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Electronic Supporting Information

Azo-oximate metal-carbonyl to metallocarboxylic acid *via* intermedial Ir(III) radical congener: quest for co-ligand driven stability of open- and closed-shell complexes

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Table S1 Crystallographic parameters of **2a**$^+$, **3a**$^+$, **4a, 5a** and **6a**.

	2a$^+$I$_3^-$	**3a$^+$BF$_4^-$**	**4a·C$_6$H$_6$**	**5a**	**6a.CH$_3$CN**
Empirical formula	$C_{50}H_{40}N_3O_2P_2I_3ClIr$	$C_{50}H_{40}N_3O_2P_2BClF_4Ir$	$C_{55}H_{46}N_3OP_2Cl_2Ir$	$C_{44}H_{35}N_6O_2PClIr$	$C_{52}H_{44}N_4O_3P_2ClIr$
fw	1385.14	1091.25	1089.99	938.42	1062.50
T /K	273K	298K	298K	136K	148(2)
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	*P*21/c	*P*21/n	*P*bcn	*P*21/c	*P*21/c
a / Å	13.752(4)	9.1118(7)	36.7741(7)	19.401(15)	11.8114(3)
b / Å	36.699(10)	20.1880(14)	11.0140(2)	9.181(6)	20.2555(6)
c / Å º	29.745(8)	24.642(2)	23.7863(5)	21.597(16)	19.2959(5)
α/deg	90	90	90	90	90
β/ deg	93.752(9)	98.939(2)	90	102.98(3)	105.5810(10)
γ/ deg	90	90	90	90	90
V /Å^3	14979(7)	4477.8(6)	9634.20(3)	3749(5)	4446.8(2)
Z	12	4	8	4	4
D$_c$ /Mgm^{-3}	1.843	1.619	1.503	1.641	1.587
μ/mm^{-1}	4.687	3.174	2.992	3.723	3.184
F(000)	7920	2168	4368	1840	2128
cryst size/mm^3	0.12×0.08×0.04	0.12×0.08×0.05	0.42×0.31×0.20	0.3×0.2×0.1	0.3×0.2×0.1
θ/deg	1.801–27.094	2.71–27.16	1.109–27.608	2.417–27.527	2.43–27.15
measured reflns	220645	66097	11161	38605	9826
Unique reflns/R_{int}	32790/ 0.0747	11161/ 0. 0279	7887/0. 0737	8573/0.1035	8891/0.1188
[a]GOF on *F*^{2}	1.051	1.021	1.076	1.067	0.830
[b]R1,[c] wR2 [$I > 2\sigma(I)$]	0.0467, 0.1404	0.0273, 0.0845	0.0495, 0.0957	0.0574, 0.1544	0.0345, 0.0998
R1, wR2	0.0719, 0.1611	0.0383, 0.0962	0.0792, 0.1032	0.0734, 0.1658	0.0390, 0.1084

[a]GOF = $\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$. [b]R1 = $\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[c]wR2 = $[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$, $P = (F_o^2+2F_c^2)/3$

Table S2 Crystallographic parameters of **2b**$^+$, **3b**$^+$ and **4b**.

	2b$^+$I$_3^-$	**3b$^+$BF$_4^-$**	**3b$^+$PF$_6^-$**	**5b.CH$_2$Cl$_2$**	**6b.CH$_3$CN**
Empirical formula	$C_{51}H_{42}N_3O_2P_2I_3ClIr$	$C_{51}H_{42}N_3O_2P_2BClF_4Ir$	$C_{51}H_{42}N_3O_2P_3ClF_6Ir$	$C_{47}H_{41}N_6O_2PCl_3Ir$	$C_{53}H_{46}N_4O_3P_2ClIr$
fw	1399.16	1105.28	1163.43	1051.38	1076.53
T /K	273K	136K	233K	273K	273K
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P* –1	*P*21/c	*P*21/c	*P*21/n	*P*21/c
a / Å	11.5360(9)	9.0249(14)	9.1651(7)	17.2850(18)	11.9113(11)
b / Å	12.0602(10)	21.080(4)	21.6867(16)	15.3182(14)	20.1469(18)
c / Å º	19.3812(15)	24.197(4)	24.310(2)	18.997(2)	20.1158(18)
α/deg	76.118(2)	90	90	90	90
β/ deg	88.795(2)	99.328(5)	99.734(3)	116.831(3)	105.698(3)
γ/ deg	70.420(2)	90	90	90	90
V /Å^3	2461.1(3)	4542.6(14)	4762.3(7)	4488.4(8)	4647.3(7)
Z	2	4	4	4	4
D_c /Mgm^{-3}	1.888	1.618	1.623	1.556	1.539
μ/mm^{-1}	4.756	3.130	3.028	3.234	3.048
F(000)	1336	2204	2312	2096	2160
cryst size/mm^3	0.3×0.2×0.1	0.3×0.2×0.1	0.03×0.02×0.01	0.20×0.15×0.10	0.8×0.06×0.06
θ/deg	2.36–27.49	2.50–27.482	1.942–27.113	1.792–27.212	2.51–27.08
measured reflns	91549	48346	70933	58086	319764
Uniquereflns/R_{int}	11299/0.0453	10356/0. 0776	10498 /0.0598	9935/0.1303	10263
[a]GOF on F^2	0.774	0.936	1.067	0.989	1.029
[b]R1,[c]wR2 [$I > 2\sigma(I)$]	0.0253, 0.0842	0.0404, 0.1161	0.0370, 0.1161	0.0631, 0.1468	0.0297, 0.1003
R1, wR2	0.0293, 0.0924	0.0480, 0.1282	0.0542, 0.1346	0.1250, 0.1863	0.0369, 0.1192

[a]GOF = $\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$. [b]R1 = $\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[c]wR2 = $[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$, $P = (F_o^2+2F_c^2)/3$.

Table S3 Selected Metrical Parameters of **2a**$^{+}$and **3a**$^{+}$.

	2a^{+}I$_3^{-}$			**3a^{+}BF$_4^{-}$**	
	Expt.	**Theo.**		**Expt.**	**Theo.**
Ir1–N1	2.012(5)	2.0363	Ir1–N1	2.057(3)	2.0363
Ir1–N3	2.103(5)	2.1232	Ir1–N3	2.024(3)	2.1232
Ir1–Cl1	2.413(16)	2.4728	Ir1–Cl1	2.3765(8)	2.4728
Ir1–P1	2.424(17)	2.5299	Ir1–P1	2.4354(9)	2.5299
Ir1–P2	2.424(17)	2.5135	Ir1–P2	2.4201(9)	2.5135
N2–N3	1.308(7)	1.2875	N2–N3	1.283(4)	1.2875
N1–C1	1.355(8)	1.3631	N1–C1	1.352(4)	1.3631
C1–C2	1.476(8)	1.4778	C1–C2	1.478(5)	1.4778
N1–O1	1.254(6)	1.2500	N1–O1	1.262(3)	1.2500
N2– C1	1.353(8)	1.3524	N2– C1	1.349(4)	1.3524
N3–C8	1.431(7)	1.4336	N3–C8	1.440(4)	1.4336
Ir1–C14	1.897(7)	1.9002	Ir1–C14	1.909(3)	1.9100
N1–Ir1–Cl1	175.40(15)	175.298	N1–Ir1–Cl1	98.56(8)	175.2987
N3–Ir1–N1	77.23(19)	76.5143	N3–Ir1–N1	76.44(11)	76.5143
Cl1–Ir1–C14	168.0(2)	91.7729	Cl1–Ir1–C14	84.73(11)	91.7729
C14–Ir1–N3	168.0(2)	169.2363	C14–Ir1–N3	100.51(13)	169.2363
C14–Ir1–N1	90.9(2)	92.7419	C14–Ir1–N1	175.56(12)	92.7419

Table S4 Selected Metrical Parameters of **4a**, **5a** and **6a**.

4a			**5a**			**6a**		
	Expt.	**Theo.**		**Expt.**	**Theo.**		**Expt.**	**Theo.**
Ir1–N1	2.011(5)	2.0216	Ir1–N1	2.040(6)	2.0693	Ir1–N1	2.010(3)	2.0352
Ir1–N3	2.087(4)	2.1031	Ir1–N3	2.052(6)	2.1193	Ir1–N3	2.134(3)	2.2255
Ir1–Cl1	2.3737(14)	2.4461	Ir1–N4	2.033(6)	2.0626	Ir1–Cl1	2.4026(7)	2.4656
Ir1–Cl2	2.4006(14)	2.4812	Ir1–N6	2.072(5)	2.1125	Ir1–C14	2.118(3)	2.0946
Ir1–P1	2.3924(13)	2.4613	Ir1–P1	2.331(2)	2.4092	Ir1–P1	2.4051(8)	2.4737
Ir1–P2	2.3945(13)	2.4638	Ir1–Cl1	2.375(2)	2.4423	Ir1–P2	2.3721(8)	2.4560
N2–N3	1.308(6)	1.2932	N2–N3	1.302(8)	1.2801	N2–N3	1.291(3)	1.2815
N1–C1	1.338(7)	1.2932	N5–N6	1.290(8)	1.2856	N1–C1	1.350(4)	1.3559
C1–C2	1.488(8)	1.4791	N1–O1	1.260(7)	1.2490	N1–O1	1.286(3)	1.2735
N1–O1	1.256(6)	1.2444	N4–O2	1.262(7)	1.2426	N2–C1	1.362(4)	1.3622
N2– C1	1.337(7)	1.3395	N2–C1	1.367(9)	1.3540	C14–O2	1.354(3)	1.3532
N3–C8	1.427(7)	1.43832	N4–C14	1.358(8)	1.3489	C14–O3	1.159(4)	1.2162
N1–Ir1–Cl1	89.21(14)	92.0524	N1–Ir1–N3	76.0(2)	75.0581	N1–Ir1–Cl1	173.02(7)	172.13
N3–Ir1–N1	77.05(18)	77.2848	N4–Ir1–N6	75.6(2)	75.5797	N3–Ir1–N1	75.55(9)	74.90
N3–Ir1–Cl2	103.36(13)	101.6882	N1–Ir1–N4	101.4(2)	100.0991	Cl1–Ir1–C14	89.59(8)	91.11
Cl1–Ir1–Cl2	90.42(5)	88.9814	N3–Ir1–N6	106.2(2)	108.2903	O2–C14–O3	119.7(3)	117.8
N1–Ir1–Cl2	178.1(13)	178.7562	P1–Ir1–Cl1	177.9(6)	175.6155	C14–Ir1–N3	171.04(10)	171.62

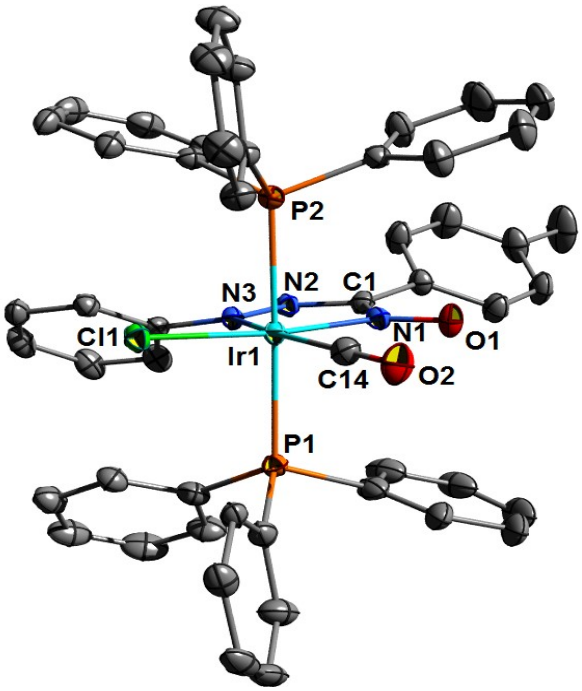


Fig. S1. ORTEP view of $\mathbf{2b^{+}I_3^{-}}$: Hydrogen atoms and $\mathbf{I_3^{-}}$ are omitted for clarity, and thermal ellipsoids are set at 50% probability.): Ir1–N1 2.014(3), Ir1–N3 2.085(2), Ir1–Cl1 2.408(8), Ir1–P1 2.409(8), Ir1–P2 2.4120(8), N2–N3 1.298(4),N1–C1 1.355(8), C1–C2 1.476(8), N1–O1 1.247(3), N2–C1 1.346(4), N3–C8 1.443(4), Ir1–C141.913(3), C14–O2 1.110(4), N1–Ir1–Cl1 173.85(7), N1–Ir1–N376.96(10), Cl1–Ir1–C14 93.81(10), C14–Ir1–N3 166.02(12), C14– Ir1–N1 89.43(2).

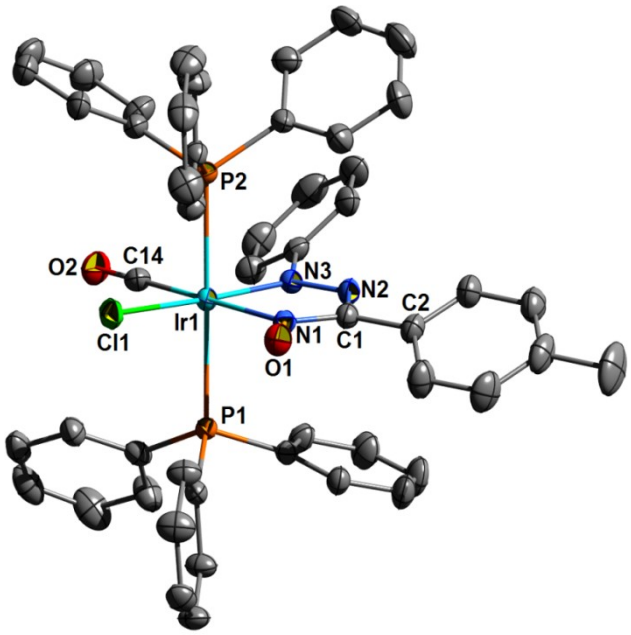


Fig. S2. ORTEP view of $\mathbf{3b^{+}BF_4^{-}}$: Hydrogen atoms and $\mathbf{BF_4^{-}/PF_6^{-}}$ ion are omitted for clarity, and thermal ellipsoids are set at 50% probability. Ir1–N1 2.059(4), Ir1–N3 2.021(4), Ir1–Cl1

2.3830(13), Ir1–P1 2.4311(13), Ir1–P2 2.4253(13), N2–N3 1.283(5), N1–C1 1.357(6), C1–C2 1.474(7), N1–O1 1.250(5), N2–C1 1.353(6), N3–C8 1.443(6), Ir1–C14 1.917(5), C14–O2 1.112(6), N1–Ir1–Cl1 100.38(11), N3–Ir1–N1 76.58(15),Cl1–Ir1–C14 82.59(17), C14–Ir1–N3 100.5(2), C14–Ir1–N1 176.78(19), P1–Ir1–P2 175.22(4).

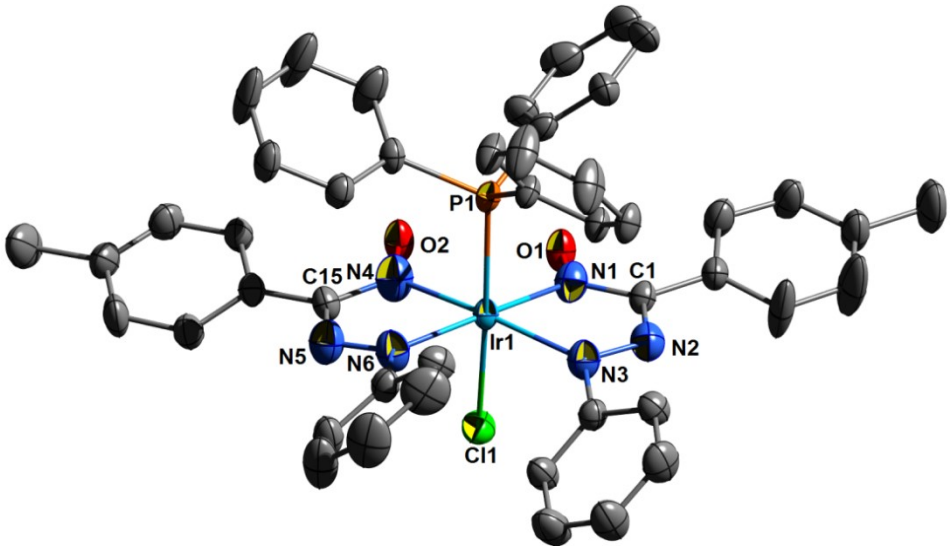


Fig. S3. ORTEP view of **5b·CH_2Cl_2**: Hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at 50% probability. Selected bond lengths (Å) and angles (deg): Ir1–N1 2.014(7), Ir1–N3 2.075(6), Ir1–N4 2.031(7) Ir1–N6 2.063(7) Ir1–Cl1 2.385(3), Ir1–P1 2.341(3), N2–N3 1.284(10), N5–N6 1.296(9), N1–O1 1.262(8), N4–O2 1.252(9), N1–C1 1.339(10), N2–C1 1.365(11), N4–C15 1.340(11), N5–C15 1.370(11), C1–C2 1.486(13), C15–C16 1.457(11), N1–Ir1–N3 75.30(3), N4–Ir1–N6 76.10(3), N1–Ir1–N6 174.10(3), N1–Ir1–N4 99.80(3), N3–Ir1–N6 108.2(3), P1–Ir1–Cl1 174.24(8), N1–Ir1–Cl1 87.50(2).

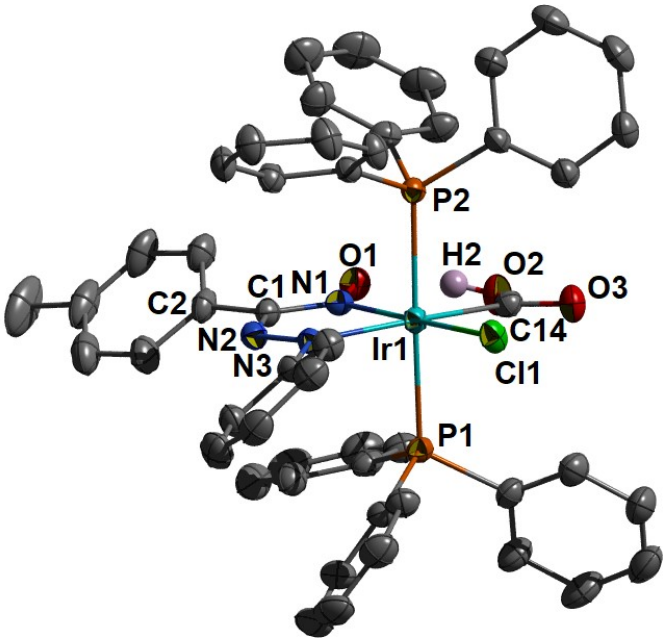


Fig. S4. Molecular diagram of **6b·CH$_3$CN**: Aromatic hydrogen atoms and solvent CH_3CN molecule are omitted for clarity, and thermal ellipsoids are set at 50% probability. Selected bond lengths (Å) and angles (deg): Ir1–N1 2.015(3), Ir1–N3 2.152(3), Ir1–Cl1 2.4054(9), Ir1–P1 2.4082(9), Ir1–P2 2.3750(9), N2–N3 1.279(4), N1–C1 1.342(5), C1–C2 1.476(5), N1–O1 1.286(4), N2–C1 1.352(5), Ir1–C14 2.076(3), C14–O2 1.340(4), C14–O3 1.207(4), O2–H2 0.8200, N1–Ir1–Cl1 172.50(8), N3–Ir1–N1 75.40(11), Cl1–Ir1–C14 90.28(10), O2–C14–O3 116.2(3), C14–Ir1–N3 171.22(12), C14– Ir1–N1 96.70(12).

Table S5 Optimized Bond length(Å) and Bond Angles(°) of Complex **2a** and **3a**.

	2a	**3a**
Ir1–N1	2.03992	2.09673
Ir1–N3	2.13151	2.10726
Ir1–Cl1	2.53359	2.47376
Ir1–P1	2.48797	2.48437
Ir1–P2	2.50978	2.48161
N2–N3	1.34652	1.35572
N1–C1	1.32774	1.38212
C1–C2	1.48362	1.48393
N1–O1	1.14862	1.27807
N2– C1	1.32774	1.31985
N3–C8	1.41325	1.40778
Ir1–C14	1.89418	1.89431
C14–O2	1.14862	1.15492
N1–Ir1–Cl1	177.58882	91.17806
N3–Ir1–N1	77.08915	76.59099
Cl1–Ir1–C14	87.7918	89.68410
C14–Ir1–N3	169.66485	102.54342

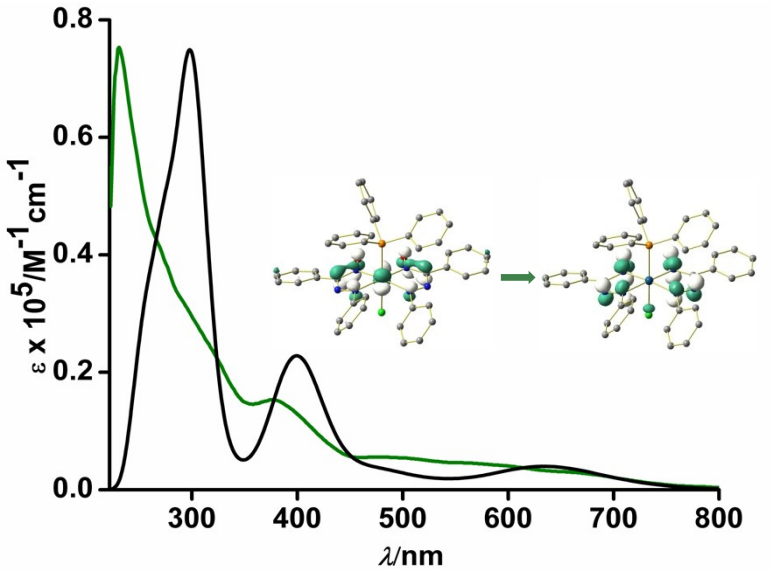


Fig. S4. Theoretical (black) and experimental absorption spectra (green) of **5a** in dichloromethane.

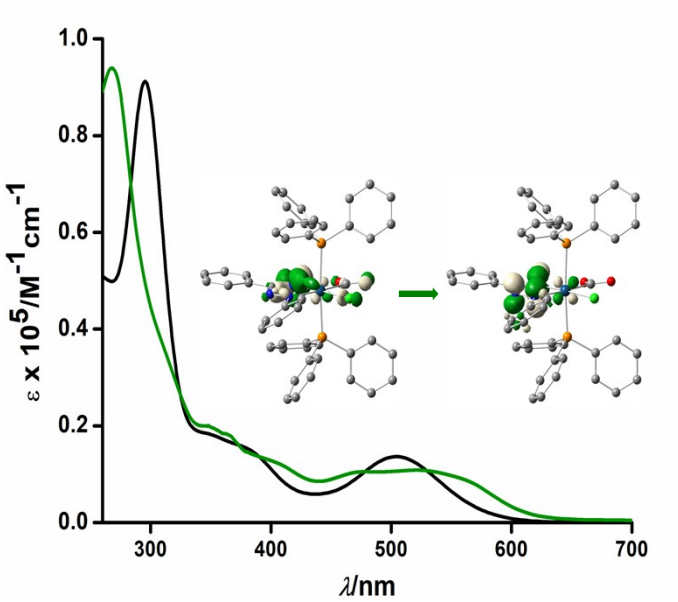


Fig. S5. Theoretical (black) and experimental absorption spectra (green) of **6a** in dichloromethane.

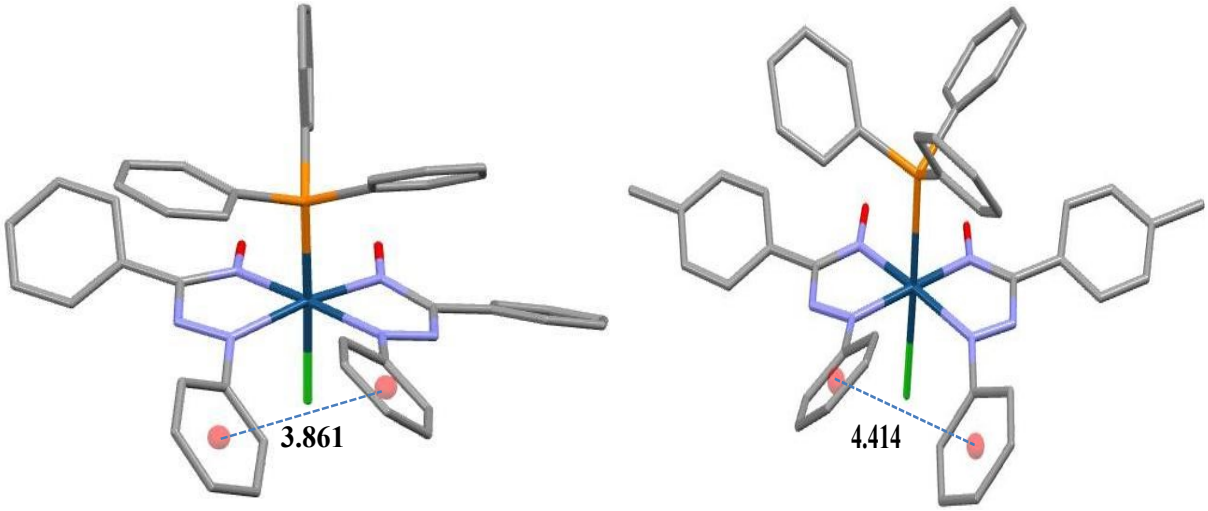


Fig. S6. Intramolecular π–π stacking interactions in **5a**(left) and **5b**.

Table S6 Intramolecular π–π stacking parameters for compound **5**.

Stacking parameters	**5a**	**5b**
$d(c_i–c_j)$ Å/α°	3.861(5)/24.7(4)	4.414(7)/ 26.0(6)
$d(\perp c_i–P_j)$ Å/β°	3.330(3)/ 30.40	3.302(5)/36.6
$d(\perp c_j–P_i)$ Å/β°	3.281(3)/ 31.80	3.290(5)/ 36.9

[a]c = ring centroid, α = dihedral angle between rings, β and β' (slip angle) = angle between the vector $c_i–c_j$ and the normal to plane P_i or P_j from c_i and c_j respectively, $d(c_i–c_j)$ = centroid-centroid distance, $d(\perp c_i–P_j)$ = ⊥ distance from c_i of P_i on ring P_i.

Electronic Structure and Frontier Molecular Orbital Compositions

Energy levels and pictures of certain selected orbitals of the complex **2** are depicted in Fig. S15, ESI†. The partial frontier molecular orbital compositions are listed in Tables S7, S10, S13, S16, S19 and S22, ESI†. The HOMO of the diamagnetic $\mathbf{2}^{+}$, $\mathbf{3}^{+}$, **4**, **5** and **6** are principally composed of azo-oxime-phenyl orbitals (~90%) having π-symmetry withslight participation of d_{Ir}(~5 %), while the LUMO and LUMO+1 have been found to be of azo-oxime π*-orbitals (~80%) over the ligand. The estimated $d_{N-N(azo)}$ in above-mentioned complexes have been observed to be longer as compared tothat of **1** (d_{N-N} (azo) = 1.25 Å) and this is indicative of significant population of azo π* *via* $d_{Ir} \rightarrow$ azo π* back-bonding in complexes. Unrestricted calculation was performed in the case of **2**, where each molecular orbital is differentiated into α and β components, according to the electron spin. FMOs demonstrate the symmetry breaking and it is characteristic of a ligand-centered radical complex, with the spin-*α* and spin-*β* components of each orbital localized differently inthe molecule. The highest singly occupied spin-*α* orbital (SOMO) is delocalized over the ligand framework (71% azo-oxime π* and 22% phenyl) and lies ~2.0 eV below the vacant spin-*β* counterpart. In addition, the highest singly occupied spin-*β* orbital is polarized toward azo-oxime-phenyl scaffold (56% azo-oxime and 44% phenyl) and lies ~2.8 eV below the LUMO of spin-α counterpart. The computed azo bond distance in **2a** has been found to be appreciably longer by 0.06 Å relative to that in $\mathbf{2a}^{+}$(d_{N-N} (azo) = 1.288 Å, Table S3), which is consistent with the anion radical ligand description of the former.

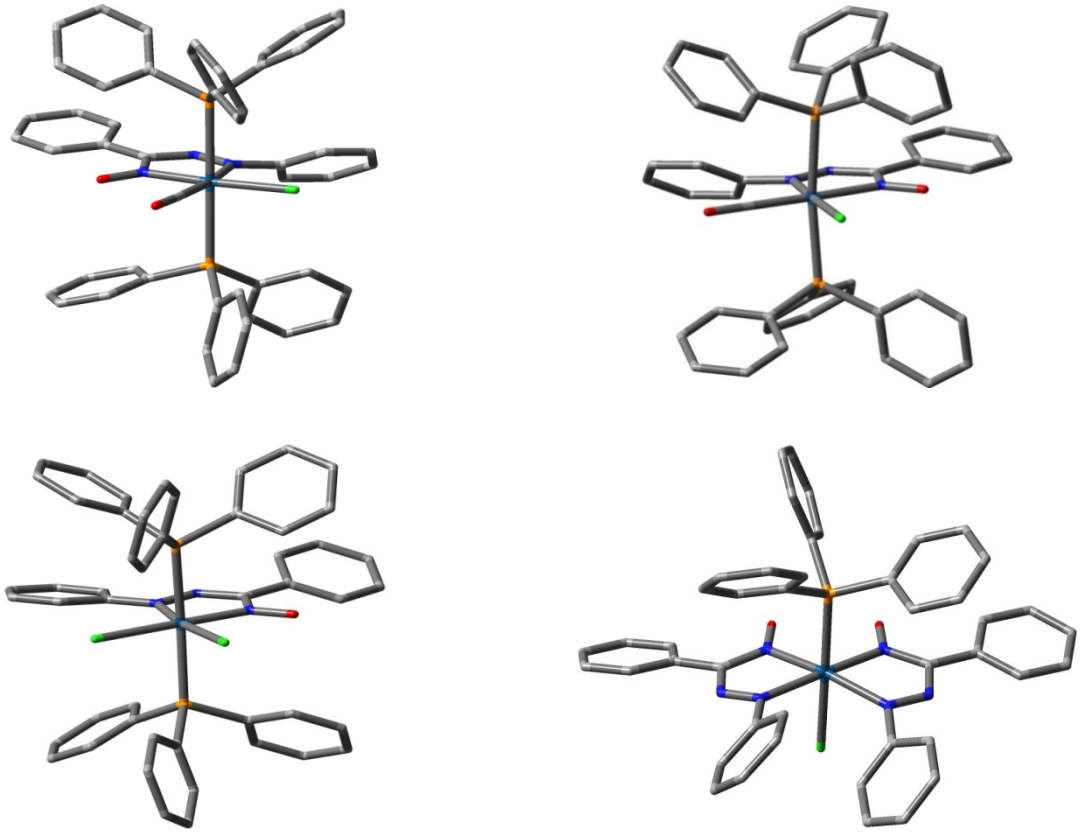


Fig. S7. Optimized geometries of **2a**$^{+}$**I**$_3^{-}$(top-left) **3a**$^{+}$**BF**$_4^{-}$ (top-right), **4a** (bottom-left) and **5a** (bottom-right).

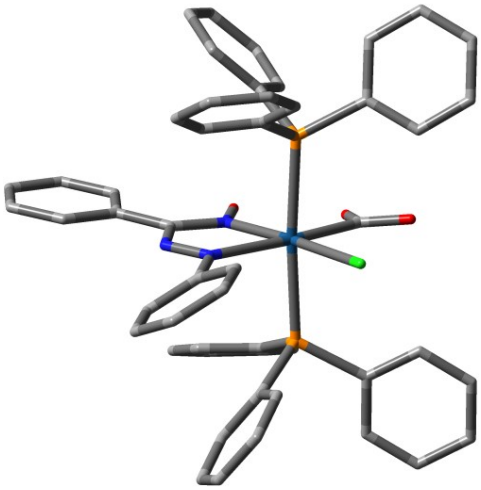


Fig. S8. Optimized geometries of **6a**.

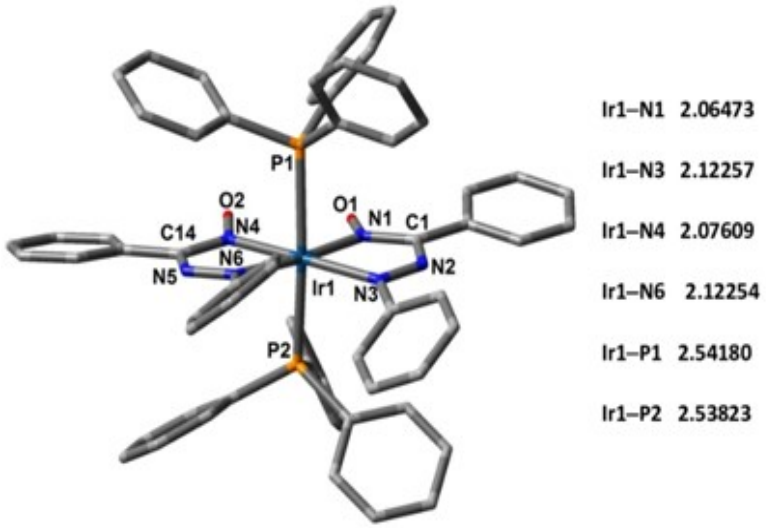


Fig. S9. Optimized geometry of **7a**$^{+}$ with theoretical bond length(Å).

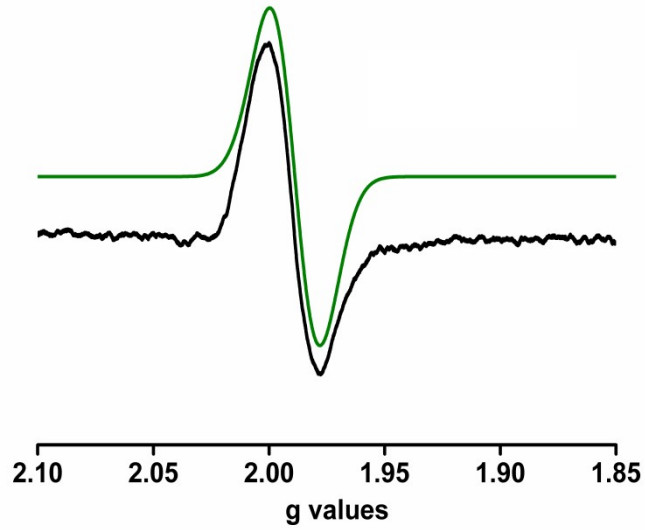


Fig. S10. X-band EPR spectrum of **2b** in dichloromethane at 298 K: Experimental (black); Simulated (green). Instrument settings: microwave frequency, 9.424 GHz; microwave power, 0.998 mW; modulation frequency, 70 kHz

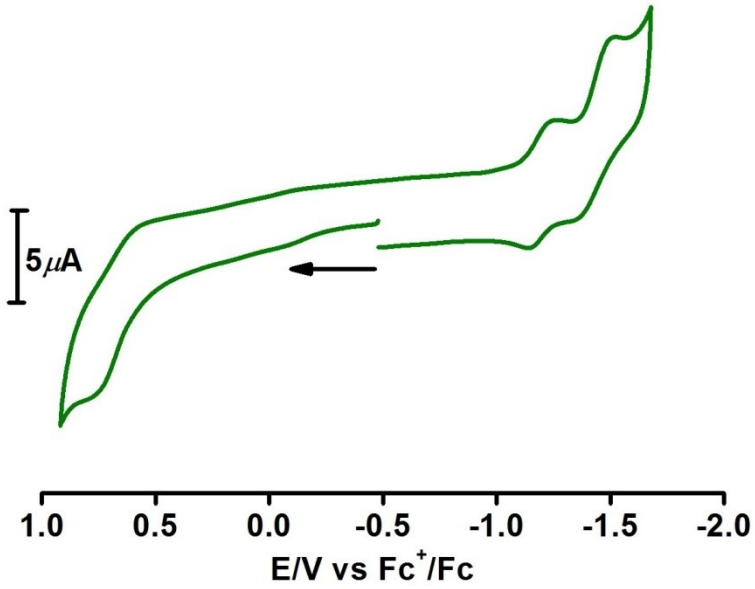


Fig. S11. cyclic voltammogram of complex **3a**$^{+}$ in CH_2Cl_2.

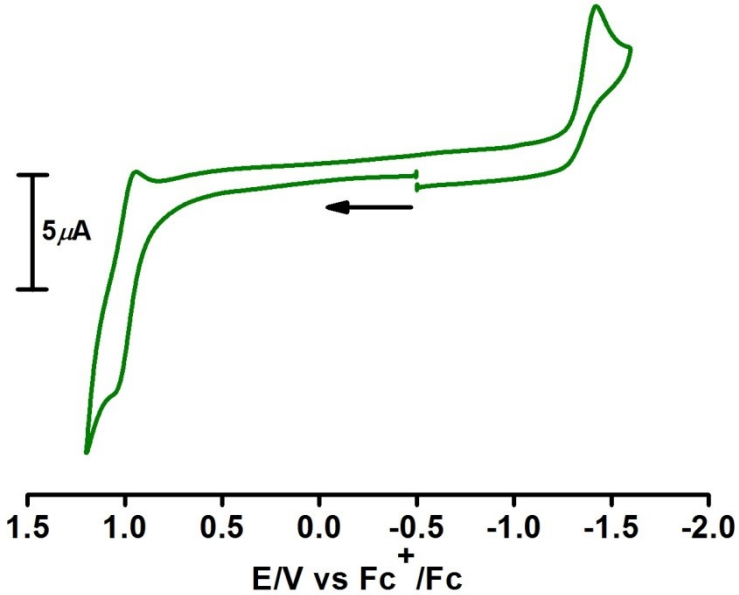


Fig. S12. cyclic voltammogram of complex **4a** in CH_2Cl_2.

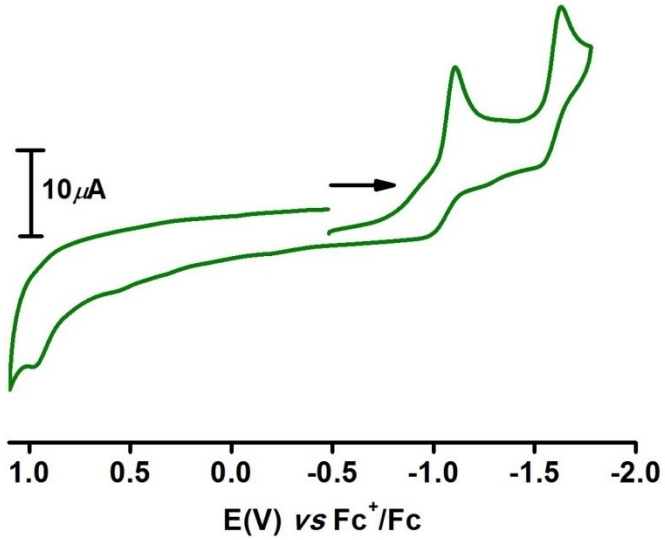


Fig. S13. cyclic voltammogram of complex **5a** in CH_2Cl_2.

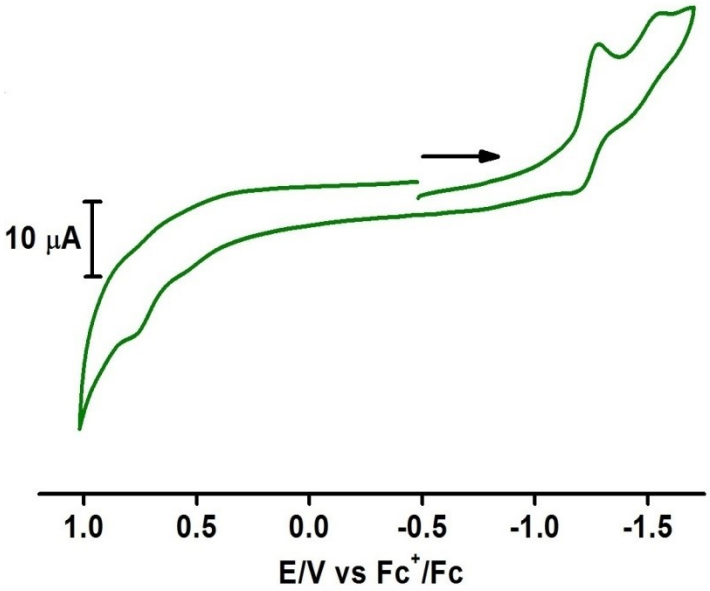


Fig. S14. cyclic voltammogram of complex **6a** in CH_2Cl_2.

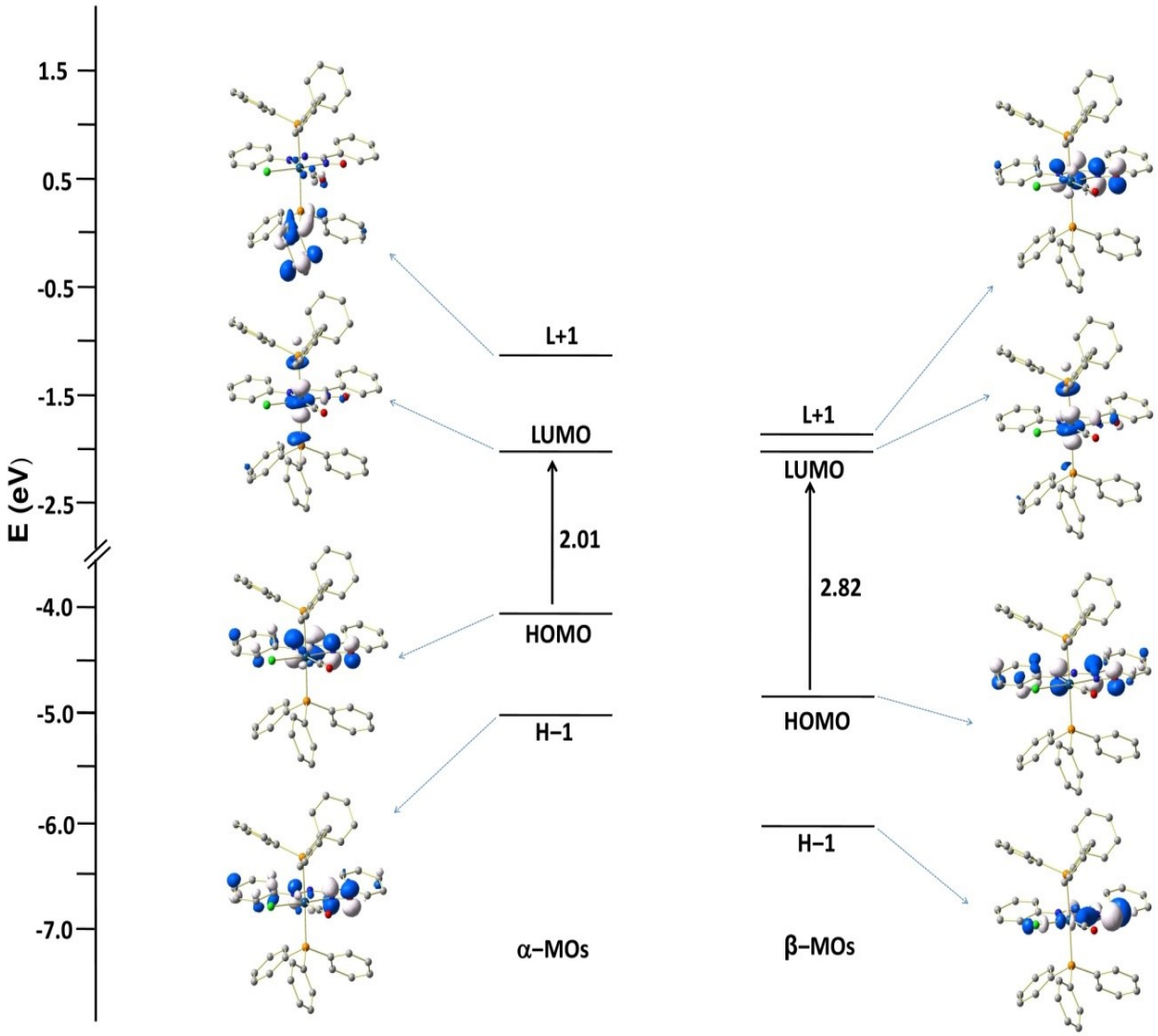


Fig. S15. A portion of MO diagram of complex **2a**.

Table S7 Frontier Molecular Orbital Composition (%) in the Ground State for **2a**.

Orbital	α–MO	Energy (eV)	Contribution (%)							Main Bond Type
			Metal	Ligand						
			Ir	Azo	Oxime	Ph	PPh_3	Cl	CO	
227	L+5	–0.99	6	1	1	1	80	1	10	$\pi^*(PPh_3)$
226	L+4	–1.01	7	0	14	0	71	1	8	$\pi^*(PPh_3$+Oxime)
225	L+3	–1.09	39	1	5	0	32	5	19	$d_{x^2-y^2}$(Ir)+ π^*(CO+PPh_3)
224	L+2	–1.14	3	0	2	0	92	0	4	$\pi^*(PPh_3)$
223	L+1	–1.27	2	0	1	0	89	0	8	$\pi^*(PPh_3)$
222	LUMO	–2.02	28	1	5	0	65	2	1	d_{z^2}(Ir)+π^*(PPh_3)
221	SOMO	–4.03	4	40	31	22	2	0	1	π(Azo+Oxime+Ph)
220	H–1	–5.49	4	8	44	40	2	1	0	π(Oxime+Ph)
219	H–2	–6.21	6	5	67	12	0	8	1	π(Oxime+Ph)
218	H–3	–6.41	0	1	1	91	3	4	0	π(Ph)
217	H–4	–6.44	0	8	1	75	16	1	0	π(Ph+ PPh_3)
216	H–5	–6.56	1	3	3	89	2	2	0	π(Ph)
Orbital	β–MO	Energy (eV)	Contribution (%)							Main Bond Type
			Metal	Ligand						
			Ir	Azo	Oxime	Ph	PPh_3	Cl	CO	
226	L+5	–0.99	13	2	12	0	62	2	13	$\pi^*(PPh_3$+CO)
225	L+4	–1.07	31	0	7	0	44	3	17	$d_{x^2-y^2}$(Ir)+ $\pi^*(PPh_3$+CO)
224	L+3	–1.14	3	0	2	0	92	0	4	$\pi^*(PPh_3)$
223	L+2	–1.27	1	0	1	0	91	0	7	$\pi^*(PPh_3)$
222	L+1	–1.86	7	30	38	13	10	1	2	π^* (Azo+Oxime+Ph+ PPh_3)
221	LUMO	–2.02	23	4	8	1	61	2	1	d_{z^2}(Ir)+ $\pi^*(PPh_3)$
220	HOMO	–4.84	1	18	35	44	2	0	1	π(Azo+Oxime+Ph)
219	H–1	–6.02	7	6	68	9	0	8	2	π(Oxime)
218	H–2	–6.3	0	9	4	78	9	0	0	π(Ph)
217	H–3	–6.35	0	0	0	91	5	3	0	π(Ph)
216	H–4	–6.56	1	5	1	88	1	3	1	π(Ph)
215	H–5	–6.59	13	0	1	7	46	32	0	d_{xz}+π(PPh_3)+p(Cl)

Table S8 Main optical transition at the TD-DFT/B3LYP/6-31+G(d,p) Level for the complex **2a** with composition in terms of molecular orbital contribution of the transition, Computed Vertical excitation energies, and oscillator strength in dichloromethane.

Transition	**CI**	**Composition**	**E (eV)**	**Oscillator strength (*f*)**	λ_{theo} **(nm)**
$S_0 \rightarrow S_2$	0.75531	HOMO-$\beta\rightarrow$ LUMO-β (57%)	1.9166	0.0920	646.89
$S_0 \rightarrow S_8$	0.56920	HOMO -$\alpha\rightarrow$ L+5-α (32%)	2.5921	0.1026	478.31
$S_0 \rightarrow S_{64}$	0.53906	H–4- $\alpha\rightarrow$LUMO- α (29%)	4.0561	0.0480	305.67

Table S9 Natural transition orbitals (NTOs) for complex **2a** illustrating the nature of singlet excited states in the absorption bands in the range 250–700 nm. For each state, the respective number of the state, transition energy (eV), and the oscillator strength (in parentheses) are listed. Shown are only occupied (holes) and unoccupied (electrons) NTO pairs that contribute more than 35% to each excited state.

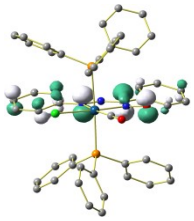
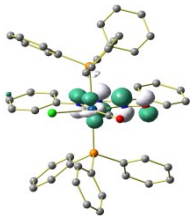
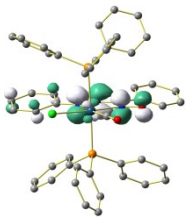
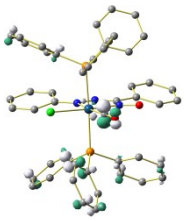
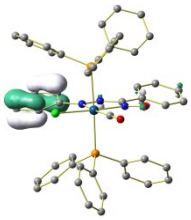
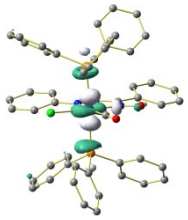
		Hole	Electron
538 nm	S_2 w = 1.1409 1.9166 (0.0920) 646.89 nm ILCT+LMCT π(azo+oxime+Ph) → π*(azo+oxime)+ d_z^2(Ir)		
357 nm	S_8 w = 0.6479 2.5921 (0.1026) 478.31 LLCT π(Azo+Oxime) → π* (CO)		
270 nm	S_{64} w = 0.5811 4.0561 (0.0480) 305.67nm ILCT+LMCT π(Ph) → d_z^2(Ir)+σ *(Ir–P)		

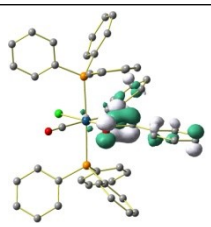
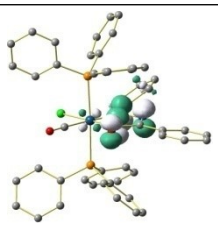
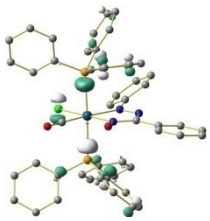
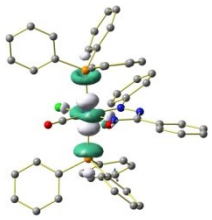
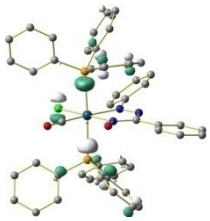
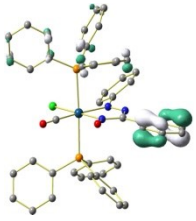
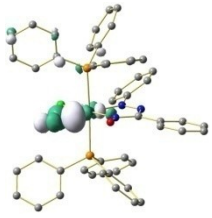
Table S10 Frontier Molecular Orbital Composition (%) in the Ground State for **2a**$^+$.

Orbital	MO	Energy (EV)	Contribution (%)							Main Bond Type
			Metal	Ligand						
			Ir	Azo	Oxime	Ph	PPh_3	Cl	CO	
226	L+5	–3.55	4	0	3	4	70	0	18	π*(PPh_3+CO)
225	L+4	–3.75	11	0	3	2	36	0	49	d_{xz}(Ir)+π*(PPh_3+CO)
224	L+3	–3.82	4	1	4	3	40	0	48	π*(PPh_3+CO)
223	L+2	–4.02	50	7	10	2	0	10	25	$d_{x^2-y^2}$(Ir)+π*(Oxime+CO)+p(Cl)
222	L+1	–4.76	32	0	5	0	59	4	0	Ir+π*(PPh_3)
221	LUMO	–5.67	4	41	38	12	4	0	2	π*(Oxime+Azo+Ph)
220	HOMO	–8.32	2	9	34	51	3	1	0	π(Ph+Oxime)
219	H–1	–9.03	4	1	0	19	67	8	0	π(PPh_3+Ph)
218	H–2	–9.11	0	0	0	84	14	1	0	π(PPh_3+Ph)
217	H–3	–9.22	1	2	0	32	61	3	0	π(PPh_3+Ph)
216	H–4	–9.30	1	1	1	55	38	4	0	π(PPh_3+Ph)
215	H–5	–9.36	0	1	2	23	72	2	0	π(PPh_3+Ph)
HOMO–LUMO gap = 2.65 eV										

Table S11 Main optical transition at the TD-DFT/B3LYP/6-31+G(d,p) Level for the complex **2a**$^+$ with composition in terms of molecular orbital contribution of the transition, Computed vertical excitation energies, and oscillator strength in dichloromethane.

Transition	CI	Composition	E (eV)	Oscillator strength (*f*)	λ_{theo} (nm)
$S_0 \rightarrow S_1$	0.69219	HOMO → LUMO (96%)	2.3754	0.1179	521.95
$S_0 \rightarrow S_{21}$	0.60686	H–1 → L+1 (74%)	3.6394	0.3785	340.67
$S_0 \rightarrow S_{38}$	0.54692	H–1→ L+2 (60%)	4.2377	0.0631	292.58
$S_0 \rightarrow S_{71}$	0.34592 0.25613	H–2 → L+4 (24%) H–1→ L+6 (13%)	4.9159	0.0337	252.21

Table S12 Natural transition orbitals (NTOs) for complex **2a**$^+$ illustrating the nature of singlet excited states in the absorption bands in the range 200–700 nm. For each state, the respective number of the state, transition energy (eV), and the oscillator strength (in parentheses) are listed. Shown are only occupied (holes) and unoccupied (electrons) NTO pairs that contribute more than 10% to each excited state

		Hole	Electron
540 nm	S_1 w = 0.9582 2.3754 (0.1179) 521.95 nm ILCT π(Azo+Oxime+ Ph) → π*(Azo+Oxime)		
363 nm	S_{21} w = 0.7365 2.6132 (0.3785) 340.67 nm ILCT σ*(Ir-P) → dz^2(Ir)+σ*(Ir-P) bond		
295 nm	S_{38} w = 0.5982 4.2377 (0.0631) 292.58 nm ILCT+LMCT p(PPh_3) → $d_{x^2-y^2}$(Ir)+π*(CO+Oxime)+p(Cl)		
231 nm	S_{71} w = 0.2393 4.9159 (0.0337) 252.21 nm ILCT π(Ph) → π*(CO)+p(Cl)		

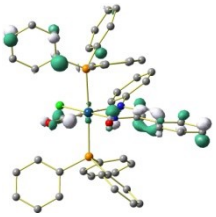
w = 0.1312 4.9159 (0.0337) 252.21 nm ILCT p(PPh_3)+p(Cl) → π*(+Azo+CO+Oxime)		

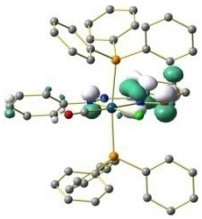
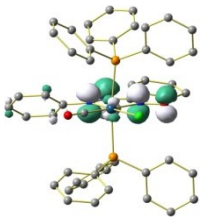
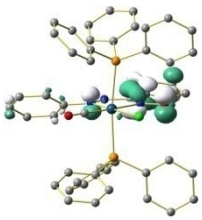
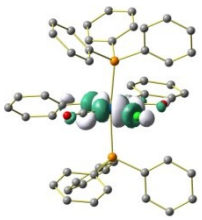
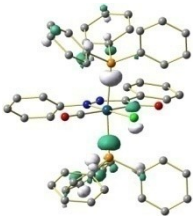
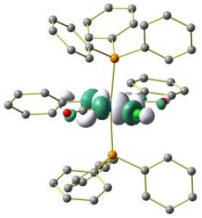
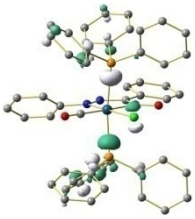
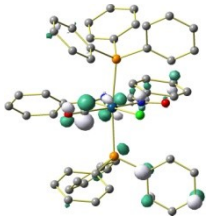
Table S13 Frontier Molecular Orbital Composition (%) in the Ground State for **3a**$^+$.

Orbital	MO	Energy (EV)	Contribution (%)							Contribution
			Metal	Ligand			PPh_3	Cl	CO	
			Ir	Azo	Oxime	Ph				
226	L+5	-3.49	0	1	12	24	62	0	1	π*(PPh_3+Ph+Oxime)
225	L+4	-3.74	16	6	5	11	21	1	39	d_{xy} (Ir)+π*(Ph+PPh_3+CO)
224	L+3	-3.75	20	0	0	16	16	2	53	d_{xy}(Ir)+π*(PPh_3+CO)
223	L+2	-3.88	41	7	11	14	6	8	13	$d_{x^2-y^2}$(Ir)+π*(Ph+CO)
222	L+1	-4.82	35	2	4	0	53	6	1	d_{z^2}(Ir)+π*(PPh_3)
221	LUMO	-5.67	4	38	39	11	5	0	2	π*(Oxime+Azo)
220	HOMO	-8.38	3	9	37	49	2	1	0	π(Ph+Oxime)
219	H–1	-9.04	5	0	1	4	73	17	0	π(PPh_3+Cl)
218	H–2	-9.11	0	0	2	89	6	2	0	π(Ph)
217	H–3	-9.14	8	1	1	7	71	13	0	π(PPh_3+Cl)
216	H–4	-9.22	2	0	0	1	94	4	0	π(PPh_3)
215	H–5	-9.27	3	0	3	2	82	10	0	π(PPh_3)
HOMO–LUMO gap = 2.71 eV										

Table S14 Main optical transition at the TD-DFT/B3LYP/6-31+G(d,p) Level for the complex **3a**$^+$ with composition in terms of molecular orbital contribution of the transition, Computed vertical excitation energies, and oscillator strength in dichloromethane.

Transition	CI	Composition	E (eV)	Oscillator strength (*f*)	λ_{theo} (nm)
$S_0 \rightarrow S_1$	0.59688 0.28740	HOMO → LUMO (71%) H–6→ LUMO (17%)	2.4472	0.0750	506.63
$S_0 \rightarrow S_{23}$	0.57663	HOMO → L+2 (67%)	3.6905	0.0998	335.95
$S_0 \rightarrow S_{45}$	0.49457	H–1→ L+2 (49%)	4.4059	0.0763	281.40
$S_0 \rightarrow S_{69}$	0.49776 0.31350	H–1 → L+6 (50%) H–1→ L+5 (20%)	4.9495	0.0431	250.50

Table S15 Natural transition orbitals (NTOs) for complex **3a**$^+$ illustrating the nature of singlet excited states in the absorption bands in the range 250–700 nm. For each state, the respective number of the state, transition energy (eV), and the oscillator strength (in parentheses) are listed. Shown are only occupied (holes) and unoccupied (electrons) NTO pairs that contribute more than 15% to each excited state.

		Hole	Electron
513 nm	S_1 w = 0.7125 2.4472 (0.0750) 506.63 nm ILCT π(Azo+Oxime+Ph) → π*(Azo+Oxime)		
375 nm	S_{23} w = 0.6650 3.6905 (0.0998) 335.95 nm ILCT+d-d transition π(Azo+Oxime+Ph) → $d_{x^2-y^2}$(Ir)+p(Cl)		
295 nm	S_{45} w = 0.4891 4.4059 (0.0763) 281.40 nm ILCT π(PPh_3)+ p(Cl) → $d_{x^2-y^2}$(Ir)+p(Cl)		
228 nm	S_{69} w = 0.4955 4.9495 (0.0431) 250.50 nm ILCT+MMCT π(PPh_3) → π*(CO)+d_{xz}(Ir)		

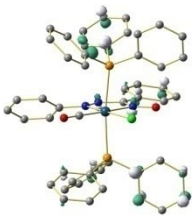
w=0.1965 4.9495 (0.0431) 250.50 nm ILCT+MMCT $\pi(PPh_3) \rightarrow \pi^*((PPh_3)$		

Table S16 Frontier Molecular Orbital Composition (%) in the Ground State for **4a**.

Orbital	MO	Energy (EV)	Contribution (%)						Main Bond Type
			Metal	Ligand					
			Ir	Azo	Oxime	Ph	PPh_3	Cl	
28	L+5	-0.91	17	62	12	0	6	5	$d_{x^2-y^2}$(Ir)+π*(Azo+Oxime)
227	L+4	-0.93	12	72	0	2	14	3	$d_{x^2-y^2}$(Ir)+π*(Azo+PPh_3)
226	L+3	-1.02	32	41	13	1	4	9	$d_{x^2-y^2}$(Ir)+π*(Azo+Oxime)
225	L+2	-1.07	2	28	15	53	2	0	π*(Azo+Oxime+Ph)
224	L+1	-1.77	31	39	1	0	24	5	d_{z^2}(Ir)+π*(Azo+ PPh_3)
223	LUMO	-2.82	7	37	40	15	1	0	π*(Azo+Oxime+Ph)
222	HOMO	-5.6	9	13	33	39	0	5	π(Azo+Oxime+Ph)
221	H–1	-6.16	38	5	1	2	0	53	d_{xy}(Ir)+π(Cl)
220	H–2	-6.26	10	25	0	2	14	48	d_{xz}(Ir)+π(Azo+PPh_3+Cl)
219	H–3	-6.4	13	36	3	5	4	38	d_{yz}(Ir)+π(Azo+Cl)
218	H–4	-6.6	4	13	31	7	0	45	π(Azo+Oxime+Cl)
217	H–5	-6.68	3	11	35	8	0	43	π(Azo+Oxime+Cl)
HOMO–LUMO gap = 2.78 eV									

Table S17 Main optical transition at the TD-DFT/B3LYP/6-31+G(d,p) Level for the complex **4a** with composition in terms of molecular orbital contribution of the transition, Computed Vertical excitation energies, and oscillator strength in dichloromethane.

Transition	**CI**	**Composition**	**E (eV)**	**Oscillator strength (*f*)**	**λ_{theo} (nm)**
$S_0 \rightarrow S_1$	0.66801	HOMO →LUMO(89%)	2.3403	0.1084	529.78
$S_0 \rightarrow S_5$	0.64297	H–3 → LUMO (83%)	3.0121	0.0748	411.62
$S_0 \rightarrow S_{29}$	0.68561	HOMO→L+3 (94%)	4.0474	0.3235	306.33

Table S18 Natural transition orbitals (NTOs) for complex **4a** illustrating the nature of singlet excited states in the absorption bands in the range 250–700 nm. For each state, the respective number of the state, transition energy (eV), and the oscillator strength (in parentheses) are listed. Shown are only occupied (holes) and unoccupied (electrons) NTO pairs that contribute more than 35% to each excited state.

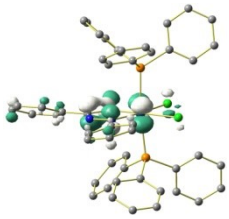
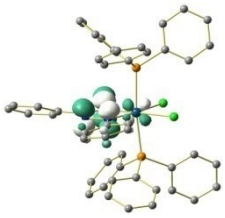
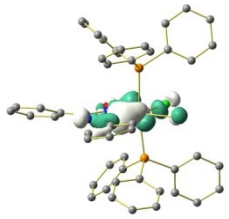
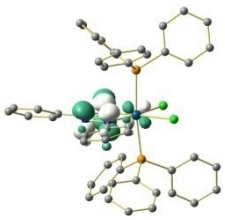
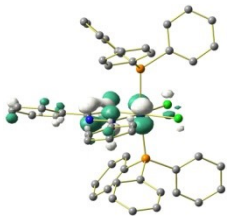
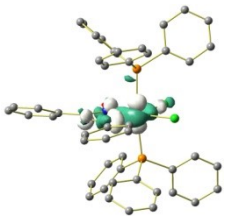
		Hole	Electron
555 nm	S_1 w = 0.8924 2.3403 (0.1084) 529.78 nm ILCT+d-d transition π(azo+oxime)+d_{xz} (Ir)→ π*(azo+oxime)		
470 nm	S_5 w = 0.8268 3.0121 (0.0748) 411.62 ILCT++LMCT π(azo)+p(Cl) → π*(azo+oxime)		
270 nm	S_{29} w = 0.9401 4.0474 (0.3235) 306.32nm ILCT+LMCT π(azo+oxime)+d_{xz} (Ir)→ d_z^2(Ir)		

Table S19 Frontier Molecular Orbital Composition (%) in the Ground State for **5a**.

Orbital	MO	Energy (EV)	Contribution (%)						Contribution
			Ir	Azo	Oxime	Ph	PPh_3	Cl	
209	L+5	-1.13	0	1	3	5	91	0	π*(PPh_3)
208	L+4	-1.3	1	2	3	1	92	1	π*(PPh_3)
207	L+3	-1.38	1	0	0	3	97	0	π*(PPh_3)
206	L+2	-1.87	29	3	4	-1	56	11	Ir +π*(PPh_3+Cl)
205	L+1	-2.48	8	40	40	11	1	0	Ir+π*(Azo+ Oxime+Ph)
204	LUMO	-3.07	2	41	45	9	1	3	π*(Azo+Oxime)
203	HOMO	-5.59	8	12	38	40	1	0	π(Azo+Oxime+Ph)
202	H–1	-5.85	0	14	41	44	1	0	π(Azo+Oxime+Ph)
201	H–2	-6.4	5	15	58	7	1	14	π(Azo+Oxime+Cl)
200	H–3	-6.63	9	4	30	20	1	36	π(Oxime+Ph+Cl)
199	H–4	-6.69	24	1	14	8	3	50	Ir+π(Oxime+Cl)
198	H–5	-6.8	5	1	1	84	1	9	π(Ph)
HOMO–LUMO gap = 2.52 eV									

Table 20 Main optical transition at the TD-DFT/B3LYP/6-31+G(d,p) Level for the complex **5a** with composition in terms of molecular orbital contribution of the transition, Computed vertical excitation energies, and oscillator strength in dichloromethane.

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Transition	CI	Composition	E (eV)	Oscillator strength (*f*)	λ_{theo} (nm)
$S_0 \rightarrow S_1$	0.68847	HOMO → LUMO (95%)	1.9472	0.0532	636.73
$S_0 \rightarrow S_5$	0.50414	HOMO → L+1 (75%)	2.6132	0.0395	474.46
$S_0 \rightarrow S_{10}$	0.37454	H–4→ LUMO (54%)	3.1095	0.0475	398.73
$S_0 \rightarrow S_{45}$	0.41184	HOMO → L+5 (34%)	4.1262	0.1536	300.48

Table S21 Natural transition orbitals (NTOs) for complex **5a** illustrating the nature of singlet excited states in the absorption bands in the range 250–700 nm. For each state, the respective number of the state, transition energy (eV), and the oscillator strength (in parentheses) are listed. Shown are only occupied (holes) and unoccupied (electrons) NTO pairs that contribute more than 35% to each excited state.

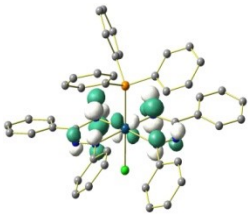
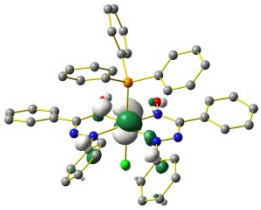
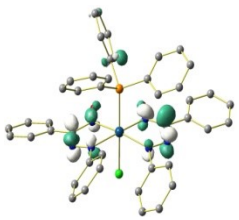
		Hole	Electron
657 nm	S_1 w = 0.9487 1.9472 (0.0532) 636.73 nm ILCT+MLCT π(azo+oxime) + d_{yz}(Ir)→ π*(azo+oxime)		
487 nm	S_5 w = 0.5083 2.6132 (0.0395) 474.46 nm ILCT+ d-d transition π(azo+oxime)+ d_{yz}(Ir) → π*(azo+oxime) + d_{xz}(Ir)		
377 nm	S_{10} w = 0.2805 3.1095 (0.0475) 398.73 nm ILCT π(Ph+oxime) →π*(azo+oxime)		
231 nm	S_{45} w = 0.545 4.1320 (0.0263) 300.48 nm ILCT+MLCT π(azo+oxime) + d_{yz}(Ir) → π*(azo+oxime)		

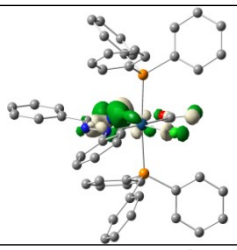
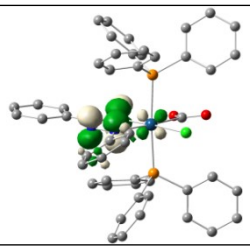
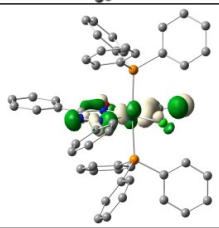
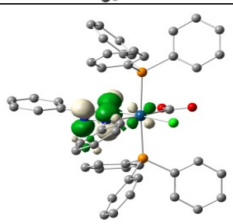
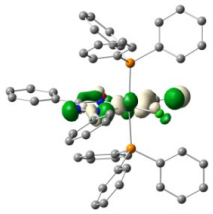
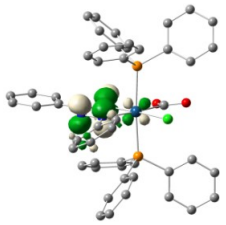
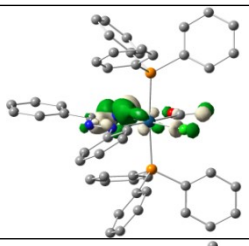
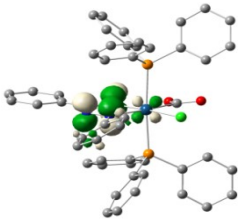
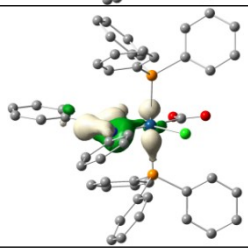
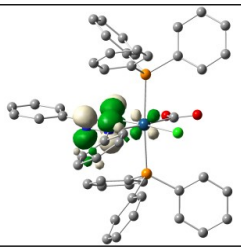
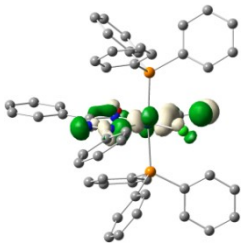
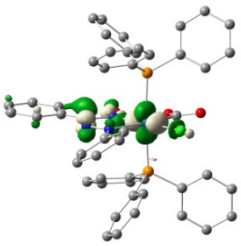
Table S22 Frontier Molecular Orbital Composition (%) in the Ground State for **6a**.

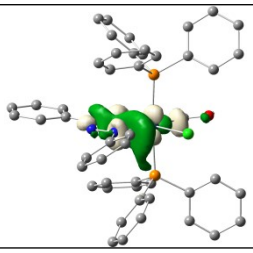
Orbital	MO	Energy (EV)	Contribution (%)							Main Bond Type
			Metal	Ligand						
			Ir	Azo	Oxime	Ph	PPh_3	Cl	COOH	
231	L+5	-0.98	4	0	5	0	89	1	2	$\pi^*(PPh_3)$
230	L+4	-1.03	11	0	3	8	75	1	2	$\pi^*(PPh_3)$
229	L+3	-1.07	1	1	2	3	92	0	0	$\pi^*(PPh_3)$
228	L+2	-1.21	0	8	16	56	19	0	0	π^*(Oxime+Ph PPh_3)
227	L+1	-1.67	26	0	5	0	67	3	0	Ir+π^*(PPh_3)
226	LUMO	-2.94	6	40	36	14	2	0	1	π^*(Oxime+Azo+Ph)
225	HOMO	-5.81	10	9	30	36	2	4	9	Ir+π(Ph+Oxime)
224	H–1	-5.96	15	10	5	10	2	3	54	Ir+π(Azo+Oxime+COOH)
223	H–2	-6.3	33	0	8	4	3	47	5	Ir+p(Cl)
222	H–3	-6.36	11	1	5	3	42	38	0	π(PPh_3)+p(Cl)
221	H–4	-6.72	9	2	2	12	67	7	0	$\pi(PPh_3$+Ph)
220	H–5	-6.78	1	0	1	1	93	0	3	$\pi(PPh_3)$
HOMO–LUMO gap = 2.87 eV										

Table S23 Main optical transition at the TD-DFT/B3LYP/6-311+G(d,p) Level for the complex **6a** with composition in terms of molecular orbital contribution of the transition, Computed vertical excitation energies, and oscillator strength in dichloromethane

Transition	**CI**	**Composition**	**E (eV)**	**Oscillator strength (*f*)**	**λ_{theo} (nm)**
$S_0 \rightarrow S_1$	0.55050 0.40893	H–1 → LUMO (61%) HOMO → LUMO (33%)	2.3961	0.0387	517.44
$S_0 \rightarrow S_2$	0.52000 0.41941	HOMO → LUMO (54%) H–1 → LUMO (35%)	2.4785	0.0757	500.24
$S_0 \rightarrow S_6$	0.51638	H–4→ LUMO (53%)	3.2381	0.0300	382.90
$S_0 \rightarrow S_{28}$	0.54244 0.34163	HOMO → L+2 (59%) HOMO → L+4 (23%)	4.1500	0.2391	298.75

Table S24 Natural transition orbitals (NTOs) for complex **6a** illustrating the nature of singlet excited states in the absorption bands in the range 250–700 nm. For each state, the respective number of the state, transition energy (eV), and the oscillator strength (in parentheses) are listed. Shown are only occupied (holes) and unoccupied (electrons) NTO pairs that contribute more than 30% to each excited state.

		Hole	Electron
536 nm	S_1 w = 0.6061 2.3961 (0.0387) 517.44 nm ^{1}ILCT+ ^{1}LLCT π(oxime)+π(COOH) → π*(azo+oxime)		
	w = 0.3344 2.3961 (0.0387) 517.44 nm ^{1}ILCT+ ^{1}LLCT π(azo+oxime)+π(COOH)→ π*(azo+oxime)		
468 nm	S_2 w = 0.5408 2.4785 (0.0757) 500.24 nm ^{1}ILCT+ ^{1}LLCT π(azo+oxime)+π(COOH) → π*(azo+oxime)		
	w = 0.3518 2.4785 (0.0757) 500.24 nm ^{1}ILCT+ ^{1}LLCT π(oxime)+π(COOH) → π*(azo+oxime)		
365 nm	S_6 w = 0.5332 3.2381 (0.0300) 382.90 nm ^{1}ILCT π(azo + σ(Ir-P) → π*(azo+oxime)		
268 nm	S_{28} w = 0.5844 4.1500 (0.2391) 298.75 nm ^{1}ILCT+^{1}LMCT π(azo+oxime)+π(COOH)→ π*(azo+oxime)+$d_{x^2-y^2}$(Ir)		

w = 0.1074 4.1500 (0.2391) 298.75 nm ^{1}ILCT+ ^{1}LLCT π(azo+oxime)+π(COOH)→ π*(azo+ oxime)		

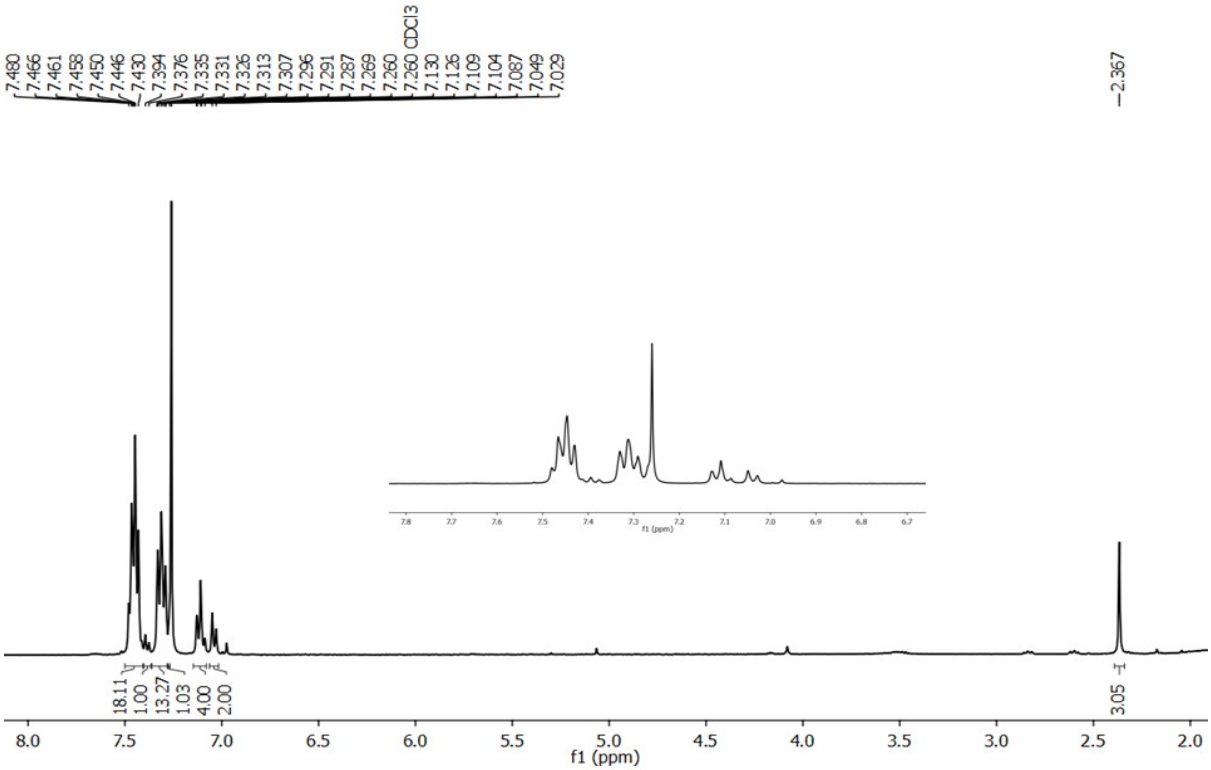


Fig. S16. ^{1}H NMR spectrum of **2b**$^+$

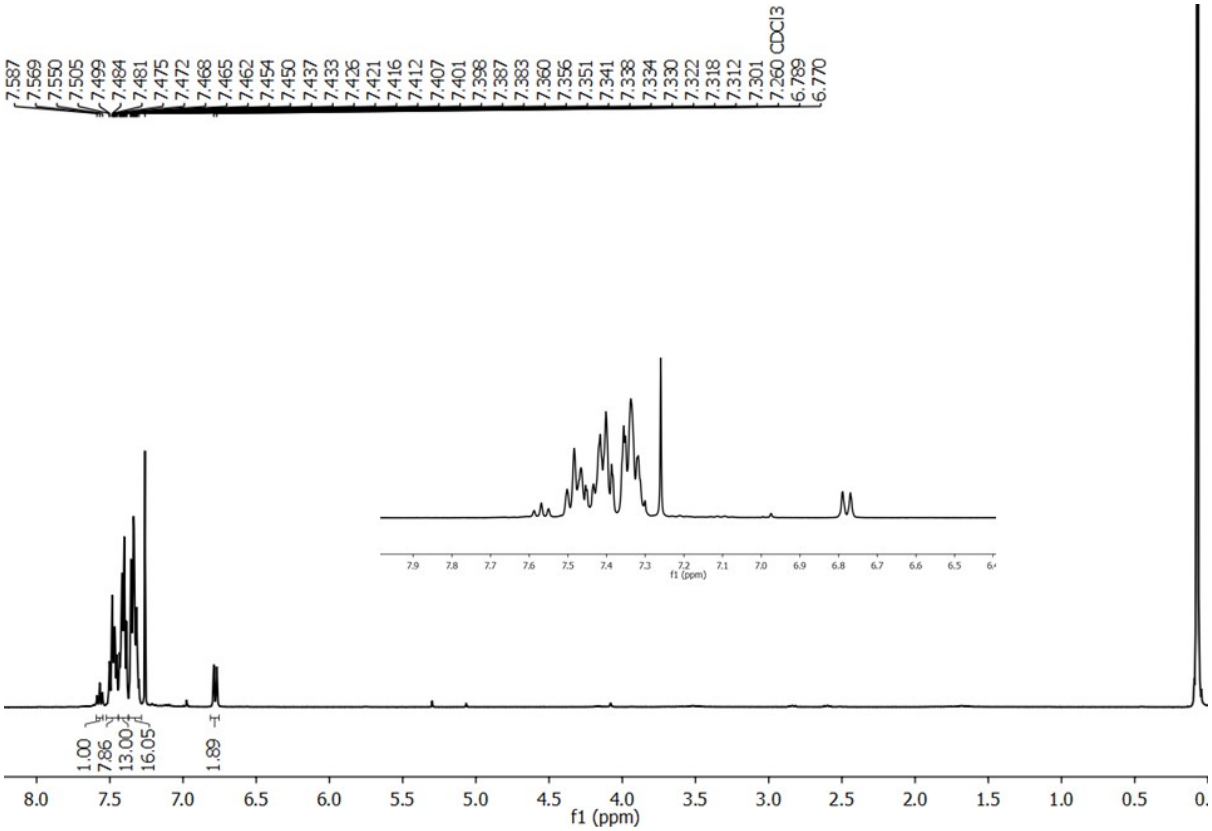


Fig. S17. [1]H NMR spectrum of **3a**[+]

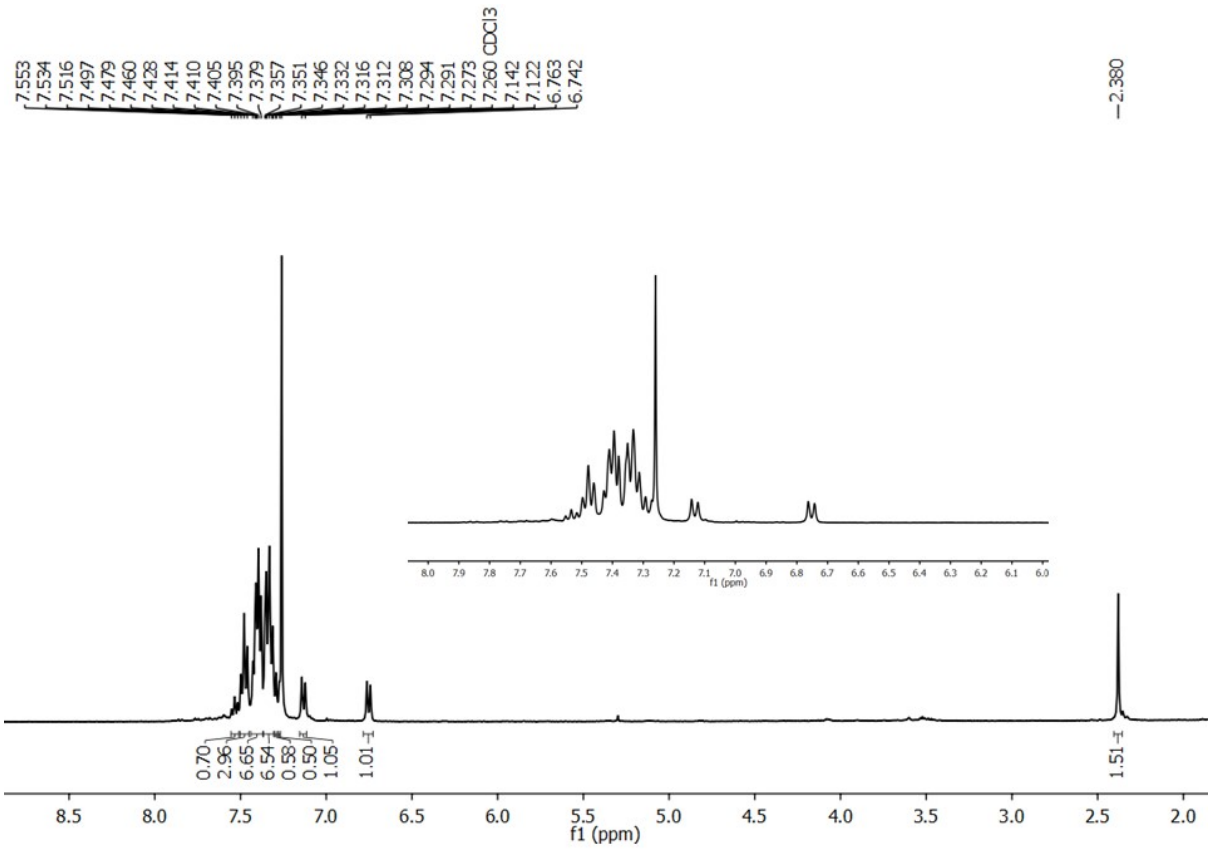


Fig. S18. [1]H NMR spectrum of **3b**[+]

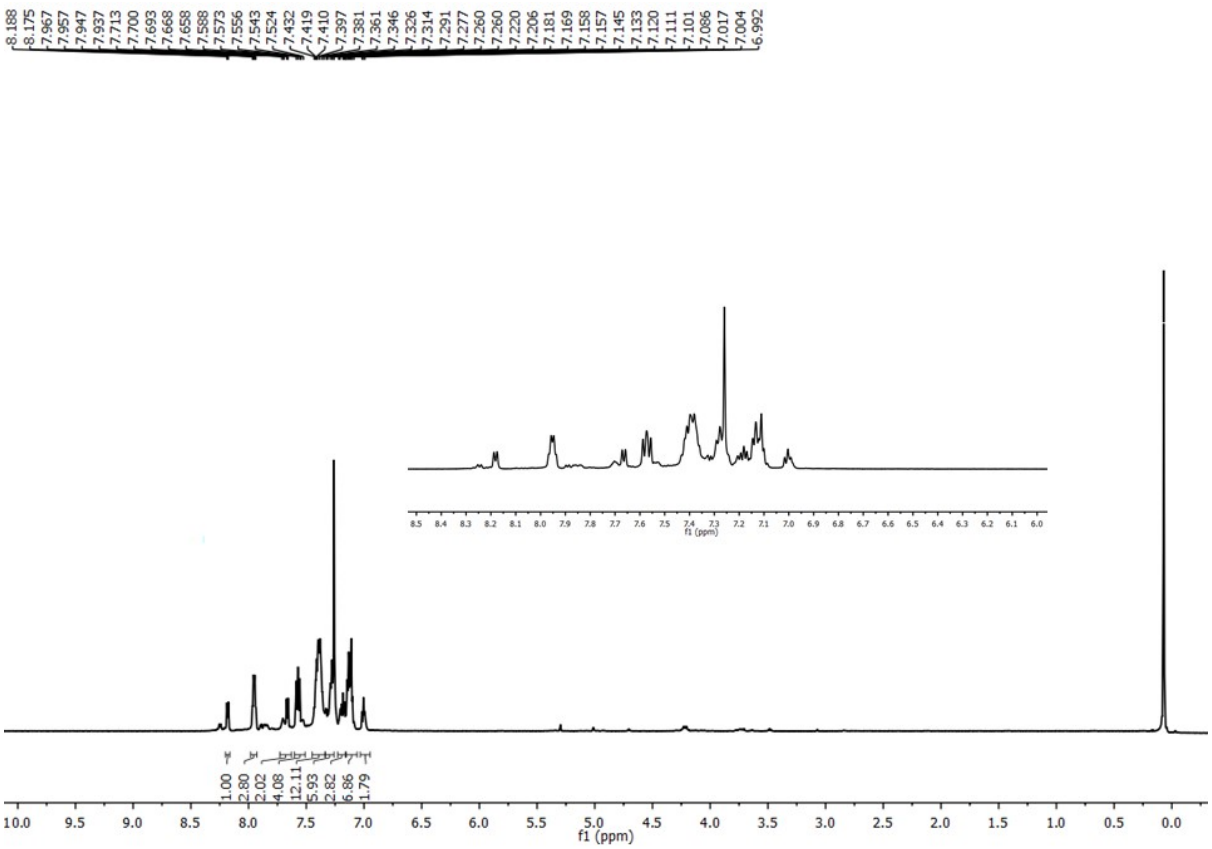


Fig. S19. [1]H NMR spectrum of **4a**

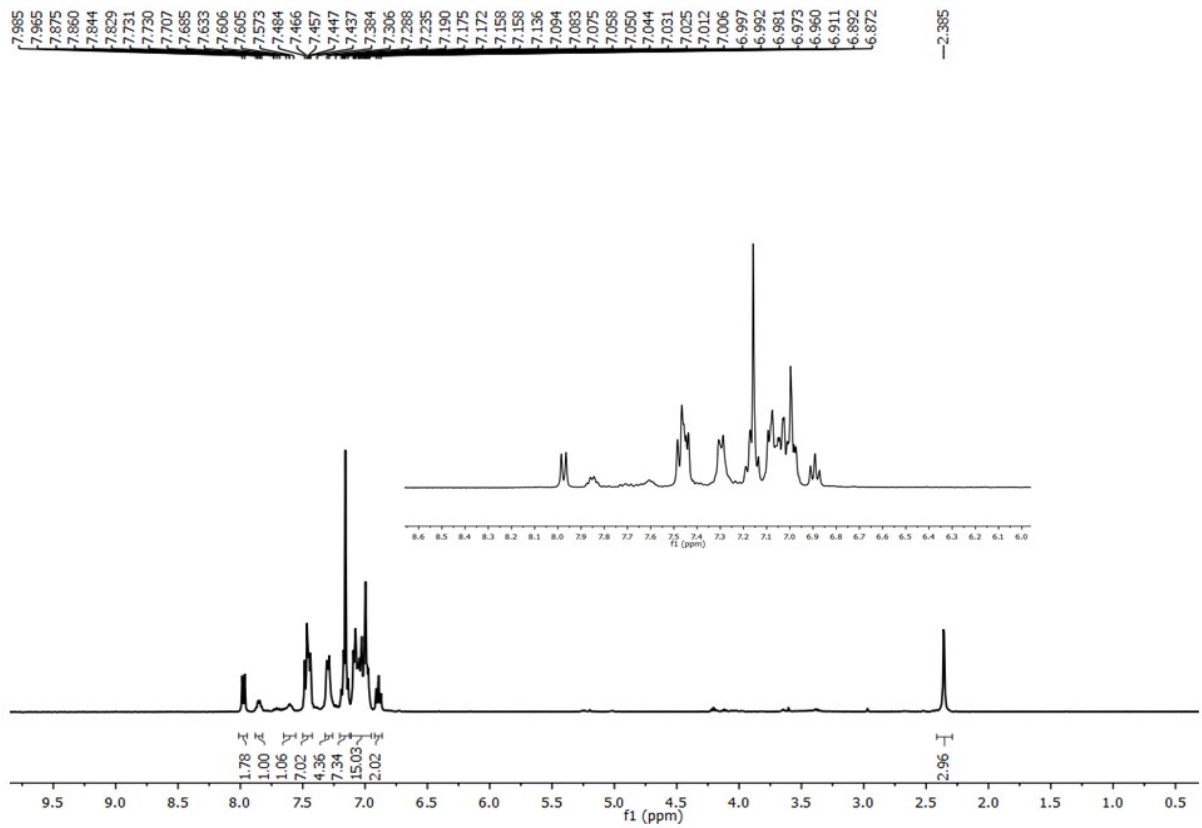


Fig. S20. [1]H NMR spectrum of **4b**

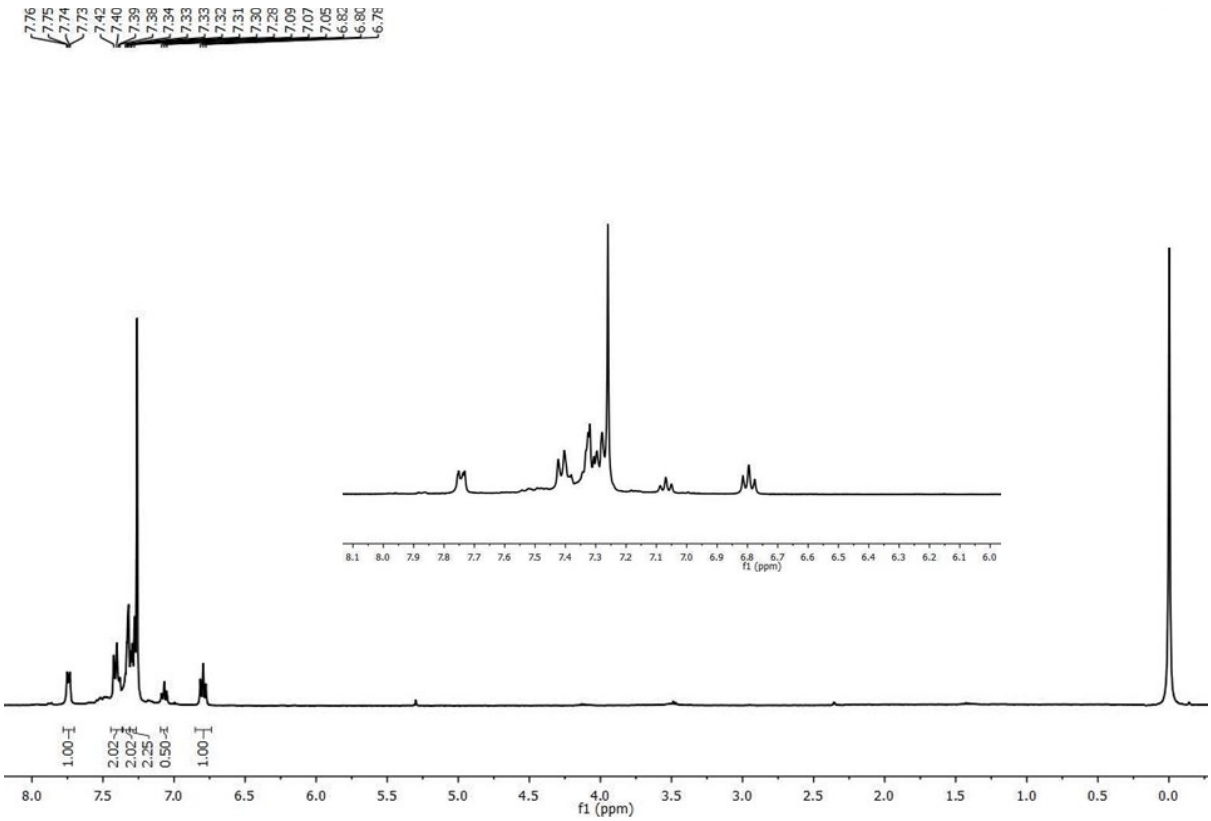


Fig. S21. [1]H NMR spectrum of **5a**

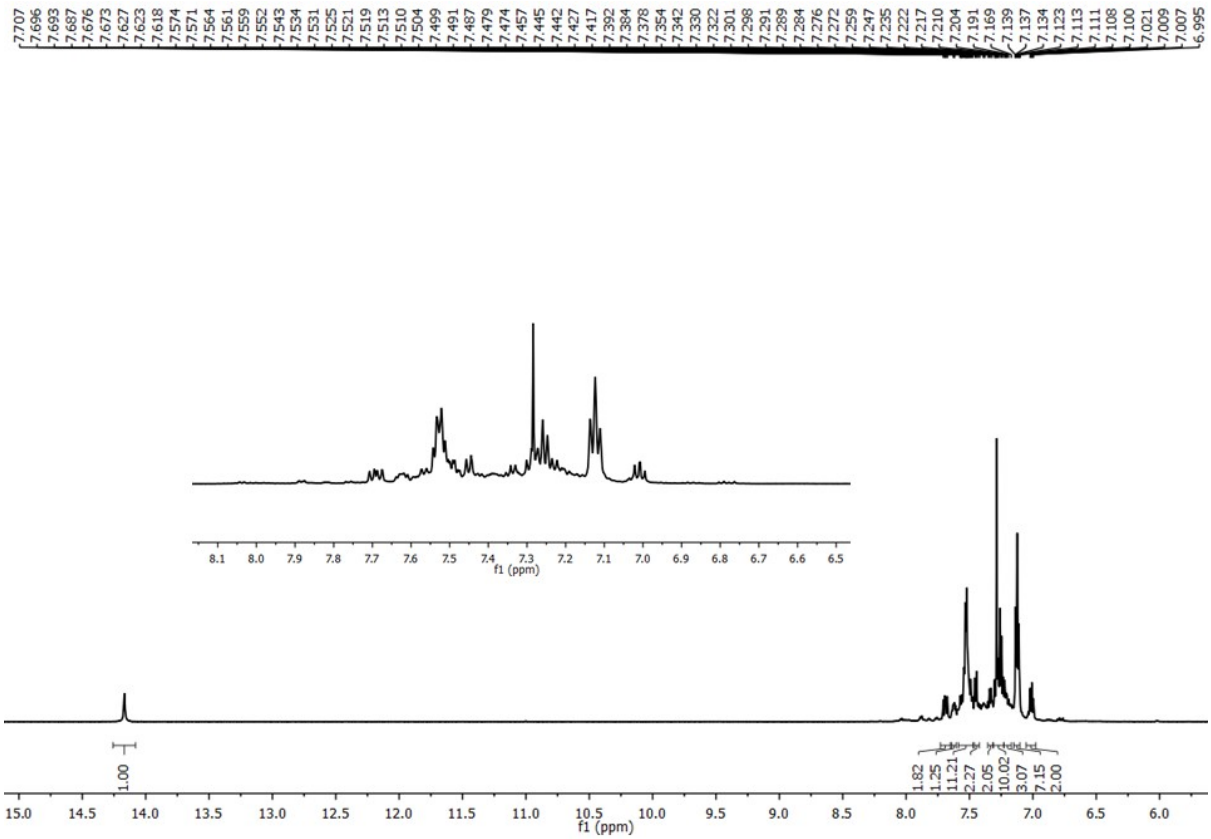


Fig. S22. [1]H NMR spectrum of **6a**

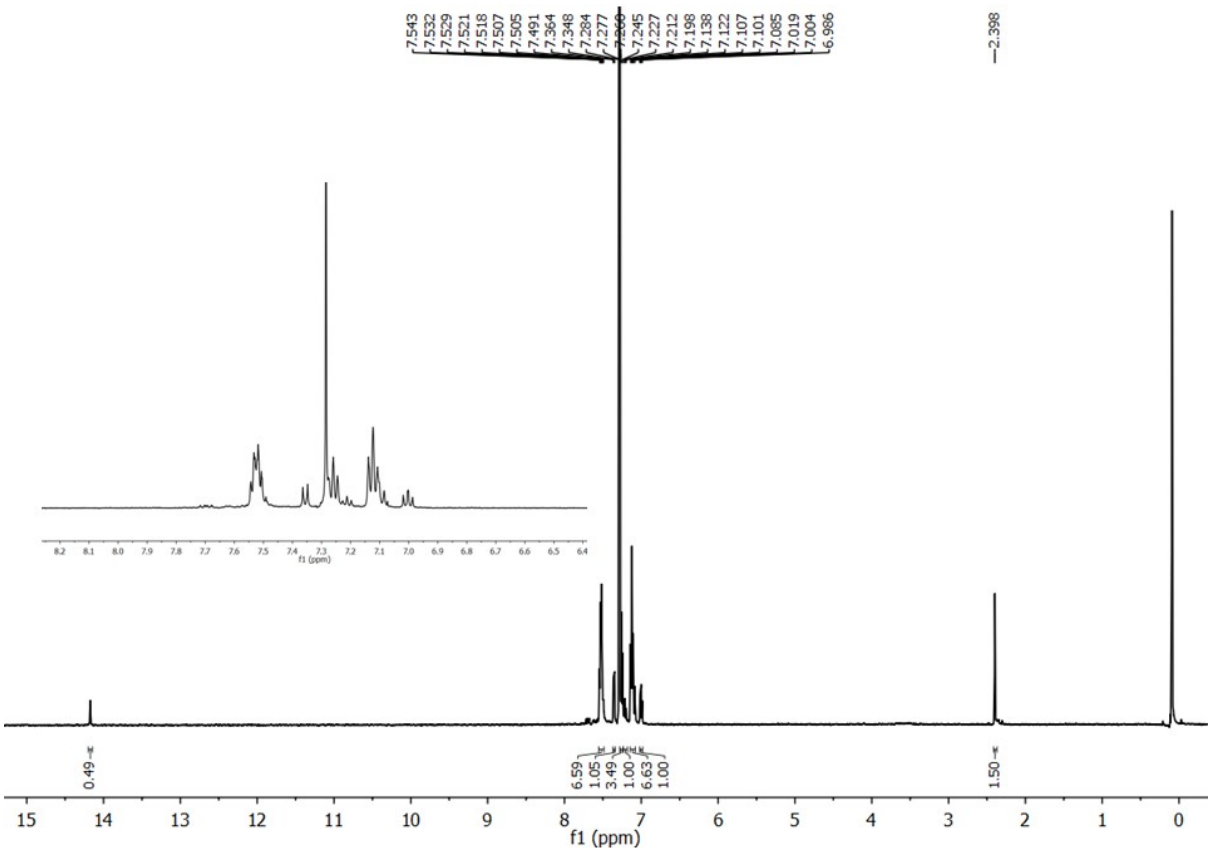


Fig. S23. ^{1}H NMR spectrum of **6b**

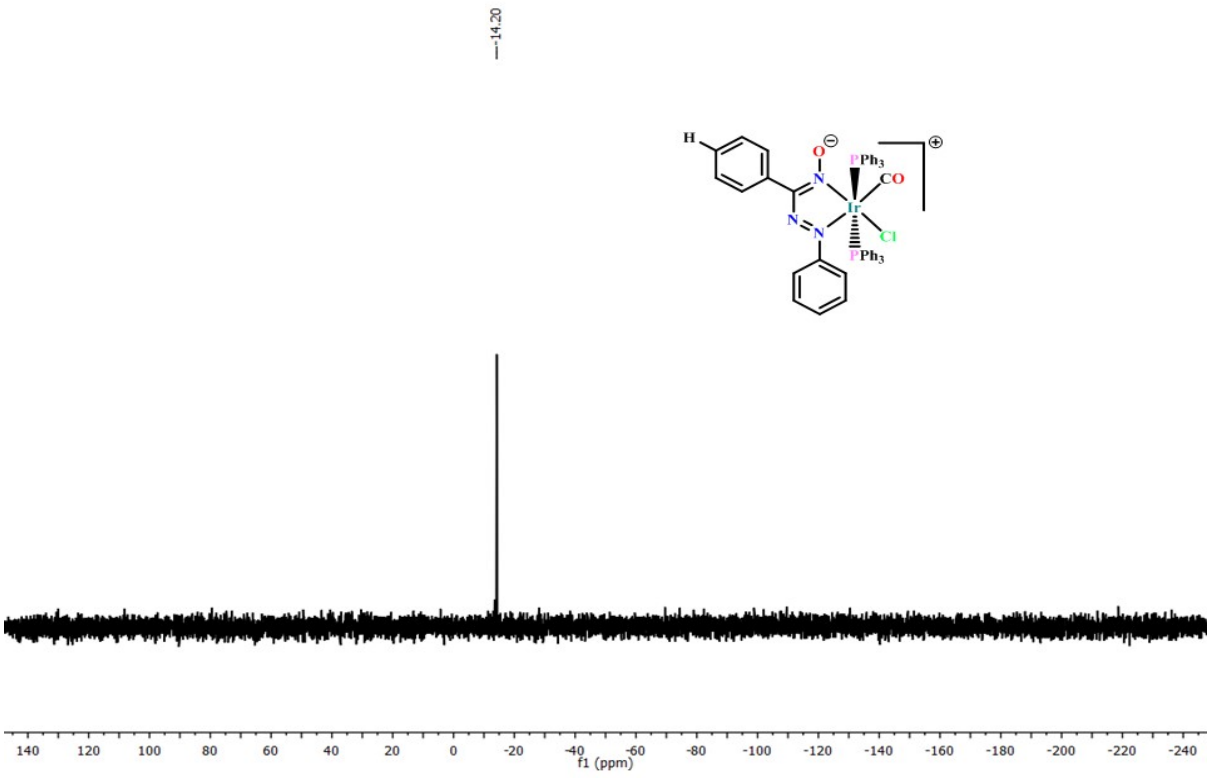


Fig. S24. ^{31}P NMR spectrum of **2a**$^{+}$

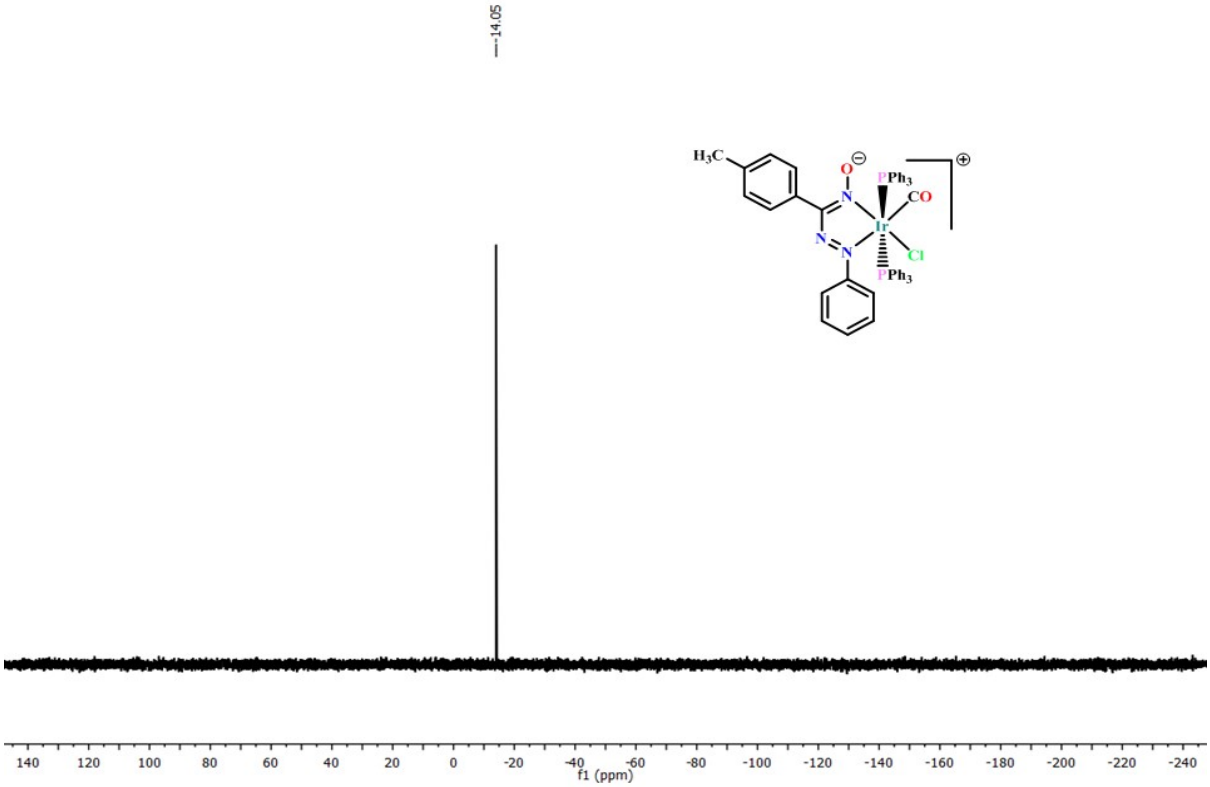


Fig. S25. ^{31}P NMR spectrum of **2b**$^{+}$

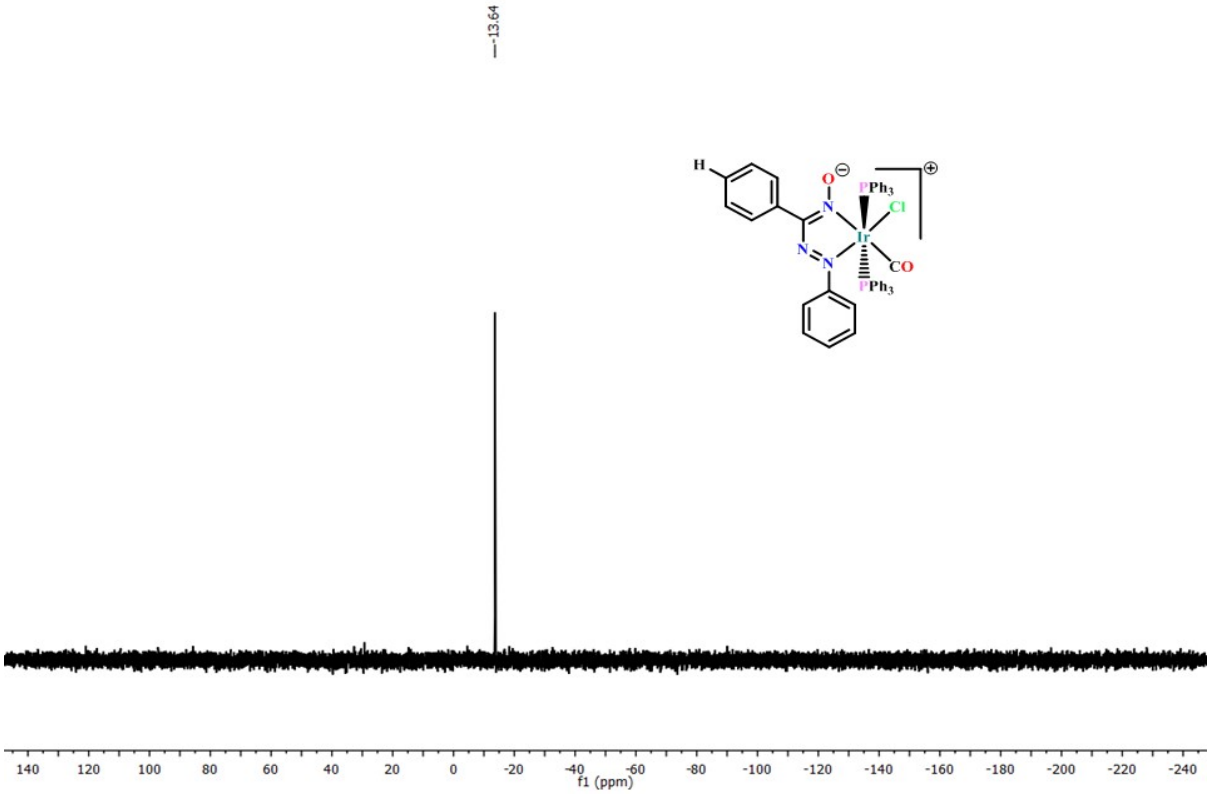


Fig. S26. ^{31}P NMR spectrum of **3a**$^{+}$

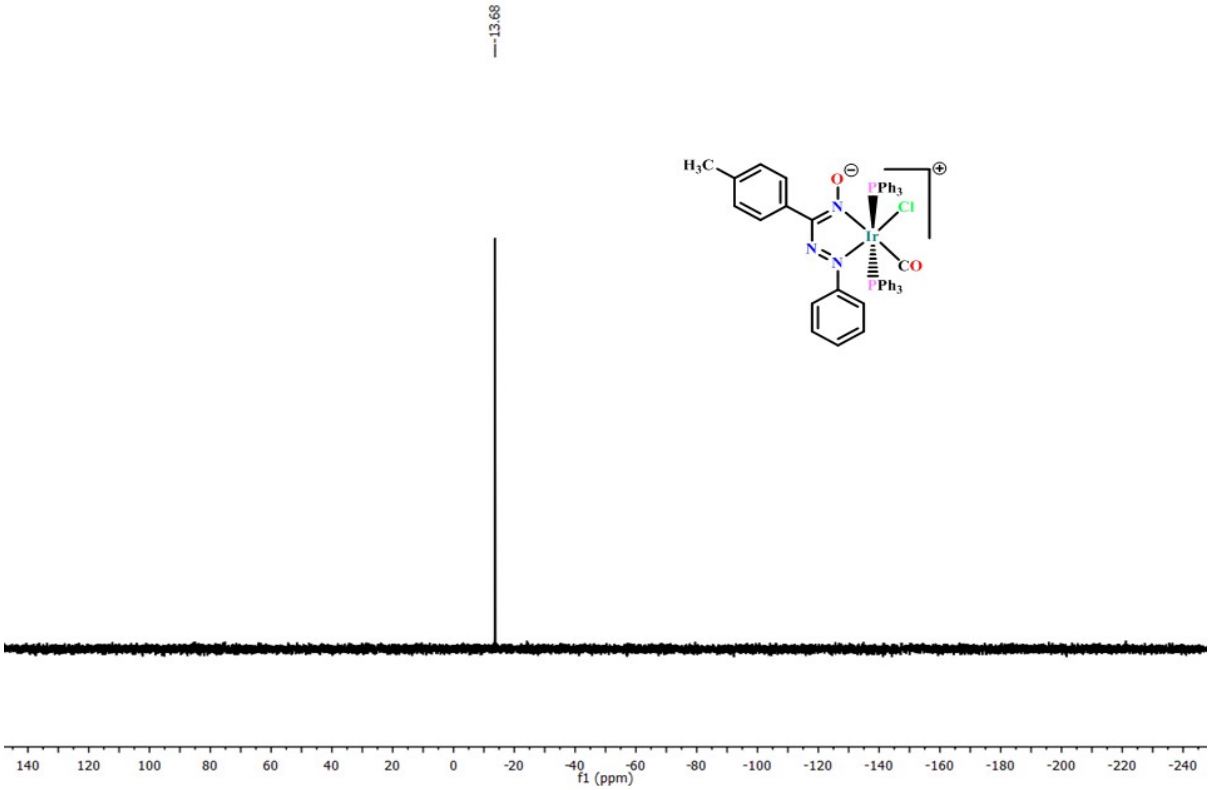


Fig. S27. ^{31}P NMR spectrum of **3b**$^{+}$

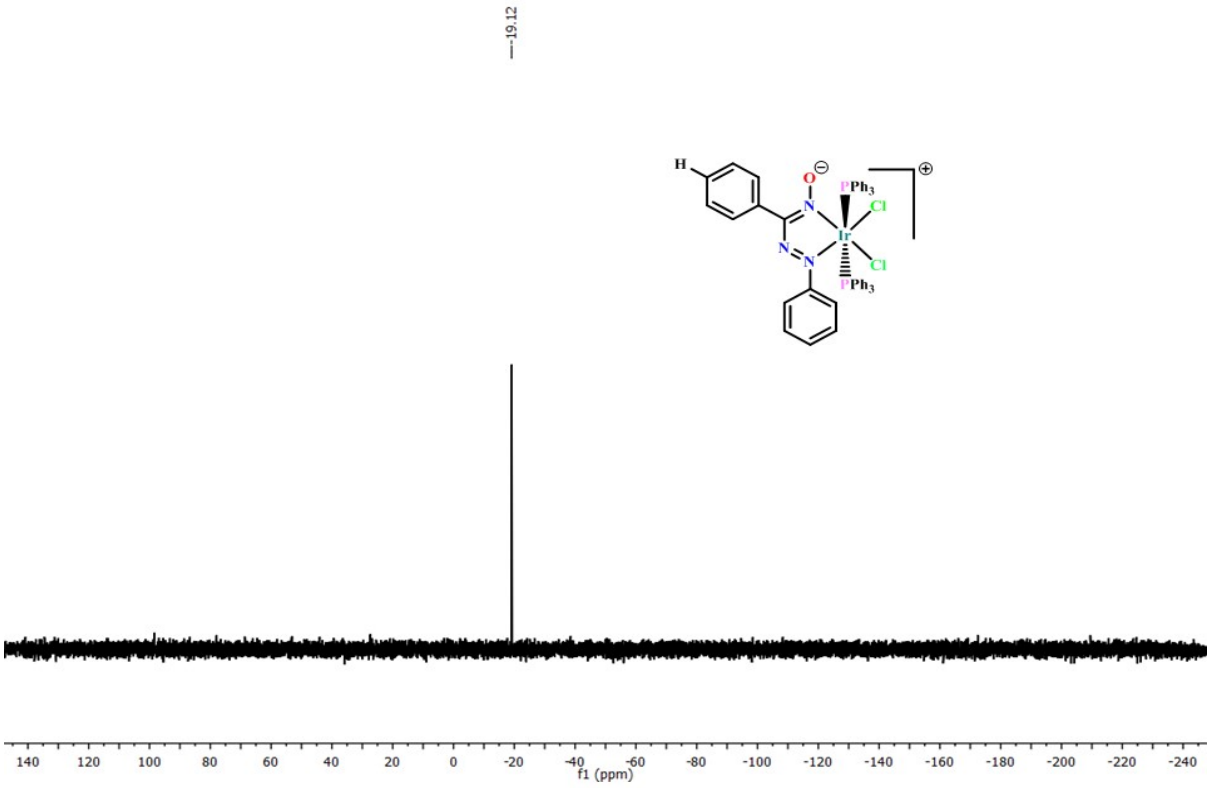


Fig. S28. ^{31}P NMR spectrum of **4a**

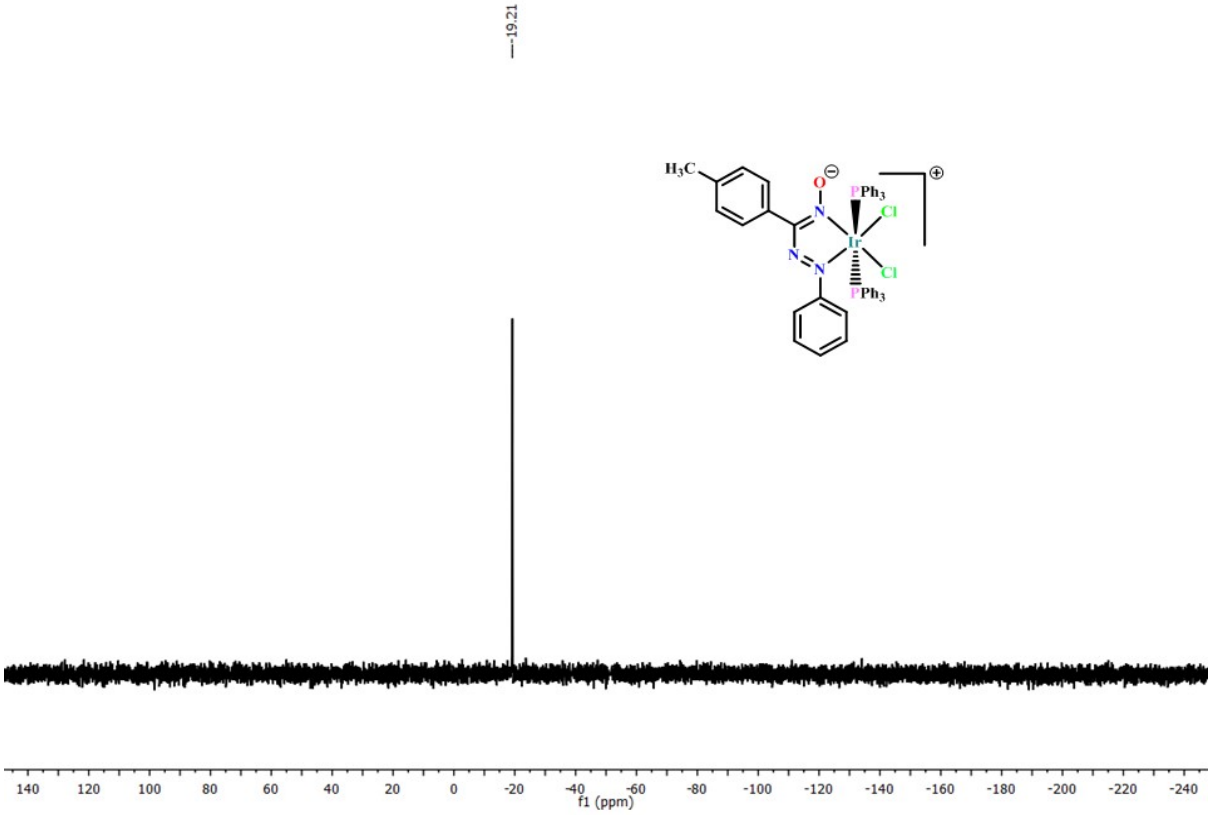


Fig. S29. ^{31}P NMR spectrum of **4b**

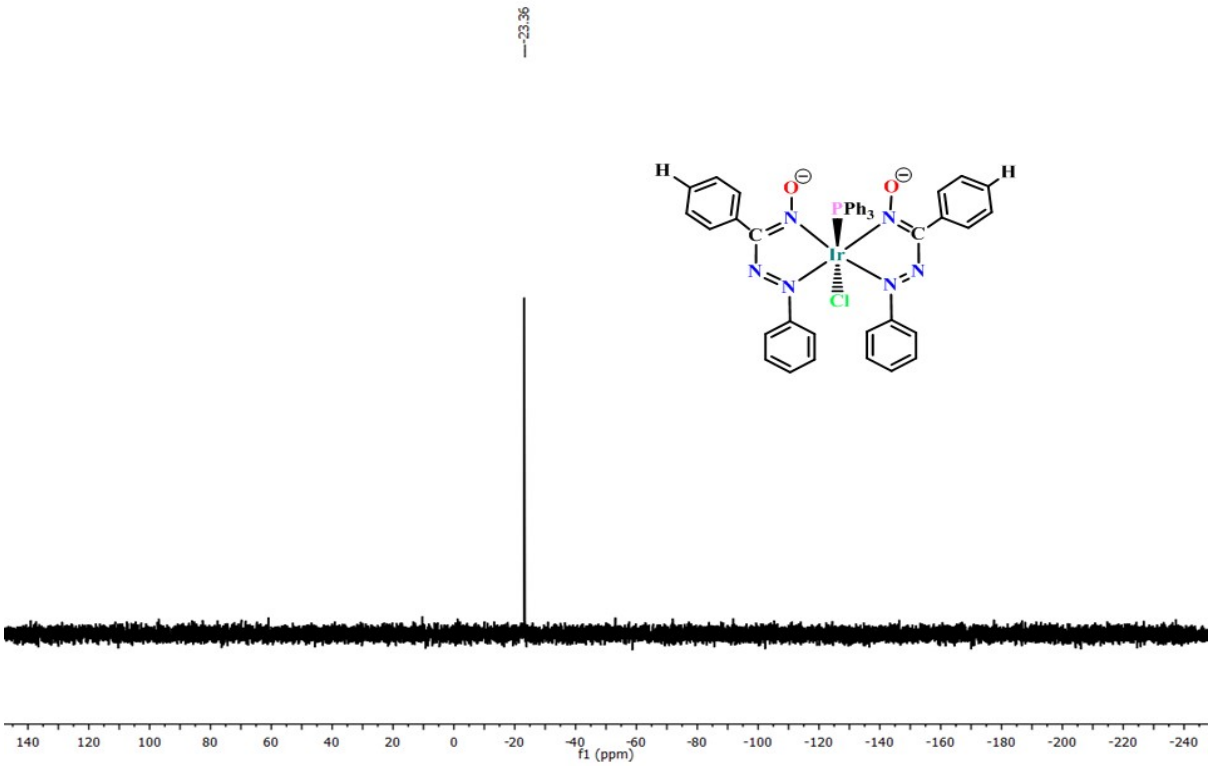


Fig. S30. ^{31}P NMR spectrum of **5a**

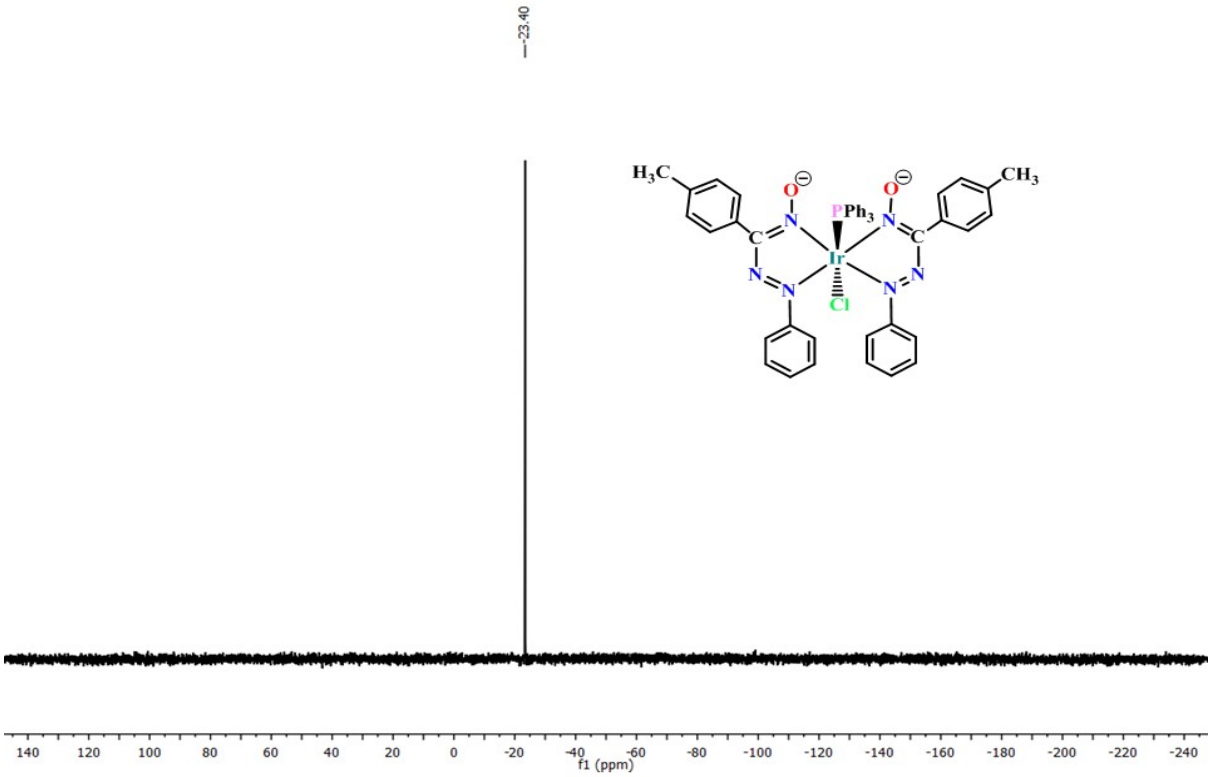


Fig. S31. ^{31}P NMR spectrum of **5b**

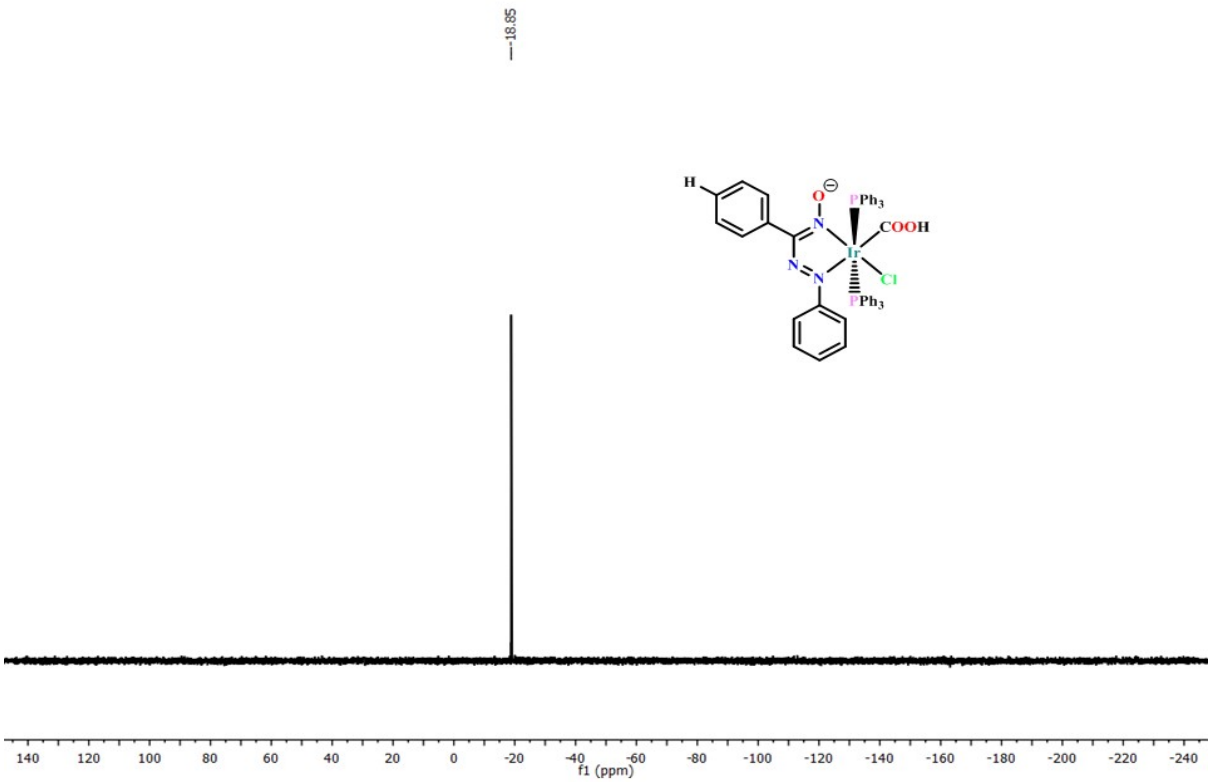


Fig. S32. ^{31}P NMR spectrum of **6a**

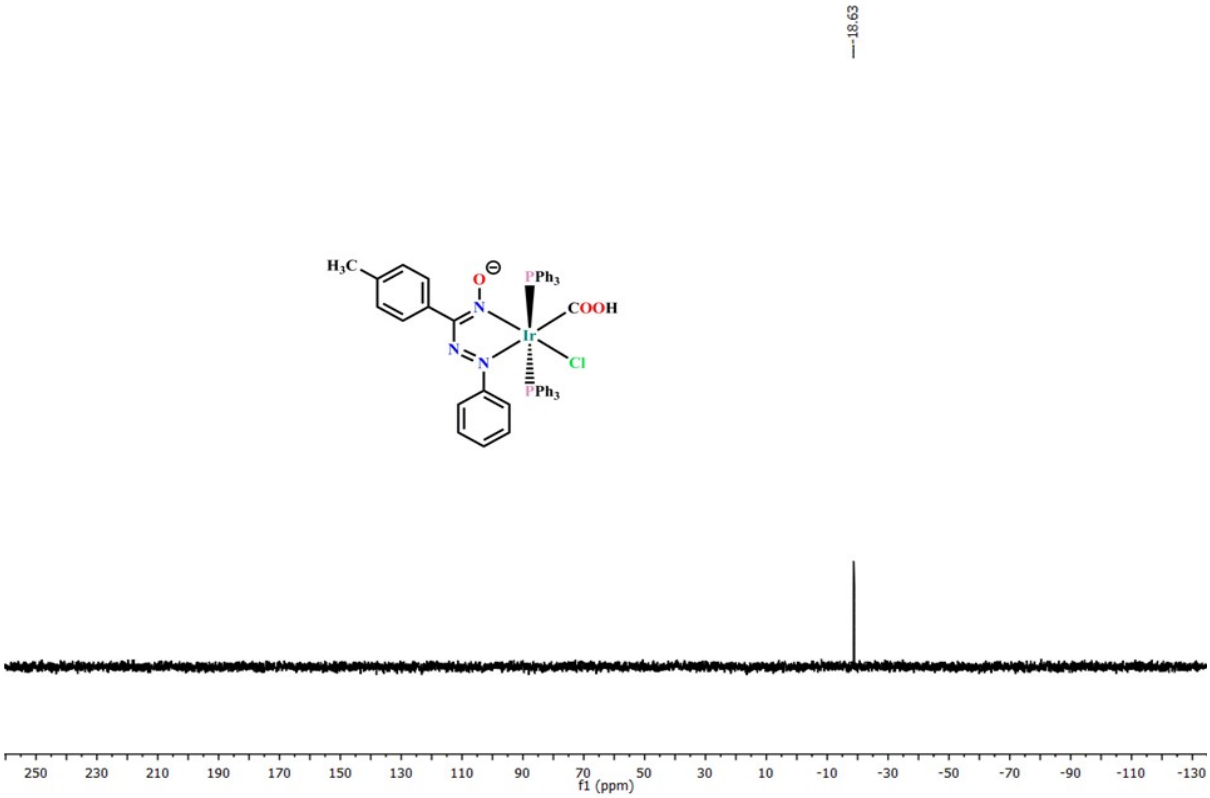


Fig. S33. ^{31}P NMR spectrum of **6b**

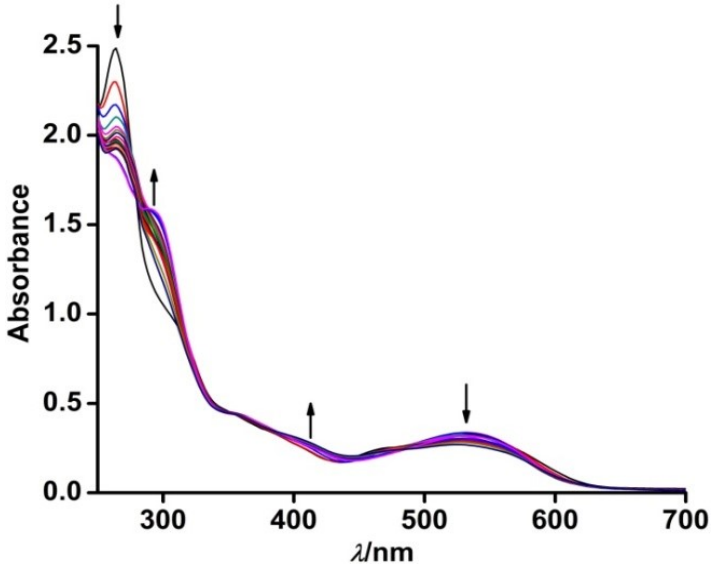


Fig. S34. Spectro-electrochemistry of **2a** in CH_2Cl_2.

Table S25 Co-ordinates of optimized geometry of **2a**.

Tag	Symbol	X	Y	Z
1	Ir	4.503412	9.479635	1.996146
2	Cl	2.945644	9.300289	0.006104
3	P	6.546299	9.46545	0.576146
4	P	2.40005	9.525732	3.364623
5	N	5.689341	9.638806	3.648273
6	N	5.478243	11.91684	3.288578
7	N	4.710916	11.58785	2.232124
8	O	6.056496	8.597347	4.313035
9	C	5.975478	10.92635	4.019724
10	C	6.804821	11.27935	5.198163
11	C	7.695237	10.38119	5.816044
12	H	7.773973	9.369853	5.441321
13	C	8.468016	10.78624	6.90853
14	H	9.151814	10.07506	7.366578
15	C	8.368438	12.08454	7.413157
16	H	8.967381	12.39191	8.267111
17	C	7.485063	12.98489	6.806482
18	H	7.391599	13.99934	7.18731
19	C	6.715039	12.58861	5.714942
20	H	6.031931	13.28932	5.248027
21	C	4.231003	12.71219	1.523032
22	C	4.319106	14.0113	2.07843
23	H	4.760278	14.13694	3.058836
24	C	3.848586	15.1194	1.373934
25	H	3.928248	16.10478	1.829109
26	C	3.279133	14.97799	0.103394
27	H	2.914264	15.84497	-0.44152
28	C	3.194965	13.69625	-0.44956
29	H	2.762618	13.55501	-1.43763
30	C	3.663691	12.58005	0.242183
31	H	3.586196	11.60376	-0.21359
32	C	6.693261	8.051735	-0.61444
33	C	7.973151	7.626624	-1.01809
34	H	8.861062	8.097717	-0.60957
35	C	8.117593	6.592109	-1.94352
36	H	9.11392	6.275482	-2.24125
37	C	6.98844	5.964498	-2.47925
38	H	7.102031	5.154913	-3.19583
39	C	5.716197	6.38444	-2.08766
40	H	4.830597	5.907457	-2.49955
41	C	5.565561	7.422749	-1.1624
42	H	4.569838	7.75201	-0.88741
43	C	6.784884	10.96145	-0.46407
44	C	7.039494	12.20814	0.134689
45	H	7.071801	12.30455	1.21514
46	C	7.238397	13.34039	-0.6558
47	H	7.428645	14.29691	-0.17706
48	C	7.166443	13.24959	-2.04855
49	H	7.311365	14.13607	-2.66061
50	C	6.893657	12.01884	-2.64931
51	H	6.826351	11.93961	-3.73125
52	C	6.705558	10.87872	-1.8636
53	H	6.499728	9.929682	-2.34661
54	C	8.102465	9.271396	1.554487
55	C	9.182646	10.16344	1.467245
56	H	9.116845	11.05004	0.847516
57	C	10.36735	9.911328	2.165741

58	H	11.19165	10.61567	2.090107
59	C	10.49197	8.762031	2.948809
60	H	11.41425	8.56669	3.489974
61	C	9.42348	7.865133	3.034452
62	H	9.505543	6.969555	3.644532
63	C	8.236008	8.118324	2.347798
64	H	7.419315	7.411552	2.437369
65	C	1.088159	10.60748	2.656885
66	C	-0.09036	10.08554	2.103162
67	H	-0.25833	9.015421	2.073325
68	C	-1.06518	10.94174	1.584122
69	H	-1.97151	10.52125	1.156012
70	C	-0.87598	12.32525	1.61244
71	H	-1.6337	12.98907	1.203821
72	C	0.294145	12.8519	2.165996
73	H	0.460814	13.92513	2.186593
74	C	1.270447	11.99951	2.682521
75	H	2.170508	12.42658	3.108541
76	C	1.620754	7.850148	3.485118
77	C	1.200011	7.332969	4.721351
78	H	1.342705	7.904291	5.631596
79	C	0.594138	6.075186	4.794338
80	H	0.279469	5.689515	5.760621
81	C	0.39568	5.320231	3.636569
82	H	-0.07427	4.341798	3.695467
83	C	0.807624	5.829652	2.40178
84	H	0.658895	5.251308	1.493498
85	C	1.418032	7.082883	2.323535
86	H	1.73021	7.467804	1.357082
87	C	2.536458	10.06478	5.126608
88	C	1.571077	10.90414	5.710824
89	H	0.751637	11.29669	5.120104
90	C	1.651061	11.24065	7.06455
91	H	0.897881	11.89451	7.496955
92	C	2.68887	10.74052	7.854729
93	H	2.753843	11.00896	8.906161
94	C	3.642937	9.894546	7.284347
95	H	4.459152	9.50247	7.884961
96	C	3.570065	9.554655	5.93124
97	H	4.327395	8.895642	5.517398
98	C	4.543086	7.586453	2.043014
99	O	4.621433	6.441499	2.090575

Table S26 Co-ordinates of optimized geometry of **2a**$^{+}$

Tag	Symbol	X	Y	Z
1	C	1.546982	11.82116	19.39997
2	C	0.360588	11.88479	20.27887
3	C	0.370067	11.50627	21.6364
4	H	1.279626	11.14021	22.089
5	C	-0.79485	11.59909	22.40241
6	H	-0.76454	11.30069	23.44703
7	C	-1.98498	12.06613	21.84264
8	H	-2.88615	12.1362	22.44567
9	C	-2.00514	12.44404	20.49567
10	H	-2.92292	12.8116	20.04448
11	C	-0.85054	12.3555	19.72288
12	H	-0.87923	12.65304	18.68092
13	C	2.063063	12.19125	15.91345
14	C	2.925828	12.84993	15.02862
15	H	3.862325	13.25657	15.38107
16	C	2.561457	12.99288	13.68891
17	H	3.231248	13.51452	13.011
18	C	1.347359	12.48224	13.22349
19	H	1.071519	12.59413	12.17856
20	C	0.489567	11.8191	14.10981
21	H	-0.45025	11.40551	13.75488
22	C	0.840719	11.67187	15.44849
23	H	0.186255	11.14626	16.1343
24	C	5.645816	11.26924	19.50825
25	C	3.59994	14.6291	20.37769
26	C	2.671783	15.68327	20.39161
27	H	2.437803	16.22799	19.48483
28	C	2.056745	16.06547	21.58741

29	H	1.342918	16.8845	21.58173
30	C	2.366306	15.40989	22.78066
31	H	1.888222	15.71086	23.70867
32	C	3.301511	14.37091	22.77785
33	H	3.556413	13.85956	23.70178
34	C	3.913433	13.98107	21.58705
35	H	4.643598	13.17947	21.61276
36	C	6.265231	14.60049	19.29292
37	C	6.467512	15.68182	20.17229
38	H	5.623013	16.19406	20.62057
39	C	7.760121	16.10621	20.48322
40	H	7.898753	16.94041	21.16534
41	C	8.867157	15.46088	19.92452
42	H	9.872665	15.78992	20.1719
43	C	8.673486	14.39332	19.04559
44	H	9.526777	13.88948	18.59996
45	C	7.381742	13.96485	18.72676
46	H	7.252176	13.15499	18.01911
47	C	4.02459	15.25372	17.51758
48	C	2.669245	15.38959	17.16463
49	H	1.904246	14.81138	17.67288
50	C	2.289007	16.2771	16.15789
51	H	1.237891	16.37909	15.90285
52	C	3.255647	17.02177	15.47499
53	H	2.957546	17.71125	14.68998
54	C	4.605265	16.87276	15.80197
55	H	5.363209	17.44254	15.27176
56	C	4.991374	15.9963	16.81974
57	H	6.04252	15.90052	17.06854
58	C	3.005275	8.45443	19.12857
59	C	1.600923	8.516628	19.08357
60	H	1.096697	8.96811	18.23483
61	C	0.835847	7.988362	20.12434
62	H	-0.248	8.0363	20.0703
63	C	1.461521	7.404315	21.22952
64	H	0.864397	6.989931	22.03703
65	C	2.855872	7.362589	21.29513
66	H	3.350522	6.920813	22.15557
67	C	3.625666	7.888858	20.25527
68	H	4.707785	7.845628	20.32489
69	C	5.600571	8.274548	17.79649
70	C	6.856075	8.880746	17.6561
71	H	6.942889	9.955259	17.5558
72	C	8.013414	8.097596	17.59054
73	H	8.97924	8.582725	17.48041
74	C	7.928758	6.706672	17.65431
75	H	8.829309	6.101142	17.60227
76	C	6.6769	6.093365	17.77488
77	H	6.598787	5.010449	17.81513
78	C	5.520387	6.868801	17.84023
79	H	4.558067	6.37411	17.92952
80	C	3.265654	8.7516	16.19023
81	C	2.365052	7.677519	16.07913
82	H	2.005587	7.157233	16.95963
83	C	1.932355	7.251323	14.82091
84	H	1.236959	6.419375	14.74957
85	C	2.399712	7.880222	13.66442
86	H	2.065651	7.542185	12.68726
87	C	3.305655	8.938711	13.7699
88	H	3.680917	9.429249	12.87628

89	C	3.738407	9.375002	15.02289
90	H	4.45086	10.18955	15.08765
91	Cl	5.786657	11.96278	16.42349
92	Ir	4.222186	11.67491	18.31673
93	N	2.819127	11.51748	19.78415
94	N	1.373879	12.06716	18.08141
95	N	2.398158	12.06224	17.30136
96	O	3.110647	11.18354	20.95293
97	O	6.454935	11.02146	20.27836
98	P	4.531597	14.12398	18.87071
99	P	4.016564	9.222814	17.80401

Table S27 Co-ordinates of optimized geometry of **3a**

Tag	Symbol	X	Y	Z
1	Ir	4.491042	9.46406	1.9206
2	P	6.61946	9.406954	0.640489
3	P	2.473151	9.429101	3.364652
4	N	5.625637	9.87187	3.636017
5	N	5.231561	12.06918	3.025713
6	N	4.535921	11.56977	1.98762
7	O	6.104465	8.98581	4.42283
8	C	5.787512	11.22382	3.873242
9	C	6.533887	11.78643	5.025817
10	C	7.520941	11.07237	5.730828
11	H	7.735515	10.04916	5.455177
12	C	8.216081	11.67523	6.783273
13	H	8.977166	11.10453	7.310579
14	C	7.942746	12.99131	7.161682
15	H	8.482973	13.45176	7.985447
16	C	6.961531	13.70953	6.468774
17	H	6.732505	14.73464	6.751018
18	C	6.268244	13.11559	5.416131
19	H	5.510531	13.67749	4.880353
20	C	3.985276	12.55791	1.149626
21	C	4.256965	13.93132	1.383655
22	H	4.899751	14.20296	2.210463
23	C	3.715769	14.92035	0.566906
24	H	3.95183	15.96126	0.780258
25	C	2.885876	14.59858	-0.51305
26	H	2.467236	15.37462	-1.14805
27	C	2.608794	13.25037	-0.74932

28	H	1.962095	12.96064	-1.57453
29	C	3.1432	12.25057	0.064397
30	H	2.877836	11.22873	-0.15376
31	C	6.899848	7.954106	-0.47588
32	C	8.204382	7.743136	-0.961
33	H	9.015458	8.391168	-0.64362
34	C	8.474941	6.70178	-1.84878
35	H	9.489457	6.555795	-2.21054
36	C	7.447323	5.848689	-2.26401
37	H	7.657796	5.033193	-2.95124
38	C	6.152688	6.045461	-1.78245
39	H	5.348176	5.380666	-2.08551
40	C	5.879655	7.089776	-0.89262
41	H	4.875439	7.194023	-0.50911
42	C	6.816796	10.84968	-0.48707
43	C	6.996765	12.14019	0.040234
44	H	7.020654	12.29788	1.113804
45	C	7.130068	13.23791	-0.81101
46	H	7.264364	14.22826	-0.3855
47	C	7.065123	13.06898	-2.19652
48	H	7.159287	13.92799	-2.85576
49	C	6.86353	11.79375	-2.72843
50	H	6.801446	11.65181	-3.80429
51	C	6.741501	10.68948	-1.88099
52	H	6.593436	9.705757	-2.31339
53	C	8.13167	9.347557	1.692761
54	C	9.194321	10.25498	1.560947
55	H	9.130248	11.08452	0.86585
56	C	10.35874	10.08915	2.316636
57	H	11.17247	10.80168	2.208658
58	C	10.47527	9.01344	3.19994
59	H	11.38242	8.884693	3.785202
60	C	9.420445	8.105456	3.330661
61	H	9.498916	7.269713	4.020906
62	C	8.250882	8.269239	2.587227
63	H	7.432447	7.568034	2.70954
64	C	1.373847	10.88367	3.101539
65	C	0.118921	10.73764	2.486688
66	H	-0.2339	9.757476	2.184126
67	C	-0.69449	11.85179	2.263167
68	H	-1.66174	11.72021	1.784969
69	C	-0.26836	13.12308	2.652724
70	H	-0.90081	13.98952	2.477695
71	C	0.981967	13.27786	3.257203
72	H	1.332788	14.26478	3.545438
73	C	1.802982	12.1703	3.471536
74	H	2.781545	12.31683	3.916507
75	C	1.324807	7.987869	3.172216
76	C	0.364802	7.776168	4.179477
77	H	0.345629	8.41572	5.056547
78	C	-0.5675	6.744356	4.069113
79	H	-1.29969	6.596767	4.858759
80	C	-0.55354	5.902158	2.952523
81	H	-1.27569	5.094063	2.868217
82	C	0.399977	6.099475	1.953036
83	H	0.431163	5.442715	1.087731
84	C	1.334992	7.134212	2.061943
85	H	2.083978	7.239468	1.29065
86	C	2.842656	9.363948	5.167813
87	C	2.332056	10.28972	6.091013

88	H	1.729326	11.12748	5.759092
89	C	2.583659	10.13203	7.456894
90	H	2.186462	10.85835	8.16136
91	C	3.33853	9.047973	7.911071
92	H	3.535943	8.928425	8.973425
93	C	3.841428	8.120055	6.995069
94	H	4.437306	7.278842	7.338546
95	C	3.600822	8.273689	5.629488
96	H	4.009263	7.555888	4.926594
97	Cl	4.720601	7.028179	2.28569
98	O	2.875456	8.86346	-0.59377
99	C	3.479136	9.123725	0.35579

Table S28 Co-ordinates of optimized geometry of **3a**$^{+}$.

Tag	Symbol	X	Y	Z
1	C	2.204262	3.427175	10.83486
2	Cl	-2.9539	5.460212	10.92031
3	Ir	-0.56144	4.936003	10.75131
4	N	1.470139	4.643279	10.63764
5	O	-0.4647	7.909546	10.42017
6	P	-0.45031	5.279874	13.24767
7	C	1.704663	2.208862	10.35511
8	H	0.772401	2.169988	9.804132
9	N	2.194939	5.685261	10.46367
10	O	-1.60767	2.090728	11.11807
11	P	-0.88212	4.843009	8.253596
12	C	2.442048	1.036276	10.53165
13	H	2.05316	0.099376	10.14307
14	N	0.222124	6.861706	10.47921
15	C	3.674603	1.07022	11.18949
16	H	4.244041	0.155943	11.32934
17	C	4.170525	2.288842	11.66616
18	H	5.124223	2.323566	12.18525
19	C	3.444752	3.465594	11.49214
20	H	3.817732	4.409199	11.87256
21	C	1.579302	6.886783	10.35056
22	C	2.421558	8.078425	10.12501
23	C	3.782064	7.878419	9.799517
24	H	4.164806	6.868388	9.707137
25	C	4.632092	8.960567	9.589905
26	H	5.673206	8.781317	9.334859
27	C	4.150855	10.26989	9.703229

28	H	4.814933	11.11408	9.538863
29	C	2.809662	10.48	10.02671
30	H	2.423155	11.49147	10.11798
31	C	1.945539	9.401465	10.23406
32	H	0.909387	9.586641	10.47714
33	C	-1.19979	3.150819	10.98337
34	C	1.268057	5.322255	13.92973
35	C	2.041705	6.464383	13.64998
36	H	1.633451	7.272688	13.05202
37	C	3.32761	6.598756	14.17351
38	H	3.904792	7.49181	13.95044
39	C	3.859746	5.598756	14.99413
40	H	4.856708	5.708412	15.41214
41	C	3.094126	4.469388	15.28963
42	H	3.488797	3.69603	15.94302
43	C	1.806815	4.328254	14.76112
44	H	1.225797	3.455552	15.03289
45	C	-1.35871	3.93963	14.11672
46	C	-0.89387	2.611879	14.08215
47	H	0.013419	2.354473	13.54258
48	C	-1.59925	1.597918	14.73075
49	H	-1.223	0.57904	14.7011
50	C	-2.78921	1.890787	15.40412
51	H	-3.34	1.099839	15.90543
52	C	-3.2715	3.200986	15.42021
53	H	-4.20225	3.43508	15.92912
54	C	-2.56309	4.222369	14.78179
55	H	-2.95271	5.233855	14.80305
56	C	-1.13668	6.853567	13.9182
57	C	-0.86423	7.134659	15.27332
58	H	-0.26036	6.454672	15.86684
59	C	-1.36821	8.2894	15.86855
60	H	-1.15468	8.490267	16.91476
61	C	-2.14005	9.184901	15.11914
62	H	-2.52887	10.0877	15.58235
63	C	-2.40621	8.913927	13.7771
64	H	-3.00265	9.604441	13.18735
65	C	-1.9124	7.751667	13.17356
66	H	-2.13787	7.557453	12.1353
67	C	-2.19013	5.927864	7.547641
68	C	-2.83191	5.520216	6.36327
69	H	-2.61117	4.556944	5.915743
70	C	-3.76408	6.3559	5.745972
71	H	-4.25362	6.02858	4.83292
72	C	-4.06612	7.602587	6.301207
73	H	-4.79506	8.250174	5.821599
74	C	-3.42943	8.010574	7.475465
75	H	-3.66121	8.976285	7.916094
76	C	-2.49601	7.180314	8.101127
77	H	-2.0193	7.512537	9.01431
78	C	0.648717	5.293911	7.338588
79	C	0.680591	6.457108	6.549737
80	H	-0.19687	7.08834	6.465801
81	C	1.842164	6.809286	5.857639
82	H	1.849721	7.712124	5.25355
83	C	2.981772	6.006769	5.937132
84	H	3.881464	6.280421	5.393047
85	C	2.960813	4.85033	6.722663
86	H	3.842656	4.219374	6.793678
87	C	1.807287	4.500571	7.425514

88	H	1.819256	3.603086	8.033978
89	C	-1.38992	3.160686	7.703428
90	C	-0.6512	2.387835	6.794464
91	H	0.279667	2.759152	6.380996
92	C	-1.12786	1.137327	6.386198
93	H	-0.549	0.550223	5.678451
94	C	-2.34476	0.654301	6.871468
95	H	-2.71456	-0.31489	6.548369
96	C	-3.09348	1.428356	7.764922
97	H	-4.04796	1.065991	8.13635
98	C	-2.62164	2.673193	8.180305
99	H	-3.22017	3.272645	8.861839

Table S29 Co-ordinates of optimized geometry of **4a**.

Tag	Symbol	X	Y	Z
1	Ir	4.587147	9.550171	2.047914
2	Cl	4.763933	7.129013	2.348587
3	Cl	3.264428	9.153028	-0.01351
4	P	6.593178	9.403666	0.629231
5	P	2.497986	9.436603	3.34899
6	N	5.682151	9.909549	3.70891
7	N	5.282421	12.10758	3.147567
8	N	4.63064	11.65136	2.128054
9	O	6.171353	9.038285	4.45069
10	C	5.850404	11.24117	3.99678
11	C	6.576659	11.78107	5.166746
12	C	7.569274	11.06553	5.863384
13	H	7.81483	10.05612	5.564665
14	C	8.240707	11.65308	6.938792
15	H	9.006629	11.08286	7.458767
16	C	7.937535	12.95296	7.348801
17	H	8.459705	13.4006	8.190676
18	C	6.951389	13.67171	6.664758
19	H	6.699428	14.68378	6.972137
20	C	6.281652	13.09474	5.587854
21	H	5.519558	13.65994	5.06174
22	C	4.108945	12.70093	1.29438
23	C	4.501358	14.03984	1.507963
24	H	5.214343	14.2707	2.289106
25	C	3.982178	15.05754	0.714039
26	H	4.298921	16.0827	0.891429
27	C	3.069228	14.77005	-0.30893

28	H	2.669065	15.56781	-0.92947
29	C	2.687217	13.44554	-0.52153
30	H	1.980467	13.19817	-1.3094
31	C	3.197641	12.41567	0.272608
32	H	2.892312	11.39557	0.092454
33	C	6.843219	7.907128	-0.43734
34	C	8.14327	7.659482	-0.91695
35	H	8.967235	8.304635	-0.62851
36	C	8.395153	6.580633	-1.76526
37	H	9.406254	6.405475	-2.1241
38	C	7.352562	5.728825	-2.14323
39	H	7.547681	4.883984	-2.79928
40	C	6.061816	5.968751	-1.66978
41	H	5.244303	5.310626	-1.95272
42	C	5.803316	7.050409	-0.82116
43	H	4.798358	7.222893	-0.46428
44	C	6.741788	10.79956	-0.56583
45	C	7.013512	12.10442	-0.1198
46	H	7.150748	12.30548	0.93807
47	C	7.110444	13.16039	-1.0273
48	H	7.324765	14.16129	-0.66267
49	C	6.913953	12.9346	-2.39225
50	H	6.983011	13.75899	-3.09734
51	C	6.616787	11.64653	-2.84256
52	H	6.449041	11.46132	-3.90037
53	C	6.532531	10.58509	-1.93788
54	H	6.302467	9.590979	-2.30481
55	C	8.160079	9.385387	1.613113
56	C	9.220425	10.28626	1.429448
57	H	9.145931	11.08564	0.700933
58	C	10.40137	10.14937	2.166237
59	H	11.21292	10.85603	2.011731
60	C	10.54004	9.107307	3.085609
61	H	11.46014	8.999976	3.654707
62	C	9.491243	8.200515	3.266081
63	H	9.589017	7.38377	3.976593
64	C	8.307197	8.336358	2.539683
65	H	7.499251	7.627022	2.689976
66	C	1.374653	10.86713	3.040785
67	C	0.192832	10.69442	2.302117
68	H	-0.0785	9.712511	1.929842
69	C	-0.64521	11.7815	2.03856
70	H	-1.55445	11.62763	1.463121
71	C	-0.31845	13.05421	2.510958
72	H	-0.97285	13.89828	2.308875
73	C	0.861977	13.23891	3.236092
74	H	1.135669	14.22754	3.594985
75	C	1.707285	12.15771	3.48928
76	H	2.628104	12.32864	4.037667
77	C	1.383617	7.971443	3.136621
78	C	0.422115	7.731037	4.135931
79	H	0.375834	8.363618	5.016956
80	C	-0.48161	6.675093	4.012752
81	H	-1.21634	6.504073	4.795519
82	C	-0.43401	5.839401	2.892368
83	H	-1.13339	5.012284	2.797744
84	C	0.519649	6.071498	1.90005
85	H	0.569818	5.425197	1.027526
86	C	1.426386	7.130369	2.017073
87	H	2.158675	7.2982	1.240205

88	C	2.792043	9.391547	5.173964
89	C	2.205938	10.28156	6.087922
90	H	1.562257	11.08323	5.743807
91	C	2.425678	10.13225	7.460759
92	H	1.964787	10.83044	8.155071
93	C	3.224028	9.089464	7.93596
94	H	3.394312	8.975003	9.003534
95	C	3.800228	8.192805	7.03183
96	H	4.42336	7.377799	7.390293
97	C	3.589518	8.339083	5.660007
98	H	4.044161	7.637324	4.967989

Table S30 Co-ordinates of optimized geometry of **5a**.

Tag	Symbol	X	Y	Z
1	Ir	3.359458	5.285404	9.683189
2	P	1.525548	4.206886	8.552675
3	C	0.282856	3.506674	9.722673
4	C	0.64545	2.462595	10.59017
5	H	1.656214	2.066724	10.57735
6	C	-0.28523	1.921386	11.4781
7	H	0.008587	1.105898	12.13421
8	C	-1.58599	2.431648	11.53013
9	H	-2.30717	2.017025	12.22939
10	C	-1.95007	3.481294	10.68487
11	H	-2.95513	3.892393	10.7247
12	C	-1.02501	4.013363	9.781975
13	H	-1.32749	4.823505	9.12737
14	C	0.507088	5.243587	7.407249
15	C	0.321361	6.616328	7.6312
16	H	0.830171	7.118665	8.44431
17	C	-0.51768	7.356084	6.790467
18	H	-0.64089	8.420441	6.971968
19	C	-1.1796	6.740951	5.727419
20	H	-1.82687	7.321817	5.075089
21	C	-1.00319	5.371442	5.50259
22	H	-1.51365	4.88011	4.678201
23	C	-0.16657	4.627204	6.334621
24	H	-0.04314	3.56666	6.143256
25	C	1.99673	2.806117	7.441004

26	C	2.87152	3.086192	6.376985
27	H	3.264811	4.088517	6.24157
28	C	3.22942	2.089	5.470288
29	H	3.908706	2.324901	4.655602
30	C	2.717937	0.794795	5.610206
31	H	2.999994	0.016963	4.905511
32	C	1.837204	0.51065	6.655263
33	H	1.422441	-0.48806	6.765606
34	C	1.473716	1.510596	7.564026
35	H	0.772297	1.272218	8.355808
36	N	4.875271	4.34446	8.551931
37	C	5.58496	3.120686	8.751065
38	C	4.899918	1.969436	9.154379
39	H	3.835125	2.014099	9.341315
40	C	5.58321	0.760985	9.290887
41	H	5.037951	-0.12874	9.593914
42	C	6.957822	0.695431	9.049815
43	H	7.489768	-0.24508	9.166544
44	C	7.647301	1.852829	8.669301
45	H	8.719852	1.817228	8.496062
46	C	6.968815	3.060699	8.516021
47	H	7.495091	3.963168	8.225956
48	N	5.352454	5.053948	7.591834
49	C	4.765924	6.238099	7.320853
50	C	5.308346	7.042461	6.205673
51	C	5.022596	8.410105	6.022978
52	H	4.356762	8.91666	6.706962
53	C	5.599013	9.11718	4.964238
54	H	5.368658	10.17328	4.847867
55	C	6.45901	8.485643	4.064156
56	H	6.899997	9.042021	3.240902
57	C	6.748074	7.127426	4.235719
58	H	7.417227	6.619168	3.545623
59	C	6.18333	6.415685	5.291445
60	H	6.422263	5.365888	5.422923
61	N	3.698674	6.572736	8.107749
62	O	3.073094	7.631217	7.927687
63	N	3.192855	4.277694	11.5402
64	C	3.984845	3.231593	12.13143
65	C	3.36547	2.227384	12.88997
66	H	2.287065	2.235406	13.00407
67	C	4.141208	1.2463	13.50863
68	H	3.655914	0.466834	14.09084
69	C	5.535202	1.274533	13.39358
70	H	6.13912	0.515103	13.88341
71	C	6.146416	2.291912	12.65592
72	H	7.229261	2.335122	12.57762
73	C	5.378477	3.2672	12.01732
74	H	5.848922	4.078966	11.47636
75	N	2.365127	4.7885	12.37244
76	C	1.671844	5.888161	11.99344
77	C	0.706252	6.456731	12.9576
78	C	0.594544	5.848012	14.22833
79	H	1.2316	5.004595	14.46763
80	C	-0.31245	6.319499	15.17357

81	H	-0.37105	5.833987	16.14476
82	C	-1.13776	7.411303	14.88176
83	H	-1.84358	7.781185	15.6213
84	C	-1.0352	8.023741	13.6322
85	H	-1.66228	8.878627	13.39097
86	C	-0.12447	7.561174	12.67776
87	H	-0.04894	8.060062	11.72296
88	N	1.996081	6.397007	10.77302
89	O	1.509723	7.47642	10.37491
90	Cl	5.14689	6.542301	10.77425

Table S31 Co-ordinates of optimized geometry of **6a**.

Tag	Symbol	X	Y	Z
1	Ir	2.153663	12.94875	3.51251
2	Cl	1.825258	12.52117	1.106564
3	P	-0.23161	13.50961	3.679874
4	P	4.581564	12.56331	3.236594
5	N	2.365472	13.0313	5.534985
6	O	2.595304	14.10419	6.18156
7	N	1.782337	10.87139	4.219361
8	C	2.521543	14.97754	3.143392
9	N	1.904993	10.75814	5.490033
10	C	5.5205	13.48979	1.937266
11	C	-1.41335	12.09011	3.513516
12	C	-0.99545	14.69779	2.480282
13	C	4.999301	10.79981	2.869888
14	C	2.246915	11.86203	6.211207
15	C	4.911257	13.97972	0.773466
16	H	3.843341	13.88575	0.635813
17	C	-0.57734	14.27486	5.322713
18	C	1.715502	9.393576	2.270467
19	H	2.307666	10.11306	1.721966
20	C	-0.31344	15.22458	1.376937
21	H	0.7239	14.97849	1.199067
22	C	5.554465	12.99603	4.753974
23	C	1.34645	9.660995	3.594936
24	C	-0.66875	13.48992	6.485337
25	H	-0.59477	12.4086	6.425941

26	C	-1.30052	11.2845	2.367053
27	H	-0.48583	11.4475	1.668803
28	C	5.683267	14.61134	-0.2076
29	H	5.193288	14.99644	-1.09795
30	C	5.501365	10.43256	1.611018
31	H	5.665131	11.18591	0.848313
32	C	4.789859	9.794628	3.831123
33	H	4.383909	10.04218	4.806052
34	C	5.501024	14.33259	5.188433
35	H	4.881288	15.05503	4.668178
36	C	2.430832	11.66406	7.669521
37	C	6.911236	13.6423	2.099017
38	H	7.404665	13.27462	2.992847
39	C	-0.64156	15.67238	5.44504
40	H	-0.54499	16.30259	4.567352
41	C	-2.48834	11.87473	4.390776
42	H	-2.62113	12.49929	5.266751
43	C	1.314276	8.200605	1.666477
44	H	1.613938	7.999207	0.641334
45	C	-2.34913	15.03553	2.676609
46	H	-2.90018	14.6286	3.519434
47	C	5.100581	8.463651	3.549914
48	H	4.935388	7.70395	4.309439
49	C	0.561177	8.731835	4.302396
50	H	0.255022	8.957211	5.317506
51	C	-2.23786	10.28196	2.113312
52	H	-2.13296	9.668815	1.222356
53	C	6.257148	14.75421	6.282636
54	H	6.201517	15.79217	6.599999
55	C	6.39038	12.09815	5.435752
56	H	6.482841	11.06981	5.106635
57	C	5.605532	8.109116	2.295646
58	H	5.841133	7.071186	2.074917
59	C	-0.85146	14.08564	7.734259
60	H	-0.91982	13.46035	8.620364
61	C	-3.4197	10.86301	4.136358
62	H	-4.24517	10.7109	4.827497
63	C	7.060832	14.75959	-0.04276
64	H	7.654005	15.2563	-0.80675
65	C	7.674688	14.27131	1.115475
66	H	8.74653	14.38313	1.258646
67	C	-0.9744	16.08832	0.494421
68	H	-0.42827	16.49395	-0.35303
69	C	-3.00024	15.89654	1.795417
70	H	-4.04393	16.14986	1.964063
71	C	7.073202	13.84911	6.96695
72	H	7.6569	14.17727	7.823286
73	C	-3.2977	10.06396	2.997732
74	H	-4.02509	9.280954	2.798451
75	C	-0.93192	15.47663	7.84307
76	H	-1.07111	15.94081	8.81608
77	C	5.797732	9.095907	1.326744
78	H	6.18293	8.831965	0.34514
79	C	-0.81961	16.26666	6.696903
80	H	-0.86415	17.35	6.771478

81	C	2.763472	12.69091	8.578198
82	H	2.890973	13.70054	8.220137
83	C	0.162978	7.547244	3.689102
84	H	-0.45529	6.84154	4.238223
85	C	0.540676	7.272866	2.368475
86	H	0.226564	6.347909	1.891411
87	C	7.139063	12.52198	6.538601
88	H	7.778385	11.81026	7.054801
89	C	2.273247	10.35593	8.185091
90	H	2.023122	9.548353	7.507761
91	C	-2.31148	16.42688	0.697816
92	H	-2.81844	17.09787	0.008641
93	C	2.435819	10.089	9.542095
94	H	2.30685	9.071836	9.904114
95	C	2.927496	12.41177	9.938179
96	H	3.185053	13.22425	10.61335
97	C	2.764668	11.11707	10.43213
98	H	2.89266	10.90945	11.49152
99	O	2.575468	15.80517	4.212627
100	H	2.527516	15.27414	5.054702
101	O	2.684468	15.46321	2.040339

Table S32 Co-ordinates of optimized geometry of **7a**$^{+}$.

Tag	Symbol	X	Y	Z
1	Ir	5.066535	7.373514	12.65643
2	P	4.658707	8.321671	14.97532
3	C	4.629953	10.16437	14.97559
4	C	5.788068	10.89419	14.65524
5	H	6.705106	10.38136	14.38356
6	C	5.782157	12.28891	14.69259
7	H	6.691503	12.83663	14.45922
8	C	4.612884	12.97786	15.02861
9	H	4.607255	14.06399	15.05231
10	C	3.45303	12.2625	15.33093
11	H	2.537646	12.78794	15.58801
12	C	3.459506	10.86509	15.3101
13	H	2.551659	10.32775	15.55984
14	C	3.059143	7.845633	15.76818
15	C	1.883869	7.685393	15.01662
16	H	1.900648	7.754951	13.93747
17	C	0.670645	7.420309	15.65886
18	H	-0.22769	7.291646	15.06121
19	C	0.612014	7.313557	17.04912
20	H	-0.33305	7.104091	17.543
21	C	1.776974	7.479105	17.8042
22	H	1.744132	7.404358	18.8877
23	C	2.992211	7.74393	17.17188
24	H	3.880019	7.875427	17.77937
25	C	5.886303	7.841632	16.26994

26	C	6.001142	6.479596	16.60117
27	H	5.394488	5.736192	16.09559
28	C	6.867932	6.065356	17.6121
29	H	6.939513	5.008994	17.85568
30	C	7.631145	7.004499	18.31276
31	H	8.305016	6.68168	19.10154
32	C	7.509441	8.360356	18.00396
33	H	8.081447	9.100904	18.55647
34	C	6.640572	8.779702	16.9915
35	H	6.546267	9.840024	16.78872
36	N	6.558023	6.071189	13.42111
37	C	7.955514	6.249732	13.68954
38	C	8.433529	7.495163	14.10825
39	H	7.752796	8.329867	14.19527
40	C	9.777554	7.656258	14.44576
41	H	10.12969	8.62652	14.78436
42	C	10.66294	6.581244	14.34848
43	H	11.71078	6.709318	14.60486
44	C	10.18927	5.33567	13.91894
45	H	10.86949	4.492268	13.83684
46	C	8.844461	5.164241	13.59903
47	H	8.474927	4.194561	13.28746
48	N	6.138152	4.89711	13.74479
49	C	4.818962	4.633044	13.64518
50	C	4.346498	3.289142	14.04507
51	C	3.029947	2.830279	13.83913
52	H	2.294649	3.479787	13.3878
53	C	2.665894	1.535804	14.21898
54	H	1.6455	1.203109	14.04803
55	C	3.590572	0.676948	14.81454
56	H	3.297639	-0.3263	15.11185
57	C	4.898971	1.123819	15.02838
58	H	5.63085	0.469153	15.49422
59	C	5.273694	2.41001	14.64894
60	H	6.29087	2.74469	14.81853
61	N	4.038096	5.683598	13.2477
62	O	2.796489	5.591648	13.22378
63	N	6.009848	9.125782	11.91825
64	C	7.386676	9.434821	11.65233
65	C	7.849936	10.7587	11.74691
66	H	7.169123	11.53897	12.06621
67	C	9.170753	11.05679	11.41725
68	H	9.524281	12.08098	11.50024
69	C	10.03557	10.04908	10.9722
70	H	11.06195	10.28736	10.70795
71	C	9.56961	8.736663	10.87142
72	H	10.22836	7.94552	10.52511
73	C	8.254308	8.424986	11.22118
74	H	7.903651	7.40458	11.13835
75	N	5.215946	10.07669	11.58459
76	C	3.881341	9.854668	11.65724
77	C	2.978854	10.95531	11.25919
78	C	3.55321	12.12391	10.71155
79	H	4.626675	12.1731	10.57216
80	C	2.760302	13.20837	10.34633

81	H	3.227595	14.09363	9.922755
82	C	1.372934	13.16062	10.52051
83	H	0.754083	14.00688	10.23455
84	C	0.792816	12.01175	11.06082
85	H	-0.28396	11.95854	11.19861
86	C	1.579169	10.91531	11.42353
87	H	1.10779	10.03122	11.82709
88	N	3.516227	8.597204	12.01668
89	O	2.314333	8.231594	11.95889
90	P	5.022343	6.431407	10.29608
91	C	3.734675	5.131315	10.05948
92	C	4.05192	3.907601	9.443009
93	C	2.40016	5.38497	10.4293
94	C	3.055166	2.960131	9.199061
95	H	5.068425	3.687113	9.139875
96	C	1.408751	4.43574	10.17138
97	H	2.130014	6.315611	10.91476
98	C	1.73111	3.222461	9.558783
99	H	3.31795	2.020061	8.721913
100	H	0.382615	4.649417	10.45838
101	H	0.956251	2.486254	9.362441
102	C	6.561818	5.632319	9.660318
103	C	7.043597	5.883786	8.364153
104	C	7.208043	4.661115	10.44426
105	C	8.160514	5.198251	7.878185
106	H	6.549063	6.602539	7.721747
107	C	8.319009	3.973442	9.952585
108	H	6.832351	4.415528	11.42979
109	C	8.80398	4.2448	8.670187
110	H	8.518227	5.406998	6.873644
111	H	8.800099	3.220402	10.57061
112	H	9.669093	3.709798	8.288296
113	C	4.621946	7.733161	9.045985
114	C	3.392111	7.743974	8.367468
115	C	5.56889	8.728793	8.741326
116	C	3.115974	8.729197	7.415159
117	H	2.646075	6.984161	8.564622
118	C	5.291944	9.705098	7.78397
119	H	6.536347	8.739915	9.230029
120	C	4.061462	9.712399	7.120985
121	H	2.157969	8.719909	6.902864
122	H	6.040679	10.46014	7.560198
123	H	3.84428	10.47604	6.379312

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