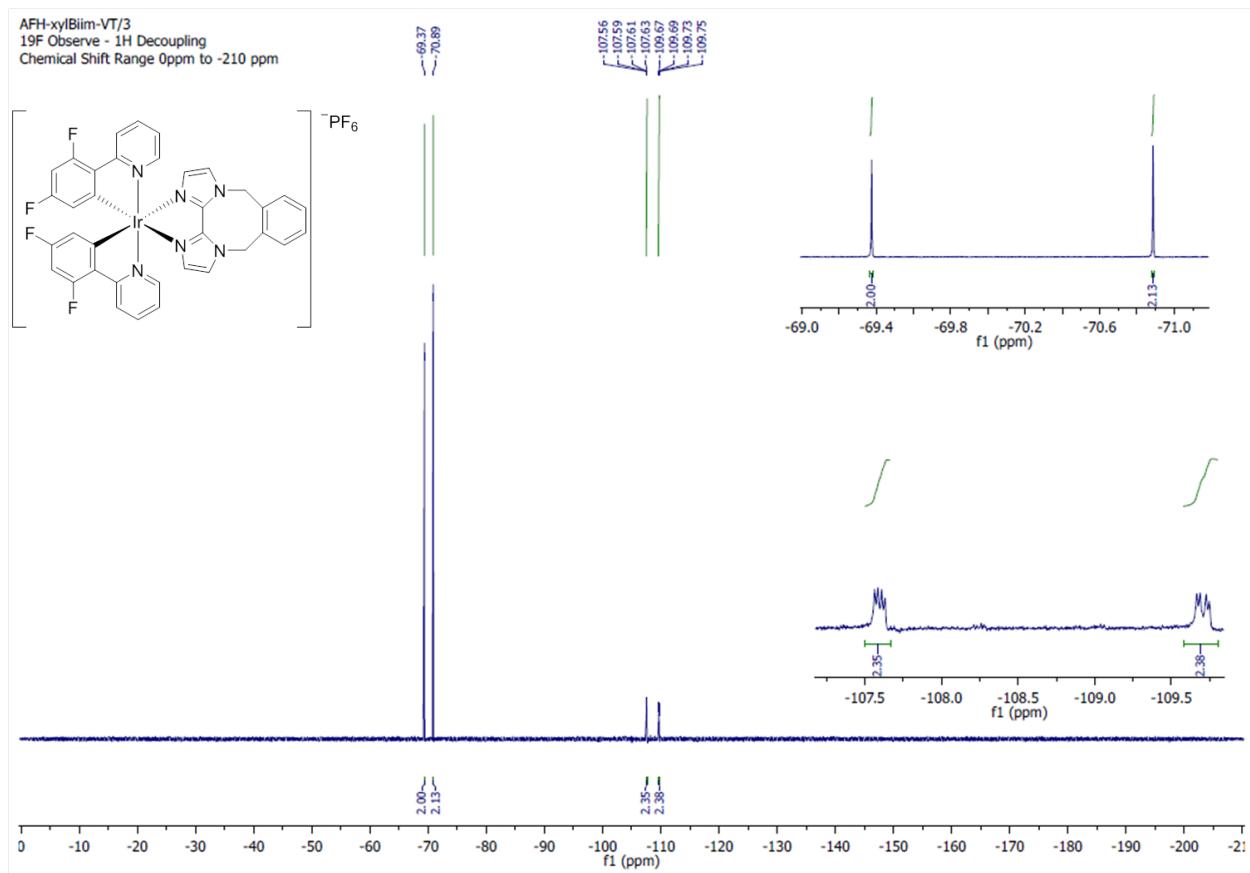


Figure S15. ^{19}F { ^1H } NMR spectrum of $[(\text{dFppy})_2\text{Ir}(\text{Xylbiim})](\text{PF}_6)$, 3, in $\text{DMSO}-d_6$.

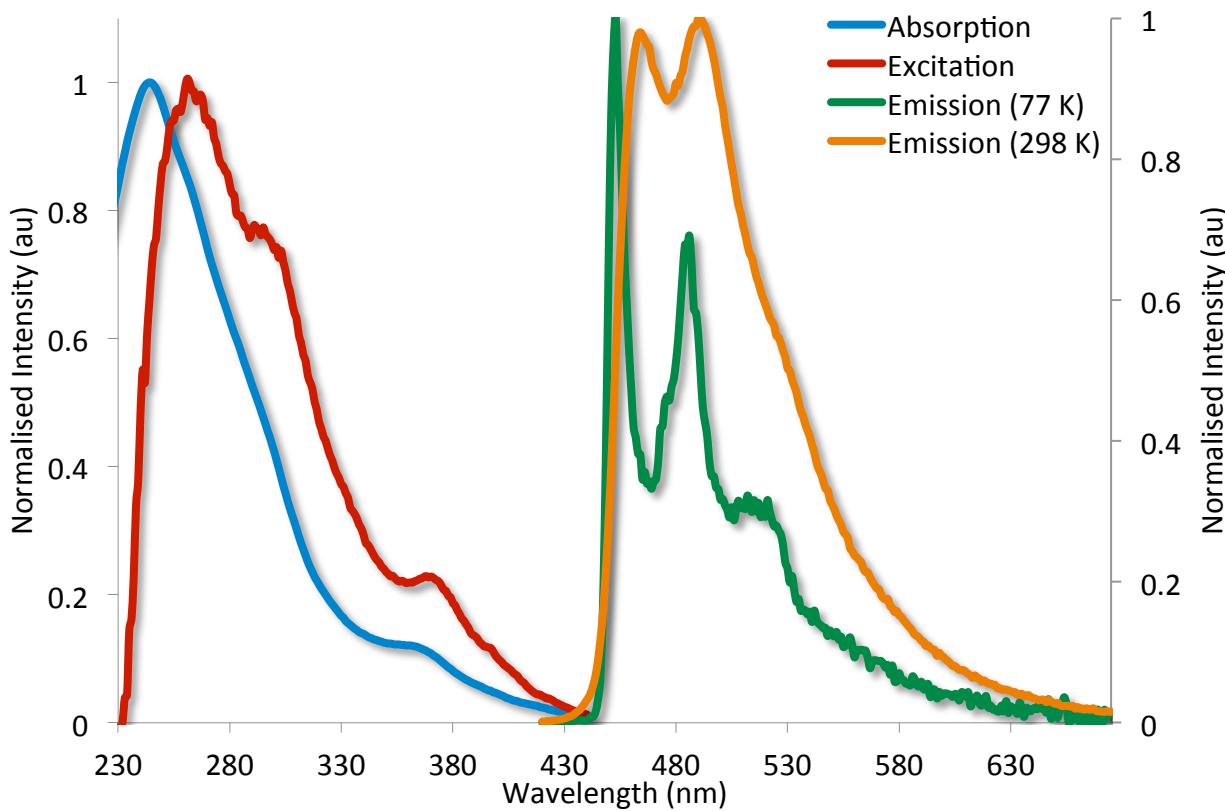


Figure S16. Summary of photophysical data for complex **1**, $[(\text{dFppy})_2\text{Ir}(\text{biim})](\text{PF}_6)$. Normalised absorption spectra in HPLC grade MeOH. Normalised excitation and 298 K emission spectra in HPLC grade MeOH. Normalised 77 K emission spectra, in 1:1 MeOH/EtOH glass.

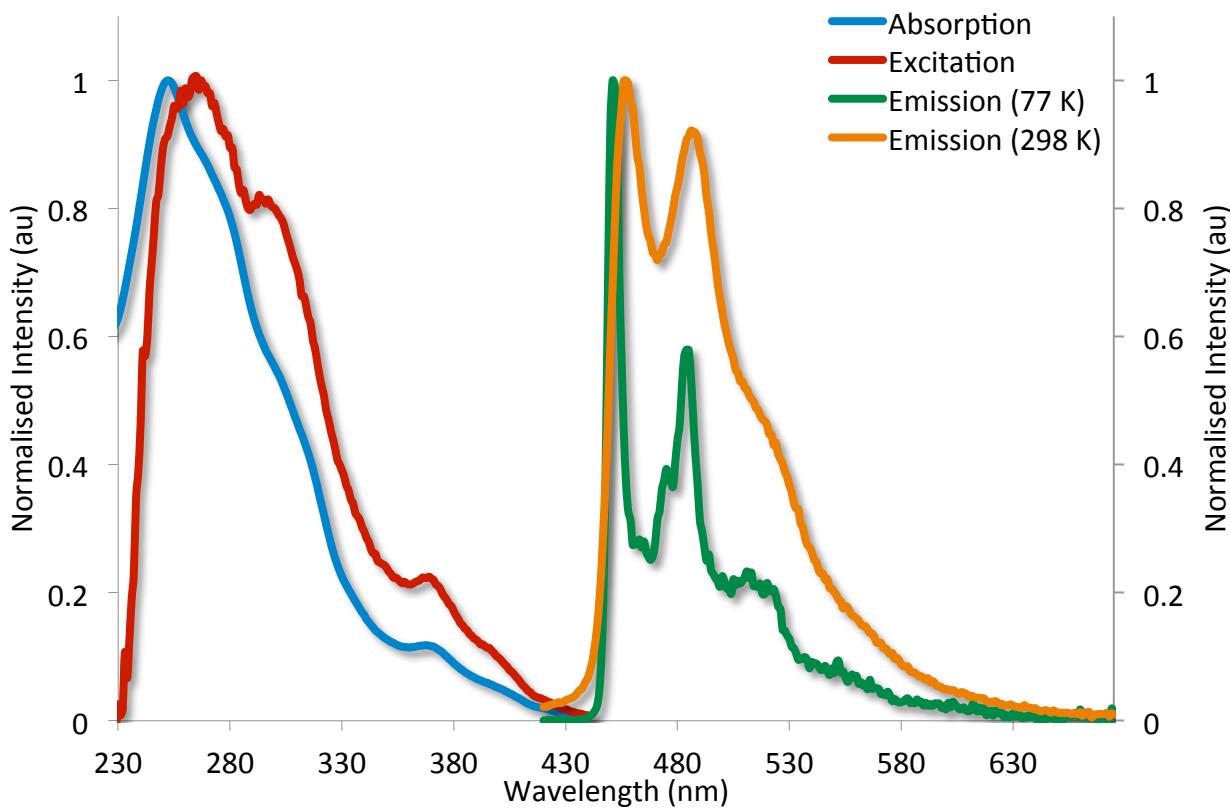


Figure S17. Summary of photophysical data for complex **2**, $[(\text{dFppy})_2\text{Ir}(\text{dMebiim})](\text{PF}_6)$. Normalised absorption spectra in HPLC grade MeOH. Normalised excitation and 298 K emission spectra in HPLC grade MeOH. Normalised 77 K emission spectra, in 1:1 MeOH/EtOH glass.

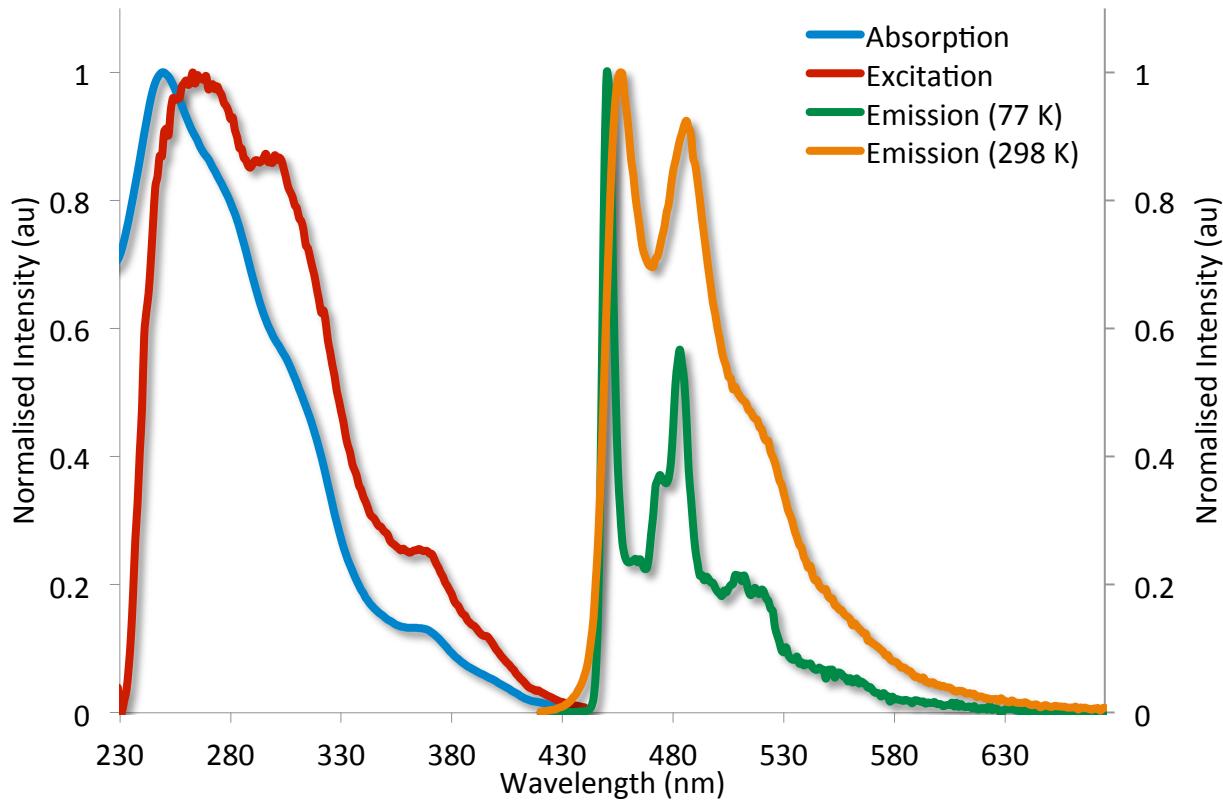


Figure S18. Summary of photophysical data for complex **3**, $[(dFppy)_2Ir(Xylbiim)](PF_6)$. Normalised absorption spectra in HPLC grade MeOH. Normalised excitation and 298 K emission spectra in HPLC grade MeOH. Normalised 77 K emission spectra, in 1:1 MeOH/EtOH glass.

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

Compound	Absorption at 298 K [Molar Absorptivities ($\times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)] ^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

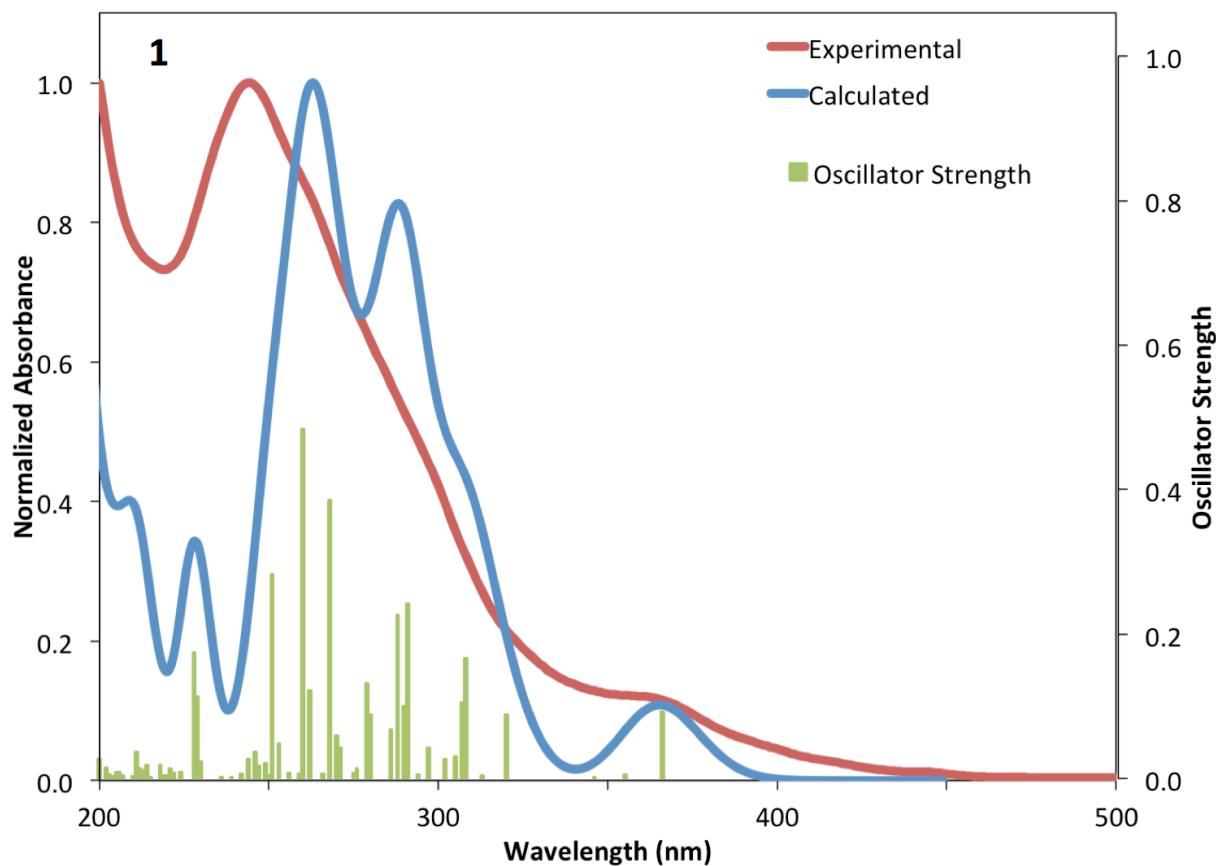


Figure S19. Experimental (red) and calculated UV-Vis spectrum (blue – fwhm = 1000 cm^{-1}) obtained from TDDFT calculations with the corresponding vertical excitations (green) for **1**.

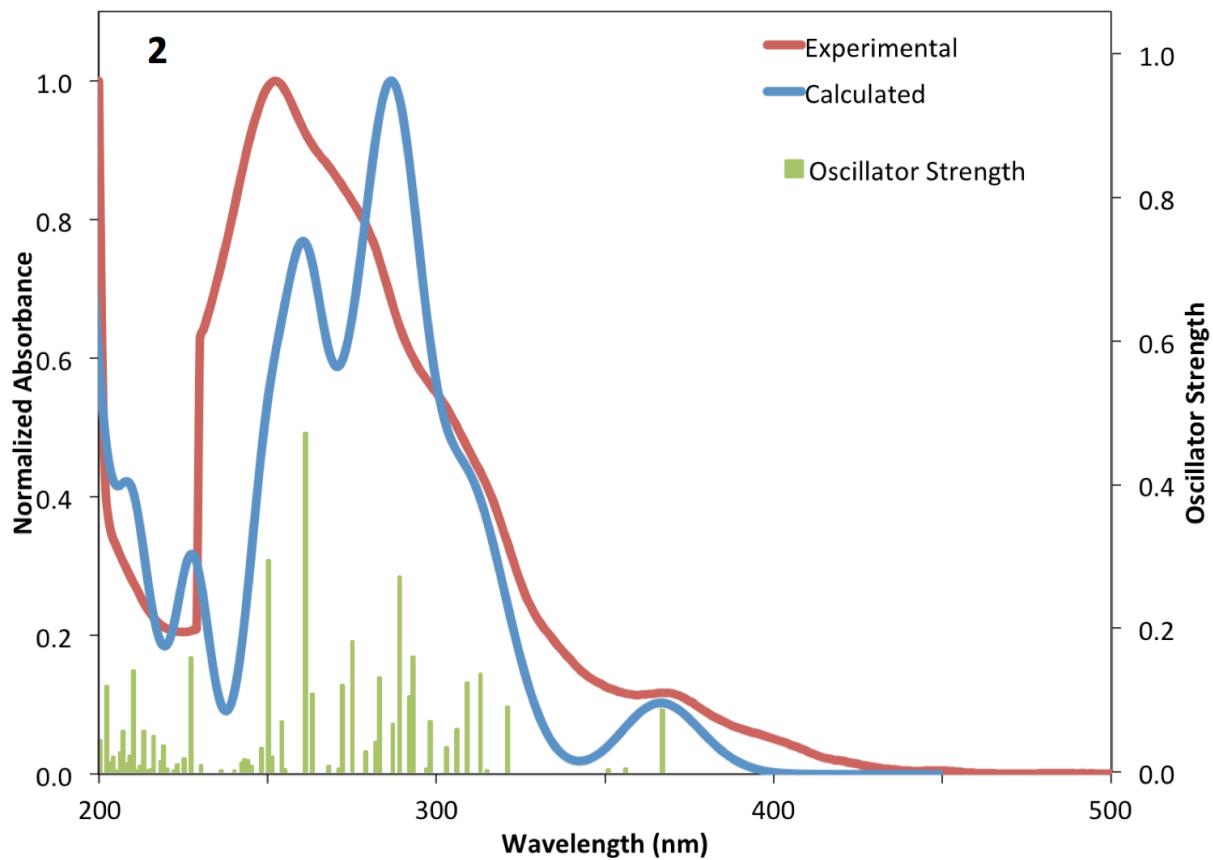


Figure S20. Experimental (red) and calculated UV-Vis spectrum (blue – fwhm = 1000 cm⁻¹) obtained from TDDFT calculations with the corresponding vertical excitations (green) for **1**.

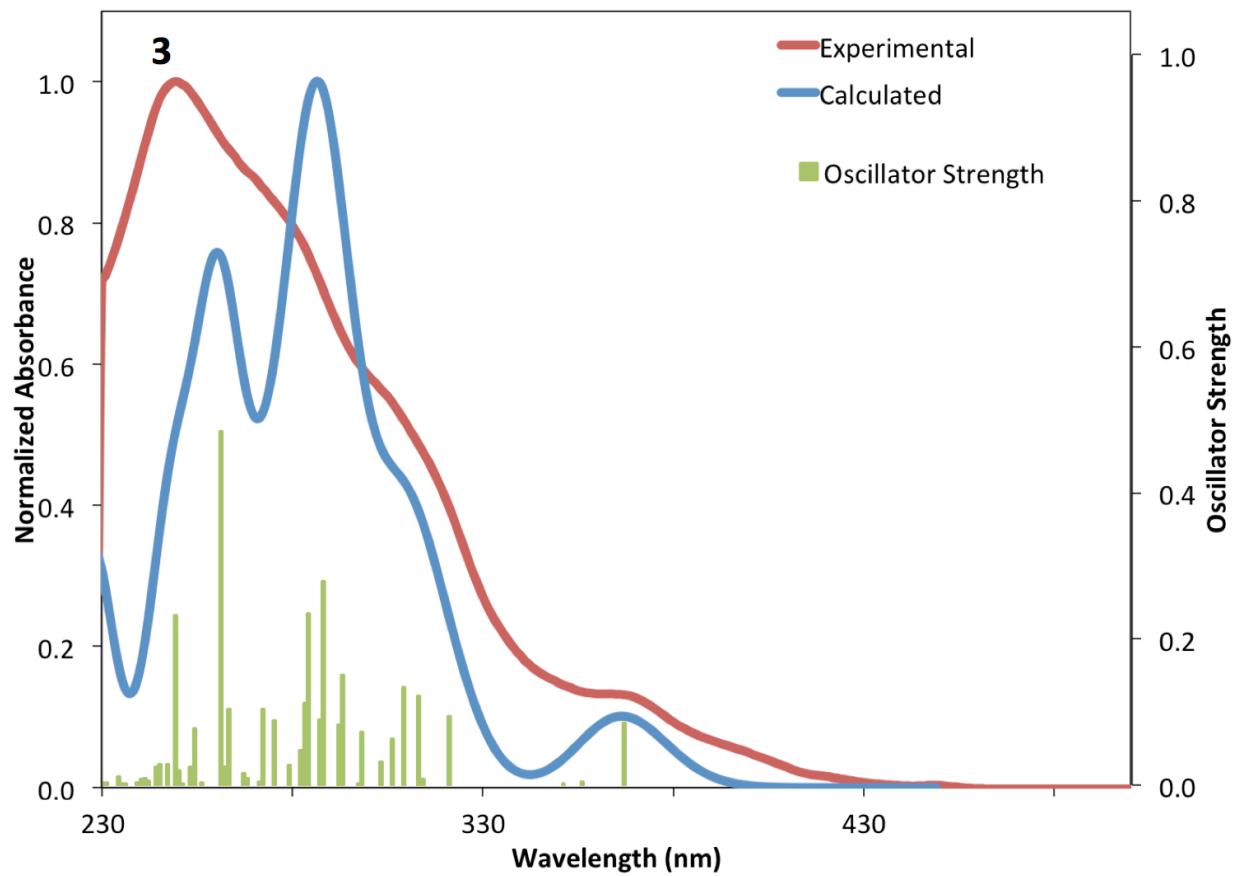


Figure S21. Experimental (red) and calculated UV-Vis spectrum (blue – fwhm = 1000 cm^{-1}) obtained from TDDFT calculations with the corresponding vertical excitations (green) for **1**.