β-diketonate Ancillary Ligands in Heteroleptic Iridium Complexes: a balance between synthetic advantages and photophysical troubles

Marta Penconi[a§], Marco Cazzaniga[a§], Sagar Kesarkar[a§], Clara Baldoli[a], Patrizia R. Mussini[b], Davide Ceresoli[a*] and Alberto Bossi[a*]

[a]Istituto di Scienze e Tecnologie Molecolari ISTM – CNR Via Golgi 19, 20133 Milano, PST via Fantoli 16/15, 20138 Milano and SmartMatLab Centre@ISTM, Via Golgi 19, 20133 Milano, Italy
* e-mails: davide.ceresoli@cnr.it; alberto.bossi@istm.cnr.it
[b]Dipartimento di Chimica, Università degli Studi di Milano and SmartMatLab Centre, Via Golgi 19, 20133 Milano, Italy
§ Authors contribute equally to the work.

Supporting Information

Index:

1. Experimental Section

General information. Reagents and solvents were purchased from Aldrich and TCI, and were used without further purification. All solvents, unless otherwise stated are degassed under argon prior the use. The ligand H*dtdk* was previously synthesized by some of us[1] while H*tta* and H*dpm,* commercially available, were used as received. NMR were recorded on Bruker Advance 400 MHz and the residual signal of the deuterated solvent was used as internal standard (e.g. 5.32 ppm for ^{1}H and 53.84 ppm for ^{13}C of CD_2Cl_2). The chemical shifts are given in ppm and coupling constants in Hz. **Ir3**,[2] **Ir2acac**,[3] **Ir2tta**[4] and **Ir2BPhenPF$_6$**,[5] were synthesised according to known synthetic procedures.

Gradient HPLC-MS analysis are performed on Agilent 1100 equipped with PDA UV-Vis detector and a Ion Trap Bruker Esquire 3000 Plus Mass Detector, range from 50-3000 Da; analysis were conducted on reverse phase Waters Atlantis 4.6 mm x 5.0 cm, 3 μm column. Acetonitrile with 0.05% trifluoroacetic acid (TFA) and H_2O with 0.05% TFA were used as a solvent mixture, with average run time of 10 minutes. UV/Vis

---

[1] C. Freund, W. Porzio, U. Giovanella, F. Vignali, M. Pasini, S. Destri, A. Mech, S. Di Pietro, L. Di Bari, P. Mineo, *Inorg. Chem.* 2011, ***50***, 5417.
[2] Dedeian, K.; Djurovich, P. I.; Garces, F. O.; Carlson, G.; Watts, R. J. *Inorg. Chem*. 1991, **30**, 1685
[3] Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razaq, F.; Kwong, R.; Tsyba, I.; Bortz, M.; Mui, B.; Bau, R.; Thompson, M. E. *Inorg. Chem*. 2001, **40**, 1704-1711.
[4] K. Beydoun, M. Zaarour, J. A. G. Williams, T. Roisnel, V. Dorcet, A. Planchat, A. Boucekkine, D. Jacquemin, H. Doucet, V. Guerchais, *Inorg. Chem*. 2013, **52**(21), 12416-12428
[5] C. Dragonetti,. L. Falciola, P. Mussini, S. Righetto, D. Roberto, R. Ugo, A. Valore, F. De Angelis, S.Fantacci, A. Sgamellotti, M. Ramon, M. Muccini, *Inorg. Chem*. 2007, ***46*** , 8533−8547

absorption spectra were obtained on Agilent 8453 spectrophotometer in 1 cm path length quartz cell with dichloromethane.

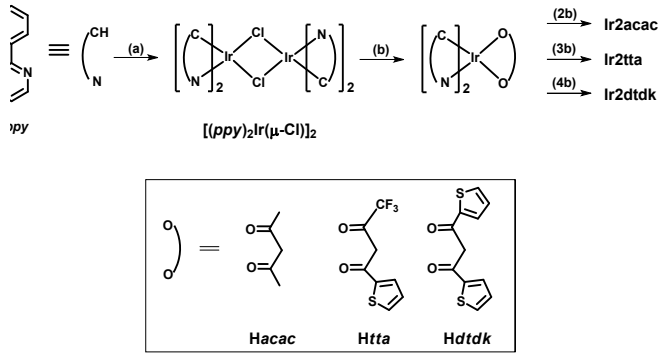
DSC were measured in open vessel mode under nitrogen flow on a Mettler Toledo STAR^e SYSTEM DSC 500; samples of 2-3 mg were weighted in an Aluminium crucible; temperature range were set from room temperature up to 450°C for all complexes other than **Ir3** that was set up to 470°C.

TGA analysis were performed under dry nitrogen flow on a Mettler Toledo STAR^e SYSTEM TGA/DSC 3+; samples of 3-4 mg were weighted in an Al_2O_3 crucible; temperature range were set from room temperature up to 500°C for all complexes except for **Ir2BPhen** that was set up to 600°C.

Prior photophysical characterizations the samples were further re-precipitated with hexane from concentered dichloromethane solutions; samples are considered suitable when purity is ascertained to be over 99% determined by HPLC analysis and NMR.

General procedure for the synthesis of Ir(ppy)$_2$(*O^O*) complexes:[3] 1 eq. of $[Ir(C^{\wedge}N)_2Cl]_2$ was placed in a round bottom flask connected to argon line and 2-ethoxyethanol was added to it. 3 eq. of ligand H*acac*/ H*tta*/ H*dtdk* and 7 eq. of K_2CO_3 were added to the solution, and the mixture was heated at 120 ^{o}C for 12 hours. The reaction was monitored by TLC. After cooling the reaction mixture at room temperature, distilled water was added and the crude product was filtered off and washed with water followed by 1 portion of diethyl ether and hexane. The solid was dried under high vacuum and further purified by flash column using dichloromethane as the eluent. [Yields obtained: **Ir2acac** = 67 % (yellow solid), **Ir2tta** = 74 % (orange solid), **Ir2dtdk** = 74 % (orange solid)].

Ir2dtdk, although it can be isolated in high purity, it seems that may exists in two possible stable conformers, one of higher simmetry and a second with lower symmetry characterized by indipendent set of resonances for all the protons as it appears in fig. SI 2a (it is excluded the possibility of a stereo-isomer given preliminary photolysis experiments and HPLC studies). Altenatively, due to the electron reachness of the dtdk system, the dtdk ligand could lead to the opening of the 6- metallacycle (i.e. braking of a Ir-O bond) resulting again in an asymmetric coordinatively-open compound[6]



Scheme SI 1. Synthesis of the *β*-diketonate: (a) $IrCl_3.nH_2O$, 2-ethoxyethanol, H_2O, 120^{o}C; (b) O^O, K_2CO_3, 2-ethoxyethanol, 120^{o}C; O^O: Acetylacetone (H*acac*); 2-Thienoyltrifluoroacetone (H*tta*);1,3-di(thiophen-2-yl)propane-1,3-dione (H*dtdk*)

Complex **Ir2dtdk** *major conformer*: ^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 8.62 (d, *J*=5.8 Hz, 2H), 7.90 (d, *J*=8.1Hz, 2H), 7.75 (t, *J*=7.9Hz, 2H), 7.62 (d, *J*=7.8Hz, 2H), 7.60 (d, *J*=3.8Hz, 2H), 7.43 (d, *J*=4.7Hz, 2H),

[6] Y. Li, Y. Liu, M. Zhou, *Dalton Trans*., 2012, **41**, 3807

7.13 (t, *J*=7.8Hz, 2H), 7.02 (dd, *J*=4.7Hz, 2H), 6.88 (t, *J*=7.4Hz, 2H), 6.74 (t, *J*=7.4, 2H), 6.47 (s, 1H), 6.29 (t, *J*=7.6Hz, 2H).

^{1}H-NMR (300 MHz, DMSO-*d6*) δ = 8.50 (d, *J*=5.5 Hz, 2H), 8.14 (d, *J*=8.1Hz, 2H), 7.89 (m(t+d), 4H), 7.71 (d, *J*=7.6Hz, 2H), 7.66 (d, *J*=4.7Hz, 2H), 7.35(t, *J*=6.4Hz, 2H), 7.08 (dd, *J*=4.3Hz, 2H), 6.8 (d, *J*=7.4Hz, 2H), 6.65 (t, *J*=7.4Hz, 2H), 6.60 (s, 1H), 6.14 (d, *J*=7.4, 2H).

^{13}C-NMR (100 MHz, CD_2Cl_2) δ = 172.9, 168.1, 147.7, 147.4, 145.7 (Cq), 148.8, 137.9, 133.6, 129.8, 129.4, 128.5, 127.6, 124.4, 122.5, 121.4, 119.1, 94.5 (CH)

LC-MS= 735.8 $[M]^+$, 541.9 $[M\text{-dtdk}+CH_3CN]^+$, 500.9 $[M\text{-dtdk}]^+$; M^2 (735.8) = 500.9 [M-*dtdk*]$^+$

Anal. Calc. for $C_{33}H_{23}IrN_2O_2S_2$: C, 53.86; H, 3.15; Ir, 26.12; N, 3.81; O, 4.35; S, 8.71; Found: C, 53.05; H, 3.3; N, 3.63.

Complex **Ir2dtdk** *minor conformer*: ^{1}H-NMR (300 MHz, DMSO-*d6*) δ = 8.81 (d, *J*=5.7 Hz, 1H), 9.54 (d, *J*=5.7 Hz, 1H), 8.26 (d, *J*=8.0 Hz, 1H), 8.05 (m, 6H), 7.78 (m, 2H), 7.57 (t, *J*=6.5Hz, 1H), 7.45 (t, *J*=6.6Hz, 1H), 7.29 (m, 2H), 7.11(1H), 6.89 (t, *J*=7.7Hz, 2H), 6.74 (m, 2H), 6.25 (d, *J*=7.6Hz, 1H), 5.66 (d, J=7.5Hz, 1H), 4.75 (s, 1H).

Complex **Ir2tta**: (400 MHz, CD_2Cl_2) δ = 8.50 (d, *J* = 5.6 Hz, 1H), 8.47 (d, *J* = 5.5 Hz, 1H), 7.92 (m, 2H), 7.81 (m, 2H), 7.67 (d, *J* = 3.8 Hz, 1H), 7.62 (d, *J*=7.8, 2H), 7.56 (d, *J*=5.0, 1H), 7.21 (t, *J*=6.6, 1H), 7.17 (t, *J* = 6.6 Hz, 1H), 7.04 (m, 1H), 6.90 (m, 2H), 6.74 (m, 2H), 6.28 (d, *J*=7.6 Hz, 1H), 6.24 (s, 1H), 6.22 (d, *J* = 8.0 Hz, 1H).

^{13}C-NMR (100 MHz, CD_2Cl_2) δ = 176.9, 168.6, 168.5, 146.3, 145.6, 145.1, 144.5 (Cq), 148.5, 138.3, 133.7, 132.2, 129.6, 129.5, 129.0, 124.6, 124.4, 122.74, 122.69, 122.0, 121.9, 119.4, 119.3, 93.3 (CH)

LC-MS (ESI, m/z)= 721.06 $[M]^+$; M^2 (735.8) = 500.6 [M-*tta*]$^+$

1.1 HPLCs and NMRs

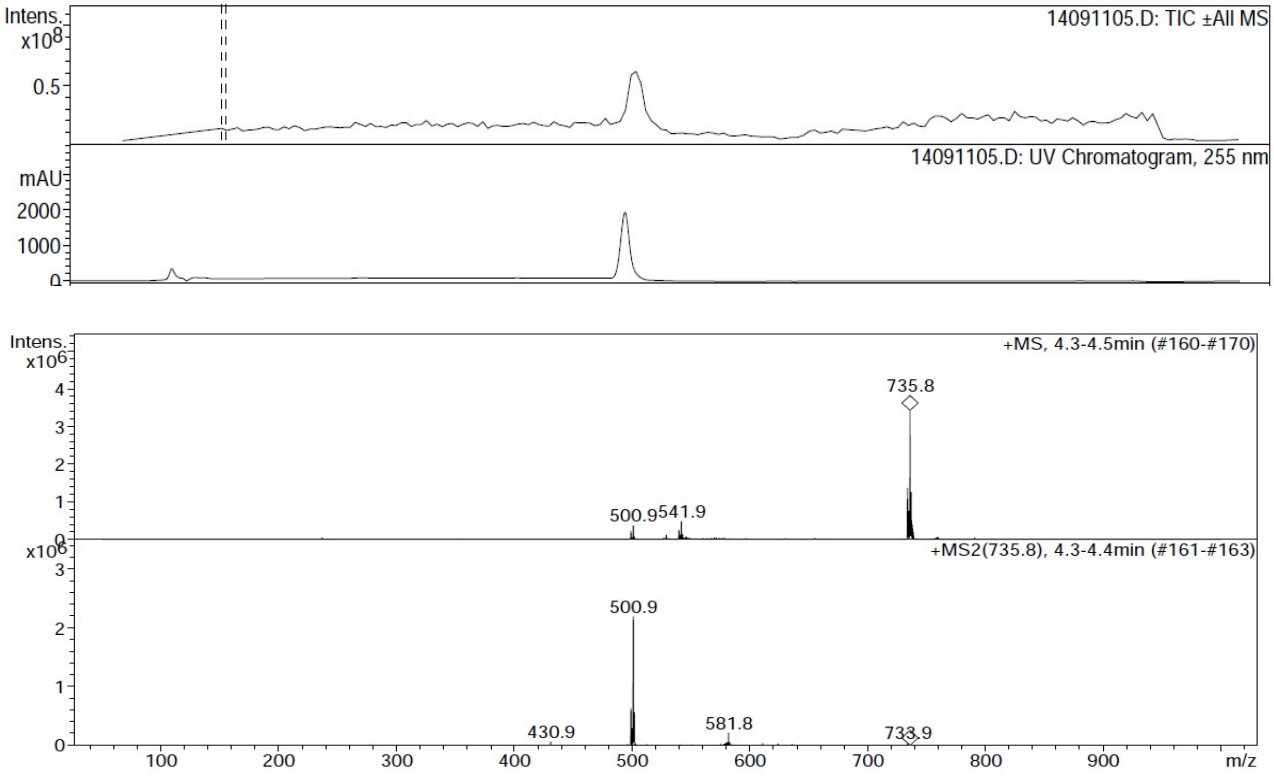
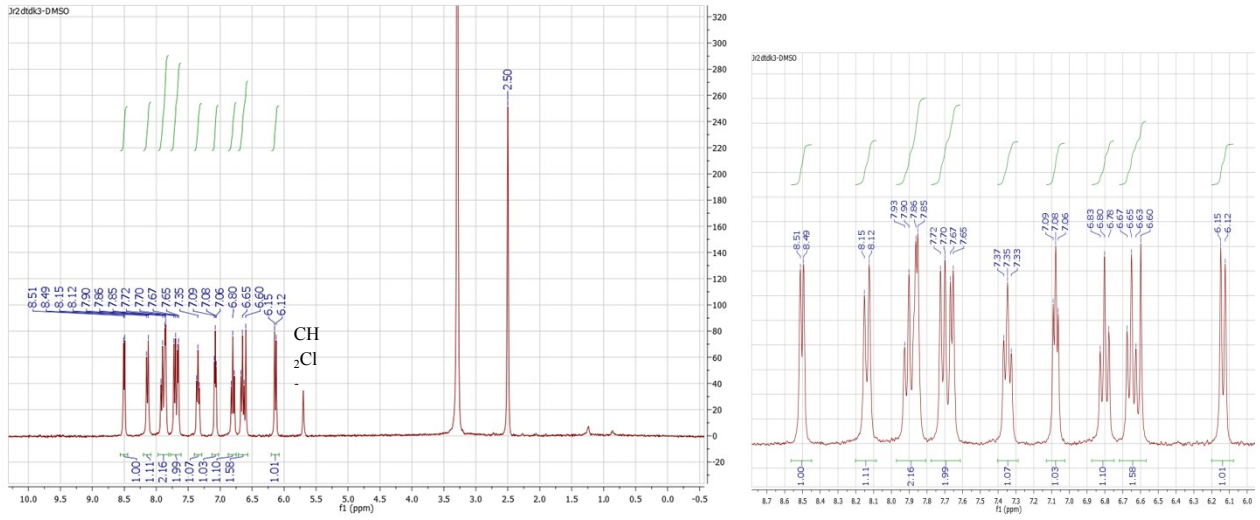
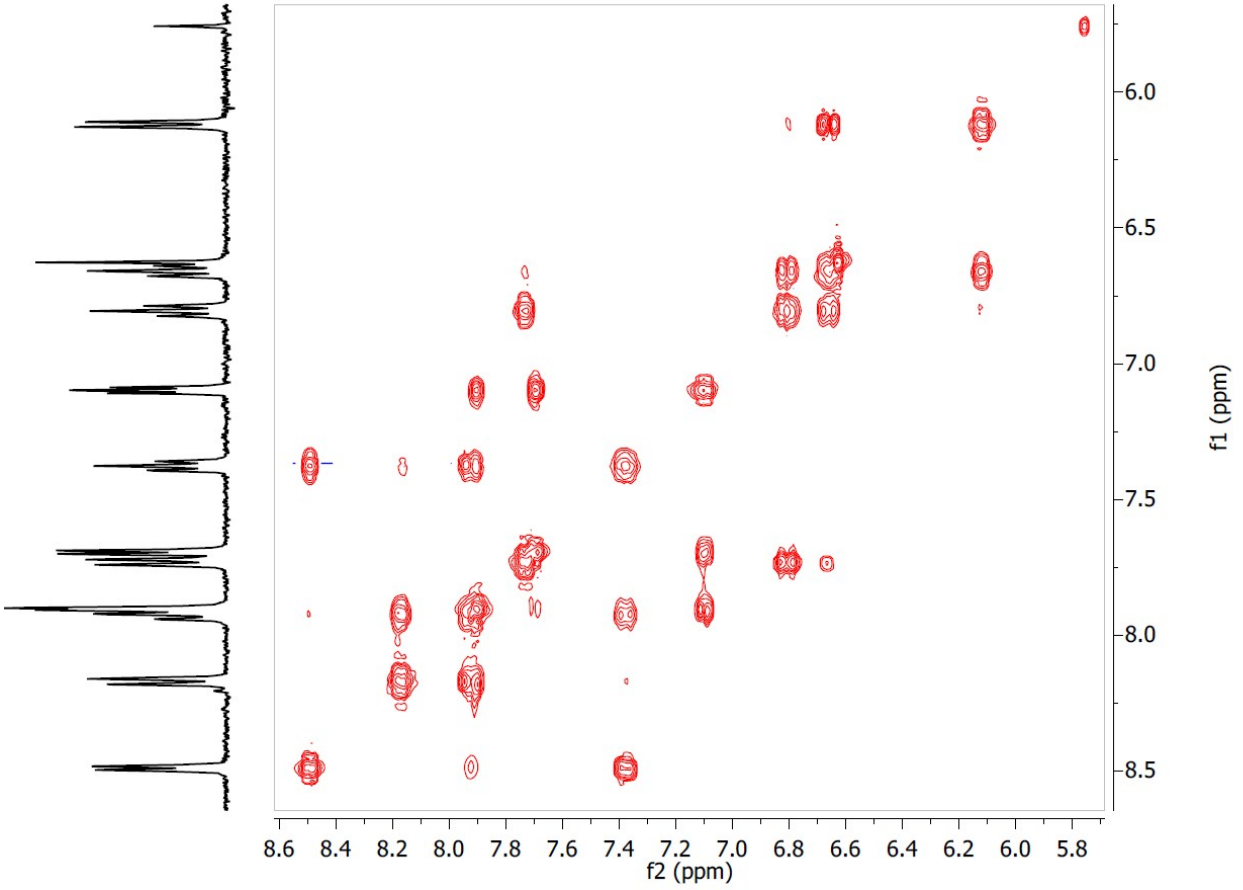


Figure SI 1: LC-MS analysis of **Ir2dtdk.**


Jr2.dtdk3-DMSO
2.50
CH2Cl2
f1 (ppm)


f1 (ppm)
f2 (ppm)

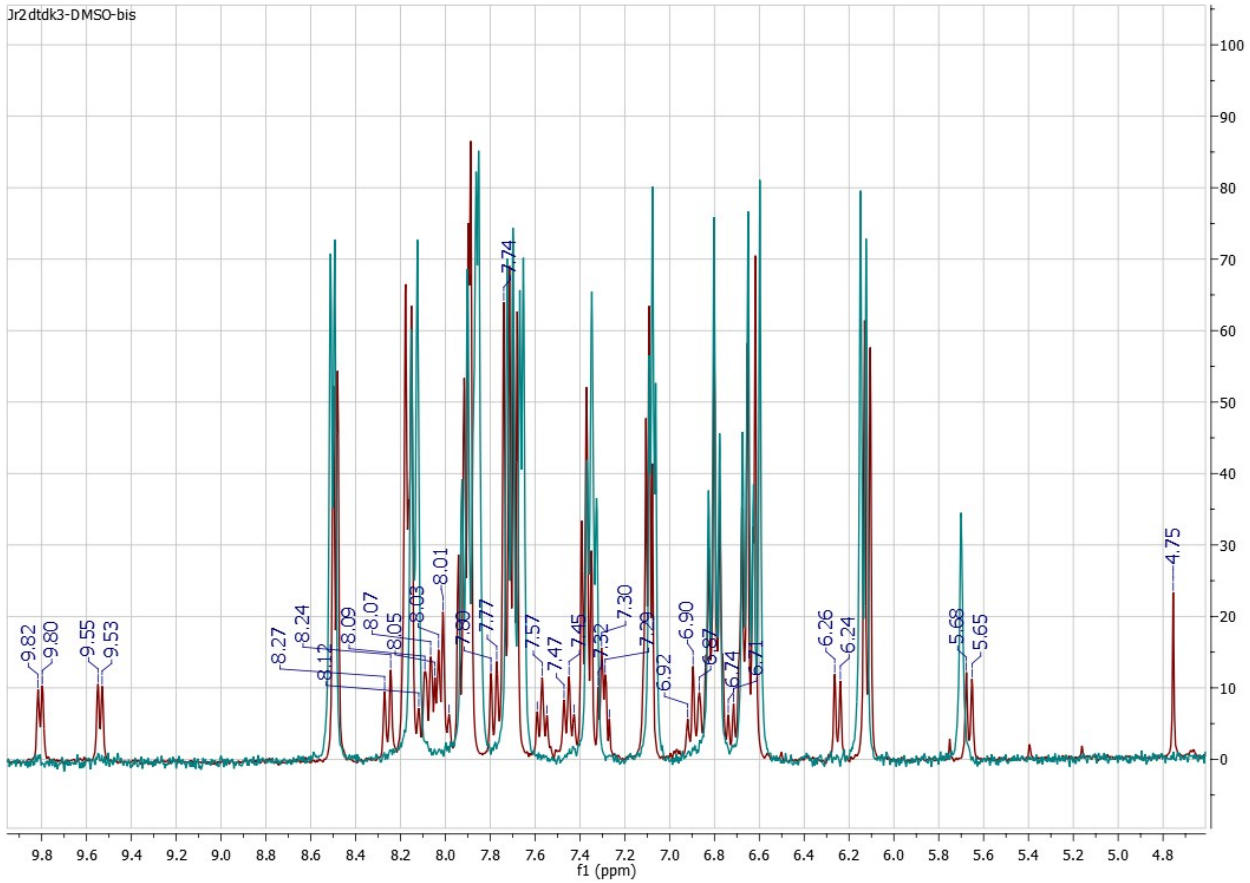
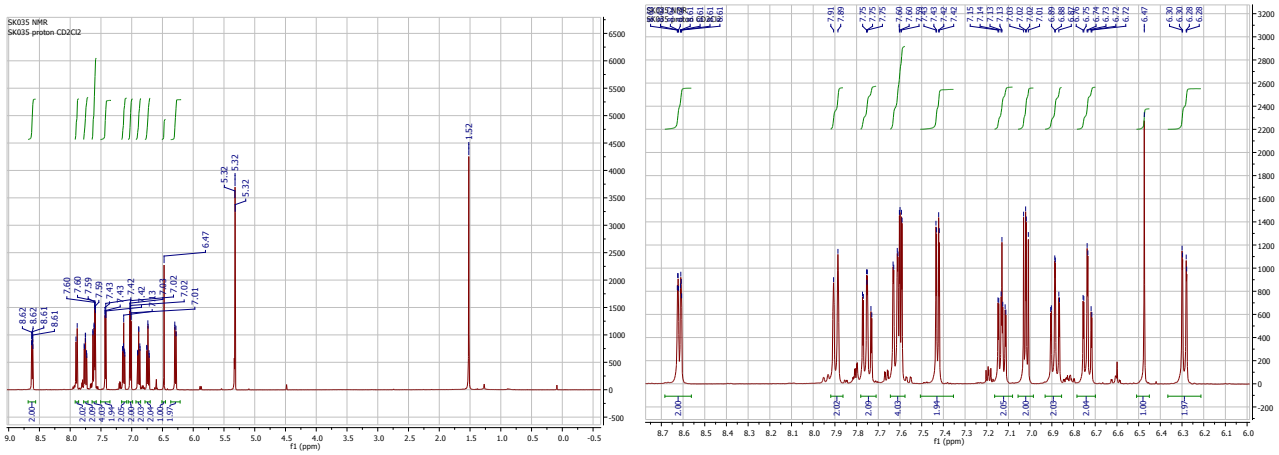
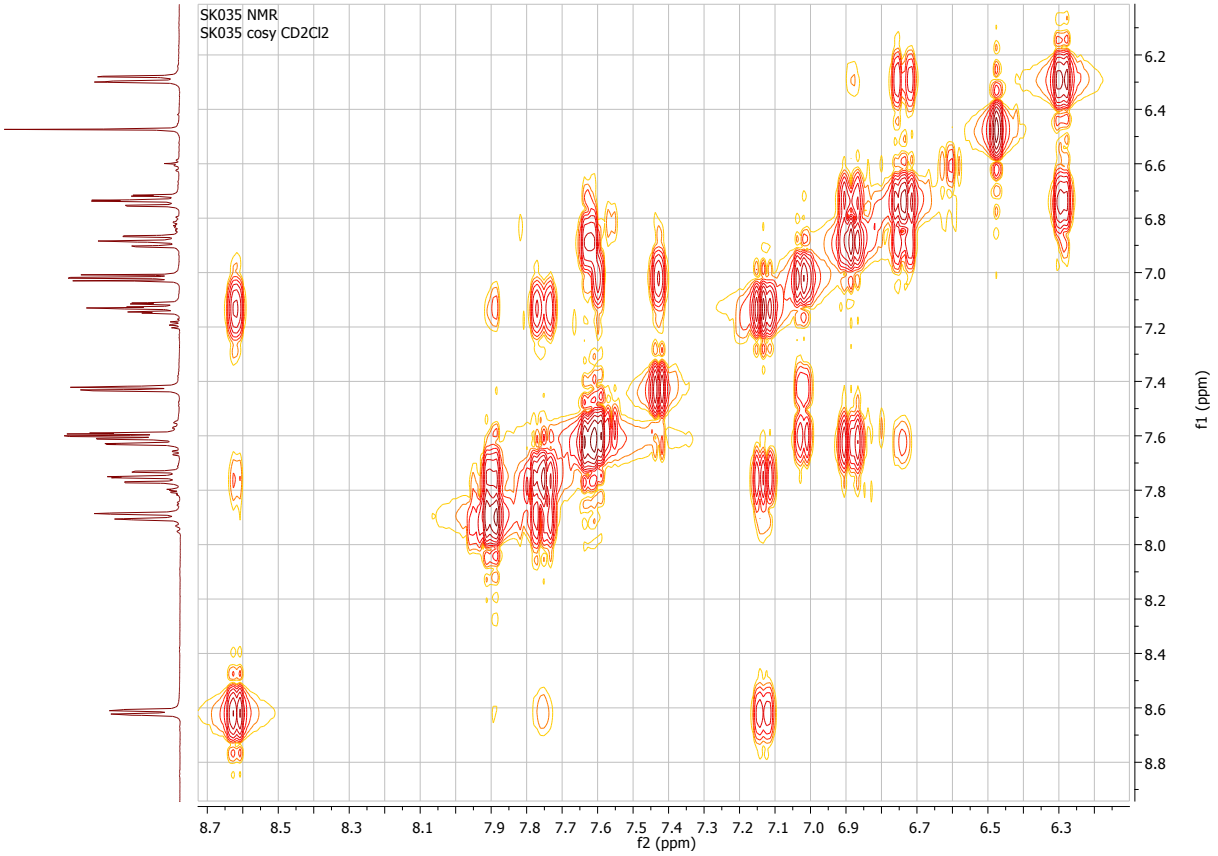
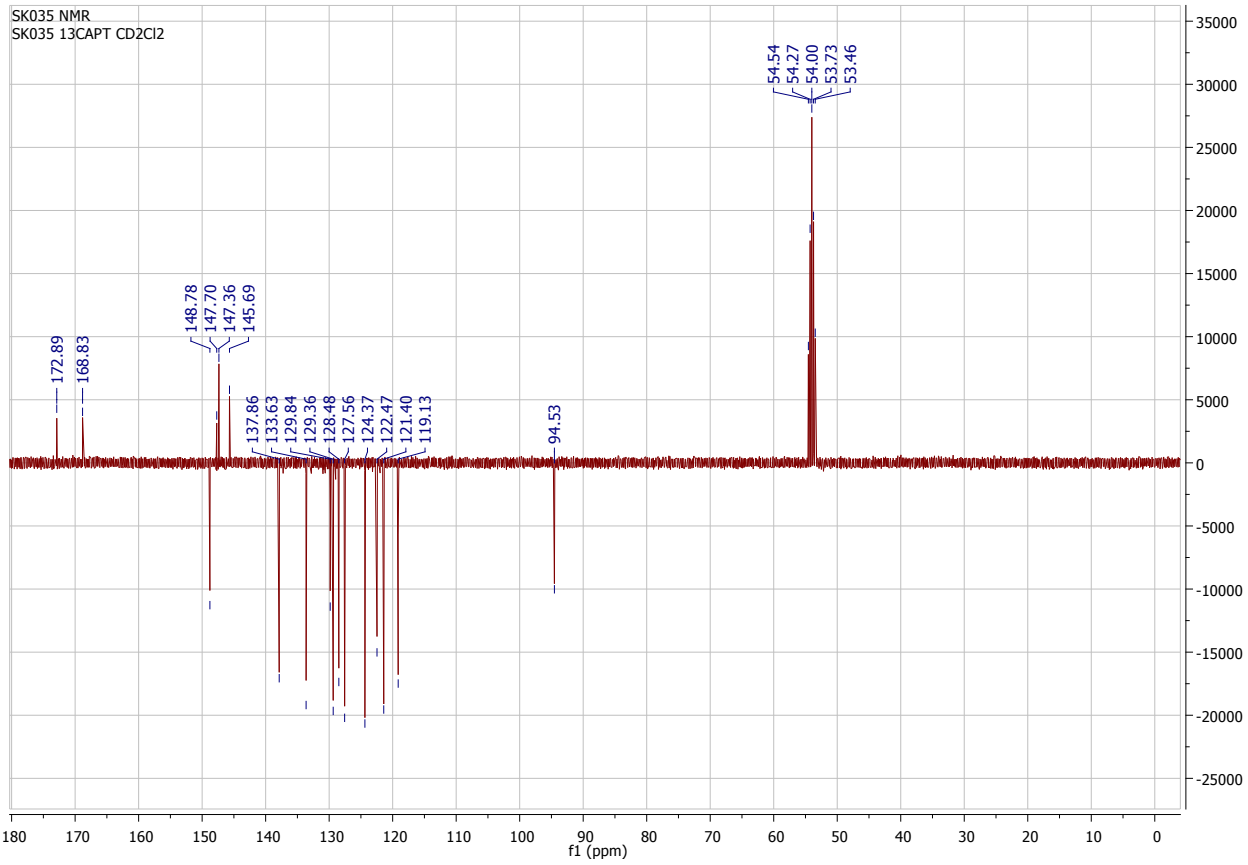


Figure SI 2a: [1]H-NMR, and COSY of **Ir2dtdk** in DMSO-*d6*. *Top* two panels and middle one for the major conformer; *bottom* panel, overlaid spectra of the pure title compound (green line) and a mixture with the a possible conformer or open form (red line).


SK035 NMR
SK035 proton CD2Cl2
f1 (ppm)


SK035 NMR
SK035 cosy CD2Cl2
f2 (ppm)
f1 (ppm)



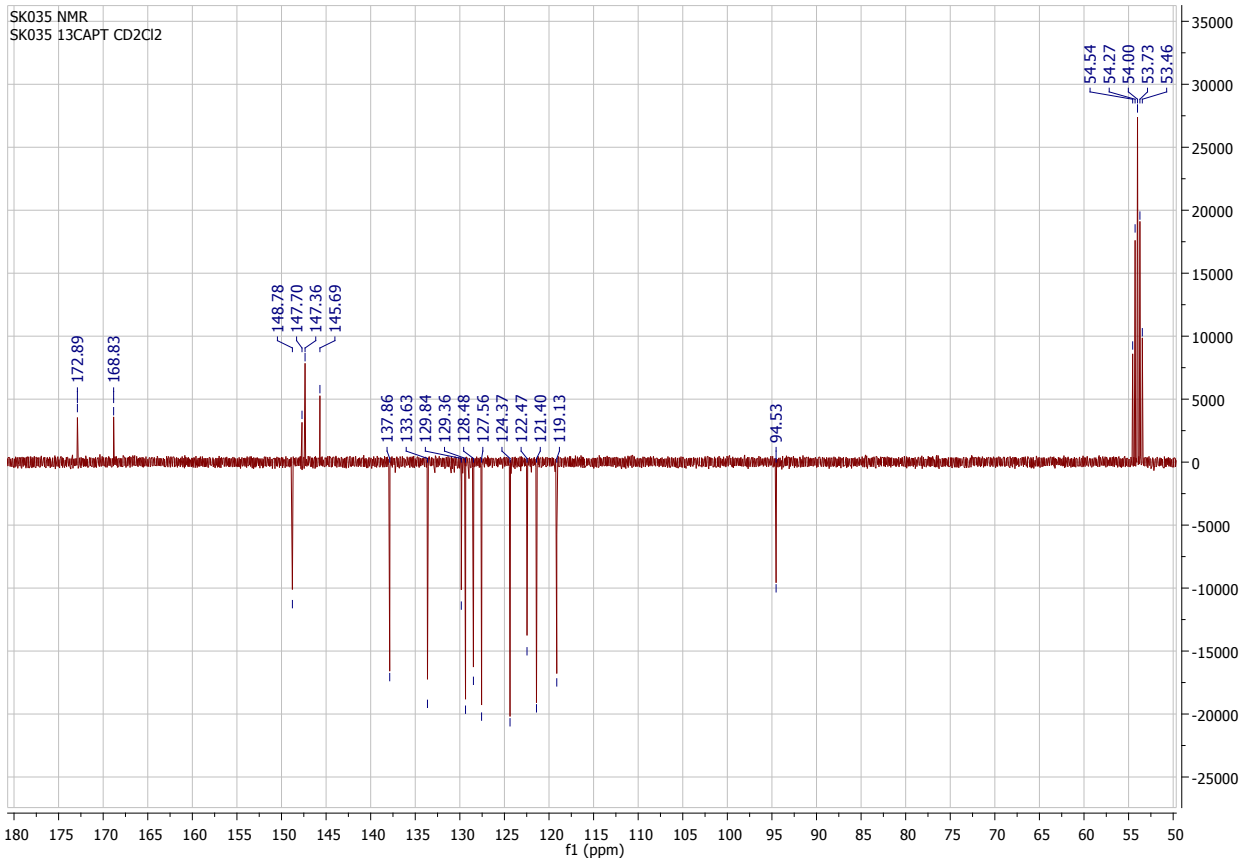


Figure SI 2b: ^{1}H-NMR, COSY and ^{13}C-NMR of **Ir2dtdk** in CD_2Cl_2.

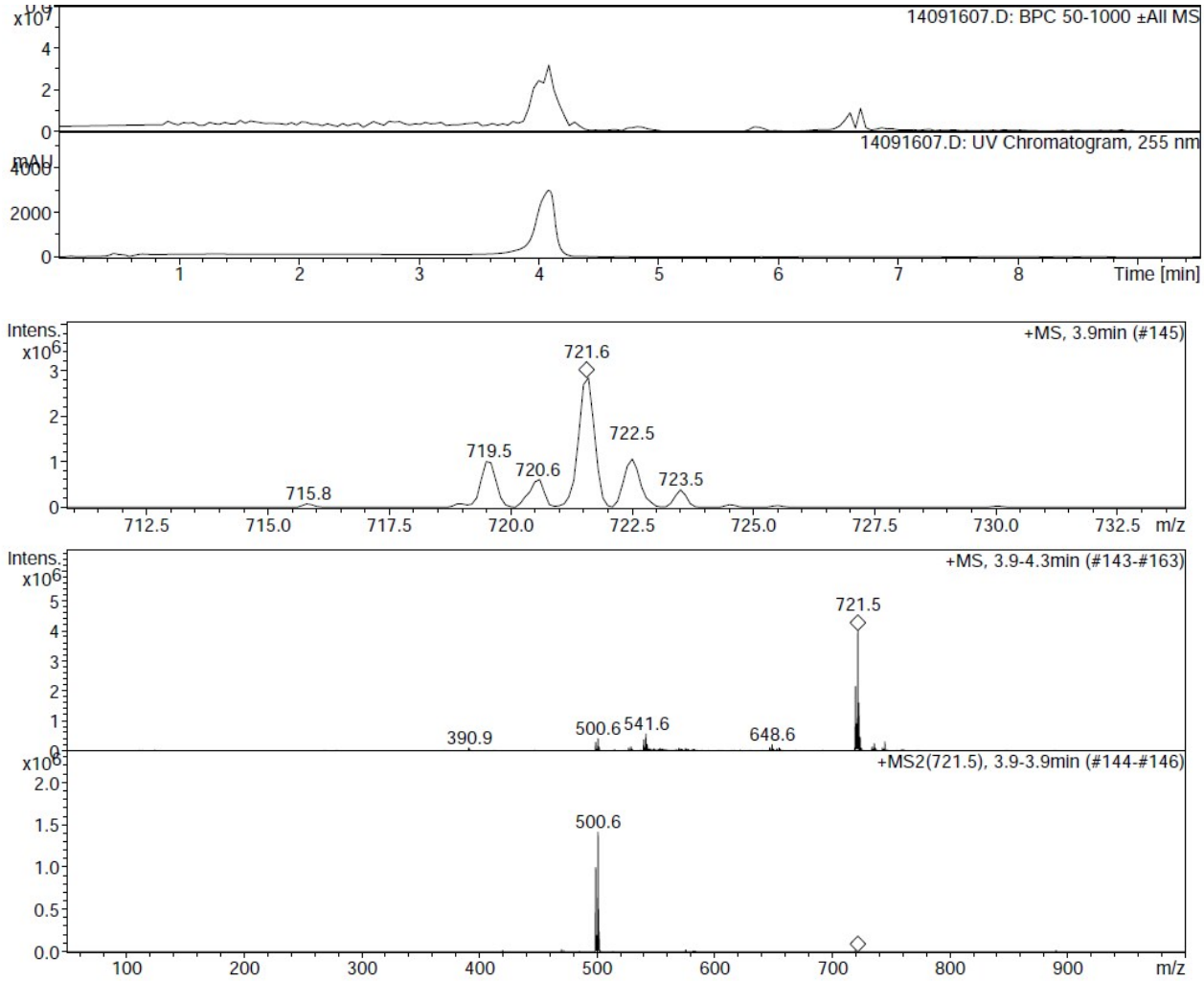
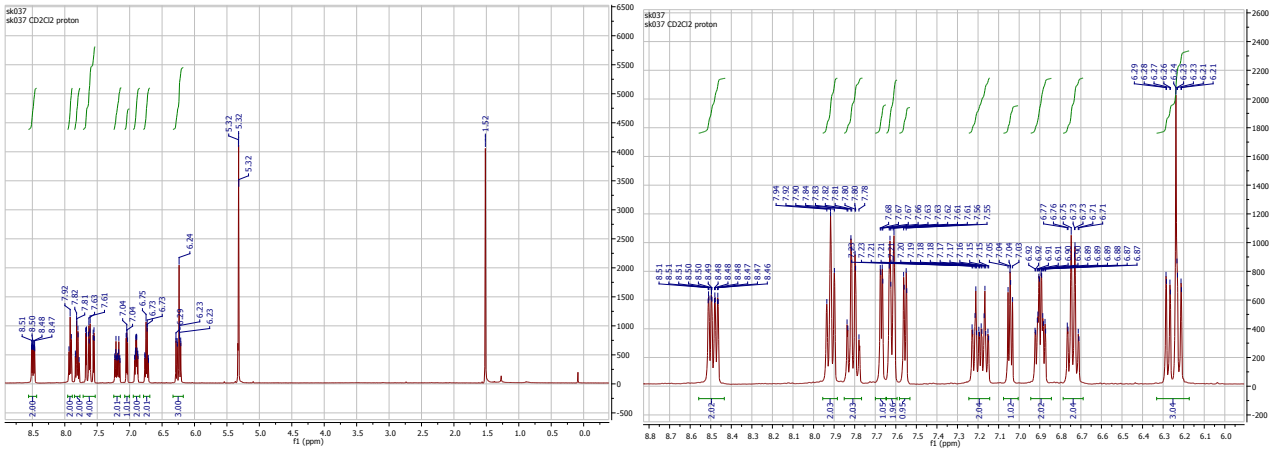
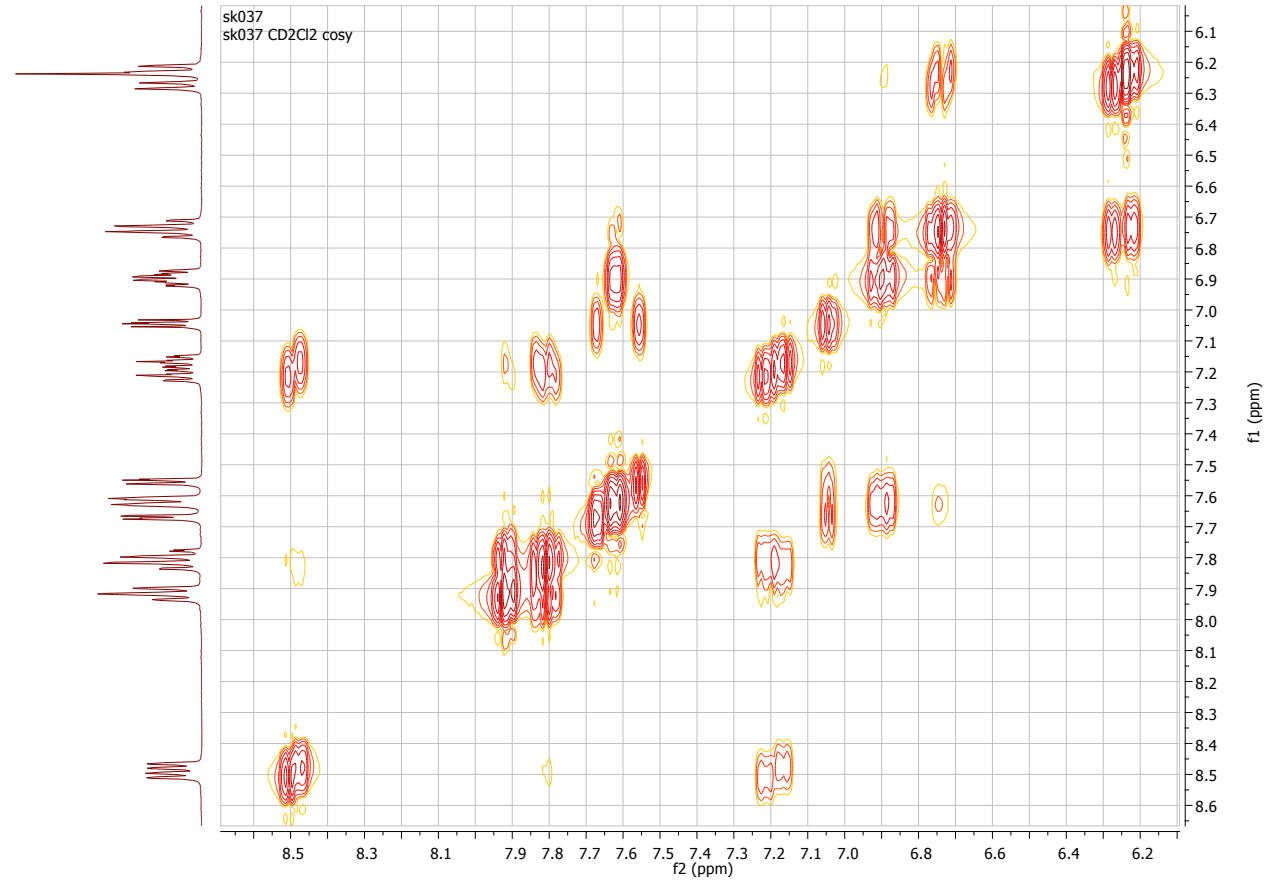
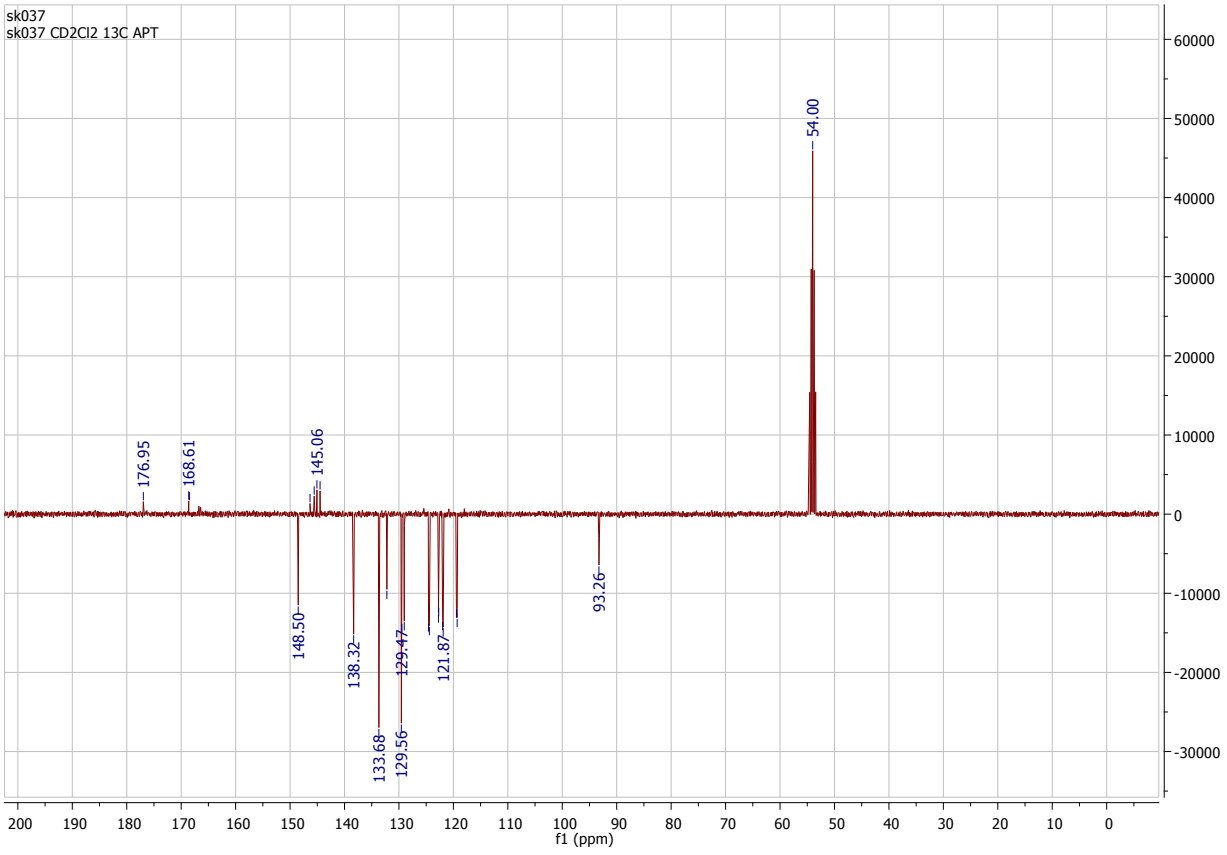


Figure SI 3: LC-MS analysis of complex **Ir2tta**.




sk037
sk037 CD2Cl2 cosy
f2 (ppm)
f1 (ppm)


sk037
sk037 CD2Cl2 13C APT
176.95
168.61
145.06
148.50
138.32
133.68
129.56
129.47
121.87
93.26
54.00
f1 (ppm)

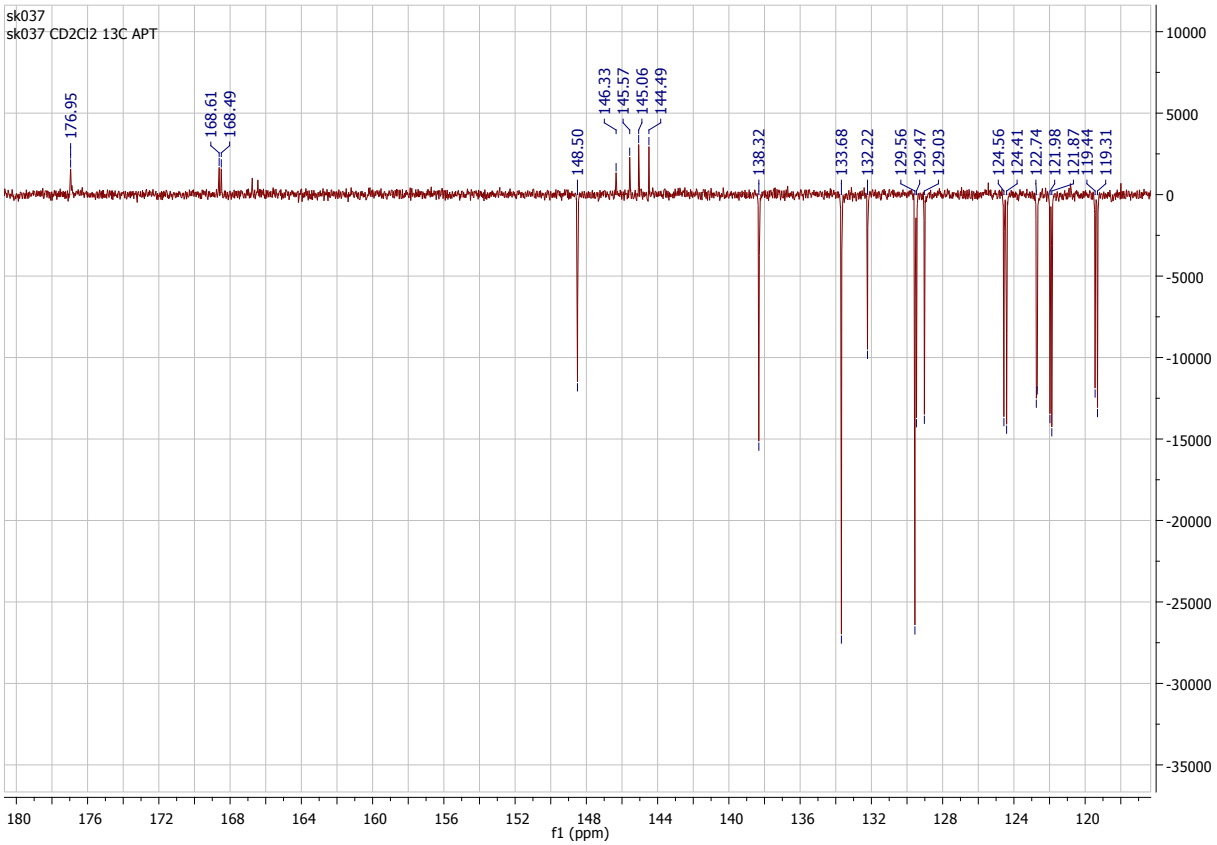


Figure SI 4: ^{1}HNMR, COSY and ^{13}C-NMR of complex **Ir2tta**.

1.2 Thermal studies

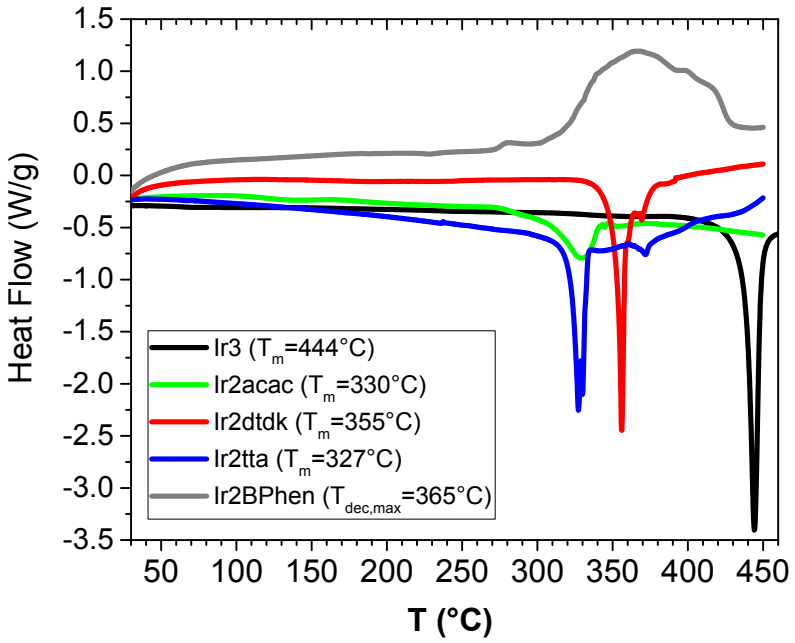


Figure SI 5.1: DSC thermal profiles for the five studied complexes

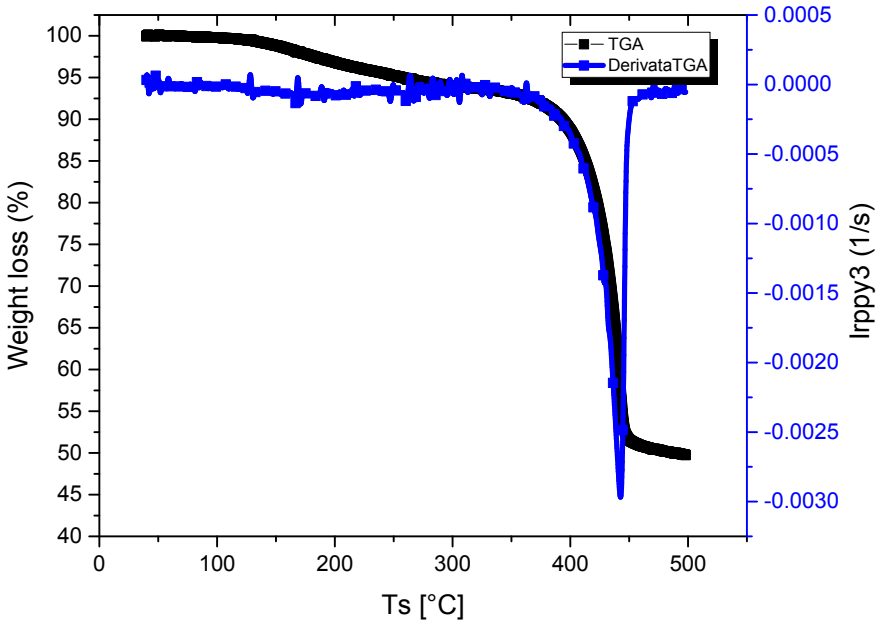


Figure SI 5.2: TGA thermal profile of **Ir3**

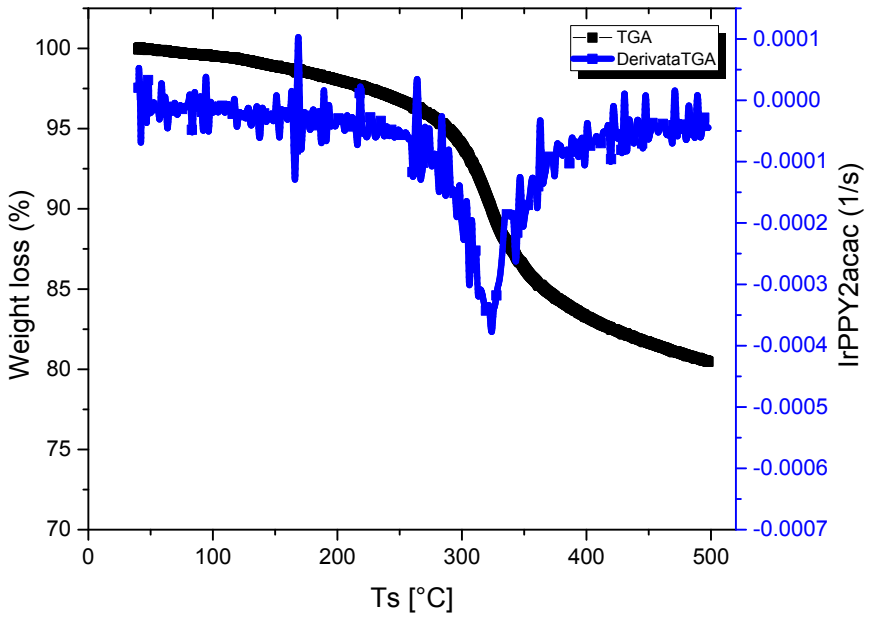


Figure SI 5.3: TGA thermal profile of **Ir2acac**

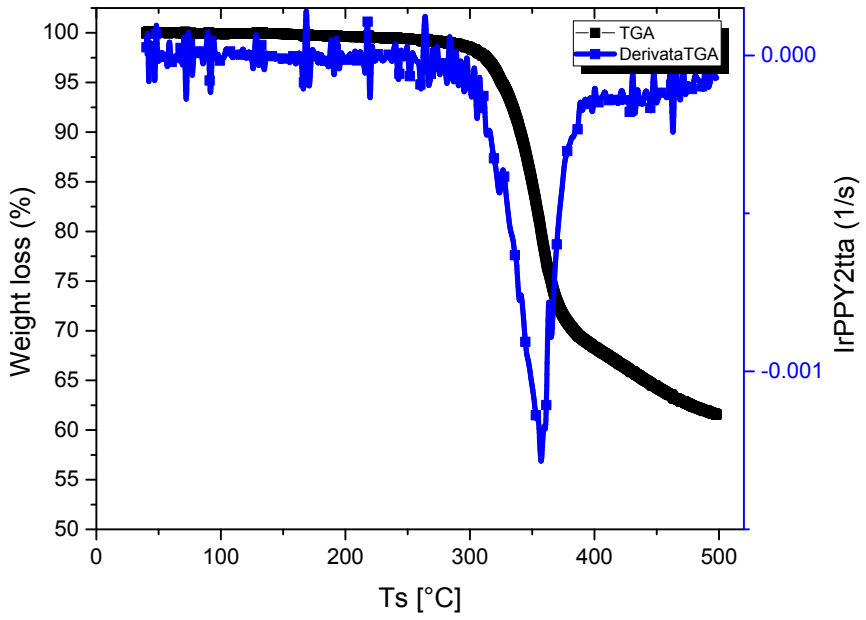


Figure SI 5.4: TGA thermal profile of **Ir2tta**

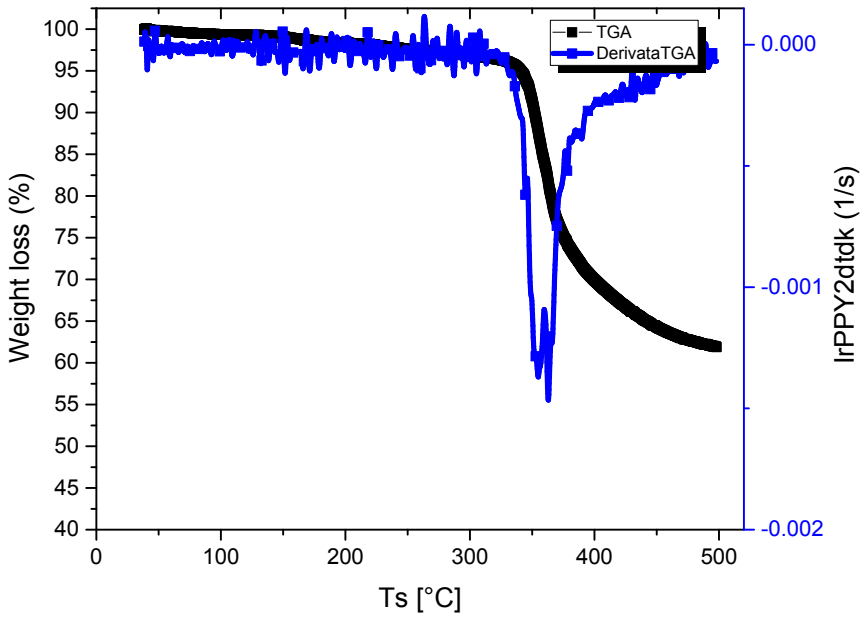


Figure SI 5.5: TGA thermal profile of **Ir2dtdk**

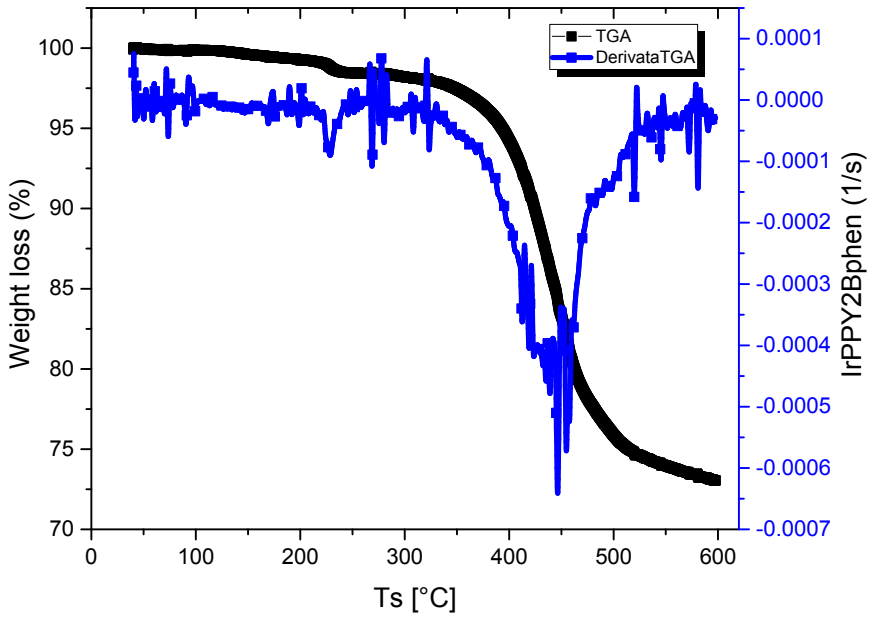


Figure SI 5.6: TGA thermal profile of **Ir2BPhen**

2. Optical characterization

Table SI 1. Photophysical parameters of the complexes.

	Rigidochromic effect /cm^{-1}	77 K		
		$\Delta E(0\text{-}1)_{S0}$ /cm^{-1}	S_M	Stokes shift /cm^{-1}
Ir3	825	1410	0.58	461
Ir2acac	532	1313	0.53	604
Ir2tta	853	1195	-	-
Ir2dtdk	866	-	-	-
Ir2BPhen	2486	1144	0.85	-

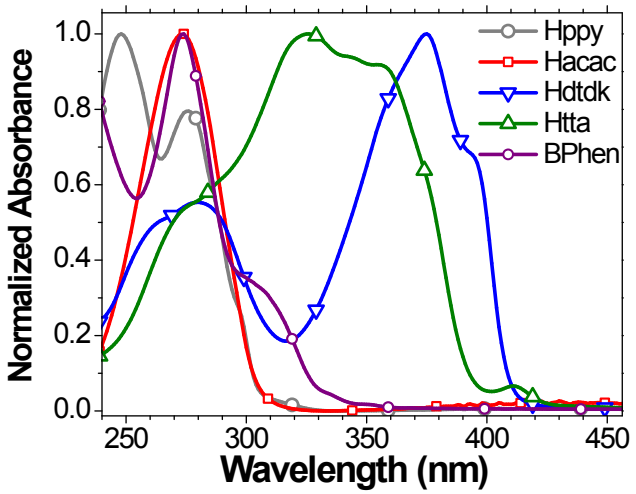


Figure SI 6: Absorption spectra of the free ligands in CH_2Cl_2.

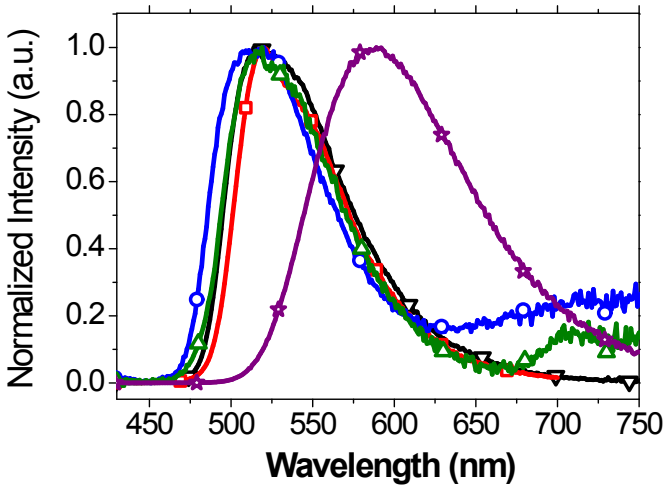


Figure SI 7: Emission spectra in deaerated CH_2Cl_2 solution at 298 K of complexes **Ir3** (black inverted triangles), **Ir2acac** (red squares), **Ir2dtdk** (blue circles), **Ir2tta** (green triangles) and **Ir2BPhen** (purple stars).

3. Electrochemical Features of the ancillary ligands

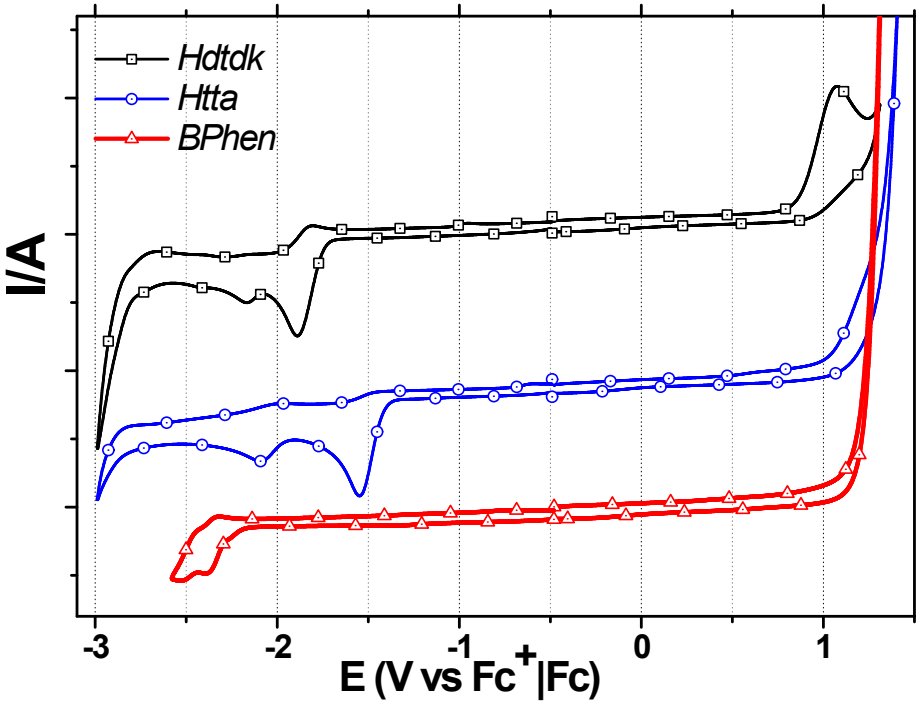


Figure SI 8: Cyclic voltammograms of the ancillary ligands recorded versus Fc^+/Fc in DMF at 298 K under a N_2 atmosphere (scan rate = 100 mV s^{-1})

4. DFT/TDDFT calculations

Tables SI 2 to SI 11 report the calculated optical absorption energies, oscillator strength and dominant orbital transitions with coefficients from TDDFT (H = HOMO, L = LUMO).

Table SI 2: Ir3 – Singlet excitations

Excited state	Transition (eV)	Transition λ (nm)	Oscillator strength	Dominant excitations (coefficient)
S1	2.83	438	0.0049	H→L (0.70)
S2	2.89	430	0.0020	H→L+1 (0.69)
S3	2.89	429	0.0021	H→L+2 (0.69)
S4	3.06	406	0.0222	H−1→L (0.59)
S5	3.06	406	0.0229	H−2→L (0.59)
S6	3.08	403	0.0026	H−2→L+1 (0.46), H−1→L+2 (0.46)
S7	3.16	392	0.0521	H−2→L+1 (-0.42), H−1→L+2 (0.42)
S8	3.16	392	0.0530	H−2→L+2 (0.41), H−1→L+1 (0.43)
S9	3.18	389	0.0001	H→L+3 (0.57)
S10	3.38	367	0.0461	H−2→L+2 (-0.38), H−1→L+1 (0.37), H→L+3 (0.40)
S11	3.39	366	0.0053	H−1→L+3 (0.68)
S12	3.39	366	0.0052	H−2→L+3 (0.68)
S13	3.50	354	0.0352	H→L+4 (0.69)
S14	3.50	354	0.0346	H→L+5 (0.69)
S15	3.64	340	0.0002	H−2→L+5 (-0.47), H−1→L+4 (0.49)
S16	3.66	339	0.0094	H−2→L+4 (0.29), H−2→L+5 (0.40), H−1→L+4 (0.39), H−1→L+5 (-0.30)
S17	3.66	339	0.0096	H−2→L+4 (0.40), H−2→L+5 (-0.30), H−1→L+4 (-0.29), H−1→L+5 (-0.39)
S18	3.69	336	0.0096	H−2→L+4 (0.47), H−1→L+5 (0.47)
S19	4.11	302	0.0056	H−4→L (0.63)
S20	4.11	302	0.0056	H−3→L (0.63)
S21	4.17	297	0.0011	H−4→L+2 (-0.40), H−3→L+1 (0.43)
S22	4.20	295	0.0477	H−4→L+1 (0.45), H−3→L+2 (-0.45)
S23	4.20	295	0.0475	H−4→L+2 (0.45), H−3→L+1 (0.44)
S24	4.21	294	0.0428	H−4→L+1 (0.31), H−3→L+2 (0.32), H→L+6 (0.47)
S25	4.22	293	0.0003	H−5→L (0.40), H→L+6 (0.43)
S26	4.27	291	0.1737	H−5→L (0.47), H→L+6 (-0.30)
S27	4.29	289	0.0070	H−5→L+1 (0.63)
S28	4.29	289	0.0069	H−5→L+2 (0.63)
S29	4.38	283	0.0003	H−1→L+6 (0.70)
S30	4.39	283	0.0003	H−2→L+6 (0.70)
S31	4.43	280	0.0249	H−4→L+3 (0.55)
S32	4.43	280	0.0250	H−3→L+3 (0.55)
S33	4.49	276	0.0005	H−6→L (0.52), H−5→L+3 (0.36)
S34	4.54	273	0.0422	H−6→L (-0.34), H−5→L+3 (0.54)
S35	4.56	272	0.0171	H−6→L+1 (0.57)
S36	4.56	272	0.0170	H−6→L+2 (0.57)
S37	4.62	268	0.0032	H−7→L (0.54)
S38	4.62	268	0.0034	H−8→L (0.54)
S39	4.64	267	0.0366	H−9→L (-0.27), H−4→L+4 (0.35), H−3→L+5 (0.36)
S40	4.67	265	0.0225	H−9→L (0.48)
S41	4.68	265	0.0064	H−9→L+2 (0.25), H−8→L+2 (-0.21), H−7→L+1 (0.23), H−4→L+5 (0.26), H−3→L+4 (0.27), H→L+8 (-0.23)
S42	4.68	265	0.0068	H−9→L+1 (0.25), H−8→L+1 (0.21), H−7→L+2 (0.21), H−4→L+4 (-0.27), H−3→L+5 (0.27), H→L+7 (0.24)
S43	4.71	263	0.0057	H→L+7 (0.46), H→L+8 (-0.39)
S44	4.71	263	0.0053	H→L+7 (0.42), H→L+8 (0.43)
S45	4.71	263	0.0013	H−4→L+5 (0.47), H−3→L+4 (-0.38)
S46	4.75	261	0.0434	H−9→L+1 (0.18), H−9→L+2 (-0.15), H−8→L (-0.20), H−8→L+2 (0.23), H−7→L+1 (-0.21), H−7→L+2 (0.22), H−5→L+5 (0.19), H−4→L+5 (0.25), H−3→L+4 (0.25)
S47	4.75	261	0.0424	H−9→L+1 (0.16), H−9→L+2 (0.18), H−8→L+1 (0.19), H−8→L+2 (-0.17), H−7→L (0.20), H−7→L+1 (0.19), H−7→L+2 (0.26), H−5→L+4 (-0.18), H−4→L+4 (0.25), H−3→L+5 (-0.24)
S48	4.76	260	0.0097	H−8→L+1 (0.40), H−7→L+2 (-0.32), H→L+10 (-0.27)
S49	4.79	259	0.0004	H−9→L+1 (0.47)
S50	4.79	259	0.0004	H−9→L+2 (0.46)

Table SI 3: Ir3 – Triplet excitations

Excited state	Transition (eV)	Transition λ (nm)	Oscillator strength	Dominant excitations (coefficient)
T1	2.60	477	--	H→L (0.59)
T2	2.61	475	--	H→L+1 (0.53)
T3	2.61	474	--	H→L+2 (0.53)
T4	2.83	439	--	H−2→L+2 (-0.44), H−1→L+1 (0.45)
T5	2.86	434	--	H−2→L (0.30), H−2→L+2 (0.26), H−1→L (0.36), H−1→L+1 (0.27)
T6	2.86	434	--	H−2→L (0.36), H−2→L+1 (-0.27), H−1→L (-0.29), H−1→L+2 (0.26)
T7	2.98	416	--	H−2→L+2 (-0.27), H−1→L (0.40), H−1→L+1 (-0.27), H→L+2 (-0.32)
T8	2.98	416	--	H−2→L (0.40), H−2→L+1 (0.28), H−1→L+2 (-0.28), H→L+1 (-0.31)
T9	3.01	412	--	H−2→L+1 (0.41), H−1→L+2 (0.41), H→L (-0.30)
T10	3.09	401	--	H→L+3 (0.63)
T11	3.17	391	--	H−2→L+3 (0.30), H−1→L+3 (0.27), H→L+4 (0.28)
T12	3.17	391	--	H−2→L+3 (-0.27), H−1→L+3 (0.30), H→L+5 (0.28)
T13	3.22	385	--	H−5→L+1 (-0.23), H−4→L (-0.29), H−2→L+3 (0.23), H−1→L+3 (0.35)
T14	3.22	385	--	H−5→L+2 (0.23), H−3→L (0.29), H−2→L+3 (0.35), H−1→L+3 (-0.22)
T15	3.24	382	--	H−5→L (0.31), H−4→L+1 (0.29), H−3→L+2 (0.29)
T16	3.41	363	--	H−2→L+5 (-0.27), H−1→L+4 (0.40), H→L+4 (0.24)
T17	3.41	363	--	H→L+4 (0.51)
T18	3.41	363	--	H−2→L+5 (-0.31), H→L+5 (0.50)
T19	3.57	347	--	H−2→L+5 (0.41), H−1→L+4 (0.41)
T20	3.58	347	--	H−2→L+4 (0.41), H−1→L+5 (-0.41)
T21	3.63	341	--	H−2→L+4 (0.47), H−1→L+5 (0.47)
T22	3.85	322	--	H−3→L (-0.19), H−3→L+3 (0.30)
T23	3.85	322	--	H−4→L (-0.19), H−4→L+3 (0.30)
T24	3.86	321	--	H−5→L+3 (0.30), H−4→L+1 (-0.22), H−4→L+4 (0.22), H−3→L+2 (-0.22), H−3→L+5 (0.22)
T25	4.00	310	--	H−7→L+1 (-0.12), H−6→L (0.15), H−6→L+3 (-0.14), H−5→L+3 (0.15), H−2→L+5 (0.15), H−2→L+12 (0.19), H−1→L+4 (-0.15), H−1→L+11 (-0.19), H→L+10 (0.21), H→L+13 (0.13)
T26	4.02	308	--	H−8→L (0.14), H−2→L+10 (0.22), H→L+12 (0.23)
T27	4.02	308	--	H−7→L (0.14), H−1→L+10 (-0.22), H→L+11 (0.23)
T28	4.12	301	--	H−4→L (0.46)
T29	4.12	301	--	H−3→L (0.45)
T30	4.14	299	--	H−5→L (0.43)
T31	4.17	298	--	H−7→L (0.32), H−5→L+1 (0.26)
T32	4.17	297	--	H−8→L (0.32), H−5→L+2 (0.26)
T33	4.18	297	--	H−4→L+2 (0.40), H−3→L+1 (-0.40)
T34	4.22	294	--	H→L+6 (0.68)
T35	4.27	290	--	H−9→L (0.19), H−8→L+2 (-0.22), H−7→L+1 (-0.23), H−5→L (0.30), H−4→L+1 (-0.18), H→L+10 (-0.19)
T36	4.27	290	--	H−5→L+1 (0.50)
T37	4.28	290	--	H−5→L+2 (0.50)
T38	4.31	288	--	H−6→L (0.55)
T39	4.35	285	--	H−6→L+2 (0.51)
T40	4.35	285	--	H−6→L+1 (0.51)
T41	4.38	283	--	H−1→L+6 (0.69)
T42	4.38	283	--	H−2→L+6 (0.69)
T43	4.51	275	--	H−9→L+1 (0.27), H−6→L+1 (0.24), H−4→L+3 (0.37)
T44	4.51	275	--	H−9→L+2 (0.27), H−6→L+2 (0.24), H−3→L+3 (0.37)
T45	4.51	275	--	H−9→L (0.50)
T46	4.57	271	--	H−9→L+2 (0.35), H−3→L+3 (-0.24)
T47	4.57	271	--	H−9→L+1 (0.35), H−4→L+3 (-0.24)
T48	4.57	271	--	H−5→L+3 (0.45), H−4→L+4 (-0.31), H−3→L+5 (-0.33)
T49	4.62	269	--	H−14→L (0.20), H−13→L+1 (-0.19), H−12→L+2 (0.19), H−9→L (0.22), H−5→L+3 (0.19), H→L+10 (-0.21), H→L+13 (0.17)
T50	4.63	268	--	H−14→L+2 (-0.15), H−13→L (-0.14), H−13→L+1 (-0.15), H−12→L (-0.19), H−12→L+2 (-0.14), H−7→L (0.22), H→L+8 (-0.15), H→L+14 (-0.14)

Table SI 4: Ir2(acac) – Singlet excitations

Excited state	Transition (eV)	Transition λ (nm)	Oscillator strength	Dominant excitations (coefficient)
S1	2.72	457	0.0310	H→L+1 (0.69)
S2	2.74	453	0.0004	H→L (0.70)
S3	3.20	388	0.0218	H−1→L (0.64)
S4	3.21	386	0.0018	H→L+3 (0.56), H→L+4 (0.41)
S5	3.24	382	0.0019	H−1→L+1 (0.64)
S6	3.25	382	0.0309	H→L+2 (0.65)
S7	3.35	371	0.0000	H→L+3 (-0.37), H→L+4 (0.54)
S8	3.57	347	0.0766	H−2→L+1 (0.66)
S9	3.59	345	0.0113	H−2→L (0.64)
S10	3.72	333	0.0007	H−1→L+2 (0.66)
S11	3.74	331	0.0055	H−1→L+3 (0.59)
S12	3.79	327	0.0036	H−1→L+4 (0.56)
S13	3.90	318	0.0458	H−3→L (0.62)
S14	3.92	316	0.0083	H−3→L+1 (0.65)
S15	4.07	305	0.0237	H−2→L+2 (0.62)
S16	4.12	301	0.0360	H−2→L+3 (0.61)
S17	4.15	299	0.0187	H−5→L (0.66)
S18	4.15	299	0.0076	H−5→L+1 (0.37), H−4→L (-0.36), H−2→L+4 (0.39)
S19	4.18	297	0.0007	H−5→L+1 (0.52)
S20	4.21	294	0.0000	H→L+5 (0.70)
S21	4.25	291	0.0662	H−4→L+1 (0.59)
S22	4.26	291	0.0392	H−4→L (0.45), H−2→L+4 (0.40)
S23	4.34	286	0.0009	H−6→L+1 (-0.42), H−3→L+2 (0.51)
S24	4.36	285	0.0182	H−6→L (0.56)
S25	4.38	283	0.0014	H−7→L+3 (0.36), H−7→L+4 (0.27), H−3→L+3 (0.31), H−3→L+4 (0.29)
S26	4.44	279	0.0084	H→L+6 (0.67)
S27	4.49	276	0.0258	H−7→L+1 (-0.33), H−6→L+1 (0.38), H−5→L+2 (-0.26), H−3→L+2 (0.33)
S28	4.49	276	0.0140	H−7→L (0.46), H−3→L+3 (0.43)
S29	4.50	275	0.0159	H−7→L (-0.33), H−7→L+3 (-0.26), H−3→L+4 (0.42)
S30	4.54	273	0.1632	H−7→L (0.35), H−3→L+3 (-0.29), H−3→L+4 (0.30), H→L+9 (0.27)
S31	4.54	273	0.0424	H−7→L+1 (0.59)
S32	4.61	269	0.0058	H−1→L+5 (0.66)
S33	4.64	267	0.0368	H−4→L+2 (0.41), H→L+9 (0.37)
S34	4.65	267	0.0272	H→L+8 (0.55)
S35	4.67	266	0.0102	H−5→L+2 (0.54)
S36	4.68	265	0.0010	H→L+7 (0.67)
S37	4.71	263	0.0106	H−5→L+4 (-0.36), H−4→L+2 (0.48)
S38	4.75	261	0.0197	H−4→L+3 (0.53), H−4→L+4 (0.44)
S39	4.77	260	0.0015	H→L+8 (0.29), H→L+10 (0.37), H→L+13 (-0.32)
S40	4.79	259	0.0312	H−4→L+3 (-0.36), H−4→L+4 (0.48)
S41	4.79	259	0.3308	H−5→L+4 (0.34), H−4→L+2 (0.23), H→L+9 (-0.27)
S42	4.85	256	0.0130	H−1→L+10 (-0.38), H−1→L+13 (0.43)
S43	4.86	255	0.0187	H−6→L+3 (-0.29), H−5→L+3 (0.47), H−5→L+4 (0.33)
S44	4.87	255	0.0001	H−6→L+2 (0.64)
S45	4.92	252	0.0008	H−1→L+6 (0.67)
S46	4.94	251	0.0034	H−6→L+4 (0.58)
S47	4.97	249	0.0042	H−8→L (0.64)
S48	4.98	249	0.0022	H−8→L+1 (0.61)
S49	5.02	247	0.0186	H−7→L+2 (0.60)
S50	5.03	247	0.0260	H−7→L+2 (0.32), H−2→L+5 (0.31), H−2→L+13 (-0.23), H−1→L+9 (-0.28), H→L+10 (0.25)

Table SI 5: Ir2(acac) – Triplet excitations

Excited state	Transition (eV)	Transition λ (nm)	Oscillator strength	Dominant excitations (coefficient)
T1	2.47	501	--	H→L+1 (0.66)
T2	2.48	501	--	H→L (0.67)
T3	2.86	433	--	H−1→L+1 (0.49)
T4	2.87	431	--	H−1→L (0.49)
T5	2.91	426	--	H−1→L+3 (0.45), H−1→L+4 (0.36)
T6	3.07	404	--	H→L+2 (0.65)
T7	3.13	397	--	H−1→L+1 (0.34), H→L+3 (-0.35), H→L+4 (0.38)
T8	3.15	393	--	H→L+3 (0.50), H→L+4 (0.48)
T9	3.22	385	--	H−4→L+1 (-0.27), H−3→L (-0.26), H−2→L+1 (0.25), H−1→L (0.38)
T10	3.23	384	--	H−4→L (-0.23), H−3→L+1 (-0.23), H−2→L (0.28), H−1→L+1 (0.27), H→L+3 (0.28), H→L+4 (-0.26)
T11	3.36	369	--	H−2→L (0.53)
T12	3.38	367	--	H−2→L+1 (0.54)
T13	3.62	343	--	H−1→L+2 (0.59)
T14	3.66	339	--	H−3→L (0.51)
T15	3.69	336	--	H−5→L+1 (-0.27), H−3→L+1 (0.43)
T16	3.70	335	--	H−1→L+3 (-0.36), H−1→L+4 (0.46)
T17	3.83	324	--	H−4→L (0.24), H−3→L+2 (0.39)
T18	3.84	323	--	H−2→L+3 (0.50), H−2→L+4 (0.42)
T19	3.85	322	--	H−5→L (0.30), H−4→L+1 (0.24), H−4→L+2 (0.22), H−3→L+3 (-0.20), H−3→L+4 (0.25)
T20	3.94	315	--	H−5→L (0.26), H−2→L+2 (-0.31), H→L+9 (0.35)
T21	3.94	315	--	H→L+10 (0.47)
T22	4.00	310	--	H−2→L+2 (0.42), H→L+9 (0.35)
T23	4.01	309	--	H−6→L+3 (-0.26), H−6→L+4 (-0.21), H−5→L+3 (-0.28), H−5→L+4 (-0.20), H−2→L+2 (0.33)
T24	4.05	306	--	H−2→L+3 (-0.38), H−2→L+4 (0.44)
T25	4.11	302	--	H−6→L+1 (0.29), H−5→L+1 (0.42), H−4→L (-0.26)
T26	4.12	301	--	H−6→L (0.28), H−5→L (0.43), H−4→L+1 (-0.28)
T27	4.18	296	--	H→L+5 (0.58)
T28	4.23	293	--	H−7→L+3 (0.42), H−7→L+4 (0.31)
T29	4.25	292	--	H−6→L+1 (0.46), H−4→L (0.38)
T30	4.25	291	--	H−6→L (0.48), H−4→L+1 (0.39)
T31	4.29	289	--	H→L+5 (0.32), H→L+13 (0.44)
T32	4.40	282	--	H−1→L+13 (0.44)
T33	4.41	281	--	H−7→L+1 (0.40), H−3→L+2 (0.30)
T34	4.42	280	--	H−7→L (0.35), H−3→L+4 (0.31), H→L+6 (-0.26)
T35	4.43	280	--	H→L+6 (0.53)
T36	4.46	278	--	H−7→L (0.31), H−3→L+3 (0.48)
T37	4.49	276	--	H−7→L+1 (0.56)
T38	4.50	275	--	H−7→L (-0.26), H−3→L+3 (0.25), H−3→L+4 (0.41)
T39	4.55	272	--	H−11→L+1 (0.22), H−10→L (-0.21), H−5→L+2 (0.30), H→L+10 (-0.25)
T40	4.55	272	--	H−11→L (-0.24), H−10→L+1 (0.27), H−7→L (0.18), H−3→L+11 (-0.20), H→L+12 (0.21)
T41	4.60	269	--	H−6→L+2 (0.34), H−5→L+2 (0.47)
T42	4.61	269	--	H−1→L+5 (0.25), H→L+7 (-0.32), H→L+14 (0.39)
T43	4.62	268	--	H−1→L+5 (0.58)
T44	4.64	267	--	H−2→L+13 (0.50)
T45	4.67	265	--	H−5→L+3 (-0.35), H−5→L+4 (0.43)
T46	4.69	264	--	H→L+8 (0.66)
T47	4.71	263	--	H−4→L+3 (0.56), H−4→L+4 (0.35)
T48	4.71	263	--	H→L+7 (0.56)
T49	4.77	260	--	H−6→L+2 (0.37), H−4→L+4 (0.41)
T50	4.80	258	--	H−6→L+3 (-0.31), H−6→L+4 (0.35), H−4→L+2 (0.38)

Table SI 6: Ir2(dtdk) – Singlet excitations

Excited state	Transition (eV)	Transition λ (nm)	Oscillator strength	Dominant excitations (coefficient)
S1	2.33	532	0.0027	H→L (0.70)
S2	2.75	451	0.0296	H→L+2 (0.69)
S3	2.77	447	0.0000	H→L+1 (0.70)
S4	2.85	435	0.0415	H−1→L (0.68)
S5	3.20	388	0.1129	H−2→L (0.66)
S6	3.24	382	0.0142	H−1→L+1 (0.62)
S7	3.29	377	0.0290	H→L+3 (0.64)
S8	3.29	377	0.0016	H−1→L+2 (0.60)
S9	3.38	366	0.0001	H→L+4 (0.65)
S10	3.47	357	0.0296	H−3→L (0.64)
S11	3.55	349	0.3285	H−4→L (0.54), H−2→L+2 (-0.32)
S12	3.57	347	0.0826	H−2→L+2 (0.58)
S13	3.61	344	0.0003	H−2→L+1 (0.61)
S14	3.68	337	0.0292	H→L+5 (0.68)
S15	3.75	330	0.0024	H−5→L (0.68)
S16	3.77	328	0.0007	H−1→L+3 (0.62)
S17	3.83	324	0.0053	H−1→L+4 (0.62)
S18	3.86	321	0.0217	H−6→L (0.64)
S19	3.91	317	0.0525	H−3→L+1 (0.62)
S20	3.91	317	0.0115	H−3→L+2 (0.67)
S21	3.96	313	0.0305	H−4→L+1 (0.58)
S22	3.98	312	0.0059	H−9→L (-0.35), H−8→L (0.45)
S23	3.99	311	0.0001	H−4→L+2 (0.63)
S24	4.07	305	0.0309	H−2→L+3 (0.60)
S25	4.12	301	0.0158	H−1→L+5 (0.60)
S26	4.14	299	0.0040	H−5→L+1 (0.38), H−2→L+4 (0.43), H−1→L+5 (0.27)
S27	4.25	292	0.0261	H−5→L+1 (0.50), H−2→L+4 (-0.32)
S28	4.25	292	0.0594	H−5→L+2 (0.59)
S29	4.29	289	0.0264	H−6→L+2 (0.48), H−3→L+3 (-0.39)
S30	4.30	289	0.0402	H−6→L+1 (0.57)
S31	4.33	286	0.0079	H−7→L (0.58)
S32	4.39	283	0.0002	H→L+6 (0.70)
S33	4.40	282	0.0263	H−9→L (0.54), H−8→L (0.43)
S34	4.43	280	0.0012	H−4→L+3 (0.69)
S35	4.48	277	0.0459	H−2→L+5 (0.69)
S36	4.50	275	0.0579	H−6→L+2 (0.31), H−3→L+3 (0.49)
S37	4.51	275	0.1274	H−3→L+4 (0.47), H→L+7 (0.30)
S38	4.52	274	0.0266	H−12→L (0.56), H−10→L (-0.36)
S39	4.52	274	0.0018	H−4→L+4 (0.68)
S40	4.56	272	0.0343	H−12→L (0.34), H−10→L (0.53)
S41	4.57	271	0.0725	H→L+7 (0.60)
S42	4.65	266	0.0435	H→L+8 (0.52)
S43	4.65	266	0.0520	H−5→L+3 (0.50)
S44	4.69	265	0.0044	H−11→L (0.43), H−9→L+1 (0.29), H−8→L+1 (-0.43)
S45	4.72	263	0.0193	H−9→L+2 (-0.36), H−8→L+2 (0.55)
S46	4.74	262	0.1452	H−11→L (-0.24), H−5→L+3 (0.39), H→L+9 (0.26)
S47	4.74	262	0.0081	H−3→L+5 (0.59)
S48	4.76	260	0.0035	H−7→L+1 (0.30), H−6→L+3 (0.34), H−5→L+4 (0.41)
S49	4.77	260	0.0164	H−11→L (0.38), H−8→L+1 (0.28), H−1→L+6 (-0.33)
S50	4.77	260	0.0096	H−1→L+6 (0.42)

Table SI 7: Ir2(dtdk) – Triplet excitations

Excited state	Transition (eV)	Transition λ (nm)	Oscillator strength	Dominant excitations (coefficient)
T1	2.21	560	--	H−1→L (0.64)
T2	2.29	541	--	H→L (0.70)
T3	2.50	496	--	H→L+2 (0.66)
T4	2.51	494	--	H→L+1 (0.66)
T5	2.76	449	--	H−2→L (0.56)
T6	2.80	442	--	H−4→L (0.43), H−3→L (0.36)
T7	2.89	429	--	H−3→L+2 (0.27), H−1→L+2 (0.45)
T8	2.91	426	--	H−1→L+1 (0.46)
T9	3.11	399	--	H→L+3 (0.65)
T10	3.16	392	--	H−1→L+2 (0.35), H→L+4 (0.51)
T11	3.24	383	--	H−5→L+2 (-0.29), H−1→L+1 (0.40)
T12	3.25	381	--	H−7→L (-0.31), H−2→L (0.37)
T13	3.26	380	--	H−5→L+1 (0.21), H−2→L+1 (-0.25), H−1→L+2 (-0.27), H→L+4 (0.33)
T14	3.36	369	--	H−2→L+1 (0.55)
T15	3.37	367	--	H−2→L+2 (0.56)
T16	3.46	358	--	H−4→L (-0.39), H−3→L (0.54)
T17	3.52	352	--	H−8→L (0.45)
T18	3.65	340	--	H−1→L+3 (0.50)
T19	3.67	338	--	H−7→L (-0.29), H−5→L (-0.30), H−1→L+5 (0.38)
T20	3.67	338	--	H−4→L+1 (0.27), H−3→L+1 (-0.33), H→L+5 (0.35)
T21	3.69	336	--	H→L+5 (0.54)
T22	3.71	334	--	H−6→L+2 (0.24), H−6→L+3 (0.21), H−5→L+4 (0.21), H−4→L+2 (0.32), H−3→L+2 (-0.25), H−1→L+3 (-0.27)
T23	3.74	332	--	H−1→L+4 (0.54)
T24	3.76	330	--	H−5→L (0.59)
T25	3.79	327	--	H−9→L (0.61)
T26	3.81	325	--	H−11→L (0.47), H−8→L (0.39)
T27	3.83	324	--	H−10→L (0.57)
T28	3.85	322	--	H−6→L+2 (-0.20), H−5→L+1 (-0.26), H−5→L+4 (0.24), H−4→L+3 (-0.20), H−3→L+3 (0.33), H→L+4 (0.22)
T29	3.86	322	--	H−6→L (-0.27), H−6→L+1 (0.27), H−5→L+2 (0.20), H−5→L+3 (-0.18), H−4→L+1 (0.23), H−3→L+4 (-0.24), H−1→L+4 (-0.21)
T30	3.88	320	--	H−4→L+1 (0.47), H−3→L+1 (0.31)
T31	3.89	319	--	H−4→L+2 (0.46), H−3→L+2 (0.34)
T32	3.92	316	--	H−6→L (0.57)
T33	3.96	313	--	H→L+11 (0.41)
T34	3.98	312	--	H−3→L+1 (0.20), H−2→L+3 (-0.31), H→L+9 (-0.23), H→L+10 (0.31)
T35	4.00	310	--	H−2→L+3 (0.54)
T36	4.06	305	--	H−2→L+4 (0.65)
T37	4.23	293	--	H−6→L+2 (-0.33), H−5→L+1 (0.43), H→L+17 (0.27)
T38	4.24	293	--	H−6→L+1 (0.47), H−5→L+2 (-0.46)
T39	4.24	292	--	H−6→L+2 (0.34), H→L+17 (0.42)
T40	4.34	286	--	H−12→L (0.30), H−7→L (0.28), H−4→L+5 (0.32), H−3→L+5 (0.30), H−1→L+5 (0.26)
T41	4.37	284	--	H−4→L+3 (0.33), H−3→L+3 (0.48)
T42	4.39	282	--	H−2→L+5 (0.53)
T43	4.40	282	--	H−2→L+5 (-0.27), H−1→L+17 (0.36)
T44	4.41	281	--	H→L+6 (0.54)
T45	4.41	281	--	H−12→L (0.47), H→L+6 (0.32)
T46	4.45	279	--	H−4→L+3 (0.44)
T47	4.45	278	--	H−3→L+4 (0.49)
T48	4.47	277	--	H−4→L+4 (0.43)
T49	4.50	275	--	H−4→L+4 (0.43)
T50	4.54	273	--	H→L+7 (0.42)

Table SI 8: Ir2(tta) – Singlet excitations

Excited state	Transition (eV)	Transition λ (nm)	Oscillator strength	Dominant excitations (coefficient)
S1	2.31	537	0.0026	H→L (0.70)
S2	2.78	446	0.0299	H→L+1 (0.56), H→L+2 (-0.41)
S3	2.81	441	0.0012	H→L+1 (0.41), H→L+2 (0.56)
S4	2.89	429	0.0156	H−1→L (0.69)
S5	3.23	384	0.1360	H−2→L (0.67)
S6	3.31	374	0.0039	H→L+3 (0.61)
S7	3.35	370	0.0302	H−1→L+1 (0.57)
S8	3.38	367	0.0100	H−1→L+2 (0.50), H→L+4 (0.43)
S9	3.43	361	0.0005	H−3→L (0.70)
S10	3.44	360	0.0040	H−1→L+2 (-0.33), H→L+4 (0.53)
S11	3.64	341	0.0697	H−2→L+2 (0.56)
S12	3.68	337	0.0102	H−4→L (-0.38), H−2→L+1 (0.48)
S13	3.73	333	0.0156	H−4→L (0.53)
S14	3.79	327	0.0111	H−5→L (0.63)
S15	3.86	321	0.0017	H−1→L+3 (0.54)
S16	3.89	319	0.0206	H−3→L+1 (0.42), H−3→L+2 (0.41), H−1→L+4 (0.36)
S17	3.96	313	0.0119	H−3→L+1 (0.43), H−1→L+3 (-0.35), H−1→L+4 (-0.26)
S18	3.97	312	0.0410	H−6→L (0.30), H−3→L+2 (-0.30), H−1→L+4 (0.43)
S19	4.00	310	0.0262	H−8→L (0.40), H−7→L (-0.33), H−1→L+4 (0.27)
S20	4.04	307	0.2458	H−6→L (0.56)
S21	4.12	301	0.0153	H−2→L+3 (0.58)
S22	4.17	297	0.0174	H−4→L+1 (0.36), H−4→L+2 (0.37), H−2→L+4 (0.39)
S23	4.21	294	0.0077	H−5→L+1 (0.49), H−4→L+1 (0.44)
S24	4.25	292	0.0400	H−5→L+2 (0.55)
S25	4.27	291	0.0589	H−5→L+2 (0.41), H−4→L+2 (-0.41)
S26	4.31	288	0.0025	H→L+5 (0.65)
S27	4.33	287	0.0485	H−6→L+1 (-0.28), H−5→L+1 (0.25), H−3→L+3 (0.27), H−2→L+4 (0.35)
S28	4.37	283	0.0004	H−6→L+1 (0.36), H−6→L+2 (-0.32), H−3→L+3 (0.45)
S29	4.39	282	0.0204	H−6→L+1 (0.46), H−6→L+2 (0.36), H−3→L+4 (0.29)
S30	4.44	279	0.0076	H−8→L (0.45), H−7→L (0.50)
S31	4.49	276	0.0037	H→L+6 (0.68)
S32	4.51	275	0.0894	H−6→L+1 (-0.20), H−3→L+3 (0.31), H−3→L+4 (0.30), H−2→L+4 (-0.19)
S33	4.55	273	0.1069	H−6→L+2 (-0.33), H−3→L+4 (0.38), H→L+9 (0.23)
S34	4.56	272	0.0031	H−10→L (0.62)
S35	4.62	268	0.0807	H−4→L+3 (-0.31), H−3→L+4 (0.29), H→L+7 (0.42)
S36	4.67	265	0.0160	H−4→L+3 (0.44), H→L+7 (0.46)
S37	4.68	265	0.0485	H→L+8 (0.36), H→L+9 (0.24), H→L+15 (0.35)
S38	4.73	262	0.0661	H−5→L+3 (0.40), H−4→L+3 (0.30), H−4→L+4 (0.26)
S39	4.74	261	0.0707	H−9→L (0.54)
S40	4.75	261	0.0606	H−5→L+3 (0.49)
S41	4.79	259	0.0848	H−4→L+4 (0.57)
S42	4.82	257	0.0115	H−8→L+1 (0.42), H−7→L+1 (-0.41)
S43	4.83	257	0.0501	H−5→L+4 (0.52)
S44	4.84	256	0.0072	H−8→L+2 (0.45), H−7→L+2 (-0.43)
S45	4.85	256	0.0291	H−5→L+4 (-0.24), H−1→L+8 (0.21), H−1→L+11 (-0.23), H−1→L+15 (0.32)
S46	4.89	254	0.0005	H−11→L (0.58)
S47	4.89	254	0.0038	H−6→L+3 (0.54)
S48	4.91	252	0.0005	H−6→L+3 (0.29), H→L+8 (0.41), H→L+10 (-0.25)
S49	4.95	250	0.0077	H−1→L+5 (0.51)
S50	4.98	249	0.0141	H−6→L+4 (0.66)

Table SI 9: Ir2(tta) – Triplet excitations

Excited state	Transition (eV)	Transition λ (nm)	Oscillator strength	Dominant excitations (coefficient)
T1	2.26	550	--	H→L (0.66)
T2	2.32	534	--	H−1→L (0.58)
T3	2.52	492	--	H→L+1 (0.56), H→L+2 (-0.34)
T4	2.53	489	--	H→L+1 (0.34), H→L+2 (0.56)
T5	2.73	455	--	H−2→L (0.52)
T6	2.93	423	--	H−2→L+1 (-0.25), H−1→L+1 (-0.27), H−1→L+2 (0.35)
T7	2.95	420	--	H−2→L+1 (0.26), H−1→L+1 (0.30), H−1→L+2 (0.32)
T8	3.14	394	--	H→L+3 (0.64)
T9	3.16	393	--	H−6→L (0.43), H−2→L (0.39)
T10	3.21	387	--	H→L+4 (0.53)
T11	3.28	378	--	H−1→L+1 (0.36), H−1→L+2 (0.22)
T12	3.29	376	--	H−4→L+2 (-0.26), H−3→L+2 (0.25), H−1→L+2 (0.23), H→L+4 (0.33)
T13	3.40	364	--	H−3→L (0.41), H−2→L+1 (-0.39)
T14	3.42	362	--	H−3→L (0.45), H−2→L+1 (0.30)
T15	3.46	359	--	H−2→L+2 (0.60)
T16	3.49	355	--	H−7→L (0.44), H−5→L (-0.29)
T17	3.68	337	--	H−3→L+1 (0.43)
T18	3.69	336	--	H−3→L+2 (0.41), H−1→L+3 (-0.25)
T19	3.70	335	--	H−4→L (0.55)
T20	3.72	333	--	H−9→L (0.34), H−8→L (0.36), H−7→L (0.33), H−4→L (-0.25)
T21	3.77	329	--	H−1→L+3 (0.49)
T22	3.78	328	--	H−8→L (0.49)
T23	3.81	326	--	H−3→L+4 (0.25), H−1→L+4 (0.33)
T24	3.86	321	--	H−6→L (0.26), H−5→L (0.40), H−1→L+4 (0.36)
T25	3.86	321	--	H−5→L+1 (0.21), H−4→L+2 (-0.24), H−3→L+3 (0.34), H−1→L+3 (-0.27), H→L+4 (-0.22)
T26	3.90	318	--	H−6→L (-0.18), H−5→L (-0.27), H−5→L+1 (-0.25), H−4→L+2 (-0.24), H−1→L+4 (0.30)
T27	3.95	314	--	H→L+11 (0.42)
T28	3.99	311	--	H−1→L+4 (0.25), H→L+9 (0.41)
T29	4.07	305	--	H−2→L+3 (0.59)
T30	4.14	299	--	H−2→L+4 (0.60)
T31	4.17	297	--	H−4→L+1 (0.58)
T32	4.21	295	--	H−5→L+2 (0.48)
T33	4.23	293	--	H−5→L+2 (0.27), H→L+15 (0.42)
T34	4.27	291	--	H−6→L+2 (0.41), H−4→L+2 (-0.25), H→L+5 (0.26)
T35	4.28	290	--	H→L+5 (0.55)
T36	4.34	286	--	H−6→L+1 (0.63)
T37	4.40	282	--	H−1→L+5 (0.46)
T38	4.42	281	--	H−1→L+15 (0.41)
T39	4.44	279	--	H−10→L (0.51), H→L+5 (0.32)
T40	4.45	279	--	H−3→L+3 (0.35)
T41	4.47	278	--	H−4→L+3 (-0.25), H−3→L+4 (0.42)
T42	4.50	275	--	H→L+6 (0.63)
T43	4.52	274	--	H→L+7 (-0.20), H→L+17 (0.32)
T44	4.56	272	--	H−13→L+1 (-0.18), H−5→L+3 (-0.18), H→L+7 (-0.20), H→L+11 (-0.16), H→L+17 (0.25)
T45	4.58	271	--	H−13→L+2 (0.20), H−12→L+2 (0.24), H−6→L+2 (-0.17), H→L+7 (0.17), H→L+11 (-0.15), H→L+14 (-0.19), H→L+17 (-0.15)
T46	4.64	267	--	H−2→L+15 (0.43)
T47	4.69	264	--	H→L+7 (0.58)
T48	4.70	264	--	H−5→L+3 (0.35), H−4→L+3 (0.33), H−4→L+4 (0.31)
T49	4.74	261	--	H−8→L+1 (-0.40), H−7→L+1 (0.42)
T50	4.76	260	--	H−5→L+4 (0.40)

Table SI 10: Ir2(BPhen) – Singlet excitations

Excited state	Transition (eV)	Transition λ (nm)	Oscillator strength	Dominant excitations (coefficient)
S1	2.21	561	0.0004	H→L (0.70)
S2	2.39	519	0.0008	H→L+1 (0.70)
S3	2.96	418	0.0020	H−2→L (0.62)
S4	2.98	417	0.0499	H−1→L (0.68)
S5	3.00	413	0.0363	H→L+2 (0.70)
S6	3.10	400	0.0095	H→L+3 (0.64)
S7	3.11	399	0.0290	H−1→L+1 (0.69)
S8	3.13	396	0.0176	H−3→L (0.45), H−2→L+1 (-0.40)
S9	3.22	385	0.1160	H−3→L (0.44), H−2→L+1 (0.51)
S10	3.28	378	0.0674	H−3→L+1 (0.67)
S11	3.31	374	0.0015	H−4→L (0.62)
S12	3.41	364	0.0531	H−5→L (0.69)
S13	3.45	359	0.0102	H→L+4 (0.68)
S14	3.46	358	0.0521	H−4→L+1 (0.65)
S15	3.53	351	0.0265	H−5→L+1 (0.69)
S16	3.68	337	0.0001	H→L+5 (0.69)
S17	3.74	332	0.0049	H→L+6 (0.68)
S18	3.74	331	0.0067	H−6→L (0.58)
S19	3.75	330	0.0135	H−6→L (0.35), H−1→L+2 (0.52)
S20	3.76	330	0.0162	H−2→L+2 (0.47), H−1→L+3 (0.35)
S21	3.80	327	0.1379	H−6→L+1 (0.66)
S22	3.84	322	0.0754	H−2→L+2 (-0.37), H−1→L+3 (0.54)
S23	3.87	320	0.0172	H−3→L+2 (0.36), H−2→L+3 (0.46), H−1→L+2 (-0.30)
S24	3.93	316	0.0212	H−7→L (0.56)
S25	3.95	314	0.0007	H−9→L+1 (0.39), H−8→L (0.58)
S26	3.96	313	0.0018	H−9→L (0.49), H−8→L+1 (0.31), H−7→L (-0.37)
S27	3.97	312	0.1312	H−7→L+1 (0.61)
S28	4.00	310	0.0655	H−3→L+3 (0.62)
S29	4.00	310	0.0065	H−7→L+1 (-0.28), H−3→L+2 (0.46), H−2→L+3 (-0.33)
S30	4.07	305	0.0012	H→L+7 (0.69)
S31	4.10	303	0.0290	H−1→L+4 (0.49)
S32	4.12	301	0.0030	H−9→L (-0.39), H−8→L+1 (0.58)
S33	4.12	301	0.0031	H−9→L+1 (0.57), H−8→L (-0.39)
S34	4.12	301	0.0283	H−4→L+2 (0.49), H−2→L+4 (-0.33)
S35	4.20	296	0.0003	H−5→L+2 (0.54), H−4→L+3 (0.37)
S36	4.21	294	0.0128	H−5→L+3 (0.46), H−4→L+2 (0.29), H−2→L+4 (0.35)
S37	4.22	294	0.0003	H−10→L (0.43)
S38	4.27	290	0.0252	H−5→L+3 (0.41), H−2→L+4 (-0.38), H−1→L+5 (0.28)
S39	4.28	289	0.0131	H−10→L (-0.36), H−4→L+3 (-0.26), H−1→L+4 (0.39)
S40	4.33	286	0.0083	H−3→L+4 (0.60)
S41	4.34	286	0.0107	H−11→L (0.38), H−10→L+1 (0.58)
S42	4.37	284	0.0001	H−12→L (0.69)
S43	4.44	279	0.0078	H−2→L+5 (0.45), H−1→L+6 (0.45)
S44	4.46	278	0.0476	H−2→L+6 (0.40), H−1→L+5 (0.40)
S45	4.47	277	0.0143	H−13→L (0.60)
S46	4.52	274	0.0208	H−4→L+4 (0.57)
S47	4.53	273	0.0054	H−5→L+4 (0.42), H−3→L+6 (0.27), H−1→L+6 (-0.32)
S48	4.54	273	0.0033	H−12→L+1 (0.64)
S49	4.55	272	0.1509	H−3→L+5 (-0.37), H−2→L+6 (0.40)
S50	4.57	272	0.0906	H−3→L+5 (0.54), H−1→L+5 (-0.35)

Table SI 11: Ir2(BPhen) – Triplet excitations

Excited state	Transition (eV)	Transition λ (nm)	Oscillator strength	Dominant excitations (coefficient)
T1	2.18	569	--	H→L (0.70)
T2	2.38	522	--	H→L+1 (0.70)
T3	2.54	488	--	H−3→L+1 (0.38), H−2→L (0.23)
T4	2.65	468	--	H−3→L (0.50), H−1→L (0.36)
T5	2.67	464	--	H→L+2 (0.60)
T6	2.73	454	--	H→L+3 (0.55)
T7	2.91	426	--	H−2→L (0.53)
T8	3.02	411	--	H−1→L (0.57)
T9	3.09	401	--	H−2→L+1 (-0.26), H−2→L+3 (0.27), H−1→L+2 (-0.26), H→L+3 (0.34)
T10	3.10	400	--	H−2→L+2 (0.30), H−1→L+1 (0.30), H−1→L+3 (-0.24), H→L+2 (0.31)
T11	3.12	397	--	H−4→L+1 (0.28), H−2→L+1 (0.47)
T12	3.14	394	--	H−1→L+1 (0.56)
T13	3.25	381	--	H−6→L (0.43), H−5→L (-0.34), H−3→L (0.26)
T14	3.27	379	--	H−4→L (0.46), H−3→L+1 (-0.28), H−2→L (-0.34)
T15	3.28	378	--	H→L+4 (0.54)
T16	3.37	368	--	H−6→L+1 (0.35), H−4→L (0.29), H−3→L+1 (0.39)
T17	3.40	365	--	H→L+5 (0.48)
T18	3.42	362	--	H−6→L (0.33), H−5→L (0.39), H−4→L+1 (0.31)
T19	3.43	362	--	H−10→L+1 (0.34), H−7→L (0.41)
T20	3.44	361	--	H−4→L+1 (0.47)
T21	3.52	352	--	H−5→L+1 (0.36), H−4→L+2 (0.36)
T22	3.55	350	--	H−10→L (-0.23), H−6→L (0.21), H−4→L+3 (0.32), H−3→L+2 (-0.26), H−2→L+3 (0.20)
T23	3.55	349	--	H−10→L (0.32), H−7→L+1 (0.29), H−4→L+3 (0.19), H−3→L+2 (-0.20)
T24	3.56	348	--	H−5→L+1 (0.45), H−4→L+2 (-0.28)
T25	3.62	342	--	H→L+4 (0.37), H→L+6 (0.47)
T26	3.65	339	--	H−5→L+2 (0.29), H−1→L+2 (0.47)
T27	3.66	339	--	H−11→L (0.38), H−6→L+1 (0.25), H−1→L+3 (-0.28)
T28	3.68	337	--	H−1→L+3 (0.41)
T29	3.75	331	--	H−9→L+1 (0.44), H−8→L (0.46)
T30	3.76	330	--	H−3→L+2 (0.50), H−2→L+3 (0.37)
T31	3.76	330	--	H−9→L (0.49), H−8→L+1 (0.42)
T32	3.78	328	--	H−3→L+3 (0.47), H−2→L+2 (0.35)
T33	3.83	324	--	H−11→L+1 (0.50)
T34	3.89	319	--	H−1→L+4 (0.27), H→L+5 (0.39)
T35	3.89	319	--	H−3→L+3 (0.37), H→L+6 (0.27)
T36	3.98	312	--	H−10→L (-0.34), H−7→L+1 (0.42)
T37	4.00	310	--	H−11→L (0.32), H−7→L (0.43)
T38	4.03	308	--	H−1→L+4 (0.22), H→L+7 (-0.34), H→L+16 (0.35)
T39	4.05	306	--	H−10→L (0.28), H−9→L+1 (-0.21), H−8→L (0.22), H−8→L+9 (0.19), H→L+7 (0.27)
T40	4.06	305	--	H−10→L+1 (0.36), H−9→L (0.23), H−9→L+9 (0.23), H−6→L+1 (0.30)
T41	4.07	305	--	H→L+7 (0.54)
T42	4.09	303	--	H−4→L+2 (0.21), H−4→L+4 (-0.19), H−1→L+5 (0.18), H→L+12 (-0.22), H→L+14 (0.30)
T43	4.11	301	--	H−11→L+1 (-0.33), H−7→L+1 (-0.24), H−3→L+4 (0.33), H−1→L+4 (0.26)
T44	4.13	300	--	H−9→L+1 (0.46), H−8→L (-0.38)
T45	4.14	299	--	H−9→L (-0.38), H−8→L+1 (0.45)
T46	4.14	299	--	H−2→L+4 (0.48)
T47	4.18	297	--	H−5→L+2 (0.43), H−4→L+3 (0.44)
T48	4.19	296	--	H−5→L+3 (0.51), H−4→L+2 (0.34)
T49	4.22	293	--	H−12→L (0.61)
T50	4.24	292	--	H→L+17 (0.22), H→L+18 (0.36)

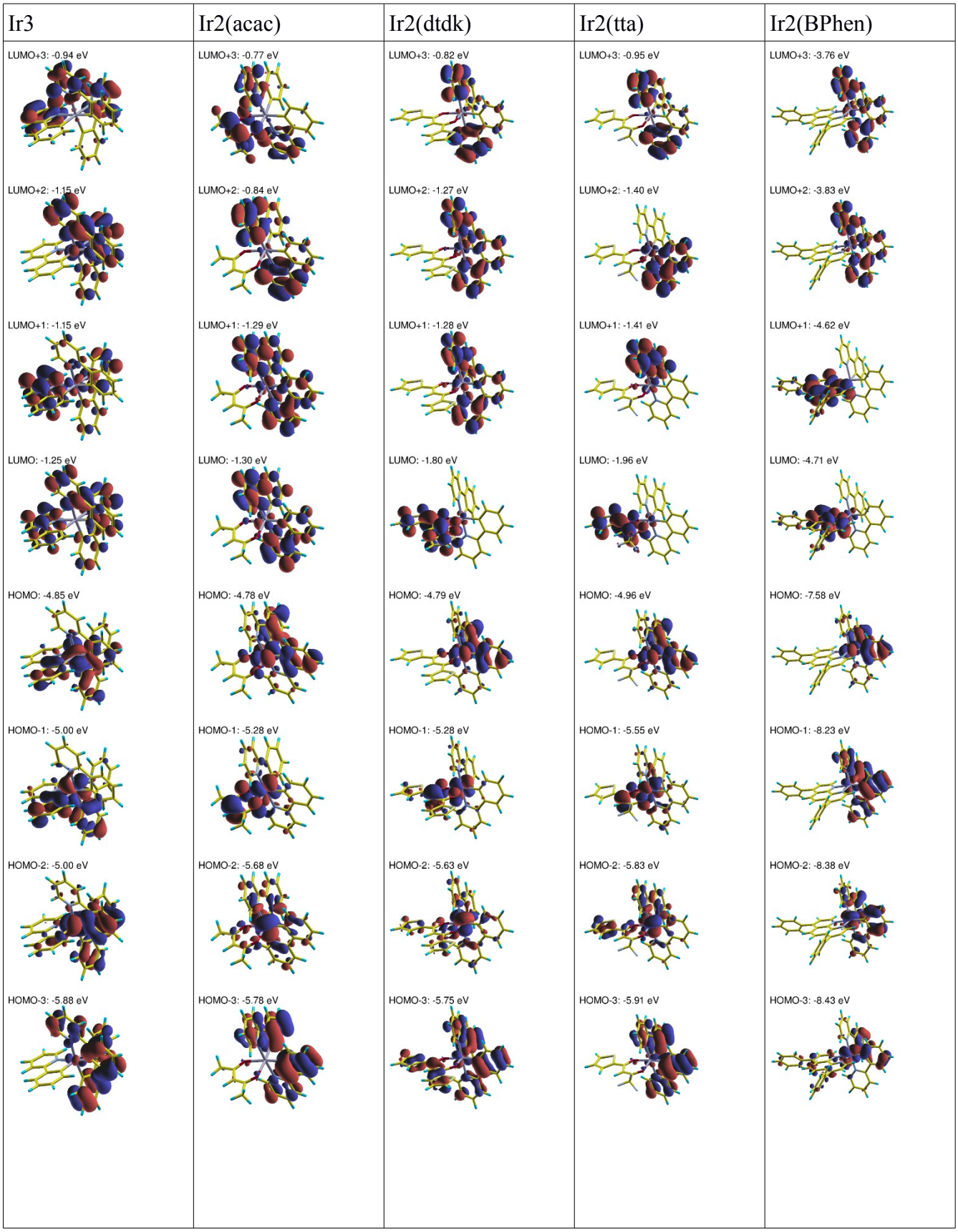


Figure SI 9: Frontier molecular orbitals calculated at the B3LYP level. The value of the isosurface is ±0.03 bohr^{-3}. Blue and red denote positive and negative values, respectively.

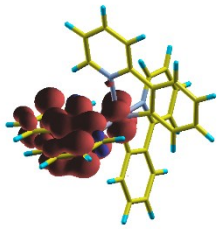
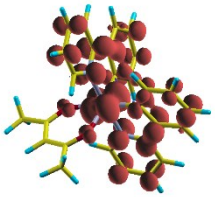
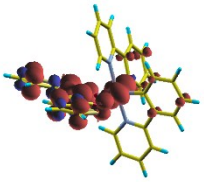
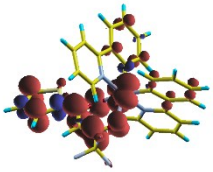
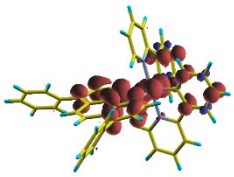
Ir3	Ir2(acac)	Ir2(dtdk)	Ir2(tta)	Ir2(BPhen)
				

Figure SI 10: Spin density in the triplet geometry, from B3LYP calculations. The value of the isosurface is ±0.003 bohr^{-3}. Red and blue denote positive and negative values.

Table SI 12: Mulliken charge and spin on the Ir atom of the molecules relaxed in the triplet ground state.

Complex	**Ir Mulliken charge**	**Ir Mulliken spin**
Ir3	−0.2206	0.3840
Ir2(acac)	+0.0288	0.5858
Ir2(dtdk)	+0.0756	0.4830
Ir2(tta)	+0.0663	0.5488
Ir2(BPhen)	+0.1127	0.5499

Table SI 13: Distance in Å between Ir and its first neighbours in the S0 and T1 geometry.

Complex	**S0 geometry**	**T1 geometry**
Ir3	C(2.031), C(2.031), C(2.031), N(2.169), N(2.169), N(2.170)	C(1.988), C(2.028), C(2.045), N(2.132), N(2.182), N(2.196)
Ir2(acac)	C(2.005), C(2.005), N(2.058), N(2.058), O(2.180), O(2.180)	C(1.980), C(1.980), N(2.061), N(2.061), O(2.186), O(2.186)
Ir2(dtdk)	C(2.004), C(2.004), N(2.057), N(2.058), O(2.180), O(2.180)	C(2.018), C(2.022), N(2.052), N(2.074), O(2.091), O(2.100)
Ir2(tta)	C(2.003), C(2.004), N(2.059), N(2.061), O(2.177), O(2.193)	C(2.021), C(2.021), N(2.052), N(2.078), O(2.088), O(2.090)
Ir2(BPhen)	C(2.025), C(2.025), N(2.076), N(2.076), N(2.193), N(2.193)	C(2.004), C(2.004), N(2.073), N(2.073), N(2.171), N(2.171)

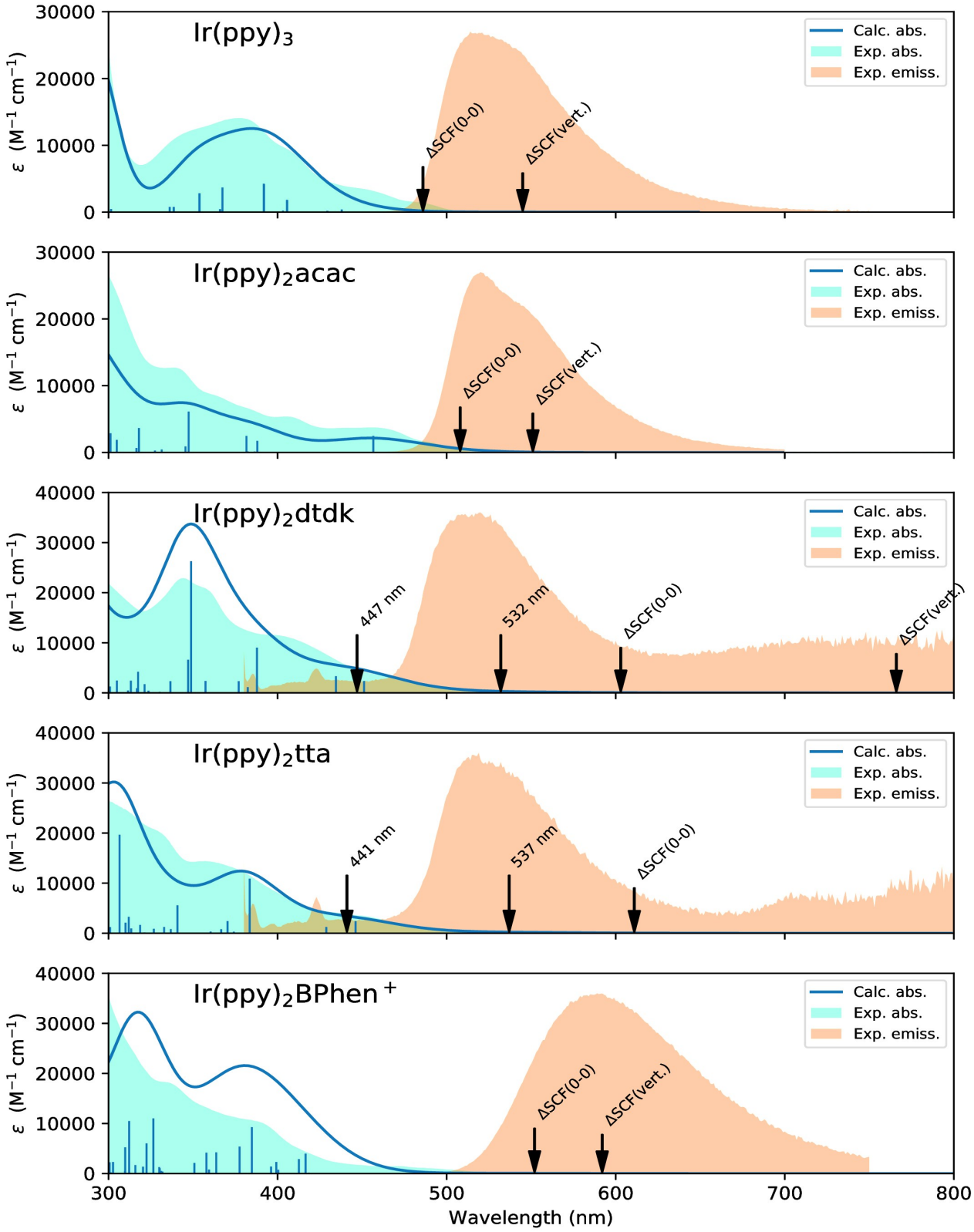


Figure SI 11: Calculated absorption spectra and emission lines from (TD)DFT. The calculated emission wavelengths are marked by the vertical arrows. The arrows denoted by "ΔSCF" are the estimate phosphorescence (T1 → S0) wavelengths. In the case of **Ir2dtdk** and **Ir2tta**, we also report the wavelengths of the low-lying singlets MLLCT transitions, that can be thermally populated from their respective triplets.