Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Room temperature transmetalation from tris(pentafluorophenyl)borane to cyclometalated iridium(III)

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Table S1. Crystallographic summary.

	4b•CH_2Cl_2	**7b**•0.5CH_2Cl_2	**8b**
CCDC	1535294	1535295	1535296
Crystal data			
Chemical formula	$C_{39}H_{38}Cl_2F_{10}IrN_3P$	$C_{41.50}H_{30}ClF_9IrN_3$	$C_{45}H_{33}F_5IrN_3S_2$
M_r	1032.79	969.33	967.06
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Orthorhombic, *Pbca*
a, *b*, *c* (Å)	12.213(4), 12.217(4), 13.801(5)	18.168(4), 10.156(2), 20.551(5)	19.6492(18), 18.2345(16), 21.0900(19)
α, β, γ (°)	92.120(4), 101.748(4), 95.488(5)	90, 94.693(3), 90	90, 90, 90
V (Å^3)	2003.5 (12)	3779.2 (15)	7556.4 (12)
Z	2	4	8
μ (mm^{-1})	3.59	3.68	3.71
Crystal size (mm)	0.43 × 0.31 × 0.26	0.39 × 0.29 × 0.10	0.32 × 0.20 × 0.19
Data collection			
T_{min}, T_{max}	0.563, 0.746	0.542, 0.746	0.651, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12070, 8646, 8183	23138, 8692, 8040	45278, 8747, 7599
R_{int}	0.016	0.026	0.035
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.641	0.651	0.652
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.030, 0.076, 1.09	0.029, 0.078, 1.05	0.053, 0.114, 1.22
No. of reflections	8646	8692	8747
No. of parameters	568	539	509
No. of restraints	178	183	15
	$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2 + 4.8448P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 9.8773P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0001P)^2 + 89.6803P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.67, -1.16	1.96, -0.87	4.60, -3.68

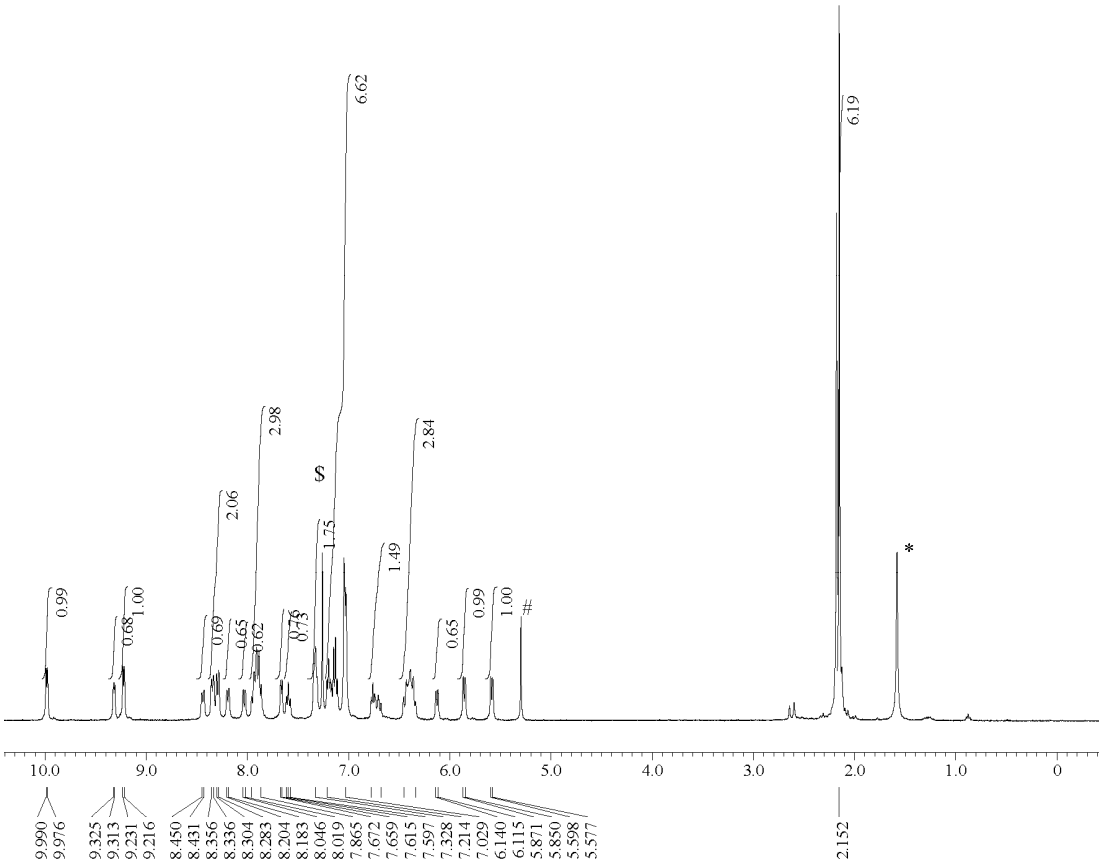

Figure S1. ^{1}H NMR spectrum of $Ir(F_2ppy)_2(CNAr^{dmp})(Cl)$ (**1a**), recorded at 400 MHz in $CDCl_3$ at room temperature. Residual solvent peaks for water (*), methylene chloride ($^{\#}$) and chloroform ($) are marked accordingly.

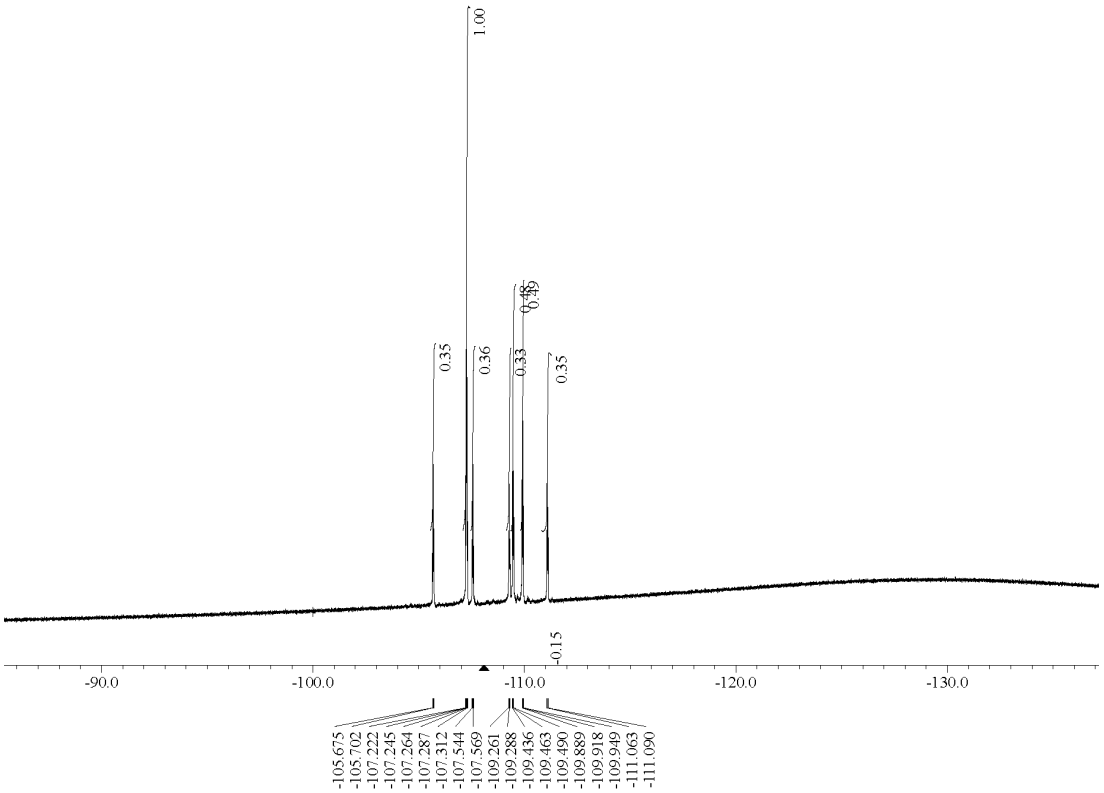

Figure S2. ^{19}F NMR spectrum of $Ir(F_2ppy)_2(CNAr^{dmp})(Cl)$ (**1a**), recorded at 376 MHz in $CDCl_3$ at room temperature.

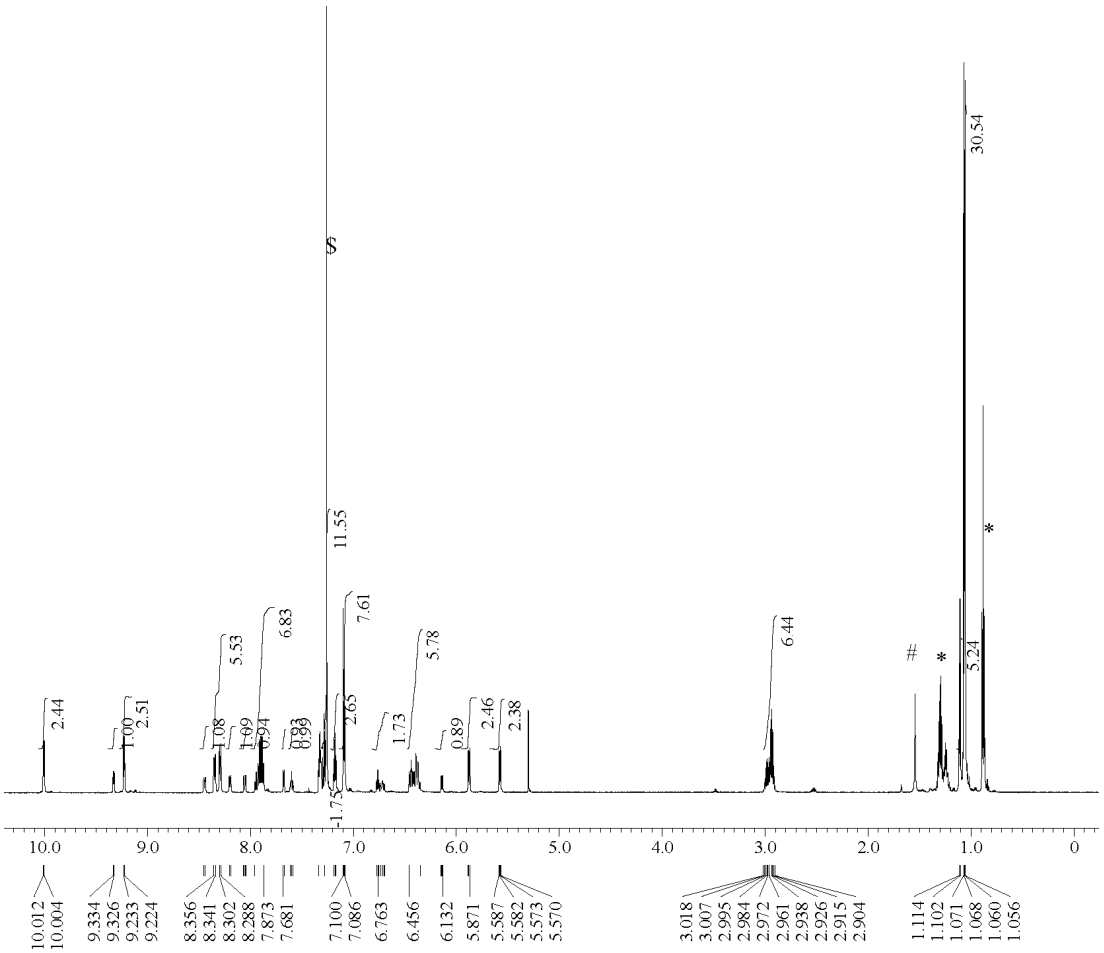

Figure S3. ^{1}H NMR spectrum of Ir(F_2ppy)$_2$(CNAr^{dipp})(Cl) (**1b**), recorded at 600 MHz in $CDCl_3$ at room temperature. Residual solvent peaks for pentane (*), water ($^{\#}$) and chloroform ($) are marked accordingly.

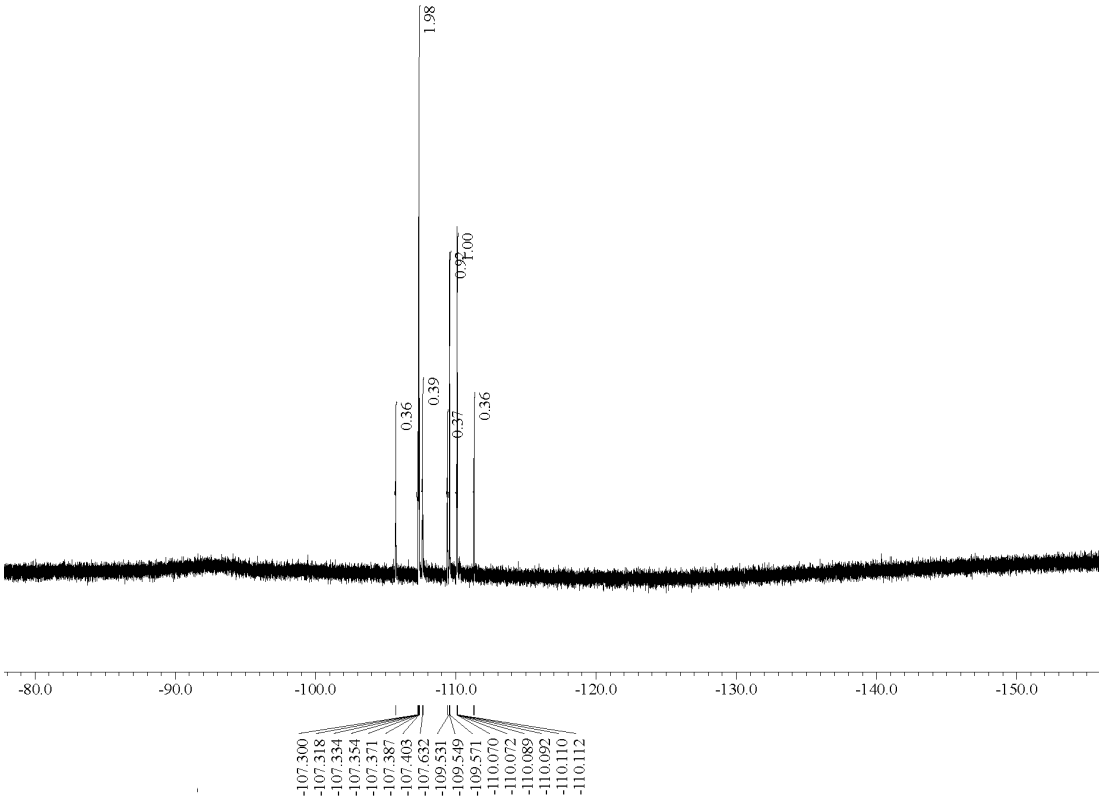

Figure S4. ^{19}F NMR spectrum of $Ir(F_2ppy)_2(CNAr^{dipp})(Cl)$ (**1b**), recorded at 565 MHz in $CDCl_3$ at room temperature.

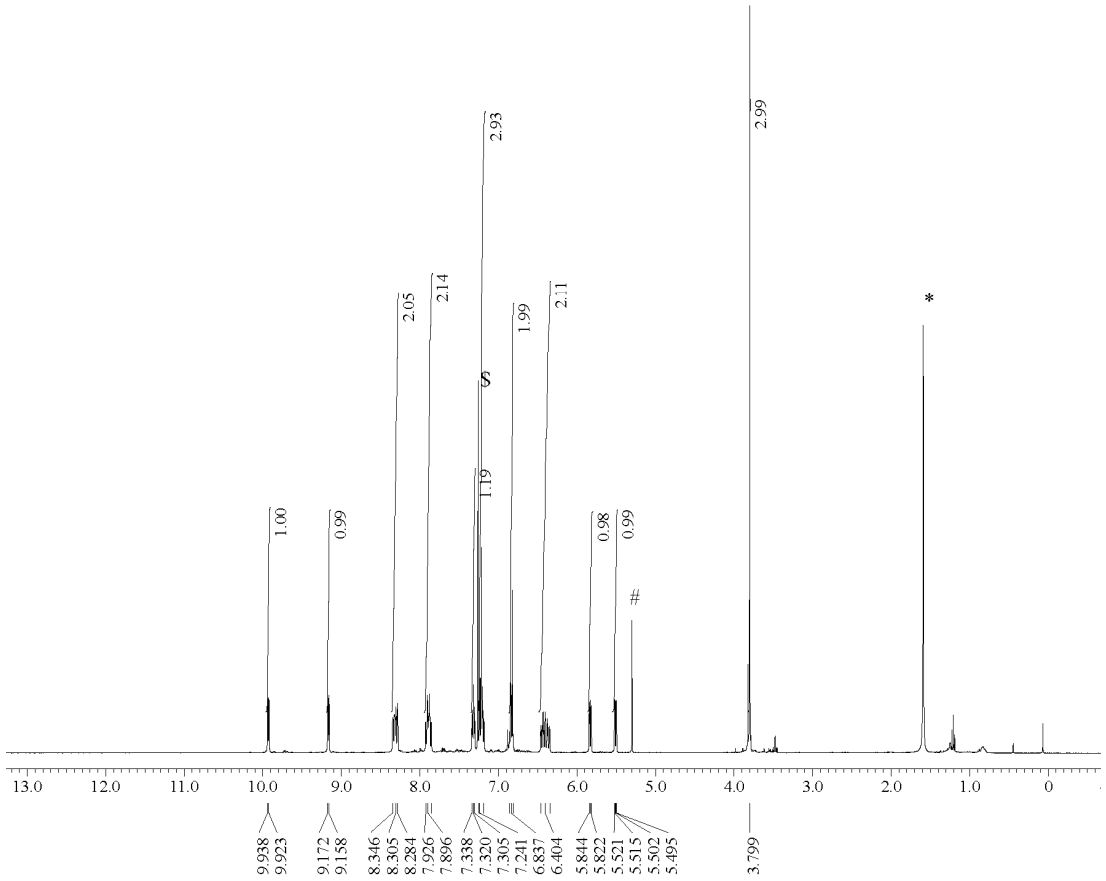

Figure S5. ^{1}H NMR spectrum of $Ir(F_2ppy)_2(CNAr^{OMe})(Cl)$ (**1c**), recorded at 400 MHz in $CDCl_3$ at room temperature. Residual solvent peaks for water (*), methylene chloride ($^{\#}$) and chloroform ($) are marked accordingly.

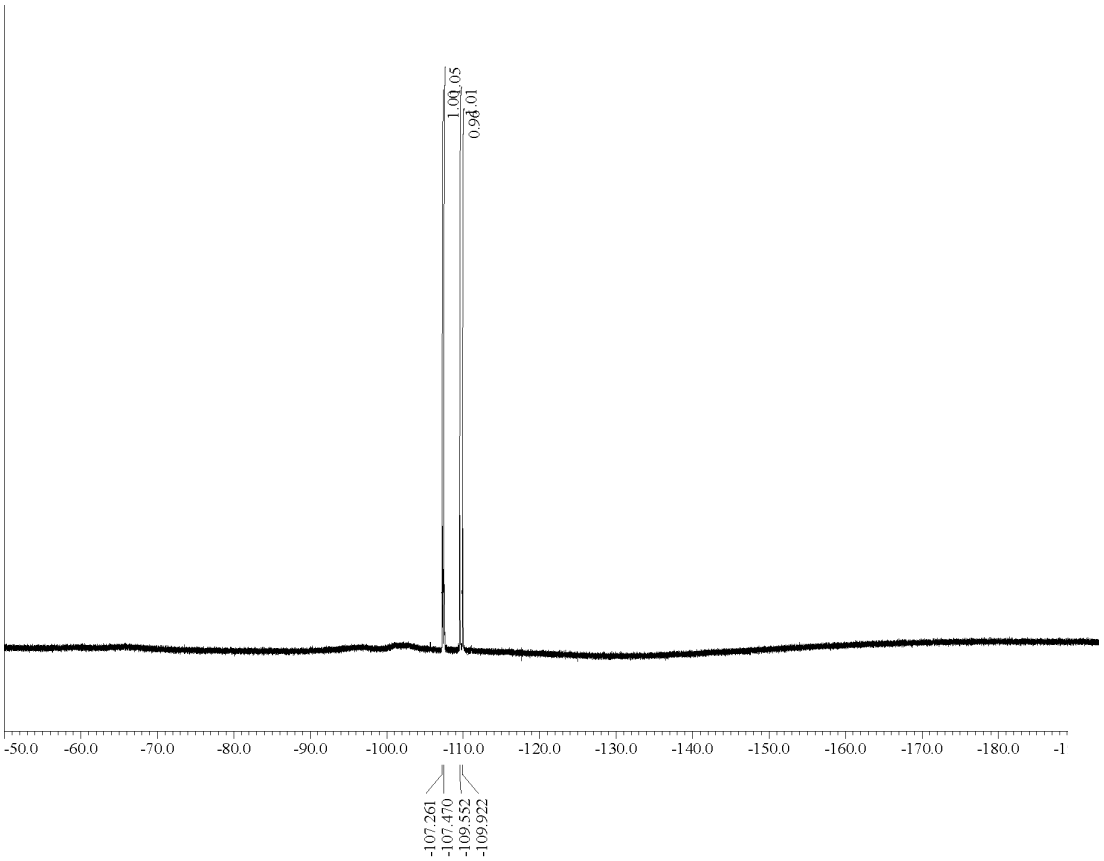

Figure S6. ^{19}F NMR spectrum of $Ir(F_2ppy)_2(CNAr^{OMe})(Cl)$ (**1c**), recorded at 376 MHz in $CDCl_3$ at room temperature.

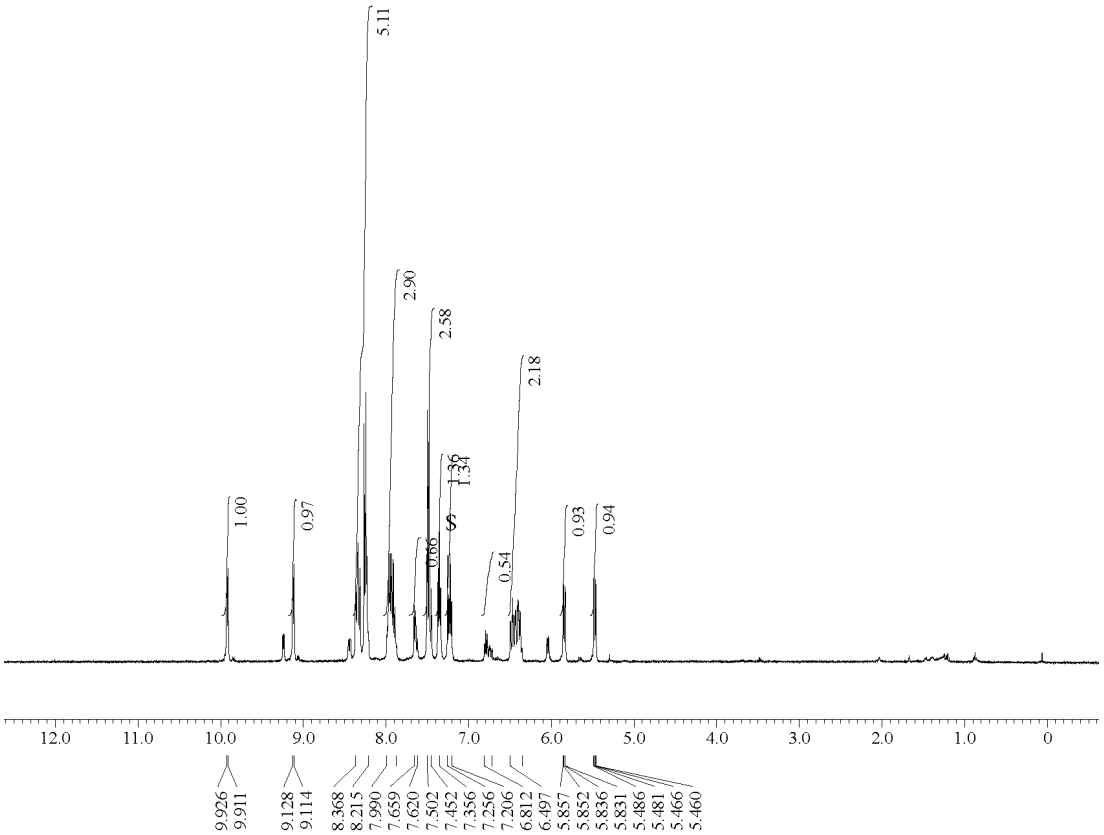

Figure S7. ^{1}H NMR spectrum of Ir(F_2ppy)$_2$(CNAr^{NO2})(Cl) (**1d**), recorded at 400 MHz in $CDCl_3$ at room temperature.

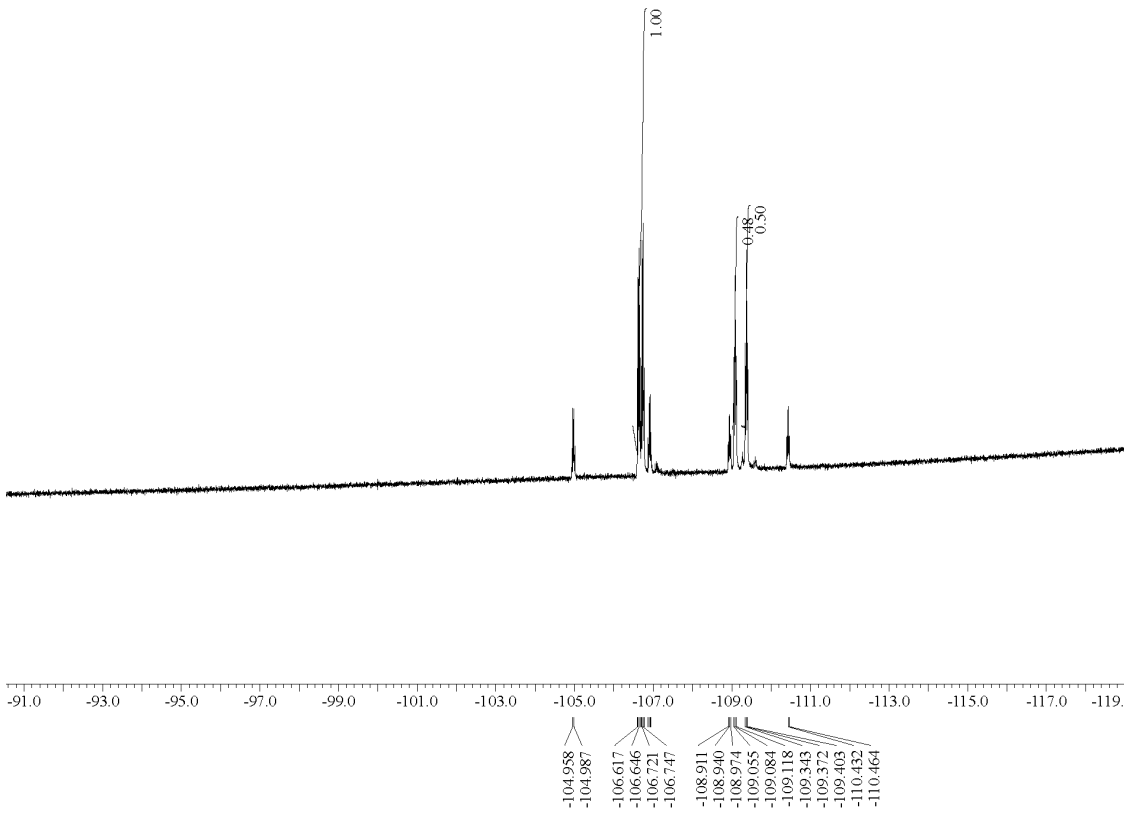

Figure S8. ^{19}F NMR spectrum of $Ir(F_2ppy)_2(CNAr^{NO2})(Cl)$ (**1d**), recorded at 376 MHz in $CDCl_3$ at room temperature.

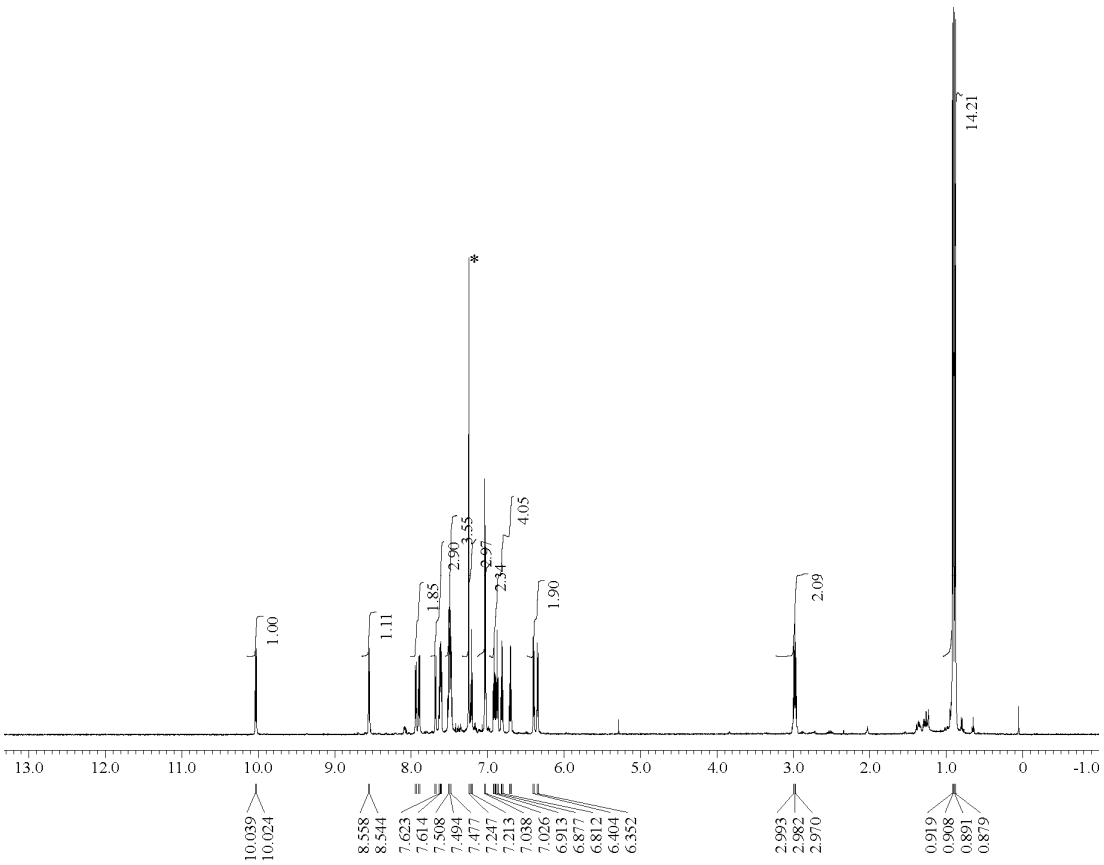

Figure S9. ^{1}H NMR spectrum of $Ir(bt)_2(CNAr^{Dipp})(Cl)$ (**2b**), recorded at 600 MHz in $CDCl_3$ at room temperature.

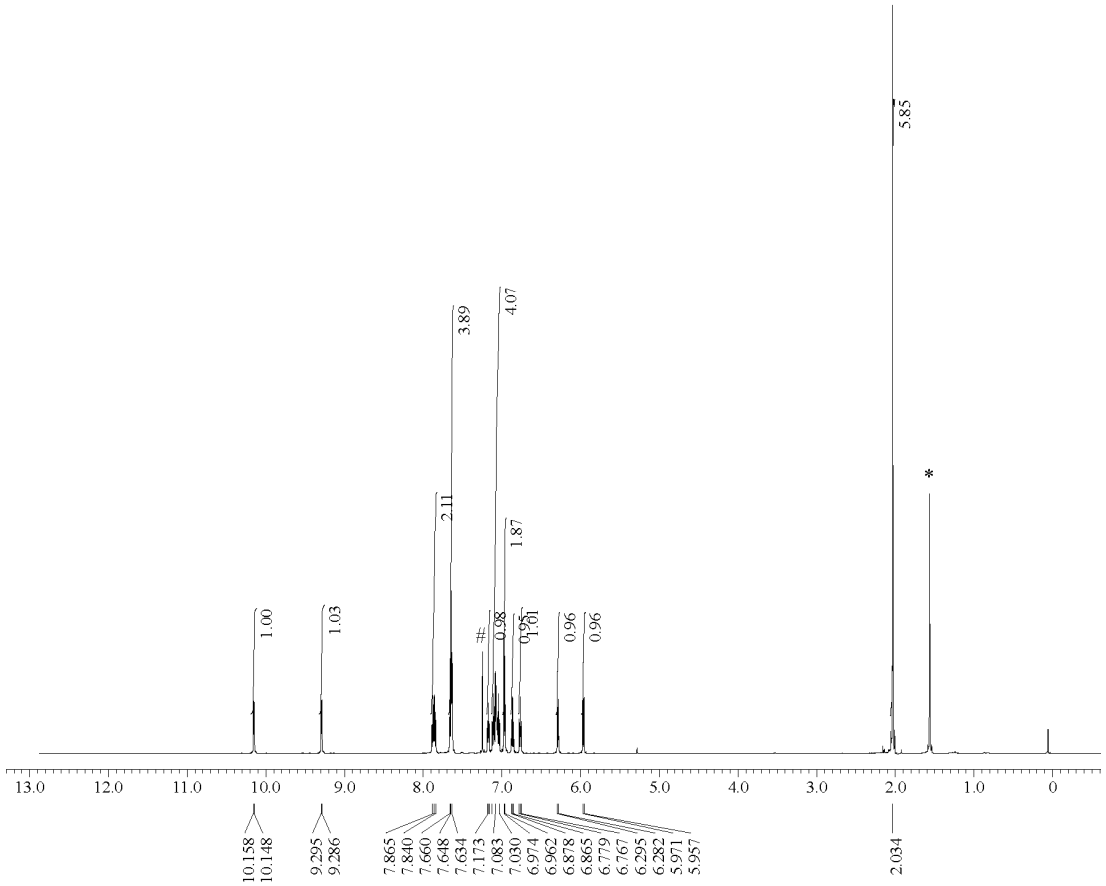

Figure S10. ^{1}H NMR spectrum of Ir(btp)$_2$(CNAr^{dmp})(Cl) (**3a**), recorded at 600 MHz in $CDCl_3$ at room temperature. Residual solvent peaks for water (*) and chloroform (#) are marked accordingly.

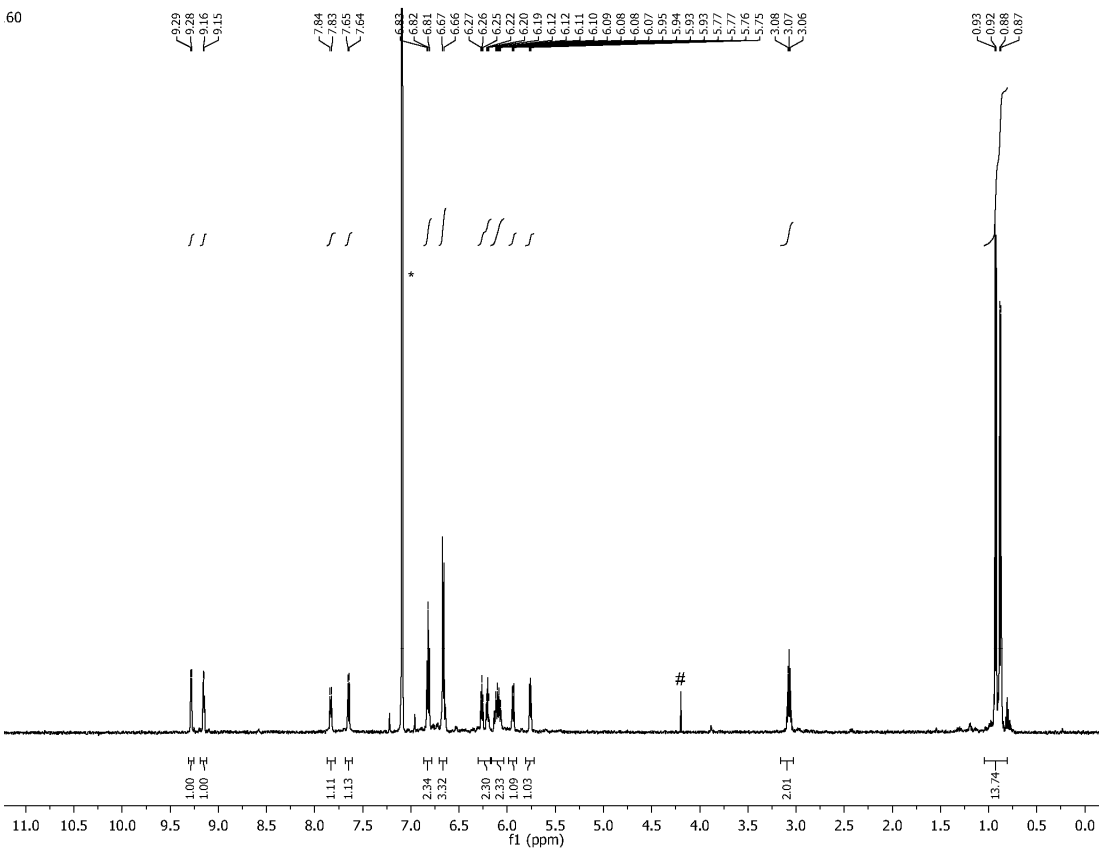

Figure S11. ^{1}H NMR spectrum of $Ir(F_2ppy)_2(CNAr^{dipp})(FPF_5)$ (**4b**), recorded at 600 MHz in C_6D_6 at room temperature. Residual solvent peaks for methylene chloride ($^{\#}$) and benzene (*) are marked accordingly.

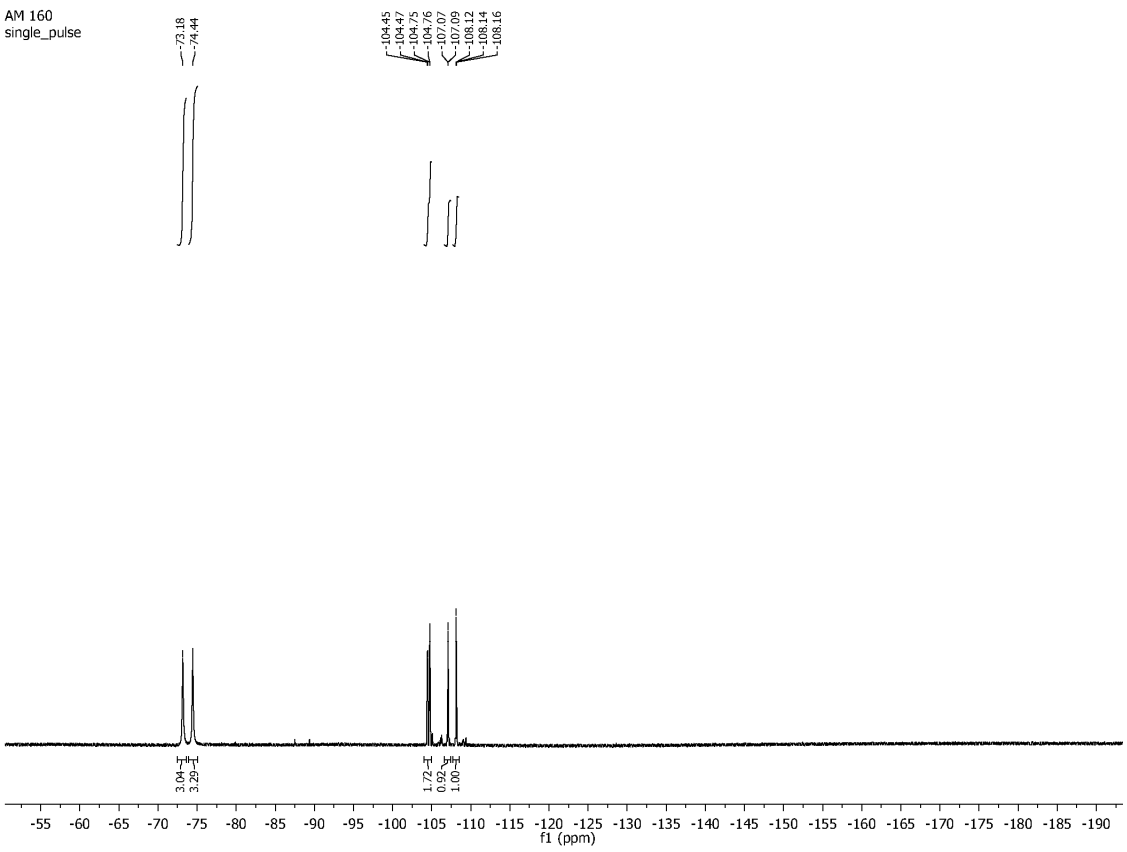

Figure S12. ^{19}F NMR spectrum of $Ir(F_2ppy)_2(CNAr^{dipp})(FPF_5)$ (**4b**), recorded at 565 MHz in C_6D_6 at room temperature.

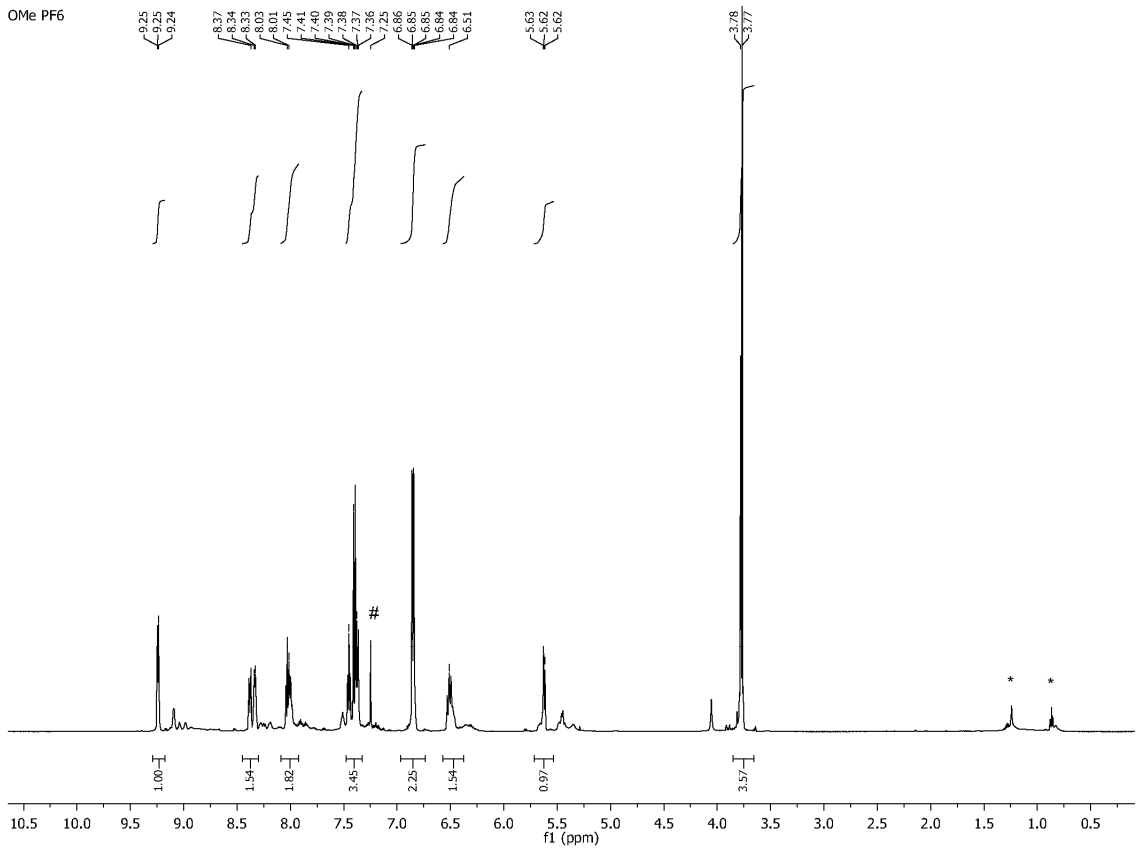

Figure S13. ^{1}H NMR spectrum of $Ir(F_2ppy)_2(CNAr^{OMe})(PF_6)$ (**4c**), recorded at 400 MHz in $CDCl_3$ at room temperature. Residual solvent peaks for pentane (*) and chloroform ($^{\#}$) are marked accordingly.

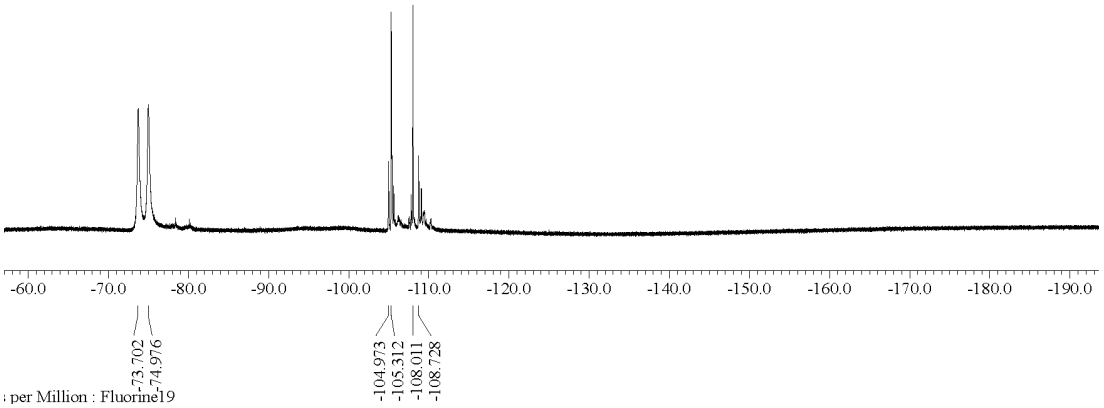

Figure S14. ^{19}F NMR spectrum of $Ir(F_2ppy)_2(CNAr^{OMe})(PF_6)$ (**4c**), recorded at 565 MHz in C_6D_6 at room temperature.

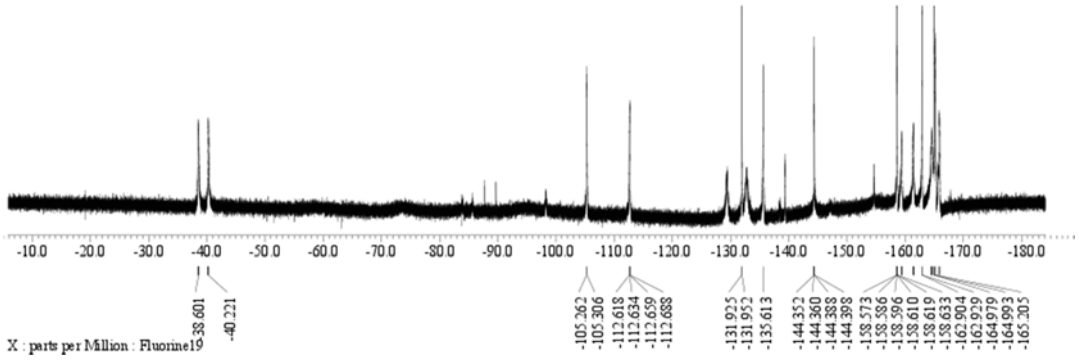

Figure S15. In situ ^{19}F NMR spectrum following the reaction of $Ir(bt)_2(CNAr^{dipp})(Cl)$ (**2b**) with $B(C_6F_5)_3$ and $AgPF_6$ for 12 h in CH_2Cl_2. No workup was performed prior to recording the spectrum, which was obtained at 565 MHz in CH_2Cl_2 at room temperature.

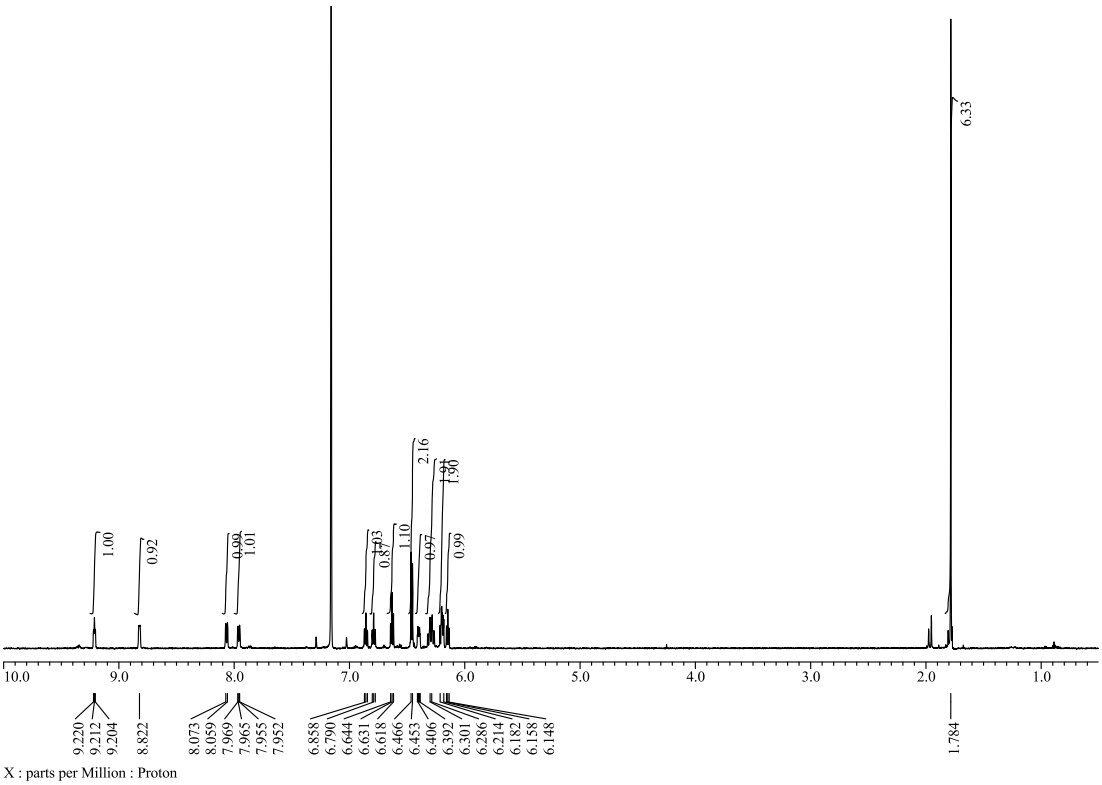

Figure S16. ^{1}H NMR spectrum of Ir(F_2ppy)$_2$(CNAr^{dmp})(C_6F_5) (**7a**), recorded at 600 MHz in C_6D_6 at room temperature.

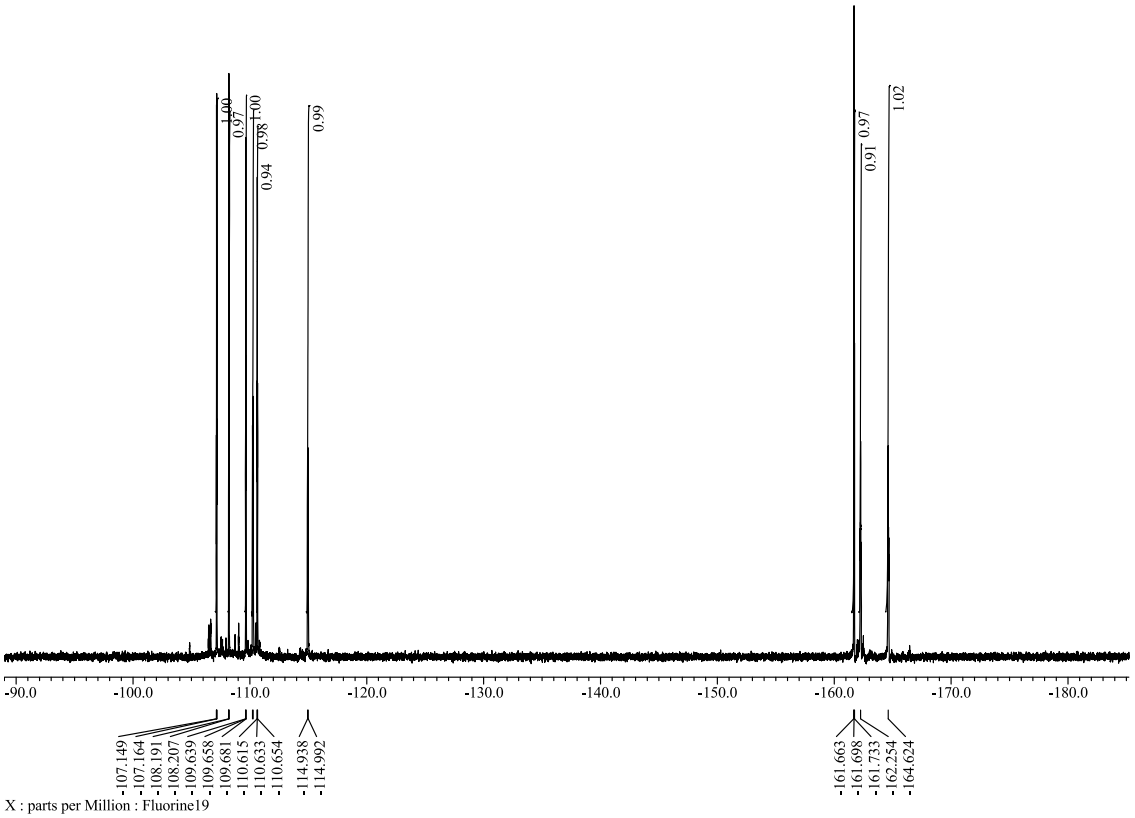

Figure S17. ^{19}F NMR spectrum of $Ir(F_2ppy)_2(CNAr^{dmp})(C_6F_5)$ (**7a**), recorded at 565 MHz in C_6D_6 at room temperature.

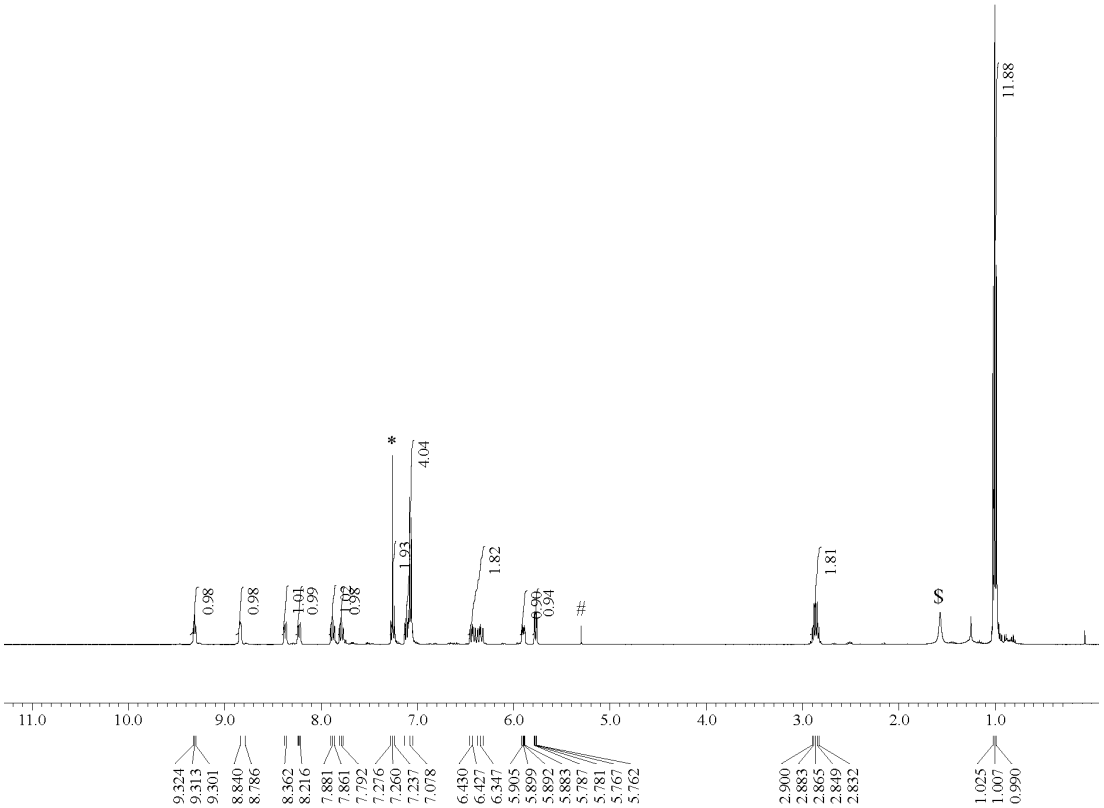

Figure S18. ^{1}H NMR spectrum of $Ir(F_2ppy)_2(CNAr^{dipp})(C_6F_5)$ (**7b**), recorded at 400 MHz in $CDCl_3$ at room temperature. Residual solvent peaks for water ($^{\$}$), methylene chloride ($^{\#}$) chloroform (*) are marked accordingly.

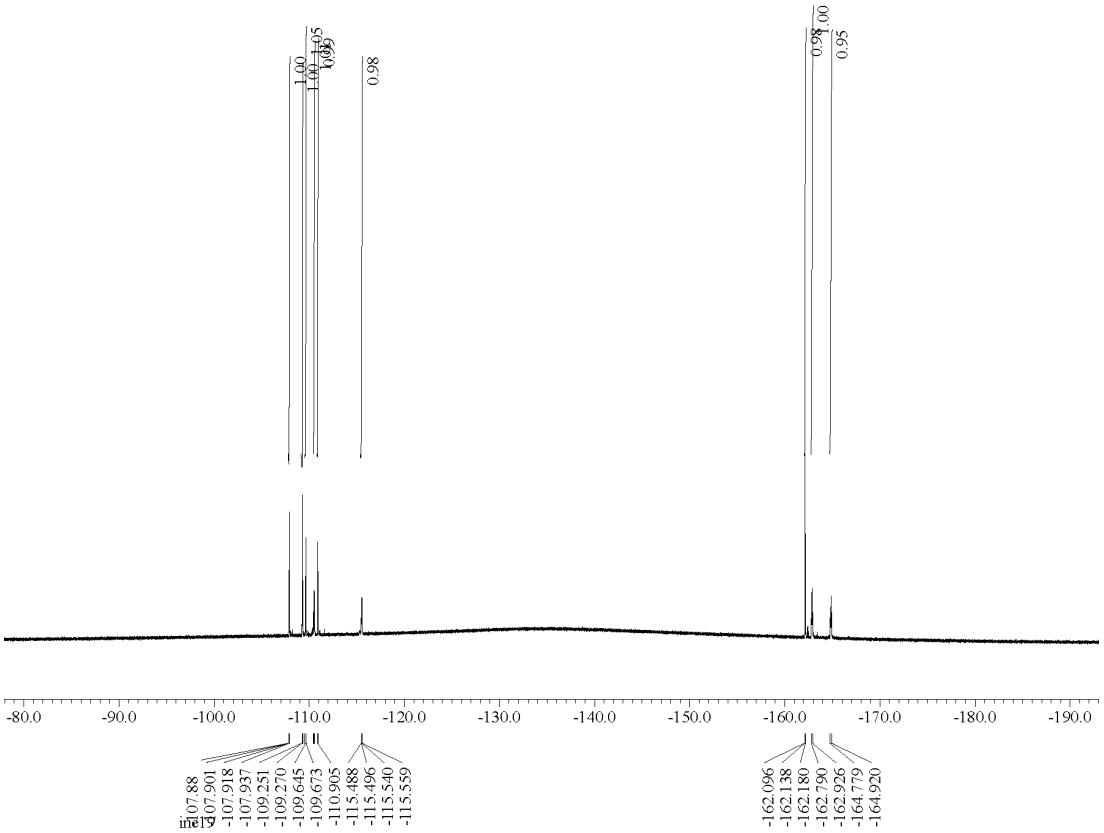

Figure S19. ^{19}F NMR spectrum of $Ir(F_2ppy)_2(CNAr^{dipp})(C_6F_5)$ (**7b**), recorded at 470 MHz in $CDCl_3$ at room temperature.

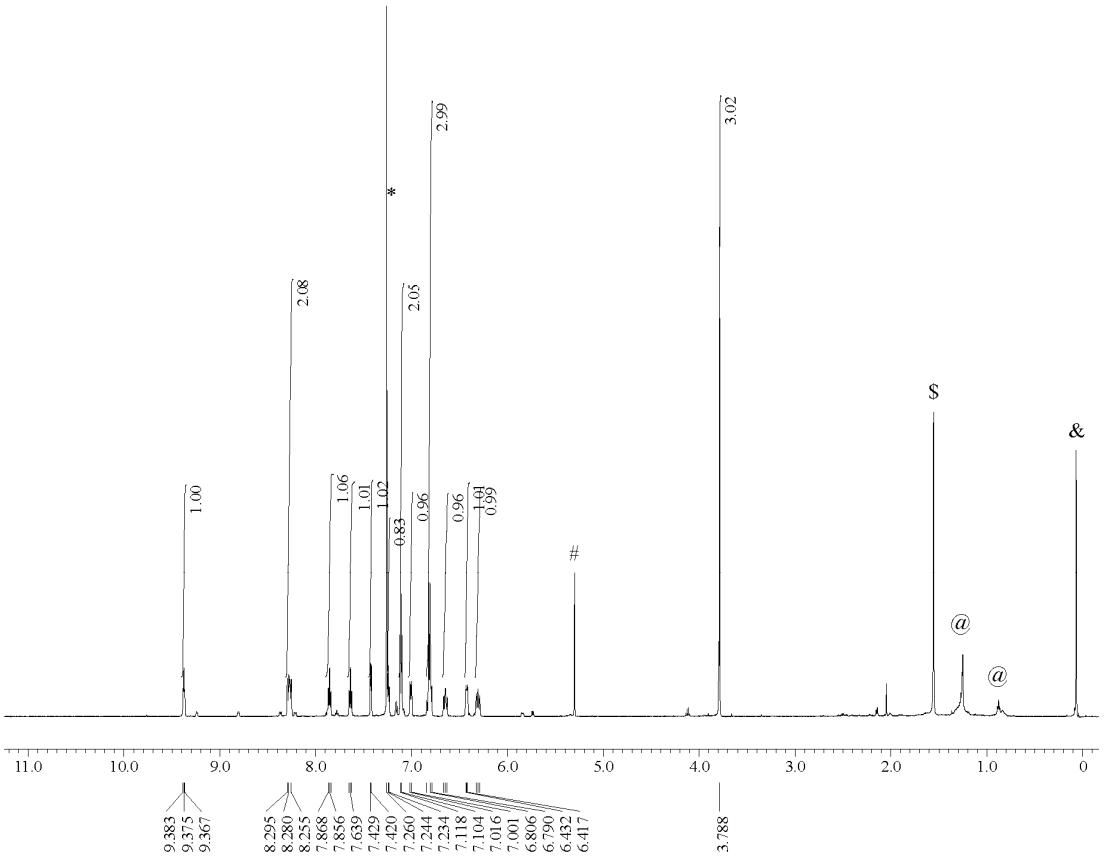

Figure S20. ^{1}H NMR spectrum of Ir(F_2ppy)$_2$(CNAr^{OMe})(C_6F_5) (**7c**), recorded at 600 MHz in $CDCl_3$ at room temperature. Residual solvent peaks for tetramethylsilane ($^{\&}$), hexanes ($^{@}$), water ($^{\$}$), methylene chloride ($^{\#}$) and chloroform (*) are marked accordingly.

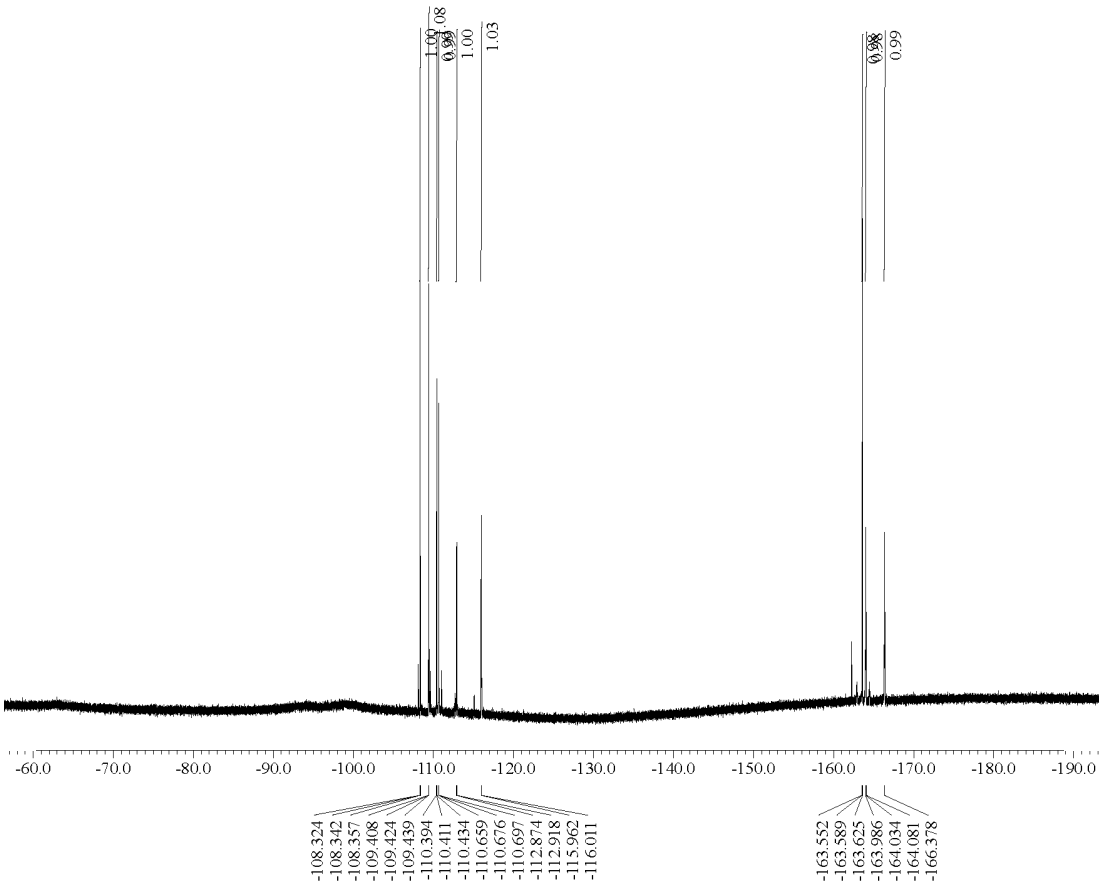

Figure S21. ^{19}F NMR spectrum of $Ir(F_2ppy)_2(CNAr^{OMe})(C_6F_5)$ (**7c**), recorded at 565 MHz in $CDCl_3$ at room temperature.

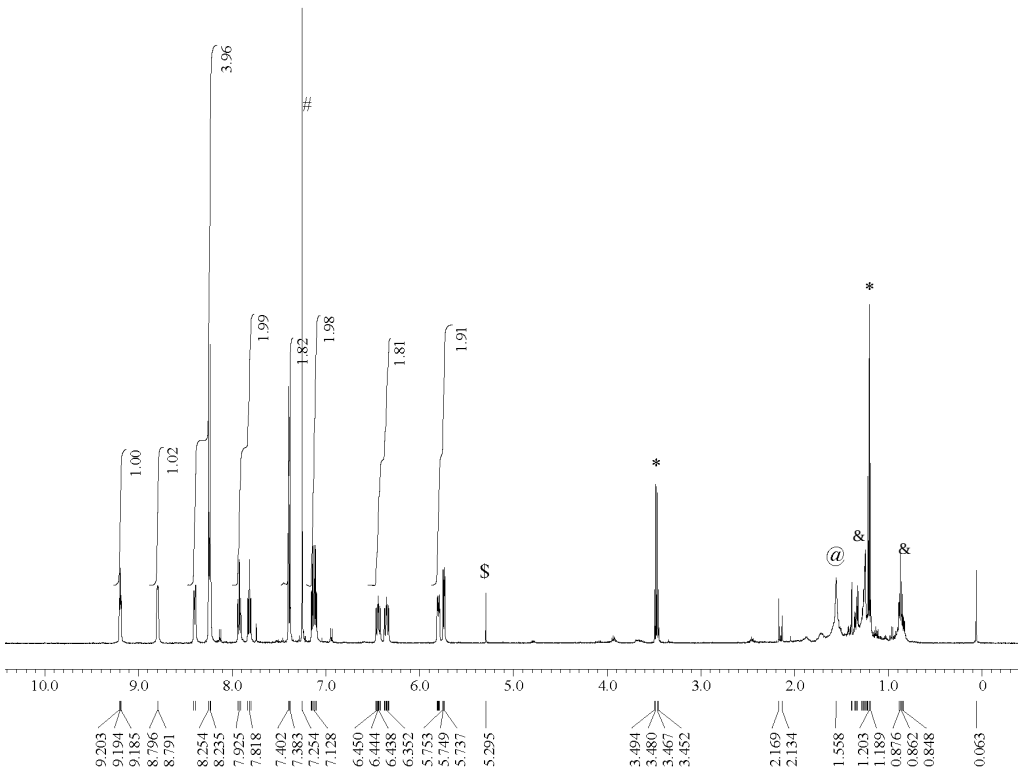

Figure S22. ^{1}H NMR spectrum of Ir(F_2ppy)$_2$(CNAr^{NO2})(C_6F_5) (**7d**), recorded at 500 MHz in $CDCl_3$ at room temperature. Residual solvent peaks for water ($^{@}$), diethyl ether (*), hexanes (&) methylene chloride ($^{\$}$), and chloroform ($^{\#}$) are marked accordingly.

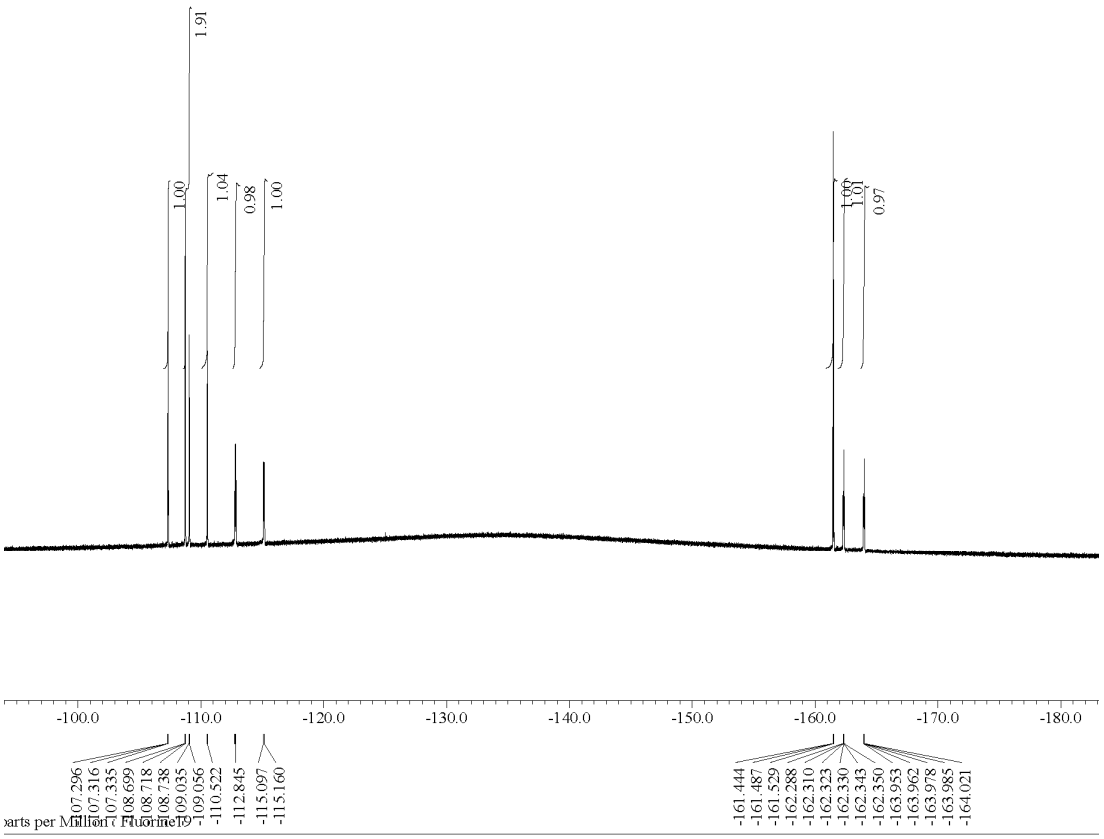

Figure S23. ^{19}F NMR spectrum of $Ir(F_2ppy)_2(CNAr^{NO2})(C_6F_5)$ (**7d**), recorded at 470 MHz in $CDCl_3$ at room temperature.

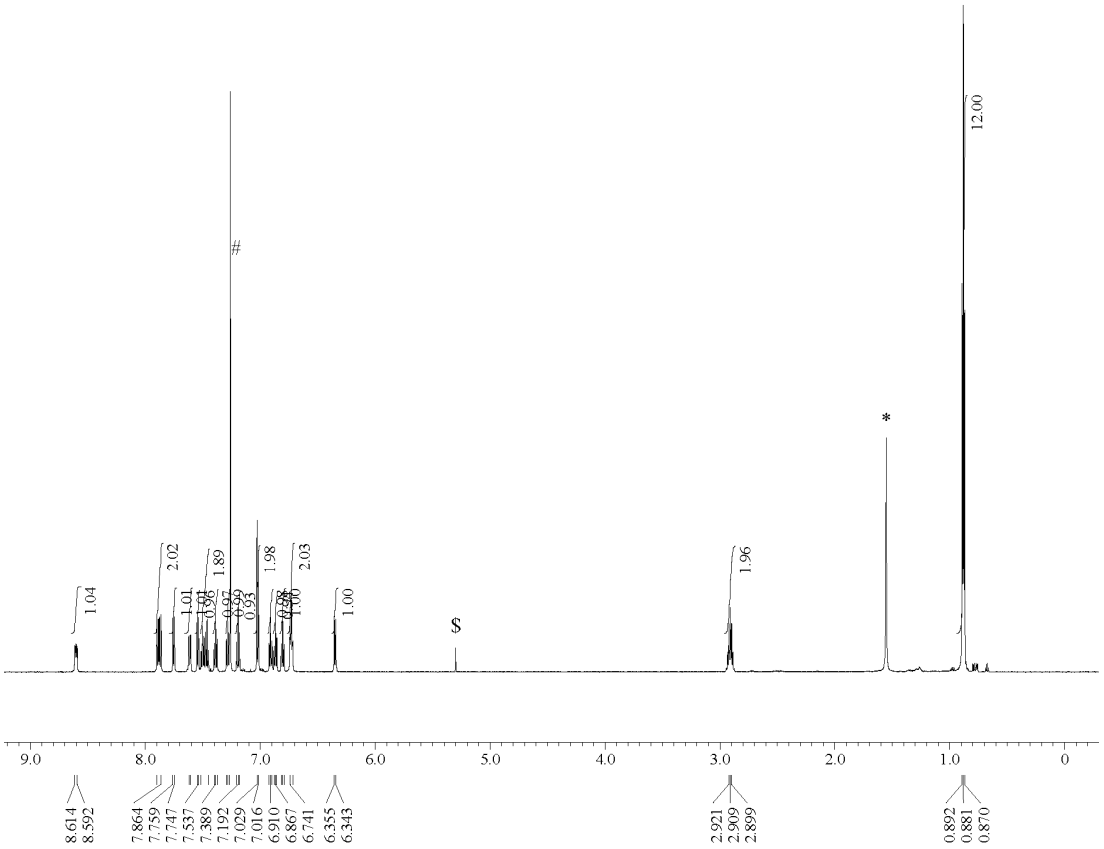

Figure S24. ^{1}H NMR spectrum of Ir(bt)$_2$(CNAr^{dipp})(C$_6$F$_5$) (**8b**), recorded at 600 MHz in CDCl$_3$ at room temperature. Residual solvent peaks for water (*), methylene chloride ($^{\$}$), and chloroform ($^{\#}$) are marked accordingly.

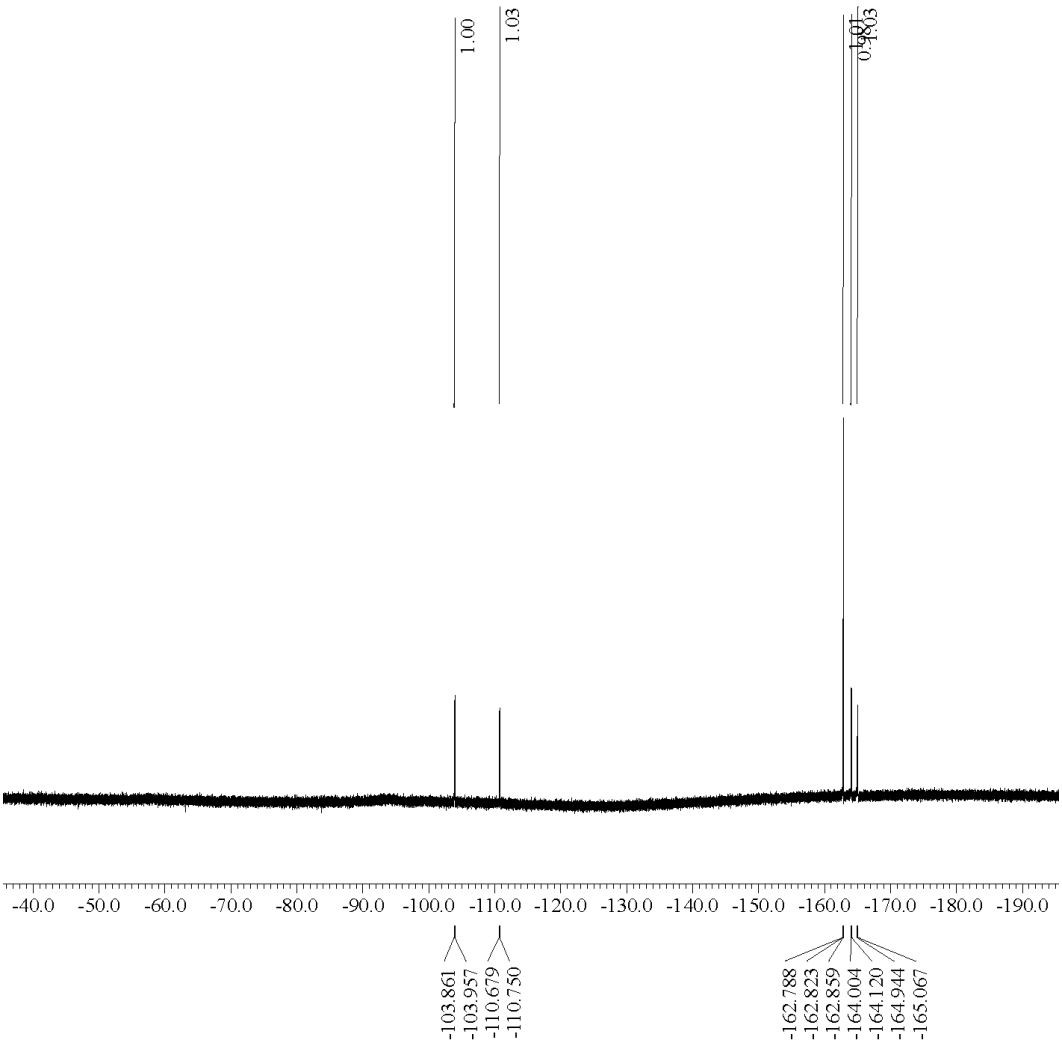

Figure S25. ^{19}F NMR spectrum of $Ir(bt)_2(CNAr^{dipp})(C_6F_5)$ (**8b**), recorded at 565 MHz in $CDCl_3$ at room temperature.

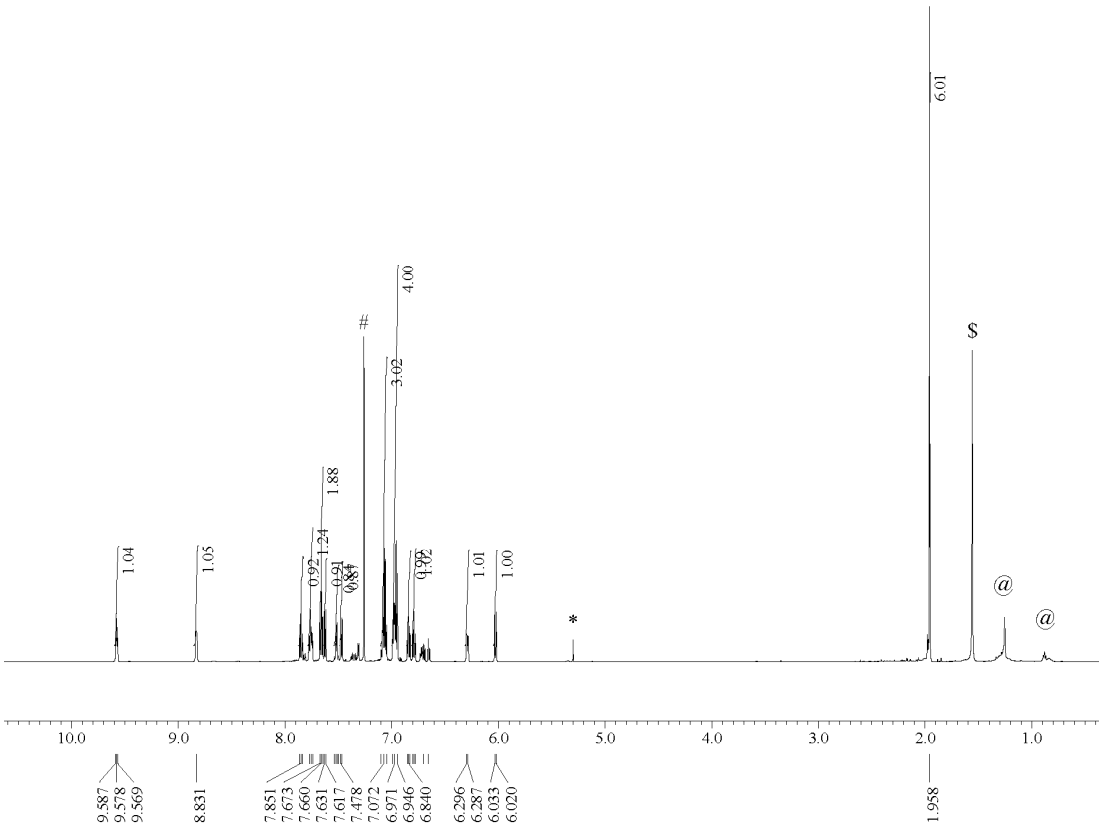

Figure S26. ^{1}H NMR spectrum of Ir(btp)$_2$(CNAr^{dmp})(C$_6$F$_5$) (**9a**), recorded at 600 MHz in CDCl$_3$ at room temperature. Residual solvent peaks for hexanes ($^{@}$), water ($^{\$}$), methylene chloride (*), and chloroform ($^{\#}$) are marked accordingly.

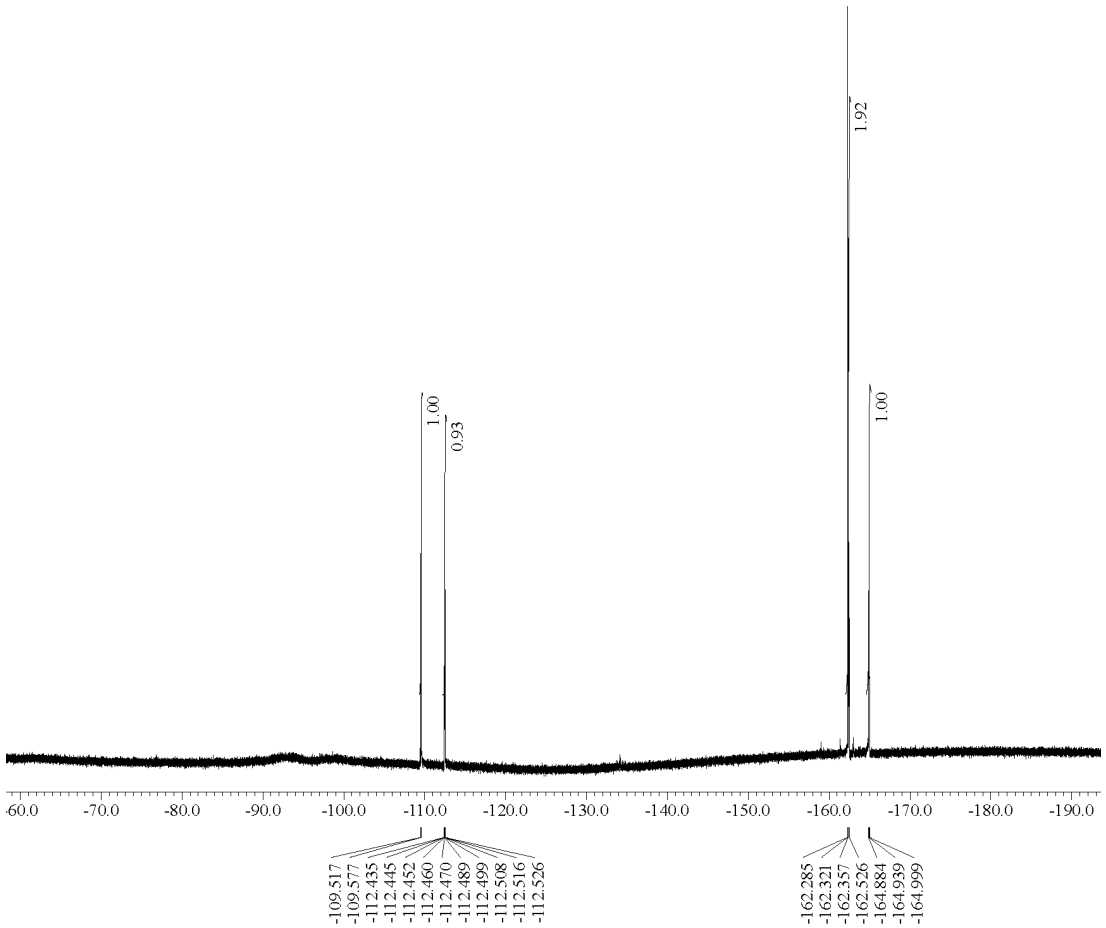

Figure S27. ^{19}F NMR spectrum of $Ir(btp)_2(CNAr^{dmp})(C_6F_5)$ (**9a**), recorded at 565 MHz in $CDCl_3$ at room temperature.

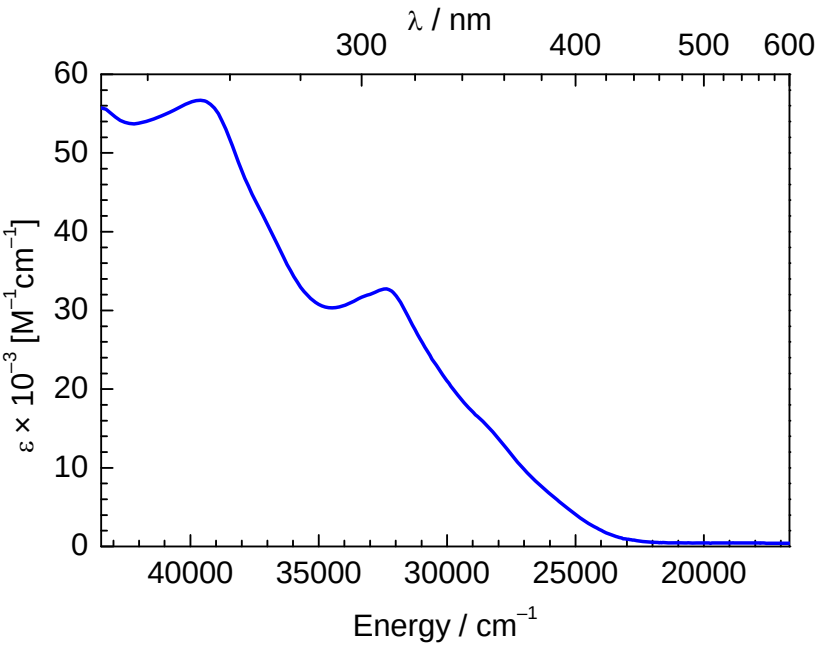

Figure S28. UV-vis absorption spectrum of $Ir(F_2ppy)_2(CNAr^{NO2})(C_6F_5)$ (**7d**), recorded at room temperature in CH_2Cl_2. This compound does not luminesce at room temperature.