Supporting Information

Efficient electroluminescence of bluish green iridium complexes with 2-(3,5-*bis*(trifluoromethyl)phenyl)pyrimidine and 2-(3,5-*bis*(trifluoromethyl)phenyl)-5-fluoropyrimidine main ligands

Hua-Bo Han[1], Zheng-Guang Wu[1], You-Xuan Zheng*[1,2]

[1] State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of Advanced Organic Materials, Collaborative Innovation Center of Advanced Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China, yxzheng@nju.edu.cn

[2] Shenzhen Research Institute of Nanjing University, Shenzhen 518057, P. R. China

General information

^{1}H NMR spectra were measured on a Bruker AM 500 spectrometer. Electrospray ionization mass spectra (ESI-MS) were obtained with ESI-MS (LCQ Fleet, Thermo Fisher Scientific) and Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (autoflex TOF/TOF, Bruker Daltonics). Elemental analyses for C, H and N were performed on an Elementar Vario MICRO analyzer. TG-DSC measurements were carried out on a DSC 823e analyzer (METTLER). UV-vis absorption and photoluminescence spectra were measured on a Shimadzu UV-3100 and a Hitachi F-4600 spectrophotometer at room temperature, respectively. The emission spectra at 77 K were measured on Hitachi F-4600 spectrophotometer. Cyclic voltammetry measurements were conducted on a MPI-A multifunctional electrochemical and chemiluminescent system at room temperature using Fc^+/Fc as the internal standard and scan rate of 0.05 V s^{-1}. The luminescence quantum efficiencies were calculated by comparison of the emission intensities (integrated areas) of a standard sample (*fac*-$Ir(ppy)_3$) and the unknown sample.[1] The decay lifetimes were measured with an HORIBA Scientific 3-D fluorescence spectrometer.

X-ray crystallography

X-ray crystallographic measurements of the single crystals were carried out on a Bruker SMART CCD diffractometer (Bruker Daltonic Inc.) using monochromated Mo Kα radiation

(λ = 0.71073 Å) at room temperature. Cell parameters were retrieved using SMART software and refined using *SAINT* [2] program in order to reduce the highly redundant data sets. Data were collected using a narrow-frame method with scan width of 0.30° in ω and an exposure time of 5 s per frame. Absorption corrections were applied using *SADABS* [3] supplied by Bruker. The structures were solved by Patterson methods and refined by full-matrix least-squares on F^2 using the program *SHELXS-2014*.[4] The positions of metal atoms and their first coordination spheres were located from direct-methods E-maps, other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and during the final cycles refined anisotropically. Hydrogen atoms were placed in calculated position and refined as riding atoms with a uniform value of U_{iso}.

OLEDs fabrication and measurement

All OLEDs were fabricated on the pre-patterned ITO-coated glass substrate with a sheet resistance of 15 Ω / sq. The deposition rate for organic compounds (TAPC (1,1-*bis*(4-(di-p-tolylamino)phenyl)cyclohexane, mCP (1,3-bis(9H-carbazol-9-yl)benzene, PPO21 3-(diphenylphosphoryl)-9-(4-(diphenyl-phosphoryl)phenyl)-9H-carbazole, TmPyPB (1,3,5-*tri*(m-pyrid-3-yl-phenyl) benzene)) is 1 Å/s. The phosphors and the host PPO21 was co-evaporated to form emitting layer from two separate sources. The cathode of LiF and Al were deposited with deposition rates of 0.1 and 3 Å/s, respectively. The characteristic curves of the devices were measured with a computer which controlled KEITHLEY 2400 source meter with a calibrated silicon diode in air without device encapsulation. On the basis of the uncorrected PL and EL spectra, the Commission Internationale de l'Eclairage (CIE) coordinates were calculated using a test program of the Spectra scan PR650 spectrophotometer.

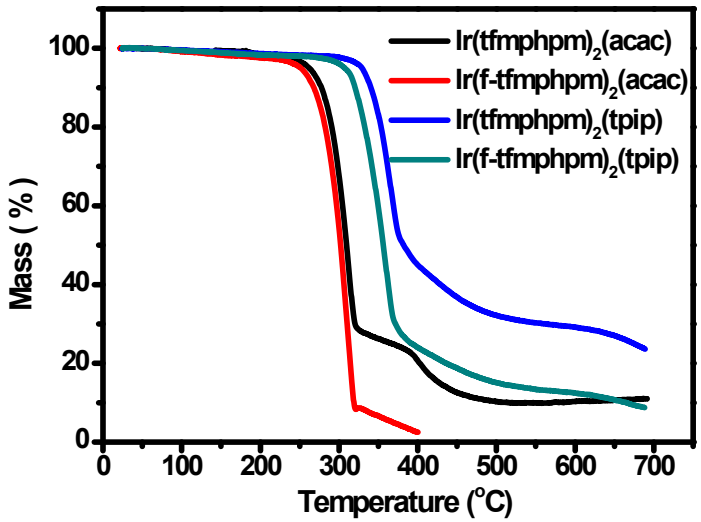


Fig. S1. The TGA curves of **Ir(tfmphpm)$_2$(acac)**, **Ir(f-tfmphpm)$_2$(acac)**, **Ir(tfmpphm)$_2$(tpip)** and **Ir(f-tfmphpm)$_2$(tpip)**.

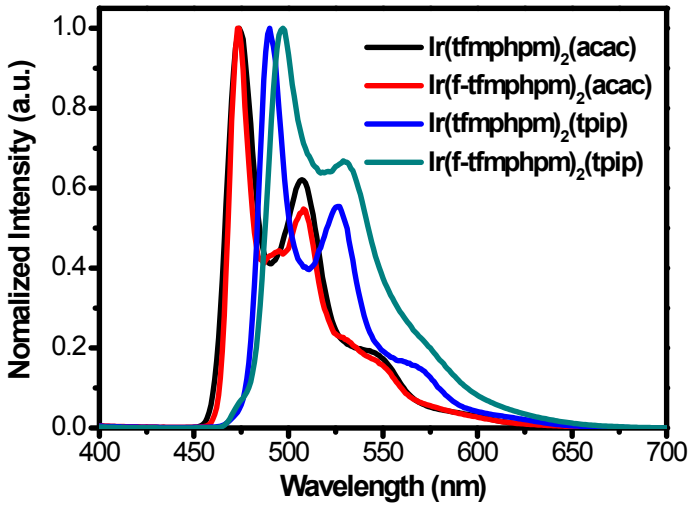


Fig. S2. Normalized PL spectra of **Ir(tfmphpm)$_2$(acac)**, **Ir(f-tfmphpm)$_2$(acac)**, **Ir(tfmpphm)$_2$(tpip)** and **Ir(f-tfmphpm)$_2$(tpip)** in degassed CH_2Cl_2 solutions (5×10^{-5} mol·L^{-1}) at 77 K.

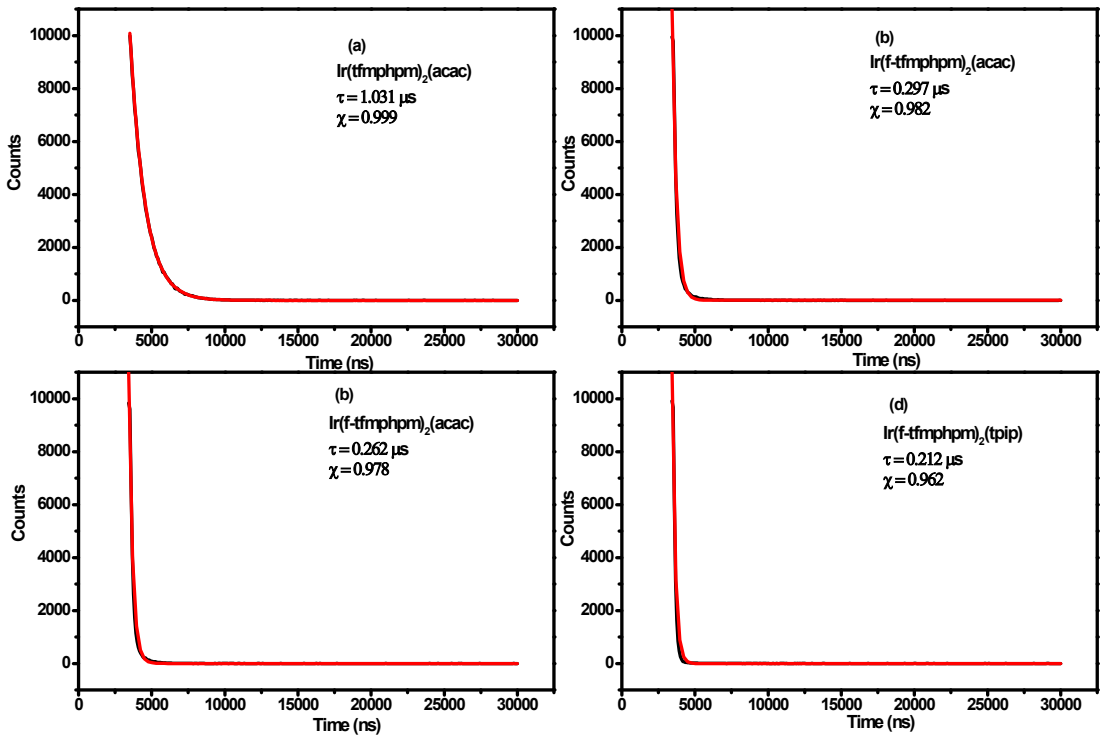


Fig. S3. The lifetime curves of **Ir(tfmphpm)$_2$(acac)**, **Ir(f-tfmphpm)$_2$(acac)**, **Ir(tfmphpm)$_2$(tpip)** and **Ir(f-tfmphpm)$_2$(tpip)** complexes.

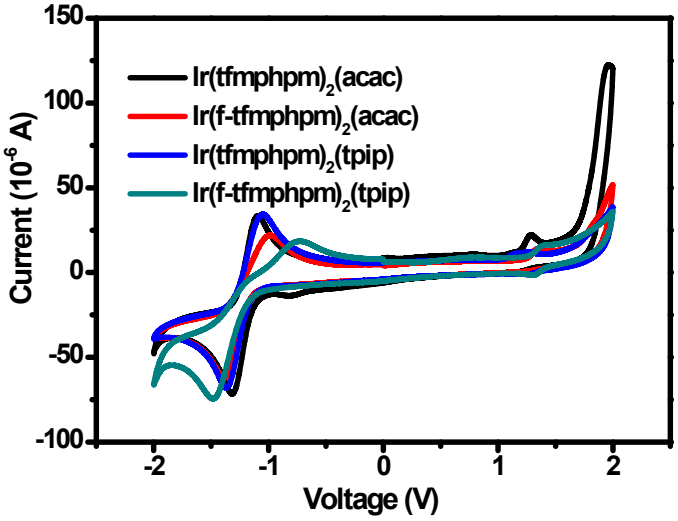


Fig. S4. The cyclic voltammogram curves of **Ir(tfmphpm)$_2$(acac)**, **Ir(f-tfmphpm)$_2$(acac)**, **Ir(tfmphpm)$_2$(tpip)** and **Ir(f-tfmphpm)$_2$(tpip)** in the range of -2 – 2 V.

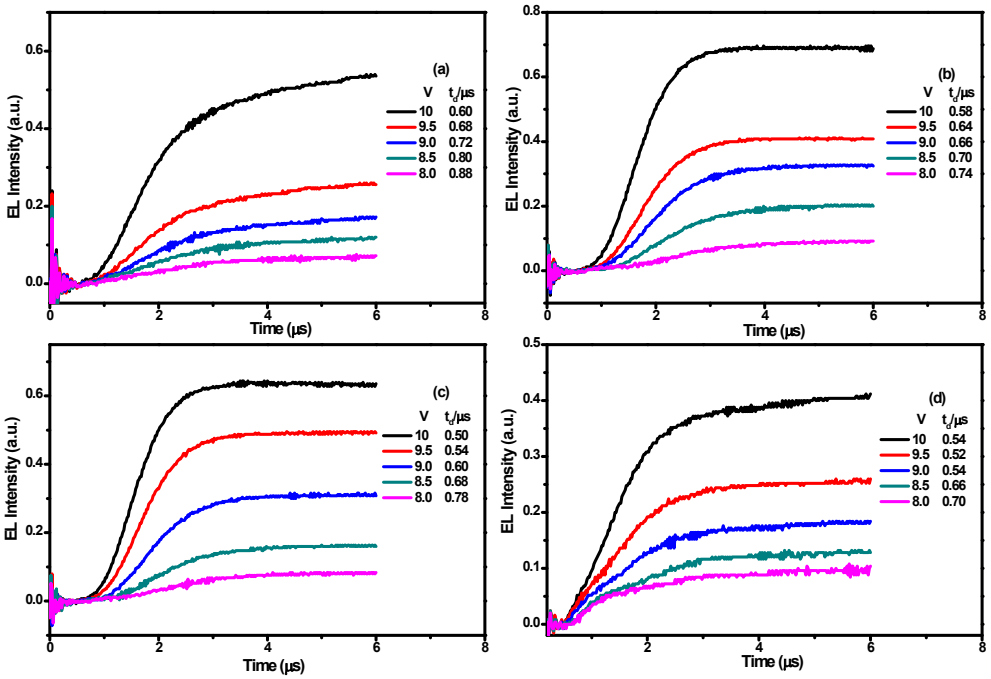


Fig. S5 (a), (b), (c) and (d) the transient EL signals for the device structure of ITO/ TAPC (50 nm)/ Ir complexes (60 nm) / LiF (1 nm) / Al (100 nm) under different applied fields of **Ir(tfmphpm)$_2$(acac)**, **Ir(f-tfmphpm)$_2$(acac)**, **Ir(tfmphpm)$_2$(tpip)** and **Ir(f-tfmphpm)$_2$(tpip)** complexes.

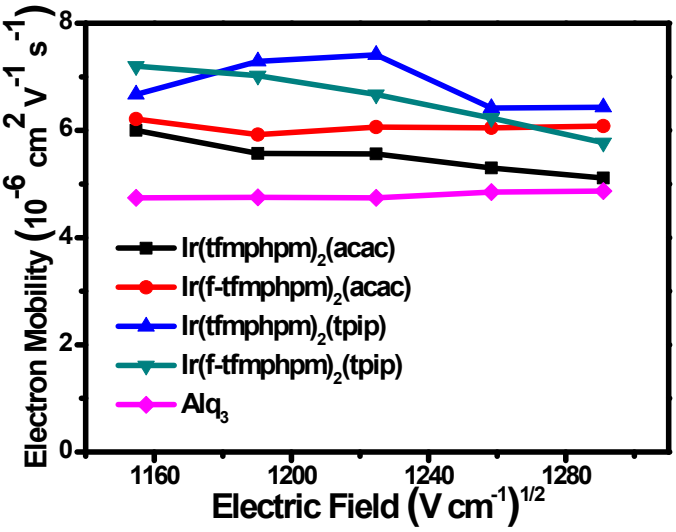


Fig. S6 Electric field dependence of charge electron mobility in the thin films of **Ir(tfmphphm)$_2$(acac)**, **Ir(f-tfmphphm)$_2$(acac)**, **Ir(tfmphphm)$_2$(tpip)**, **Ir(f-tfmphphm)$_2$(tpip)** and Alq_3.

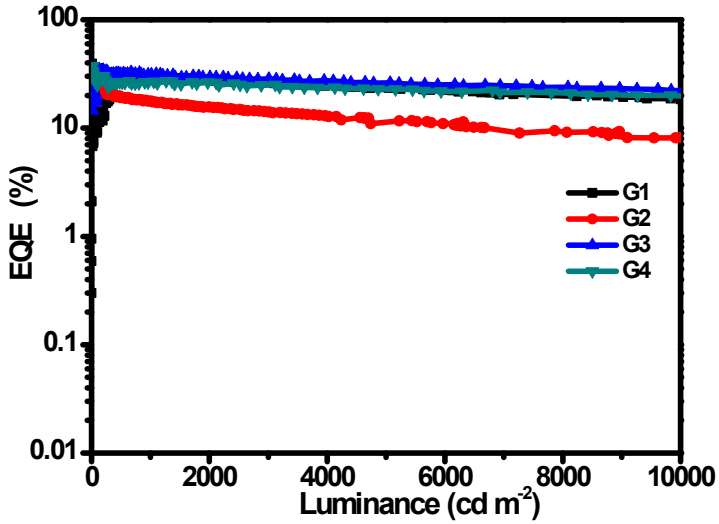
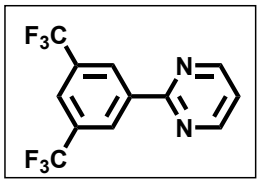
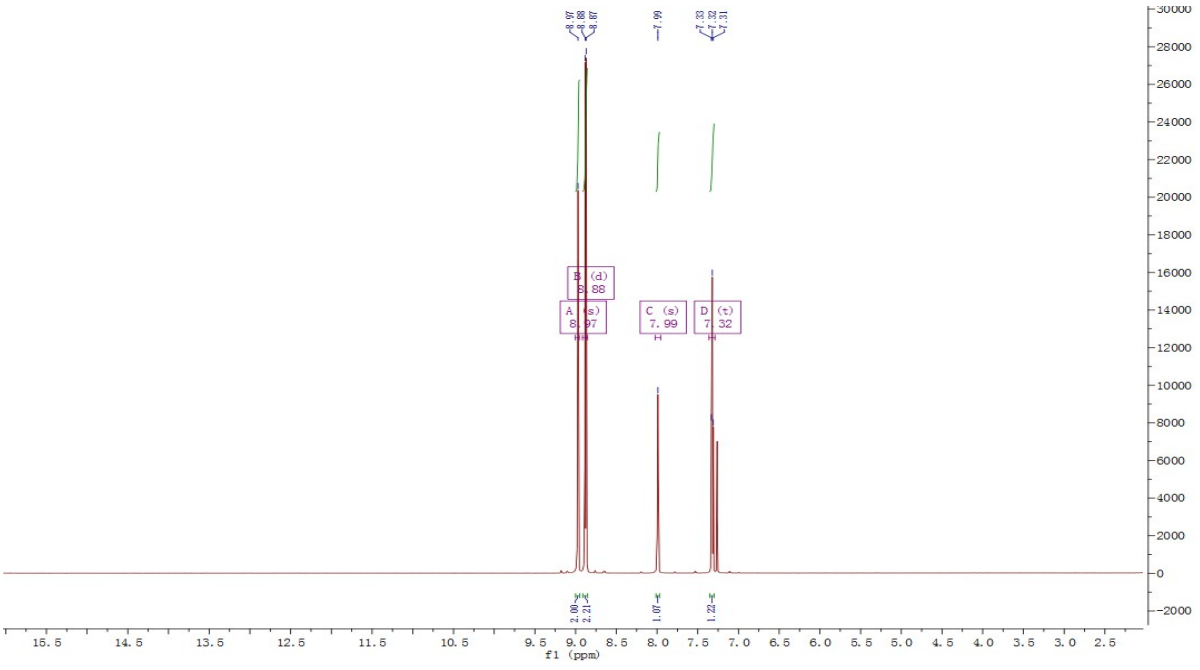
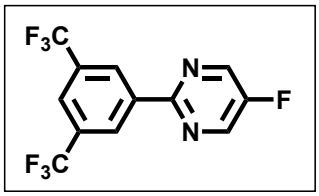


Fig. S7 The curves of external quantum efficiency (EQE) - luminance of devices **G1, G2, G3** and **G4**.







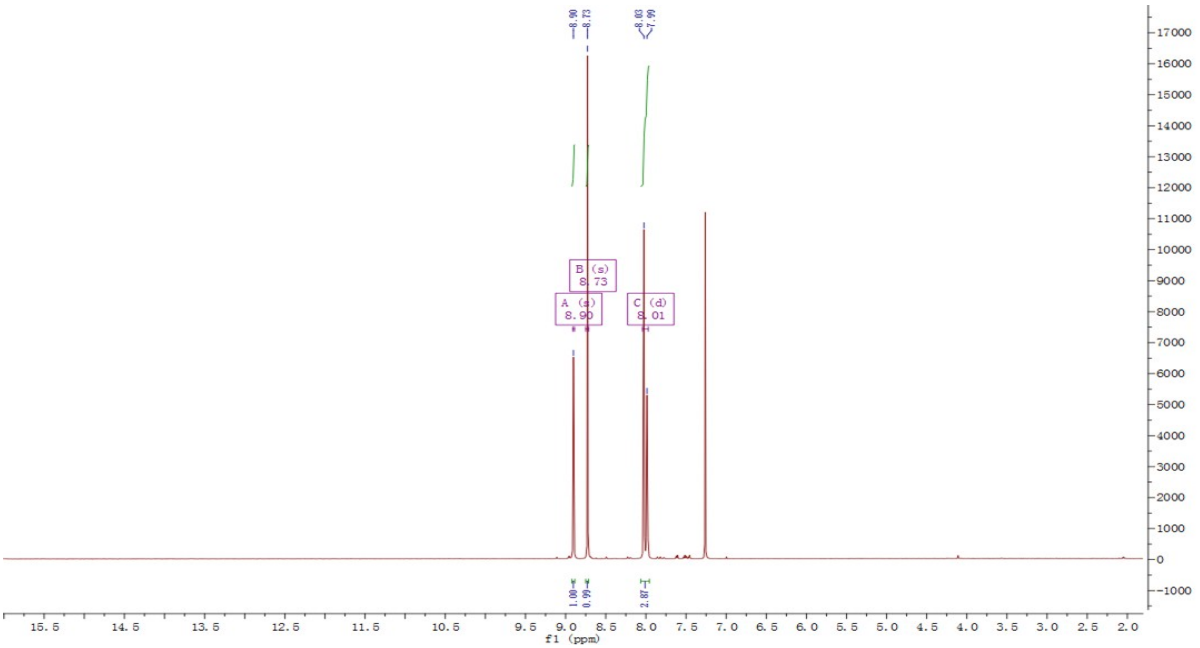
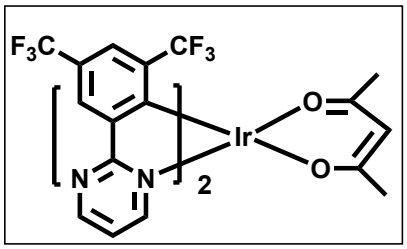
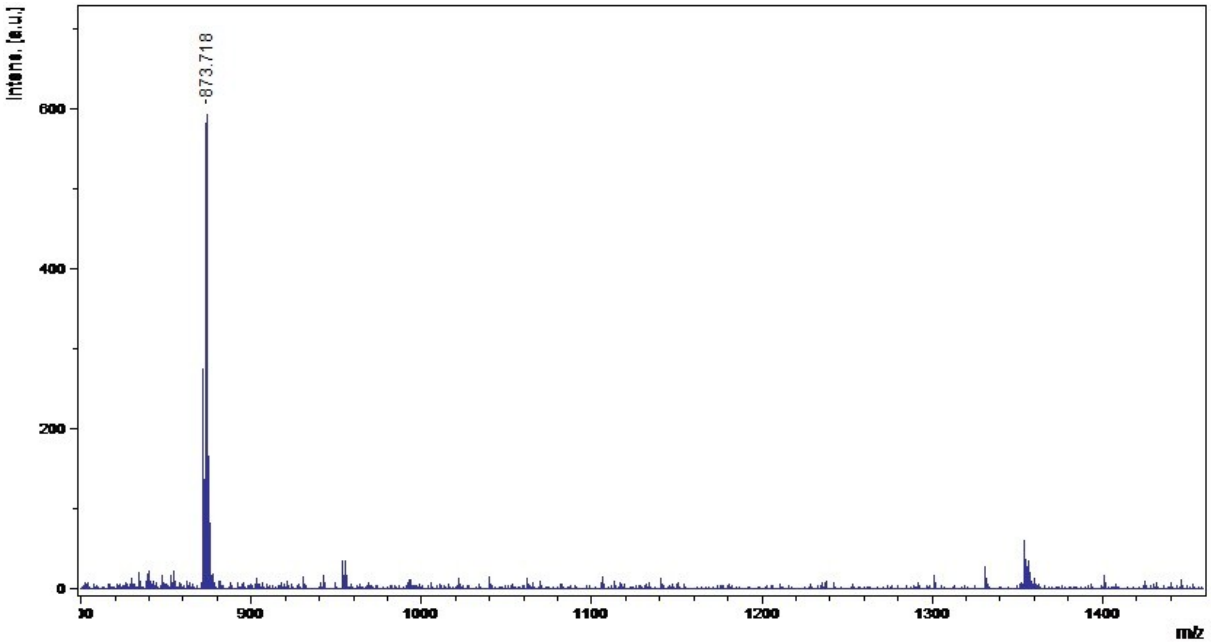
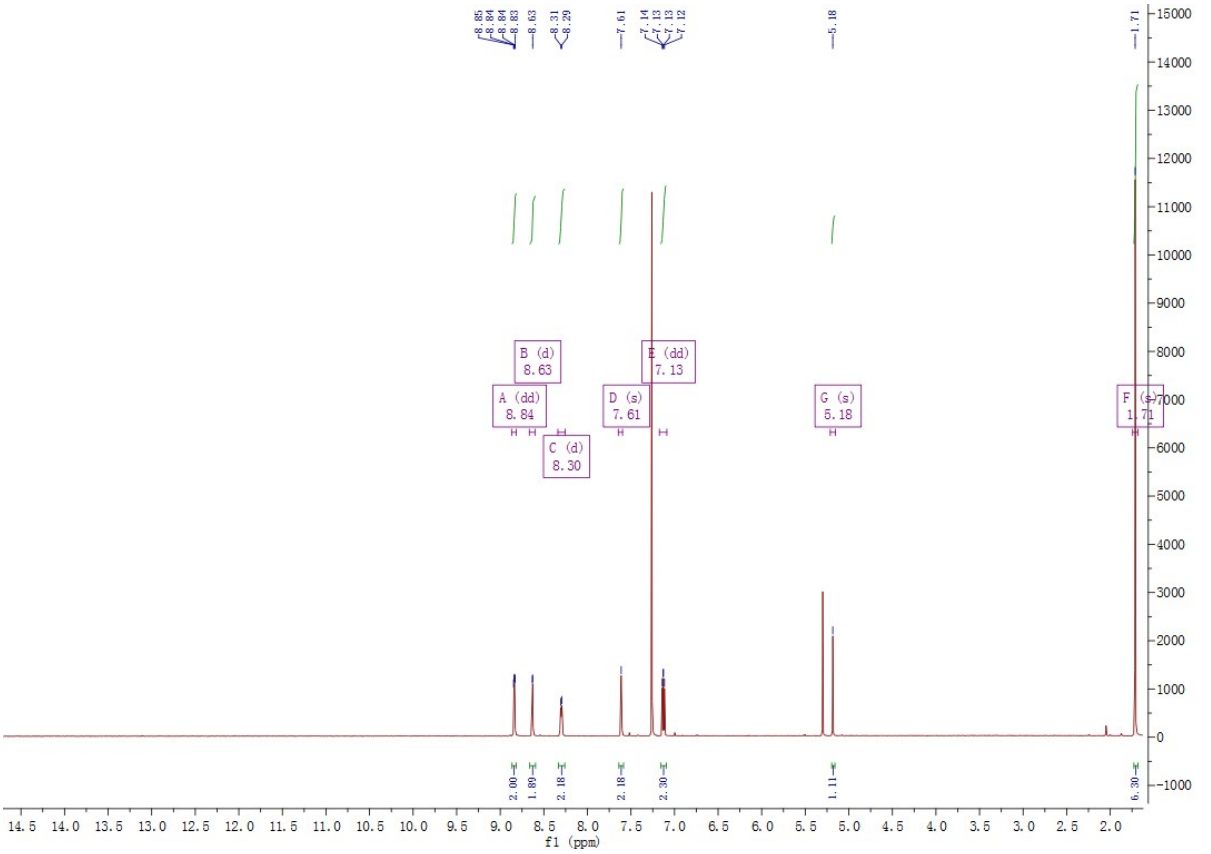


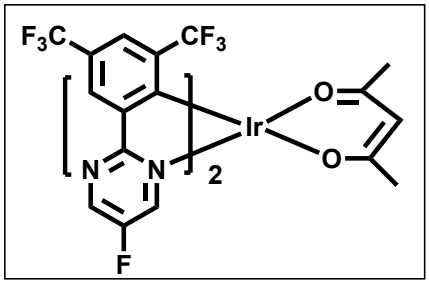
Fig. S8. The ^{1}H NMR pectra of **tfmphpm** and **f-tfmphpm**.



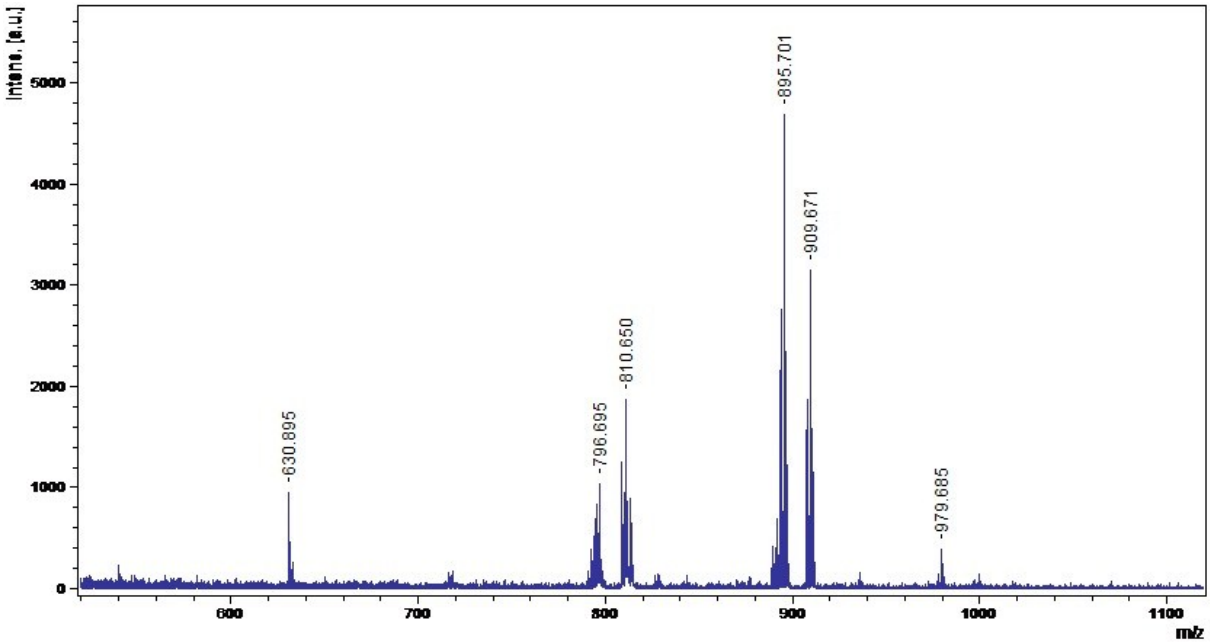
m/z: calcd for $C_{29}H_{17}F_{12}IrN_4O_2$, 873.679.

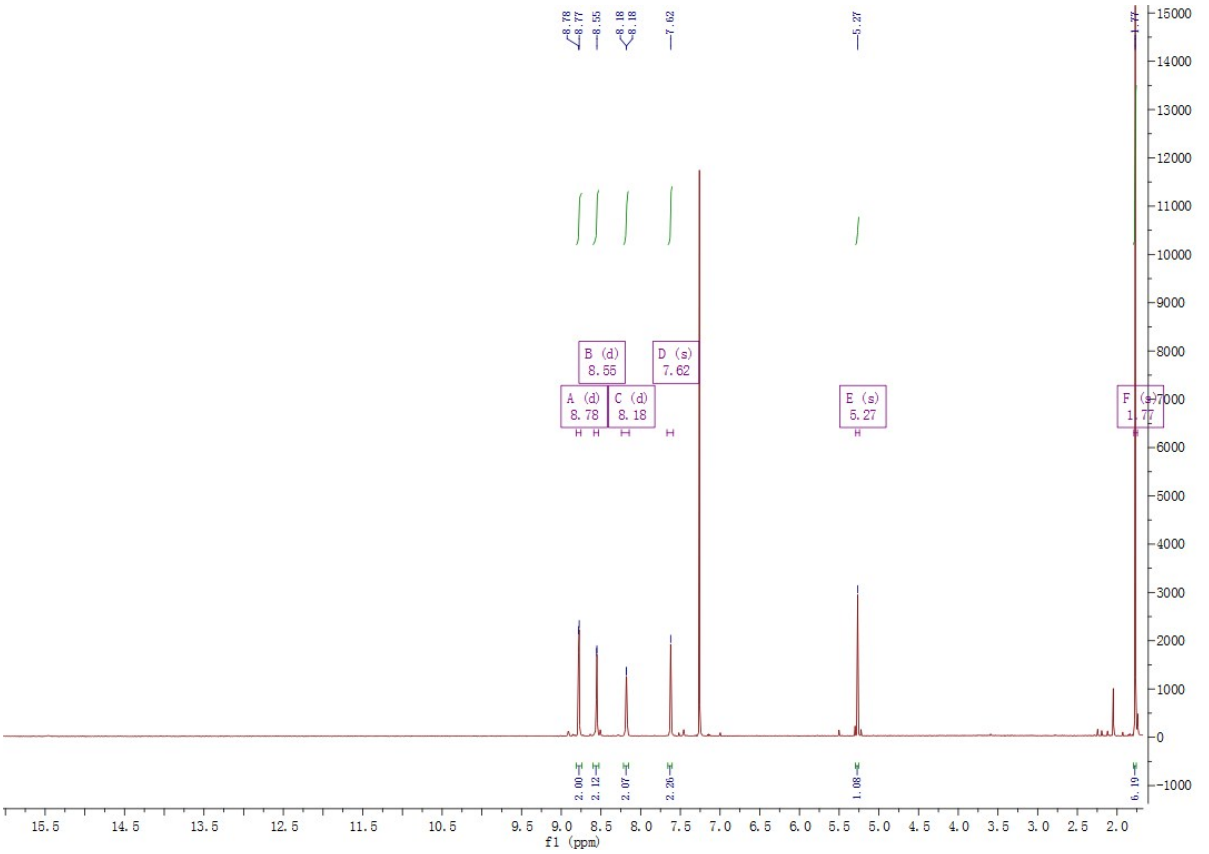


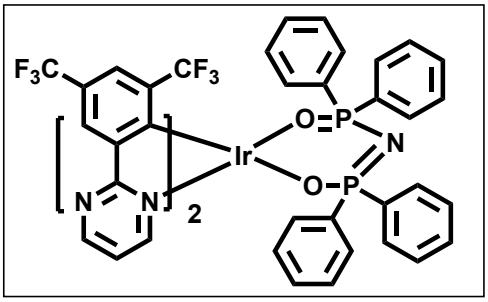




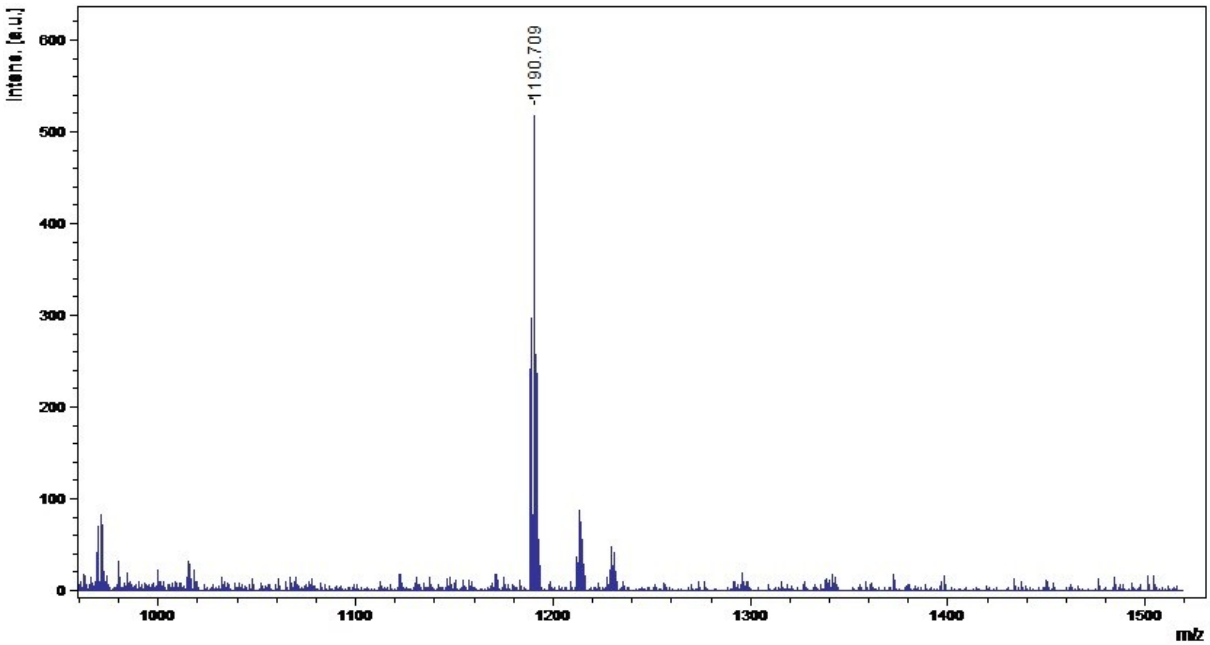
m/z: calcd for $C_{29}H_{15}F_{14}IrN_4O_2$, 909.660.

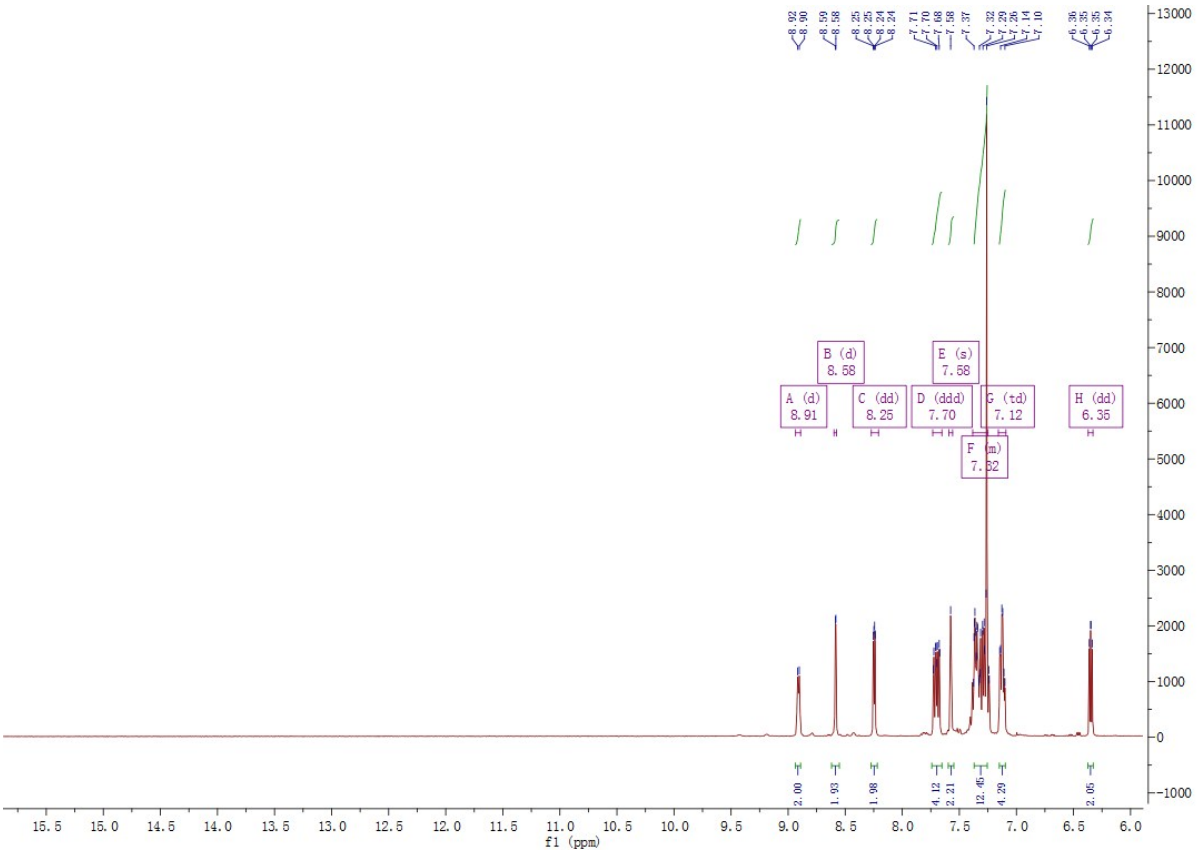


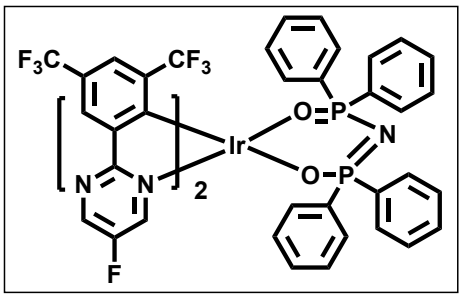




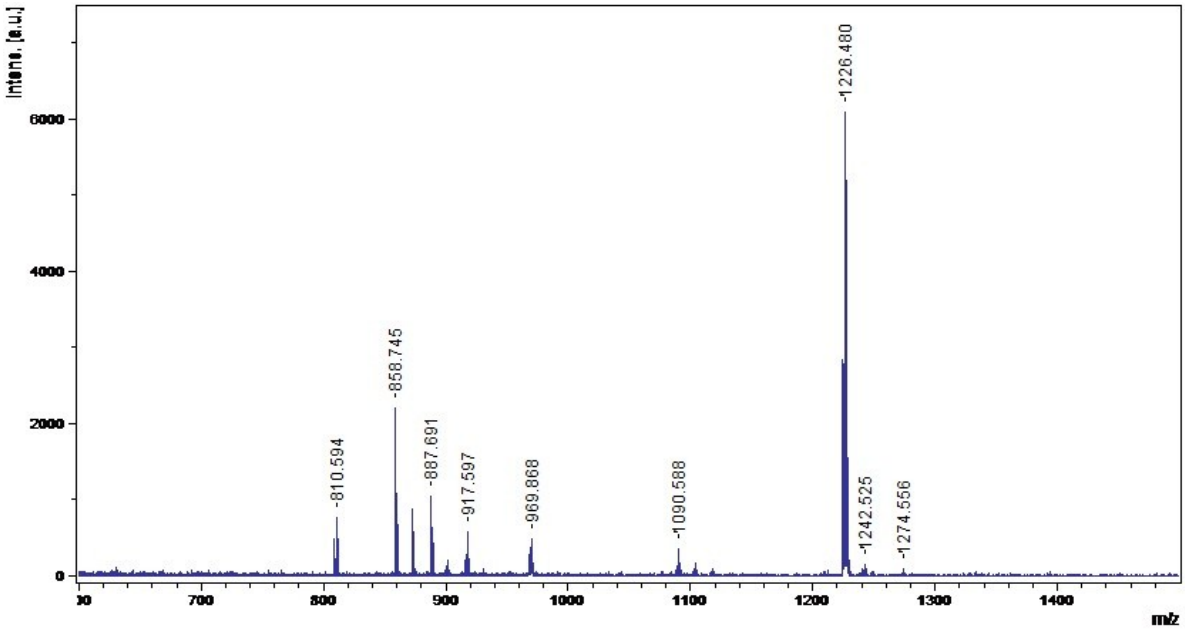
m/z: calcd for $C_{48}H_{30}F_{12}IrN_5O_2P_2$, 1190.946.







m/z: calcd for $C_{48}H_{28}F_{14}IrN_5O_2P_2$, 1126.927.



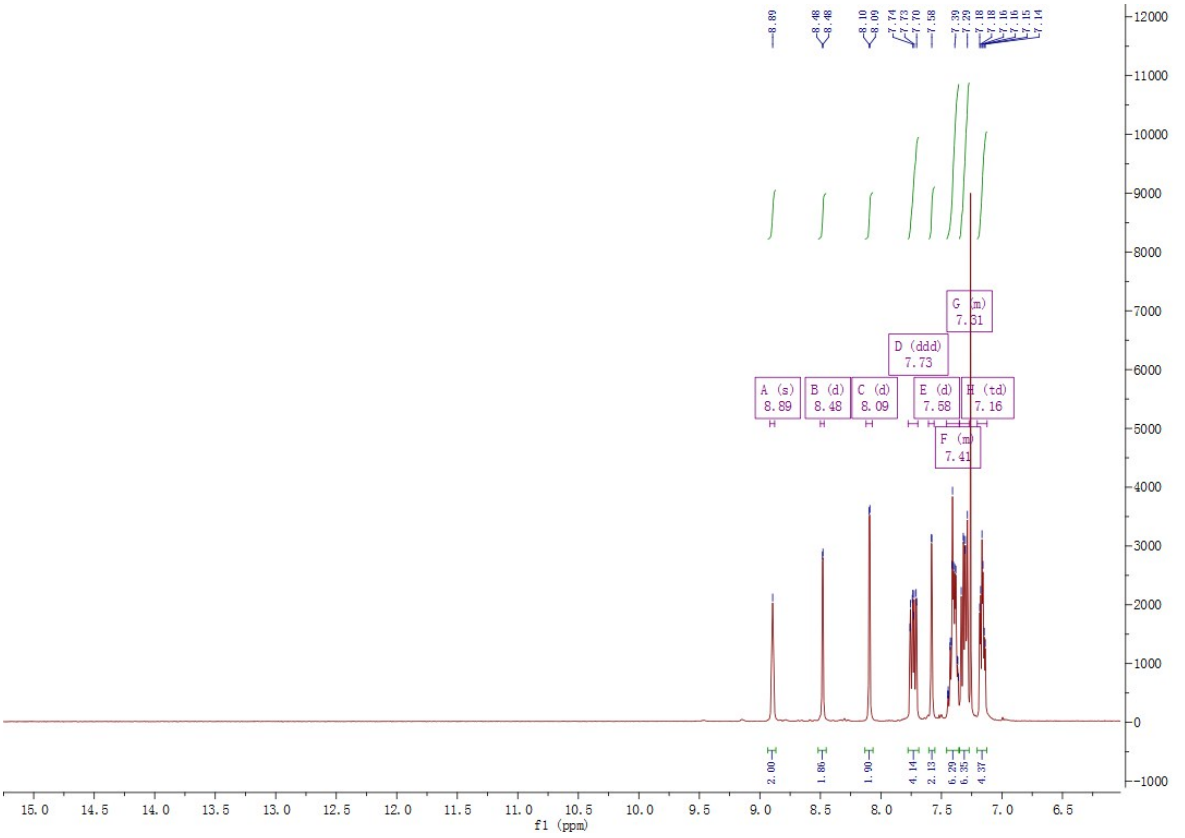


Fig. S9. The Mass Spectra and ^{1}H NMR spectra of **Ir(tfmphpm)$_2$(acac)**, **Ir(f-**

tfmphpm)$_2$(acac), **Ir(tfmphpm)$_2$(tpip)**, **Ir(f-tfmphpm)$_2$(tpip)**.

Table S1. Crystallographic data of **Ir(f-tfmphpm)$_2$(acac)**, **Ir(tfmphpm)$_2$(tpip)** and **Ir(f-tfmphpm)$_2$(tpip)**.

	Ir(tfmphpm)$_2$(acac)	**Ir(tfmphpm)$_2$(tpip)**	**Ir(f-fmphpm)$_2$(tpip)**
Formula	$C_{29}H_{15}F_{14}IrN_4O_2$	$C_{48}H_{28}F_{12}IrN_5O_2P_2$	$C_{48}H_{28}F_{14}IrN_5O_2P_2$
FW	909.90	1190.93	1226.92
T (K)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	Triclinic	Monoclinic
Space group	C 1 2/c 1	P -1	P2(1)/c
a (Å)	19.7352(17)	10.713(7)	10.7026(8)
b (Å)	10.5902(10)	11.791(3)	23.3672(19)
c (Å)	16.4426(15)	18.760(5)	18.9711(14)
α (deg)	90	80.084(5)	90
β (deg)	117.554	84.606(5)	100.879
γ (deg)	90	87.756(5)	90
V (Å^3)	3046.7(5)	2323.3(11)	4659.2(6)
Z	4	2	4
ρ_{calcd} (mg/cm^3)	1.983	1.703	1.749
μ (Mo Kα) (mm^{-1})	4.503	3.036	3.037
F (000)	1738.7	1168.0	2400.0
Reflns collected	10124	12809	39465
Unique	3519	8051	10660
Data/restraints/params	3519 / 6 / 258	8051 / 8 / 631	10660 / 6 / 649
GOF on F^2	1.034	1.007	1.201
$R_1{}^a$, $wR_2{}^b$ [$I > 2\sigma(I)$]	0.0221, 0.0483	0.0737, 0.1996	0.0701, 0.1778
$R_1{}^a$, $wR_2{}^b$ (all data)	0.0263, 0.0503	0.0950, 0.2220	0.0801, 0.1816
CCDC NO	1828771	1828766	1584888

$R_1{}^a = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2{}^b = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)]^{1/2}$

Table S2a The selected bond lengths and angels of **Ir(f-tfmphpm)$_2$(acac)**.

Selected bonds Å					
F(7A)-C(15)	1.251(7)	N(2)-C(7)	1.336(5)	C(10)-H(10)	0.93
Ir(1)-N(1)	2.043(3)	C(9)-C(8)	1.414(5)	C(5)-C(6)	1.365(7)
Ir(1)-N(1)#1	2.043(3)	C(9)-C(11)	1.418(5)	C(6)-H(6)	0.93
Ir(1)-C(9)	2.049(3)	F(4)-C(14)	1.339(5)	C(12)-C(15)	1.502(6)
Ir(1)-C(9)#1	2.049(3)	C(4)-C(5)	1.367(6)	F(5)-C(15)	1.283(8)
Ir(1)-O(1)#1	2.112(3)	C(4)-H(4)	0.93	C(3)-C(2)	1.389(6)
Ir(1)-O(1)	2.112(3)	C(11)-C(13)	1.389(5)	C(3)-C(1)	1.515(7)
O(1)-C(3)	1.272(5)	C(11)-C(14)	1.497(6)	F(6)-C(15)	1.269(9)
F(1)-C(5)	1.343(5)	C(13)-C(12)	1.381(7)	C(1)-H(1A)	0.96
N(1)-C(4)	1.341(5)	C(13)-H(13)	0.93	C(1)-H(1B)	0.96
N(1)-C(7)	1.347(5)	C(7)-C(8)	1.458(5)	C(1)-H(1C)	0.96
F(2)-C(14)	1.328(6)	C(10)-C(12)	1.368(7)	C(2)-C(3)#1	1.389(6)
F(3)-C(14)	1.340(6)	C(10)-C(8)	1.395(5)	C(2)-H(2)	0.93
N(2)-C(6)	1.331(6)				

Selected angels°			
N(1)-Ir(1)-N(1)#1	171.97(16)	C(8)-C(10)-H(10)	120.2
N(1)-Ir(1)-C(9)	81.18(13)	F(1)-C(5)-C(6)	120.2(4)
N(1)#1-Ir(1)-C(9)	104.35(13)	F(1)-C(5)-C(4)	119.6(4)
N(1)-Ir(1)-C(9)#1	104.35(13)	C(6)-C(5)-C(4)	120.2(4)
N(1)#1-Ir(1)-C(9)#1	81.18(13)	C(10)-C(8)-C(9)	123.8(4)
C(9)-Ir(1)-C(9)#1	95.13(19)	C(10)-C(8)-C(7)	118.9(3)
N(1)-Ir(1)-O(1)#1	84.39(11)	C(9)-C(8)-C(7)	117.3(3)
N(1)#1-Ir(1)-O(1)#1	89.94(11)	N(2)-C(6)-C(5)	120.9(4)
C(9)-Ir(1)-O(1)#1	87.99(13)	N(2)-C(6)-H(6)	119.5
C(9)#1-Ir(1)-O(1)#1	171.06(12)	C(5)-C(6)-H(6)	119.5
N(1)-Ir(1)-O(1)	89.94(11)	C(10)-C(12)-C(13)	119.1(4)
N(1)#1-Ir(1)-O(1)	84.39(11)	C(10)-C(12)-C(15)	120.2(5)
C(9)-Ir(1)-O(1)	171.06(12)	C(13)-C(12)-C(15)	120.7(5)
C(9)#1-Ir(1)-O(1)	87.99(13)	O(1)-C(3)-C(2)	126.4(5)
O(1)#1-Ir(1)-O(1)	90.18(17)	O(1)-C(3)-C(1)	114.4(5)
C(3)-O(1)-Ir(1)	123.9(3)	C(2)-C(3)-C(1)	119.2(5)
C(4)-N(1)-C(7)	118.3(3)	F(2)-C(14)-F(4)	105.6(4)
C(4)-N(1)-Ir(1)	125.8(3)	F(2)-C(14)-F(3)	106.0(4)
C(7)-N(1)-Ir(1)	115.3(2)	F(4)-C(14)-F(3)	106.4(4)
C(6)-N(2)-C(7)	117.2(4)	F(2)-C(14)-C(11)	113.5(4)
C(8)-C(9)-C(11)	114.2(3)	F(4)-C(14)-C(11)	112.5(4)
C(8)-C(9)-Ir(1)	111.1(3)	F(3)-C(14)-C(11)	112.3(4)
C(11)-C(9)-Ir(1)	134.7(3)	F(7A)-C(15)-F(6)	106.5(7)
N(1)-C(4)-C(5)	119.1(4)	F(7A)-C(15)-F(5)	107.6(7)
N(1)-C(4)-H(4)	120.5	F(6)-C(15)-F(5)	100.7(6)
C(5)-C(4)-H(4)	120.5	F(7A)-C(15)-C(12)	114.1(5)
C(13)-C(11)-C(9)	121.7(4)	F(6)-C(15)-C(12)	112.4(6)
C(13)-C(11)-C(14)	116.0(4)	F(5)-C(15)-C(12)	114.4(5)
C(9)-C(11)-C(14)	122.3(3)	C(3)-C(1)-H(1A)	109.5
C(12)-C(13)-C(11)	121.6(4)	C(3)-C(1)-H(1B)	109.5
C(12)-C(13)-H(13)	119.2	H(1A)-C(1)-H(1B)	109.5
C(11)-C(13)-H(13)	119.2	C(3)-C(1)-H(1C)	109.5
N(2)-C(7)-N(1)	124.3(4)	H(1A)-C(1)-H(1C)	109.5
N(2)-C(7)-C(8)	121.4(3)	H(1B)-C(1)-H(1C)	109.5
N(1)-C(7)-C(8)	114.3(3)	C(3)#1-C(2)-C(3)	129.0(6)
C(12)-C(10)-C(8)	119.6(4)	C(3)#1-C(2)-H(2)	115.5
C(12)-C(10)-H(10)	120.2	C(3)-C(2)-H(2)	115.5

Table S2b The selected bond lengths and angels of **Ir(tfmphpm)$_2$(tpip)**.

Selected bonds Å					
Ir(1)-C(63)	2.004(5)	C(15)-C(46)	1.495(7)	C(51)-C(221)	1.388(7)
Ir(1)-C(170)	2.030(6)	C(16)-C(54)	1.329(9)	C(51)-H(51)	0.93
Ir(1)-N(9)	2.045(4)	C(16)-C(21)	1.429(8)	C(54)-C(150)	1.416(10)

Ir(1)-N(6)	2.054(4)	C(18)-C(40)	1.398(8)	C(54)-H(54)	0.93
Ir(1)-O(3)	2.169(3)	C(18)-C(59)	1.409(9)	C(56)-H(56)	0.93
Ir(1)-O(4)	2.196(3)	C(21)-C(61)	1.348(9)	C(57)-H(57)	0.93
P(3)-O(4)	1.536(4)	C(21)-H(21)	0.93	C(59)-H(59)	0.93
P(3)-N(10)	1.592(4)	C(25)-C(36)	1.466(7)	C(61)-C(151)	1.432(10)
P(3)-C(219)	1.784(6)	C(29)-C(32)	1.389(7)	C(61)-H(61)	0.93
P(3)-C(18)	1.796(5)	C(29)-C(47)	1.397(8)	C(62)-C(167)	1.404(10)
P(4)-O(3)	1.528(4)	C(29)-H(29)	0.93	C(62)-H(62)	0.93
P(4)-N(10)	1.606(4)	C(30)-C(56)	1.392(9)	C(133)-H(133)	0.93
P(4)-C(30)	1.811(5)	C(30)-C(37)	1.393(8)	C(165)-C(168)	1.408(7)
P(4)-C(16)	1.812(6)	C(32)-C(63)	1.423(7)	C(165)-H(165)	0.93
F(13)-C(225)	1.297(7)	C(36)-C(165)	1.322(7)	C(167)-H(167)	0.93
F(14)-C(225)	1.325(6)	C(36)-C(170)	1.405(7)	C(168)-C(222)	1.416(6)
F(15)-C(225)	1.284(8)	C(37)-C(50)	1.369(9)	C(168)-C(225)	1.500(7)
F(16)-C(207)	1.318(7)	C(37)-H(37)	0.93	C(170)-C(210)	1.402(8)
F(17)-C(207)	1.310(7)	C(38)-C(49)	1.368(7)	C(205)-C(217)	1.355(10)
F(18)-C(207)	1.350(8)	C(38)-H(38)	0.93	C(205)-C(206)	1.437(11)
F(19)-C(46)	1.325(7)	C(39)-C(56)	1.339(8)	C(205)-H(205)	0.93
F(20)-C(46)	1.339(6)	C(39)-C(44)	1.393(10)	C(206)-C(215)	1.376(12)
F(21)-C(46)	1.378(7)	C(39)-H(39)	0.93	C(206)-H(206)	0.93
F(22)-C(226)	1.298(9)	C(40)-C(62)	1.361(8)	C(207)-C(210)	1.524(7)
F(23)-C(226)	1.265(9)	C(40)-H(40)	0.93	C(210)-C(222)	1.401(7)
F(24)-C(226)	1.287(8)	C(41)-C(167)	1.384(11)	C(215)-C(216)	1.368(10)
N(6)-C(38)	1.336(7)	C(41)-C(59)	1.399(10)	C(215)-H(215)	0.93
N(6)-C(25)	1.383(6)	C(41)-H(41)	0.93	C(216)-C(219)	1.430(8)
N(7)-C(25)	1.354(6)	C(44)-C(50)	1.370(11)	C(216)-H(216)	0.93
N(7)-C(57)	1.367(8)	C(44)-H(44)	0.93	C(217)-C(219)	1.388(9)
N(8)-C(13)	1.328(6)	C(47)-C(133)	1.396(8)	C(217)-H(217)	0.93
N(8)-C(48)	1.371(8)	C(47)-C(226)	1.512(8)	C(221)-H(221)	0.93
N(9)-C(221)	1.323(7)	C(48)-C(51)	1.340(8)	C(222)-H(222)	0.93
N(9)-C(13)	1.407(6)	C(48)-H(48)	0.93	C(151)-C(150)	1.393(10)
C(13)-C(32)	1.440(7)	C(49)-C(57)	1.390(9)	C(151)-H(151)	0.93
C(15)-C(133)	1.427(7)	C(49)-H(49)	0.93	C(150)-H(150)	0.93
C(15)-C(63)	1.437(7)	C(50)-H(50)	0.93		

Selected angels°			
C(63)-Ir(1)-C(170)	100.2(2)	N(8)-C(48)-H(48)	118.2
C(63)-Ir(1)-N(9)	81.50(18)	C(38)-C(49)-C(57)	117.9(5)
C(170)-Ir(1)-N(9)	102.94(18)	C(38)-C(49)-H(49)	121.1
C(63)-Ir(1)-N(6)	103.53(18)	C(57)-C(49)-H(49)	121.1
C(170)-Ir(1)-N(6)	82.07(18)	C(37)-C(50)-C(44)	120.3(6)
N(9)-Ir(1)-N(6)	172.31(17)	C(37)-C(50)-H(50)	119.9
C(63)-Ir(1)-O(3)	173.42(17)	C(44)-C(50)-H(50)	119.9
C(170)-Ir(1)-O(3)	85.14(18)	C(48)-C(51)-C(221)	118.2(5)
N(9)-Ir(1)-O(3)	93.67(15)	C(48)-C(51)-H(51)	120.9
N(6)-Ir(1)-O(3)	80.84(15)	C(221)-C(51)-H(51)	120.9
C(63)-Ir(1)-O(4)	87.55(16)	C(16)-C(54)-C(150)	121.2(6)
C(170)-Ir(1)-O(4)	167.90(16)	C(16)-C(54)-H(54)	119.4
N(9)-Ir(1)-O(4)	87.28(14)	C(150)-C(54)-H(54)	119.4
N(6)-Ir(1)-O(4)	87.13(14)	C(39)-C(56)-C(30)	123.3(6)
O(3)-Ir(1)-O(4)	87.76(12)	C(39)-C(56)-H(56)	118.3
O(4)-P(3)-N(10)	117.9(2)	C(30)-C(56)-H(56)	118.3
O(4)-P(3)-C(219)	105.9(2)	N(7)-C(57)-C(49)	123.2(5)
N(10)-P(3)-C(219)	110.0(2)	N(7)-C(57)-H(57)	118.4
O(4)-P(3)-C(18)	110.3(2)	C(49)-C(57)-H(57)	118.4
N(10)-P(3)-C(18)	108.4(2)	C(41)-C(59)-C(18)	118.8(7)
C(219)-P(3)-C(18)	103.3(2)	C(41)-C(59)-H(59)	120.6
O(3)-P(4)-N(10)	118.3(2)	C(18)-C(59)-H(59)	120.6
O(3)-P(4)-C(30)	107.4(2)	C(21)-C(61)-C(151)	120.8(6)
N(10)-P(4)-C(30)	109.8(2)	C(21)-C(61)-H(61)	119.6
O(3)-P(4)-C(16)	107.2(2)	C(151)-C(61)-H(61)	119.6
N(10)-P(4)-C(16)	108.7(2)	C(40)-C(62)-C(167)	120.1(6)
C(30)-P(4)-C(16)	104.7(2)	C(40)-C(62)-H(62)	120
P(4)-O(3)-Ir(1)	128.96(19)	C(167)-C(62)-H(62)	120
P(3)-O(4)-Ir(1)	126.69(19)	C(32)-C(63)-C(15)	114.5(4)
C(38)-N(6)-C(25)	120.3(4)	C(32)-C(63)-Ir(1)	111.4(4)

C(38)-N(6)-Ir(1)	126.9(3)	C(15)-C(63)-Ir(1)	134.1(3)
C(25)-N(6)-Ir(1)	110.3(3)	C(47)-C(133)-C(15)	120.3(5)
C(25)-N(7)-C(57)	116.0(5)	C(47)-C(133)-H(133)	119.9
C(13)-N(8)-C(48)	116.4(4)	C(15)-C(133)-H(133)	119.9
C(221)-N(9)-C(13)	118.3(4)	C(36)-C(165)-C(168)	120.3(4)
C(221)-N(9)-Ir(1)	127.4(3)	C(36)-C(165)-H(165)	119.9
C(13)-N(9)-Ir(1)	112.2(3)	C(168)-C(165)-H(165)	119.9
P(3)-N(10)-P(4)	126.7(3)	C(41)-C(167)-C(62)	119.2(6)
N(8)-C(13)-N(9)	122.8(4)	C(41)-C(167)-H(167)	120.4
N(8)-C(13)-C(32)	124.2(4)	C(62)-C(167)-H(167)	120.4
N(9)-C(13)-C(32)	112.9(4)	C(165)-C(168)-C(222)	116.9(4)
C(133)-C(15)-C(63)	120.8(5)	C(165)-C(168)-C(225)	123.8(4)
C(133)-C(15)-C(46)	115.2(5)	C(222)-C(168)-C(225)	119.3(4)
C(63)-C(15)-C(46)	123.8(5)	C(210)-C(170)-C(36)	113.9(5)
C(54)-C(16)-C(21)	120.2(6)	C(210)-C(170)-Ir(1)	133.8(4)
C(54)-C(16)-P(4)	118.0(5)	C(36)-C(170)-Ir(1)	112.2(4)
C(21)-C(16)-P(4)	121.5(4)	C(217)-C(205)-C(206)	118.6(7)
C(40)-C(18)-C(59)	119.0(5)	C(217)-C(205)-H(205)	120.7
C(40)-C(18)-P(3)	123.2(4)	C(206)-C(205)-H(205)	120.7
C(59)-C(18)-P(3)	117.7(5)	C(215)-C(206)-C(205)	119.5(7)
C(61)-C(21)-C(16)	119.9(6)	C(215)-C(206)-H(206)	120.3
C(61)-C(21)-H(21)	120	C(205)-C(206)-H(206)	120.3
C(16)-C(21)-H(21)	120	F(17)-C(207)-F(16)	109.1(5)
N(7)-C(25)-N(6)	122.2(4)	F(17)-C(207)-F(18)	105.1(5)
N(7)-C(25)-C(36)	120.7(4)	F(16)-C(207)-F(18)	104.3(5)
N(6)-C(25)-C(36)	117.1(4)	F(17)-C(207)-C(210)	111.8(5)
C(32)-C(29)-C(47)	118.1(5)	F(16)-C(207)-C(210)	113.4(5)
C(32)-C(29)-H(29)	120.9	F(18)-C(207)-C(210)	112.6(5)
C(47)-C(29)-H(29)	120.9	C(222)-C(210)-C(170)	121.9(4)
C(56)-C(30)-C(37)	115.9(5)	C(222)-C(210)-C(207)	113.3(5)
C(56)-C(30)-P(4)	122.8(4)	C(170)-C(210)-C(207)	124.6(5)
C(37)-C(30)-P(4)	121.3(4)	C(216)-C(215)-C(206)	119.0(8)
C(29)-C(32)-C(63)	125.1(5)	C(216)-C(215)-H(215)	120.5
C(29)-C(32)-C(13)	117.6(4)	C(206)-C(215)-H(215)	120.5
C(63)-C(32)-C(13)	117.3(4)	C(215)-C(216)-C(219)	123.8(7)
C(165)-C(36)-C(170)	126.1(5)	C(215)-C(216)-H(216)	118.1
C(165)-C(36)-C(25)	119.1(4)	C(219)-C(216)-H(216)	118.1
C(170)-C(36)-C(25)	114.5(4)	C(205)-C(217)-C(219)	124.5(7)
C(50)-C(37)-C(30)	121.5(6)	C(205)-C(217)-H(217)	117.7
C(50)-C(37)-H(37)	119.2	C(219)-C(217)-H(217)	117.7
C(30)-C(37)-H(37)	119.2	C(217)-C(219)-C(216)	114.3(5)
N(6)-C(38)-C(49)	120.2(5)	C(217)-C(219)-P(3)	122.3(5)
N(6)-C(38)-H(38)	119.9	C(216)-C(219)-P(3)	123.2(5)
C(49)-C(38)-H(38)	119.9	N(9)-C(221)-C(51)	120.8(5)
C(56)-C(39)-C(44)	119.4(7)	N(9)-C(221)-H(221)	119.6
C(56)-C(39)-H(39)	120.3	C(51)-C(221)-H(221)	119.6
C(44)-C(39)-H(39)	120.3	C(210)-C(222)-C(168)	120.4(4)
C(62)-C(40)-C(18)	121.6(5)	C(210)-C(222)-H(222)	119.8
C(62)-C(40)-H(40)	119.2	C(168)-C(222)-H(222)	119.8
C(18)-C(40)-H(40)	119.2	F(15)-C(225)-F(13)	108.5(5)
C(167)-C(41)-C(59)	121.3(7)	F(15)-C(225)-F(14)	106.2(5)
C(167)-C(41)-H(41)	119.4	F(13)-C(225)-F(14)	103.2(4)
C(59)-C(41)-H(41)	119.4	F(15)-C(225)-C(168)	111.7(5)
C(50)-C(44)-C(39)	118.8(6)	F(13)-C(225)-C(168)	113.2(5)
C(50)-C(44)-H(44)	120.6	F(14)-C(225)-C(168)	113.5(5)
C(39)-C(44)-H(44)	120.6	F(23)-C(226)-F(24)	104.3(6)
F(19)-C(46)-F(20)	105.8(5)	F(23)-C(226)-F(22)	105.1(7)
F(19)-C(46)-F(21)	106.2(4)	F(24)-C(226)-F(22)	104.4(6)
F(20)-C(46)-F(21)	107.7(5)	F(23)-C(226)-C(47)	115.3(6)
F(19)-C(46)-C(15)	112.9(5)	F(24)-C(226)-C(47)	114.3(6)
F(20)-C(46)-C(15)	113.0(4)	F(22)-C(226)-C(47)	112.3(6)
F(21)-C(46)-C(15)	110.9(5)	C(150)-C(151)-C(61)	118.2(6)
C(133)-C(47)-C(29)	120.7(5)	C(150)-C(151)-H(151)	120.9
C(133)-C(47)-C(226)	119.3(5)	C(61)-C(151)-H(151)	120.9
C(29)-C(47)-C(226)	120.0(5)	C(151)-C(150)-C(54)	119.7(6)

C(51)-C(48)-N(8)	123.5(5)	C(151)-C(150)-H(150)	120.2
C(51)-C(48)-H(48)	118.2	C(54)-C(150)-H(150)	120.2

Table S2c The selected bond lengths and angels of **Ir(f-tfmphpm)$_2$(tpip)**.

Selected bonds Å					
C(42)-C(36)	1.35(2)	C(3)-C(17)	1.381(16)	C(24)-C(35)	1.375(15)
C(42)-C(47)	1.39(2)	C(3)-H(3)	0.93	C(24)-C(27)	1.388(16)
C(42)-H(42)	0.93	C(4)-C(12)	1.410(13)	C(25)-C(41)	1.377(17)
Ir(1)-C(8)	2.014(10)	F(10)-C(31)	1.341(14)	C(25)-H(25)	0.93
Ir(1)-C(4)	2.017(9)	C(5)-N(4)	1.321(17)	C(26)-H(26)	0.93
Ir(1)-N(1)	2.019(8)	C(5)-C(31)	1.368(17)	C(27)-C(44)	1.392(16)
Ir(1)-N(3)	2.023(8)	C(5)-H(5)	0.93	C(27)-H(27)	0.93
Ir(1)-O(2)	2.159(7)	C(6)-C(18)	1.398(14)	C(28)-F(1)	1.334(15)
Ir(1)-O(1)	2.162(6)	C(6)-C(7)	1.399(14)	C(28)-C(29)	1.494(15)
P(1)-O(1)	1.523(6)	C(6)-H(6)	0.93	C(29)-C(30)	1.382(17)
P(1)-N(5)	1.594(9)	C(8)-C(20)	1.419(15)	C(30)-H(30)	0.93
P(1)-C(17)	1.801(11)	C(8)-C(9)	1.426(15)	C(31)-C(39)	1.371(15)
P(1)-C(7)	1.807(10)	C(9)-C(13)	1.395(13)	C(32)-H(32)	0.93
P(2)-O(2)	1.518(8)	C(9)-C(16)	1.457(15)	C(33)-C(37)	1.363(19)
P(2)-N(5)	1.585(9)	C(10)-C(21)	1.380(15)	C(33)-C(44)	1.397(18)
P(2)-C(19)	1.806(11)	C(10)-C(12)	1.400(14)	C(33)-H(33)	0.93
P(2)-C(24)	1.814(10)	C(10)-H(10)	0.93	C(34)-H(34)	0.93
N(1)-C(26)	1.351(13)	C(11)-C(34)	1.381(17)	C(35)-C(37)	1.402(17)
N(1)-C(15)	1.356(12)	C(11)-H(11)	0.93	C(35)-H(35)	0.93
F(6)-C(22)	1.342(12)	F(3)-C(28)	1.312(14)	C(36)-H(36)	0.93
N(3)-C(39)	1.341(13)	C(12)-C(38)	1.508(14)	C(37)-H(37)	0.93
N(3)-C(16)	1.363(12)	C(13)-C(29)	1.345(17)	C(39)-H(39)	0.93
F(5)-C(22)	1.339(13)	C(13)-H(13)	0.93	C(40)-C(41)	1.35(2)
F(11)-C(14)	1.333(12)	C(14)-C(26)	1.371(15)	C(40)-C(46)	1.41(2)
F(7)-C(38)	1.358(14)	C(14)-C(23)	1.372(16)	C(40)-H(40)	0.93
F(9)-C(38)	1.342(15)	N(4)-C(16)	1.333(14)	C(41)-H(41)	0.93
F(8)-C(38)	1.350(12)	F(2)-C(28)	1.326(17)	F(13)-C(48)	1.340(12)
F(4)-C(22)	1.362(12)	C(17)-C(45)	1.382(18)	F(14)-C(48)	1.335(12)
N(2)-C(15)	1.333(12)	C(18)-C(34)	1.359(17)	F(12)-C(48)	1.344(12)
N(2)-C(23)	1.348(14)	C(18)-H(18)	0.93	C(43)-C(46)	1.454(17)
C(1)-C(7)	1.379(14)	C(19)-C(43)	1.369(17)	C(43)-H(43)	0.93
C(1)-C(11)	1.390(14)	C(19)-C(25)	1.414(15)	C(44)-H(44)	0.93
C(1)-H(1)	0.93	C(20)-C(30)	1.390(14)	C(45)-C(47)	1.39(2)
C(2)-C(32)	1.370(13)	C(20)-C(22)	1.490(16)	C(45)-H(45)	0.93
C(2)-C(4)	1.431(13)	C(21)-C(32)	1.383(14)	C(46)-H(46)	0.93
C(2)-C(15)	1.465(13)	C(21)-C(48)	1.491(14)	C(47)-H(47)	0.93
C(3)-C(36)	1.365(18)	C(23)-H(23)	0.93		

Selected angels°			
C(36)-C(42)-C(47)	119.0(14)	C(30)-C(20)-C(8)	122.1(11)
C(36)-C(42)-H(42)	120.5	C(30)-C(20)-C(22)	116.6(10)
C(47)-C(42)-H(42)	120.5	C(8)-C(20)-C(22)	121.2(9)
C(8)-Ir(1)-C(4)	99.6(4)	C(10)-C(21)-C(32)	119.2(9)
C(8)-Ir(1)-N(1)	104.7(4)	C(10)-C(21)-C(48)	118.2(9)
C(4)-Ir(1)-N(1)	81.8(4)	C(32)-C(21)-C(48)	122.6(9)
C(8)-Ir(1)-N(3)	81.4(4)	F(5)-C(22)-F(6)	105.8(9)
C(4)-Ir(1)-N(3)	103.3(4)	F(5)-C(22)-F(4)	105.1(9)
N(1)-Ir(1)-N(3)	171.5(3)	F(6)-C(22)-F(4)	104.5(8)
C(8)-Ir(1)-O(2)	87.8(3)	F(5)-C(22)-C(20)	114.1(9)
C(4)-Ir(1)-O(2)	168.9(3)	F(6)-C(22)-C(20)	113.9(9)
N(1)-Ir(1)-O(2)	88.3(3)	F(4)-C(22)-C(20)	112.5(9)
N(3)-Ir(1)-O(2)	85.9(3)	N(2)-C(23)-C(14)	120.8(10)
C(8)-Ir(1)-O(1)	172.1(4)	N(2)-C(23)-H(23)	119.6
C(4)-Ir(1)-O(1)	83.1(3)	C(14)-C(23)-H(23)	119.6
N(1)-Ir(1)-O(1)	83.1(3)	C(35)-C(24)-C(27)	119.9(10)
N(3)-Ir(1)-O(1)	90.7(3)	C(35)-C(24)-P(2)	119.8(9)
O(2)-Ir(1)-O(1)	90.8(2)	C(27)-C(24)-P(2)	120.2(8)
O(1)-P(1)-N(5)	118.2(4)	C(41)-C(25)-C(19)	120.1(13)
O(1)-P(1)-C(17)	105.6(5)	C(41)-C(25)-H(25)	119.9
N(5)-P(1)-C(17)	106.7(5)	C(19)-C(25)-H(25)	119.9
O(1)-P(1)-C(7)	105.5(4)	N(1)-C(26)-C(14)	119.5(10)

N(5)-P(1)-C(7)	111.8(5)	N(1)-C(26)-H(26)	120.2
C(17)-P(1)-C(7)	108.5(5)	C(14)-C(26)-H(26)	120.2
O(2)-P(2)-N(5)	118.5(4)	C(24)-C(27)-C(44)	119.6(11)
O(2)-P(2)-C(19)	107.2(5)	C(24)-C(27)-H(27)	120.2
N(5)-P(2)-C(19)	110.2(5)	C(44)-C(27)-H(27)	120.2
O(2)-P(2)-C(24)	108.8(4)	F(3)-C(28)-F(2)	106.1(11)
N(5)-P(2)-C(24)	107.2(5)	F(3)-C(28)-F(1)	105.9(12)
C(19)-P(2)-C(24)	104.1(5)	F(2)-C(28)-F(1)	104.7(12)
P(1)-O(1)-Ir(1)	128.4(4)	F(3)-C(28)-C(29)	113.7(11)
C(26)-N(1)-C(15)	117.9(9)	F(2)-C(28)-C(29)	113.8(11)
C(26)-N(1)-Ir(1)	126.8(7)	F(1)-C(28)-C(29)	111.9(10)
C(15)-N(1)-Ir(1)	114.2(6)	C(13)-C(29)-C(30)	119.5(10)
C(39)-N(3)-C(16)	117.9(9)	C(13)-C(29)-C(28)	121.1(12)
C(39)-N(3)-Ir(1)	126.5(7)	C(30)-C(29)-C(28)	119.4(11)
C(16)-N(3)-Ir(1)	114.3(7)	C(29)-C(30)-C(20)	120.7(11)
C(15)-N(2)-C(23)	117.2(9)	C(29)-C(30)-H(30)	119.6
C(7)-C(1)-C(11)	120.8(10)	C(20)-C(30)-H(30)	119.6
C(7)-C(1)-H(1)	119.6	F(10)-C(31)-C(5)	121.2(11)
C(11)-C(1)-H(1)	119.6	F(10)-C(31)-C(39)	119.6(10)
C(32)-C(2)-C(4)	123.8(9)	C(5)-C(31)-C(39)	119.2(11)
C(32)-C(2)-C(15)	120.7(9)	C(2)-C(32)-C(21)	119.6(9)
C(4)-C(2)-C(15)	115.5(8)	C(2)-C(32)-H(32)	120.2
C(36)-C(3)-C(17)	121.6(13)	C(21)-C(32)-H(32)	120.2
C(36)-C(3)-H(3)	119.2	C(37)-C(33)-C(44)	121.0(11)
C(17)-C(3)-H(3)	119.2	C(37)-C(33)-H(33)	119.5
C(12)-C(4)-C(2)	114.5(8)	C(44)-C(33)-H(33)	119.5
C(12)-C(4)-Ir(1)	134.3(7)	C(18)-C(34)-C(11)	120.7(10)
C(2)-C(4)-Ir(1)	110.8(7)	C(18)-C(34)-H(34)	119.6
N(4)-C(5)-C(31)	121.7(11)	C(11)-C(34)-H(34)	119.6
N(4)-C(5)-H(5)	119.1	C(24)-C(35)-C(37)	120.9(12)
C(31)-C(5)-H(5)	119.1	C(24)-C(35)-H(35)	119.5
C(18)-C(6)-C(7)	119.0(10)	C(37)-C(35)-H(35)	119.5
C(18)-C(6)-H(6)	120.5	C(42)-C(36)-C(3)	120.8(14)
C(7)-C(6)-H(6)	120.5	C(42)-C(36)-H(36)	119.6
C(1)-C(7)-C(6)	119.5(9)	C(3)-C(36)-H(36)	119.6
C(1)-C(7)-P(1)	120.4(8)	C(33)-C(37)-C(35)	119.0(11)
C(6)-C(7)-P(1)	120.0(8)	C(33)-C(37)-H(37)	120.5
C(20)-C(8)-C(9)	114.2(9)	C(35)-C(37)-H(37)	120.5
C(20)-C(8)-Ir(1)	134.7(8)	F(9)-C(38)-F(8)	105.7(9)
C(9)-C(8)-Ir(1)	111.0(7)	F(9)-C(38)-F(7)	108.6(10)
C(13)-C(9)-C(8)	122.3(10)	F(8)-C(38)-F(7)	105.0(9)
C(13)-C(9)-C(16)	121.3(10)	F(9)-C(38)-C(12)	113.5(9)
C(8)-C(9)-C(16)	116.3(9)	F(8)-C(38)-C(12)	112.2(9)
C(21)-C(10)-C(12)	121.3(9)	F(7)-C(38)-C(12)	111.2(9)
C(21)-C(10)-H(10)	119.4	N(3)-C(39)-C(31)	119.7(10)
C(12)-C(10)-H(10)	119.4	N(3)-C(39)-H(39)	120.1
C(34)-C(11)-C(1)	119.2(11)	C(31)-C(39)-H(39)	120.1
C(34)-C(11)-H(11)	120.4	C(41)-C(40)-C(46)	124.7(12)
C(1)-C(11)-H(11)	120.4	C(41)-C(40)-H(40)	117.6
C(10)-C(12)-C(4)	121.3(9)	C(46)-C(40)-H(40)	117.6
C(10)-C(12)-C(38)	115.6(9)	C(40)-C(41)-C(25)	120.3(13)
C(4)-C(12)-C(38)	123.1(9)	C(40)-C(41)-H(41)	119.9
C(29)-C(13)-C(9)	121.0(11)	C(25)-C(41)-H(41)	119.9
C(29)-C(13)-H(13)	119.5	P(2)-O(2)-Ir(1)	128.5(4)
C(9)-C(13)-H(13)	119.5	C(19)-C(43)-C(46)	124.0(12)
F(11)-C(14)-C(26)	120.2(10)	C(19)-C(43)-H(43)	118
F(11)-C(14)-C(23)	119.9(10)	C(46)-C(43)-H(43)	118
C(26)-C(14)-C(23)	119.9(10)	F(14)-C(48)-F(13)	106.7(8)
C(5)-N(4)-C(16)	117.6(10)	F(14)-C(48)-F(12)	107.1(9)
N(2)-C(15)-N(1)	124.6(9)	F(13)-C(48)-F(12)	106.5(9)
N(2)-C(15)-C(2)	120.9(9)	F(14)-C(48)-C(21)	111.9(9)
N(1)-C(15)-C(2)	114.5(8)	F(13)-C(48)-C(21)	112.1(8)
N(4)-C(16)-N(3)	123.8(10)	F(12)-C(48)-C(21)	112.3(8)
N(4)-C(16)-C(9)	122.7(9)	C(27)-C(44)-C(33)	119.7(12)
N(3)-C(16)-C(9)	113.5(9)	C(27)-C(44)-H(44)	120.2

P(2)-N(5)-P(1)	127.1(6)	C(33)-C(44)-H(44)	120.2
C(3)-C(17)-C(45)	118.4(11)	C(17)-C(45)-C(47)	119.4(14)
C(3)-C(17)-P(1)	120.6(9)	C(17)-C(45)-H(45)	120.3
C(45)-C(17)-P(1)	120.6(9)	C(47)-C(45)-H(45)	120.3
C(34)-C(18)-C(6)	120.7(11)	C(40)-C(46)-C(43)	112.6(13)
C(34)-C(18)-H(18)	119.7	C(40)-C(46)-H(46)	123.7
C(6)-C(18)-H(18)	119.7	C(43)-C(46)-H(46)	123.7
C(43)-C(19)-C(25)	118.2(11)	C(42)-C(47)-C(45)	120.6(16)
C(43)-C(19)-P(2)	122.7(9)	C(42)-C(47)-H(47)	119.7
C(25)-C(19)-P(2)	119.1(9)	C(45)-C(47)-H(47)	119.7

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