Supporting Information for

Cyano-Isocyanide Iridium(III) Complexes with Pure Blue Phosphorescence

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Table S1. Summary of crystallographic data for **1a** and **1b**.

	1a	**1b**·0.5(butanone)
CCDC	2052924	2052925
Crystal data		
Chemical formula	$C_{33}H_{33}ClF_4IrN_7$	$C_{36}H_{36}F_4IrN_8O_{0.50}$
M_r	831.31	856.93
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Temperature (K)	123	123
a, b, c (Å)	12.7442 (13), 15.6879 (16), 16.8691 (17)	10.9536 (18), 12.944 (2), 14.027 (2)
α, β, γ (°)	91.805 (1), 90.111 (1), 100.189 (1)	80.706 (2), 71.159 (2), 72.482 (2)
V (Å^3)	3317.7 (6)	1790.4 (5)
Z	4	2
μ (mm^{-1})	4.16	3.79
Crystal size (mm)	0.42 × 0.37 × 0.16	0.25 × 0.25 × 0.20
Data collection		
T_{min}, T_{max}	0.534, 0.746	0.619, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20240, 14346, 12639	36903, 7860, 7485
R_{int}	0.019	0.024
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.641	0.641
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.061, 1.05	0.029, 0.082, 1.09
No. of reflections	14346	7860
No. of parameters	850	475
No. of restraints	25	115
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.49, −1.14	5.43, −1.17

Table S2. Summary of crystallographic data for **2a** and **4b**.

	2a	**4b**
CCDC	2052926	2052928
Crystal data		
Chemical formula	$C_{35}H_{35}ClF_6IrN_7$	$C_{37}H_{28}F_{15}IrN_8$
M_r	895.35	1061.87
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	123	123
a, b, c (Å)	16.388 (3), 12.399 (3), 22.516 (5)	24.122 (5), 14.154 (3), 24.620 (5)
β (°)	110.532 (2)	116.579 (2)
V (Å^3)	4284.7 (15)	7517 (3)
Z	4	8
μ (mm^{-1})	3.24	3.67
Crystal size (mm)	0.35 × 0.25 × 0.07	0.34 × 0.34 × 0.28
Data collection		
T_{min}, T_{max}	0.485, 0.746	0.670, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	24983, 9406, 7092	46312, 17240, 14807
R_{int}	0.033	0.033
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.641	0.651
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.055, 0.173, 1.05	0.027, 0.065, 1.06
No. of reflections	9406	17240
No. of parameters	521	1182
No. of restraints	512	516
	$w = 1/[\sigma^2(F_o^2) + (0.0993P)^2 + 16.9104P]$ where $P = (F_o^2 + 2F_c^2)/3$	
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.63, −1.42	1.42, −0.95

Table S3. Summary of crystallographic data for **2b** and **6b**.

	2b	**6b**·2$CHCl_3$
CCDC	2052927	2052930
Crystal data		
Chemical formula	$C_{36}H_{35}F_6IrN_8$	$C_{34}H_{27}Cl_6F_6IrN_6$
M_r	885.92	1038.51
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Temperature (K)	123	123
a, b, c (Å)	18.678 (7), 18.690 (7), 18.823 (8)	11.2660 (5), 13.8765 (7), 14.2695 (7)
α, β, γ (°)	101.956 (4), 101.367 (4), 101.440 (4)	98.388 (2), 102.747 (2), 113.206 (2)
V (Å^3)	6103 (4)	1931.15 (16)
Z	6	2
μ (mm^{-1})	3.34	3.94
Crystal size (mm)	0.45 × 0.28 × 0.22	0.50 × 0.36 × 0.10
Data collection		
T_{min}, T_{max}	0.505, 0.746	0.384, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	84821, 21547, 16542	51673, 8832, 7684
R_{int}	0.050	0.057
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.595	0.649
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.079, 0.184, 1.12	0.040, 0.097, 1.07
No. of reflections	21547	8832
No. of parameters	1404	482
No. of restraints	1579	
	$w = 1/[\sigma^2(F_o^2) + 177.6116P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0252P)^2 + 14.0924P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	4.69, −3.70	2.34, −2.17

Table S4. Summary of crystallographic data for **5b**.

	5b
CCDC	2052929
Crystal data	
Chemical formula	$C_{32}H_{25}F_6IrN_6$
M_r	799.78
Crystal system, space group	Trigonal, $R\bar{3}$:H
Temperature (K)	123
a, c (Å)	27.512 (3), 25.610 (3)
V (Å^3)	16788 (4)
Z	18
μ (mm^{-1})	3.64
Crystal size (mm)	0.50 × 0.10 × 0.10
Data collection	
T_{min}, T_{max}	0.376, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	29555, 7070, 5558
R_{int}	0.038
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.610
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.147, 1.10
No. of reflections	7070
No. of parameters	410
No. of restraints	48
	$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2 + 196.5672P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.02, −1.11

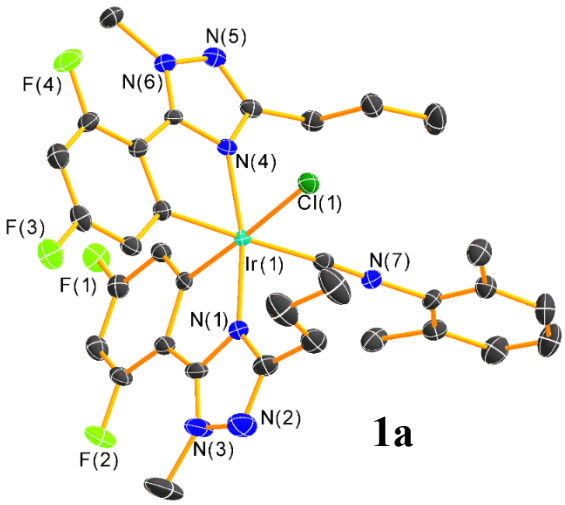

Figure S1. X-ray crystal structure of **1a**. Hydrogen atoms are omitted for clarity and only one of the two crystallographically independent molecules is shown. Ellipsoids are shown at the 50% probability level.

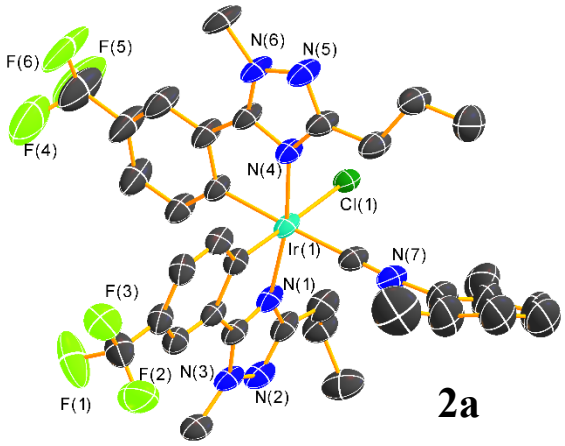

Figure S2. X-ray crystal structure of **2a**. Hydrogen atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level.

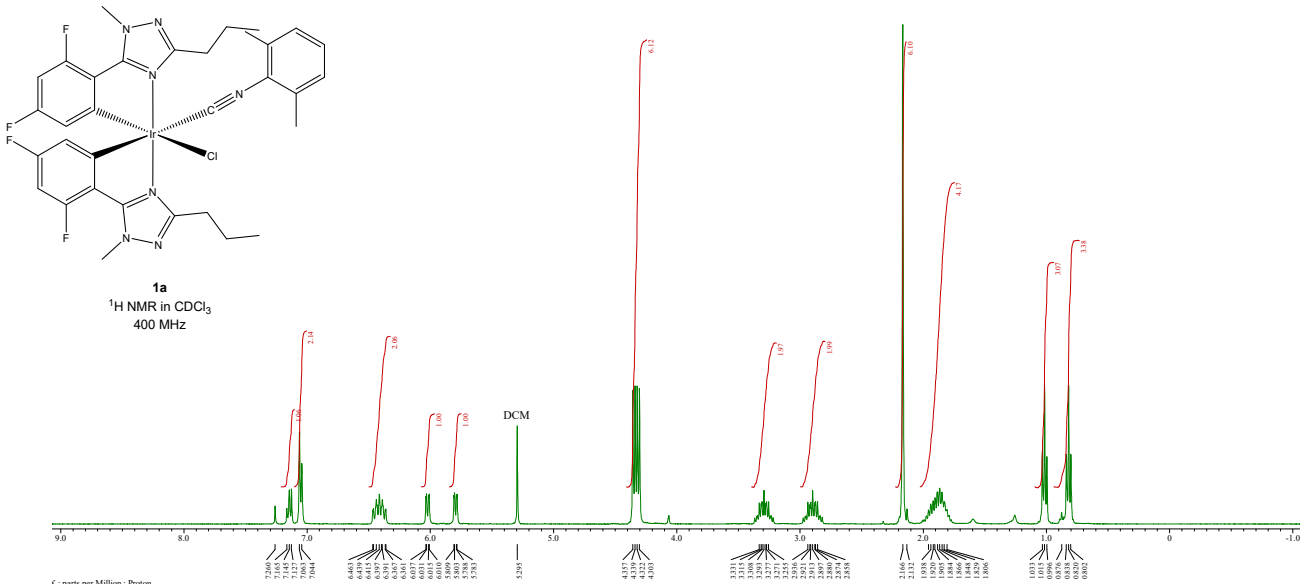

Figure S3. ^{1}H NMR spectrum of Ir(F_2ptz)$_2$(CNAr^{dmp})(Cl) (**1a**), recorded at 400 MHz in $CDCl_3$. Peak positions are shown below the horizontal axis.

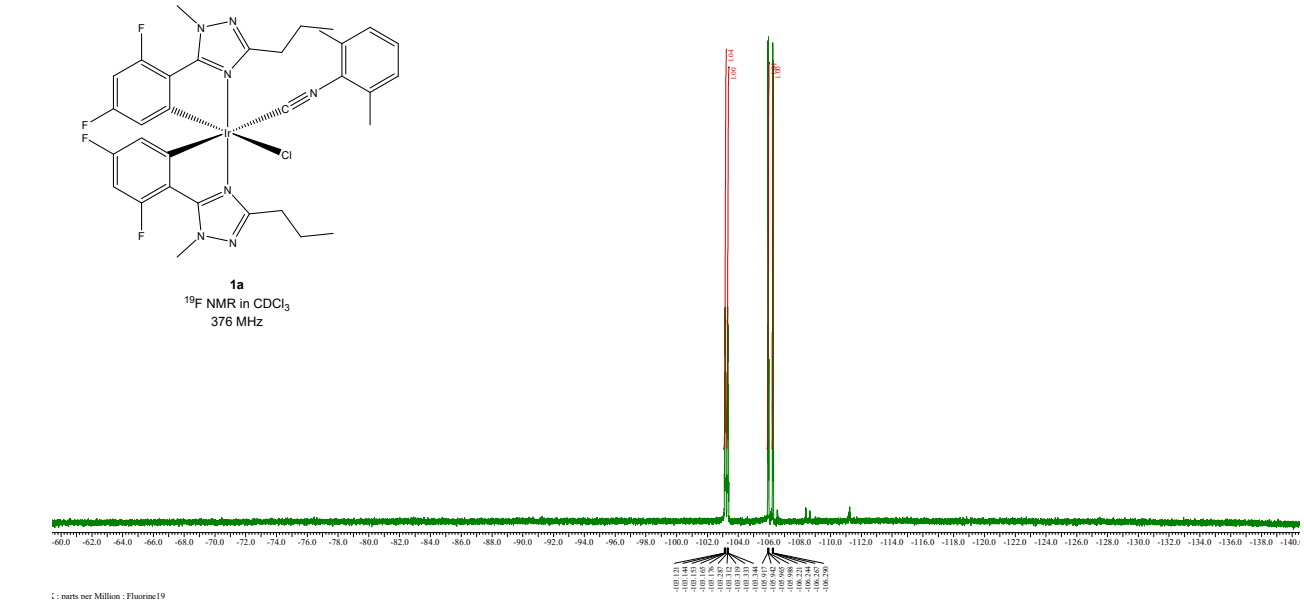

Figure S4. ^{19}F NMR spectrum of Ir(F_2ptz)$_2$(CNAr^{dmp})(Cl) (**1a**), recorded at 376 MHz in $CDCl_3$. Peak positions are shown below the horizontal axis.

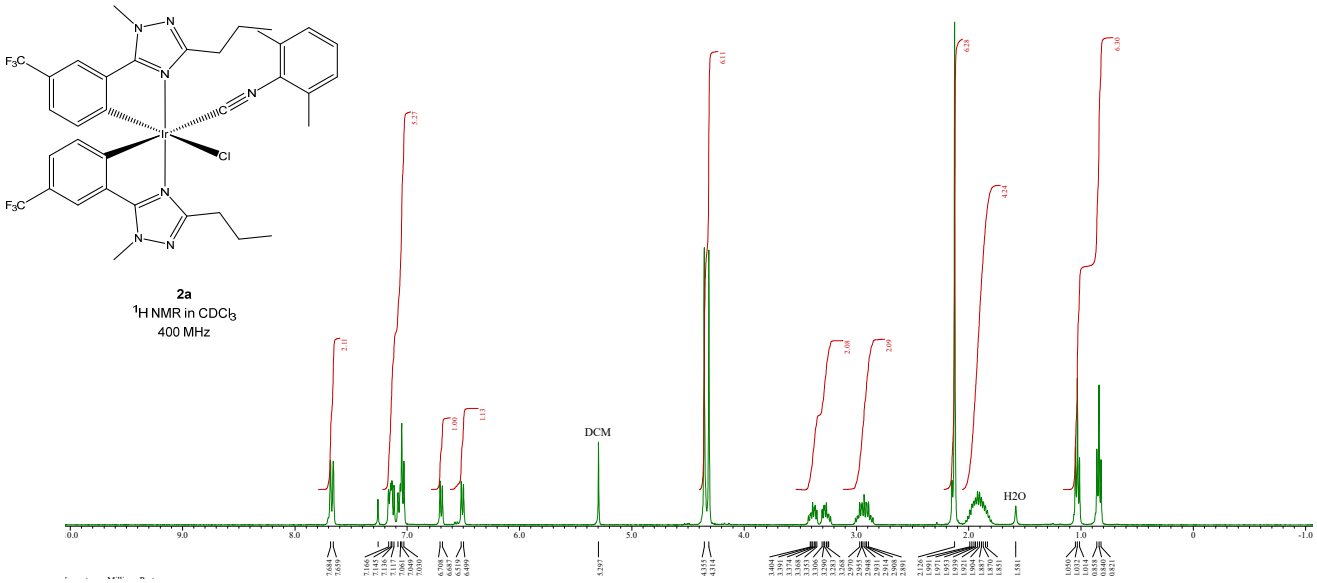

Figure S5. ^{1}H NMR spectrum of Ir(CF$_3$ptz)$_2$(CNAr^{dmp})(Cl) (**2a**), recorded at 400 MHz in CDCl$_3$. Peak positions are shown below the horizontal axis.

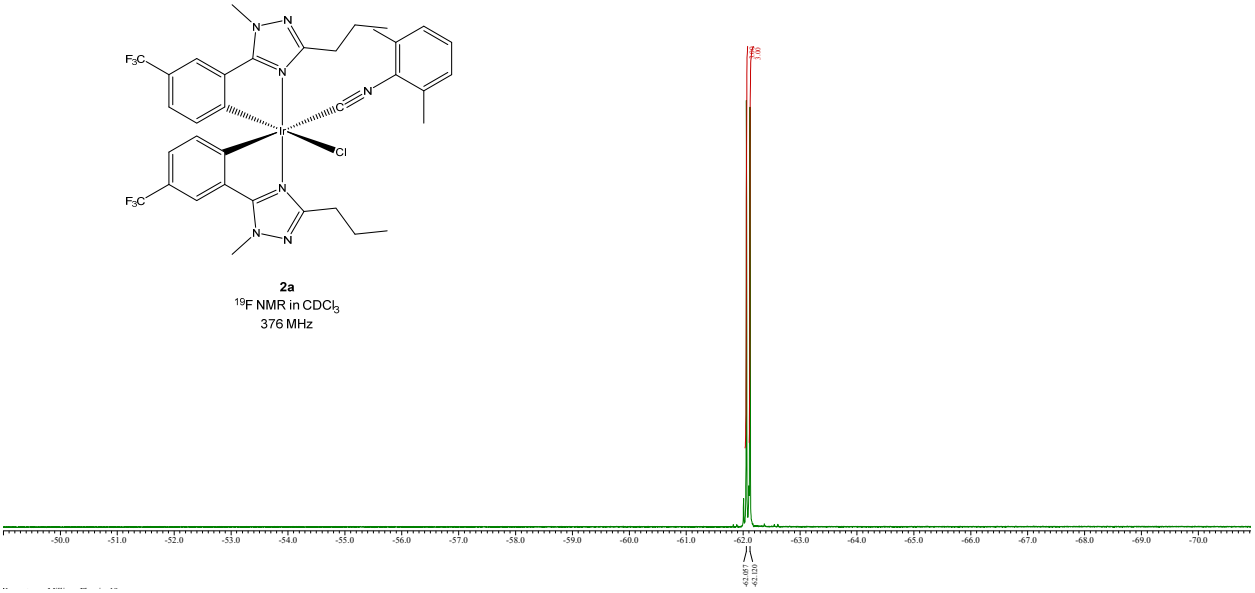

Figure S6. ^{19}F NMR spectrum of Ir(CF$_3$ptz)$_2$(CNAr^{dmp})(Cl) (**2a**), recorded at 376 MHz in CDCl$_3$. Peak positions are shown below the horizontal axis.

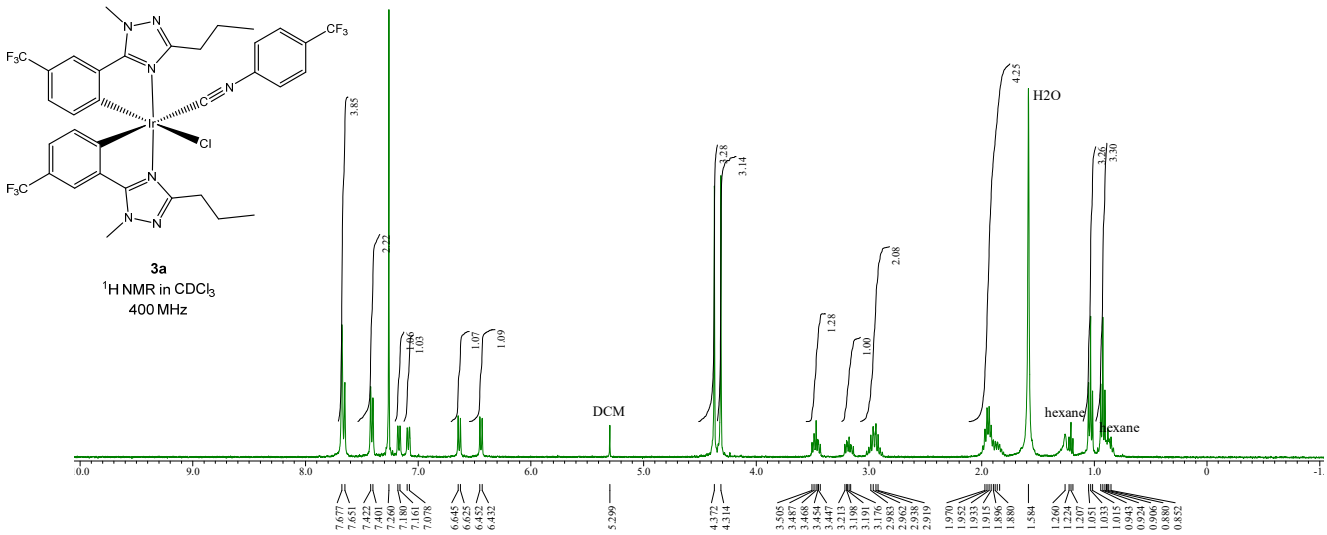

Figure S7. ^{1}H NMR spectrum of $Ir(CF_3ptz)_2(CNAr^{4\text{-}CF3})(Cl)$ (**3a**), recorded at 400 MHz in $CDCl_3$. Peak positions are shown below the horizontal axis.

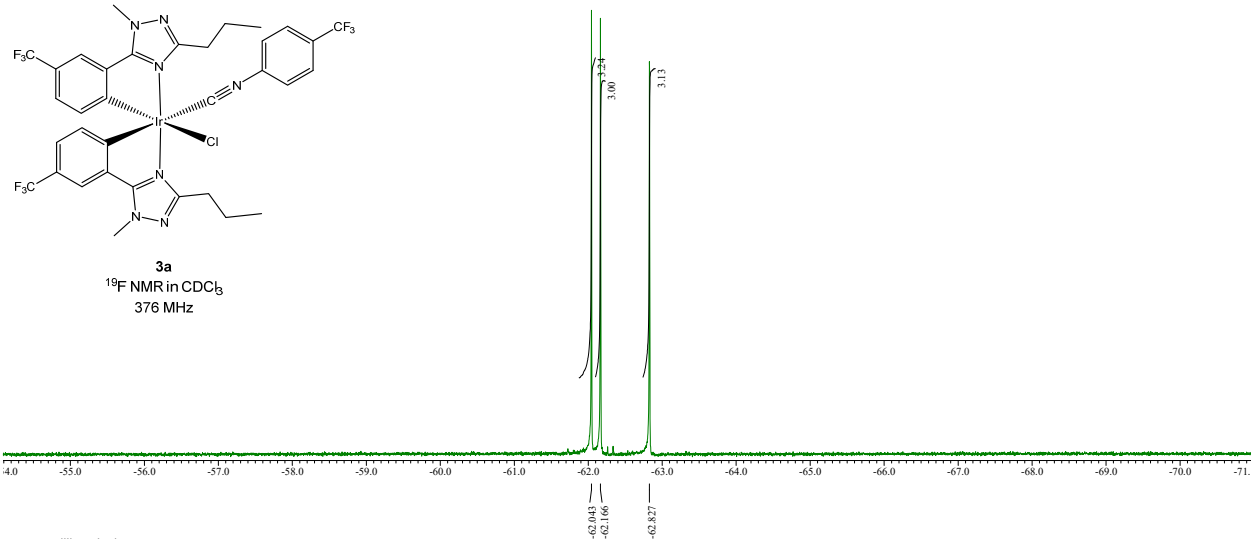

Figure S8. ^{19}F NMR spectrum of $Ir(CF_3ptz)_2(CNAr^{4\text{-}CF3})(Cl)$ (**3a**), recorded at 376 MHz in $CDCl_3$. Peak positions are shown below the horizontal axis.

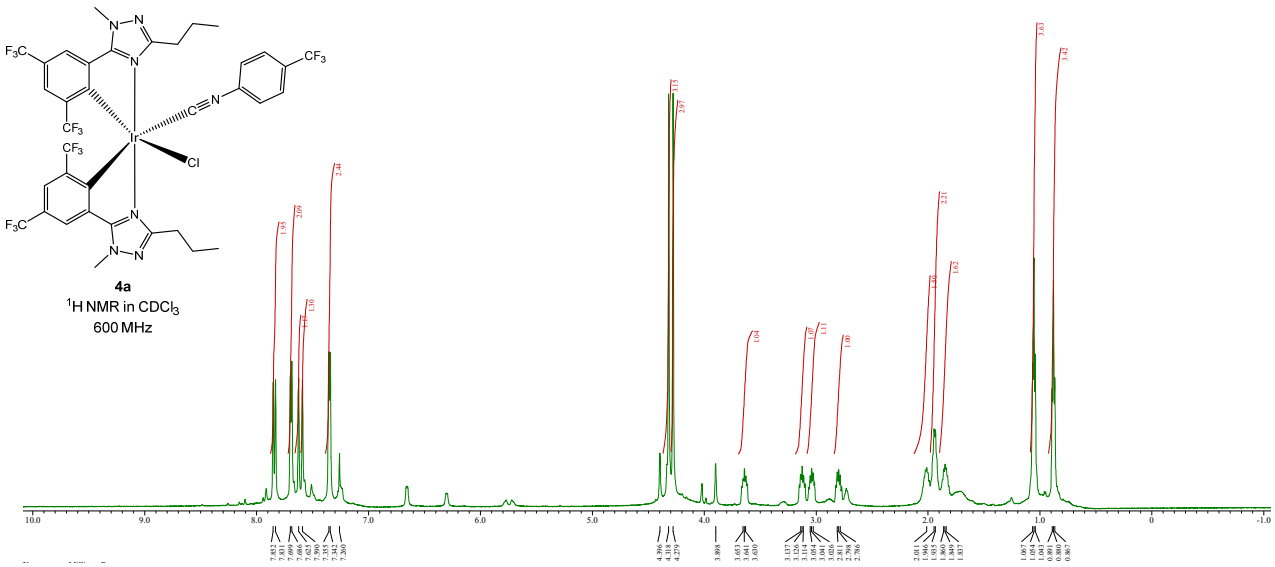

Figure S9. ^{1}H NMR spectrum of $Ir((CF_3)_2ptz)_2(CNAr^{4\text{-}CF3})(Cl)$ (**4a**), recorded at 600 MHz in $CDCl_3$. Peak positions are shown below the horizontal axis.

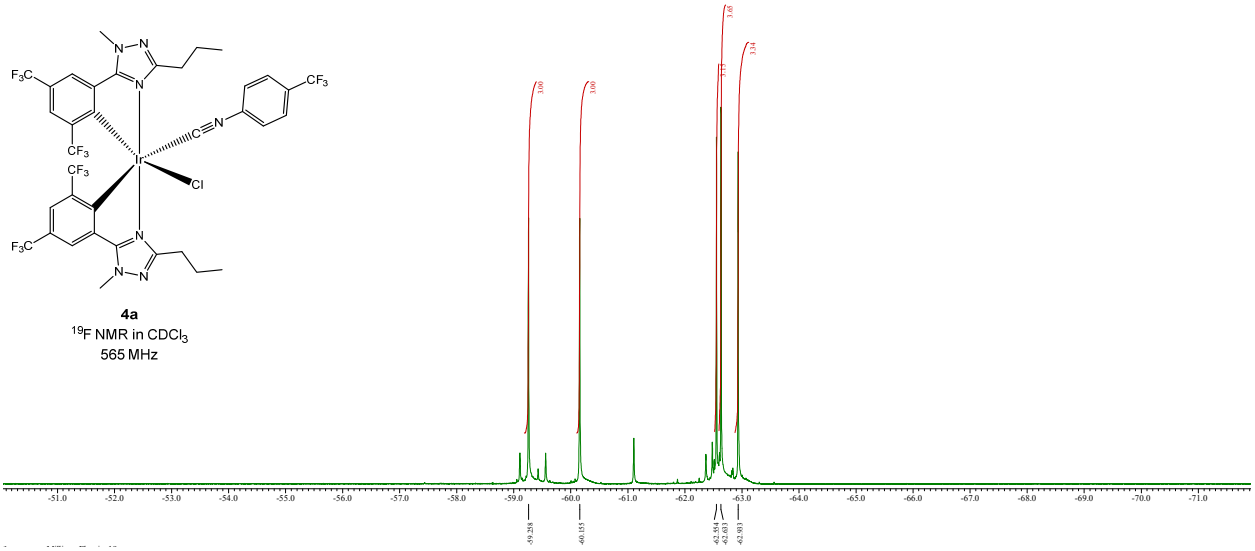

Figure S10. ^{19}F NMR spectrum of $Ir((CF_3)_2ptz)_2(CNAr^{4\text{-}CF3})(Cl)$ (**4a**), recorded at 565 MHz in $CDCl_3$. Peak positions are shown below the horizontal axis.

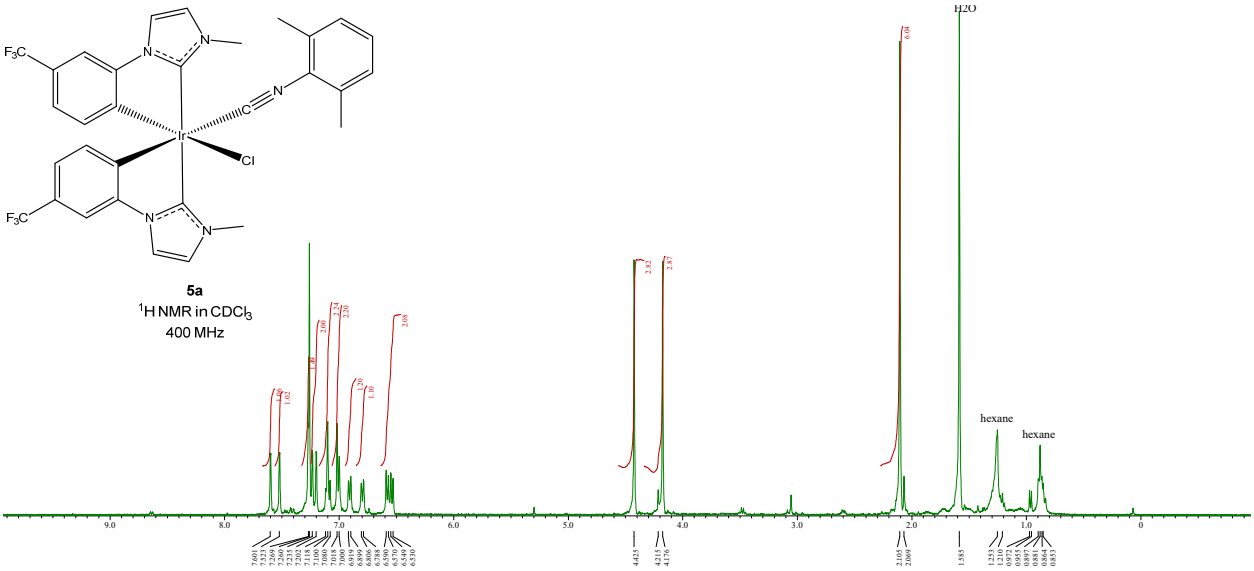

Figure S11. ^{1}H NMR spectrum of Ir(pCF_3pmi)$_2$(CNAr^{dmp})(Cl) (**5a**), recorded at 400 MHz in $CDCl_3$. Peak positions are shown below the horizontal axis.

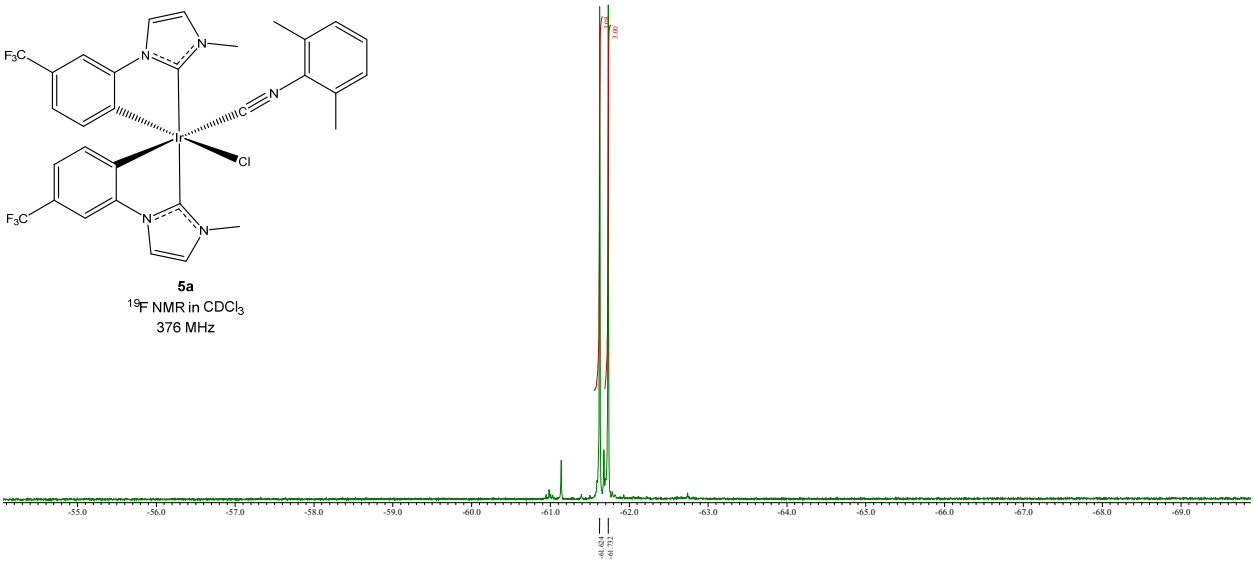

Figure S12. ^{19}F NMR spectrum of Ir(pCF_3pmi)$_2$(CNAr^{dmp})(Cl) (**5a**), recorded at 376 MHz in $CDCl_3$. Peak positions are shown below the horizontal axis.

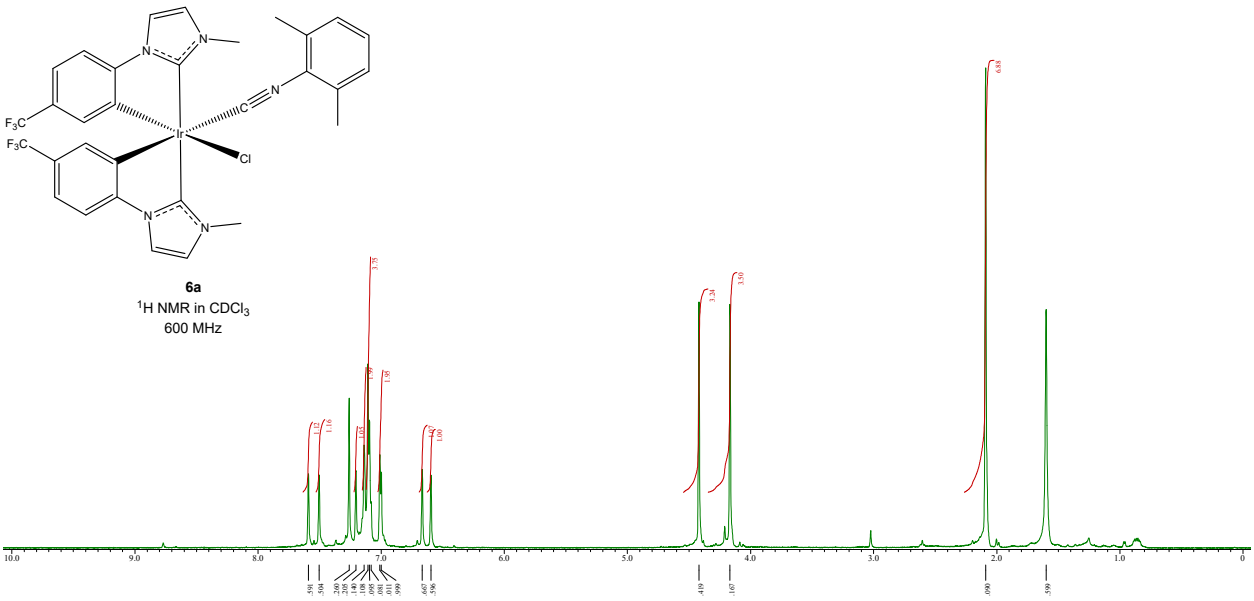

Figure S13. ^{1}H NMR spectrum of Ir(mCF$_3$pmi)$_2$(CNAr^{dmp})(Cl) (**6a**), recorded at 600 MHz in CDCl$_3$. Peak positions are shown below the horizontal axis.

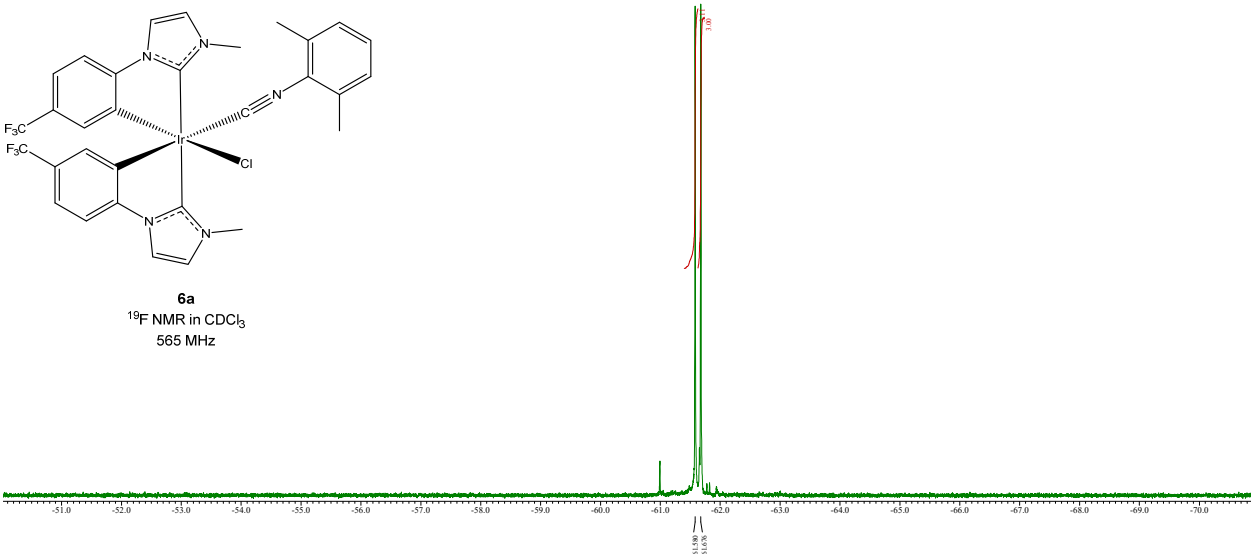

Figure S14. ^{19}F NMR spectrum of Ir(mCF$_3$pmi)$_2$(CNAr^{dmp})(Cl) (**6a**), recorded at 565 MHz in CDCl$_3$. Peak positions are shown below the horizontal axis.

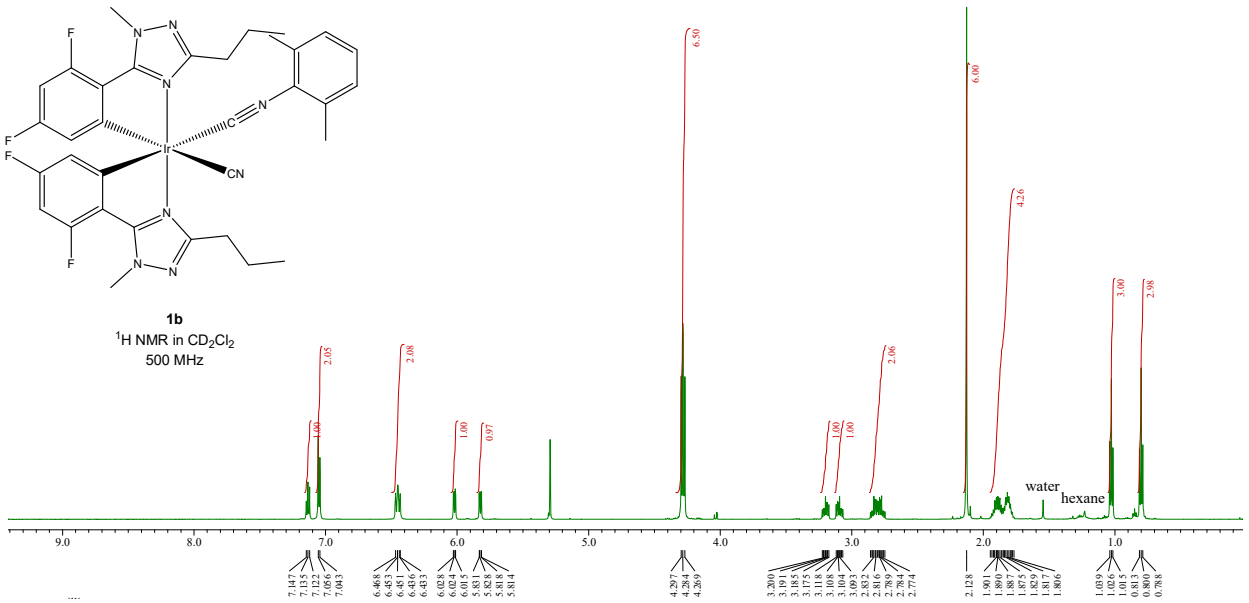

Figure S15. ^{1}H NMR spectrum of Ir(F_2ptz)$_2$(CNAr^{dmp})(CN) (**1b**), recorded at 500 MHz in CD_2Cl_2. Peak positions are shown below the horizontal axis.

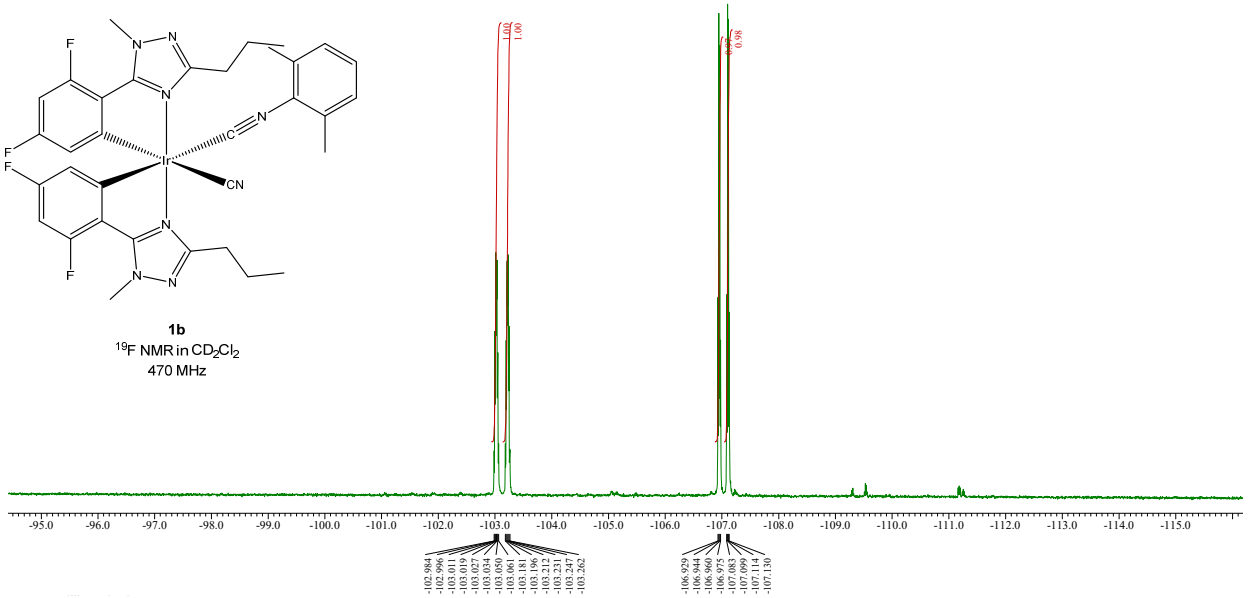

Figure S16. ^{19}F NMR spectrum of Ir(F_2ptz)$_2$(CNAr^{dmp})(CN) (**1b**), recorded at 470 MHz in CD_2Cl_2. Peak positions are shown below the horizontal axis.

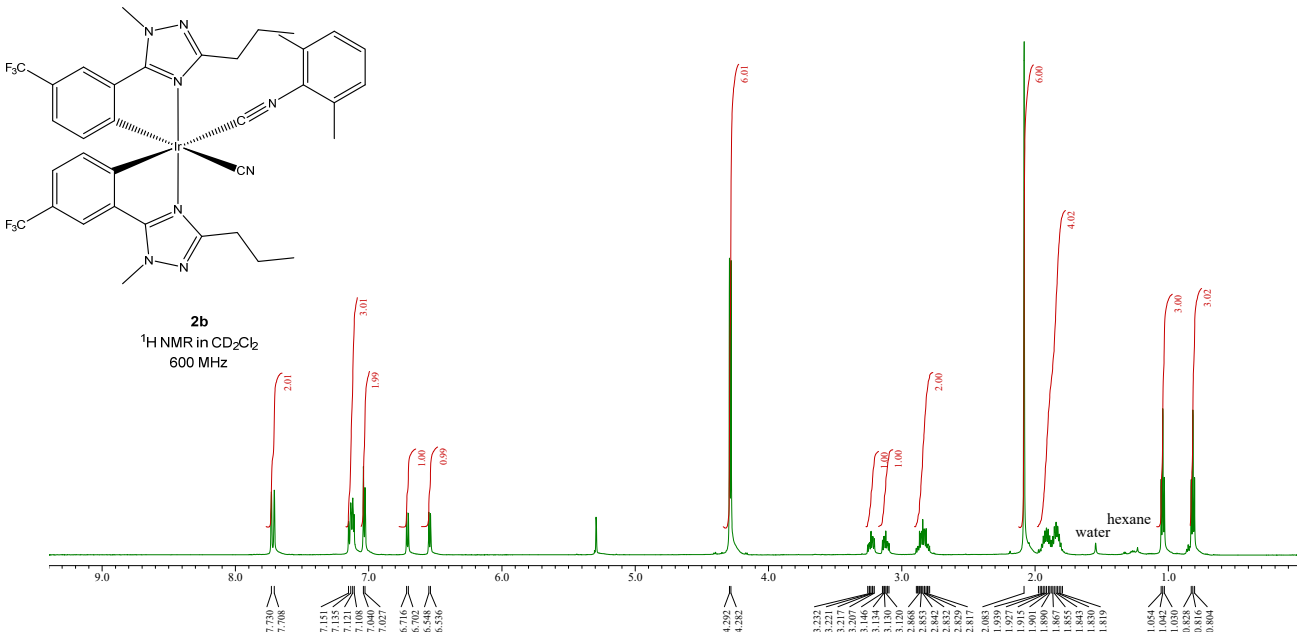

Figure S17. ^{1}H NMR spectrum of Ir(CF$_3$ptz)$_2$(CNAr^{dmp})(CN) (**2b**), recorded at 600 MHz in CD_2Cl_2. Peak positions are shown below the horizontal axis.

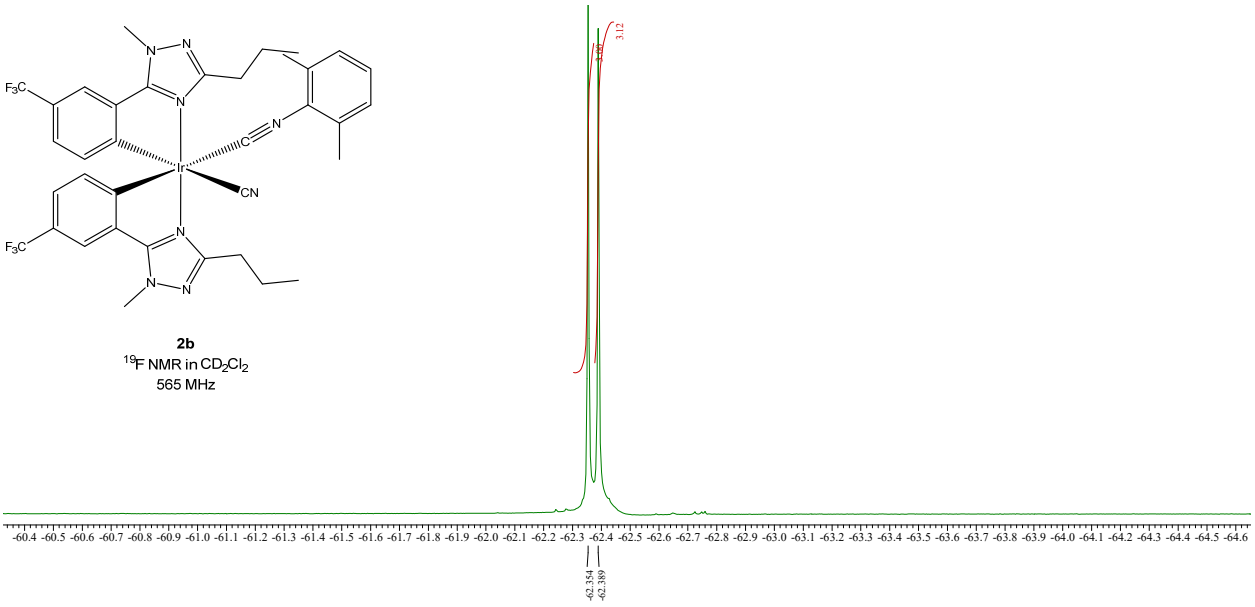

Figure S18. ^{19}F NMR spectrum of Ir(CF$_3$ptz)$_2$(CNAr^{dmp})(CN) (**2b**), recorded at 565 MHz in CD_2Cl_2. Peak positions are shown below the horizontal axis.

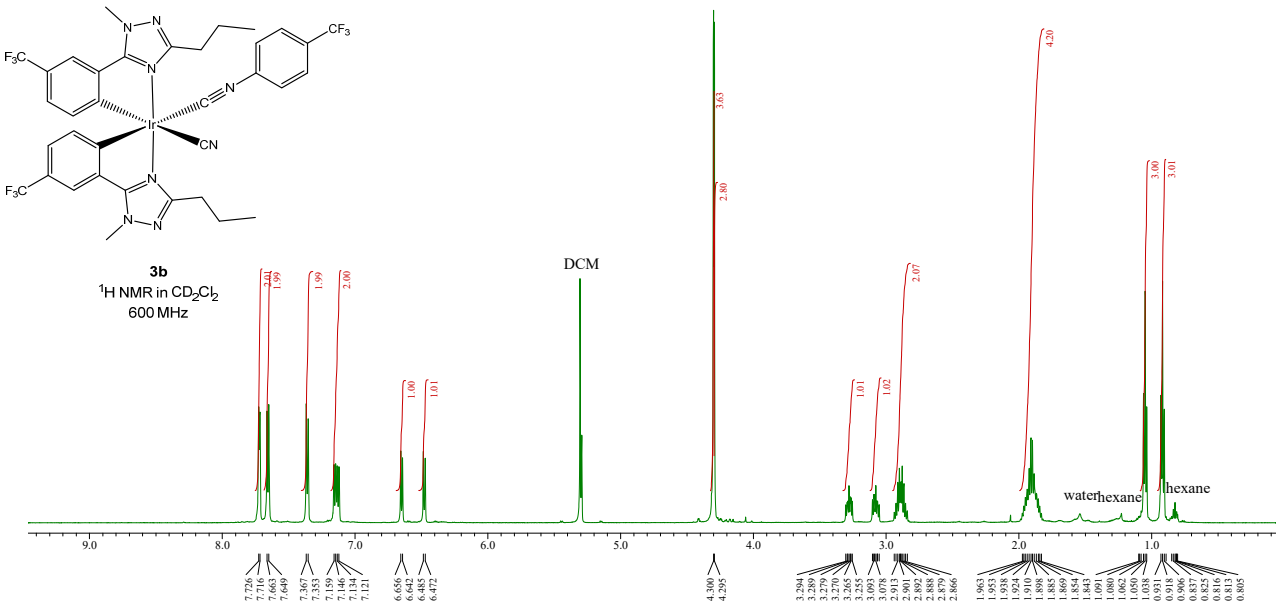

Figure S19. ^{1}H NMR spectrum of Ir(CF$_3$ptz)$_2$(CNAr$^{4\text{-CF3}}$)(CN) (**3b**), recorded at 600 MHz in CD_2Cl_2. Peak positions are shown below the horizontal axis.

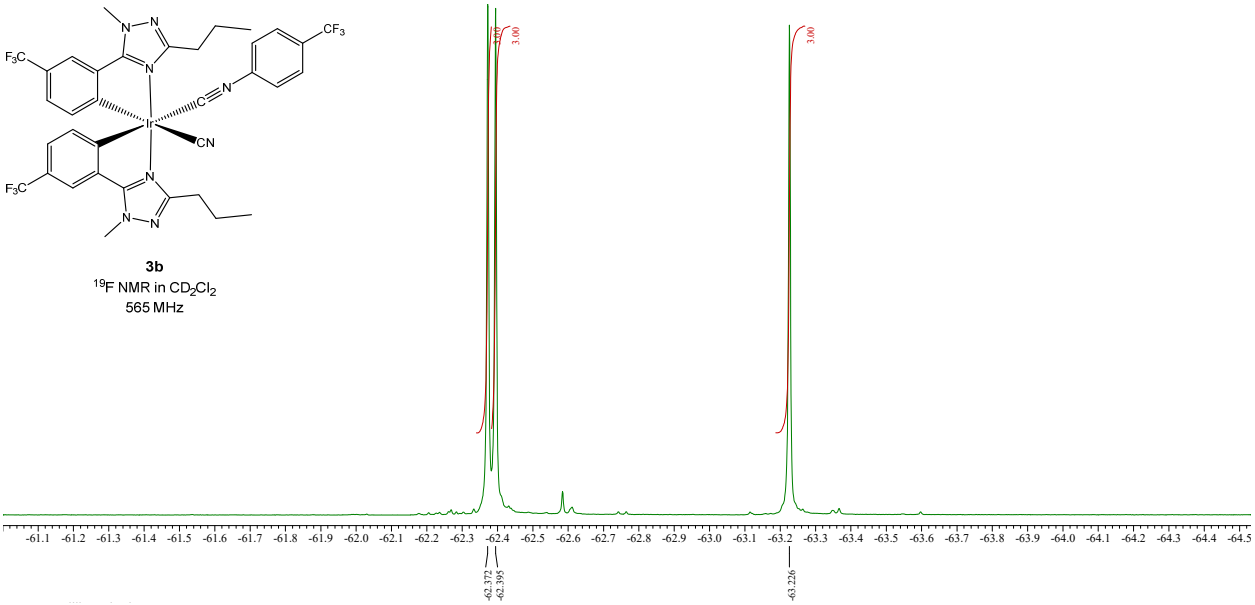

Figure S20. ^{19}F NMR spectrum of Ir(CF$_3$ptz)$_2$(CNAr$^{4\text{-CF3}}$)(CN) (**3b**), recorded at 565 MHz in CD_2Cl_2. Peak positions are shown below the horizontal axis.

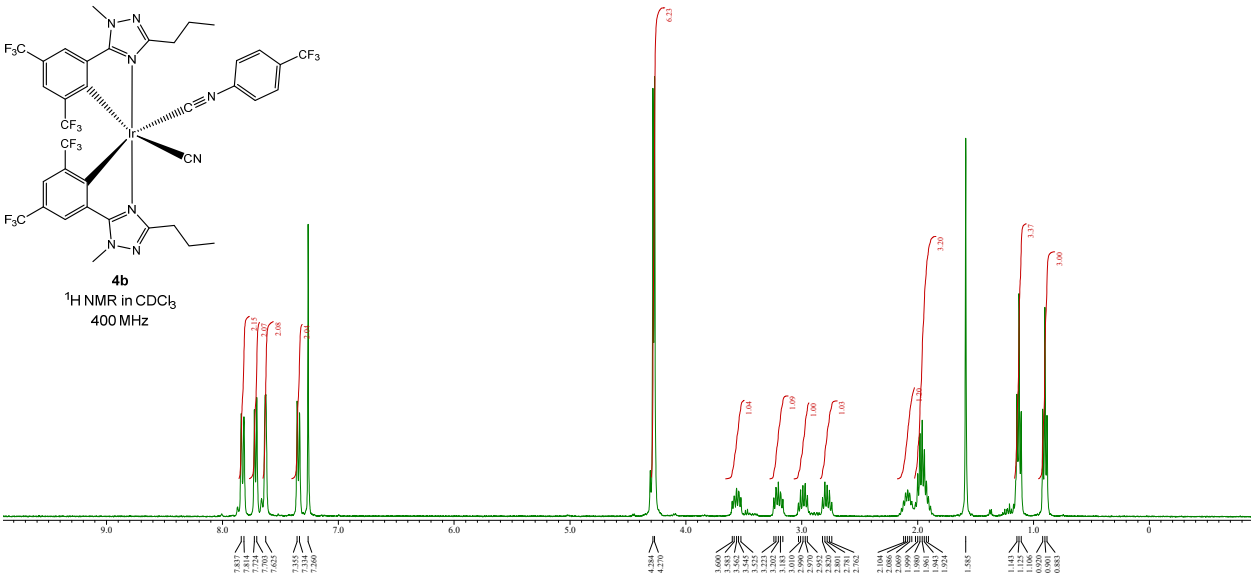

Figure S21. ^{1}H NMR spectrum of Ir((CF$_3$)$_2$ptz)$_2$(CNAr$^{4\text{-CF3}}$)(CN) (**4b**), recorded at 400 MHz in $CDCl_3$. Peak positions are shown below the horizontal axis.

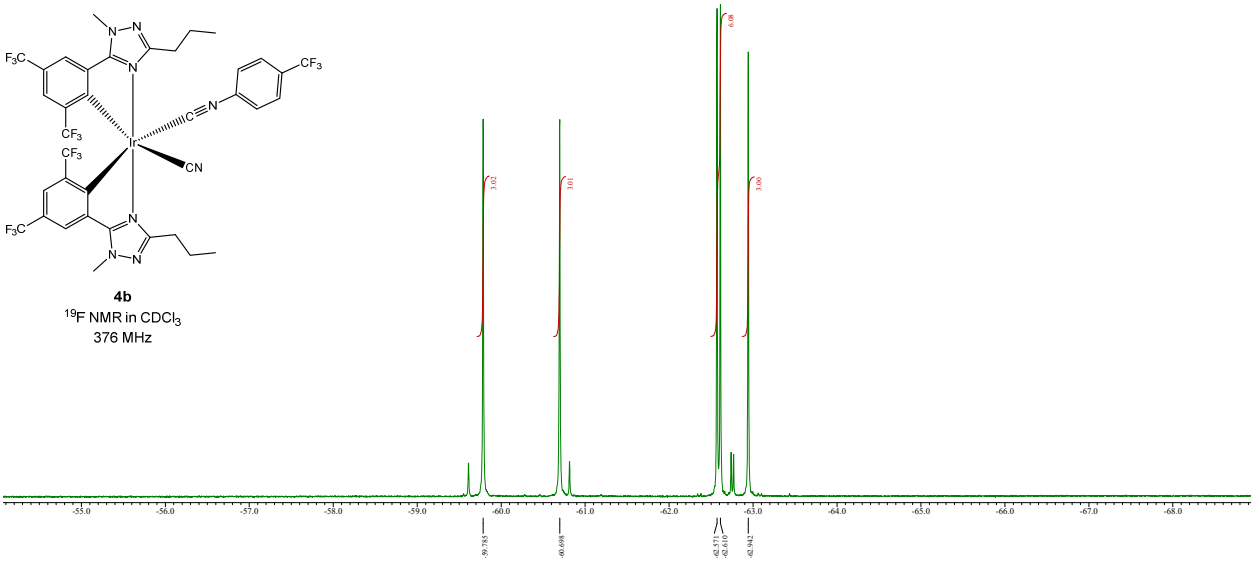

Figure S22. ^{19}F NMR spectrum of Ir((CF$_3$)$_2$ptz)$_2$(CNAr$^{4\text{-CF3}}$)(CN) (**4b**), recorded at 376 MHz in $CDCl_3$. Peak positions are shown below the horizontal axis.

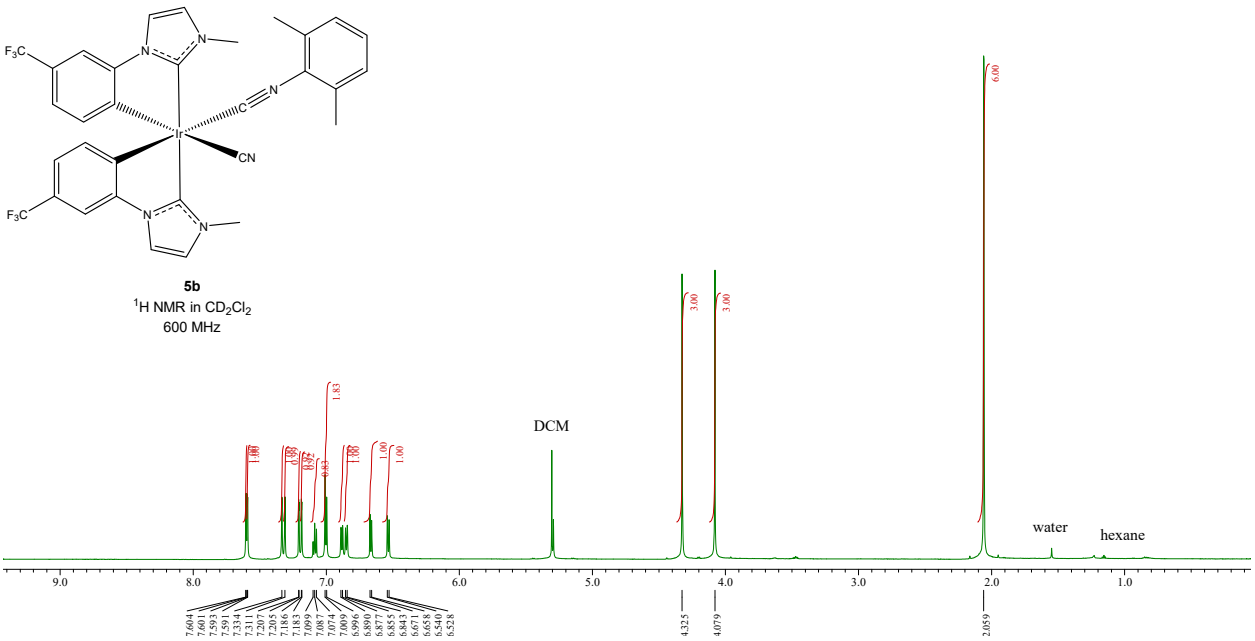

Figure S23. ^{1}H NMR spectrum of Ir(pCF_3pmi)$_2$(CNAr^{dmp})(CN) (**5b**), recorded at 600 MHz in CD_2Cl_2. Peak positions are shown below the horizontal axis.

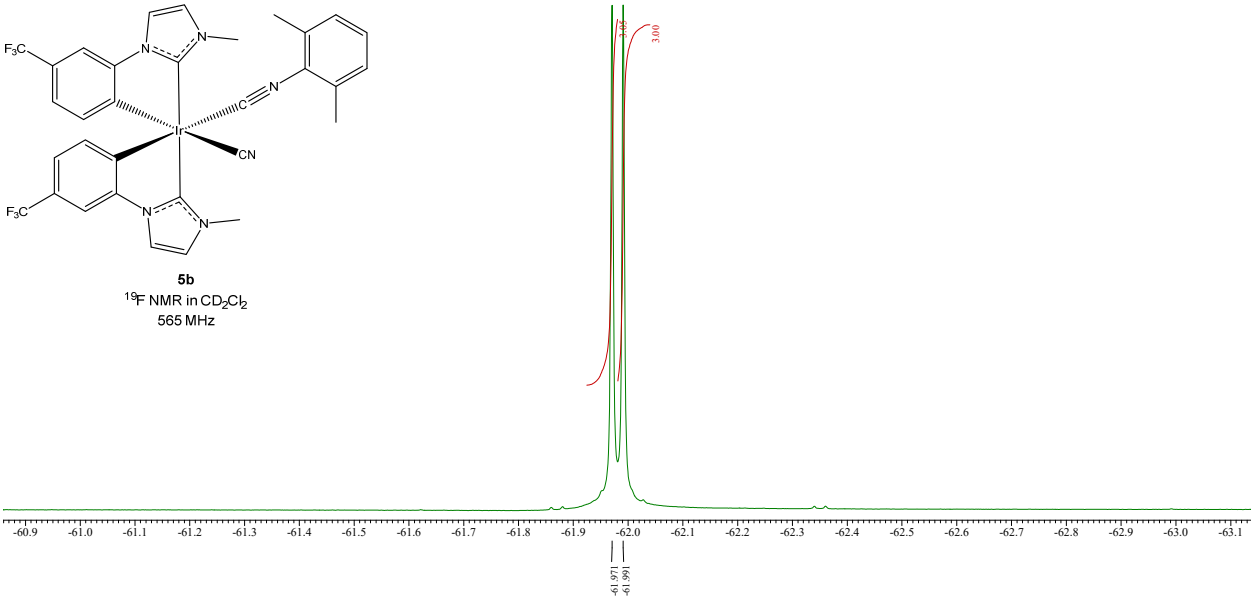

Figure S24. ^{19}F NMR spectrum of Ir(pCF_3pmi)$_2$(CNAr^{dmp})(CN) (**5b**), recorded at 565 MHz in CD_2Cl_2. Peak positions are shown below the horizontal axis.

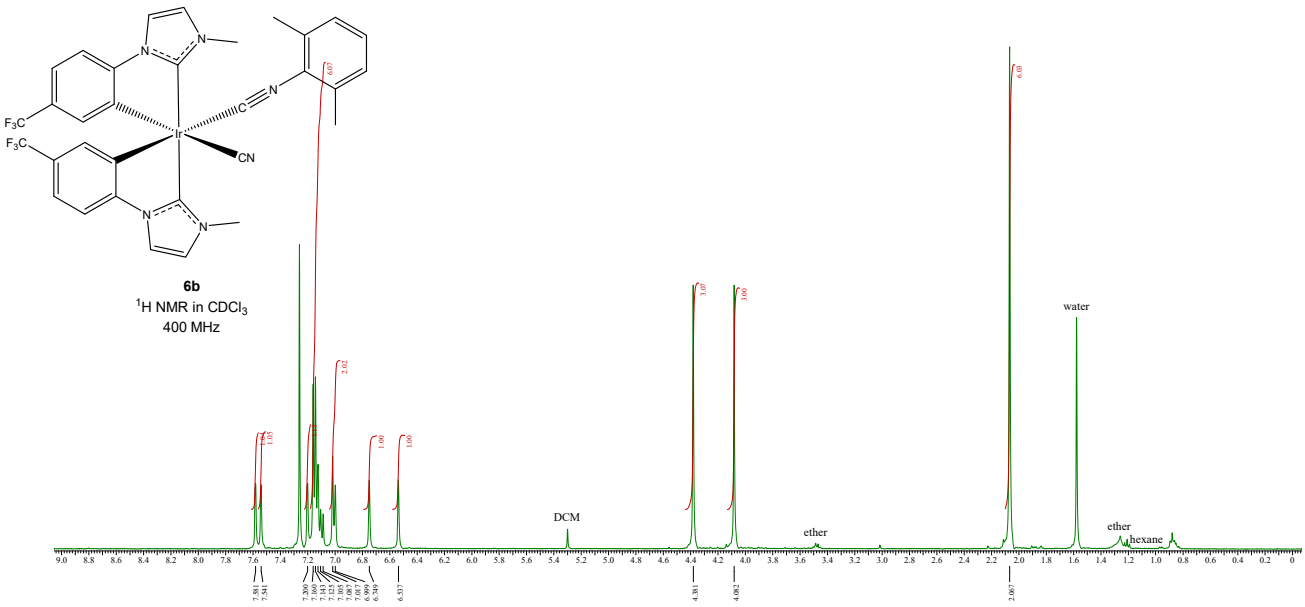

Figure S25. ^{1}H NMR spectrum of Ir(mCF_3pmi)$_2$(CNAr^{dmp})(CN) (**6b**), recorded at 400 MHz in $CDCl_3$. Peak positions are shown below the horizontal axis.

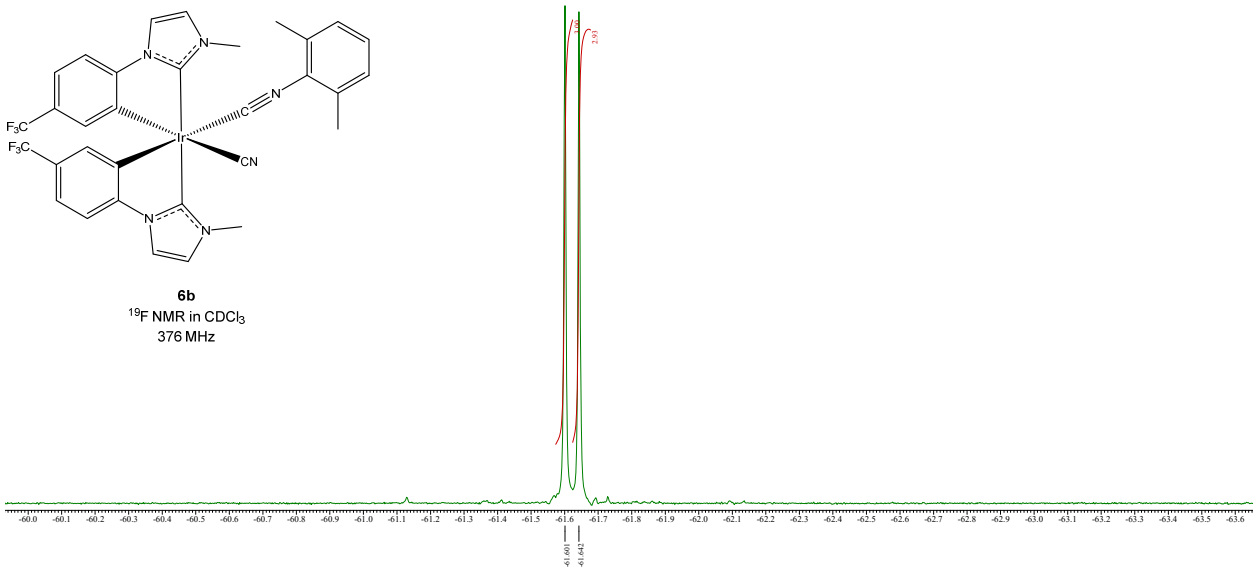

Figure S26. ^{19}F NMR spectrum of Ir(mCF_3pmi)$_2$(CNAr^{dmp})(CN) (**6b**), recorded at 376 MHz in $CDCl_3$. Peak positions are shown below the horizontal axis.

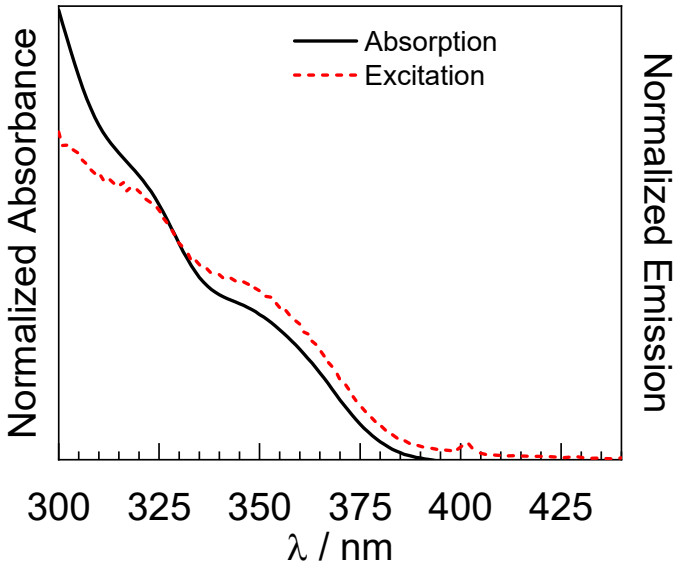

Figure S27. Excitation spectrum of $Ir(CF_3ptz)_2(CNAr^{dmp})(Cl)$ (**2a**), overlaid with its normalized absorption spectrum. Spectra were recorded in CH_2Cl_2 at room temperature, with λ_{em} = 455 nm for the excitation spectrum.

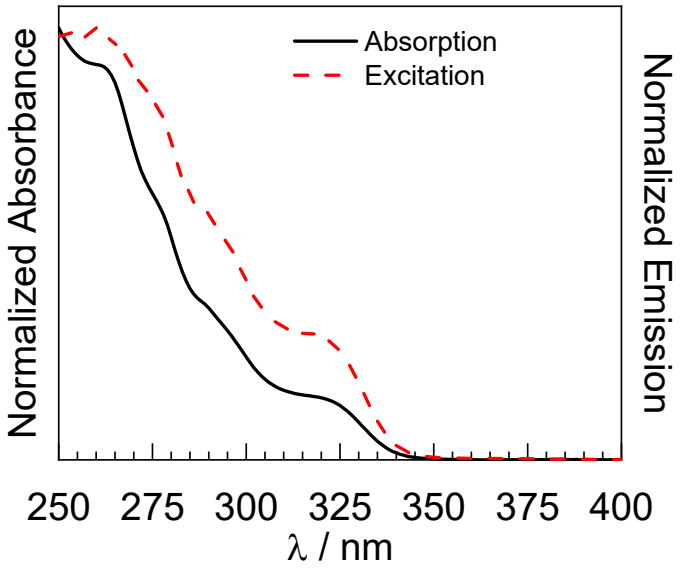

Figure S28. Excitation spectrum of $Ir(F_2ptz)_2(CNAr^{dmp})(CN)$ (**1b**), overlaid with its normalized absorption spectrum. Spectra were recorded in CH_2Cl_2 at room temperature, with λ_{em} = 437 nm for the excitation spectrum.

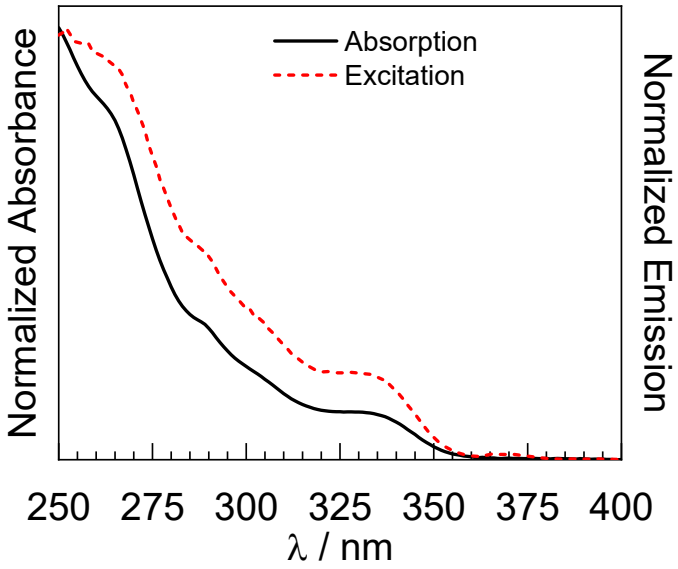

Figure S29. Excitation spectrum of $Ir(CF_3ptz)_2(CNAr^{dmp})(CN)$ (**2b**), overlaid with its normalized absorption spectrum. Spectra were recorded in CH_2Cl_2 at room temperature, with λ_{em} = 445 nm for the excitation spectrum.

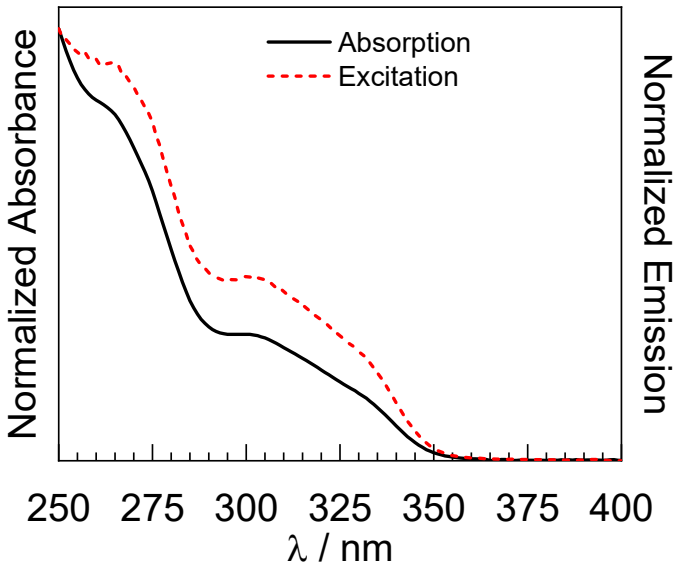

Figure S30. Excitation spectrum of $Ir(CF_3ptz)_2(CNAr^{4\text{-}CF3})(CN)$ (**3b**), overlaid with its normalized absorption spectrum. Spectra were recorded in CH_2Cl_2 at room temperature, with λ_{em} = 444 nm for the excitation spectrum.

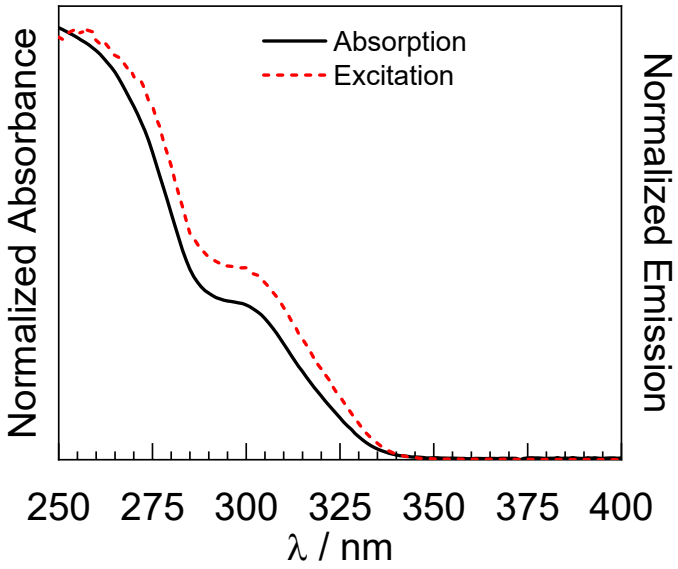

Figure S31. Excitation spectrum of $Ir((CF_3)_2ptz)_2(CNAr^{4\text{-}CF3})(CN)$ (**4b**), overlaid with its normalized absorption spectrum. Spectra were recorded in CH_2Cl_2 at room temperature, with λ_{em} = 460 nm for the excitation spectrum.

Table S5. Summary of radiative and nonradiative rate constants for the compounds that luminesce in solution.

	λ / nm	Φ_{PL}	τ / μs	k_r / s^{-1}	k_{nr} / s^{-1}
2a	426, 455, 485(sh)	0.0024	4.0	6.0×10^2	2.5×10^5
1b	411, 437, 464, 495(sh)	0.047	6.4	7.3×10^3	1.5×10^5
2b	418, 445, 472, 508(sh)	0.090	7.6	1.2×10^4	1.2×10^5
3b	417, 444, 472, 507(sh)	0.064	4.0	1.6×10^4	2.3×10^5
4b	432(sh), 462, 484(sh)	0.17	31	5.5×10^3	2.7×10^4

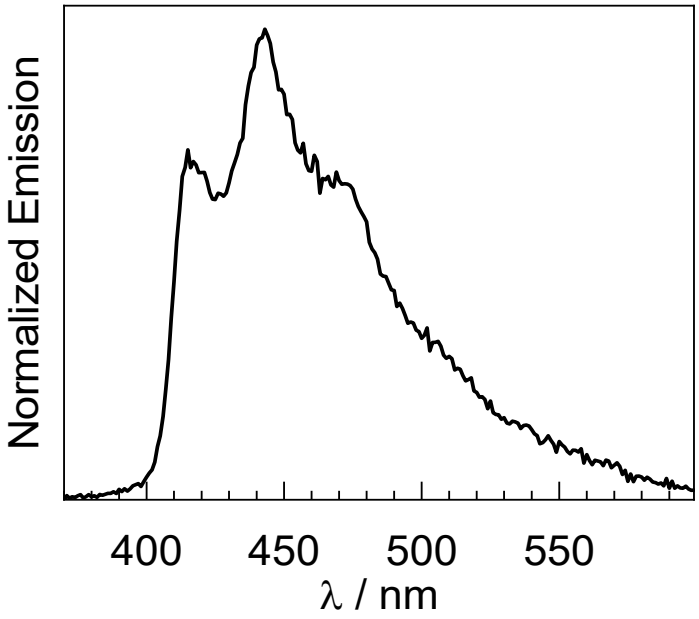

Figure S32. Photoluminescence spectrum of $Ir(F_2ptz)_2(CNAr^{dmp})(Cl)$ (**1a**). Spectrum was recorded in 2 wt% PMMA thin film at room temperature. Sample was excited at λ = 310 nm.

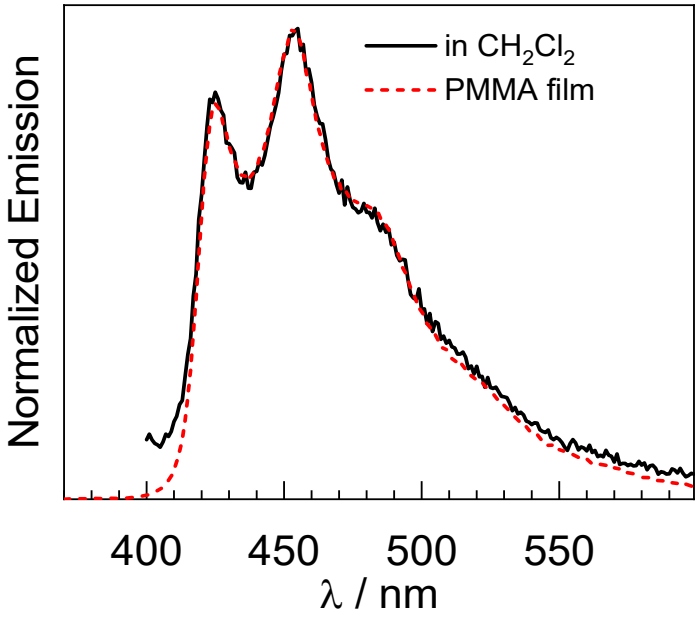

Figure S33. Photoluminescence spectra of $Ir(CF_3ptz)_2(CNAr^{dmp})(Cl)$ (**2a**). Spectra were recorded in CH_2Cl_2 and 2 wt% PMMA thin film at room temperature. Excitation wavelengths for photoluminescence are 310 and 346 nm.

Table S6. Summary of photophysical data for complexes **1a**–**6a**.

	UV-vis Absorption	Photoluminescence					
		CH_2Cl_2, RT			PMMA, RT		
	λ / nm (ε × 10^{-3} / $M^{-1}cm^{-1}$)	λ / nm	Φ_{PL}	τ / μs	λ / nm	Φ_{PL}	(CIEx, CIEy)
1a	253 (45), 307 (9.2), 334 (4.9)	a	a	a	415, 443, 474(sh)	0.013	(0.16, 0.15)
2a	254 (40), 322 (6.1), 349 (3.3)	426, 455, 485(sh)	0.0024	4.0	425, 453, 484(sh)	0.043	(0.15, 0.14)
3a	256 (37), 312 (10), 346 (6.5)	a	a	a	b	b	b
4a	263 (34), 307 (13), 340 (4.4)	a	a	a	b	b	b
5a	288 (19), 320 (6.4)	a	a	a	b	b	b
6a	297 (16), 322 (7.4)	a	a	a	b	b	b

[a] These compounds are not luminescent at room temperature in solution. [b] These compounds are not luminescent at room temperature in PMMA thin film.

Table S7. Optimized Cartesian coordinates for **2a′** in the ground state (S_0).

	X	Y	Z
Cl	-0.56467	-3.71409	1.11997
Ir	-0.12057	-1.24790	0.74158
N	-0.92739	-0.47641	2.49919
N	-1.93250	0.10010	4.39304
N	-1.51217	1.21447	3.71986
N	0.41246	-1.80510	-1.18360
N	1.22867	-2.56096	-3.10605
N	-0.10251	-2.27632	-3.23315
N	2.56525	-2.07447	2.17695
F	-0.21833	5.72140	1.02397
F	1.88992	5.40652	0.60665
F	0.47407	5.51896	-1.03270
F	-6.30503	0.13481	-2.38440
F	-6.26319	-2.02956	-2.51701
F	-5.24832	-0.83830	-4.02318
C	-1.81991	-2.33618	3.95686
H	-2.40439	-2.80919	3.16611
H	-0.88143	-2.89085	4.00792
H	-2.34604	-2.40047	4.90864
C	-1.56409	-0.91100	3.62863
C	-1.76581	2.53202	4.27959
H	-0.82638	3.04874	4.48443
H	-2.30809	2.37937	5.20922
H	-2.37255	3.12672	3.59449
C	-0.90446	0.86652	2.57391
C	0.18426	0.75201	0.45367
C	0.78512	1.36457	-0.65263
H	1.15307	0.75192	-1.46691
C	0.91322	2.74634	-0.73366
H	1.37383	3.20259	-1.60220
C	0.43787	3.56218	0.29727
C	-0.16582	2.99413	1.41208
H	-0.53239	3.64117	2.19610
C	-0.29376	1.60497	1.48670
C	0.63943	5.04524	0.22283
C	2.84877	-2.46239	-1.23920
H	3.19345	-1.54010	-0.76735
H	2.80267	-3.23519	-0.46849

H	3.55940	-2.76530	-2.00689
C	1.50752	-2.27313	-1.85050
C	-0.76842	-2.51046	-4.50427
H	-1.58229	-3.22636	-4.37857
H	-0.02172	-2.92111	-5.17905
H	-1.15688	-1.57562	-4.91232
C	-0.59936	-1.82373	-2.07011
C	-1.94661	-1.07519	-0.25018
C	-3.17963	-0.67681	0.27625
H	-3.25729	-0.41277	1.32431
C	-4.32288	-0.61093	-0.51357
H	-5.26704	-0.29371	-0.08611
C	-4.26166	-0.94209	-1.86905
C	-3.05826	-1.34821	-2.43286
H	-3.03089	-1.59575	-3.48412
C	-1.91782	-1.41230	-1.62898
C	-5.51139	-0.91575	-2.69612
C	1.61050	-1.65701	1.63652
C	3.42947	-3.01910	2.71270
C	3.02036	-4.35892	2.72831
H	2.04265	-4.61486	2.33389
C	3.88225	-5.31448	3.25327
H	3.57627	-6.35389	3.27033
C	5.12999	-4.94234	3.75586
H	5.79524	-5.69432	4.16371
C	5.52208	-3.60464	3.73499
H	6.49046	-3.31524	4.12567
C	4.67385	-2.63308	3.21289
H	4.96035	-1.58917	3.18724

Point group (P.G.) = C_1

Total electronic energy = –2666.63836 a.u.

Table S8. Optimized Cartesian coordinates for **2b′** in the ground state (S_0).

	X	Y	Z
Ir	1.65807	-0.23213	-0.21194
N	2.69208	-1.66866	-1.30198
C	3.43572	0.83997	-0.00902
F	1.06869	2.78604	-6.58944
F	-0.20168	1.04338	-6.82150
N	3.87339	-3.32002	-2.20131
F	1.93932	0.86591	-7.14132
N	3.39775	-2.48954	-3.17717
F	-4.46719	-3.58564	0.38483
N	0.35161	1.20010	0.54345
F	-4.38712	-3.56294	-1.78280
N	-0.80544	2.93402	1.30616
F	-5.15991	-1.83644	-0.70039
N	-1.64925	1.91548	0.95588
N	2.55419	-1.12917	2.67492
N	4.44969	1.36419	0.20970
C	3.72925	-3.34886	0.26960
H	4.31550	-2.63498	0.85289
H	2.80537	-3.54724	0.81669
H	4.29422	-4.27394	0.16475
C	3.43344	-2.79256	-1.07644
C	3.71570	-2.76207	-4.56983
H	2.80394	-2.93989	-5.14278
H	4.33464	-3.65552	-4.58155
H	4.26882	-1.92723	-5.00323
C	2.68483	-1.48721	-2.63546
C	1.40264	0.46883	-2.16516
C	0.72592	1.61843	-2.58572
H	0.27834	2.27736	-1.85107
C	0.61500	1.94660	-3.93254
H	0.09350	2.84687	-4.23620
C	1.18810	1.12568	-4.90703
C	1.87609	-0.02167	-4.53354
H	2.32030	-0.63801	-5.30164
C	1.98359	-0.34030	-3.17712
C	1.00489	1.45568	-6.35766
C	1.65333	3.23968	1.26852
H	2.31211	2.71020	1.95911

H	2.21134	3.34565	0.33688
H	1.40847	4.22178	1.67087
C	0.40191	2.47100	1.04537
C	-3.08481	2.09010	1.10819
H	-3.58570	1.98830	0.14396
H	-3.23923	3.09372	1.49605
H	-3.48685	1.35945	1.81229
C	-0.95150	0.86424	0.49434
C	-0.18618	-1.20715	-0.41677
C	-0.43732	-2.48409	-0.93128
H	0.39289	-3.09771	-1.26347
C	-1.72937	-2.98836	-1.03607
H	-1.90190	-3.97741	-1.44460
C	-2.82065	-2.21742	-0.62638
C	-2.61912	-0.94293	-0.11081
H	-3.47750	-0.36103	0.19268
C	-1.31639	-0.44626	-0.01149
C	-4.20252	-2.79477	-0.68572
C	2.11326	-0.87808	1.61683
C	3.47654	-1.12252	3.71462
C	3.23880	-1.86861	4.86967
H	2.32893	-2.44966	4.95359
C	4.18244	-1.84799	5.89190
H	4.00779	-2.42370	6.79309
C	5.34586	-1.09141	5.75837
H	6.07726	-1.07931	6.55794
C	5.57020	-0.34948	4.59779
H	6.47369	0.23947	4.49315
C	4.63981	-0.35586	3.56506
H	4.79104	0.21467	2.65434

Point group (P.G.) = C_1

Total electronic energy = –2299.24973 a.u.

Table S9. Optimized Cartesian coordinates for **4b′** in the ground state (S_0).

	X	Y	Z
Ir	0.37336	-0.87698	0.23037
F	0.38077	-4.11535	-3.69266
F	0.39685	-1.95742	-3.58779
F	1.55285	-3.14051	-2.16480
F	-4.81990	-5.53435	-1.00873
F	-5.04358	-4.14307	-2.66006
F	-3.77630	-5.89029	-2.88906
F	-2.61145	4.21484	-3.78195
F	-2.77742	2.47801	-5.07287
F	-3.56012	2.18406	1.00820
F	-3.29566	0.04379	1.13303
F	-1.70777	1.38856	1.78886
N	-0.89845	-1.35854	1.80004
N	-1.95380	-1.81560	3.69514
N	-2.50656	-2.51701	2.66313
N	1.57545	-0.44500	-1.41176
N	3.11895	-0.07984	-2.95928
N	1.95362	0.54977	-3.29311
N	1.66921	1.57751	1.69480
N	2.29541	-3.06780	1.58451
C	1.61294	-2.28597	1.06482
C	-0.04989	-0.26415	3.92220
H	0.98433	-0.55736	3.73139
H	-0.17254	0.78308	3.64298
H	-0.26509	-0.37466	4.98400
C	-0.97253	-1.13110	3.14608
C	-3.61609	-3.41701	2.93310
H	-4.54127	-3.03043	2.50098
H	-3.71658	-3.47265	4.01399
H	-3.40250	-4.40902	2.53342
C	-1.85877	-2.24413	1.51859
C	-0.83639	-2.43306	-0.65577
C	-0.80699	-3.12900	-1.88323
C	-1.85955	-3.94519	-2.30946
H	-1.79928	-4.44951	-3.26342
C	-2.97741	-4.13834	-1.51196
C	-3.01047	-3.57265	-0.24687
H	-3.86077	-3.76329	0.39065

C	-1.95050	-2.77133	0.17315
C	0.37848	-3.08395	-2.81666
C	-4.14714	-4.92951	-2.01711
C	3.87209	-1.45370	-1.04852
H	4.00526	-1.03858	-0.04781
H	3.53819	-2.48172	-0.91430
H	4.81979	-1.43443	-1.58524
C	2.86641	-0.67014	-1.80856
C	1.87702	1.27223	-4.55194
H	1.20354	0.76326	-5.24426
H	2.88182	1.28275	-4.96638
H	1.53912	2.29595	-4.38464
C	1.02226	0.33057	-2.35163
C	-0.85512	0.53993	-0.85344
C	-2.05958	1.20758	-0.55760
C	-2.76031	1.95417	-1.51012
H	-3.69610	2.42833	-1.24896
C	-2.26333	2.09305	-2.79760
C	-1.02388	1.55332	-3.11280
H	-0.63083	1.69510	-4.10864
C	-0.32791	0.82429	-2.15011
C	-2.65262	1.19679	0.82888
C	-3.00088	2.91593	-3.81238
C	1.23097	0.63362	1.16129
C	1.90183	2.75023	2.39118
C	0.81716	3.58266	2.69191
H	-0.17691	3.29650	2.37213
C	1.04658	4.75618	3.40051
H	0.21308	5.40589	3.63939
C	2.33852	5.09669	3.80155
H	2.50957	6.01333	4.35335
C	3.41006	4.25884	3.49482
H	4.41336	4.52191	3.80776
C	3.19974	3.07967	2.78816
H	4.01787	2.41398	2.54415
F	-4.33393	2.90453	-3.60705

Point group (P.G.) = C_1

Total electronic energy = –2973.53499 a.u.

Table S10. Optimized Cartesian coordinates for **2a′** in the lowest triplet excited state (T_1).

	X	Y	Z
Cl	-0.49582	-3.74466	1.10030
Ir	-0.10789	-1.25659	0.70242
N	-0.88022	-0.49076	2.48242
N	-1.85371	0.08226	4.39286
N	-1.45488	1.19823	3.70914
N	0.40993	-1.79432	-1.21018
N	1.20136	-2.50535	-3.16976
N	-0.10788	-2.19506	-3.32474
N	2.58550	-2.08235	2.16338
F	-0.21993	5.70954	0.99312
F	1.88431	5.39905	0.55305
F	0.45086	5.51179	-1.07104
F	-6.06646	0.34958	-2.59731
F	-6.49702	-1.72538	-2.12984
F	-5.39912	-1.22627	-3.94036
C	-1.73183	-2.35490	3.95563
H	-2.32071	-2.83187	3.17045
H	-0.78819	-2.90170	3.99666
H	-2.24717	-2.42407	4.91292
C	-1.49187	-0.92783	3.62403
C	-1.71234	2.51529	4.26850
H	-0.77476	3.03938	4.46293
H	-2.24422	2.36083	5.20381
H	-2.33040	3.10344	3.58798
C	-0.86630	0.85196	2.55277
C	0.18750	0.74492	0.41205
C	0.76952	1.35782	-0.70280
H	1.12434	0.74612	-1.52340
C	0.89273	2.74035	-0.78401
H	1.33712	3.19896	-1.65963
C	0.43275	3.55275	0.25609
C	-0.15196	2.98207	1.37987
H	-0.50718	3.62729	2.17053
C	-0.27660	1.59275	1.45493
C	0.63044	5.03668	0.18170
C	2.81499	-2.48834	-1.29018
H	3.18348	-1.58440	-0.80059
H	2.75464	-3.27524	-0.53467

H	3.51121	-2.79056	-2.07090
C	1.47199	-2.25281	-1.87991
C	-0.76641	-2.41492	-4.59502
H	-1.53457	-3.18764	-4.50408
H	-0.00423	-2.74325	-5.29789
H	-1.22122	-1.49002	-4.95737
C	-0.64966	-1.77087	-2.11720
C	-1.94090	-1.09281	-0.21244
C	-3.16229	-0.73423	0.32159
H	-3.23303	-0.49626	1.37670
C	-4.33192	-0.67432	-0.45002
H	-5.28099	-0.40024	-0.00918
C	-4.27193	-0.98958	-1.85512
C	-3.11402	-1.35049	-2.46513
H	-3.10992	-1.58229	-3.51974
C	-1.90186	-1.41995	-1.67834
C	-5.55034	-0.90221	-2.63723
C	1.64535	-1.66532	1.59942
C	3.42586	-3.01805	2.75207
C	2.99935	-4.35129	2.80249
H	2.02912	-4.60902	2.39093
C	3.83564	-5.29755	3.38287
H	3.51664	-6.33218	3.42791
C	5.07440	-4.92212	3.90485
H	5.71950	-5.66690	4.35599
C	5.48382	-3.59062	3.84793
H	6.44529	-3.29904	4.25367
C	4.66147	-2.62827	3.27033
H	4.96123	-1.58918	3.21610

Point group (P.G.) = C_1

Total electronic energy = –2666.53048 a.u.

Table S11. Optimized Cartesian coordinates for **2b′** in the lowest triplet excited state (T_1).

	X	Y	Z
Ir	1.66498	-0.25036	-0.22593
N	2.67963	-1.68484	-1.31044
C	3.46209	0.79710	-0.00729
F	1.55040	2.74351	-6.58256
F	-0.28638	1.59302	-6.69287
N	3.85608	-3.33180	-2.24797
F	1.60915	0.66382	-7.21773
N	3.36839	-2.54228	-3.23306
F	-4.45675	-3.60223	0.39066
N	0.36440	1.17743	0.55156
F	-4.38905	-3.57335	-1.77739
N	-0.78830	2.91048	1.32063
F	-5.15474	-1.84965	-0.68555
N	-1.63434	1.89507	0.96597
N	2.56413	-1.13295	2.67859
N	4.48063	1.30137	0.23598
C	3.75138	-3.34032	0.22931
H	4.34923	-2.62487	0.79912
H	2.84127	-3.54025	0.79879
H	4.31553	-4.26346	0.10689
C	3.41700	-2.77662	-1.10394
C	3.70379	-2.80897	-4.61623
H	2.79828	-2.94354	-5.21237
H	4.28751	-3.72641	-4.63209
H	4.29804	-1.99221	-5.03446
C	2.64281	-1.48354	-2.69135
C	1.38937	0.48858	-2.13833
C	0.73158	1.62350	-2.55544
H	0.28964	2.28477	-1.81897
C	0.60988	1.96732	-3.91412
H	0.09038	2.86561	-4.21970
C	1.18900	1.11231	-4.91630
C	1.86115	-0.02297	-4.59594
H	2.28578	-0.63678	-5.37595
C	1.99680	-0.38554	-3.19846
C	1.02218	1.51936	-6.35230
C	1.67256	3.21027	1.27688
H	2.33215	2.67877	1.96520

H	2.22605	3.31356	0.34209
H	1.43328	4.19359	1.67952
C	0.41788	2.44596	1.05748
C	-3.06979	2.07399	1.11443
H	-3.56836	1.96752	0.14957
H	-3.22261	3.08038	1.49571
H	-3.47534	1.34877	1.82218
C	-0.93895	0.84433	0.49978
C	-0.18113	-1.22486	-0.42675
C	-0.43408	-2.49884	-0.94519
H	0.39505	-3.10985	-1.28472
C	-1.72739	-3.00126	-1.04706
H	-1.90327	-3.98707	-1.46187
C	-2.81523	-2.23201	-0.62585
C	-2.61031	-0.96044	-0.10381
H	-3.46658	-0.38076	0.20970
C	-1.30714	-0.46396	-0.01098
C	-4.19786	-2.80844	-0.67918
C	2.12367	-0.90471	1.61636
C	3.46651	-1.10537	3.73548
C	3.21118	-1.83546	4.89691
H	2.30354	-2.42107	4.97281
C	4.13517	-1.79250	5.93620
H	3.94727	-2.35515	6.84293
C	5.29594	-1.03012	5.81251
H	6.01195	-1.00067	6.62545
C	5.53762	-0.30477	4.64499
H	6.43911	0.28858	4.54831
C	4.62711	-0.33335	3.59500
H	4.79168	0.22370	2.67821

Point group (P.G.) = C_1

Total electronic energy = –2299.14016 a.u.

Table S12. Optimized Cartesian coordinates for **4b′** in the lowest triplet excited state (T_1).

	X	Y	Z
Ir	0.41914	-0.83430	0.24550
F	0.76236	-4.39347	-3.32867
F	0.72170	-2.23940	-3.53679
F	1.79668	-3.16722	-1.88445
F	-5.17645	-4.75644	-1.53027
F	-4.32688	-4.27110	-3.47374
F	-3.71076	-6.07996	-2.44527
F	-2.92894	3.91441	-3.89430
F	-3.19047	2.06320	-4.99603
F	-3.38272	2.35804	1.14002
F	-3.25416	0.21396	1.37550
F	-1.53775	1.47303	1.83815
N	-0.85769	-1.36234	1.78917
N	-2.06548	-1.77502	3.61127
N	-2.64251	-2.39485	2.56101
N	1.55032	-0.37564	-1.43212
N	3.00043	-0.01187	-3.06600
N	1.77500	0.49067	-3.39857
N	1.71265	1.59975	1.77052
N	2.45049	-2.92929	1.59839
C	1.72267	-2.19481	1.07123
C	-0.03624	-0.39131	3.94955
H	0.98768	-0.70831	3.74284
H	-0.11970	0.67510	3.73161
H	-0.26717	-0.55679	5.00066
C	-0.97903	-1.16681	3.10588
C	-3.85311	-3.17125	2.74468
H	-4.70869	-2.66277	2.29242
H	-4.01365	-3.26520	3.81604
H	-3.73674	-4.16127	2.30195
C	-1.90180	-2.18231	1.41284
C	-0.71856	-2.37750	-0.67820
C	-0.58437	-3.20109	-1.77910
C	-1.63310	-4.04463	-2.24282
H	-1.48882	-4.66609	-3.11328
C	-2.91650	-4.02779	-1.59959
C	-3.11206	-3.33852	-0.45453
H	-4.08301	-3.31133	0.01751

C	-1.98126	-2.62346	0.11720
C	0.67109	-3.24838	-2.61297
C	-4.03699	-4.78154	-2.25492
C	3.93454	-1.14640	-1.07519
H	4.06347	-0.62133	-0.12611
H	3.69685	-2.18019	-0.82966
H	4.85988	-1.09941	-1.64787
C	2.84020	-0.52529	-1.86295
C	1.58831	1.09476	-4.70711
H	0.91004	0.49027	-5.31220
H	2.56687	1.12358	-5.17931
H	1.19943	2.10938	-4.60756
C	0.89923	0.27618	-2.40399
C	-0.89020	0.52473	-0.80979
C	-2.07678	1.19856	-0.46915
C	-2.86643	1.85495	-1.42064
H	-3.78820	2.33636	-1.12437
C	-2.47394	1.89548	-2.74984
C	-1.24571	1.35980	-3.11827
H	-0.93023	1.43516	-4.14864
C	-0.46193	0.72228	-2.15933
C	-2.55858	1.30038	0.95674
C	-3.30666	2.61779	-3.76768
C	1.27244	0.67450	1.20837
C	2.00014	2.74112	2.49686
C	0.95640	3.61433	2.82509
H	-0.05104	3.38312	2.50306
C	1.24302	4.75664	3.56329
H	0.44167	5.43791	3.82330
C	2.55087	5.02605	3.96680
H	2.76644	5.91877	4.54172
C	3.58121	4.14781	3.63276
H	4.59682	4.35549	3.94761
C	3.31381	2.99916	2.89603
H	4.09905	2.30279	2.63057
F	-4.61636	2.62345	-3.44487

Point group (P.G.) = C_1

Total electronic energy = –2973.42707 a.u.

Table S13. Optimized Cartesian coordinates for the triplet ligand-field state, ^{3}(*d*–*d*), of **2a′**.

	X	Y	Z
Cl	-3.55013	0.30693	0.05543
Ir	-0.10085	-0.40588	-0.12725
N	0.67124	-1.02180	1.68109
N	1.18258	-1.56082	3.76920
N	2.31448	-1.49931	3.00106
N	-0.76477	0.43624	-1.89430
N	-1.76447	0.96722	-3.80133
N	-1.76615	2.03562	-2.94790
N	-2.13408	-2.79265	-0.03523
F	6.87063	-0.85817	0.10556
F	6.49267	-2.14204	-1.60556
F	6.70062	-0.00136	-1.89056
F	-0.21528	6.28810	2.04519
F	-2.34318	5.93596	1.81555
F	-1.15144	6.49673	0.08862
C	-1.24451	-1.21654	3.29285
H	-1.73785	-0.39657	2.76618
H	-1.74330	-2.13845	2.98152
H	-1.36288	-1.10151	4.36950
C	0.19916	-1.26805	2.93889
C	3.61301	-1.75686	3.60288
H	4.09330	-2.61058	3.12140
H	3.43623	-1.98121	4.65163
H	4.25287	-0.87653	3.51884
C	2.00538	-1.17093	1.73536
C	1.91284	-0.56725	-0.57868
C	2.53382	-0.29737	-1.80724
H	1.92958	0.00886	-2.65333
C	3.91182	-0.40079	-1.95580
H	4.37886	-0.18473	-2.90945
C	4.71089	-0.77268	-0.86903
C	4.13706	-1.04055	0.36998
H	4.77715	-1.31325	1.19747
C	2.75354	-0.93977	0.51531
C	6.19033	-0.93804	-1.06195
C	-0.95784	-1.37658	-3.62188
H	0.08386	-1.68233	-3.49996
H	-1.57478	-2.06888	-3.04318

H	-1.23899	-1.44184	-4.67197
C	-1.15962	0.01031	-3.12793
C	-2.47283	3.25315	-3.31211
H	-3.20508	3.49326	-2.54003
H	-2.98208	3.05365	-4.25134
H	-1.77473	4.08228	-3.44272
C	-1.16911	1.71432	-1.79299
C	-0.44339	1.56575	0.48144
C	-0.18429	2.12532	1.73367
H	0.18915	1.50656	2.54078
C	-0.39856	3.48077	1.96537
H	-0.19085	3.90946	2.93863
C	-0.87206	4.30143	0.93998
C	-1.14094	3.77278	-0.31956
H	-1.49822	4.42926	-1.09998
C	-0.93436	2.41415	-0.54546
C	-1.14270	5.75097	1.21902
C	-1.51536	-1.79017	-0.07981
C	-3.23239	-3.63475	0.06747
C	-4.52359	-3.10000	-0.02063
H	-4.64110	-2.02957	-0.14796
C	-5.60855	-3.96338	0.08237
H	-6.61245	-3.55980	0.01951
C	-5.41510	-5.33238	0.27030
H	-6.26946	-5.99467	0.34991
C	-4.12315	-5.85023	0.35764
H	-3.97029	-6.91306	0.50413
C	-3.02406	-5.00481	0.25446
H	-2.01233	-5.38670	0.31542

Point group (P.G.) = C_1

Total electronic energy = –2666.52968 a.u.

Table S14. Optimized Cartesian coordinates for the triplet ligand-field state, ^{3}(*d*–*d*), of **2b′**.

	X	Y	Z
Ir	-0.51543	0.03392	0.26363
N	-0.42872	-1.80346	1.19968
C	2.38280	-0.50542	0.23021
F	1.48954	-3.80455	-5.35256
F	-0.52231	-4.52619	-4.98013
N	-0.26342	-3.59461	2.49747
F	1.14826	-5.37980	-3.88613
N	-0.00809	-3.92443	1.19504
F	-7.43032	0.96378	-0.14230
N	-0.74889	1.72191	-0.91510
F	-7.34245	-0.90327	-1.24450
N	-0.66469	3.48881	-2.25451
F	-6.97101	0.98538	-2.26515
N	-1.94309	3.00793	-2.18170
N	1.21315	1.61898	2.34478
N	3.26915	0.09345	-0.24432
C	-0.81293	-1.46561	3.65817
H	0.00309	-0.76228	3.84195
H	-1.71967	-0.87968	3.48958
H	-0.94288	-2.10022	4.53360
C	-0.50797	-2.30003	2.46692
C	0.35257	-5.29117	0.85329
H	-0.42637	-5.75530	0.24509
H	0.45599	-5.83389	1.78936
H	1.30124	-5.30250	0.31497
C	-0.10678	-2.84132	0.40717
C	0.00180	-1.22707	-1.35288
C	0.19180	-0.86300	-2.68485
H	0.17474	0.18214	-2.96981
C	0.42772	-1.82942	-3.65713
H	0.59319	-1.54062	-4.68830
C	0.47323	-3.18167	-3.30737
C	0.29247	-3.57452	-1.98550
H	0.33549	-4.62621	-1.74025
C	0.07035	-2.60115	-1.01040
C	0.65364	-4.21869	-4.37627
C	1.49598	2.83305	-1.21752
H	1.66295	3.22431	-0.20975

H	2.00484	1.86812	-1.26684
H	1.92868	3.52687	-1.93702
C	0.04025	2.69059	-1.47426
C	-3.00012	3.65456	-2.94300
H	-3.44626	2.95142	-3.64852
H	-2.53868	4.47462	-3.48705
H	-3.76840	4.04558	-2.27353
C	-1.99597	1.93979	-1.37035
C	-2.57339	0.01574	-0.06918
C	-3.50866	-0.91304	0.40687
H	-3.17924	-1.71913	1.05261
C	-4.85255	-0.82897	0.05831
H	-5.56485	-1.55499	0.43209
C	-5.29267	0.18943	-0.79176
C	-4.39564	1.12814	-1.29405
H	-4.76139	1.89748	-1.95920
C	-3.05079	1.04332	-0.93422
C	-6.75449	0.30550	-1.11503
C	0.66071	0.95888	1.53641
C	2.29772	2.23139	2.96621
C	2.09348	2.91319	4.16890
H	1.09987	2.94869	4.59863
C	3.17206	3.53373	4.78975
H	3.02178	4.06346	5.72317
C	4.43992	3.47544	4.21197
H	5.27836	3.96126	4.69771
C	4.62978	2.79167	3.01093
H	5.61548	2.74135	2.56314
C	3.56469	2.16294	2.37444
H	3.69463	1.61063	1.45013

Point group (P.G.) = C_1

Total electronic energy = –2299.10440 a.u.