PCCP

Electronic Supplementary Information

Influences of bulky substituent on the photophysical properties of homoleptic Iridium(III) complexes

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Contents

General Procedures: All compounds were synthesized in a dry N_2 atmosphere. All solvent used were distilled over sodium–benzophenone or calcium chloride under nitrogen prior to use. All solvents were stored over molecular sieves. Glassware, syringes, magnetic stirring bars, and needles were dried in a convection oven for over 4 h. Reactions were checked using thin-layer chromatography (TLC; Merck Co.). The spots developed to TLC were identified under UV light at 254 or 365 nm. Column chromatography was performed on 60 G silica gel (particle size 5−40 μm; Merck Co.). The ^{1}H-NMR spectra were recorded on a Varian Mercury 300 spectrometer (operating at 300.1 MHz). All proton chemical shifts were measured relative to internal residual benzene from the lock solvent (99.5% $CDCl_3$). High Resolution Tandem Mass Spectrometry (Jeol LTD JMS-HX 110/110A) was performed at the Korean Basic Science Institute (Seoul). 2-(2-bromophenyl)pyridine,[1] Ph-ppy,[2] MePh-ppy,[2] Me-ppy,[3] and $Ir(ppy)_3$[4] were synthesized using previously reported methods.

Reference

1 Y. L. Rao, H. Amarne, S. B. Zhao, T. M. McCormick, S. Martic, Y. Sun, R. Y. Wang and S. Wang, *J. Am. Chem. Soc*., 2008, **130**, 12898–12900.
2 W. Y. Yu, W. N. Sit, Z. Zhou and A. S. Chan, *Org. Lett*., 2009, **11**, 3174–3177.
3 A. J. Paterson, C. J. Heron, C. L. McMullin, M. F. Mahon, N. J. Press and C. G. Frost, *Org. Biomol. Chem*., 2017, **15**, 5993–6000.
A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau and M. E. Thompson, *J. Am. Chem. Soc*., 2003, **125**, 7377–7387.

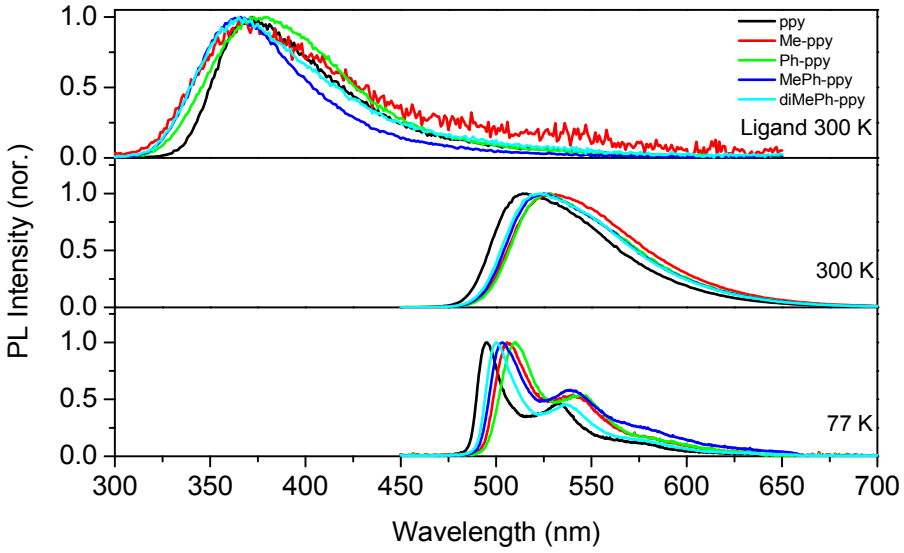

Fig. S1 (top) The emission spectra of **ppy**, **Me-ppy**, **Ph-ppy**, **MePh-ppy**, and **diMePh-ppy** in CH_2Cl_2 measured at 300 K (λ_{ex} = 275 nm), (middle) the emission spectra **Ir(ppy)$_3$**, **Ir(Me-ppy)$_3$**, **Ir(Ph-ppy)$_3$**, **Ir(MePh-ppy)$_3$**, and **Ir(diMePh-ppy)$_3$** in CH_2Cl_2 measured at 300 K (λ_{ex} = 300 nm) and (bottom) the emission spectra in MTHF at 77 K (λ_{ex} = 355 nm).

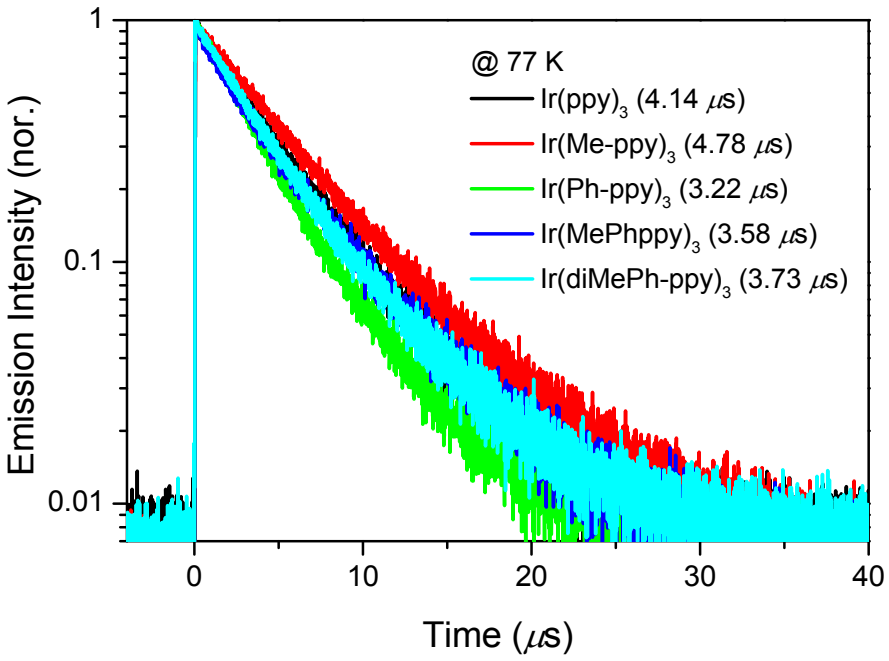

Fig. S2 Phosphorescence emission decay profiles for **Ir(ppy)$_3$**, **Ir(Me-ppy)$_3$**, **Ir(Ph-ppy)$_3$**, **Ir(MePh-ppy)$_3$**, and **Ir(diMePh-ppy)$_3$** in MTHF measured at 77 K (λ_{ex} = 355 nm).

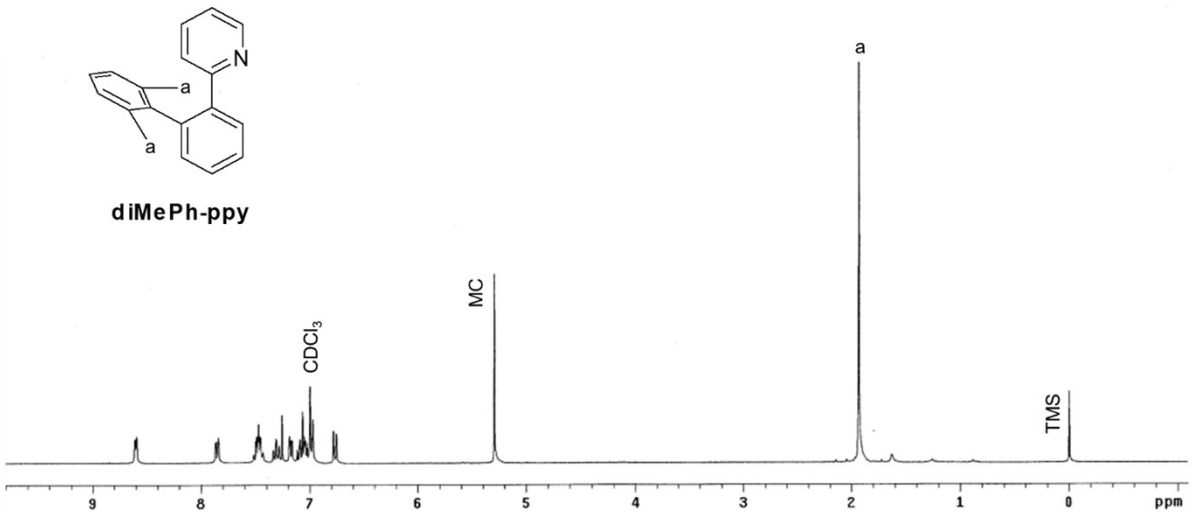

Fig. S3 ^{1}H-NMR spectrum of **diMePh-ppy** in $CDCl_3$

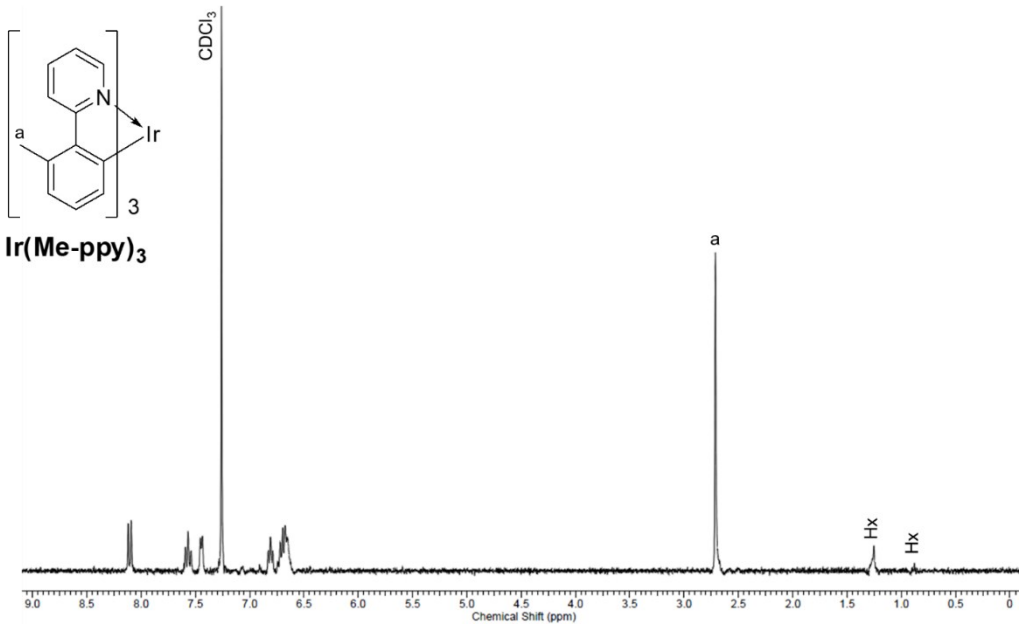

Fig. S4 ^{1}H-NMR spectrum of **Ir(Me-ppy)$_3$** in $CDCl_3$.

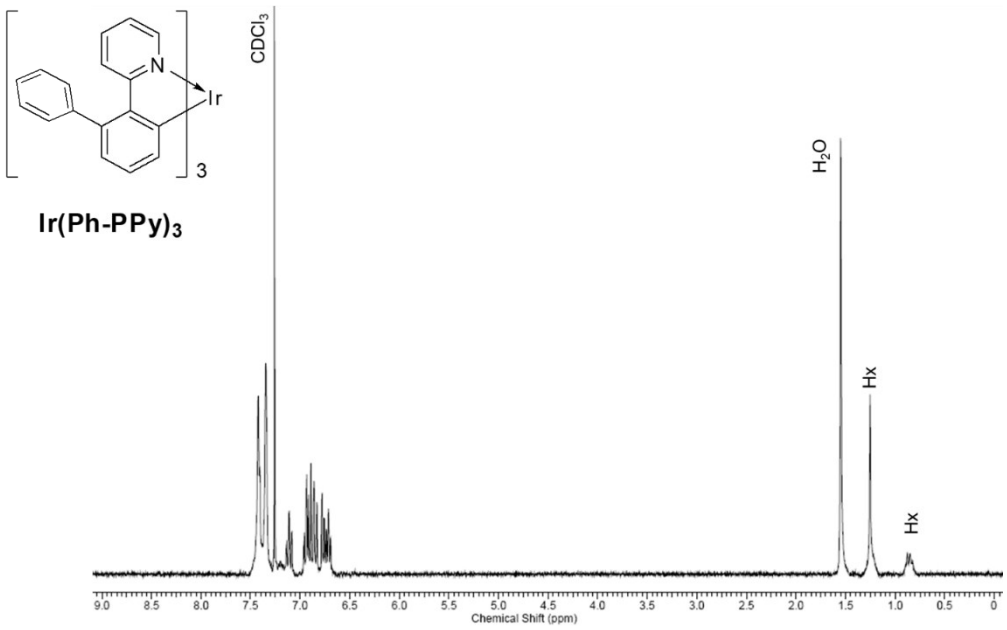

Fig. S5 ^{1}H-NMR spectrum of **Ir(Ph-ppy)$_3$** in $CDCl_3$.

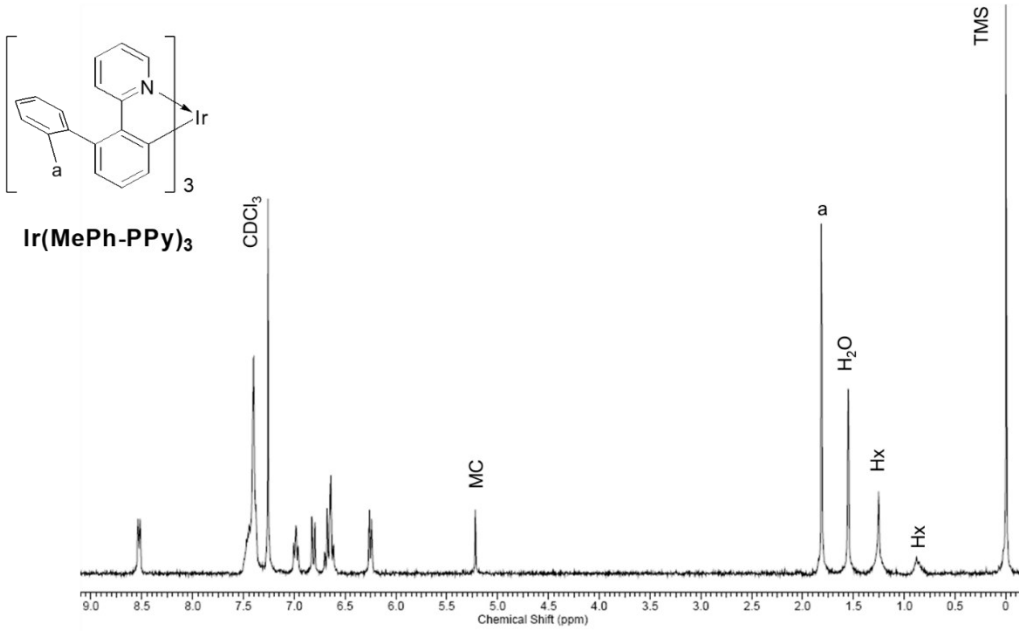

Fig. S6 ^{1}H-NMR spectrum of **Ir(MePh-ppy)$_3$** in $CDCl_3$.

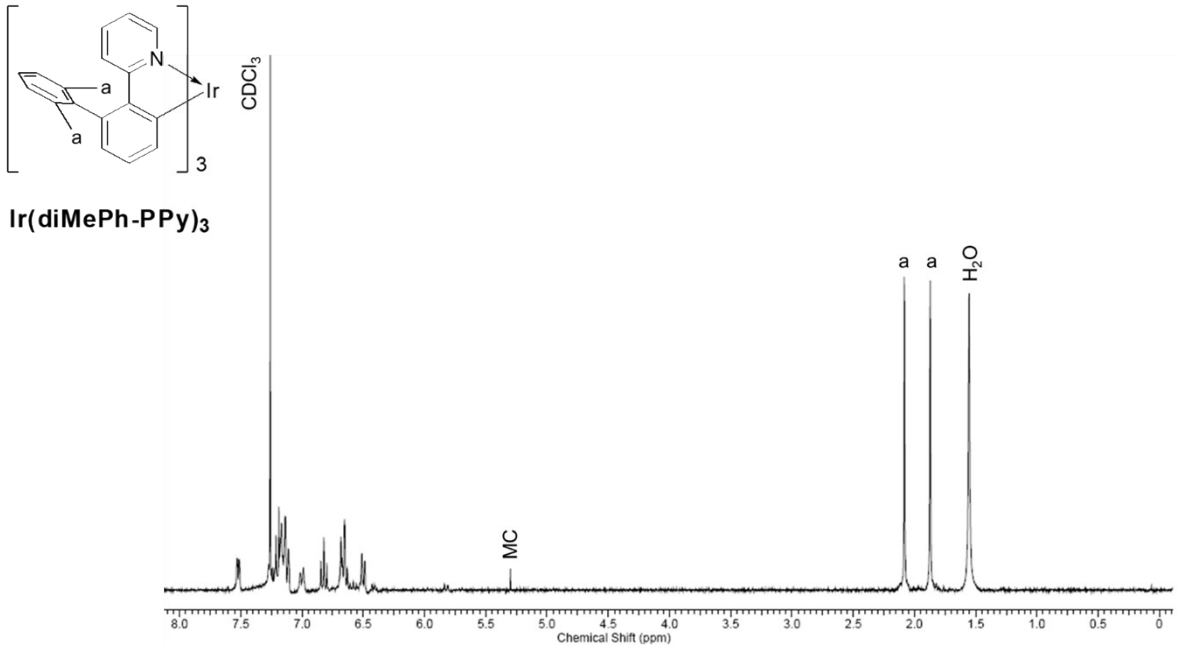

Fig. S7 ^{1}H-NMR spectrum of **Ir(diMePh-ppy)$_3$** in $CDCl_3$.

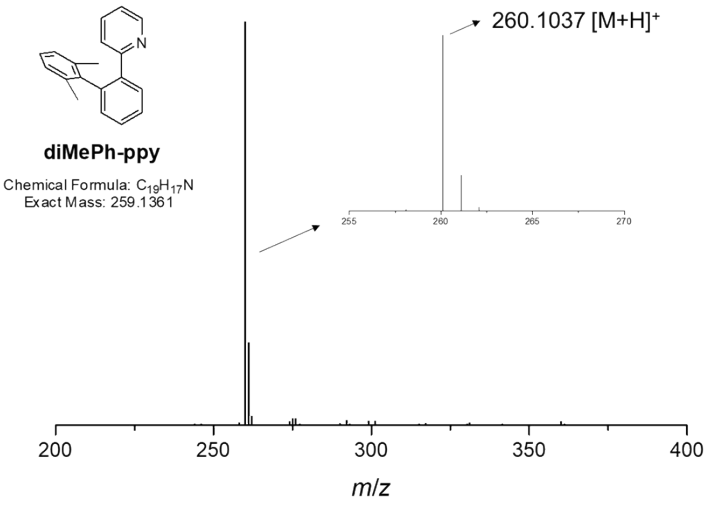

Fig. S8 ESI-Mass spectrum of **diMePh-ppy**.

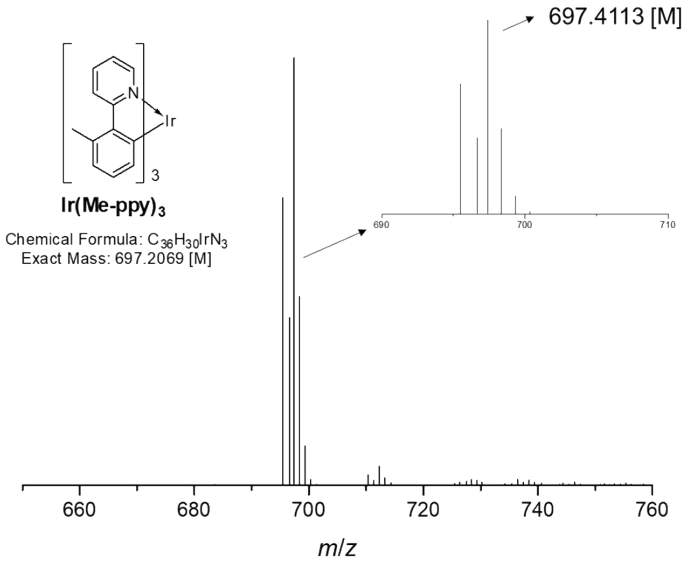

Fig. S9 ESI-Mass spectrum of **Ir(Me-ppy)$_3$**.

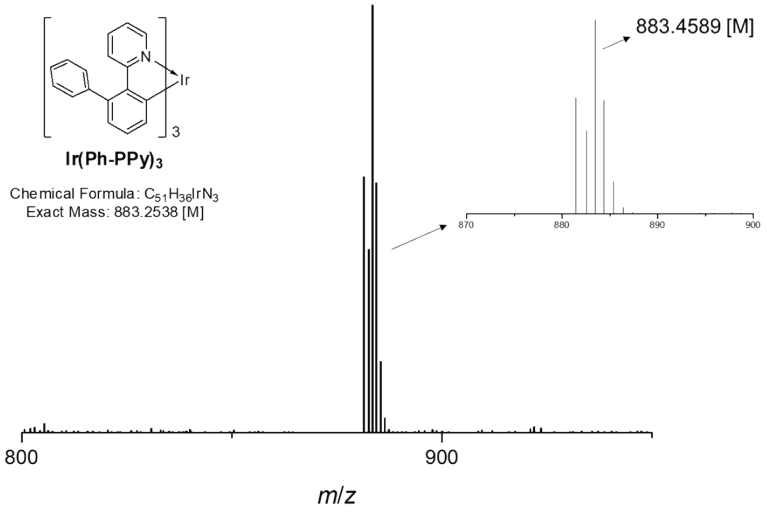

Fig. S10 ESI-Mass spectrum of **Ir(Ph-ppy)$_3$**.

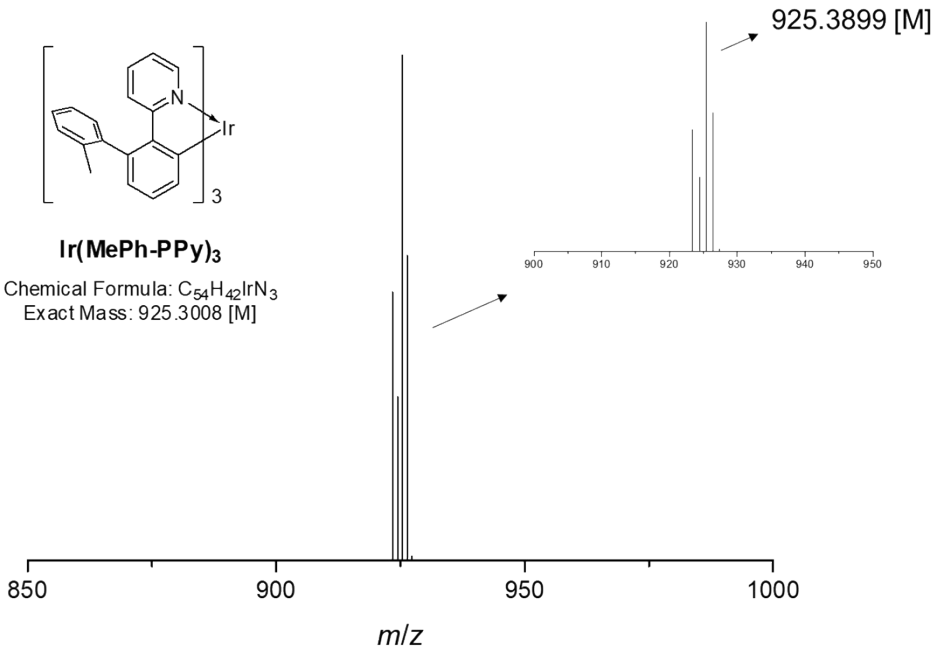

Fig. S11 ESI-Mass spectrum of **Ir(MePh-ppy)$_3$**.

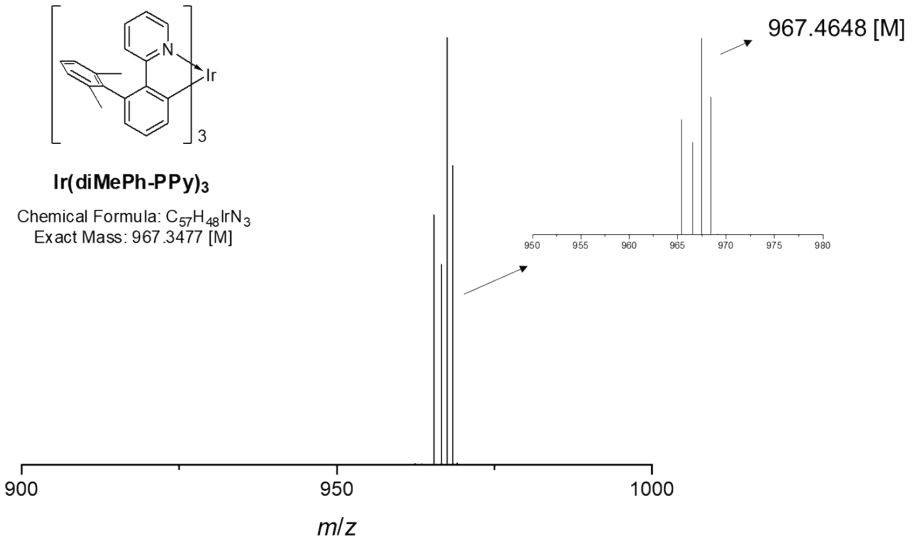

Fig. S12 ESI-Mass spectrum of **Ir(diMePh-ppy)$_3$**.

Table S1. Electrochemical and computed molecular orbital energy data of **Ir(ppy)$_3$**, **Ir(Me-ppy)$_3$**, **Ir(Ph-ppy)$_3$**, **Ir(MePh-ppy)$_3$**, and **Ir(diMePh-ppy)$_3$**

complex	Experimetal value				DFT calculations		
	$E_{1/2}^{ox}$ (V)	$E_{HOMO}{}^{a}$ (eV)	$E_{LUMO}{}^{b}$ (eV)	$E_g{}^{c}$ (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
Ir(ppy)$_3$	0.38	−5.18	−2.67	2.51	−5.15	−1.38	3.77
Ir(Me-ppy)$_3$	0.28	−5.08	−2.63	2.45	−5.07	−1.34	3.73
Ir(Ph-ppy)$_3$	0.37	−5.17	−2.73	2.44	−5.13	−1.52	3.61
Ir(MePh-ppy)$_3$	0.34	−5.14	−2.67	2.47	−5.14	−1.45	3.68
Ir(diMePh-ppy)$_3$	0.33	−5.13	−2.64	2.49	−5.14	−1.40	3.74

The HOMO (E_{HOMO}), LUMO (E_{LUMO}), and Energy gap (E_g) value were evaluated according to the following eq.: ${}^{a}E_{HOMO}$ (eV) = − (E_{ox} − E_{Fc/Fc^+} + 4.8), ${}^{b}E_{LUMO}$ (eV) = − (E_{HOMO} + E_g), and ${}^{c}E_g{}^{opt}$ = 1240/$\lambda_{77\ K}$

Table S2 Transitions related to $S_0 \rightarrow T_1$ and $S_0 \rightarrow S_1$. The energies (λ_{cal} and E_{cal}), oscillator strengths (f), orbital contributions (>20%), and assignments of for **Ir(ppy)$_3$**, **Ir(Me-ppy)$_3$**, **Ir(Ph-ppy)$_3$**, **Ir(MePh-ppy)$_3$**, and **Ir(diMePh-ppy)$_3$** evaluated by TD-DFT calculations

	State	λ_{cal} (E_{cal})	f	Orbital contribution	Assignment
Ir(ppy)$_3$	T_1	470 nm (2.63 eV)	0	HOMO->LUMO (62%)	MLCT,[a] ILCT[b]
	S_1	428 nm (2.89 eV)	0.006	HOMO->LUMO (97%)	MLCT, ILCT
	S_2	421 nm (2.94 eV)	0.0024	HOMO->L+1 (96%)	MLCT, ILCT
	S_3	421 nm (2.94 eV)	0.0024	HOMO->L+2 (96%)	MLCT, ILCT, LLCT[c]
Ir(Me-ppy)$_3$	T_1	473 nm (2.62 eV)	0	HOMO->LUMO (62%)	MLCT, ILCT
	S_1	433 nm (2.86 eV)	0.0046	HOMO->LUMO (97%)	MLCT, ILCT
	S_2	431 nm (2.87 eV)	0.0016	HOMO->L+2 (89%)	MLCT, ILCT, LLCT
	S_3	431 nm (2.87 eV)	0.0016	HOMO->L+1 (89%)	MLCT, ILCT, LLCT
Ir(Ph-ppy)$_3$	T_1	473 nm (2.62 eV)	0	HOMO->LUMO (71%)	MLCT, ILCT
	S_1	435 nm (2.85 eV)	0.0044	HOMO->LUMO (98%)	MLCT, ILCT
	S_2	421 nm (2.94 eV)	0.0025	HOMO->L+1 (65%), HOMO->L+2 (32%)	MLCT, ILCT, LLCT
	S_3	421 nm (2.94 eV)	0.0025	HOMO->L+1 (32%), HOMO->L+2 (65%)	MLCT, ILCT, LLCT
Ir(MePh-ppy)$_3$	T_1	473 nm (2.62 eV)	0	HOMO->LUMO (71%)	MLCT, ILCT
	S_1	435 nm (2.85 eV)	0.0044	HOMO->LUMO (98%)	MLCT, ILCT
	S_2	421 nm (2.94 eV)	0.0025	HOMO->L+1 (67%), HOMO->L+2 (30%)	MLCT, ILCT
	S_3	421 nm (2.94 eV)	0.0025	HOMO->L+1 (30%), HOMO->L+2 (67%)	MLCT, ILCT
Ir(diMePh-ppy)$_3$	T_1	468 nm (2.64 eV)	0	HOMO->LUMO (67%)	MLCT, ILCT
	S_1	429 nm (2.89 eV)	0.0044	HOMO->LUMO (97%)	MLCT, ILCT
	S_2	422 nm (2.93 eV)	0.0019	HOMO->L+1 (62%), HOMO->L+2 (35%)	MLCT, ILCT, LLCT
	S_3	422 nm (2.93 eV)	0.0019	HOMO->L+1 (35%), HOMO->L+2 (62%)	MLCT, ILCT, LLCT

[a]Metal to ligand charge transfer. [b]Inter ligand charge transfer. [c]Ligand to ligand charge transfer.

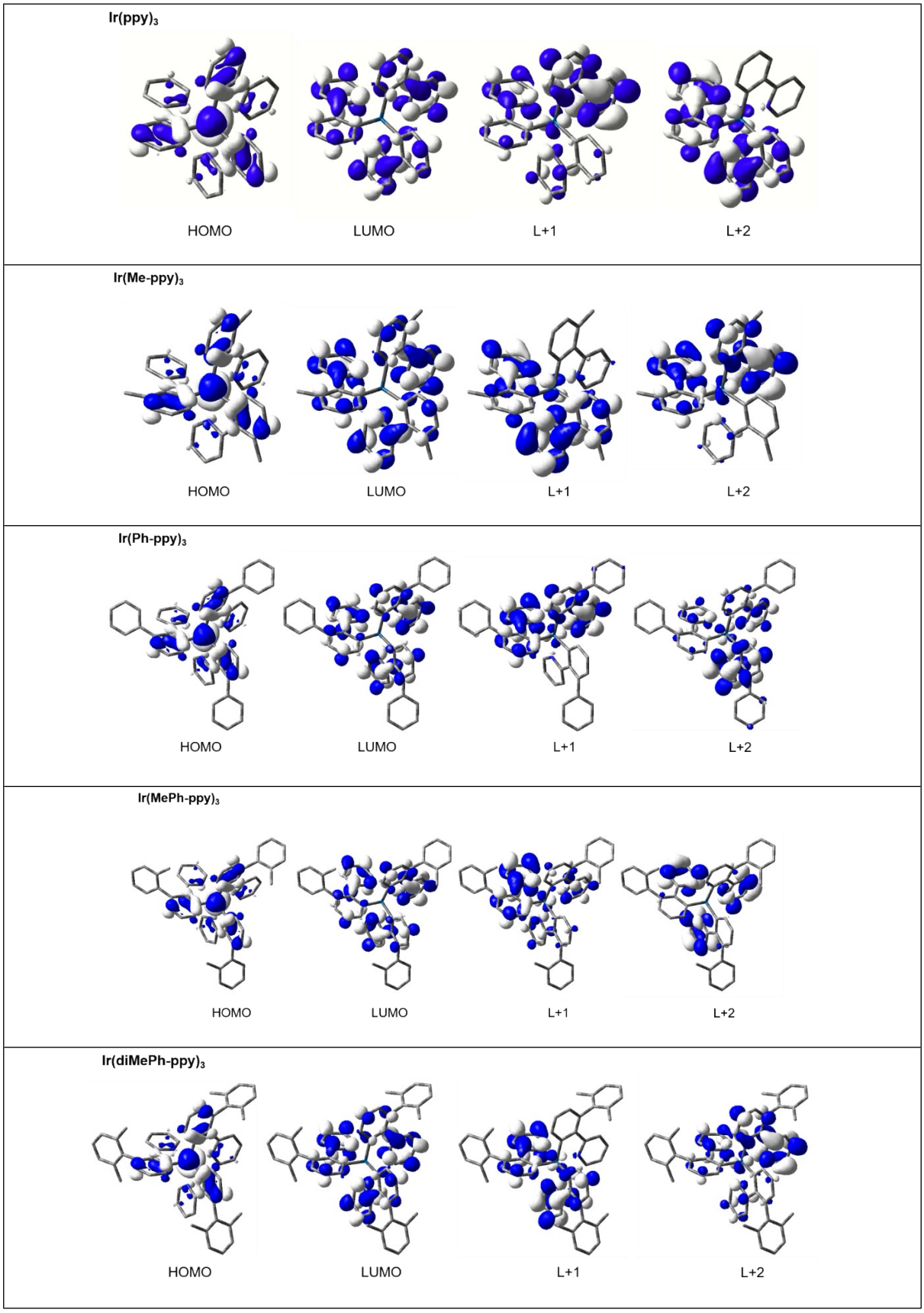

Table S3 Cartesian Coordinates of **ppy**, **Me-ppy**, **Ph-ppy**, **MePh-ppy**, and **diMePh-ppy**

Optimized geometry of singlet **ppy**

Symbol	X	Y	Z
C	2.8605130	1.1690100	-0.2268440
C	3.5417030	-0.0268210	0.0090750
C	2.8156300	-1.1998560	0.2317050
C	1.4225640	-1.1759750	0.2217730
C	0.7247500	0.0226920	-0.0042030
C	1.4659610	1.1941840	-0.2338350
H	3.4143180	2.0843010	-0.4137660
H	4.6274430	-0.0453930	0.0151810
H	3.3360440	-2.1353150	0.4156050
H	0.8550010	-2.0840060	0.3912530
H	0.9572390	2.1294160	-0.4441680
C	-0.7639790	0.0254880	-0.0020140
C	-1.5044760	1.1924640	0.2524780
C	-2.8952790	1.1351000	0.2365010
H	-1.0029310	2.1259280	0.4800460
C	-2.7073890	-1.1963330	-0.2462690
C	-3.5194360	-0.0844080	-0.0222270
H	-3.4809850	2.0280700	0.4326620
H	-3.1544820	-2.1691300	-0.4437300
H	-4.5999170	-0.1773380	-0.0433130
N	-1.3707300	-1.1556880	-0.2409440

Optimized geometry of singlet **Me-ppy**

Symbol	X	Y	Z
C	2.6131790	-1.6139410	-0.3286200
C	3.4395620	-0.5078460	-0.1232060
C	2.8699710	0.7363590	0.1386740
C	1.4798830	0.9241590	0.1847940
C	0.6458300	-0.1963890	-0.0403950
C	1.2323170	-1.4524150	-0.2774930
H	3.0399590	-2.5930170	-0.5248620
H	4.5200370	-0.6140320	-0.1547200
H	3.5162940	1.5901810	0.3255250
H	0.5774580	-2.3046070	-0.4255020
C	-0.8461930	-0.1332720	-0.0263400
C	-1.5622420	0.8867430	-0.6739460
C	-2.9548020	0.8642020	-0.6526900
H	-1.0373620	1.6708450	-1.2060140
C	-2.8146280	-1.1590620	0.6085620
C	-3.6032260	-0.1771780	0.0087800
H	-3.5219840	1.6432180	-1.1531770
H	-3.2820590	-1.9955670	1.1253620
H	-4.6854800	-0.2360480	0.0534880
N	-1.4766730	-1.1504310	0.5980240
C	0.9556130	2.3061850	0.5124120
H	0.7522070	2.8927950	-0.3915590
H	0.0287090	2.2715070	1.0899760
H	1.6973510	2.8624550	1.0921250

Optimized geometry of singlet **Ph-ppy**

Symbol	X	Y	Z
C	1.0585590	3.5369130	0.0173710
C	-0.3296560	3.6775990	-0.0100900
C	-1.1360530	2.5419080	-0.0108440
C	-0.5897030	1.2466670	0.0025900
C	0.8197040	1.1072590	-0.0048920
C	1.6185570	2.2624760	0.0216040
H	1.7009140	4.4122830	0.0285050
H	-0.7835300	4.6640650	-0.0151960
H	-2.2162240	2.6505390	0.0115110
H	2.6965520	2.1403880	0.0280080
C	1.5252370	-0.2070750	-0.0910900
C	1.1369300	-1.1964430	-1.0093160
C	1.8718270	-2.3755590	-1.0888650
H	0.2803160	-1.0349170	-1.6530010
C	3.2962780	-1.5018590	0.6195060
C	2.9757790	-2.5412110	-0.2523880
H	1.5907150	-3.1490860	-1.7971450
H	4.1551070	-1.5886770	1.2827360
H	3.5770320	-3.4437990	-0.2777660
N	2.6014160	-0.3599210	0.7060330
C	-1.5324810	0.0930850	0.0879130
C	-1.4106130	-0.8711190	1.1029490
C	-2.6056990	-0.0165000	-0.8115620
C	-2.3287740	-1.9150940	1.2094360
H	-0.5984680	-0.7926800	1.8191240
C	-3.5223960	-1.0641170	-0.7078920
H	-2.7125570	0.7176240	-1.6049390
C	-3.3870380	-2.0174710	0.3028240
H	-2.2211840	-2.6461970	2.0054300
H	-4.3406600	-1.1350530	-1.4185820
H	-4.1006650	-2.8317920	0.3855580

Optimized geometry of singlet **PhMe-ppy**

Symbol	X	Y	Z
C	-1.4378480	3.4468330	-0.1102630
C	-0.0686770	3.7154630	-0.1266440
C	0.8391350	2.6578230	-0.1319590
C	0.4134330	1.3191980	-0.1306680
C	-0.9762730	1.0498240	-0.1426720
C	-1.8786550	2.1264120	-0.1159080
H	-2.1582760	4.2592620	-0.1001320
H	0.2922190	4.7396840	-0.1265510
H	1.9056140	2.8625970	-0.1174870
H	-2.9408250	1.9061220	-0.1125010
C	-1.5529890	-0.3268320	-0.2069560
C	-1.0530160	-1.3065220	-1.0802870
C	-1.6686010	-2.5546080	-1.1257080
H	-0.2063460	-1.0871960	-1.7186410
C	-3.2052820	-1.7633590	0.5234840
C	-2.7677760	-2.7975520	-0.3030630
H	-1.2992980	-3.3218640	-1.7994930
H	-4.0644800	-1.9094780	1.1757260
H	-3.2778050	-3.7549740	-0.3041530
N	-2.6253380	-0.5578030	0.5786790
C	1.4669130	0.2544590	-0.0871650
C	2.3139350	0.0962210	-1.1949720
C	1.6720750	-0.5437670	1.0618710
C	3.3331070	-0.8563900	-1.1998380

H	2.1585790	0.7258180	-2.0667870
C	2.7021460	-1.4936350	1.0387580
C	3.5237890	-1.6604630	-0.0767970
H	3.9705080	-0.9659900	-2.0721920
H	2.8673040	-2.1071380	1.9207900
H	4.3128160	-2.4067190	-0.0622670
C	0.8381670	-0.3727210	2.3109120
H	1.2572620	-0.9531330	3.1368690
H	0.7945350	0.6767810	2.6200510
H	-0.1959410	-0.7014500	2.1632650

Optimized geometry of singlet **diPhMe-ppy**

Symbol	X	Y	Z
C	1.2108780	3.5260610	0.0141290
C	-0.1719810	3.6562680	0.1508590
C	-0.9695710	2.5140460	0.1744300
C	-0.4224370	1.2257080	0.0537970
C	0.9794740	1.0971350	-0.0922780
C	1.7726450	2.2580380	-0.0987490
H	1.8477220	4.4054150	-0.0041170
H	-0.6269140	4.6377450	0.2459700
H	-2.0435330	2.6111120	0.3054160
H	2.8468650	2.1444680	-0.1970900
C	1.6855290	-0.2133960	-0.2242600
C	1.2141020	-1.2501470	-1.0456390
C	1.9512790	-2.4271950	-1.1473730
H	0.2940300	-1.1325190	-1.6030210
C	3.5409190	-1.4626740	0.3511580
C	3.1414440	-2.5454480	-0.4312980
H	1.6033750	-3.2357470	-1.7831730
H	4.4667380	-1.5108290	0.9217730
H	3.7472190	-3.4440330	-0.4795530
N	2.8440440	-0.3249980	0.4592190
C	-1.3608220	0.0571440	0.1495630
C	-1.4332130	-0.6882380	1.3480750
C	-2.2104060	-0.2556930	-0.9356080
C	-2.3416650	-1.7507900	1.4328080
C	-3.1024020	-1.3287840	-0.8140580
C	-3.1693390	-2.0752970	0.3601900
H	-2.4000850	-2.3239560	2.3543240
H	-3.7485390	-1.5773800	-1.6517910
H	-3.8667440	-2.9042480	0.4406320
C	-2.1700140	0.5362300	-2.2249310
H	-2.7579210	0.0400930	-3.0013710
H	-2.5759480	1.5454070	-2.0939390
H	-1.1478120	0.6587940	-2.5980010
C	-0.5665510	-0.3498940	2.5404500
H	-0.6638180	0.7046150	2.8193460
H	-0.8456260	-0.9573190	3.4052160
H	0.4954720	-0.5250790	2.3372690

Table S4 Cartesian Coordinates of **Ir(ppy)$_3$**, **Ir(Me-ppy)$_3$**, **Ir(Ph-ppy)$_3$**, **Ir(MePh-ppy)$_3$**, and **Ir(diMePh-ppy)$_3$**

Optimized geometry of singlet **Ir(ppy)$_3$**

Symbol	X	Y	Z
C	3.2942600	2.5739230	-1.2251140
C	2.1926320	1.9658940	-0.5998250
C	3.8765390	1.9846970	-2.3399780
C	3.3555230	0.7831690	-2.8279640
C	2.2674320	0.2253290	-2.1694810
C	-0.2138160	-4.3515890	-2.3367150
C	-0.9963430	-3.3014630	-2.8247500
C	-0.9380430	-2.0799790	-2.1665110
H	3.7792080	0.2871100	-3.6937770
H	1.8244490	-0.7068990	-2.5021610
H	-1.6376550	-3.4218980	-3.6904420
H	-1.5258180	-1.2316290	-2.4994490
C	1.4076720	-2.5300170	0.5848270
C	2.2650350	-3.4544260	1.2105870
C	2.9991420	-3.0893740	2.3337320
H	2.3636050	-4.4651540	0.8245110
C	2.0278200	-0.8677820	2.2155040
C	2.8753380	-1.7877360	2.8348470
H	1.9508460	0.1332040	2.6293000
H	3.4439890	-1.4912240	3.7135890
H	1.1953100	-4.9474100	-0.8324390
C	0.6087650	-2.8817520	-0.5968450
C	0.5872700	-4.1399450	-1.2219600
C	1.4897630	2.4837540	0.5817300
C	1.8635800	3.6884660	1.2063130
C	-0.2614400	2.1950640	2.2118070
C	1.1804470	4.1445350	2.3283310
H	2.6910170	4.2769910	0.8199330
C	0.1131540	3.3893180	2.8295810
H	-1.0908390	1.6298770	2.6263170
H	-0.4280400	3.7358180	3.7073690
H	3.6918520	3.5032810	-0.8356290
C	1.2655080	-1.1969560	1.0760360
N	-0.1610100	-1.8693930	-1.0891570
H	-0.2302560	-5.3238230	-2.8194760
C	-2.8003870	0.9124170	-0.5996080
C	-1.3315290	1.8498470	-2.1689960
C	-3.8788770	1.5591920	-1.2263040
C	-2.8959070	0.0464700	0.5832890
C	-2.3597650	2.5104560	-2.8285880
H	-0.3026300	1.9343820	-2.5010780
C	-3.6608650	2.3578820	-2.3415620
H	-4.8825280	1.4365180	-0.8375760
C	-4.1255360	-0.2326760	1.2087510
C	-1.6706230	-0.4959130	1.0764250
H	-2.1427780	3.1254490	-3.6945670
H	-4.4943570	2.8575330	-2.8255160
H	-5.0498410	0.1866050	0.8212040
C	-1.7673570	-1.3180390	2.2177340
C	-2.9882670	-1.5910290	2.8366400
H	-0.8621380	-1.7502420	2.6336210
H	-3.0163490	-2.2297940	3.7167820
Ir	-0.0006620	0.0002770	0.0379800
H	4.7277840	2.4545990	-2.8228270
C	0.4048340	1.6965860	1.0735830
N	1.6980290	0.7941990	-1.0920080
N	-1.5384640	1.0724210	-1.0912570
C	-4.1771720	-1.0487360	2.3334540
H	3.6593460	-3.8065990	2.8126740
H	1.4729500	5.0749690	2.8062520
H	-5.1287410	-1.2610740	2.8120990

Optimized geometry of triplet **Ir(ppy)$_3$**

Symbol	X	Y	Z
C	-0.7382050	-4.1183910	-1.1824310
C	-0.3092400	-2.9223210	-0.5834680
C	-1.6376270	-4.0828710	-2.2401230
C	-2.1097760	-2.8490700	-2.6956750
C	-1.6513600	-1.6991260	-2.0665270
C	-2.8538040	3.2803250	-2.3428100
C	-1.5749780	3.0371520	-2.8528370
C	-0.7683430	2.1240630	-2.1876110
H	-2.8144750	-2.7750760	-3.5159500
H	-1.9854140	-0.7158770	-2.3780640
H	-1.2096640	3.5405450	-3.7405440
H	0.2332220	1.8892720	-2.5308550
C	-2.7356450	0.9223920	0.6432530
C	-3.9822420	1.0282930	1.2877810
C	-4.2542180	0.2767240	2.4259790
H	-4.7472900	1.6984440	0.9064980
C	-2.0364770	-0.6977150	2.2864570
C	-3.2744350	-0.5899730	2.9236630
H	-1.2919030	-1.3731140	2.6978130
H	-3.4775120	-1.1814340	3.8134760
H	-4.2621060	2.7926370	-0.7995700
C	-2.4145770	1.6966380	-0.5656520
C	-3.2728040	2.6099620	-1.2006650
C	0.6231180	-2.8242350	0.5482100
C	1.2097110	-3.9607970	1.1345070
C	1.8001580	-1.4249720	2.1236880
C	2.0828080	-3.8328870	2.2090980
H	0.9876590	-4.9532780	0.7539090
C	2.3757880	-2.5566300	2.7026870
H	2.0371250	-0.4469390	2.5305920
H	3.0558490	-2.4442260	3.5437220
H	-0.3701250	-5.0695350	-0.8179320
C	-1.7221820	0.0486670	1.1359360
N	-1.1725930	1.4751450	-1.0819570
H	-3.5172310	3.9865830	-2.8322550
C	2.6583720	1.2311540	-0.6560700
C	2.1289710	-0.4518230	-2.2473620
C	3.8809710	1.4829830	-1.3590340
C	2.2260970	1.8774530	0.5192730
C	3.3113420	-0.2430200	-2.9468740
H	1.4211200	-1.2084430	-2.5734660
C	4.2082200	0.7675640	-2.4811400
H	4.5500330	2.2538530	-0.9917400
C	2.9679440	2.9062170	1.1888720
C	0.9080980	1.4712580	1.0769970
H	3.5329310	-0.8395920	-3.8240970
H	5.1356950	0.9635300	-3.0099740
H	3.9387130	3.2119320	0.8117070
C	0.4475560	2.1462180	2.2229560
C	1.1874560	3.1485010	2.8469880

H	-0.5123630	1.8609080	2.6419350
H	0.8119600	3.6456980	3.7360160
Ir	0.0131110	0.0195060	0.0626220
H	-1.9698410	-5.0066260	-2.7034470
C	0.9097660	-1.5157270	1.0360350
N	-0.7749590	-1.7299960	-1.0480050
N	1.7770760	0.2433960	-1.1579130
C	2.4577070	3.5150320	2.3118350
H	-5.2175960	0.3636530	2.9197260
H	2.5302250	-4.7151820	2.6569380
H	3.0357560	4.2942140	2.8032140

Optimized geometry of singlet **Ir(Me-ppy)$_3$**

Symbol	X	Y	Z
C	1.7816260	3.7936440	1.2242420
C	1.5067660	2.5479510	0.6258020
C	1.0262940	4.2533010	2.2974460
C	-0.0218410	3.4744940	2.7848990
C	-0.2729740	2.2665050	2.1490520
C	-4.1978810	-1.2393420	2.2952750
C	-2.9992760	-1.7557340	2.7845440
C	-1.8272290	-1.3685030	2.1495560
H	-0.6359870	3.7908760	3.6203010
H	-1.0865690	1.6230590	2.4643710
H	-2.9663470	-2.4448050	3.6207430
H	-0.8630610	-1.7495810	2.4665370
C	-2.7687030	0.9541620	-0.5157840
C	-3.8049580	1.7240130	-1.1260250
C	-3.4805600	2.5288010	-2.2231150
C	-1.1651940	1.8690920	-2.1025350
C	-2.1783310	2.5961790	-2.7179480
H	-0.1524900	1.9428120	-2.4853060
H	-1.9582250	3.2283910	-3.5755860
H	-5.1143500	0.0169320	0.8472510
C	-2.9606990	0.0288810	0.6237230
C	-4.1771580	-0.3567180	1.2210110
C	2.2122380	1.9188830	-0.5139960
C	3.3969470	2.4311790	-1.1247490
C	2.1993960	0.0753830	-2.1035160
C	3.9302920	1.7487400	-2.2230030
C	3.3358020	0.5886790	-2.7189820
H	1.7548460	-0.8366340	-2.4882950
H	3.7714080	0.0830800	-3.5782150
H	2.5746320	4.4180250	0.8515260
C	-1.4167730	1.0417270	-0.9921330
N	-1.8029390	-0.5157090	1.1117370
H	-5.1469870	-1.5220850	2.7402940
C	1.4528380	-2.5786520	0.6265040
C	2.0974630	-0.8973240	2.1512060
C	2.3935740	-3.4398860	1.2253270
C	0.5561630	-2.8745310	-0.5140650
C	3.0175400	-1.7191820	2.7872490
H	1.9466690	0.1285990	2.4678920
C	3.1684750	-3.0159790	2.2993100
H	2.5375130	-4.4387180	0.8522150
C	0.4091840	-4.1563700	-1.1255500
C	-0.1933710	-1.7466350	-0.9916340
H	3.5977250	-1.3460130	3.6234960
H	3.8871290	-3.6966600	2.7453890
C	-1.0323740	-1.9416130	-2.1046780
C	-1.1536540	-3.1819820	-2.7216550
H	-1.5997610	-1.1006190	-2.4896750
H	-1.8079360	-3.3062480	-3.5819790
Ir	0.0001400	0.0004010	0.0246240
H	1.2561660	5.2162650	2.7431260
C	1.6101360	0.7057490	-0.9917040
N	0.4549520	1.8185010	1.1125550
N	1.3467220	-1.3030920	1.1134060
C	-0.4461460	-4.2768070	-2.2256430
H	-4.2658140	3.1173410	-2.6901350
H	4.8322020	2.1346060	-2.6906850
H	-0.5615680	-5.2505040	-2.6943600
C	4.1649060	3.6585770	-0.6757020
H	3.6134550	4.5896930	-0.8527600
H	4.4260580	3.6260000	0.3872530
H	5.0997660	3.7329860	-1.2370090
C	1.0886240	-5.4345300	-0.6755890
H	0.9289110	-5.6437360	0.3873300
H	0.6866770	-6.2818150	-1.2369260
H	2.1709240	-5.4218680	-0.8515390
C	-5.2520790	1.7731860	-0.6770120
H	-5.7821350	0.8299590	-0.8555920
H	-5.3544850	2.0135850	0.3863950
H	-5.7846340	2.5462330	-1.2367610

Optimized geometry of triplet **Ir(Me-ppy)$_3$**

Symbol	X	Y	Z
C	3.7669170	-1.6095890	1.5534340
C	2.6158980	-1.3184760	0.7491700
C	4.0512320	-0.8970630	2.6907440
C	3.1836090	0.1651300	3.0873550
C	2.0549560	0.3985530	2.3203680
C	-1.7821890	4.0776350	2.1286770
C	-2.2255890	2.8438490	2.6017700
C	-1.6856600	1.7031930	2.0246070
H	3.3787310	0.7673820	3.9670410
H	1.3492460	1.1770570	2.5942100
H	-2.9737610	2.7599410	3.3815350
H	-2.0062060	0.7144840	2.3320030
C	0.7414950	2.8194530	-0.4756810
C	1.4733900	3.9116000	-1.0306570
C	2.3747430	3.6527750	-2.0687680
C	1.8945850	1.2931560	-1.9879990
C	2.5776930	2.3627420	-2.5559680
H	2.0698870	0.2902670	-2.3617550
H	3.2810150	2.1945450	-3.3681180
H	-0.5052010	5.0851700	0.7603360
C	-0.2770560	2.9387220	0.5922180
C	-0.8179640	4.1236970	1.1280910
C	2.2047340	-1.9376590	-0.4618470
C	2.9545320	-2.9109680	-1.2321330
C	0.3079470	-2.2261530	-2.0581940
C	2.3358190	-3.5140160	-2.3144630
C	1.0121180	-3.2169060	-2.7298930
H	-0.6829340	-1.9476080	-2.4011360
H	0.5850490	-3.7313050	-3.5854000
H	4.4192270	-2.4219510	1.2743100
C	0.9751590	1.4834510	-0.9407480
N	-0.7512260	1.7449260	1.0610560
H	-2.1860530	5.0025710	2.5285430

C	-2.4779500	-1.6609020	0.5884990
C	-0.7985600	-2.1135910	2.1906090
C	-3.2939650	-2.6204530	1.2198760
C	-2.8035640	-0.8397120	-0.6026980
C	-1.5742790	-3.0561410	2.8499830
H	0.2054600	-1.8702430	2.5194290
C	-2.8467990	-3.3111250	2.3410200
H	-4.2760570	-2.8419130	0.8414170
C	-4.0645660	-0.8365890	-1.2733820
C	-1.7371900	0.0001170	-1.0641820
H	-1.1873280	-3.5717010	3.7213230
H	-3.4934310	-4.0464540	2.8098710
C	-1.9643090	0.8055720	-2.1922620
C	-3.1866640	0.7991860	-2.8561870
H	-1.1644980	1.4431560	-2.5554040
H	-3.3413730	1.4264920	-3.7311290
Ir	0.0039200	-0.0250910	0.0026510
H	4.9245850	-1.1456680	3.2855760
C	0.8602260	-1.5331380	-0.9660760
N	1.7387180	-0.3035910	1.2203510
N	-1.2291450	-1.4472950	1.1074020
C	-4.2212550	-0.0122340	-2.3929780
H	2.9317530	4.4826000	-2.4950360
H	2.9037560	-4.2489230	-2.8816920
H	-5.1788590	-0.0073790	-2.9064800
C	4.3894740	-3.2988450	-0.9498010
H	5.0336270	-2.4238680	-0.8081190
H	4.4956200	-3.9278730	-0.0566660
H	4.7914210	-3.8722560	-1.7898650
C	-5.2821000	-1.6478050	-0.8781950
H	-5.6012430	-1.4530140	0.1513830
H	-6.1214490	-1.3921390	-1.5294860
H	-5.1185570	-2.7270650	-0.9772830
C	1.3870960	5.3547060	-0.5757290
H	0.4342550	5.8252090	-0.8459540
H	1.5157120	5.4624900	0.5060910
H	2.1755500	5.9387070	-1.0568370

Optimized geometry of singlet **Ir(Ph-ppy)$_3$**

Symbol	X	Y	Z
C	0.6970890	4.0497760	1.6846440
C	0.5793820	2.8850080	0.9030700
C	-0.0069090	4.1751060	2.8758130
C	-0.8321180	3.1315620	3.2982670
C	-0.8765270	1.9853620	2.5170520
C	-3.6194560	-2.0889370	2.8754090
C	-2.3034970	-2.2820250	3.2990610
C	-1.2877840	-1.7492900	2.5177740
H	-1.4088010	3.1893280	4.2144340
H	-1.4694370	1.1272500	2.8122540
H	-2.0661970	-2.8094410	4.2160120
H	-0.2481790	-1.8345560	2.8128330
C	-2.8970810	-0.1923190	-0.3704050
C	-4.0953490	-0.0574080	-1.1292940
C	-4.1084130	0.8205610	-2.2200570
C	-1.7634390	1.3044820	-1.9069150
C	-2.9565420	1.5141980	-2.5930860
H	-0.8662650	1.8136570	-2.2433590
H	-2.9870770	2.1913940	-3.4437220
H	-4.8786350	-1.2530210	1.3615360
C	-2.7932460	-0.9401130	0.9012630
C	-3.8617620	-1.4185420	1.6828760
C	1.2815990	2.6014150	-0.3672140
C	1.9968640	3.5722560	-1.1259870
C	2.0120080	0.8722380	-1.9047210
C	2.7631480	3.1456140	-2.2175460
C	2.7887330	1.8014980	-2.5912600
H	2.0049510	-0.1592290	-2.2415110
H	3.3901580	1.4901850	-3.4424300
H	1.3492860	4.8478230	1.3646530
C	-1.6863200	0.4439550	-0.7949370
N	-1.5187760	-1.0851950	1.3708900
H	-4.4518350	-2.4530640	3.4697360
C	2.2091360	-1.9467410	0.9059810
C	2.1505070	-0.2403090	2.5241640
C	3.1573210	-2.6319640	1.6888240
C	1.6157600	-2.4122670	-0.3660460
C	3.1189860	-0.8528130	3.3070670
H	1.7021020	0.7014160	2.8194290
C	3.6132070	-2.0875450	2.8829570
H	3.5246220	-3.5944780	1.3673000
C	2.1020520	-3.5155420	-1.1251190
C	0.4563570	-1.6863930	-0.7902610
H	3.4539410	-0.3841160	4.2254260
H	4.3444300	-2.6257410	3.4782150
C	-0.2509800	-2.1886010	-1.8997000
C	0.1676750	-3.3256580	-2.5852460
H	-1.1446190	-1.6716480	-2.2337530
H	-0.4039650	-3.6947810	-3.4338250
Ir	-0.0013760	-0.0021020	0.2483820
H	0.0923150	5.0783080	3.4700000
C	1.2286290	1.2347350	-0.7920070
N	-0.1842940	1.8536410	1.3710910
N	1.6944310	-0.7717500	1.3755930
C	1.3485610	-3.9700140	-2.2144040
H	-5.0215190	0.9245050	-2.7986880
H	3.3089330	3.8852140	-2.7958490
H	1.7182340	-4.8113500	-2.7930610
C	3.4239410	-4.1850700	-0.9233170
C	4.6213480	-3.4671450	-1.0900660
C	3.5018280	-5.5610780	-0.6547840
C	5.8571060	-4.1034910	-0.9765110
C	4.7397920	-6.1982990	-0.5368210
H	2.5849620	-6.1300240	-0.5289120
C	5.9214130	-5.4717490	-0.6960000
H	6.7711640	-3.5323550	-1.1130180
H	4.7789510	-7.2623770	-0.3211920
H	6.8841000	-5.9665870	-0.6063790
C	-5.3401440	-0.8608170	-0.9257710
C	-6.5671000	-0.2340050	-0.6555610
C	-5.3244140	-2.2568140	-1.0928860
C	-7.7415090	-0.9816410	-0.5358090
H	-6.5957450	0.8446660	-0.5297010
C	-6.4969820	-3.0029900	-0.9779750
C	-7.7104450	-2.3683900	-0.6954040
H	-8.6797230	-0.4787340	-0.3187170
H	-6.4650000	-4.0803350	-1.1144930
H	-8.6231690	-2.9500320	-0.6044020
C	1.9242520	5.0520950	-0.9218350
C	0.7082320	5.7377250	-1.0892200
C	3.0812680	5.7999800	-0.6510100
C	0.6497310	7.1263990	-0.9742950

C	3.0224370	7.1909670	-0.5314020
H	4.0292100	5.2844170	-0.5252790
C	1.8067230	7.8587310	-0.6914380
H	-0.2986330	7.6384120	-1.1113330
H	3.9276250	7.7511560	-0.3143130
H	1.7605660	8.9400880	-0.6009290
H	4.5764420	-2.4049570	-1.3135990
H	-0.1924720	5.1733910	-1.3139060
H	-4.3847080	-2.7536030	-1.3173570

Optimized geometry of triplet **Ir(Ph-ppy)$_3$**

Symbol	X	Y	Z
C	1.0505220	3.8958070	1.5861520
C	0.8182980	2.7234270	0.8434450
C	0.2708280	4.1927050	2.6968970
C	-0.7464360	3.3156300	3.0769380
C	-0.9004480	2.1476760	2.3438610
C	-4.0781420	-1.3975960	2.8712920
C	-2.8235820	-1.7671490	3.3608120
C	-1.7132740	-1.4665200	2.5852210
H	-1.3874710	3.5128830	3.9284680
H	-1.6447740	1.4087500	2.6153650
H	-2.7023700	-2.2525660	4.3223920
H	-0.7067550	-1.6881220	2.9221580
C	-2.9730230	0.0714930	-0.4867050
C	-4.1100880	0.3133040	-1.3097570
C	-3.9475530	1.0670710	-2.4788150
C	-1.5680880	1.2194250	-2.1014600
C	-2.6906360	1.5341580	-2.8632780
H	-0.5904890	1.5481670	-2.4388350
H	-2.5873560	2.1149740	-3.7767510
H	-5.1462410	-0.4952990	1.2515130
C	-3.0262400	-0.5631270	0.8488860
C	-4.1785400	-0.7959450	1.6228940
C	1.5644630	2.2784700	-0.3536820
C	2.4709430	3.0955710	-1.0888220
C	2.1308480	0.3908550	-1.7765630
C	3.2354820	2.5112470	-2.1059030
C	3.0821690	1.1647410	-2.4357390
H	1.9839720	-0.6399550	-2.0812140
H	3.6826380	0.7313510	-3.2317940
H	1.8472250	4.5648900	1.2997960
C	-1.6685470	0.4766650	-0.9122520
N	-1.8075560	-0.8693450	1.3839990
H	-4.9739980	-1.5731670	3.4587940
C	1.9406560	-2.1417540	1.0916460
C	1.9139060	-0.3832740	2.6840400
C	2.9002760	-2.8301240	1.9046500
C	1.3972790	-2.5855300	-0.1341440
C	2.8850000	-0.9973480	3.4713460
H	1.4960830	0.5765230	2.9719650
C	3.3619110	-2.2720430	3.0717770
H	3.2357130	-3.8118620	1.5991250
C	1.8783770	-3.7253020	-0.9158840
C	0.1693590	-1.8736540	-0.5892330
H	3.2387040	-0.5106210	4.3725920
H	4.0757060	-2.8088440	3.6891580
C	-0.6660010	-2.5391450	-1.4916960
C	-0.3075330	-3.7724990	-2.0488650
H	-1.5927370	-2.0662950	-1.8015150
H	-0.9582540	-4.2657940	-2.7647900
Ir	-0.1042330	-0.0965540	0.2582090
H	0.4593800	5.1000800	3.2622080
C	1.3441680	0.9184030	-0.7355540
N	-0.1352330	1.8481460	1.2794880
N	1.4261370	-0.9176400	1.5602230
C	0.9768450	-4.3128450	-1.7911480
H	-4.8142630	1.2514640	-3.1064530
H	3.9260990	3.1355520	-2.6646940
H	1.2960180	-5.1854410	-2.3559320
C	3.2745500	-4.2186920	-0.8756550
C	4.3633490	-3.3204710	-0.8836690
C	3.5653140	-5.5981190	-0.8970210
C	5.6773050	-3.7815900	-0.9210100
C	4.8819800	-6.0583090	-0.9335310
H	2.7484950	-6.3136590	-0.8660720
C	5.9472850	-5.1541270	-0.9458590
H	6.4954460	-3.0663970	-0.9373020
H	5.0753710	-7.1276780	-0.9424220
H	6.9722940	-5.5123090	-0.9700330
C	-5.4743870	-0.2564110	-1.0850920
C	-6.5864250	0.5841360	-0.9180670
C	-5.6848730	-1.6458020	-1.1268310
C	-7.8703310	0.0513660	-0.7760650
H	-6.4396840	1.6601480	-0.8901250
C	-6.9667970	-2.1776720	-0.9895680
C	-8.0647380	-1.3308400	-0.8099990
H	-8.7173750	0.7178670	-0.6401540
H	-7.1098970	-3.2538620	-1.0284850
H	-9.0627070	-1.7454790	-0.7018080
C	2.6157870	4.5761810	-0.9351660
C	1.5413590	5.4335100	-1.2299940
C	3.8497440	5.1454810	-0.5827430
C	1.6934510	6.8179910	-1.1584130
C	4.0010350	6.5325040	-0.5064880
H	4.6903620	4.4948910	-0.3586020
C	2.9234250	7.3729730	-0.7923990
H	0.8528690	7.4646940	-1.3937600
H	4.9616110	6.9542700	-0.2244260
H	3.0408740	8.4511780	-0.7352530
H	4.1673470	-2.2522940	-0.8761340
H	0.5851920	5.0071670	-1.5201620
H	-4.8359410	-2.3080580	-1.2716620

Optimized geometry of singlet **Ir(MePh-ppy)$_3$**

Symbol	X	Y	Z
C	2.3844760	-3.3764090	1.6487000
C	1.5605410	-2.4973090	0.9207580
C	3.0543160	-2.9419900	2.7865370
C	2.9029520	-1.6221970	3.2114410
C	2.0615140	-0.8000610	2.4748870
C	1.0202020	4.1298720	2.7674340
C	-0.0472220	3.3411180	3.1957820
C	-0.3390480	2.1983540	2.4642550
H	3.4096540	-1.2378740	4.0894010
H	1.8888180	0.2304770	2.7630670
H	-0.6337140	3.5920500	4.0723370
H	-1.1465470	1.5365050	2.7560360
C	2.0387600	2.0825020	-0.3121190
C	3.0891340	2.7434060	-1.0132930

C	3.6659270	2.1126490	-2.1220080
C	2.1608390	0.2411950	-1.8943870
C	3.2117830	0.8671660	-2.5571200
H	1.8052260	-0.7171950	-2.2586630
H	3.6747000	0.3955080	-3.4210930
H	2.5631840	4.3666210	1.3083520
C	1.3827860	2.6047270	0.9090390
C	1.7314530	3.7614880	1.6314680
C	0.7860600	-2.8077980	-0.3027380
C	0.8450180	-4.0452630	-1.0076420
C	-0.8750200	-2.0033550	-1.8849490
C	0.0120210	-4.2342450	-2.1167920
C	-0.8489030	-3.2251670	-2.5496830
H	-1.5313280	-1.2190680	-2.2477800
H	-1.4870910	-3.3939050	-3.4142150
H	2.4937660	-4.4003360	1.3286690
C	1.5409630	0.8175450	-0.7689750
N	0.3513270	1.8337790	1.3692990
H	1.3014650	5.0255860	3.3127120
C	-2.9524600	-0.1109540	0.9135060
C	-1.7310740	-1.3838700	2.4743300
C	-4.1282450	-0.4017500	1.6308990
C	-2.8329990	0.7201490	-0.3064930
C	-2.8652950	-1.7139490	3.2029930
H	-0.7507500	-1.7414660	2.7674810
C	-4.0867560	-1.1997950	2.7682840
H	-5.0725360	0.0023750	1.3030680
C	-3.9329970	1.2942540	-1.0079650
C	-1.4897550	0.9305280	-0.7622900
H	-2.7852100	-2.3450010	4.0808360
H	-5.0031140	-1.4149380	3.3093490
C	-1.3039320	1.7623850	-1.8829200
C	-2.3742160	2.3540050	-2.5461830
H	-0.2960040	1.9425170	-2.2418540
H	-2.1999430	2.9951540	-3.4074230
Ir	-0.0053850	0.0015240	0.2652130
H	3.6870290	-3.6322650	3.3360370
C	-0.0673450	-1.7501330	-0.7595540
N	1.4057830	-1.2178330	1.3780420
N	-1.7653850	-0.6059230	1.3783380
C	-3.6790100	2.1126330	-2.1149690
H	4.4699760	2.6168650	-2.6501150
H	0.0566920	-5.1806520	-2.6476530
H	-4.5202650	2.5517970	-2.6431460
C	-5.3873980	1.0926290	-0.6933650
C	-6.0817500	-0.0571950	-1.1360000
C	-6.0915800	2.1076830	-0.0288370
C	-7.4539920	-0.1552960	-0.8710120
C	-7.4590960	1.9922270	0.2291920
H	-5.5524980	2.9939690	0.2946530
C	-8.1429510	0.8519910	-0.1917780
H	-7.9916850	-1.0375180	-1.2097510
H	-7.9827330	2.7882470	0.7507880
H	-9.2071090	0.7470000	-0.0003600
C	3.6480000	4.1008900	-0.6972420
C	4.8836330	4.1965500	-0.0399880
C	2.9998970	5.2810670	-1.1303440
C	5.4718600	5.4356860	0.2214020
H	5.3813020	3.2836430	0.2756250
C	3.6061320	6.5155630	-0.8629580
C	4.8267940	6.6017820	-0.1897000
H	6.4261950	5.4862070	0.7377360
H	3.1120970	7.4255110	-1.1947160
H	5.2715940	7.5737090	0.0042940
C	1.7533660	-5.1998600	-0.6967540
C	3.1035810	-5.2071720	-1.1181690
C	1.2259190	-6.3334930	-0.0606220
C	3.8801900	-6.3444470	-0.8607710
C	2.0154300	-7.4575300	0.1906810
H	0.1833750	-6.3249070	0.2455270
C	3.3514640	-7.4609160	-0.2091940
H	4.9182890	-6.3546710	-1.1839080
H	1.5870520	-8.3217740	0.6901580
H	3.9788680	-8.3280630	-0.0234000
C	-5.3713830	-1.1652590	-1.8785800
H	-4.8603450	-0.7850810	-2.7696410
H	-4.6062890	-1.6414510	-1.2551630
H	-6.0770150	-1.9384500	-2.1935160
C	3.7097750	-4.0196710	-1.8291370
H	3.1146150	-3.7303210	-2.7016310
H	3.7588640	-3.1415120	-1.1751380
H	4.7254680	-4.2430380	-2.1660950
C	1.6797460	5.2259750	-1.8634840
H	1.7359740	4.5678900	-2.7369320
H	0.8806820	4.8339450	-1.2238890
H	1.3791940	6.2207910	-2.2026620

Optimized geometry of triplet **Ir(MePh-ppy)$_3$**

Symbol	X	Y	Z
C	-2.8545900	2.9004470	1.8329220
C	-1.9084900	2.1887650	1.0224320
C	-3.3853800	2.3355560	2.9648650
C	-2.9909640	1.0204530	3.3410610
C	-2.0294660	0.3816510	2.5685960
C	-0.1619760	-4.2751470	2.6398400
C	0.8012450	-3.3507340	3.0433400
C	0.8777970	-2.1538420	2.3455070
H	-3.4007050	0.5271440	4.2146540
H	-1.6712930	-0.6069230	2.8391210
H	1.4673540	-3.5392870	3.8773910
H	1.5914180	-1.3871760	2.6223260
C	-1.6283720	-2.3189710	-0.3134140
C	-2.5893660	-3.1148690	-1.0018810
C	-3.2816200	-2.5588960	-2.0840200
C	-2.0785700	-0.4830430	-1.8490390
C	-3.0340560	-1.2524680	-2.5047890
H	-1.8780780	0.5248690	-2.1951830
H	-3.5823970	-0.8422350	-3.3492780
H	-1.7333530	-4.6950200	1.2546700
C	-0.8493450	-2.7649100	0.8646680
C	-0.9833360	-3.9824120	1.5575350
C	-1.3056280	2.6289680	-0.1804850
C	-1.6629210	3.8273530	-0.9265570
C	0.6756420	2.3538330	-1.6552590
C	-0.7744460	4.2829870	-1.8892790
C	0.4072420	3.5865320	-2.2476640
H	1.5341820	1.7809800	-1.9897120
H	1.0508200	3.9851610	-3.0259370
H	-3.1316710	3.9063080	1.5504750
C	-1.3540290	-0.9846460	-0.7529050
N	0.0783970	-1.8632110	1.3052620
H	-0.2773260	-5.2192380	3.1631910

C	2.9727490	0.5814520	0.9112330
C	1.5826350	1.5735430	2.5401370
C	4.0962020	0.9764990	1.6619330
C	2.9729190	-0.1733300	-0.3643740
C	2.6605420	2.0106290	3.2963890
H	0.5597000	1.7690780	2.8415730
C	3.9410930	1.6891370	2.8452420
H	5.0874690	0.7183900	1.3251020
C	4.1429920	-0.5172950	-1.1018340
C	1.6796660	-0.5676900	-0.8361490
H	2.4957840	2.5720910	4.2088170
H	4.8178870	1.9882660	3.4112540
C	1.6120240	-1.3505550	-2.0014240
C	2.7569250	-1.7225450	-2.6999510
H	0.6414240	-1.6647950	-2.3714020
H	2.6790620	-2.3296710	-3.5987560
Ir	0.0690980	0.0572980	0.2466340
H	-4.0904570	2.8926270	3.5741820
C	-0.1558900	1.8103680	-0.6643210
N	-1.4725470	0.9220390	1.4768120
N	1.7307770	0.8785780	1.3993920
C	4.0094650	-1.2992610	-2.2556170
H	-4.0140880	-3.1702480	-2.6025670
H	-1.0229970	5.1997170	-2.4190060
H	4.9039800	-1.5627260	-2.8121740
C	5.5470530	-0.0943340	-0.7802130
C	6.0243830	1.1906150	-1.1284720
C	6.4267980	-1.0235810	-0.2053390
C	7.3635080	1.5026770	-0.8597130
C	7.7579630	-0.6941250	0.0579360
H	6.0542330	-2.0132060	0.0446310
C	8.2269860	0.5781420	-0.2679660
H	7.7357470	2.4889620	-1.1256830
H	8.4200150	-1.4270860	0.5098330
H	9.2600570	0.8502050	-0.0710350
C	-2.9398270	-4.5416950	-0.6914490
C	-4.1094450	-4.8160060	0.0324670
C	-2.1633950	-5.6132110	-1.1898840
C	-4.5072370	-6.1284490	0.2949220
H	-4.7063910	-3.9855050	0.3992970
C	-2.5788690	-6.9235570	-0.9188980
C	-3.7348080	-7.1877110	-0.1809280
H	-5.4134750	-6.3181410	0.8628160
H	-1.9852990	-7.7512180	-1.2992780
H	-4.0308760	-8.2146030	0.0136360
C	-2.9169000	4.6162670	-0.7321360
C	-4.2000610	4.0807870	-1.0118060
C	-2.8178390	5.9615880	-0.3334380
C	-5.3223140	4.9034590	-0.8530550
C	-3.9474920	6.7672820	-0.1845120
H	-1.8332800	6.3706670	-0.1236010
C	-5.2103610	6.2328990	-0.4392940
H	-6.3052620	4.4934970	-1.0730030
H	-3.8392270	7.8008890	0.1321630
H	-6.1013320	6.8439410	-0.3254360
C	5.1220130	2.2139930	-1.7776470
H	4.6592810	1.8171340	-2.6876150
H	4.3041590	2.5114250	-1.1116890
H	5.6814870	3.1145370	-2.0438350
C	-4.3750560	2.6640990	-1.5032800
H	-3.7228130	2.4592300	-2.3591590
H	-4.1168480	1.9304920	-0.7320790
H	-5.4088070	2.4828500	-1.8099500
C	-0.9088920	-5.3647290	-1.9947250
H	-1.1127920	-4.7380880	-2.8695750
H	-0.1479790	-4.8429470	-1.4033090
H	-0.4756380	-6.3059560	-2.3427890

Optimized geometry of singlet **Ir(diMePh-ppy)$_3$**

Symbol	X	Y	Z
C	1.7856260	-3.7655240	1.4554290
C	1.0490150	-2.7571420	0.8055750
C	2.5851220	-3.4653900	2.5523260
C	2.6584750	-2.1501920	3.0104120
C	1.9184300	-1.1899960	2.3344380
C	1.7129430	3.9833090	2.5405680
C	0.5379390	3.3903310	3.0016710
C	0.0760700	2.2670960	2.3296820
H	3.2694750	-1.8693780	3.8607710
H	1.9369300	-0.1492900	2.6372840
H	-0.0101240	3.7815890	3.8512810
H	-0.8340170	1.7637320	2.6356310
C	2.4471750	1.5981120	-0.3738670
C	3.6584410	1.9757150	-1.0226820
C	4.0891270	1.2413070	-2.1343910
C	2.1760980	-0.2176870	-1.9687780
C	3.3549220	0.1539240	-2.6079400
H	1.6150770	-1.0658790	-2.3477560
H	3.7084300	-0.4006660	-3.4743580
H	3.2778730	3.9004460	1.0880420
C	1.8668810	2.2929540	0.7993120
C	2.3718640	3.4375100	1.4449380
C	0.1592770	-2.9149130	-0.3688160
C	-0.1136150	-4.1533270	-1.0188120
C	-1.2818510	-1.7773410	-1.9633470
C	-0.9653490	-4.1621610	-2.1302540
C	-1.5455230	-2.9848910	-2.6025660
H	-1.7384800	-0.8688770	-2.3424850
H	-2.2028620	-3.0159030	-3.4686840
H	1.7335320	-4.7825480	1.1010970
C	1.6862730	0.4774010	-0.8470190
N	0.7118080	1.7339050	1.2720050
H	2.1160630	4.8665290	3.0265940
C	-2.9172660	0.4729630	0.8064520
C	-1.9925610	-1.0606740	2.3367950
C	-4.1587670	0.3376080	1.4561610
C	-2.6104370	1.3215510	-0.3689290
C	-3.1941000	-1.2233690	3.0123340
H	-1.0998040	-1.5956440	2.6401520
C	-4.2975010	-0.5043860	2.5535640
H	-5.0143670	0.8892290	1.1008970
C	-3.5474580	2.1761650	-1.0188020
C	-1.2593240	1.2279200	-0.8429450
H	-3.2555140	-1.8927340	3.8629080
H	-5.2623170	-0.5974000	3.0427320
C	-0.9052950	2.0030260	-1.9632810
C	-1.8199020	2.8349820	-2.6017520
H	0.1099850	1.9457050	-2.3420980
H	-1.5184710	3.4210330	-3.4671410
Ir	-0.0012430	0.0038140	0.1773690
H	3.1468070	-4.2551630	3.0417910
C	-0.4343180	-1.6974820	-0.8423830

N	1.1412930	-1.4763150	1.2757620
N	-1.8528640	-0.2445110	1.2779920
C	-3.1297560	2.9193020	-2.1297550
H	5.0134240	1.5326020	-2.6254360
H	-1.1706430	-5.1088470	-2.6221110
H	-3.8474640	3.5700220	-2.6214320
C	-4.9854750	2.3794630	-0.6276190
C	-5.9951210	1.5963370	-1.2306890
C	-5.3289300	3.4083470	0.2775990
C	-7.3348400	1.8425470	-0.9030840
C	-6.6791870	3.6262460	0.5807660
C	-7.6789520	2.8491720	-0.0021790
H	-8.1122190	1.2373110	-1.3624570
H	-6.9444170	4.4150950	1.2800980
H	-8.7221220	3.0289960	0.2425500
C	4.5616170	3.1114260	-0.6272550
C	5.6160040	2.8849730	0.2854850
C	4.4046950	4.3783870	-1.2327310
C	6.4877020	3.9373770	0.5938530
C	5.2951730	5.4074150	-0.8995360
C	6.3304780	5.1929620	0.0090000
H	7.2973020	3.7653700	1.2985910
H	5.1722900	6.3841250	-1.3605910
H	7.0137680	6.0001770	0.2578960
C	0.4266680	-5.5010510	-0.6267340
C	1.6088160	-5.9869730	-1.2289790
C	-0.2951080	-6.3108480	0.2785140
C	2.0622580	-7.2711820	-0.9003960
C	0.1883960	-7.5899650	0.5829090
C	1.3604250	-8.0702660	0.0007980
H	2.9743670	-7.6442340	-1.3592450
H	-0.3638600	-8.2123950	1.2823900
H	1.7238950	-9.0642800	0.2462730
C	-5.6474230	0.4941700	-2.2059030
H	-5.1271890	0.8865200	-3.0862680
H	-4.9802800	-0.2476200	-1.7525830
H	-6.5479600	-0.0240230	-2.5457820
C	2.3918110	-5.1373720	-2.2045920
H	1.7918830	-4.8795060	-3.0838980
H	2.7055960	-4.1905230	-1.7508120
H	3.2880860	-5.6618370	-2.5461280
C	3.2859840	4.6378480	-2.2165090
H	3.3675990	3.9915320	-3.0969560
H	2.3050400	4.4375950	-1.7709890
H	3.2978120	5.6771560	-2.5552150
C	5.8056210	1.5333270	0.9364040
H	4.9230730	1.2388630	1.5154650
H	5.9671680	0.7481400	0.1901070
H	6.6647900	1.5429860	1.6122780
C	-1.5670710	-5.8116520	0.9262930
H	-1.3911660	-4.8984730	1.5060000
H	-2.3284880	-5.5662170	0.1782020
H	-1.9827460	-6.5648330	1.6008310
C	-4.2629780	4.2618570	0.9271600
H	-3.5608900	3.6538340	1.5087750
H	-3.6685020	4.7986710	0.1801750
H	-4.7096520	4.9982760	1.6003840

Optimized geometry of triplet **Ir(diMePh-ppy)$_3$**

Symbol	X	Y	Z
C	-3.3470060	2.3419590	1.7342350
C	-2.2569440	1.8352000	0.9501800
C	-3.7928930	1.6801650	2.8495810
C	-3.1649510	0.4601890	3.2394290
C	-2.0891860	0.0141390	2.4867630
C	0.7924570	-4.3167650	2.4079980
C	1.5106670	-3.2131730	2.8670360
C	1.2835510	-1.9930310	2.2461990
H	-3.4963060	-0.1051350	4.1026630
H	-1.5649210	-0.8974500	2.7579880
H	2.2259820	-3.2877610	3.6780200
H	1.8114890	-1.0988190	2.5563350
C	-1.2219880	-2.5783890	-0.3537690
C	-2.0859360	-3.5134400	-0.9930330
C	-2.8913060	-3.0779840	-2.0526900
C	-2.0230750	-0.8378250	-1.8584560
C	-2.8615750	-1.7534290	-2.4863880
H	-2.0022440	0.1885820	-2.2081160
H	-3.4935950	-1.4395980	-3.3135900
H	-0.6614930	-5.0180640	1.0076260
C	-0.3099910	-2.9020600	0.7684830
C	-0.1116610	-4.1618170	1.3636140
C	-1.7086700	2.3859080	-0.2369730
C	-2.2173460	3.5333480	-0.9673310
C	0.2225740	2.3201880	-1.8145160
C	-1.4680070	4.0369360	-2.0188600
C	-0.2416490	3.4685930	-2.4474460
H	1.1335760	1.8482010	-2.1680010
H	0.2949950	3.9074280	-3.2829270
H	-3.8151640	3.2699520	1.4402400
C	-1.1896390	-1.2142490	-0.7897310
N	0.4064190	-1.8391680	1.2400890
H	0.9341700	-5.2952920	2.8562610
C	2.8025380	1.1285810	0.8319630
C	1.2459400	1.8838200	2.4385530
C	3.8100010	1.8429060	1.5072490
C	2.9569720	0.3039930	-0.3912430
C	2.2056610	2.6032650	3.1358050
H	0.2089500	1.8599620	2.7537980
C	3.5133560	2.5755170	2.6509800
H	4.8226170	1.8256750	1.1375010
C	4.1885870	0.0962350	-1.0770750
C	1.7516910	-0.3050180	-0.8699300
H	1.9318080	3.1637560	4.0222370
H	4.3026810	3.1216030	3.1583780
C	1.8287090	-1.1138290	-2.0159260
C	3.0307270	-1.3166010	-2.6885080
H	0.9263040	-1.5855100	-2.3918280
H	3.0644870	-1.9414400	-3.5779050
Ir	0.0465470	0.0558740	0.1953030
H	-4.6140480	2.0857900	3.4325370
C	-0.4728970	1.7237170	-0.7487600
N	-1.6153770	0.6557680	1.4087800
N	1.5317510	1.1748790	1.3336330
C	4.1971390	-0.7134880	-2.2199550
H	-3.5471310	-3.7959910	-2.5366550
H	-1.8560780	4.9040330	-2.5490310
H	5.1380080	-0.8676790	-2.7405910
C	5.5265400	0.6684530	-0.6973590
C	5.9428230	1.9044180	-1.2407340
C	6.3958500	-0.0731750	0.1337040
C	7.2191800	2.3898890	-0.9280190

C	7.6647940	0.4442150	0.4245540
C	8.0770790	1.6684210	-0.0993750
H	7.5391110	3.3425610	-1.3422250
H	8.3333170	-0.1227920	1.0673170
H	9.0641500	2.0572530	0.1348200
C	-2.2358740	-4.9677940	-0.6414830
C	-3.2036670	-5.3657770	0.3074170
C	-1.4666000	-5.9365030	-1.3243420
C	-3.3746190	-6.7306220	0.5729230
C	-1.6650260	-7.2921360	-1.0319150
C	-2.6109160	-7.6908320	-0.0887600
H	-4.1164420	-7.0384270	1.3053490
H	-1.0706510	-8.0385260	-1.5526180
H	-2.7540730	-8.7457940	0.1277620
C	-3.5242970	4.2190280	-0.6905310
C	-4.7328800	3.6535050	-1.1594990
C	-3.5414000	5.4635490	-0.0191390
C	-5.9374040	4.3325500	-0.9377450
C	-4.7655390	6.1150470	0.1841200
C	-5.9588840	5.5559820	-0.2693740
H	-6.8654160	3.8962120	-1.2987950
H	-4.7783890	7.0680220	0.7072090
H	-6.9010520	6.0711560	-0.1034370
C	5.0282260	2.7099400	-2.1358380
H	4.7382790	2.1446730	-3.0279110
H	4.0997020	2.9817700	-1.6209030
H	5.5154250	3.6328370	-2.4609920
C	-4.7395420	2.3361260	-1.9003670
H	-4.1174110	2.3830980	-2.8011590
H	-4.3377640	1.5241220	-1.2845340
H	-5.7543540	2.0627910	-2.2018130
C	-0.4313650	-5.5297390	-2.3488620
H	-0.8872020	-4.9998510	-3.1922110
H	0.3154670	-4.8521310	-1.9199940
H	0.0928210	-6.4049520	-2.7414140
C	-4.0412690	-4.3441690	1.0435550
H	-3.4174440	-3.6561960	1.6254810
H	-4.6253200	-3.7286880	0.3510400
H	-4.7350430	-4.8333910	1.7321390
C	-2.2661180	6.0903620	0.5006810
H	-1.6774120	5.3751880	1.0849360
H	-1.6198110	6.4356040	-0.3139560
H	-2.4885610	6.9511230	1.1374320
C	5.9708420	-1.4011480	0.7191460
H	5.0739220	-1.2982640	1.3404950
H	5.7275190	-2.1263100	-0.0646410
H	6.7641910	-1.8248920	1.3403930

Table S5 Selected bon lengths (Å), dihedral angles (degree), and their differences ($\Delta R_{S0\text{-}T1}$ and $\Delta D_{S0\text{-}T1}$) between ground singlet state and excited triplet state for **Ir(ppy)$_3$**, **Ir(Me-ppy)$_3$**, **Ir(Ph-ppy)$_3$**, **Ir(MePh-ppy)$_3$**, and **Ir(diMePh-ppy)$_3$**[a]

	Ir(ppy)$_3$	Ir(Me-ppy)$_3$	Ir(Ph-ppy)$_3$	Ir(MePh-ppy)$_3$	Ir(diMePh-ppy)$_3$
C_{Ph}-C_{py} (Å), S_0	1.47	1.48	1.48	1.48	1.48
C_{Ph}-C_{py} (Å), T_1	1.41	1.42	1.41	1.41	1.41
$\Delta R_{S0\text{-}T1}$ (Å)	0.06	0.06	0.07	0.07	0.07
$D_{Ph\text{-}py}$ (deg), S_0	0.69	6.51	12.37	4.96	1.51
$D_{Ph\text{-}Py}$ (deg), T_1	0.21	7.54	10.97	8.63	5.35
$\Delta D_{S0\text{-}T1}$ (deg)	0.48	1.03	1.40	3.67	3.84
Ir-N_{py} (Å), S_0	2.19	2.17	2.18	2.17	2.17
Ir-N_{py} (Å), T_1	2.16	2.14	2.17	2.15	2.14
$\Delta R_{S0\text{-}T1}$ (Å)	0.03	0.03	0.01	0.02	0.03
Ir-C_{Ph} (Å), S_0	2.02	2.03	2.03	2.03	2.03
Ir-C_{Ph} (Å), T_1	2.02	1.99	1.99	1.98	1.99
$\Delta R_{S0\text{-}T1}$ (Å)	0	0.04	0.04	0.05	0.04

[a] C_{Ph}-C_{py}, $D_{Ph\text{-}Py}$, Ir-N_{py}, and Ir-C_{Ph} indicate the distance and dihedral angle between phenyl-pyridine, Ir-N, and Ir-C, respectively.