

Electronic Supporting Information

for

Bipyridine-based Iridium(III) Triplet Emitters for Organic Light-Emitting Diodes (OLEDs): Application and Impact of Phenyl Substitution at the 5'-position of the N-Coordinating Pyridine Ring

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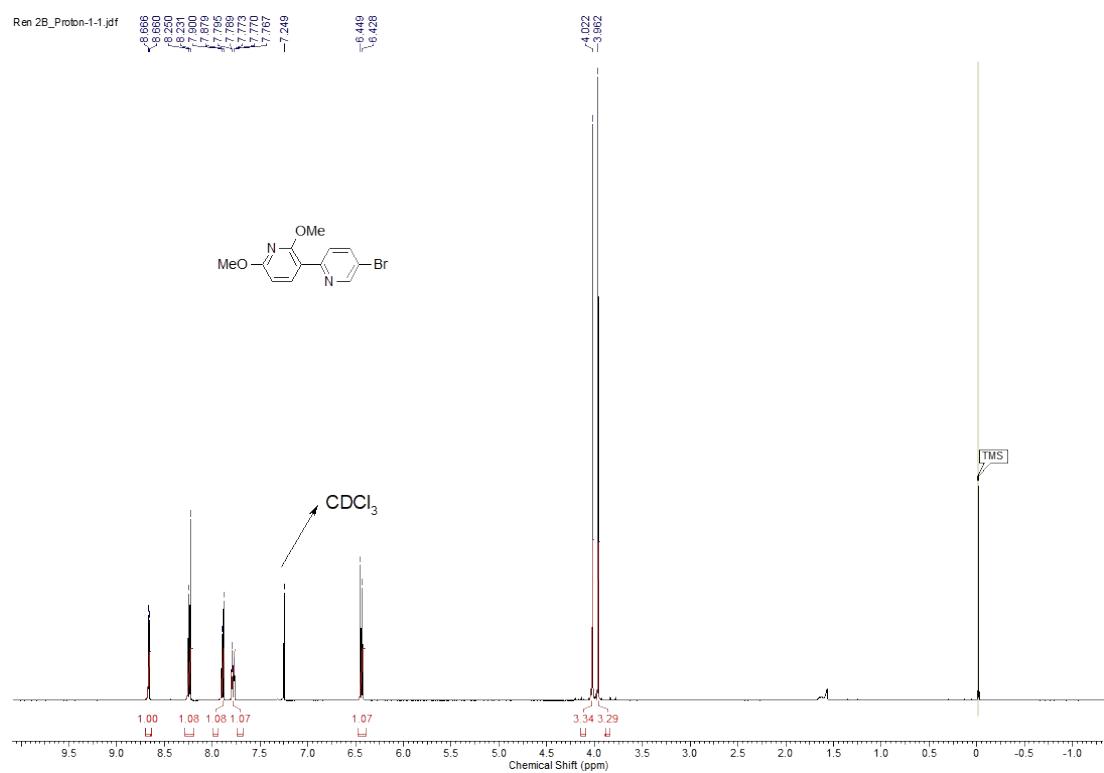


Figure S1. ^1H NMR of **B** in CDCl_3 .

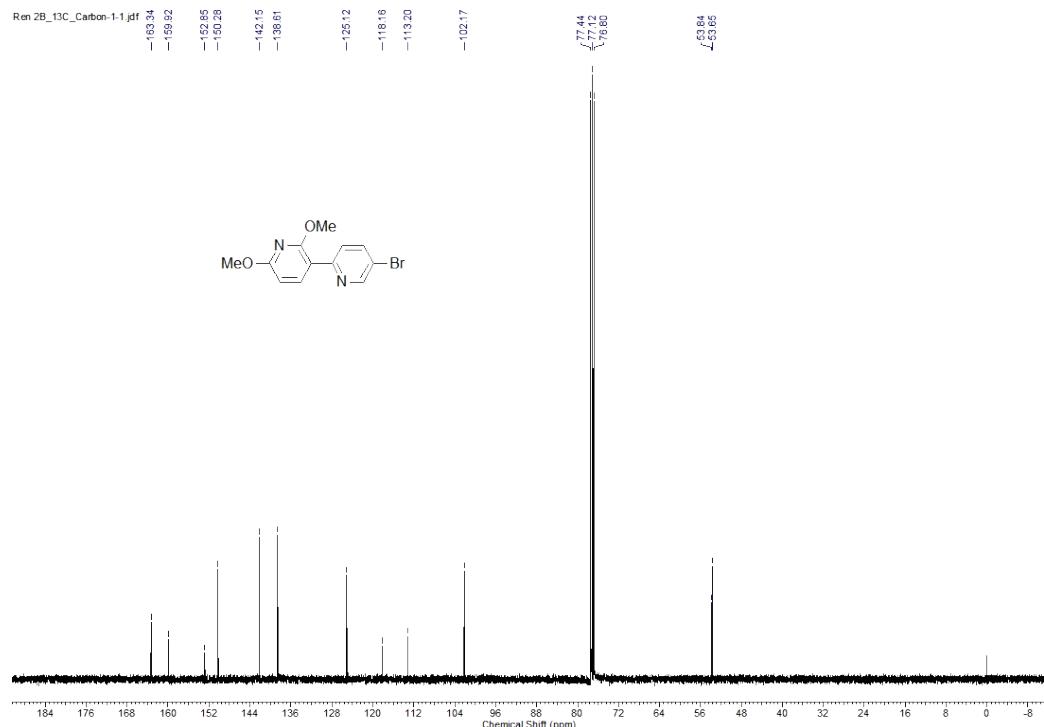


Figure S2. ^{13}C NMR of **B** in CDCl_3 .

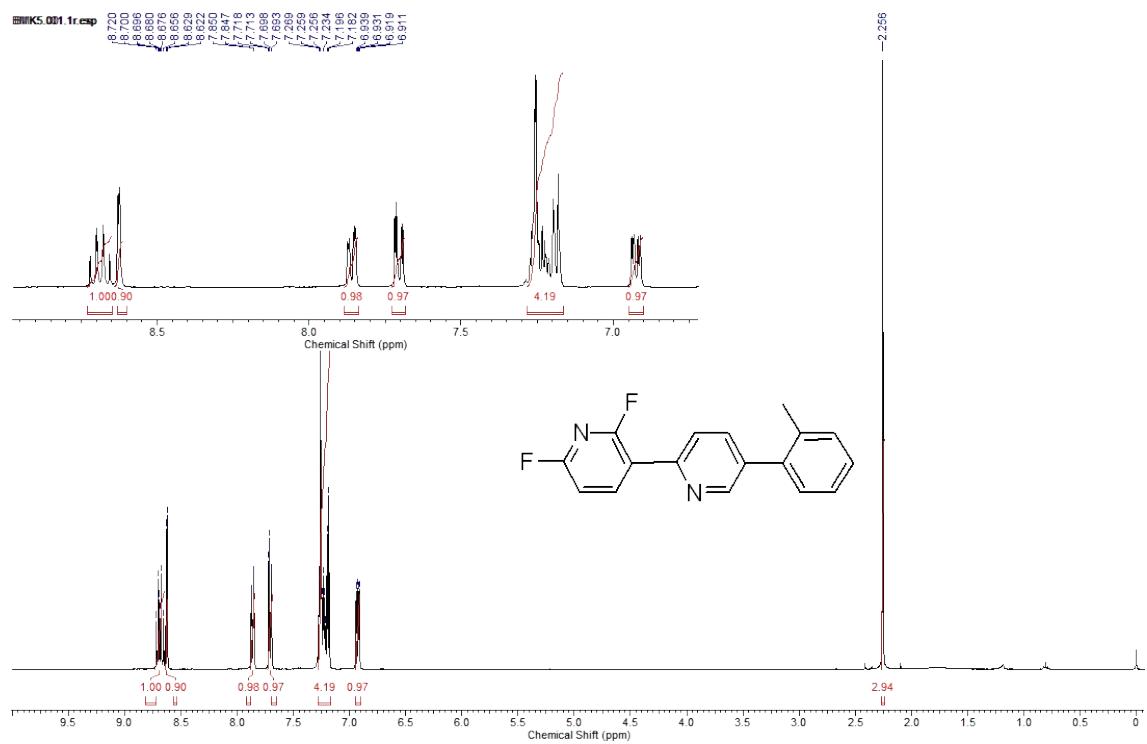


Figure S3. ^1H NMR of C in CDCl_3 .

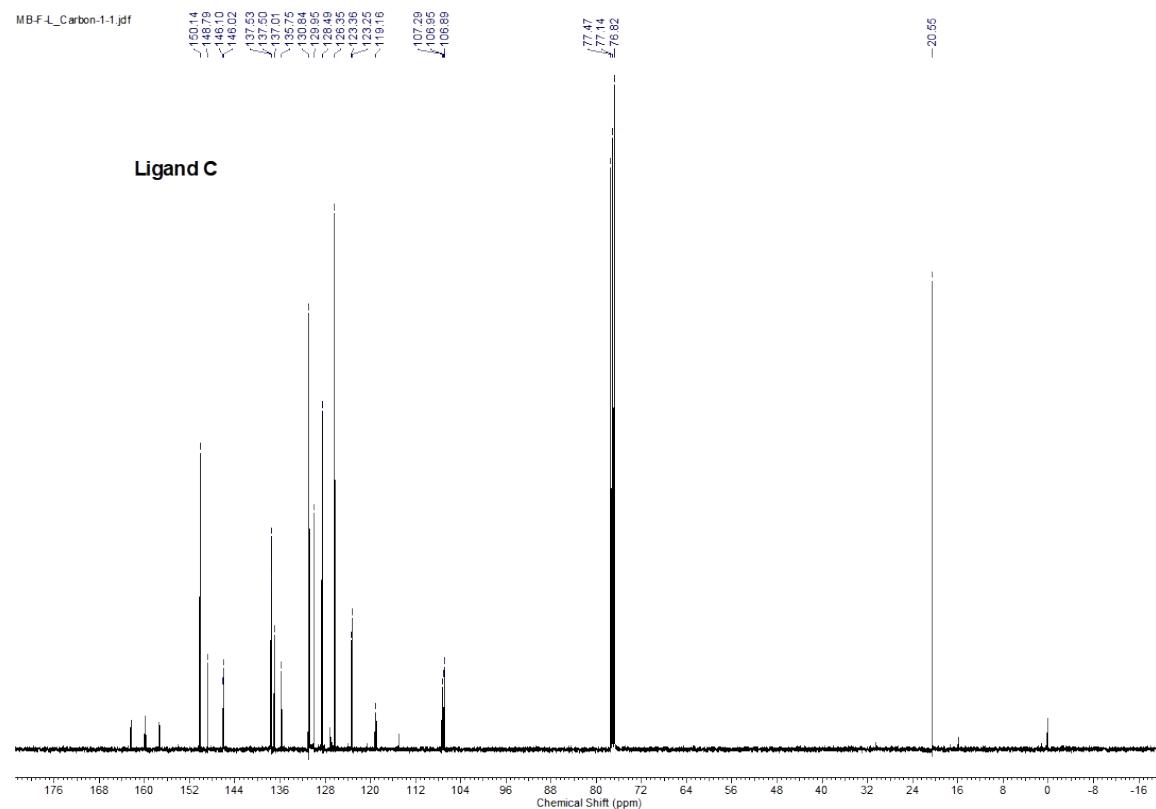


Figure S4. ^{13}C NMR of **C** in CDCl_3 .

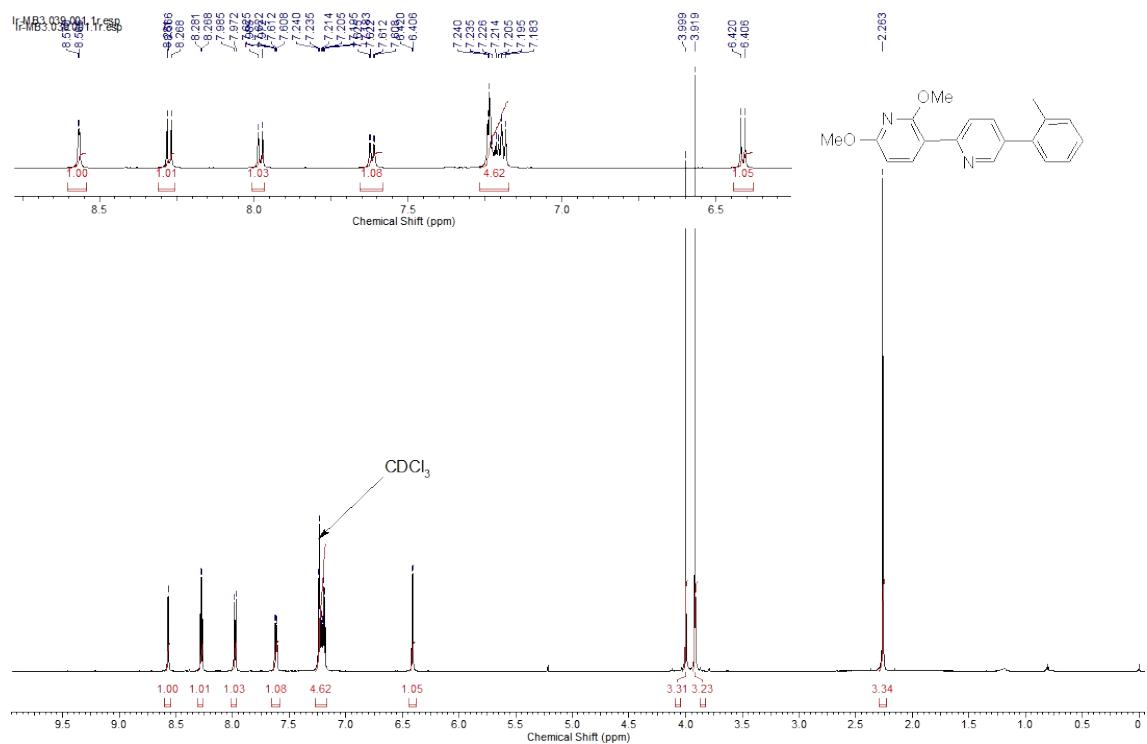


Figure S5. ^1H NMR of **D** in CDCl_3 .

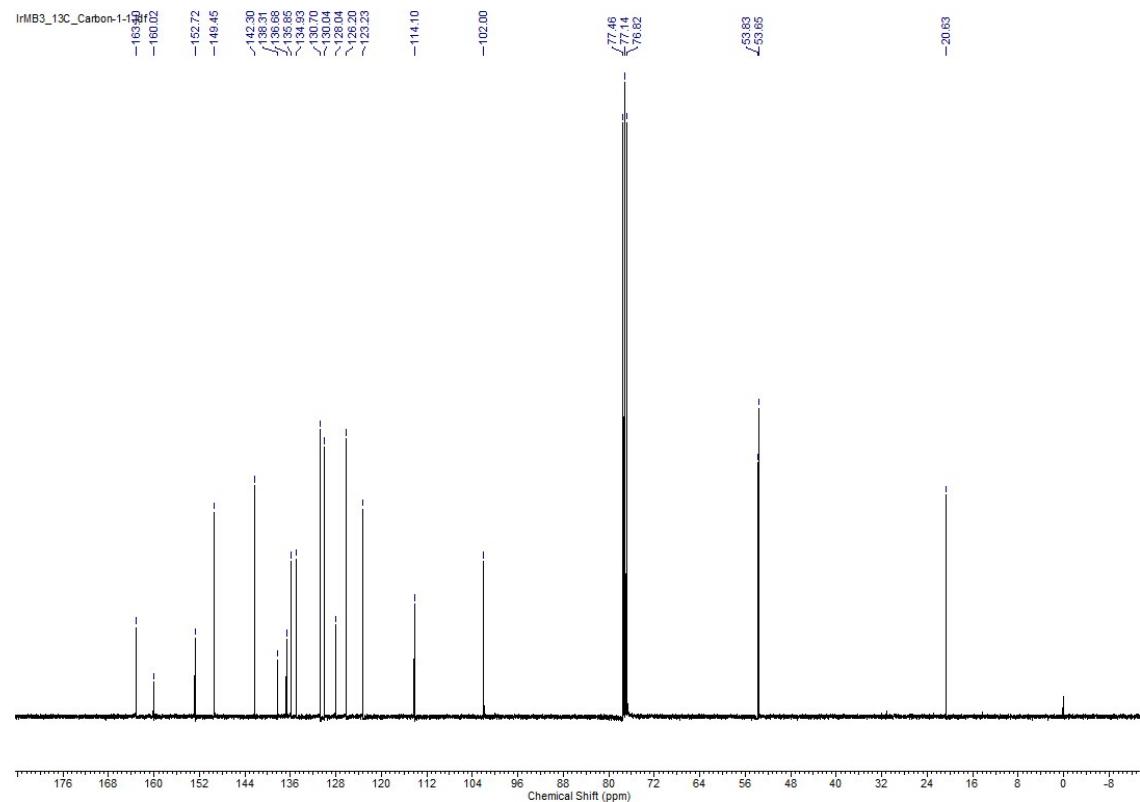


Figure S6. ^{13}C NMR of **D** in CDCl_3 .

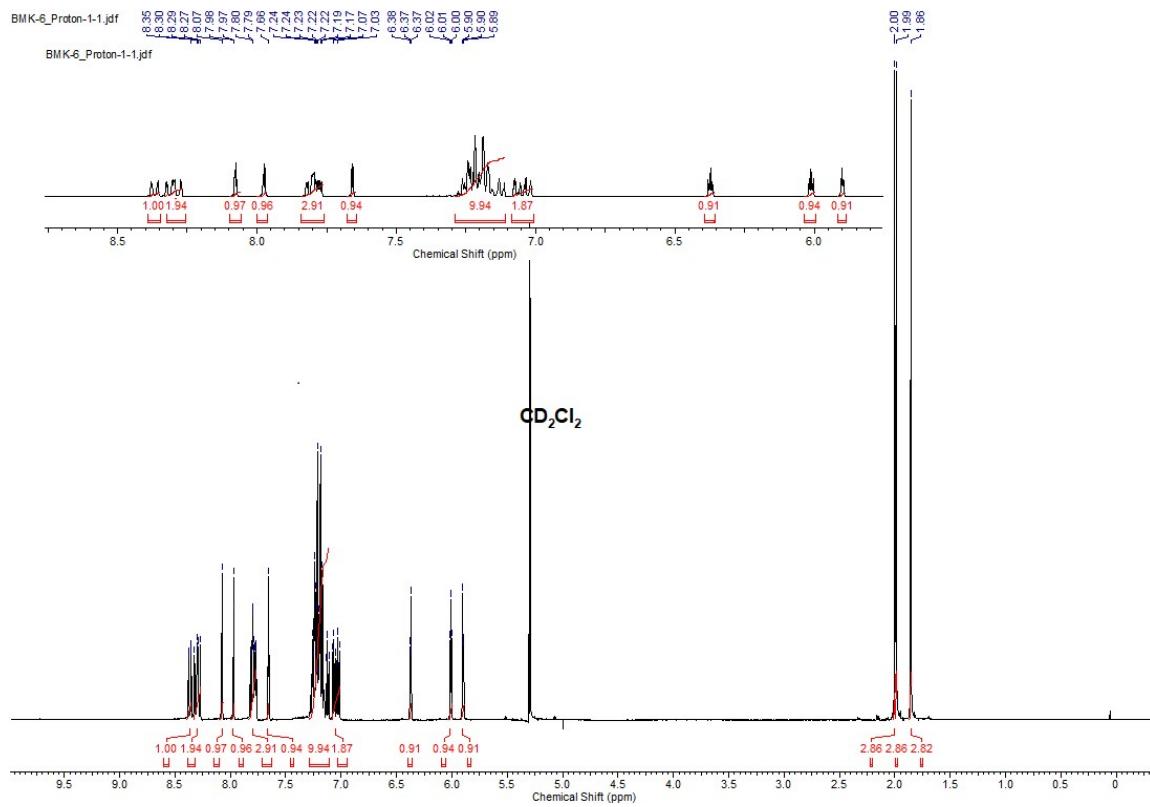


Figure S7. ^1H NMR of *mer-1* in CD_2Cl_2 .

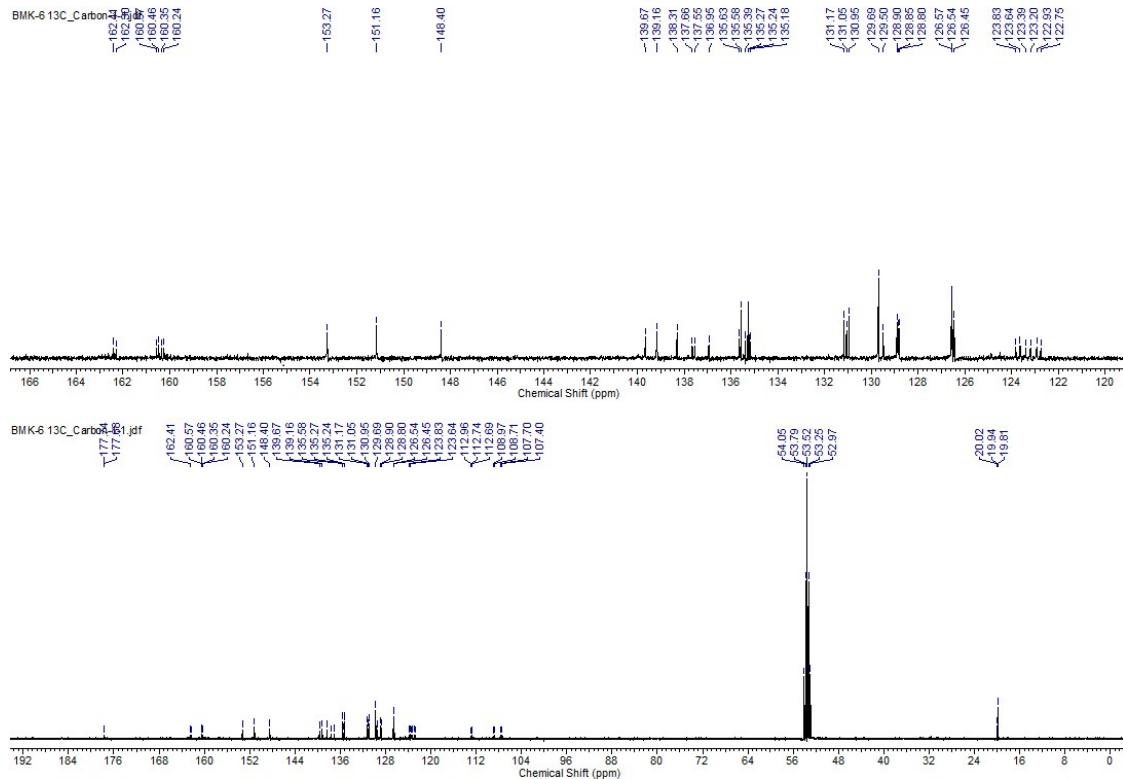


Figure S8. ^{13}C NMR of *mer-1* in CD_2Cl_2 .

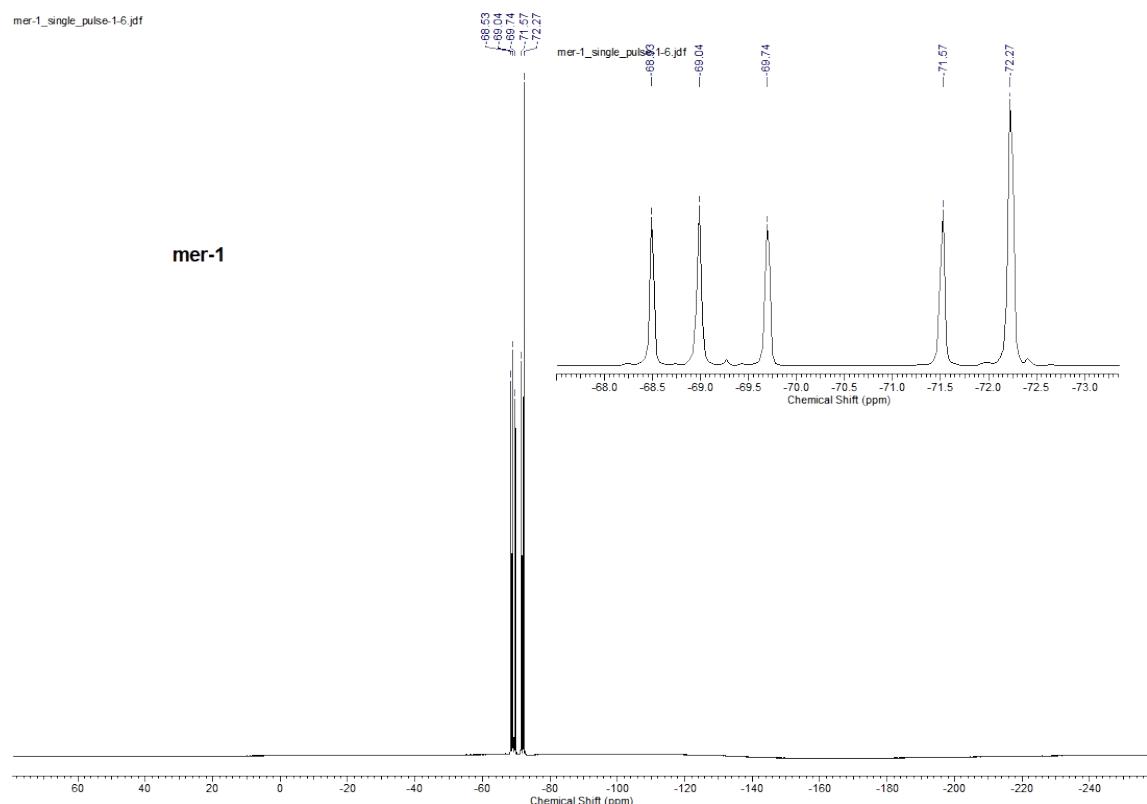


Figure S9. ^{19}F NMR of *mer-1* in CD_2Cl_2 .

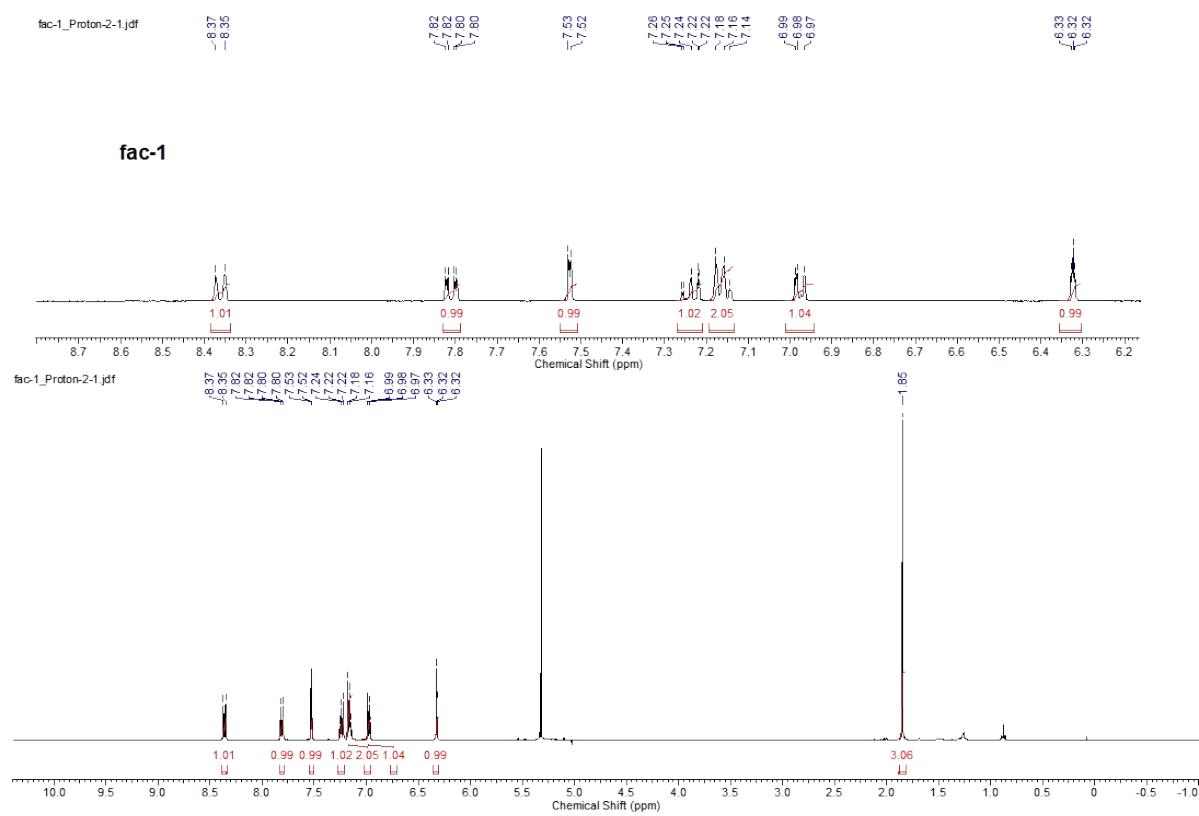


Figure S10. ^1H NMR of *fac-1* in CD_2Cl_2 .

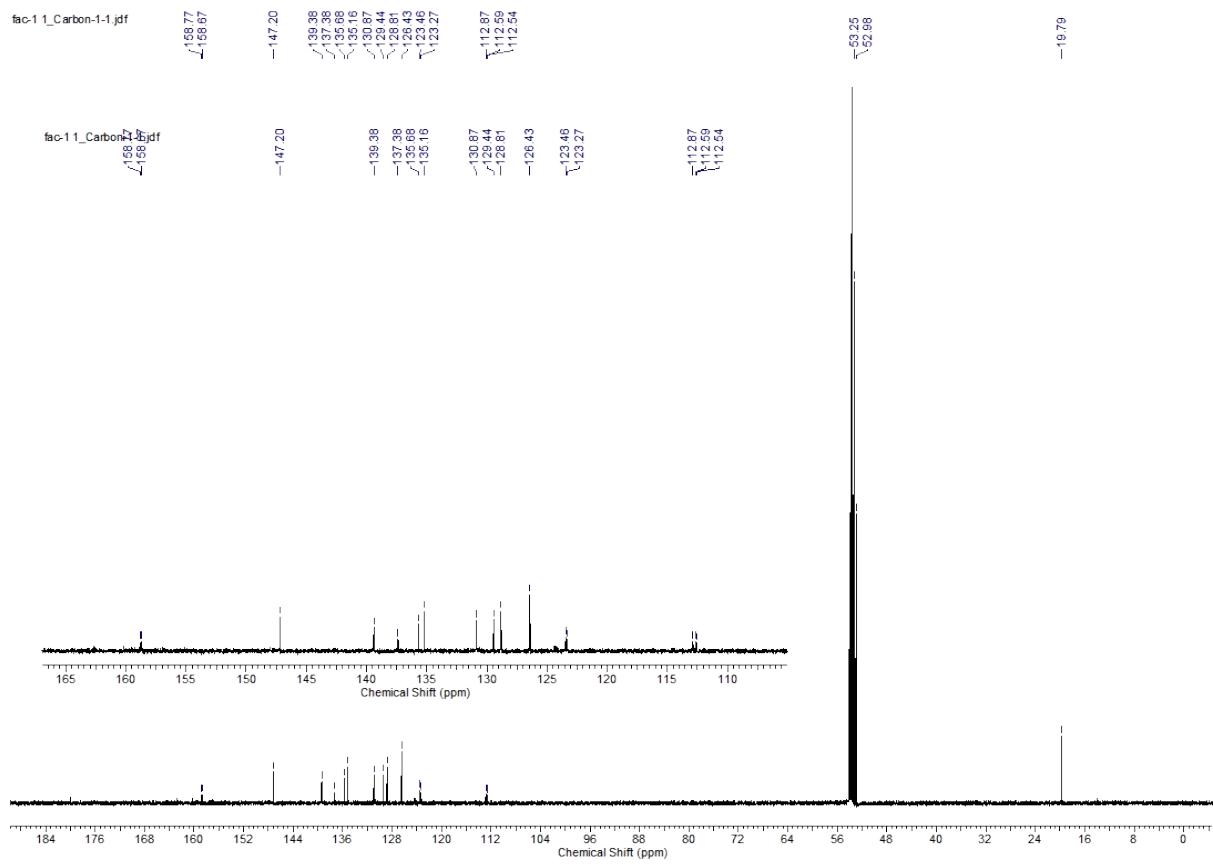


Figure S11. ^{13}C NMR of *fac-1* in CD_2Cl_2 .

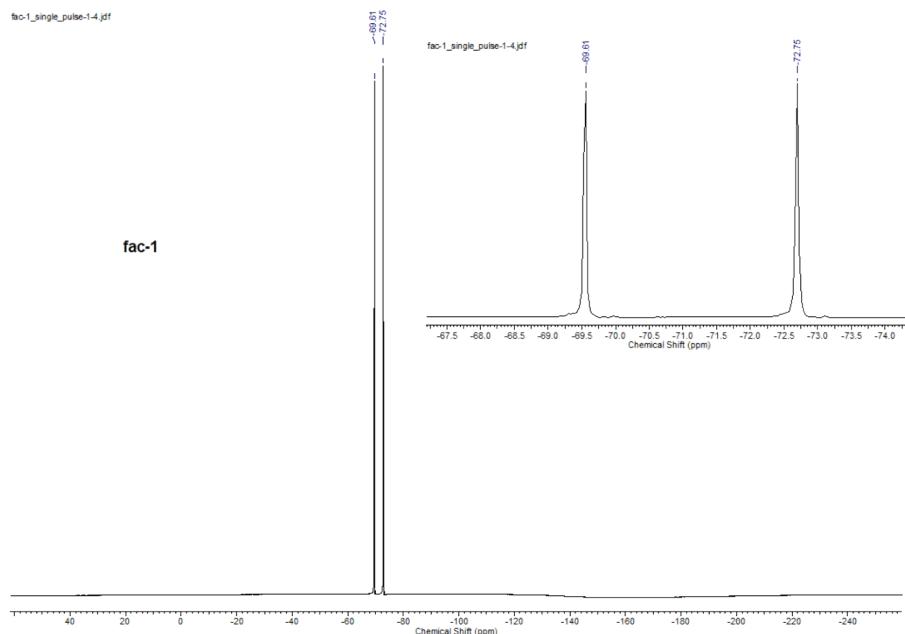


Figure S12. ^{19}F NMR of *fac-1* in CD_2Cl_2 .

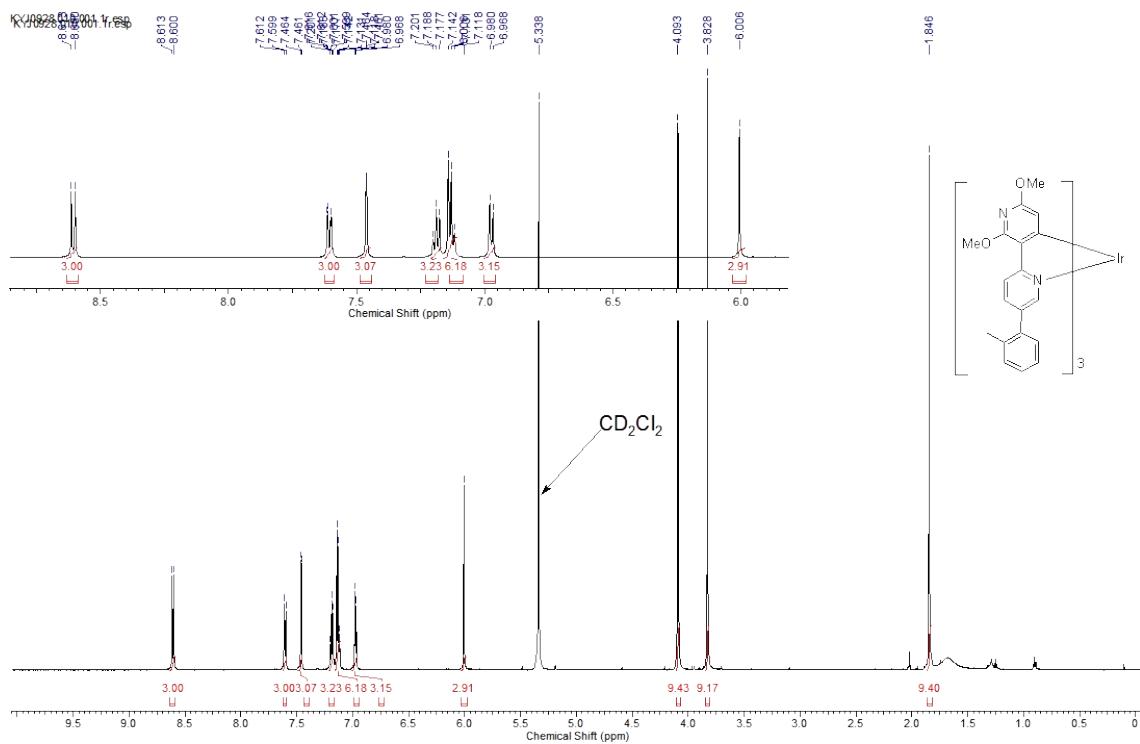


Figure S13. ^1H NMR of *fac*-2 in CD_2Cl_2 .

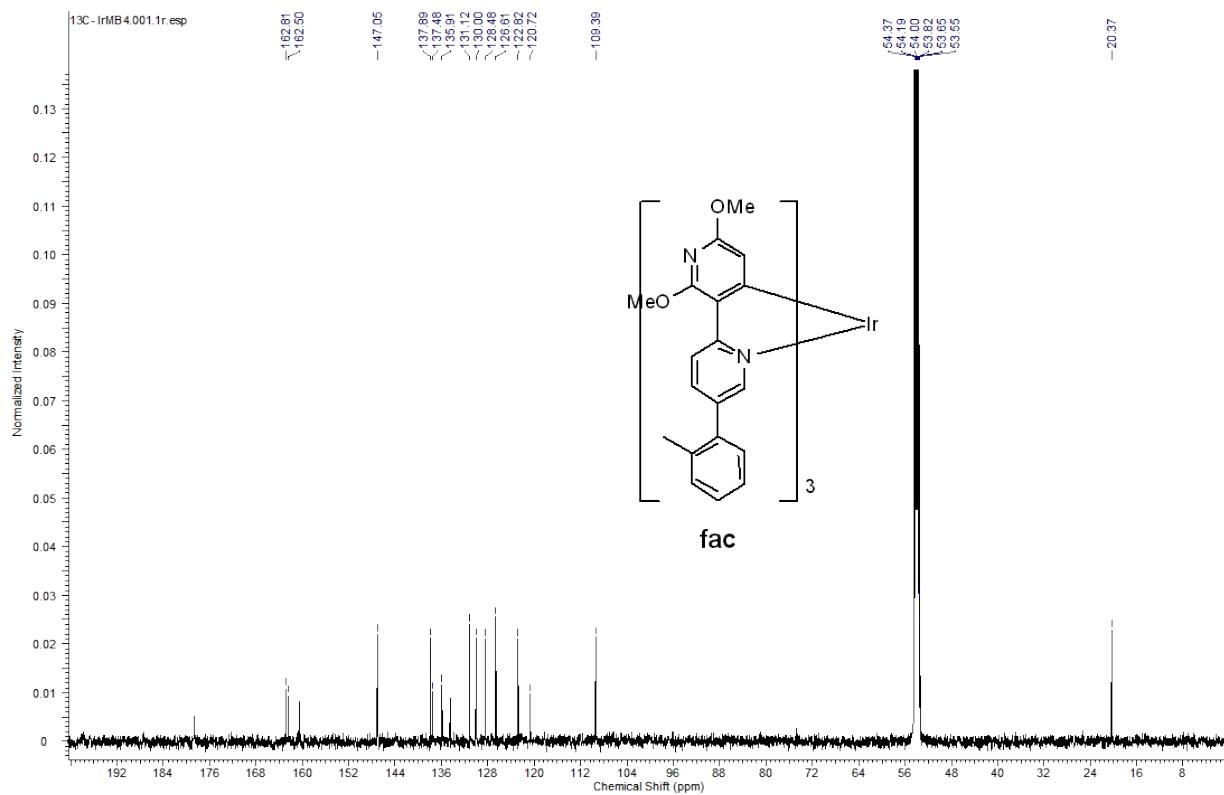


Figure S14. ^{13}C NMR of *fac*-2 in CD_2Cl_2 .

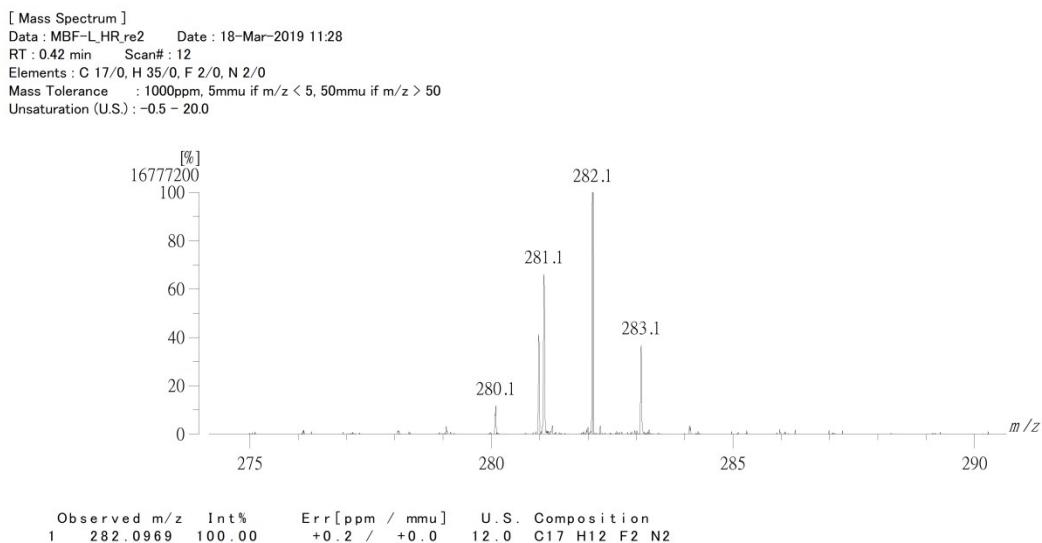


Figure S15. HRMS data of **C**.

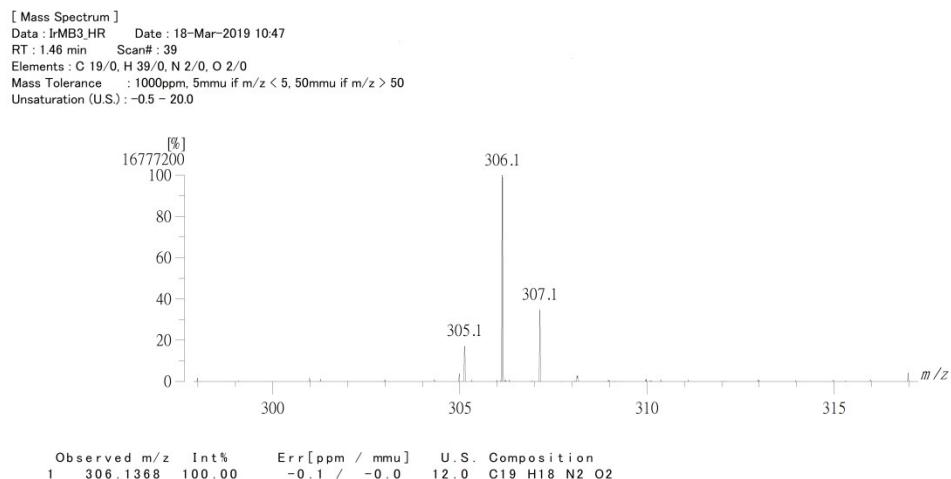


Figure S16. HRMS data of **D**.

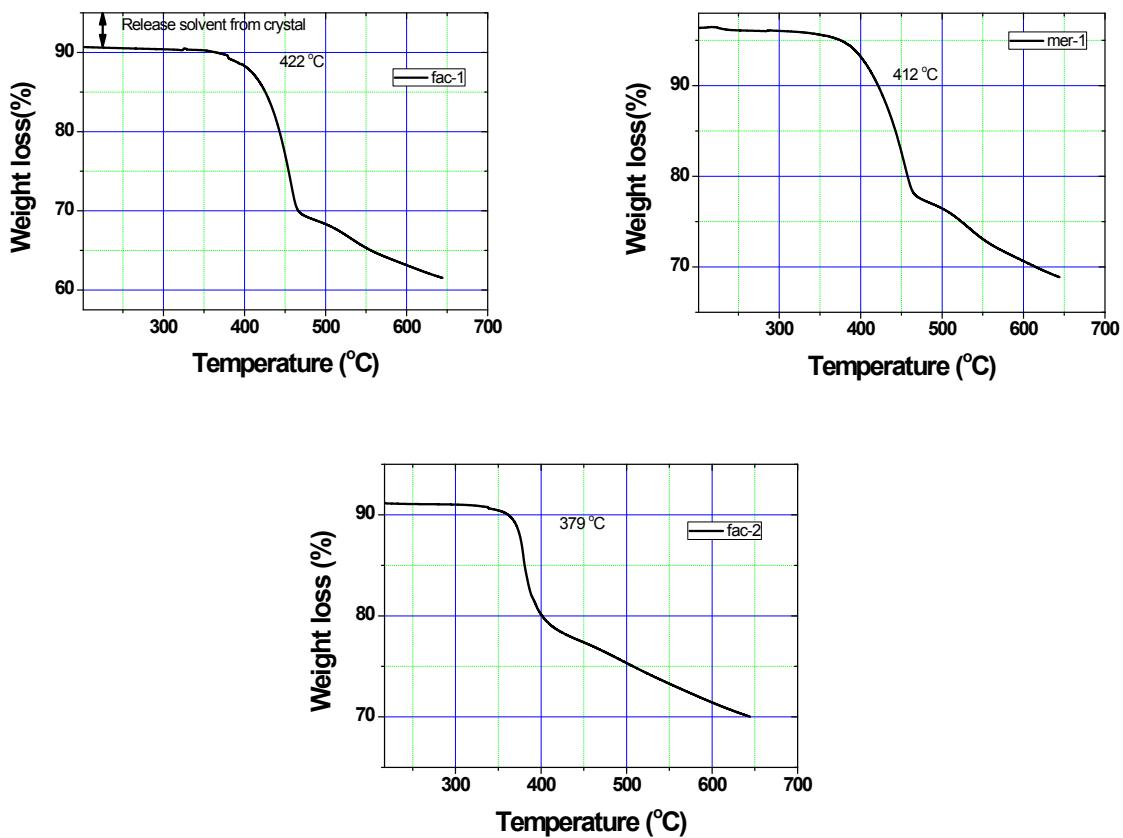


Figure S17. TGA data of *fac*-1, *mer*-1 and *fac*-2.

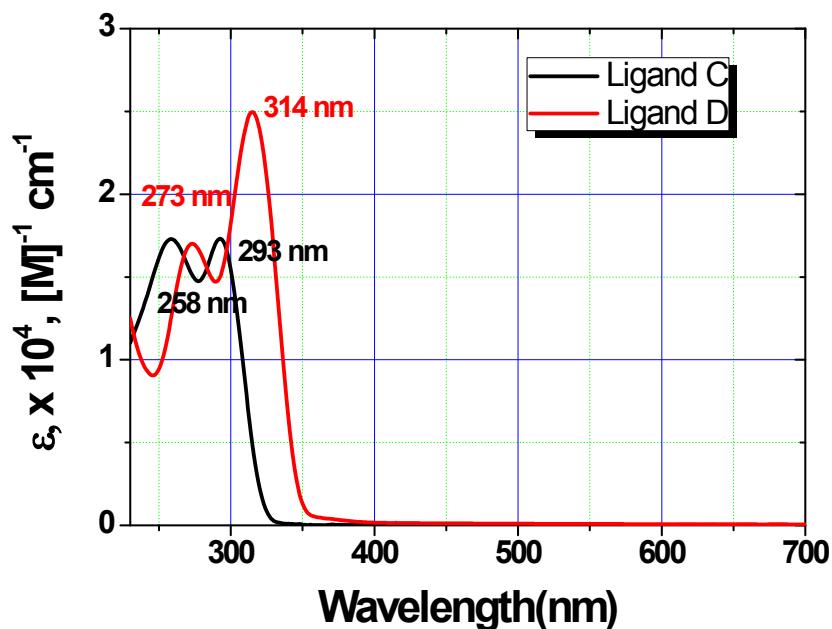


Figure S18. Absorption spectra of free ligands C and D.

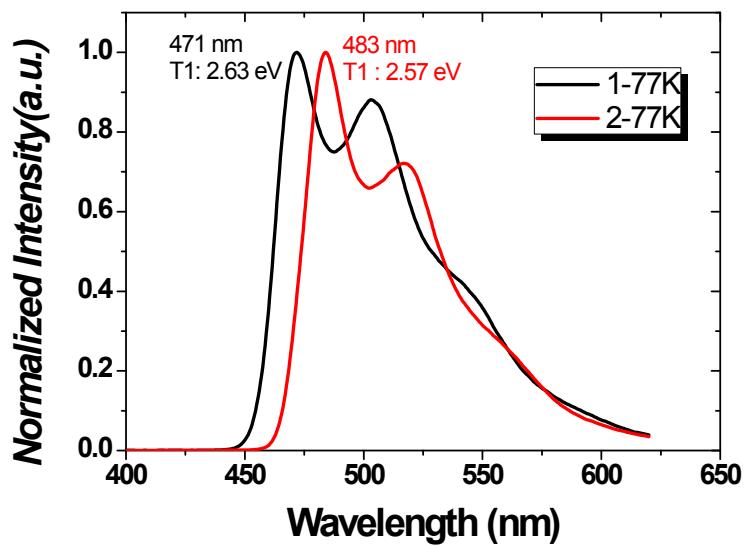


Figure S19. Emission spectra of *mer*-1 and *fac*-2 at 77K.

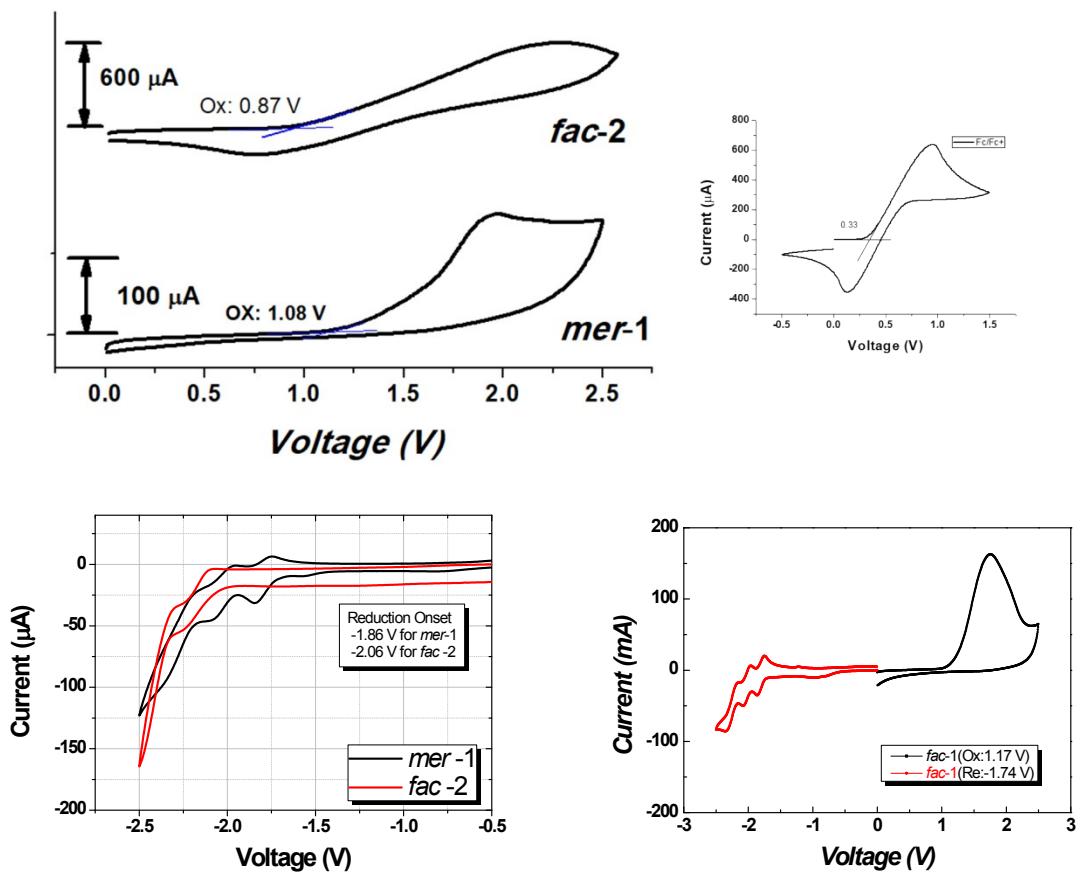


Figure S20. CV data of *fac*-1, *mer*-1 and *fac*-2 (upper right:*Fc/Fc⁺*).

Table S1. OLEDs data for *mer-1* -based device.

Doping ratio	V(V)	I(mA/cm ²)	L(cd/m ²)	x	y	EQE(%)		LE(lm/W)		J(Cd/A)	
						[1000cd/m ²]	[Max]	[1000cd/m ²]	[Max]	[1000cd/m ²]	[Max]
5%	7.2	3.2	1004.4	0.19	0.42	13.0	14.6	13.9	18.0	31.8	35.6
10%	6.8	3.8	994.7	0.18	0.40	11.4	12.3	12.5	15.1	26.8	28.9
15%	6.3	3.9	996.4	0.18	0.41	10.8	11.3	12.8	15.1	25.7	26.9

Device structure : ITO(50nm)/PEDOT:PSS(60nm)/TAPC(20nm)/mCP(10nm)/mCP:**1**(25nm:*x*%) /TSPO1(5nm)/TPBi(20nm)/LiF(1.5m)/Al(200nm)**Table S2.** OLEDs data for *fac-2* -based device.

Doping ratio	V(V)	I(mA/cm ²)	L(cd/m ²)	x	y	EQE(%)		LE(lm/W)		J(Cd/A)	
						[1000cd/m ²]	[Max]	[1000cd/m ²]	[Max]	[1000cd/m ²]	[Max]
5%	6.2	2.8	997.6	0.19	0.51	13.6	14.9	18.7	25.7	36.7	40.0
10%	6.1	2.6	1000.4	0.21	0.53	14.0	15.6	20.3	33.2	39.2	43.7
15%	5.7	3.0	1004.2	0.22	0.54	12.0	13.2	18.9	31.3	34.3	37.7

Device structure: ITO(50m)/PEDOT:PSS(60nm)/TAPC(20nm)/mCP(10nm)/mCP:**2**(25nm:*x*%) /TSPO1(5nm)/TPBi(20nm)/LiF(1.5nm)/Al(200nm)

Table S3. Crystal Data and Structure Refinement for ***fac-1*** and ***fac-2***.

Identification code	<i>fac-1</i>	<i>fac-2</i>
Empirical formula	C ₅₇ H ₄₇ F ₆ IrN ₆	C ₅₇ H ₅₁ IrN ₆ O ₆
Formula weight	1122.20	1108.23
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P2₁/n</i>
<i>a</i> (Å)	38.0031(11)	13.3302(2)
<i>b</i> (Å)	12.5069(4)	21.8273(3)
<i>c</i> (Å)	19.6910(6)	17.6527(2)
α (°)	90	90
β (°)	92.0785(19)	107.7379(7)
γ (°)	90	90
Volume (Å ³)	9353.0(5)	4892.09(12)
<i>Z</i>	8	4
Density (calculated) (Mg/m ³)	1.594	1.505
Absorption coefficient (mm ⁻¹)	2.926	2.788
F(000)	4496	2240
Crystal size (mm ³)	0.28 × 0.13 × 0.05	0.30 × 0.08 × 0.04
Theta range for data collection	1.072 to 28.298°	1.529 to 28.287°
Index ranges	-50 ≤ <i>h</i> ≤ 50 -16 ≤ <i>k</i> ≤ 15 -26 ≤ <i>l</i> ≤ 26	-17 ≤ <i>h</i> ≤ 16 -29 ≤ <i>k</i> ≤ 29 -23 ≤ <i>l</i> ≤ 17
Reflections collected	47145	50193
Independent reflections	11580 [<i>R</i> _{int} = 0.0683]	12132 [<i>R</i> _{int} = 0.0480]
Completeness to theta = 26.00°	100.0 %	99.9 %
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.5889	0.7457 and 0.6510
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	11580 / 48 / 632	12132 / 18 / 631
Goodness-of-fit on <i>F</i> ²	1.041	1.033
Final R indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0454, <i>wR</i> ₂ = 0.1033	<i>R</i> ₁ = 0.0318, <i>wR</i> ₂ = 0.0696
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0725, <i>wR</i> ₂ = 0.1153	<i>R</i> ₁ = 0.0578, <i>wR</i> ₂ = 0.0788
Largest diff. peak and hole (e.Å ⁻³)	1.346 and -1.524	0.756 and -0.669

Table S4. Selected bond lengths (\AA) and bond angles ($^\circ$) for *fac-1* and *fac-2*.

	<i>fac-1</i>		<i>fac-2</i>
Ir1-C1	2.001(5)	Ir1-C1	1.999(3)
Ir1-C18	1.999(5)	Ir1-C20	2.006(3)
Ir1-C35	1.995(5)	Ir1-C39	2.001(3)
Ir1-N1	2.135(4)	Ir1-N1	2.129(3)
Ir1-N3	2.115(4)	Ir1-N3	2.129(3)
Ir1-N5	2.130(4)	Ir1-N5	2.120(3)
C1-Ir1-C18	96.5(2)	C1-Ir1-C20	97.15(12)
C1-Ir1-C35	95.9(2)	C1-Ir1-C39	94.90(13)
C1-Ir1-N1	79.71(19)	C1-Ir1-N1	79.56(11)
C1-Ir1-N3	172.94(19)	C1-Ir1-N3	91.11(11)
C1-Ir1-N5	87.69(18)	C1-Ir1-N5	172.84(11)
C18-Ir1-C35	92.6(2)	C20-Ir1-C39	93.79(13)
C18-Ir1-N1	91.86(18)	C20-Ir1-N1	173.60(11)
C18-Ir1-N3	79.48(19)	C20-Ir1-N3	79.03(12)
C18-Ir1-N5	171.65(18)	C20-Ir1-N5	87.39(11)
C35-Ir1-N1	174.11(18)	C39-Ir1-N1	91.97(11)
C35-Ir1-N3	90.07(19)	C39-Ir1-N3	171.18(11)
C35-Ir1-N5	79.77(18)	C39-Ir1-N5	79.22(12)
N1-Ir1-N3	94.55(16)	N1-Ir1-N3	95.47(10)
N1-Ir1-N5	96.01(15)	N1-Ir1-N5	96.44(10)
N3-Ir1-N5	97.06(16)	N3-Ir1-N5	95.21(10)

Table S5. Intra- and intermolecular interactions (involving C-H···F/O hydrogen bonds, and C-H··· π , halogen··· π , and π - π interactions) for **fac-1** and **fac-2** [Å and °]. $Cg1$, $Cg2$, $Cg3$, $Cg4$, $Cg5$, $Cg6$, and $Cg7$ in **fac-1** are the centroids of the N1/C6-C10, N3/C23-C27, N4/C18-C22, N5/C40-C44, C28-C33, and C45-C50 rings, respectively. $Cg1$ and $Cg2$ in **fac-2** are the centroids of the C49-C54 and N4/C20-C24 rings, respectively.

D-H···A	d(D-H)	d(H···A)	d(D···A)	\angle (DHA)
fac-1				
C(7)-H(7)···F(2)	0.95	2.26	2.877(7)	121.6
C(24)-H(24)···F(4)	0.95	2.29	2.895(7)	120.8
C(41)-H(41)···F(6)	0.95	2.23	2.854(6)	122.3
C(41)-H(41)···F(6) ⁱ	0.95	2.43	3.314(7)	153.9
C(44)-H(44)···F(5) ⁱⁱ	0.95	2.55	3.341(6)	141.1
C36-H36···Cg3	0.95	2.96	3.732(5)	139
C49-H49···Cg2 ⁱⁱ	0.95	2.64	3.566(6)	166
C52-H52B···Cg5 ⁱⁱ	0.98	2.80	3.711(19)	155
C57-H57B···Cg6	0.98	2.78	3.639(17)	147
C57-H57C···Cg4 ⁱⁱⁱ	0.98	2.87	3.730(18)	146
F5···Cg1 ^{iv}			3.488(4)	
Cg5···Cg7 ^{iv}			3.774(3)	
[Symmetry codes: (i) - x +1, y , - z +1/2; (ii) x , - y +1, z +1/2; (iii) x , y +1, z ; (iv) x , - y +1, z -1/2.]				
fac-2				
C(7)-H(7)···O(2)	0.95	2.25	2.855(5)	120.8
C(26)-H(26)···O(4)	0.95	2.27	2.864(5)	119.8
C(45)-H(45)···O(6)	0.95	2.23	2.839(5)	121.1
C19-H19A···Cg1 ⁱ	0.98	2.89	3.717(5)	59
C55-H55C···Cg2 ⁱ	0.98	2.73	3.405(5)	35
[Symmetry codes: (i) x +1/2, - y +1/2, z +1/2.]				