Supplementary Information

Azo-triazolide Bis-cyclometalated Ir(III) Complexes via Cyclization of 3-Cyanodiarylformazanate Ligands

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Contents

Table S1. IR spectral data

Compound	ν(CN)/ cm^{-1}	ν(NH)/ cm^{-1}	Other transitions, ν/ cm^{-1}
1a	2206		1608(m), 1479, 1214
2a			1597(m), 1474(m), 1289(m)
3a			1582(m), 1434(m), 1295(m)
4a	2207		1582, 1438, 1216
1b	2202		1607(m), 1476, 1224(m)
2b	2213		1738, 1601(m), 1402, 1228(m)
3b	2205		1581(m), 1406(m), 1223(m)
Fza[1]	2219(m)	3313	1525, 1281(m)
Fzb	2222	3332	1527, 1277(m)

Reference

1 J. B. Gilroy, P. O. Otieno, M. J. Ferguson, R. McDonald and R. G. Hicks, *Inorg. Chem.*, 2008, **47**, 1279–1286.

Table S2. Crystallographic summary for **1a**, **2a**, and **3a.**

	1a·2CHCl$_3$	**2a**	**3a**
CCDC	1946976	1946977	1946978
Crystal data			
Chemical formula	$C_{42}H_{36}Cl_6IrN_7$	$C_{40}H_{30}F_4IrN_7$	$C_{44}H_{34}IrN_7S_2$
M_r	1043.68	876.91	917.10
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$
a, b, c (Å)	16.837 (3), 17.611 (3), 14.610 (3)	9.724 (4), 12.386 (5), 15.409 (6)	15.0406 (11), 13.7393 (10), 18.9988 (14)
α, β, γ (°)	90, 108.390 (2), 90	83.506 (4), 86.618 (4), 67.247 (3)	90, 105.613 (1), 90
V (Å^3)	4110.9 (14)	1700.2 (11)	3781.2 (5)
Z	4	2	4
μ (mm^{-1})	3.68	3.99	3.68
Crystal size (mm)	0.40 × 0.28 × 0.10	0.23 × 0.16 × 0.07	0.37 × 0.29 × 0.15
Data collection			
T_{min}, T_{max}	0.521, 0.746	0.416, 0.746	0.553, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25545, 9473, 8663	22822, 7662, 6820	23405, 8759, 7783
R_{int}	0.026	0.050	0.027
(sin θ/λ)$_{max}$ (Å^{-1})	0.651	0.648	0.652
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.088, 1.05	0.039, 0.089, 1.05	0.021, 0.047, 1.05
No. of reflections	9473	7662	8759
No. of parameters	528	473	491
No. of restraints	78	0	0
	$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 10.8851P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + 11.079P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0202P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.07, -1.44	3.27, -2.97	0.67, -0.83

Table S3. Selected bond lengths and angles for **1a**

	1a
d (Ir–N5)	2.160(3)
d (Ir–N3)	2.141(3)
d (N5–N6)	1.283(5)
d (N5–C1)	1.399(5)
d (C1–C2)	1.435(5)
d (C1–N4)	1.329(5)
d (C2–N7)	1.150(5)
d (N3–N4)	1.303(4)
∠N3–Ir–N5	75.88(12)

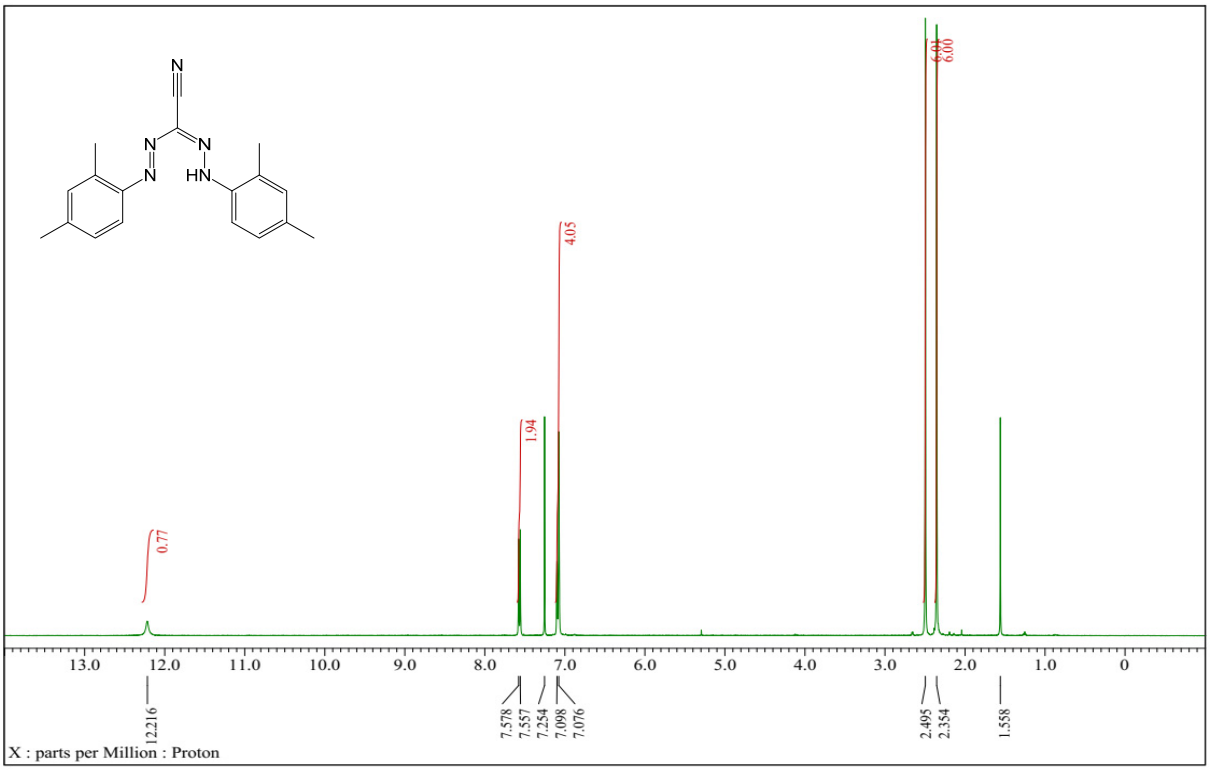

Fig. S1. Room-temperature ^{1}H NMR spectrum of **Fzb**, recorded at 400 MHz in $CDCl_3$.

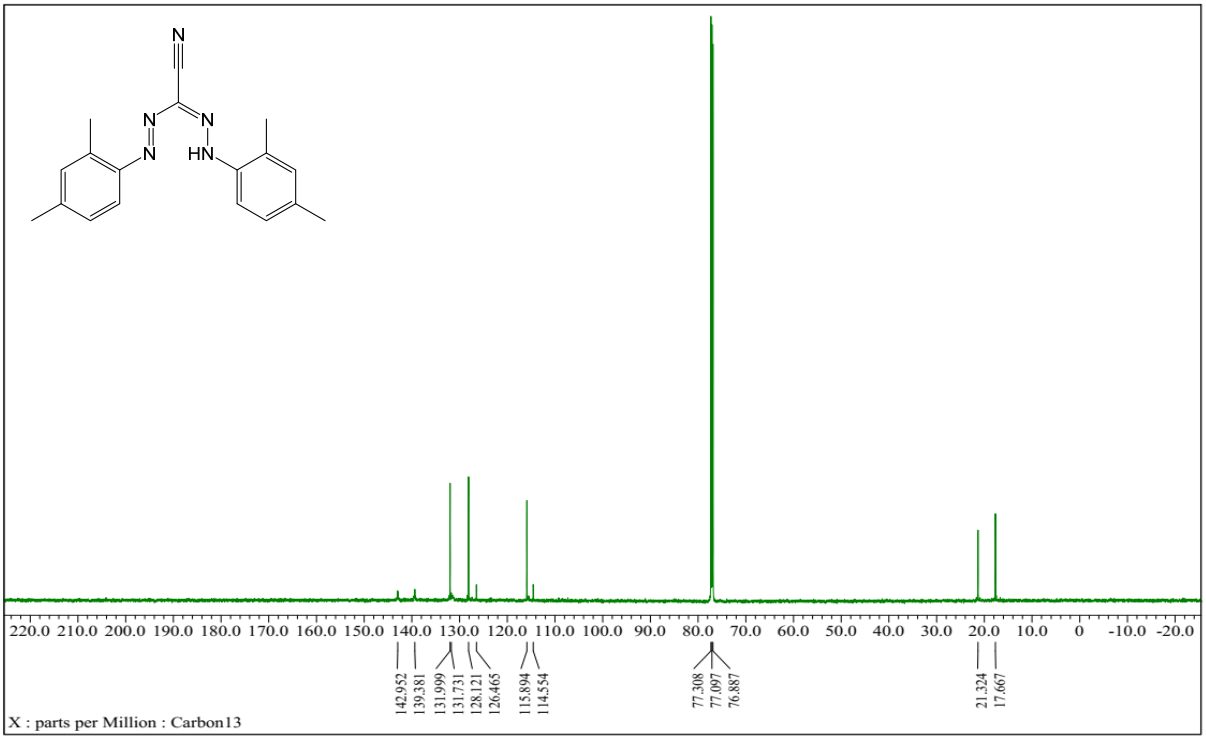

Fig. S2. Room-temperature $^{13}C\{^{1}H\}$ NMR spectrum of **Fzb**, recorded at 151 MHz in $CDCl_3$.

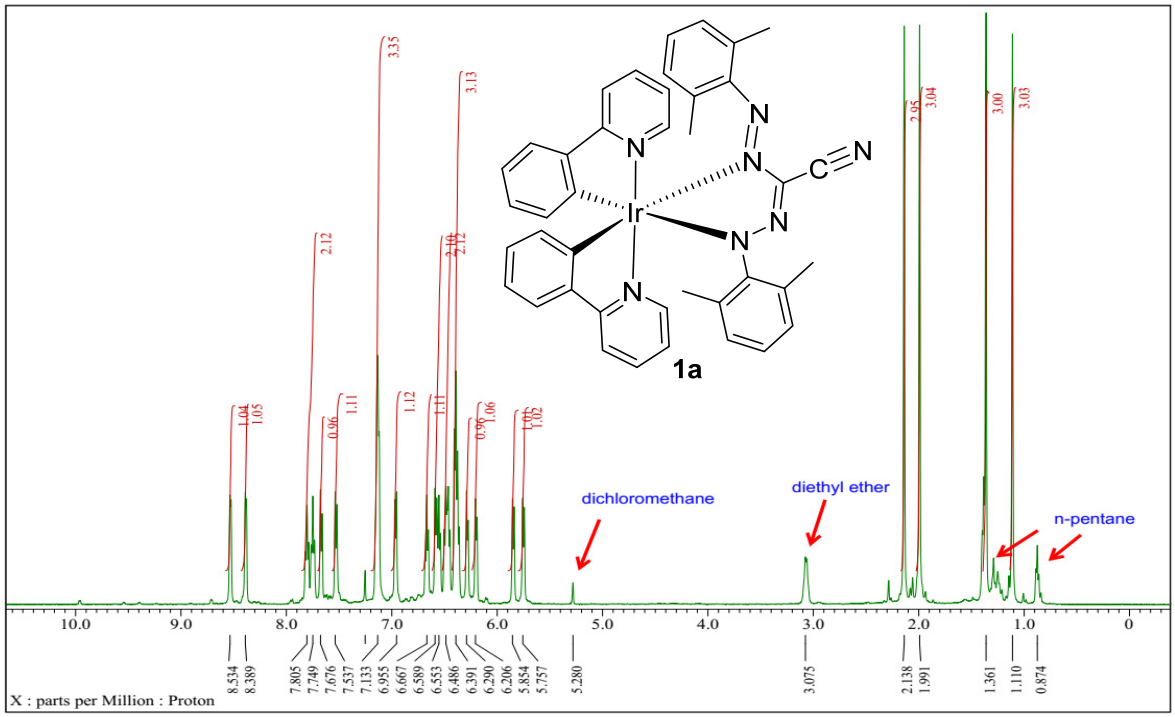

Fig. S3. Room-temperature ^{1}H NMR spectrum of **1a**, recorded at 500 MHz in $CDCl_3$.

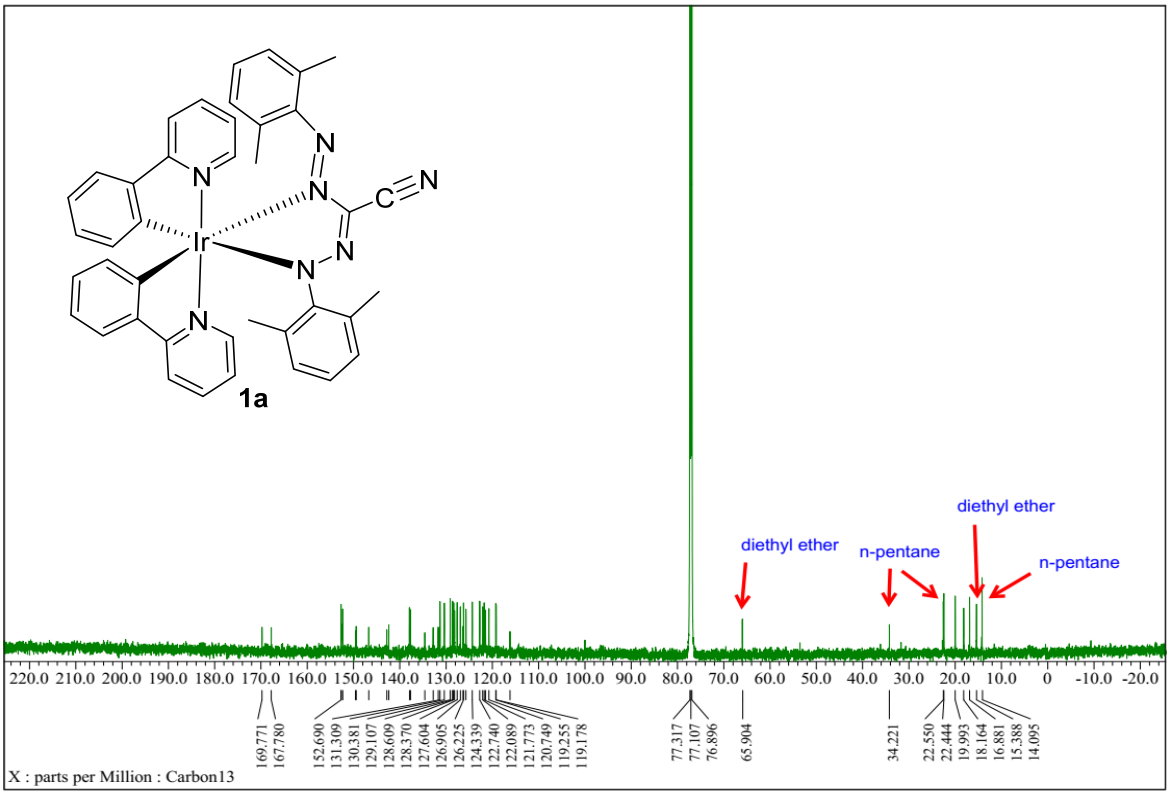

Fig. S4. Room-temperature $^{13}C\{^{1}H\}$ NMR spectrum of **1a**, recorded at 151 MHz in $CDCl_3$.

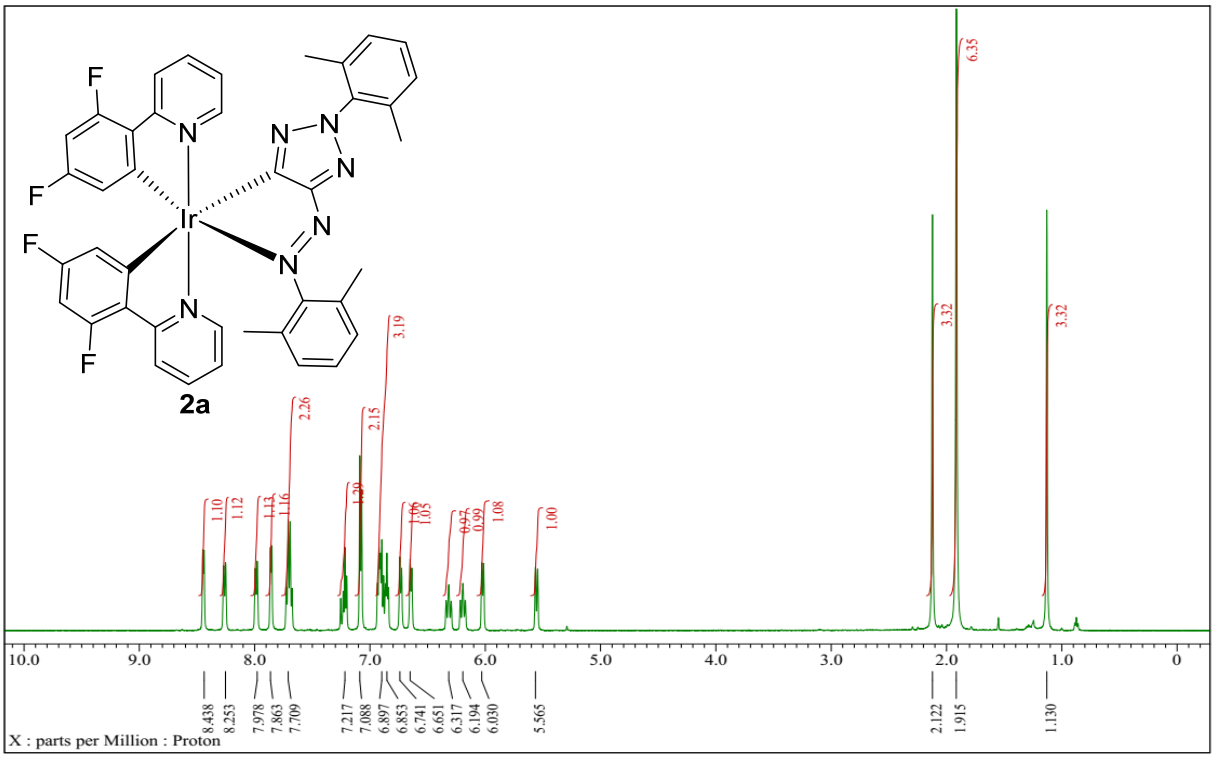

Fig. S5. Room-temperature ^{1}H NMR spectrum of **2a**, recorded at 500 MHz in $CDCl_3$.

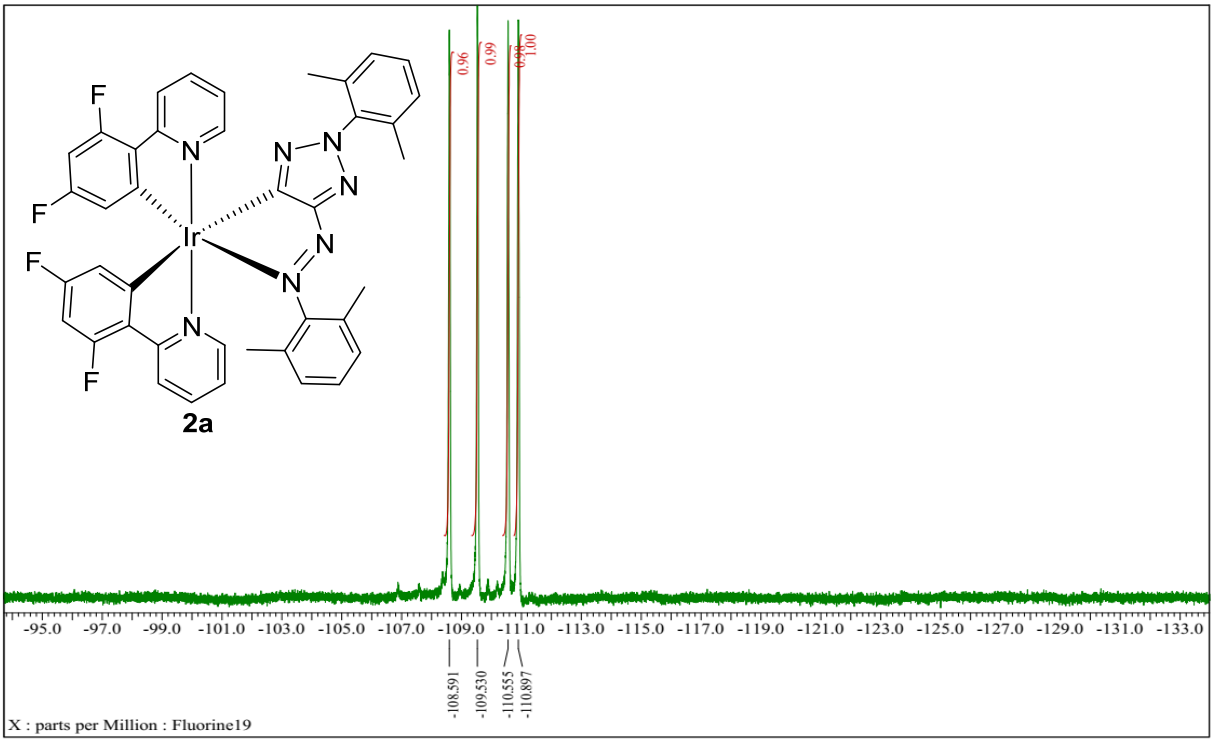

Fig. S6. Room-temperature ^{19}F NMR spectrum of **2a**, recorded at 470 MHz in $CDCl_3$.

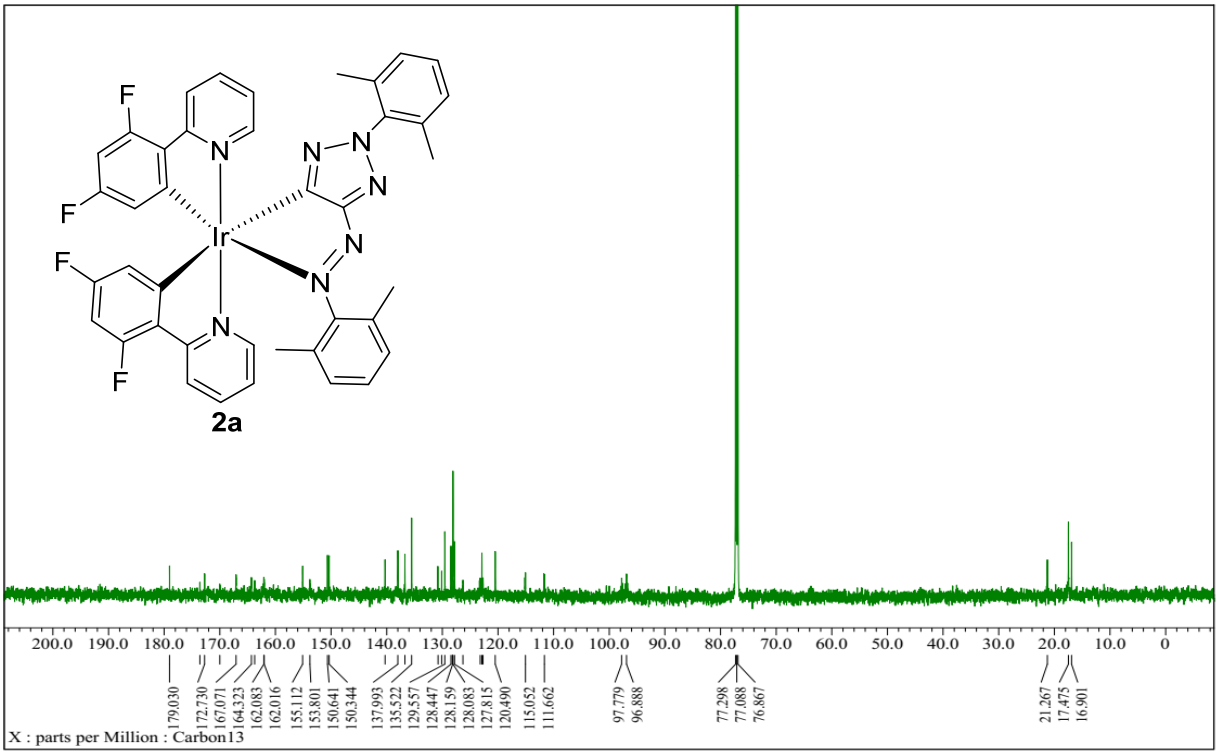

Fig. S7. Room-temperature $^{13}C\{^{1}H\}$ NMR spectrum of **2a**, recorded at 151 MHz in $CDCl_3$.

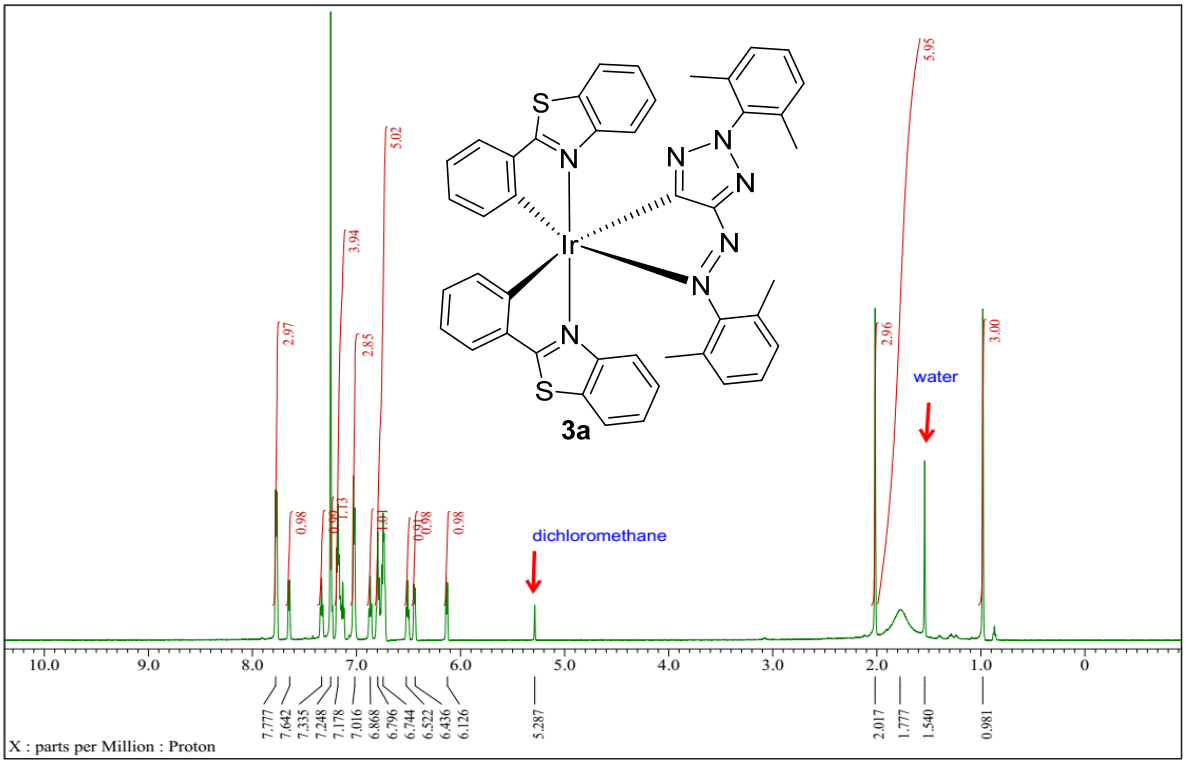

Fig. S8. Room-temperature ^{1}H NMR spectrum of **3a**, recorded at 600 MHz in $CDCl_3$.

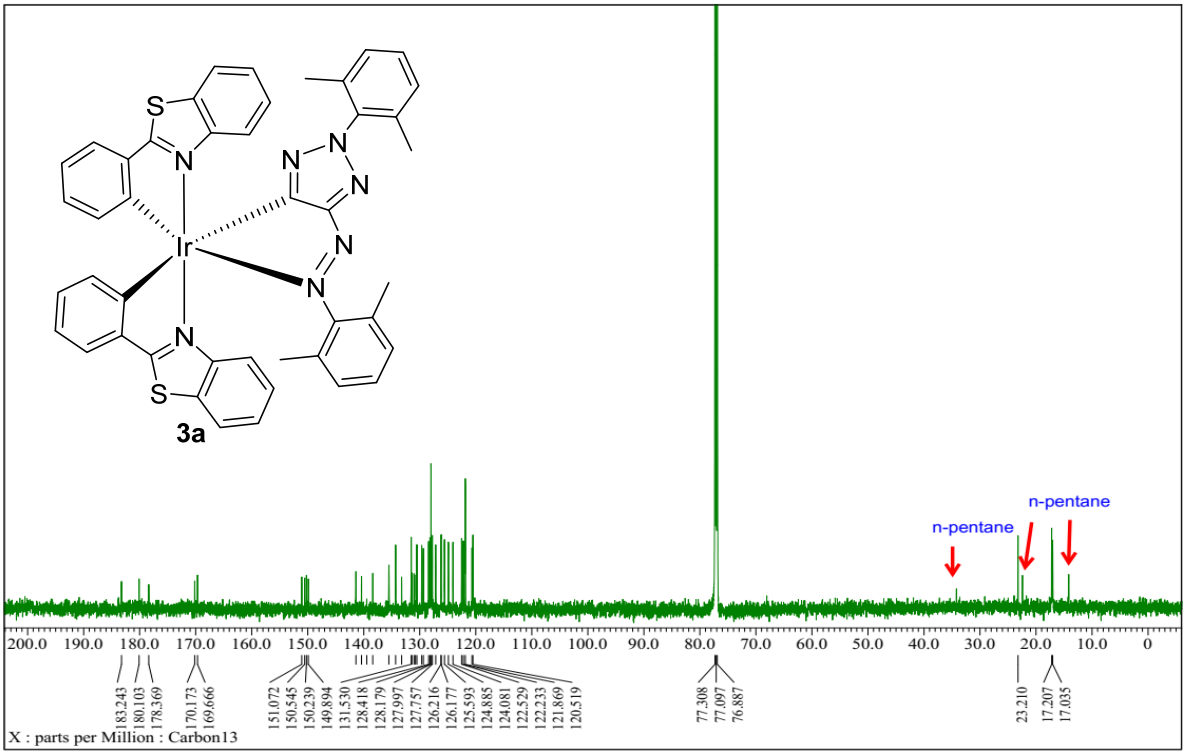

Fig. S9. Room-temperature $^{13}C\{^{1}H\}$ NMR spectrum of **3a**, recorded at 151 MHz in $CDCl_3$.

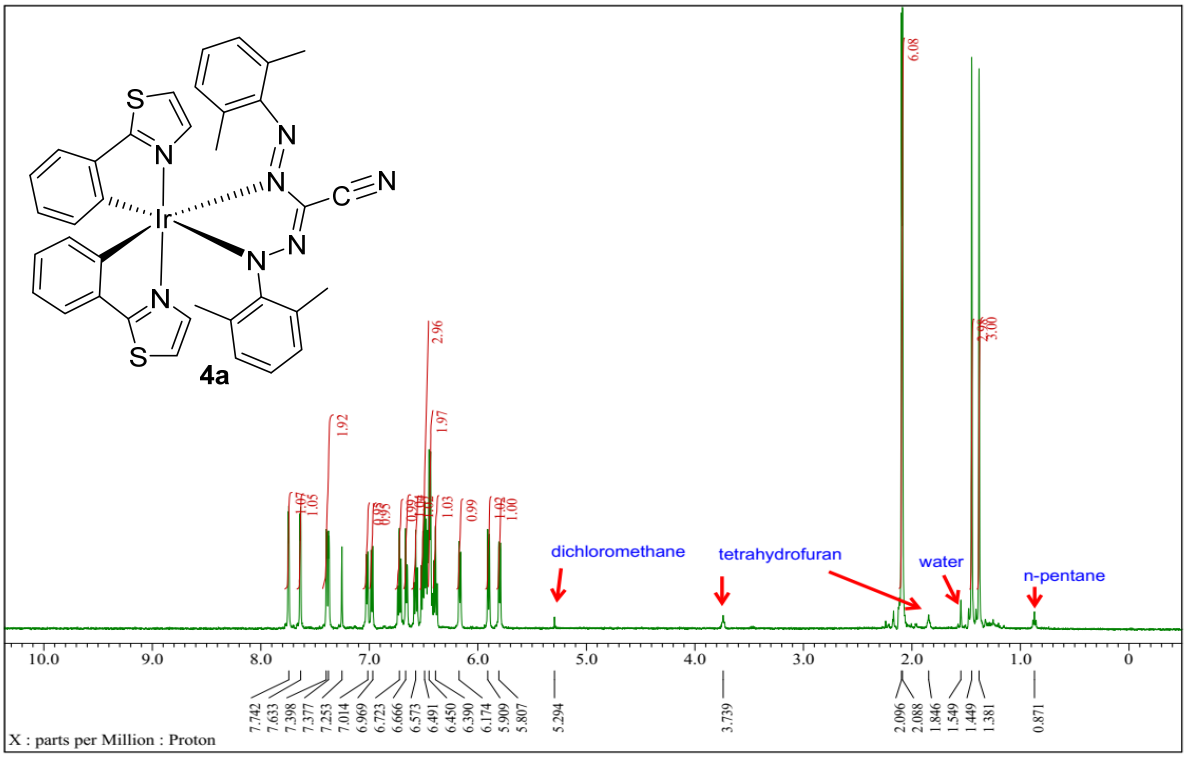

Fig. S10. Room-temperature ^{1}H NMR spectrum of **4a**, recorded at 500 MHz in $CDCl_3$.

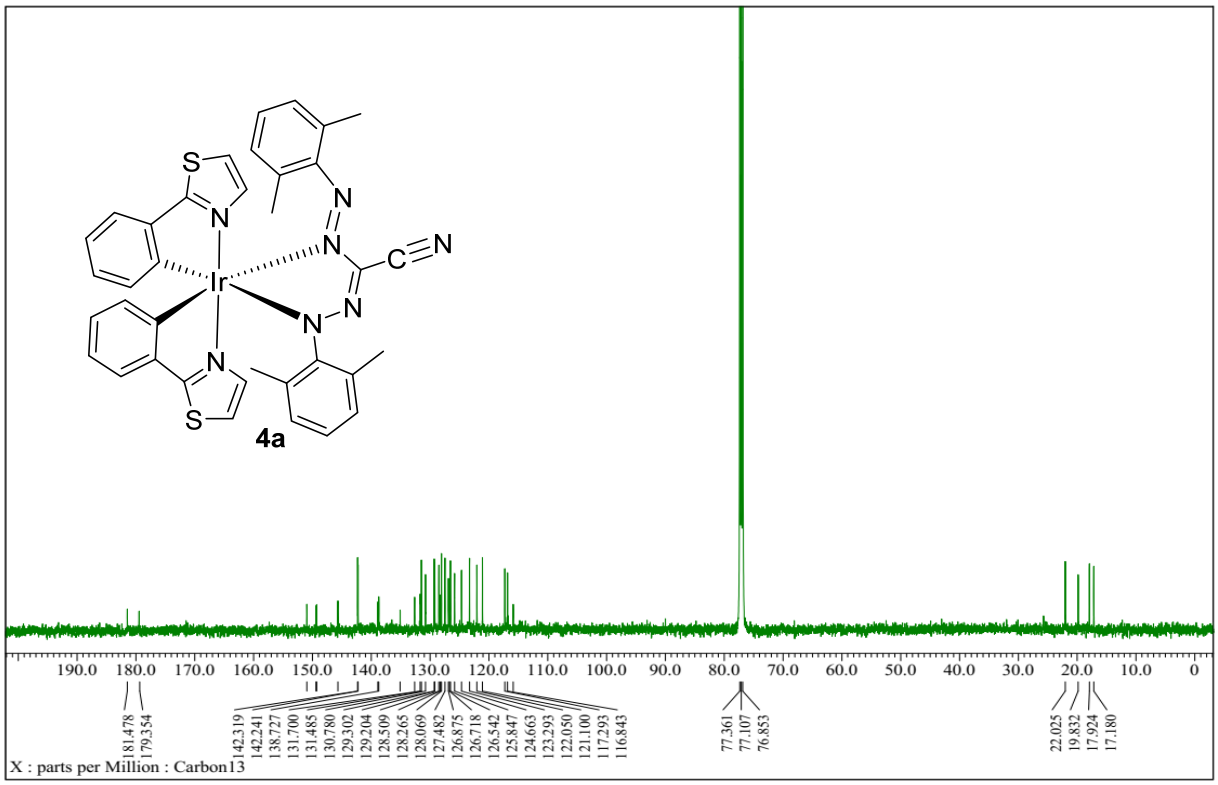

Fig. S11. Room-temperature $^{13}C\{^{1}H\}$ NMR spectrum of **4a**, recorded at 126 MHz in $CDCl_3$.

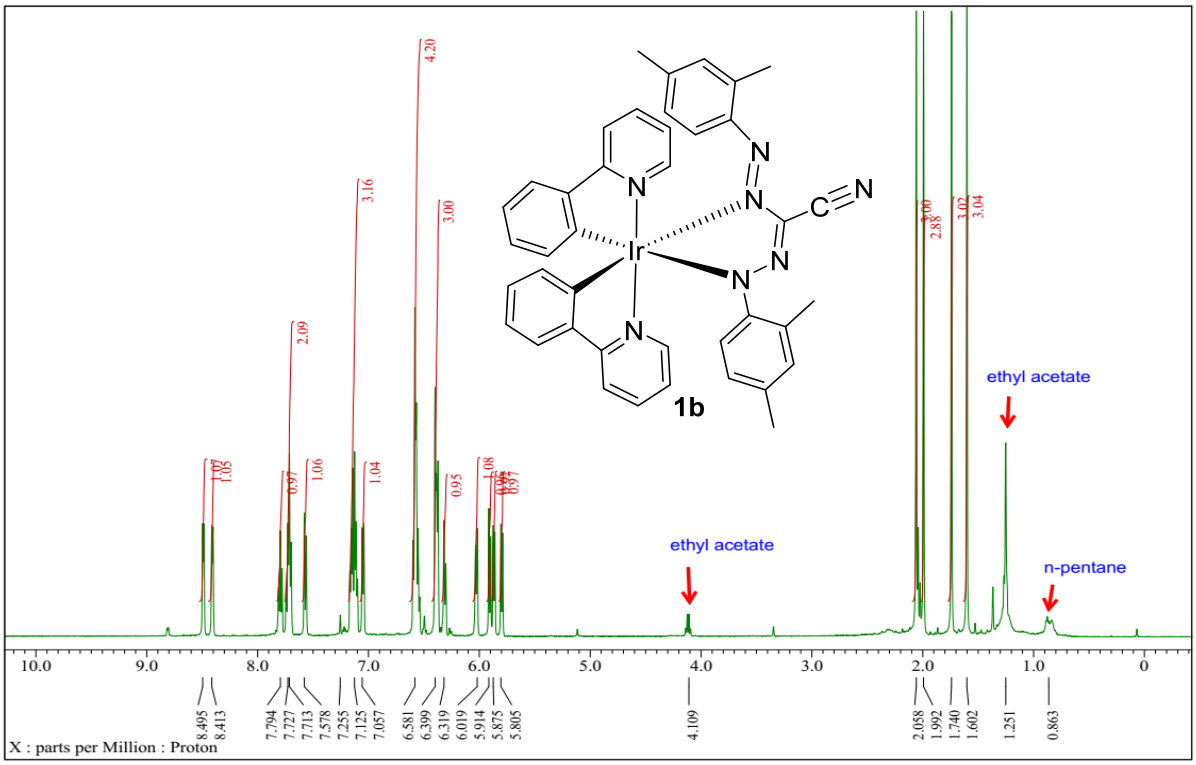

Fig. S12. Room-temperature ^{1}H NMR spectrum of **1b**, recorded at 500 MHz in $CDCl_3$.

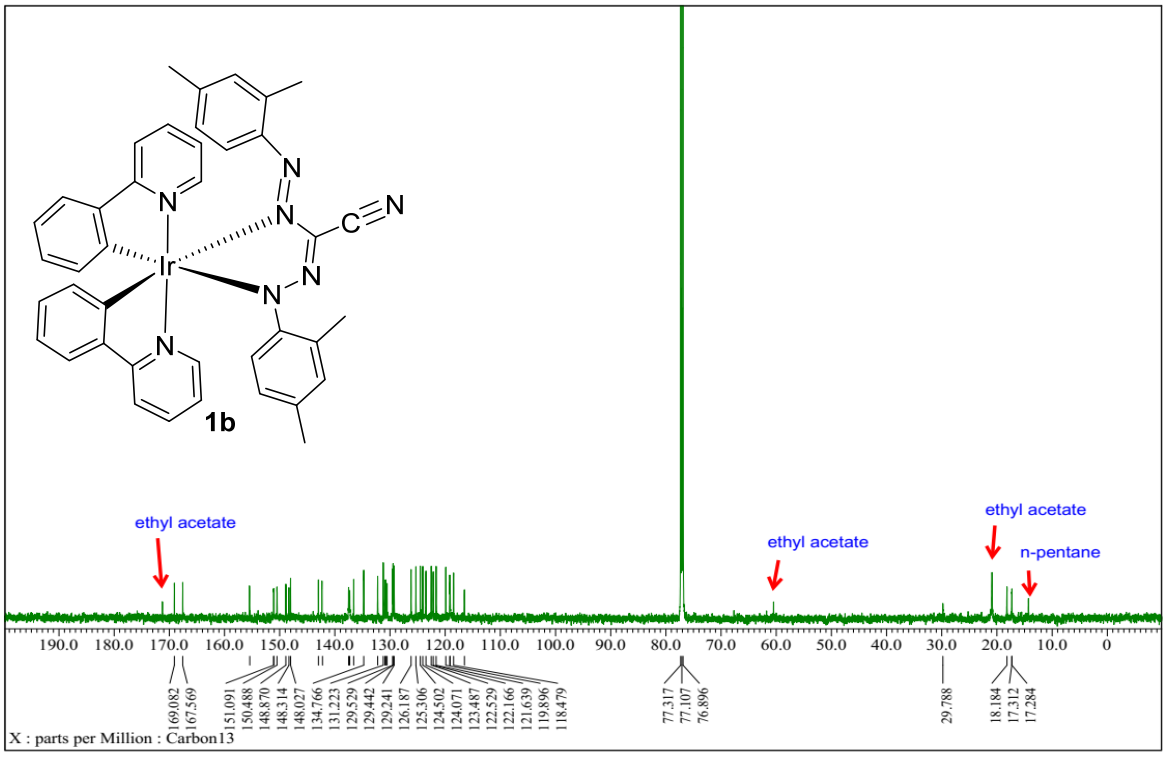

Fig. S13. Room-temperature $^{13}C\{^{1}H\}$ NMR spectrum of **1b**, recorded at 151 MHz in $CDCl_3$.

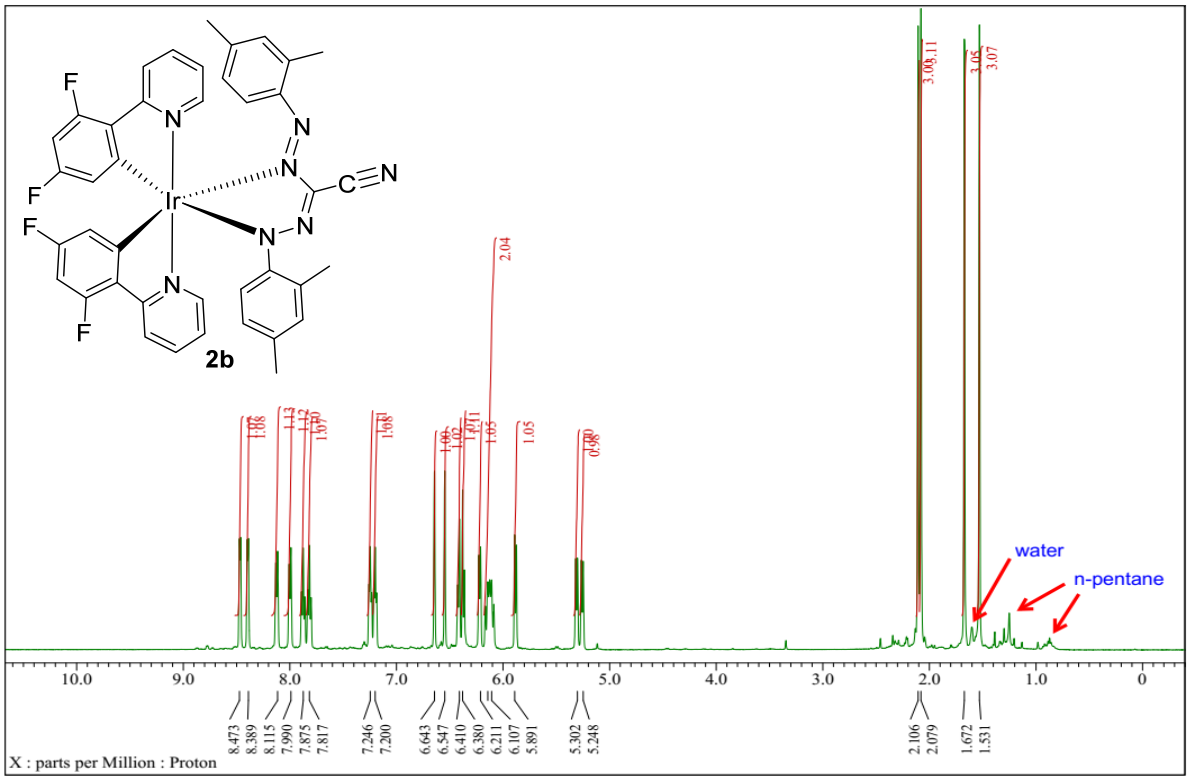

Fig. S14. Room-temperature ^{1}H NMR spectrum of **2b**, recorded at 500 MHz in $CDCl_3$.

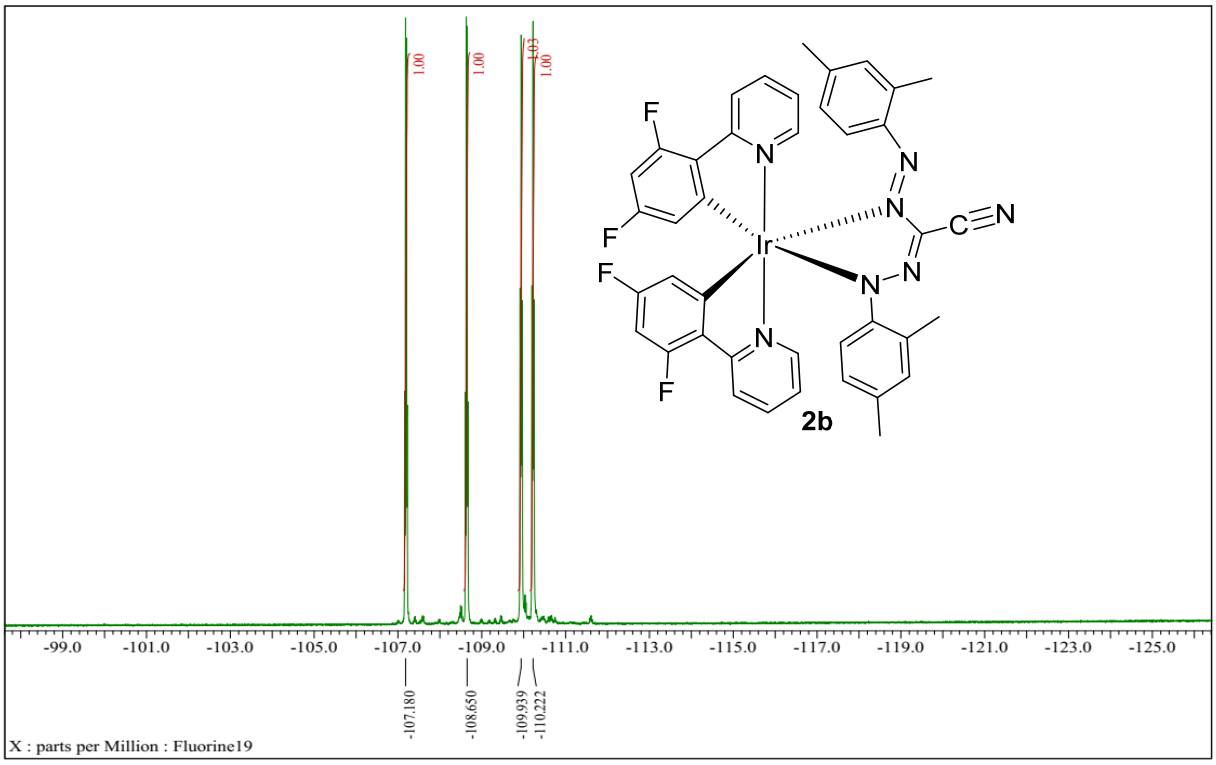

Fig. S15. Room-temperature ^{19}F NMR spectrum of **2b**, recorded at 470 MHz in $CDCl_3$.

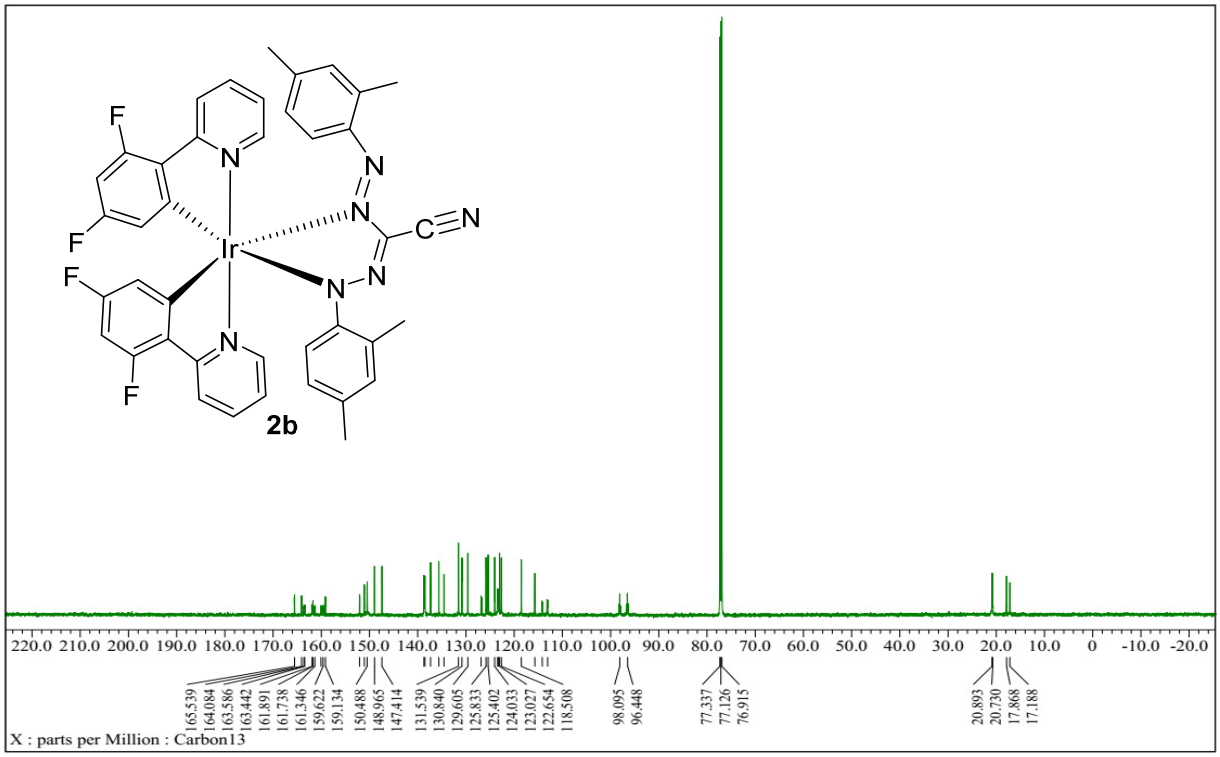

Fig. S16. Room-temperature $^{13}C\{^1H\}$ NMR spectrum of **2b**, recorded at 151 MHz in $CDCl_3$.

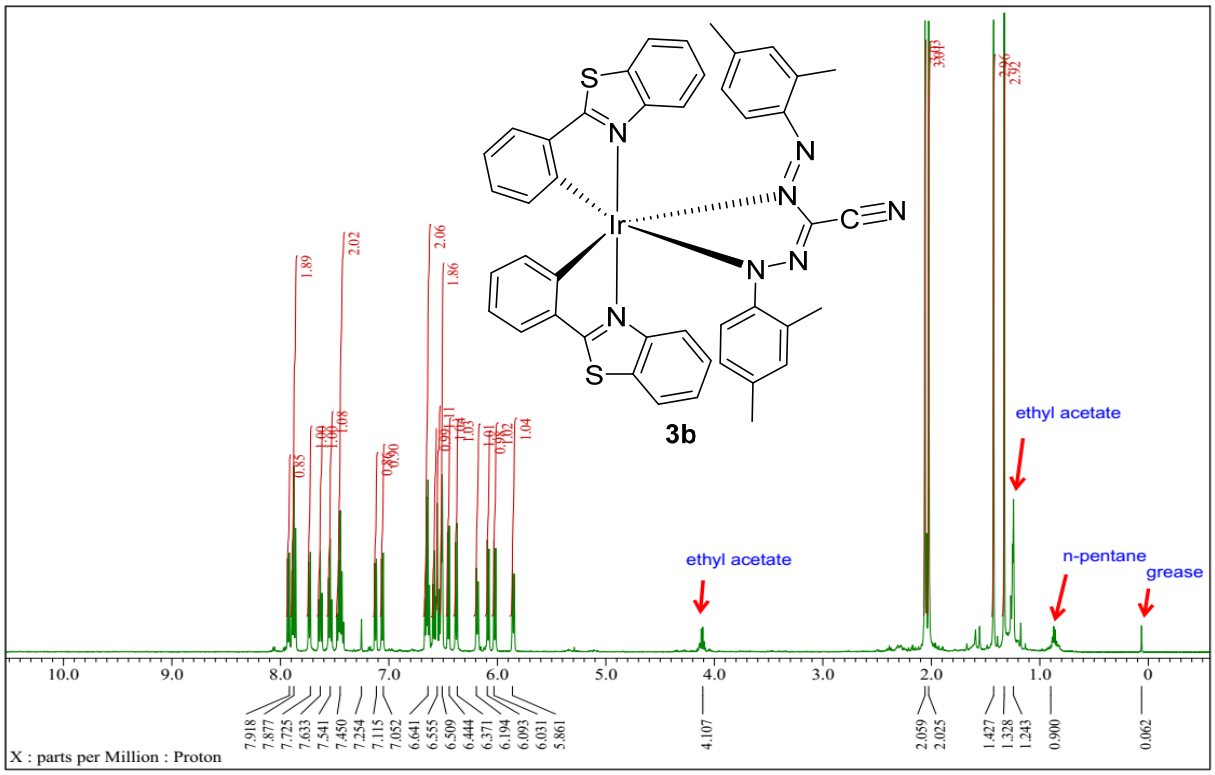

Fig. S17. Room-temperature ^{1}H NMR spectrum of **3b**, recorded at 500 MHz in $CDCl_3$.

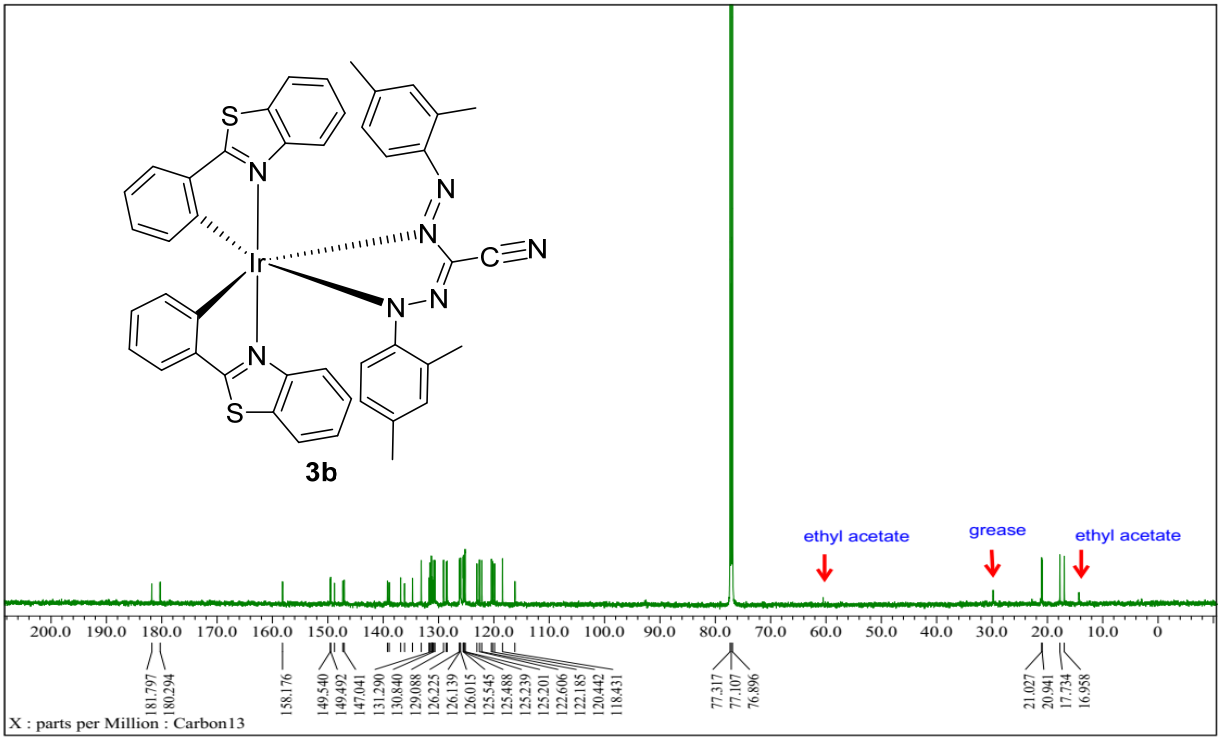

Fig. S18. Room-temperature $^{13}C\{^{1}H\}$ NMR spectrum of **3b**, recorded at 151 MHz in $CDCl_3$.

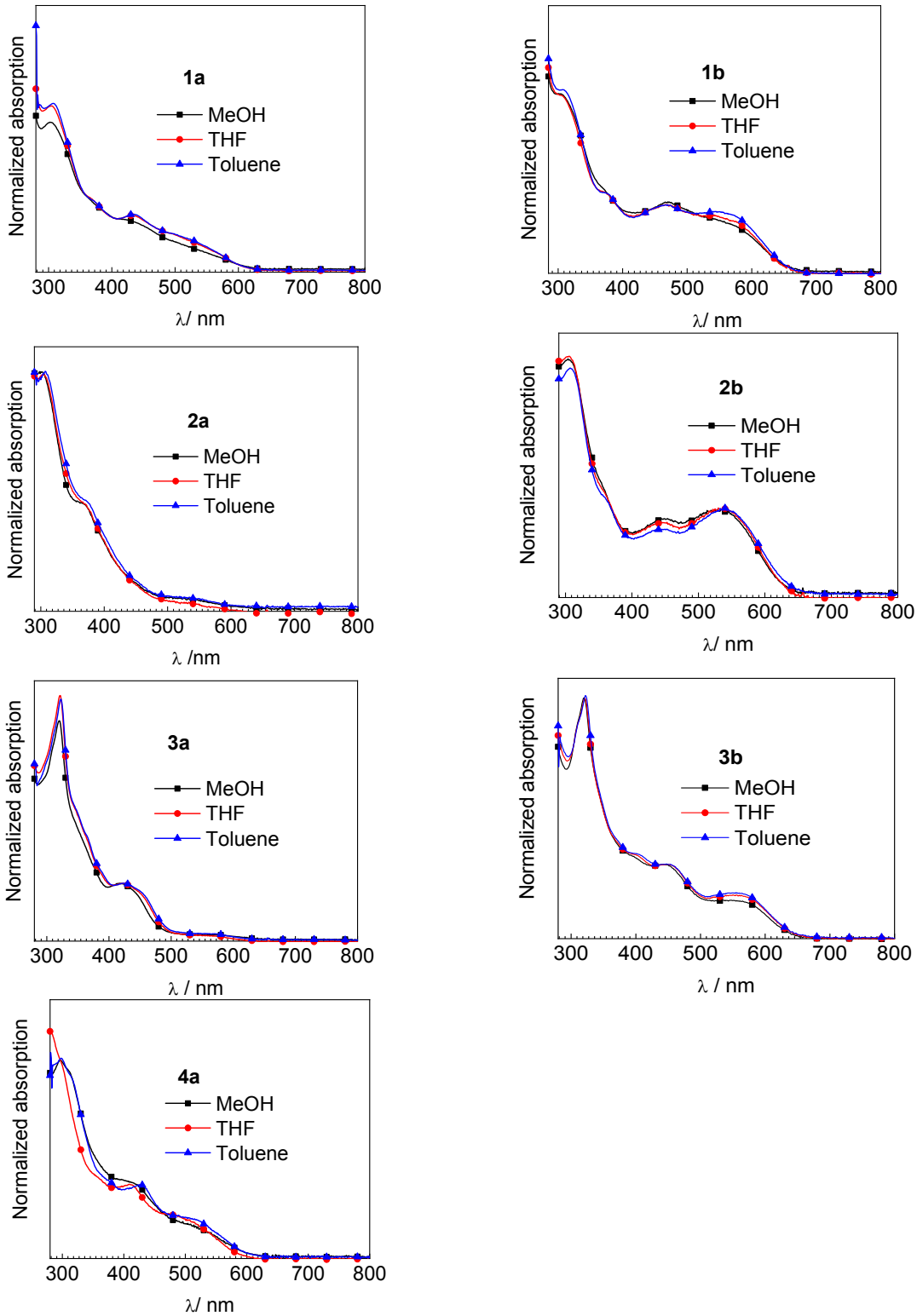

Fig. S19. UV-Vis absorption spectra of complex **1a–4a, 1b–3b**, recorded in toluene, tetrahydrofuran (THF), and methanol (MeOH) at room temperature. The spectra are normalized to the low-energy absorption maximum.

Table S4. Summary of UV-vis absorption maxima for spectra recorded in toluene, tetrahydrofuran(THF) and MeOH.

	λ/ nm		
	Toluene	THF	MeOH
1a	308, 433	305, 434	302, 427
2a	308, 373(sh)	306,369(sh)	301, 369(sh)
3a	323, 430	321, 430	320, 424
4a	298, 427, 510(sh)	413, 509(sh)	298, 408(sh), 509(sh)
1b	304(sh), 469, 551(sh)	309(sh), 469,542(sh)	309(sh), 470, 559(sh)
2b	306, 439, 540	306, 439, 536	305, 439, 535
3b	323, 403(sh), 453, 565	321, 402(sh), 453, 557	320, 452, 564

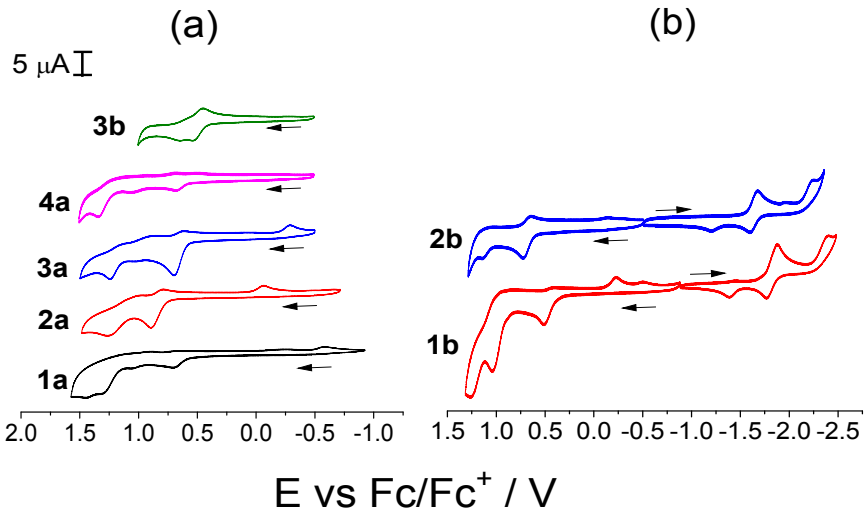

Fig. S20. Overlaid cyclic voltammograms of (a) complexes **1a**–**4a** and **3b** (only additional oxidation peaks revealed) and (b) complexes **1b** and **2b** (both additional reduction and oxidation peaks revealed) in extended scan windows. CVs were recorded in CH_2Cl_2 with 0.1 M NBu_4PF_6 supporting electrolyte, using a glassy carbon working electrode and a scan rate of 0.1 V/s. The arrows indicate the scan direction.

Table S5. Summary of electrochemical data of complexes **1a**–**4a** and **1b**–**3b** in extended scan windows**.**

	E^{ox}(V)	E^{red}(V)
1a	0.66[a], 1.04[b], 1.30[b]	−1.85
2a	0.84[a], 1.24[b]	−1.76
3a	0.66[a], 1.24[b]	−1.82
4a	0.61[a], 1.05[b], 1.34[b]	−1.88
1b	0.46[a], 1.04[b]	−1.82, −2.39[b]
2b	0.68, 1.14[b]	−1.64, −2.23[b]
3b	0.49, 0.64[b]	−1.84

[a] reversible wave, but become irreversible after additional waves. [b] Irreversible wave. $E_{p,c}$ or $E_{p,a}$ is reported.

Table S6. Optimized ground-state Cartesian coordinates for **1a**.

	X	Y	Z
Ir	0.97529	0.80906	4.69774
N	0.52450	-0.48801	6.25832
N	1.42679	1.95851	3.01937
N	2.21241	2.30476	5.74432
N	1.58080	3.31326	6.24474
N	-0.46172	2.19621	5.70651
N	-1.69744	2.17056	5.99374
N	-0.99613	5.18435	7.45491
C	0.24800	3.25898	6.27418
C	-0.44237	4.31336	6.93321
C	0.88826	-0.28443	7.53770
H	1.43507	0.62711	7.72827
C	0.58359	-1.17867	8.54718
H	0.90405	-0.97403	9.55994
C	-0.15318	-2.31881	8.22267
H	-0.41608	-3.03991	8.98772
C	-0.56627	-2.50858	6.91553
H	-1.16380	-3.36943	6.65040
C	-0.22434	-1.58120	5.92278
C	-0.17634	-0.55885	3.72077
C	-0.47095	-0.60632	2.35234
H	-0.12205	0.18676	1.70035
C	-1.19477	-1.66082	1.80525
H	-1.41337	-1.66846	0.74207
C	-1.63394	-2.71621	2.60963
H	-2.19972	-3.53437	2.17973
C	-1.33288	-2.71153	3.96256
H	-1.66733	-3.53567	4.58256
C	-0.60304	-1.65040	4.51741
C	0.74972	3.05675	2.64047
H	-0.07686	3.34232	3.27251
C	1.09484	3.79786	1.52533
H	0.51465	4.67239	1.26305
C	2.20874	3.40207	0.78545
H	2.51902	3.96494	-0.08710
C	2.92073	2.28344	1.18270
H	3.79153	1.96428	0.62741
C	2.51674	1.55022	2.30527

C	2.51393	-0.26248	3.92079
C	3.01028	-1.49185	4.36765
H	2.52938	-1.99625	5.19792
C	4.12157	-2.07992	3.77090
H	4.49298	-3.02869	4.14451
C	4.76169	-1.46068	2.69396
H	5.63257	-1.91719	2.23846
C	4.26414	-0.26378	2.20187
H	4.75336	0.20633	1.35630
C	3.14093	0.32789	2.79746
C	3.60960	2.51071	5.50245
C	4.52069	1.53693	5.96086
C	5.85606	1.62293	5.57208
H	6.55291	0.86713	5.91749
C	6.30177	2.66162	4.76300
H	7.34020	2.70833	4.45468
C	5.41121	3.65279	4.37542
H	5.75979	4.48452	3.77194
C	4.06208	3.61091	4.74255
C	4.09800	0.46253	6.92553
H	3.74149	0.90716	7.85990
H	4.93634	-0.19441	7.16312
H	3.29805	-0.15119	6.52138
C	3.17888	4.76514	4.33486
H	3.12645	5.50608	5.13684
H	2.15661	4.46494	4.12741
H	3.57888	5.25280	3.44305
C	-2.50613	1.11694	5.50066
C	-2.92108	1.04079	4.16175
C	-3.77109	-0.00419	3.79251
H	-4.07927	-0.08559	2.75614
C	-4.21666	-0.93245	4.72281
H	-4.86256	-1.74553	4.41189
C	-3.85656	-0.79651	6.06080
H	-4.23522	-1.49511	6.79970
C	-3.02386	0.23963	6.47559
C	-2.51145	2.07069	3.14443
H	-2.36653	3.05004	3.60554
H	-3.27718	2.16972	2.37224
H	-1.58373	1.78012	2.65026

C	-2.68869	0.43992	7.93084
H	-1.61884	0.34612	8.11979
H	-3.20738	-0.29126	8.55381
H	-2.97520	1.44476	8.25389

Point group (P.G.) = C_1

Number of imaginary frequency (NIm) = 0

Total electronic energy with ZPE = –2032.35834 a.u.

Table S7. Optimized ground-state Cartesian coordinates for **1a′.**

	X	Y	Z
Ir	0.12658	1.70620	0.03318
H	2.84873	5.61744	2.37911
H	-0.73542	6.73634	0.32751
H	2.38537	2.88378	-4.52793
H	4.79852	0.75813	-1.70629
N	-1.24584	2.87544	-1.00220
N	1.65161	0.62176	0.93699
N	-2.24983	-1.68948	0.55959
N	-0.66800	-1.26149	-1.03174
N	-1.56484	-2.14015	-0.47377
N	-1.49134	1.51282	1.62039
N	-2.20560	0.45964	1.62985
C	-1.76750	-0.44651	0.69483
C	-0.77348	-0.15774	-0.29518
C	-2.09117	2.38588	-1.92918
H	-1.99869	1.32691	-2.12776
C	-3.02087	3.17909	-2.57574
H	-3.68037	2.74133	-3.31332
C	-3.08625	4.53259	-2.23989
H	-3.81448	5.18221	-2.71164
C	-2.20123	5.04207	-1.30621
H	-2.22411	6.09169	-1.04835
C	-1.25219	4.20754	-0.69867
C	0.70559	3.61978	0.62107
C	1.81057	4.01811	1.38370
H	2.54481	3.27562	1.68253
C	1.98573	5.34105	1.78093
C	1.05561	6.31926	1.41575
H	1.18597	7.34618	1.73743
C	-0.02734	5.96952	0.62266
C	-0.19386	4.63770	0.21325
C	1.52715	-0.05587	2.09358
H	0.56796	0.02312	2.58280
C	2.55046	-0.81530	2.62848
H	2.39837	-1.33685	3.56421
C	3.75823	-0.88877	1.93115
H	4.58592	-1.46971	2.32108
C	3.87777	-0.22814	0.72200

H	4.79237	-0.29837	0.14946
C	2.80636	0.51967	0.21188
C	1.52159	1.77371	-1.42011
C	1.41885	2.38285	-2.68011
H	0.48970	2.85501	-2.97542
C	2.49417	2.40372	-3.56039
C	3.71772	1.82014	-3.21194
H	4.55343	1.84533	-3.90150
C	3.84998	1.21021	-1.97560
C	2.76613	1.18030	-1.08313
C	-2.00150	2.62253	2.37528
C	-1.19761	3.18317	3.38305
C	-1.62158	4.36438	3.98857
H	-1.00549	4.80762	4.76285
C	-2.81045	4.97695	3.60828
H	-3.11657	5.90684	4.07420
C	-3.61026	4.38742	2.63813
H	-4.54652	4.85481	2.35206
C	-3.23432	3.19611	2.01091
C	0.05568	2.49654	3.85201
H	0.57789	3.10584	4.59093
H	0.73759	2.31549	3.02460
H	-0.18151	1.53228	4.31293
C	-4.15493	2.57868	0.98670
H	-4.72697	1.75792	1.42643
H	-3.61443	2.16553	0.13771
H	-4.85717	3.32446	0.60963
C	-1.71445	-3.47330	-0.97199
C	-2.94239	-3.85233	-1.52940
C	-3.05698	-5.15753	-2.01217
H	-3.99559	-5.47801	-2.45081
C	-1.98299	-6.03922	-1.94571
H	-2.08839	-7.04816	-2.32874
C	-0.77417	-5.63189	-1.39037
H	0.05827	-6.32488	-1.33629
C	-0.61494	-4.33863	-0.88845
C	-4.09527	-2.88432	-1.61124
H	-4.49530	-2.66745	-0.61820
H	-4.89652	-3.28932	-2.23142
H	-3.77504	-1.93047	-2.03963

C	0.68703	-3.89434	-0.27082
H	1.35564	-4.74491	-0.12785
H	0.52030	-3.41843	0.69952
H	1.18365	-3.15352	-0.90086

P.G. = C_1

NIm = 0

Total electronic energy with ZPE = –2032.33720 a.u.

Table S8. Optimized ground-state Cartesian coordinates for **2a.**

	X	Y	Z
Ir	0.13139	1.69765	0.03194
F	2.98261	5.64334	2.58920
F	-0.95546	6.89995	0.39472
F	2.30428	2.99401	-4.75449
F	5.04232	0.74576	-1.69877
N	-1.25121	2.85432	-1.00336
N	1.66430	0.62577	0.93486
N	-2.24385	-1.69141	0.56257
N	-0.65722	-1.26834	-1.02430
N	-1.55915	-2.14342	-0.46947
N	-1.47432	1.50892	1.62130
N	-2.19128	0.45841	1.63509
C	-1.75718	-0.45057	0.70120
C	-0.76021	-0.16638	-0.28621
C	-2.07652	2.34786	-1.93897
H	-1.96418	1.29017	-2.13326
C	-3.01012	3.12307	-2.60078
H	-3.65150	2.67237	-3.34641
C	-3.09951	4.47464	-2.26930
H	-3.82914	5.11308	-2.75373
C	-2.23935	5.00563	-1.32305
H	-2.28258	6.05132	-1.06708
C	-1.28387	4.18761	-0.69921
C	0.69131	3.61419	0.62332
C	1.79164	3.98885	1.39647
H	2.54293	3.26770	1.69635
C	1.92498	5.30028	1.81953
C	1.00364	6.28959	1.50088
H	1.11234	7.30492	1.85394
C	-0.06162	5.92208	0.70164
C	-0.23808	4.61773	0.22644
C	1.53078	-0.05203	2.08962
H	0.56474	0.01866	2.56606
C	2.55346	-0.80140	2.63896
H	2.39409	-1.32297	3.57342
C	3.76870	-0.86087	1.95714
H	4.59876	-1.43100	2.35757
C	3.90279	-0.20137	0.74769

H	4.82320	-0.25870	0.19041
C	2.82893	0.53472	0.22089
C	1.51890	1.77145	-1.42373
C	1.37991	2.37616	-2.67827
H	0.45344	2.83647	-2.99195
C	2.45402	2.40603	-3.54721
C	3.69636	1.86399	-3.23789
H	4.52556	1.90465	-3.92914
C	3.82513	1.27028	-1.99945
C	2.77583	1.19574	-1.07409
C	-1.97331	2.62908	2.36921
C	-1.16386	3.18812	3.37367
C	-1.56149	4.39281	3.95008
H	-0.94145	4.83589	4.72128
C	-2.73021	5.02867	3.54496
H	-3.01294	5.97861	3.98387
C	-3.54040	4.43630	2.58557
H	-4.46172	4.92157	2.28222
C	-3.19195	3.22128	1.98822
C	0.06731	2.47914	3.86832
H	0.59193	3.08401	4.60913
H	0.75845	2.27405	3.05447
H	-0.19726	1.52491	4.33489
C	-4.12467	2.60124	0.97697
H	-4.71652	1.80572	1.43665
H	-3.59426	2.15382	0.13905
H	-4.80875	3.35364	0.58087
C	-1.71833	-3.47396	-0.97379
C	-2.94776	-3.83861	-1.53728
C	-3.07249	-5.14104	-2.02481
H	-4.01211	-5.45128	-2.46845
C	-2.00716	-6.03302	-1.95651
H	-2.12061	-7.03966	-2.34310
C	-0.79670	-5.63926	-1.39508
H	0.02876	-6.34035	-1.34005
C	-0.62704	-4.34915	-0.88856
C	-4.09147	-2.85981	-1.62019
H	-4.49631	-2.64593	-0.62840
H	-4.89232	-3.25401	-2.24762
H	-3.76093	-1.90619	-2.04122

C	0.67721	-3.91911	-0.26575
H	1.33531	-4.77703	-0.11894
H	0.51257	-3.44013	0.70341
H	1.18591	-3.18605	-0.89538

P.G. = C_1

NIm = 0

Total electronic energy with ZPE = –2429.43831 a.u.

Table S9. Optimized ground-state Cartesian coordinates for **2a′.**

	X	Y	Z
Ir	-0.21129	-0.12405	0.17305
N	-0.66128	-1.42803	1.72689
N	0.23288	1.02485	-1.50418
N	1.03214	1.35199	1.21784
N	0.40881	2.36418	1.72005
N	-1.64023	1.26855	1.16873
N	-2.88485	1.27044	1.41177
N	-2.16117	4.26138	2.91097
C	-0.92455	2.32375	1.74342
C	-1.61031	3.38595	2.39417
C	-0.27824	-1.22716	3.00043
H	0.26875	-0.31466	3.18444
C	-0.56382	-2.12447	4.01244
H	-0.22712	-1.92199	5.02032
C	-1.29881	-3.26504	3.69319
H	-1.54399	-3.99332	4.45721
C	-1.73673	-3.45537	2.39305
H	-2.32948	-4.31667	2.13362
C	-1.41729	-2.52082	1.39686
C	-1.37795	-1.47249	-0.80636
C	-1.67123	-1.47624	-2.17204
H	-1.32964	-0.68925	-2.83124
C	-2.41537	-2.51044	-2.71008
F	-2.71050	-2.48906	-4.02833
C	-2.88568	-3.57489	-1.95331
H	-3.48148	-4.36474	-2.38702
C	-2.57155	-3.57322	-0.60927
F	-3.04749	-4.60943	0.12750
C	-1.81189	-2.56525	-0.00503
C	-0.46769	2.10926	-1.87757
H	-1.29143	2.38070	-1.23624
C	-0.14920	2.85310	-2.99839
H	-0.74834	3.71577	-3.25713
C	0.96176	2.47209	-3.74765
H	1.25275	3.03499	-4.62669
C	1.70198	1.36756	-3.35893
H	2.56858	1.06142	-3.92100
C	1.32317	0.62929	-2.22848

C	1.32556	-1.19095	-0.60371
C	1.80690	-2.41297	-0.13344
H	1.33932	-2.93106	0.69326
C	2.92582	-2.97860	-0.72016
F	3.39671	-4.14811	-0.23828
C	3.59655	-2.39172	-1.78443
H	4.47509	-2.84222	-2.22310
C	3.08539	-1.20402	-2.26946
F	3.73841	-0.64218	-3.31730
C	1.95325	-0.58576	-1.72676
C	2.43059	1.54481	0.96478
C	3.33897	0.56975	1.42566
C	4.66785	0.63391	1.01072
H	5.36352	-0.12197	1.35828
C	5.10933	1.65298	0.17441
H	6.14144	1.68138	-0.15588
C	4.22365	2.64897	-0.21118
H	4.57032	3.46608	-0.83504
C	2.88117	2.62901	0.18180
C	2.92400	-0.48305	2.41754
H	2.57194	-0.01829	3.34356
H	3.76513	-1.13236	2.66561
H	2.12355	-1.10908	2.03365
C	2.00433	3.78787	-0.22578
H	1.98172	4.54259	0.56475
H	0.97318	3.49988	-0.40431
H	2.39031	4.25525	-1.13420
C	-3.68548	0.20495	0.92360
C	-4.12739	0.14389	-0.40656
C	-4.95822	-0.91697	-0.77702
H	-5.28897	-0.98639	-1.80764
C	-5.35884	-1.87329	0.14557
H	-5.98691	-2.70000	-0.16542
C	-4.97511	-1.75020	1.47824
H	-5.31708	-2.47387	2.21030
C	-4.16194	-0.69905	1.89449
C	-3.76579	1.20058	-1.41572
H	-3.58309	2.16447	-0.93653
H	-4.57546	1.33037	-2.13682
H	-2.87349	0.91714	-1.97665

C	-3.81291	-0.50751	3.34759
H	-2.73694	-0.53912	3.51954
H	-4.27659	-1.27949	3.96410
H	-4.15485	0.47181	3.69476

P.G. = C_1

NIm = 0

Total electronic energy with ZPE = –2429.45836 a.u.