

Supporting Information

Bis-tridentate Ir(III) Emitters with Complementary Carbene Cyclometalates Targeted for Efficient Blue Phosphorescence and Hyperluminescence

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General information

All solvents were dried and degassed before used, and commercially available reagents were used without further purification. All reactions were conducted under N₂ atmosphere and monitored by pre-coated TLC plates (0.20 nm with fluorescent indicator F254). ¹H, ¹³C and ¹⁹F NMR spectra were recorded with Bruker 400 MHz AVANCE III Nuclear Magnetic Resonance System. The high-resolution mass spectra were obtained using Bruker microTOF-Q instrument and acetonitrile as solvent. TGA measurements were performed on a TA Instrument TGAQ50, at a heating rate of 10 °C min⁻¹ under N₂ atmosphere.

Photophysical measurements: All photophysical measurements in this study were performed at RT (298 K). UV-visible spectra were recorded on HITACHI UH4150. The emission spectra of the solution state were measured with an Edinburgh FL 1000 instrument. The wavelength-dependent excitation and emission responses were calibrated. Steady-state absorption and emission spectra of the studied complexes were measured in diluted toluene solution at RT, and coumarin 102 was used as standard, where spectral grade solvents were employed. To specify the quantum yield in the fluid state, samples were degassed using at least three freeze-pump-thaw cycles.

Electrochemistry and thermogravimetric study: Cyclic voltammetry was conducted on a CHI660 Electrochemical Analyzer. Ag/Ag⁺ (0.01 M AgNO₃) electrode was employed as the reference electrode. Oxidation and reduction potentials were measured using platinum working electrode with 0.1 M of (NBu₄)(PF₆) as electrolyte in acetonitrile. The potentials were referenced externally to a ferrocenium/ferrocene (Fc⁺/Fc) couple. The associated data are given in Figures S4 and S5.

Single X-Ray Structural Determination. The single crystals suitable for X-ray diffraction study were obtained via slow diffusion of hexane into a saturated ethyl acetate solution of [Ir(DP)(MC1)], [Ir(DP)(MC2)] and [Ir(DP)(MC3)] at RT. Single crystal X-ray diffraction data were recorded on a Bruker D8 Venture Photon II diffractometer with microfocus X-ray sources using phi and omega scans mode (APEX3) at 233 K. The crystallographic data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Computational details of theoretical investigations: The geometries, electronic structures, and electronic excitations of the studied Ir(III) complexes were investigated by methods based on DFT[1, 2] and TD-DFT[3, 4] using the B3LYP functional[5-7] with Gaussian 16 set of programs.[8] The polarizable continuum model (PCM)[9] was used to include solvent effects of toluene. The 6-31G(d,p)[10] basis set was used for light elements such as hydrogen, carbon, nitrogen, and fluorine, while the LANL2DZ[11] basis set with the Los Alamos National Laboratory (LANL) effective

core potentials (ECPs) was used for iridium. The corresponding ground state (S_0) and lowest triplet state (T_1) geometries were optimized based on the X-ray structural data. The low-energy excited states were then calculated by the TD-DFT method based on the optimized geometries for the ground state (results provided in Table S2) or the T_1 state (results provided in the main text, Table S4 and Figure S6). Avogadro software[12] was used to visualize the orbitals presented in this work (with isosurface value of the electron density as 0.02 e/au^3). Orbital composition analysis was performed using the Hirshfeld method[13] to calculate the contribution of Ir atom to each molecular orbital with Multiwfn software.[14]

Additional computational details for relativistic TD-DFT calculations. Relativistic TD-DFT calculations were further performed to obtain more detailed information on spin-mixed electron excitations (e.g., the oscillator strength and the radiative rate for $S_0 \rightarrow T_1$ excitations) with ADF (2024 version)[15] using the B3LYP functional and Slater type TZP[16, 17] basis sets. The Conductor-like Screening Model (COSMO)[18, 19] is used to model solvent effects.

In these calculations, spin-orbit coupling (SOC) was added perturbatively[20] to one-component TDDFT[3, 21] utilizing the one-component zeroth order regular approximation (ZORA).[22-24] A total of 12 spin-mixed excitations were calculated. The radiative rate (k_r) of an excited state was then calculated according to[25-27]

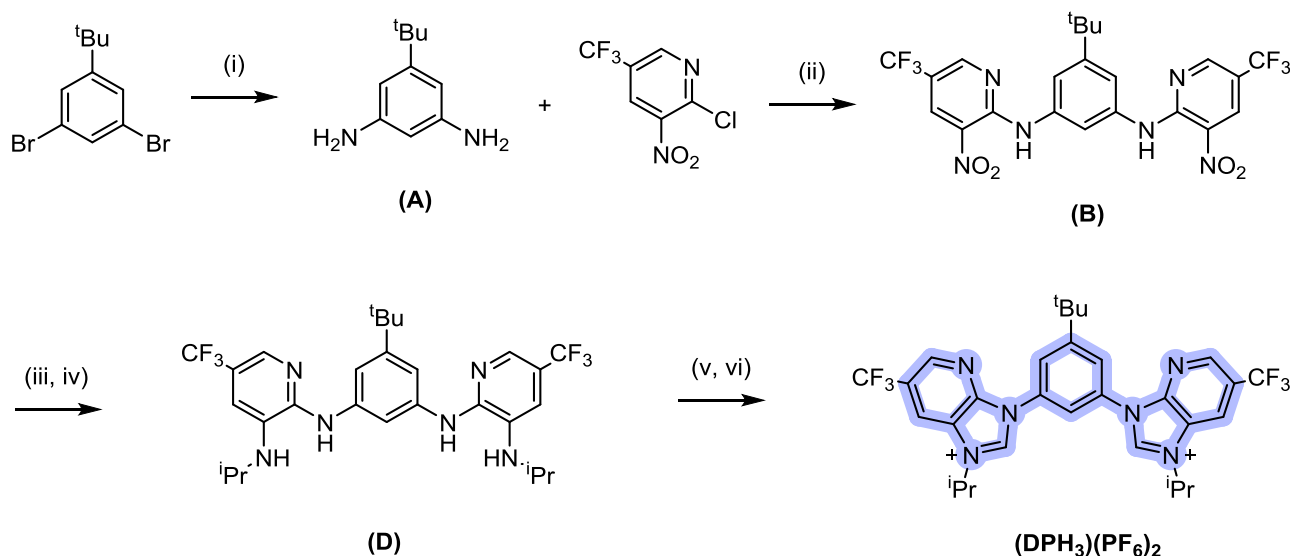
$$k_r = 2\epsilon^2 f / c^3 \quad (1)$$

where ϵ is the excitation energy, f is the corresponding oscillate strength for the electronic excitation from the ground state to excited state, c represents the speed of light in vacuum and the equation is in atomic units. The three lowest energy states found in the SOC TDDFT calculations for the complexes considered here are derived from the three substates in a triplet state with a small singlet admixture due to SOC.[28, 29] There will be small energy differences between the three substates because of their different admixtures with the singlet state, the so called zero-field splitting (ZFS). As the ZFS is small compared to $k_B T$ at room temperature, the radiative rate of the triplet state is then calculated as an average over the three substates within the assumption of fast thermalization. (The calculation results of relativistic TD-DFT were provided in Table S3.)

OLED fabrication and measurement: OLEDs were fabricated on the ITO-coated glass substrates with multiple organic layers sandwiched between the transparent bottom indium-tin-oxide (ITO) anode and the top metal cathode using a Trovato 450C system. Before device fabrication, the ITO glass substrates were pre-cleaned carefully. All material layers were deposited by vacuum evaporation in a vacuum chamber with a base pressure of 10^{-4} Pa. The deposition rate of organic

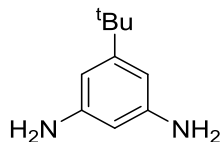
layers was kept at $1 - 2 \text{ \AA}\cdot\text{sec}^{-1}$. The doping was conducted by co-evaporation from separate evaporation sources with different evaporation rates. The current density, voltage, luminance, external quantum efficiency, electroluminescent spectra and other characteristics were measured with a Keithley 2400 source meter. The EQE measurement system is Hamamatsu C9920-12, which is equipped with Hamamatsu PMA-12 Photonic multichannel analyzer C10027-02, whose longest detection wavelength is 1200 nm. All measurements were repeated three times, among which the median value was chosen as the reported data, and the corresponding errors are generally within $\pm 5\%$.

Preparation of Tridentate Chelates



Scheme S1. Synthetic route to the tridentate dicarbene pincer chelate **(DPH₃)(PF₆)₂**; (i) NH₄OH, CuI, L-proline, K₂CO₃, DMSO, 110 °C; (ii) Et₃N, 2-propanol, 85 °C; (iii) NH₄Cl_(aq), Fe(s), methanol and THF, 70 °C; (iv) sodium triacetoxyborohydride, acetone, acetic acid, CH₂Cl₂, RT; (v) HCO₂H, 100 °C; (vi) KPF_{6(aq)}.

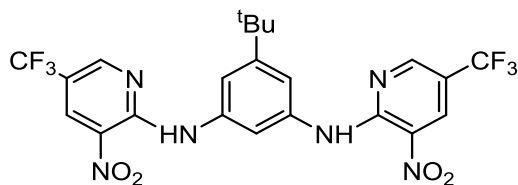
5-(*tert*-butyl)benzene-1,3-diamine (A)



This compound was prepared in accordance with the literature method.[30] In a 50 mL pressure tube, was added 25 % NH₄OH_(aq) (4.6 mL), 1,3-dibromo-5-(*tert*-butyl) benzene (1.0 g, 3.4 mmol), CuI (0.27 g, 1.4 mmol), L-proline (0.31 g, 2.7 mmol), K₂CO₃ (1.9 g, 13.6 mmol) and 20 mL DMSO. The tube was sealed, and the mixture was heated to 110 °C for 24 h. After cooled to RT, DMSO was removed under reduced pressure, and the residue was washed with water and then purified by column chromatography using a mixture of hexane and ethyl acetate (3/1, v/v) as eluent to afford a white solid. Yield: 0.46 g (82%).

Selected spectroscopic data: ¹H NMR (400 MHz, CDCl₃, 296 K) δ 6.17 (d, *J* = 2.0 Hz, 2H), 5.90 (t, *J* = 2.0 Hz, 1H), 3.53 (br, 4H), 1.25 (s, 9H).

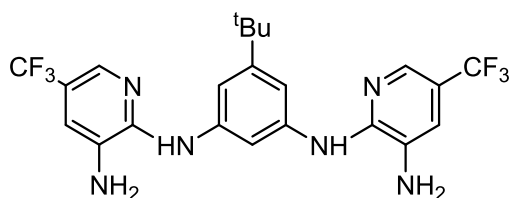
5-(*tert*-butyl)-*N*¹,*N*³-bis(3-nitro-5-(trifluoromethyl)pyridin-2-yl)benzene-1,3-diamine (B)



To a mixture of **A** (1.2 g, 7.34 mmol) and 2-chloro-3-nitro-5-(trifluoromethyl) pyridine (2.6 mL, 18.6 mmol) in 2-propanol (50 mL) was slowly added Et₃N (3.1 mL, 22.2 mmol), and the mixture was heated at 85 °C for 24 h. After cooled to RT, the red precipitate was collected, washed with deionized water and cold ethanol to afford red powder. Yield: 3.92 g (98%).

Selected spectroscopic data: ¹H NMR (400 MHz, CDCl₃, 296 K) δ 10.32 (s, 2H), 8.77 (s, 2H), 8.70 (s, 2H), 8.00 (s, 1H), 7.39 (s, 2H), 1.38 (s, 9H). ¹⁹F NMR (376 MHz, CDCl₃, 296 K) δ –61.40 (s, 6F).

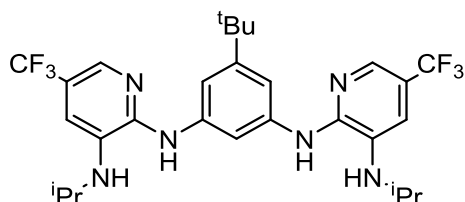
*N*²,*N*^{2'}-(5-(*tert*-butyl)-1,3-phenylene)bis(5-(trifluoromethyl)pyridine-2,3-diamine) (**C**)



Iron powder (1.11 g, 20.0 mmol) was added to a stirred solution of NH₄Cl (1.07 g, 20.0 mmol) in deionized water (10 mL) at 0 °C. A mixture of methanol and THF (1/1, v/v, 30 mL) of **B** (2.17 g, 4.0 mmol) was added dropwise and then, the mixture was heated at 70 °C overnight. After cooling to RT, the mixture was concentrated, and the resulting residue was dispersed into excess ethyl acetate and filtrated. After then, the filtrate was washed with deionized water, dried over anhydrous Na₂SO₄ and concentrated to dryness. The crude product was further purified by column chromatography using a mixture of hexane and ethyl acetate (1/1, v/v) to give a brown-colored solid. Yield: 1.55 g (80%).

Selected spectroscopic data: ¹H NMR (400 MHz, CDCl₃, 296 K) δ 8.03 (s, 2H), 7.66 (s, 1H), 7.11 (s, 2H), 7.00 (s, 2H), 6.60 (s, 2H), 3.53 (br, 4H), 1.30 (s, 9H). ¹⁹F NMR (376 MHz, CDCl₃, 296 K) δ –61.38 (s, 6F).

*N*²,*N*^{2'}-(5-(*tert*-butyl)-1,3-phenylene)bis(*N*³-isopropyl-5-(trifluoromethyl)pyridine-2,3-diamine) (**D**)

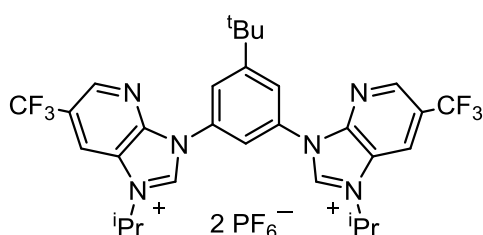


To a solution of compound **C** (1.69 g, 3.5 mmol) in CH₂Cl₂ (20 mL) was slowly added acetic acid (0.80 mL, 14.0 mmol), acetone (1.03 mL, 14.0 mmol) and sodium triacetoxyborohydride (2.97 g, 14.0 mmol) in sequence. After stirring at RT for 12 hours, the mixture was concentrated under vacuum and the residue was dissolved in ethyl acetate (200 mL). The organic phase was quenched

with 2N HCl_(aq), followed by diluted NaHCO_{3(aq)} and brine, dried over anhydrous Na₂SO₄ and concentrated. The crude product was purified by column chromatography using a mixture of hexane and ethyl acetate (3/1, v/v) to give white solid. Yield: 1.65 g (83%).

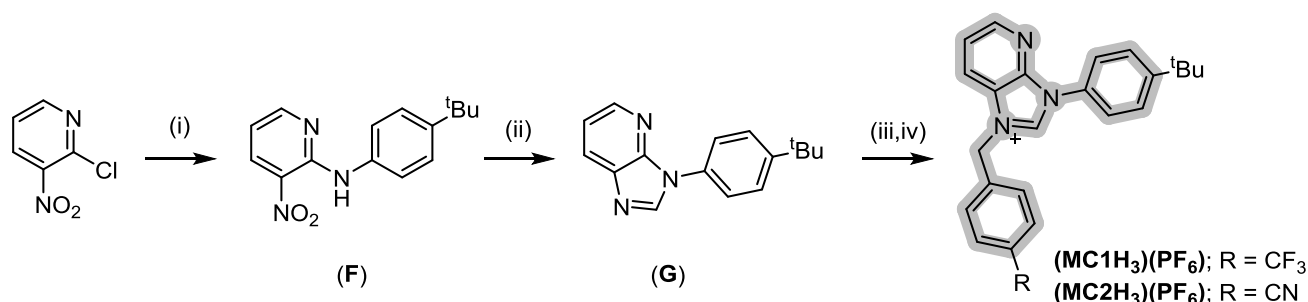
Selected spectroscopic data: ¹H NMR (400 MHz, CDCl₃, 296 K) δ 7.98 (s, 2H), 7.50 (s, 1H), 7.04 (s, 2H), 6.96 (s, 2H), 6.48 (s, 2H), 3.59 (sep, *J* = 6.4 Hz, 2H), 3.26 (s, 2H), 1.31 (s, 9H), 1.27 (d, *J* = 6.4 Hz, 12H). ¹⁹F NMR (376 MHz, CDCl₃, 296 K) δ -61.43 (s, 6F).

Di-hexafluorophosphate salt of
3,3'-(5-(*tert*-butyl)-1,3-phenylene)bis(1-isopropyl-6-(trifluoromethyl)-3H-imidazo[4,5-*b*]pyridin-1-ium) (**(DPH₃)(PF₆)₂**)



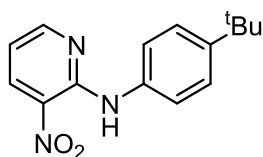
Compound **D** (1.42 g, 2.5 mmol) was dissolved in 50 mL formic acid and the mixture was heated to 100 °C for 12 h with vigorous stirring. After cooling to RT, the solvent was removed under vacuum. The residue was dissolved in acetone (15 mL), followed by the addition of 100 mL of KPF₆ (4.60 g, 40.0 mmol) in water and stirred at RT for 2 h. The precipitation was filtered, washed with deionized water and diethyl ether, and dried under vacuum to afford a pink solid of **(DPH₃)(PF₆)₂**. Yield: 2.15 g (98%).

Selected spectroscopic data of **(DPH₃)(PF₆)₂**: ¹H NMR (400 MHz, DMSO-*d*₆, 296 K) δ 10.76 (s, 2H), 9.44 (s, 2H), 9.22 (s, 2H), 8.38 (s, 1H), 8.25 (s, 2H), 5.35 (sep, *J* = 6.7 Hz, 2H), 1.75 (d, *J* = 6.7 Hz, 12H), 1.46 (s, 9H). ¹⁹F NMR (376 MHz, DMSO-*d*₆, 296 K): δ -58.88 (s, 6F), -70.13 (d, *J*_{PF} = 711 Hz, 12F).



Scheme S2. Synthetic route to the monocarbene pro-chelates **(MC1H₃)(PF₆)** and **(MC2H₃)(PF₆)**: experimental condition: (i) 4-*tert*-butylaniline, Et₃N, 2-propanol, 85 °C; (ii) Fe(s), formic acid, reflux; (iii) 1-(bromomethyl)-4-(trifluoromethyl)benzene or 4-(bromomethyl)benzonitrile, toluene, 110 °C; (iv) KPF_{6(aq)}.

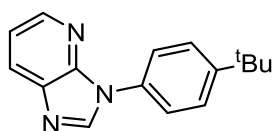
N-(4-(*tert*-butyl)phenyl)-3-nitropyridin-2-amine (**F**)



To a mixture of 4-*tert*-butylaniline (3.6 mL, 22.8 mmol) and 2-chloro-3-nitro pyridine (3.0 g, 19.0 mmol) in 2-propanol (100 mL) was slowly added Et₃N (3.3 mL, 23.7 mmol), and the mixture was heated at 85 °C for 12 h. After cooled to RT, the red precipitate was collected, washed with deionized water and cold ethanol to afford red powder. Yield: 4.9 g (95%).

Selected spectroscopic data: ¹H NMR (400 MHz, CDCl₃, 296 K) δ 10.07 (s, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 8.48 (d, *J* = 5.6 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 6.83 (dd, *J* = 8.4, 5.6 Hz, 1H), 1.33 (s, 9H).

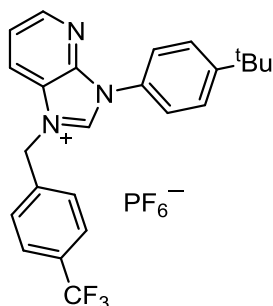
3-(4-(*tert*-butyl)phenyl)-3*H*-imidazo[4,5-*b*]pyridine (**G**)



Compound **F** (2.0 g, 7.4 mmol) and iron powder (3.3 g, 59.0 mmol) were refluxed in 50 mL formic acid for 12 h with vigorous stirring. After cooling to RT, the unreacted formic acid was removed under vacuum, and the resulting residue was dispersed into excess ethyl acetate and filtrated. After then, the filtrate was washed with deionized water, dried over anhydrous Na₂SO₄ and concentrated to dryness. The crude product was further purified by column chromatography using a mixture of hexane and ethyl acetate (2/1, v/v) to afford a white solid of **G**. Yield: 1.5 g (80%).

Selected spectroscopic data: ¹H NMR (400 MHz, CDCl₃, 296 K) δ 8.48 (d, *J* = 4.8 Hz, 1H), 8.31 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.33 (dd, *J* = 8.4, 4.8 Hz, 1H), 1.38 (s, 9H).

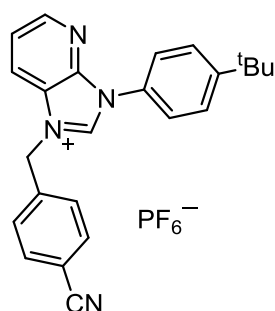
Hexafluorophosphate salt of
3-(4-(*tert*-butyl)phenyl)-1-(4-(trifluoromethyl)benzyl)-3*H*-imidazo[4,5-*b*]pyridin-1-ium (**MC1H₃**)(PF₆)



A mixture of compound **G** (0.5 g, 2.0 mmol) and 1-(bromomethyl)-4-(trifluoromethyl)benzene (0.4 mL, 2.4 mmol) in 10 mL toluene was heated at 110 °C for 12 h with vigorous stirring. After cooling to RT, the precipitation was collected and dissolved in acetone (5 mL), followed by the addition of 20 mL of KPF₆ (0.460 g, 4.0 mmol) in water and stirred at RT for 2 h. The precipitation was filtered, washed with deionized water and diethyl ether, and dried under vacuum to afford a white solid of **(MC1H₃)(PF₆)**. Yield: 0.99 g (90%).

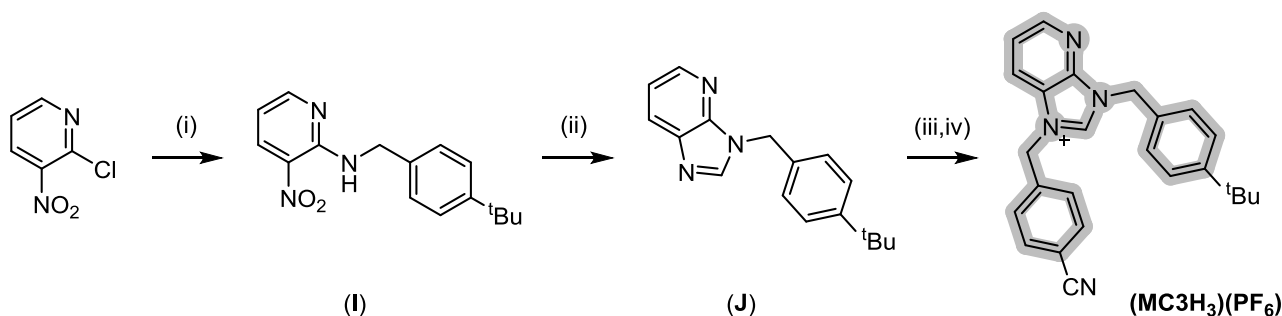
Selected spectroscopic data of **(MC1H₃)(PF₆)**: ¹H NMR (400 MHz, DMSO-*d*₆, 296 K) δ 10.63 (s, 1H), 8.80 (d, *J* = 4.8 Hz, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 7.90 – 7.80 (m, 7H), 7.76 (d, *J* = 8.4 Hz, 2H), 6.00 (s, 2H), 1.38 (s, 9H); ¹⁹F NMR (376 MHz, DMSO-*d*₆, 296 K): δ –61.09 (s, 3F), –70.19 (d, *J* = 711 Hz, 6F).

Hexafluorophosphate salt of
3-(4-(*tert*-butyl)phenyl)-1-(4-cyanobenzyl)-3*H*-imidazo[4,5-*b*]pyridin-1-ium **(MC2H₃)(PF₆)**



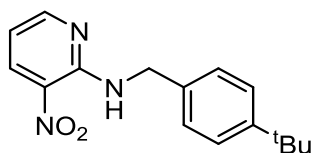
White solid of **(MC2H₃)(PF₆)** (0.6 g, 78%) was attained from **G** and 4-(bromomethyl)benzonitrile, following the same approach reported for its analogue **(MC1H₃)(PF₆)**.

Selected spectroscopic data of **(MC2H₃)(PF₆)**: ¹H NMR (400 MHz, CDCl₃, 296 K) δ 11.99 (s, 1H), 8.79 (d, *J* = 4.4 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.75 – 7.62 (m, 5H), 6.52 (s, 2H), 1.39 (s, 9H); ¹⁹F NMR (376 MHz, CDCl₃, 296 K): δ –71.55 (d, *J* = 711 Hz, 6F).



Scheme S3. Synthetic route to the monocarbene pro-chelate **(MC3H₃)(PF₆)**: experimental condition: (i) 4-*tert*-butylbenzylamine, Na₂CO₃, DMF, 100 °C; (ii) Fe(s), formic acid, reflux; (iii) 1-(bromomethyl)-4-cyanobenzene, toluene, 110 °C; (iv) KPF_{6(aq)}.

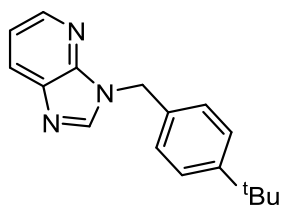
N-(4-(*tert*-butyl)benzyl)-3-nitropyridin-2-amine (**I**)



A mixture of 4-*tert*-butylbenzylamine (516 mg, 3.2 mmol), 2-chloro-3-nitro pyridine (500 mg, 3.2 mmol) and Na₂CO₃ (537 mg, 5.1 mmol) in DMF (20 mL) was heated at 100 °C for 12 h. After cooling to RT, the red precipitate was induced by the addition of deionized water, then washed with cold ethanol to afford red powder **I**. Yield: 820 mg (90%).

Selected spectroscopic data: ¹H NMR (400 MHz, CDCl₃, 296 K) δ 8.52 (br, 1H), 8.48 – 8.45 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.70 (dd, *J* = 8.0, 4.8 Hz, 1H), 4.86 (d, *J* = 5.6 Hz, 2H), 1.35 (s, 9H).

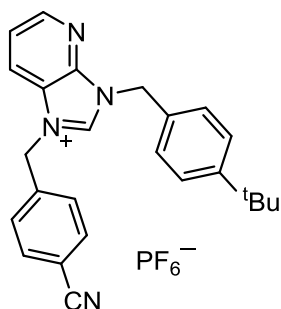
3-(4-(*tert*-butyl)benzyl)-3*H*-imidazo[4,5-*b*]pyridine (**J**)



White solid of **J** was attained following the same approach reported for its analogue **G**. Yield: 371 mg (80%).

Selected spectroscopic data: ¹H NMR (400 MHz, CDCl₃, 296 K) δ 8.52 (dd, *J* = 4.8, 1.2 Hz, 1H), 8.20 (s, 1H), 8.18 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.12 (br, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.35 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 1.32 (s, 9H).

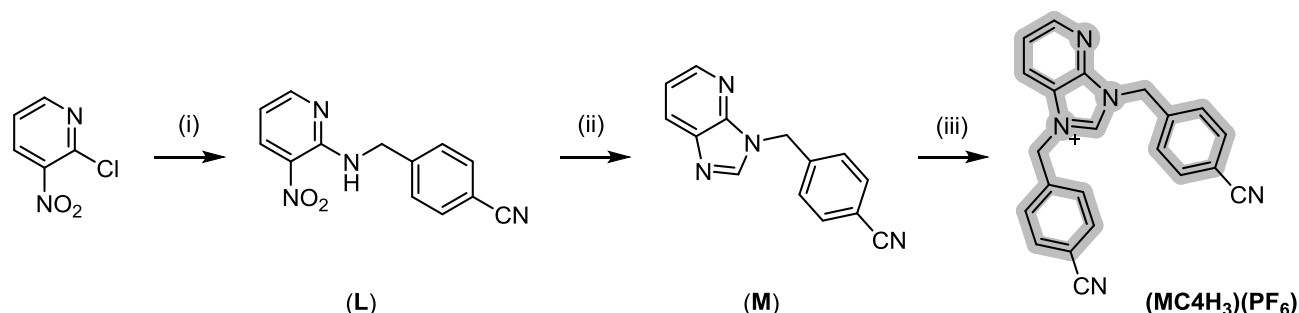
Hexafluorophosphate salt of 1,3-bis(4-(*tert*-butyl)benzyl)-3*H*-imidazo[4,5-*b*]pyridin-1-ium (**(MC3H₃)(PF₆)**)



White solid of **(MC3H₃)(PF₆)** was attained from **J** and 1-(bromomethyl)-4-cyanobenzene, following the same approach reported for its analogue **(MC1H₃)(PF₆)**. Yield: 899 mg (90%).

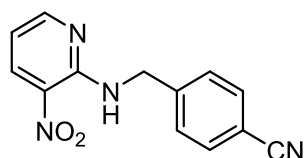
Selected spectroscopic data of **(MC3H₃)(PF₆)**: ¹H NMR (400 MHz, CDCl₃, 296 K) δ 12.05 (s, 1H), 8.76 (d, *J* = 4.8 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.55 (dd, *J* = 8.4, 4.8 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 6.24 (s, 2H), 5.83 (s, 2H), 1.29

(s, 9H); ^{19}F NMR (376 MHz, CDCl_3 , 296 K): δ -71.33 (d, J = 711 Hz, 6F).



Scheme S4. Synthetic route to the monocarbene pro-chelate **(MC4H3)(PF₆)**: (i) 4-cyanobenzylamine hydrochloride, Na_2CO_3 , DMF, 100 °C; (ii) Fe(s), formic acid, reflux; (iii) 1-(bromomethyl)-4-cyanobenzene, toluene, 110 °C; (iv) $\text{KPF}_6(\text{aq})$.

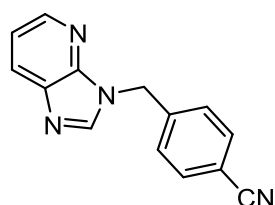
4-(((3-nitropyridin-2-yl)amino)methyl)benzonitrile (**L**)



A mixture of 4-(aminomethyl)benzonitrile hydrochloride (1.9 g, 12 mmol), 2-chloro-3-nitropyridine (2.0 g, 12 mmol) and Na_2CO_3 (3.8 g, 36 mmol) in DMF (20 mL) was heated at 130 °C for 4 h. After cooling to RT, the solvent was removed under vacuum, and the resulting residue was dispersed into excess CH_2Cl_2 and filtrated. After then, the filtrate was washed with deionized water, dried over anhydrous Na_2SO_4 and concentrated to dryness. The crude product was further purified by column chromatography using a mixture of hexane, CH_2Cl_2 and ethyl acetate (1/5/1, v/v/v) to afford a yellow solid of **G**. Yield: 2.5 g (83%).

Selected spectroscopic data: ^1H NMR (400 MHz, CDCl_3 , 296 K) δ 8.61 (br, 1H), 8.46 (d, J = 8.4 Hz, 1H), 8.40 (d, J = 4.4 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 6.73 (dd, J = 8.4, 4.4 Hz, 1H), 4.93 (d, J = 6.0 Hz, 2H).

4-((3H-imidazo[4,5-*b*]pyridin-3-yl)methyl)benzonitrile (**M**)

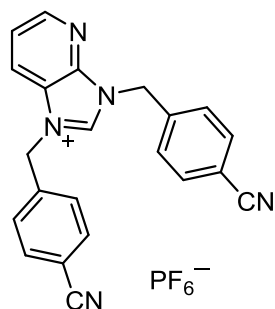


White solid of **M** (0.6 g, 78%) was attained following the same approach reported for its analogue **G**.

Selected spectroscopic data: ^1H NMR (400 MHz, CDCl_3 , 296 K) δ 8.44 (s, 1H), 8.15 – 8.11 (m,

2H), 7.63 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.32 (dd, $J = 8.0, 4.8$ Hz, 1H), 5.56 (s, 2H).

Hexafluorophosphate salt of 1,3-bis(4-cyanobenzyl)-3*H*-imidazo[4,5-*b*]pyridin-1-ium (**(MC4H₃)(PF₆)**)



White solid of **(MC4H₃)(PF₆)** (0.6 g, 78%) was attained from **M** and 1-(bromomethyl)-4-cyanobenzene, following the same approach reported for its analogue **(MC1H₃)(PF₆)**.

Selected spectroscopic data of **(MC4H₃)(PF₆)**: ^1H NMR (400 MHz, CDCl_3 , 296 K) δ 12.05 (s, 1H), 8.76 (d, $J = 4.8$ Hz, 1H), 8.02 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 8.4$ Hz, 2H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.64 (d, $J = 8.4$ Hz, 2H), 7.55 (dd, $J = 8.4, 4.8$ Hz, 1H), 7.41 (d, $J = 8.4$ Hz, 2H), 6.24 (s, 2H), 5.83 (s, 2H), 1.29 (s, 9H); ^{19}F NMR (376 MHz, CDCl_3 , 296 K): δ -71.33 (d, $J = 711$ Hz, 6F).

Preparation of Bis-tridentate Ir(III) Complexes:

Synthesis of **[Ir(DP)(MC1)]**. To a 100 mL flask was added chelate **(DPH₃)(PF₆)₂** (264 mg, 0.3 mmol), **[Ir(COD)(μ -Cl)]₂** (100 mg, 0.15 mmol), NaOAc (123 mg, 1.5 mmol) and degassed acetonitrile (20 mL) under N_2 atmosphere. This mixture was refluxed overnight under N_2 atmosphere. After then, the acetonitrile was removed under vacuum, the residue was combined with **(MC1H₃)(PF₆)** (148 mg, 0.3 mmol) and 1,2,4-trichlorobenzene (10 mL). After refluxing for 12 hours, Cs_2CO_3 (534 mg, 1.5 mmol) was added, and the resulting mixture was further refluxed for another 48 hours. Once completed, 1,2,4-trichlorobenzene was removed under vacuum. The residue was dissolved in ethyl acetate, washed with deionized water, dried over anhydrous Na_2SO_4 , and concentrated to dryness using rotary evaporator. Finally, the resulting mixture was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate (3/1, v/v) to afford a light-yellow solid. Yield: 106 mg (30.0%).

Selected spectroscopic data of **[Ir(DP)(MC1)]**: HRMS (ESI) for $\text{C}_{54}\text{H}_{50}\text{F}_9\text{IrN}_9$ [$\text{M} + \text{H}^+$]: calcd 1188.3675, found 1188.3643; ^1H NMR (400 MHz, CDCl_3 , 296 K) δ 8.75 (d, $J = 1.6$ Hz, 2H), 8.74 (s, 2H),

8.59 (dd, $J = 5.2, 1.6$ Hz, 1H), 8.40 (d, $J = 8.0$ Hz, 1H), 8.04 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.68 (d, $J = 1.6$ Hz, 2H), 7.44 (dd, $J = 8.0, 5.2$ Hz, 1H), 7.20 (d, $J = 8.0$ Hz, 1H), 7.01 (d, $J = 2.0$ Hz, 1H), 6.96 (dd, $J = 8.0, 2.0$ Hz, 1H), 6.86 (d, $J = 8.0, 2.0$ Hz, 1H), 6.12 (s, 2H), 6.00 (d, $J = 2.0$ Hz, 1H), 4.24 (sep, $J = 7.2$ Hz, 2H), 1.73 (s, 9H), 1.09 (d, $J = 7.2$ Hz, 6H), 0.87 (s, 9H), 0.81 (d, $J = 7.2$ Hz, 6H). ^{19}F NMR (376 MHz, CDCl_3 , 296 K) δ -60.20 (s, 6F), -62.16 (s, 3F).

Selected crystal data of **[Ir(DP)(MC1)]**: CCDC number: 2378796. $\text{C}_{58}\text{H}_{57}\text{F}_9\text{IrN}_9\text{O}_2$; $M = 1275.32$; monoclinic; space group C2/c ; $a = 35.111(3)$ Å, $b = 12.6722(8)$ Å, $c = 26.874(2)$ Å; $\beta = 95.620(7)^\circ$; $V = 11899.5(16)$ Å³; $Z = 8$; $\rho_{\text{Calcd}} = 1.424$ g·cm⁻³; $\mu = 4.995$ mm⁻¹; $F(000) = 5136$, $\lambda(\text{Cu-K}\alpha) = 1.54178$ Å; $T = 213$ (2) K; index range: $-43 \leq h \leq 43$, $-14 \leq k \leq 15$, $-33 \leq l \leq 33$; 77784 reflections collected, 12190 independent reflections ($R_{\text{int}} = 0.1033$), data / restraints / parameters = 12190 / 778 / 872, GOF = 1.089, final $R_1[I > 2\sigma(I)] = 0.0534$ and $wR_2(\text{all data}) = 0.1518$.

Synthesis of **[Ir(DP)(MC2)]**. Light-yellow solid of **[Ir(DP)(MC2)]** (150 mg, 40%) was attained from tridentate chelates **(DPH₃)(PF₆)₂** and **(MC2H₃)(PF₆)₂**, following the same approach reported for its analogue **[Ir(DP)(MC1)]**.

Selected spectroscopic data of **[Ir(DP)(MC2)]**: HRMS (ESI) for $\text{C}_{54}\text{H}_{50}\text{F}_6\text{IrN}_{10}$ [$M + \text{H}^+$]: calcd 1145.3753, found 1145.3784; ^1H NMR (400 MHz, CDCl_3 , 296 K) δ 8.75 (s, 2H), 8.74 (s, 2H), 8.56 (dd, $J = 4.8, 1.2$ Hz, 1H), 8.35 (d, $J = 8.0$ Hz, 1H), 8.02 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.67 (d, $J = 1.2$ Hz, 2H), 7.43 (dd, $J = 8.0, 4.8$ Hz, 1H), 7.16 (d, $J = 8.0$ Hz, 1H), 7.12 (d, $J = 1.2$ Hz, 1H), 7.01 (dd, $J = 8.0, 2.0$ Hz, 1H), 6.82 (dd, $J = 8.0, 2.0$ Hz, 1H), 6.13 (s, 2H), 5.88 (d, $J = 2.0$ Hz, 1H), 4.24 (sep, $J = 7.2$ Hz, 2H), 1.72 (s, 9H), 1.08 (d, $J = 7.2$ Hz, 6H), 0.83 (s, 9H), 0.79 (d, $J = 7.2$ Hz, 6H). ^{19}F NMR (376 MHz, CDCl_3 , 296 K) δ -60.21 (s, 6F). Anal. Calcd.: C, 56.63; H, 4.40; N, 12.23. Found: C, 56.73; H, 4.49; N, 12.13.

Selected crystal data of **[Ir(DP)(MC2)]**: CCDC number: 2426306. $\text{C}_{55}\text{H}_{51}\text{Cl}_2\text{F}_6\text{IrN}_{10}$; $M = 1229.15$; monoclinic; space group C2/c ; $a = 35.014(4)$ Å, $b = 12.8048(13)$ Å, $c = 26.671(3)$ Å; $\beta = 91.171(2)^\circ$; $V = 11956(2)$ Å³; $Z = 8$; $\rho_{\text{Calcd}} = 1.366$ g·cm⁻³; $\mu = 5.659$ mm⁻¹; $F(000) = 4928$, $\lambda(\text{Cu-K}\alpha) = 1.54178$ Å; $T = 243$ (2) K; index range: $-43 \leq h \leq 43$, $-15 \leq k \leq 13$, $-33 \leq l \leq 33$; 114762 reflections collected, 12240 independent reflections ($R_{\text{int}} = 0.0502$), data / restraints / parameters = 12240/542/773, GOF = 1.025, final $R_1[I > 2\sigma(I)] = 0.0331$ and $wR_2(\text{all data}) = 0.0981$.

Synthesis of **[Ir(DP)(MC3)]**. Light-yellow solid of **[Ir(DP)(MC3)]** (240 mg, 42%) was attained from tridentate chelates **(DPH₃)(PF₆)₂** and **(MC3H₃)(PF₆)₂**, following the same approach reported for its analogue **[Ir(DP)(MC1)]**.

Selected spectroscopic data of **[Ir(DP)(MC3)]**: HRMS (ESI) for C₅₅H₅₁F₆IrN₁₀ [M + H]⁺: calcd 1159.3910, found 1159.3870; ¹H NMR (400 MHz, CDCl₃, 296 K) δ 8.81 (d, *J* = 1.2 Hz, 2H), 8.73 (s, 2H), 8.54 (dd, *J* = 6.4, 1.6 Hz, 1H), 8.02 (dd, *J* = 10.4, 1.6 Hz, 1H), 7.73 (d, *J* = 2.4 Hz, 2H), 7.44 (dd, *J* = 10.4, 2.8 Hz, 1H), 7.11 (dd, *J* = 10.4 Hz, 1H), 7.01 – 6.97 (m, 2H), 6.75 (d, *J* = 2.4 Hz, 1H), 6.58 (dd, *J* = 10.4, 2.8 Hz, 1H), 6.04 (d, *J* = 2.8 Hz, 1H), 5.55 (s, 2H), 5.37 (s, 2H), 3.82 (sep, *J* = 7.2 Hz, 2H), 1.66 (s, 9H), 0.87 (d, *J* = 7.2 Hz, 6H), 0.76 (d, *J* = 7.2 Hz, 6H), 0.52 (s, 9H). ¹⁹F NMR (376 MHz, CDCl₃, 296 K) δ –60.21 (s, 6F). Anal. Calcd.: C, 57.03; H, 4.44; N, 12.09. Found: C, 57.00; H, 4.49; N, 12.03.

Selected crystal data of **[Ir(DP)(MC3)]**: CCDC number: 2385163. C₅₅H₅₁F₆IrN₁₀; M = 1158.26; triclinic; space group P-1; *a* = 13.1131(3) Å, *b* = 14.2294(3) Å, *c* = 18.0725(5) Å; α = 71.9620(10)°, β = 71.5620(10)°, γ = 74.3120(10)°; V = 2985.73(13) Å³; Z = 2; ρ_{Calcd} = 1.288 g·cm⁻³; μ = 4.829 mm⁻¹; F(000) = 1164, λ(Cu-Kα) = 1.54178 Å; T = 213 (2) K; index range: –16 ≤ *h* ≤ 16, –17 ≤ *k* ≤ 17, –22 ≤ *l* ≤ 22; 50232 reflections collected, 12185 independent reflections (*R*_{int} = 0.0531), data / restraints / parameters = 12185/744/791, GOF = 1.078, final *R*₁[*I* > 2σ(*I*)] = 0.0322 and *wR*₂(all data) = 0.0847.

Synthesis of **[Ir(DP)(MC4)]**. Light-yellow solid of **[Ir(DP)(MC4)]** (100 mg, 29%) was attained from tridentate chelates **(DPH₃)(PF₆)₂** and **(MC4H₃)(PF₆)₂**, following the same approach reported for its analogue **[Ir(DP)(MC1)]**.

Selected spectroscopic data of **[Ir(DP)(MC4)]**: HRMS (ESI) for C₅₂H₄₃F₆IrN₁₁ [M]⁺: calcd 1128.3236, found 1128.3192; ¹H NMR (400 MHz, CDCl₃, 296 K) δ 8.84 (s, 2H), 8.71 (s, 2H), 8.54 (d, *J* = 4.8 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.77 (s, 2H), 7.45 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 2H), 6.43 (dd, *J* = 8.0, 1.6 Hz, 2H), 5.60 (s, 2H), 5.33 (s, 2H), 5.30 (s, 2H), 3.81 (sep, *J* = 7.2 Hz, 2H), 1.66 (s, 9H), 0.87 (d, *J* = 7.2 Hz, 12H). ¹⁹F NMR (376 MHz, CDCl₃, 296 K) δ –60.26 (s, 6F). Anal. Calcd.: C, 55.36; H, 3.84; N, 13.66. Found: C, 55.30; H, 3.79; N, 13.61.

Table S1. Summary of decomposition temperature (T_d), voltammetric data and calculated energy gaps.

	T_d ($^{\circ}\text{C}$) ^a	$E^{\text{ox}}_{1/2}$ (V) (ΔE_p) ^b	$E^{\text{re}}_{\text{pc}}$ (V) ^c	HOMO (eV) ^d	energy gap (eV) ^e	LUMO (eV) ^f
[Ir(DP)(MC1)]	334	0.40 (0.09)	−2.40	−5.20	2.84	−2.36
[Ir(DP)(MC2)]	354	0.43 (0.09)	−2.40	−5.23	2.86	−2.37
[Ir(DP)(MC3)]	386	0.56 (0.08)	−2.40	−5.36	2.94	−2.42
[Ir(DP)(MC4)]	421	0.70 (0.07)	−2.32	−5.50	2.98	−2.52

^a Temperature with a weight loss of 5%; ^b Electrochemical potentials were measured in a 0.1 M acetonitrile solution of TBAPF₆. E_{ox} refers to $[(E_{\text{pa}} + E_{\text{pc}})/2]$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials referenced to the Fc/Fc⁺ couple; ^c $E^{\text{re}}_{\text{pc}}$ is the cathodic wave potential for the irreversible reduction wave; ^d HOMO = $-(E^{\text{ox}}_{\text{onset}} + 4.8)$; ^e energy gap = $1240 / [PL_{\text{onset}} \text{ (nm)}]$; ^f LUMO = HOMO + energy gap.

Table S2. The calculation results^[a] for the excitation energy (ϵ), oscillator strength (f), and main orbital contributions of the lowest singlet (S_1) and triplet (T_1) excited states, for the investigated Ir(III) complexes at their geometries optimized for the ground state.

	State	ϵ (nm/eV)	f	Orbital contribution (> 20%)
[Ir(DP)(MC1)]	T_1	446/2.78	0	HOMO $\rightarrow$ LUMO (94%)
	S_1	418/2.97	0.0033	HOMO $\rightarrow$ LUMO (98%)
[Ir(DP)(MC2)]	T_1	443/2.80	0	HOMO $\rightarrow$ LUMO (94%)
	S_1	415/2.99	0.0031	HOMO $\rightarrow$ LUMO (98%)
[Ir(DP)(MC3)]	T_1	433/2.87	0	HOMO $\rightarrow$ LUMO (92%)
	S_1	412/3.01	0.0003	HOMO $\rightarrow$ LUMO (98%)
[Ir(DP)(MC4)]	T_1	425/2.92	0	HOMO $\rightarrow$ LUMO (92%)
	S_1	404/3.07	0.0004	HOMO $\rightarrow$ LUMO (99%)

^[a] Calculated by TD-DFT using B3LYP functional and PCM for modelling the toluene solvent (see computational details for further information).

Table S3. Results of relativistic calculations of the excitation energy (ϵ), oscillator strength (f), and radiative decay rate (k_r), for the Ir(III) complexes at geometries optimized for the T_1 excited state.

	ϵ (nm/eV) ^[a]	f (10^{-4}) ^[a]	k_r (10^4 s ⁻¹) ^[a,b]
[Ir(DP)(MC1)]	541 / 2.29	3.202	7.29
[Ir(DP)(MC2)]	535 / 2.32	3.250	7.58
[Ir(DP)(MC3)]	525 / 2.36	3.384	8.19
[Ir(DP)(MC4)]	509 / 2.43	3.198	8.22

^[a] The average of the three sub-states of the T_1 state is given for ϵ , f and k_r . Relativistic calculations were used to compute spin-mixed excitations by adding perturbative spin-orbit coupling (SOC) to one-component TD-DFT. COSMO was used to model the toluene solvent. For additional information please see computational details.

^[b] Note that the calculated k_r (at 0 K) is systematically smaller than the experimental k_r (at RT), same as that found in other families of Ir(III) complexes. The former is intrinsic and independent from the non-radiative decay pathways, whereas the latter is highly dependent on the non-radiative decay pathways. The uncertainty of applied computational models and methods are also one of possible sources of deviation between calculated and experimental k_r . In general, the trend of calculated and experimental k_r is consistent. Also, the trend of calculated k_r for four Ir(III) complexes here is consistent with that determined by experiments.

Table S4. The calculation results^[a] for the excitation energy (ϵ), oscillator strength (f), and main orbital contributions, of the two lowest triplet excited states (T_1 and T_2) for the investigated Ir(III) complexes at their geometries optimized for the T_1 state. Additionally, the excitation energy gap between T_1 and T_2 is provided.

	State	ϵ (nm/eV)	f	Orbital contribution (> 20%)	Excitation energy gap T_1/T_2 (eV)
[Ir(DP)(MC1)]	T_1	539/2.30	0	HOMO $\rightarrow$ LUMO (95%)	0.21
	T_2	495/2.51	0	HOMO $\rightarrow$ LUMO+1 (94%)	
[Ir(DP)(MC2)]	T_1	532/2.33	0	HOMO $\rightarrow$ LUMO (95%)	0.21
	T_2	488/2.54	0	HOMO $\rightarrow$ LUMO+1 (94%)	
[Ir(DP)(MC3)]	T_1	523/2.37	0	HOMO $\rightarrow$ LUMO (95%)	0.23
	T_2	476/2.61	0	HOMO $\rightarrow$ LUMO+1 (93%)	
[Ir(DP)(MC4)]	T_1	509/2.44	0	HOMO $\rightarrow$ LUMO (94%)	0.25
	T_2	462/2.68	0	HOMO $\rightarrow$ LUMO+1 (92%)	

^[a] Calculated by TD-DFT using B3LYP functional and PCM for modelling the toluene solvent (see computational details for further information).

Table S5. Photophysical data of the studied Ir(III) carbene complexes (10 wt.%) deposited in a 65:35 mixture of SiCzCz : SiTrzCz2 at RT (10 wt.%).

	em $\lambda_{\max}^a$ (nm)	FWHM ^{a,b} (nm)	$\phi^{a,c}$ (%)	$\tau_{\text{obs}}^{a,d}$ (ns)	k_r (10^5 s^{-1})	k_{nr} (10^5 s^{-1})
[Ir(DP)(MC1)]	479	74	89	1013	8.8	1.1
[Ir(DP)(MC2)]	479	75	86	1010	8.5	1.4
[Ir(DP)(MC3)]	468	67	71	794	8.9	3.6
[Ir(DP)(MC4)]	465	82	46	643	7.2	8.4

^a PL spectra, lifetime, and quantum yield were recorded in doped SiCzCz : SiTrzCz2 co-host at RT; ^b Full width at half maximum; ^c Quantum yields were measured by integrated sphere; ^d Lifetimes were measured with excitation wavelength of 375 nm.

Table S6. Selected EL data of OLED devices that published in high-impact journal articles.

emitter	λ_{EL} (nm)	CIE(x,y)	EQE (%)			Ref.
			max	1000 cd m ⁻²	10000 cd m ⁻²	
[Ir(DP)(MC3)]	472	(0.15, 0.21)	18.1	18.1	15.4	This work
[Ir(DP)(MC3)] / v-DABNA	469	(0.13, 0.11)	32.7	29.3	21.8	This work
TMCz-BO	471	(0.14,0.18)	20.7	17.4	–	<i>Nat. Commun.</i> 2020 , 11, 1765
PCzTrz / v-DABNA	473	(0.13, 0.18)	33.5	23.8	~10	<i>Nat. Photon.</i> 2021 , 15, 208–215
HDT-1 / v-DABNA	471	(0.13, 0.16)	27	20	~12	<i>Nat. Photon.</i> 2021 , 15, 203–207
BD-02	460	(0.13, 0.15)	26.4	23.7	–	<i>Nat. Photon.</i> 2022 , 16, 212–218
2,5-tDPAtDIDCz	464	(0.13, 0.12)	23.4	~5	–	<i>Nat. Commun.</i> 2023 , 14, 4818
mTDBA-Si / v-DABNA	465	(0.13, 0.10)	27.3	24.1	–	<i>Nat. Commun.</i> 2023 , 14, 5589
PtON-tb-DTB	466	(0.14, 0.22)	20.9	20.4	–	<i>Nat. Commun.</i> 2024 , 15, 2977
4CzBN-PhCN / t-BuCz-DABNA	470	(0.14, 0.17)	30.8	26.2	~16	<i>Nat. Mater.</i> 2024 , 23, 1523–1530
DPAc-DCzBN / NB-2	458	(0.16, 0.19)	21.5	~15	–	<i>Nat. Mater.</i> 2024 , 23, 519–526
Ir(cb) ₃	465	(0.14, 0.26)	18.0	~16	~12	<i>Nature</i> , 2024 , 626, 300–305
f-ct6a / v-DABNA	472	(0.12, 0.13)	26.2	18.4	–	<i>Adv. Mater.</i> 2024 , 36, 2305273
Pt-imp	465	(0.13, 0.16)	24.5	23.6	~10	<i>Adv. Mater.</i> 2025 , 202510070

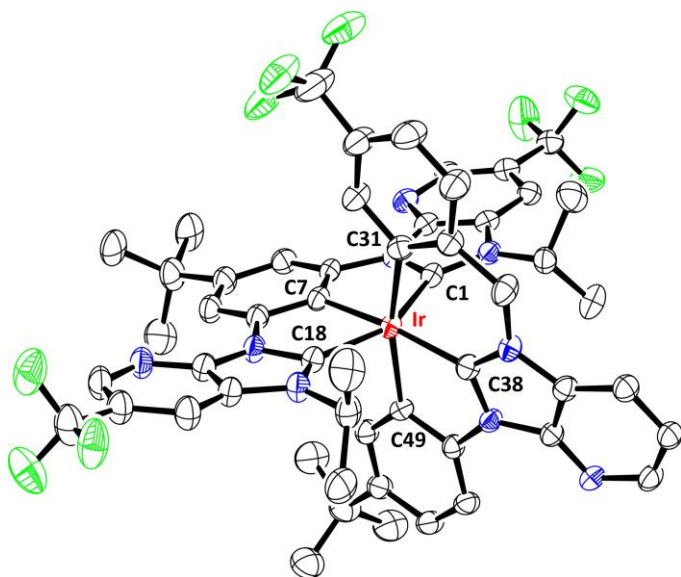


Figure S1. Structure of **[Ir(DP)(MC1)]** with thermal ellipsoids shown at 30% probability level. Selected bond lengths (Å): Ir1-C1 = 2.031(6), Ir1-C7 = 2.024(5), Ir1-C18 = 2.038(5), Ir1-C31 = 2.140(5), Ir1-C38 = 2.024(5), Ir1-C49 = 2.126(5). Selected bond angles (°): C18-Ir1-C1 = 153.1(2), C31-Ir1-C49 = 166.0(2). Hydrogen atoms were omitted for clarity.

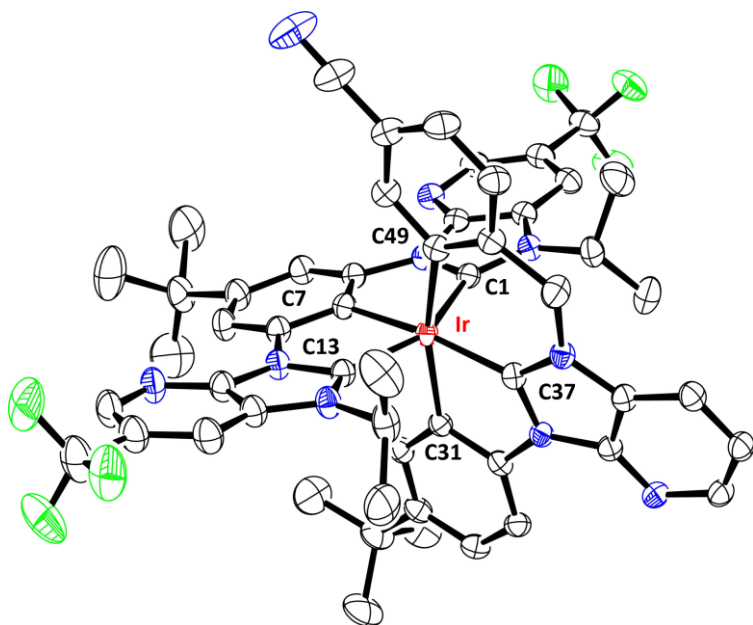


Figure S2. Structure of **[Ir(DP)(MC2)]** with thermal ellipsoids shown at 30% probability level. Selected bond lengths (Å): Ir1-C1 = 2.034(3), Ir1-C7 = 2.009(3), Ir1-C13 = 2.036(3), Ir1-C31 = 2.120(3), Ir1-C37 = 2.000(2), Ir1-C49 = 2.122(3). Selected bond angles (°): C13-Ir1-C1 = 153.08(10), C31-Ir1-C49 = 165.68(10). Hydrogen atoms were omitted for clarity.

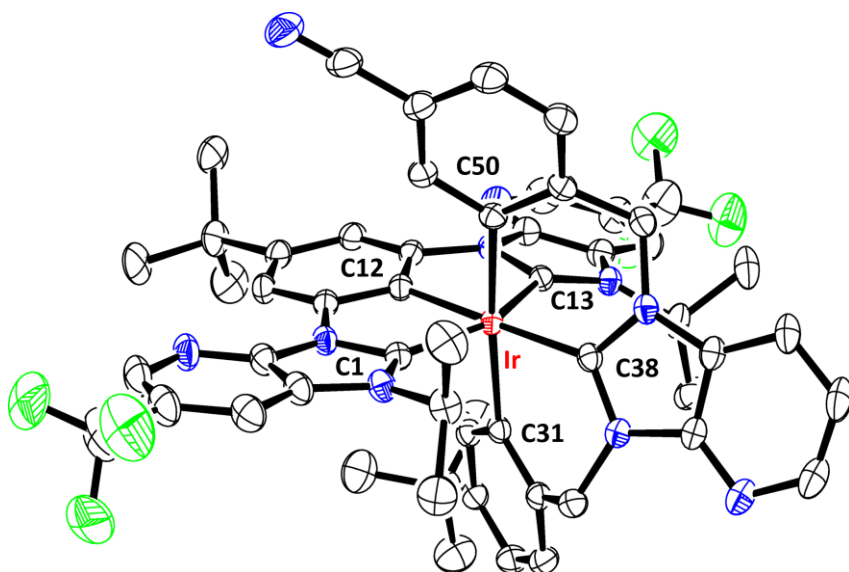


Figure S3. Structure of $[\text{Ir}(\text{DP})(\text{MC3})]$ with thermal ellipsoids shown at 30% probability level. Selected bond lengths ($\text{\AA}$): Ir1-C1 = 2.034(3), Ir1-C12 = 2.007(3), Ir1-C13 = 2.045(3), Ir1-C31 = 2.145(3), Ir1-C38 = 2.043(3), Ir1-C50 = 2.140(3). Selected bond angles ($^\circ$): C1-Ir1-C13 = 154.29(12), C31-Ir1-C50 = 174.55(11). Hydrogen atoms were omitted for clarity.

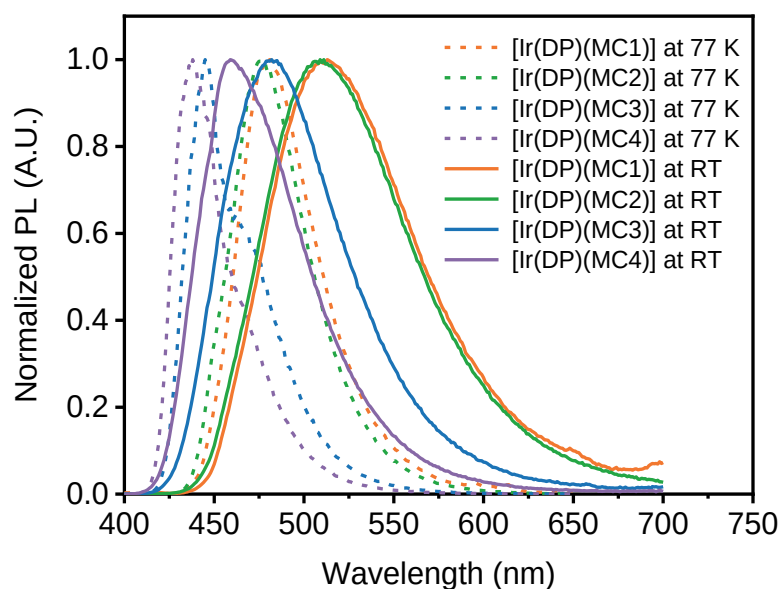


Figure S4. Photoluminescence spectra of the studied Ir(III) complexes in Me-THF at RT (solid line) and 77 K (dashed line).

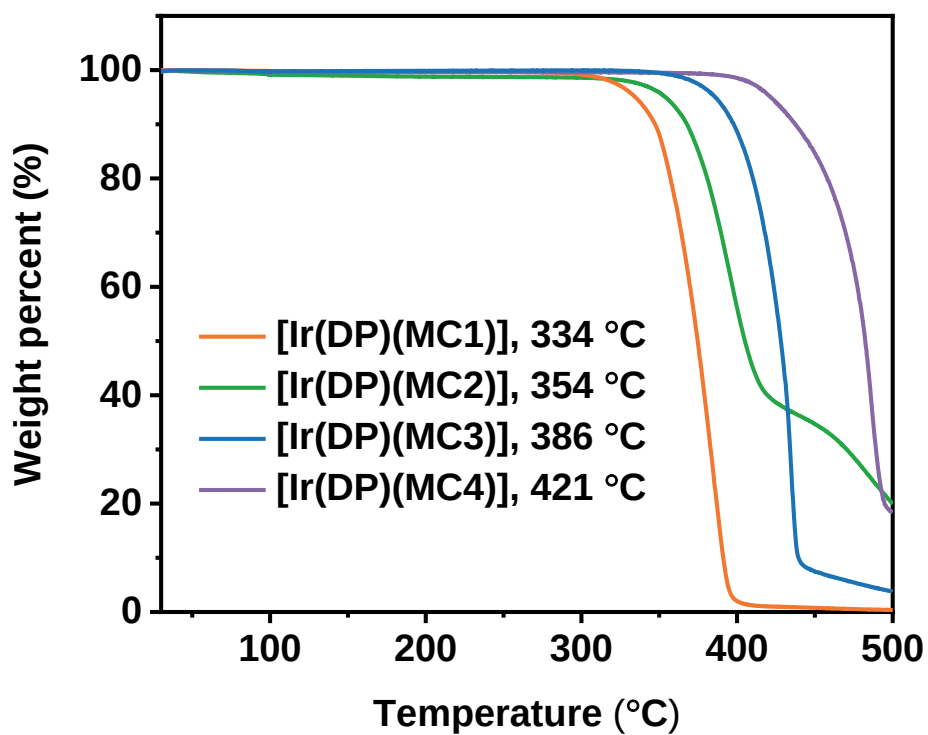


Figure S5. Thermogravimetric diagrams of studied Ir(III) complexes measured under N₂ atmosphere.

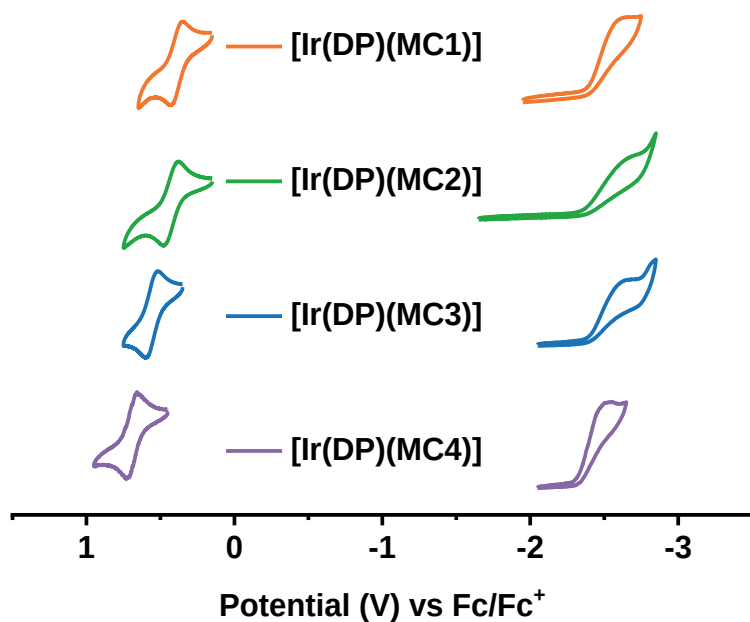


Figure S6. Electrochemical spectra measured in acetonitrile solution.

	<i>[Ir(DP)(MC1)]</i>	<i>[Ir(DP)(MC2)]</i>	<i>[Ir(DP)(MC3)]</i>	<i>[Ir(DP)(MC4)]</i>
LUMO+1				
HOMO				

Figure S7. Orbitals primarily contributing to the T_2 excited state (HOMO and LUMO+1) of the investigated Ir(III) complexes with their geometry optimized for the T_1 state.

	<i>[Ir(DP)(MC1)]</i>	<i>[Ir(DP)(MC2)]</i>	<i>[Ir(DP)(MC3)]</i>	<i>[Ir(DP)(MC4)]</i>
LUMO	 -1.76 eV; Ir: 2.6%	 -1.79 eV; Ir: 2.6%	 -1.83 eV; Ir: 2.5%	 -1.91 eV; Ir: 2.5%
HOMO	 -4.82 eV; Ir: 28.1%	 -4.89 eV; Ir: 27.3%	 -4.96 eV; Ir: 24.7%	 -5.11 eV; Ir: 22.1%

Figure S8. Frontier molecular orbitals (HOMO and LUMO) of the studied Ir(III) complexes in electronic state optimized for the singlet ground-state and in the geometry optimized for the T_1 state (a different visualization angle from Figure 2). The orbital energy level and the contribution from Ir(III) atom are also provided. Note that the HOMO to LUMO transition dominates the T_1 excited state for all four complexes (*cf.* Table 2).

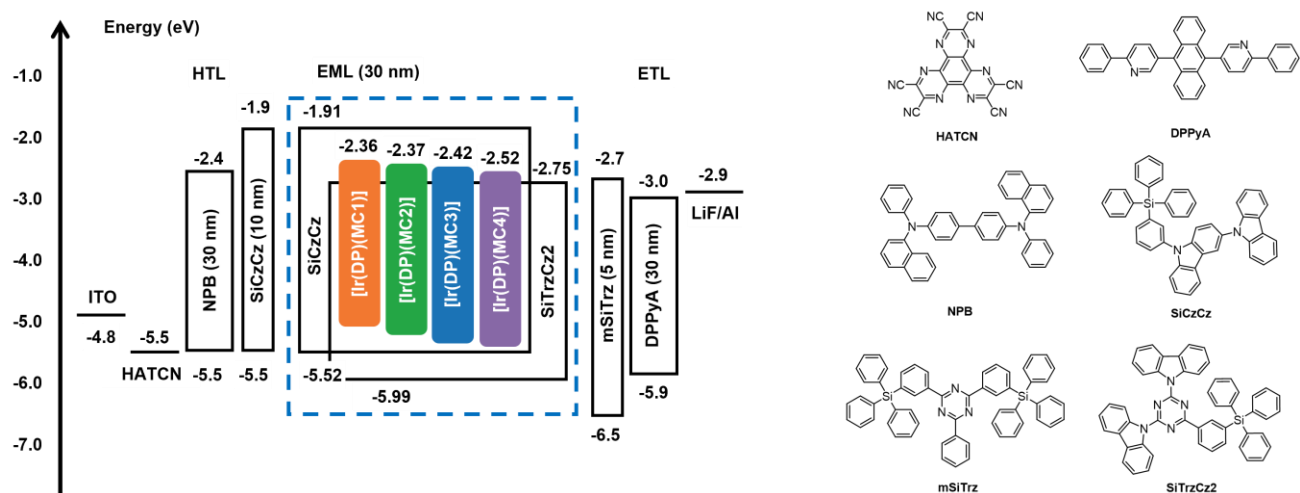


Figure S9. Schematic architecture and structures of organic materials for the fabrication of OLED devices.

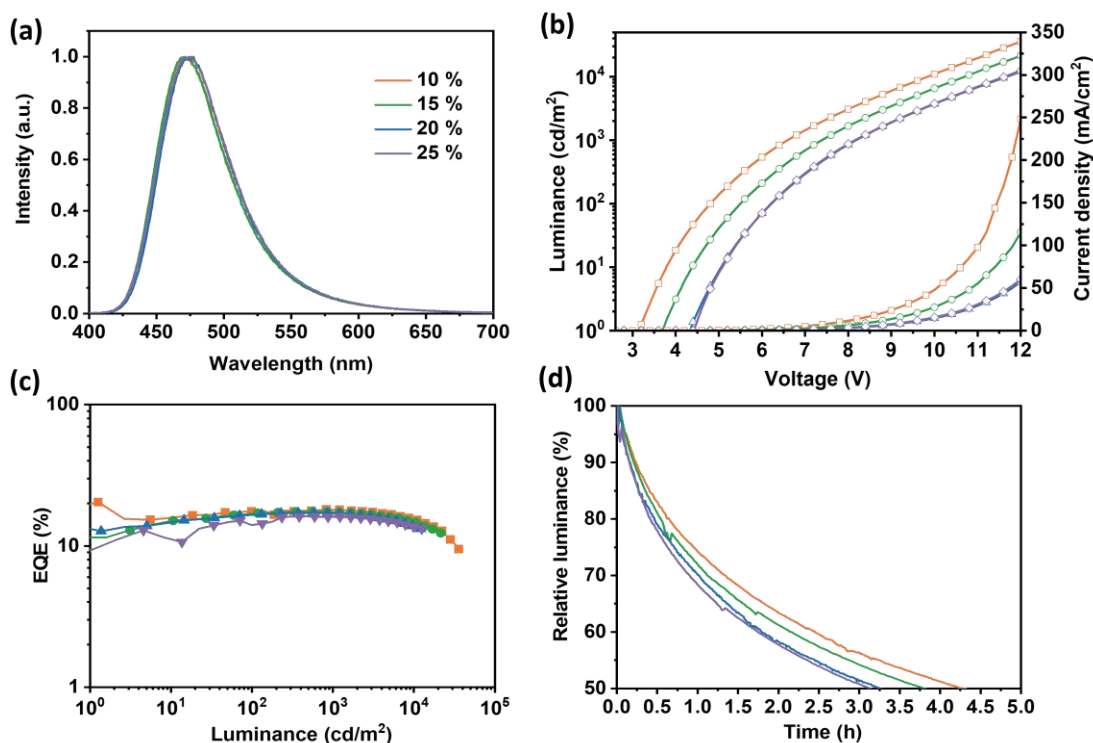


Figure S10. PhOLED bearing **[Ir(DP)(MC3)]** with doping ratio of 10 – 25 wt% in a 65:35 mixture of co-host SiCzCz: SiTrzCz2. (a) EL spectra; (b) Current density-voltage-luminance (J - V - L) curves; (c) External quantum efficiency (EQE) versus luminance. (d) Relative luminance as a function of operational time of OLED using **[Ir(DP)(MC3)]** with $L_0 = 1000 \text{ cd} \cdot \text{m}^{-2}$.

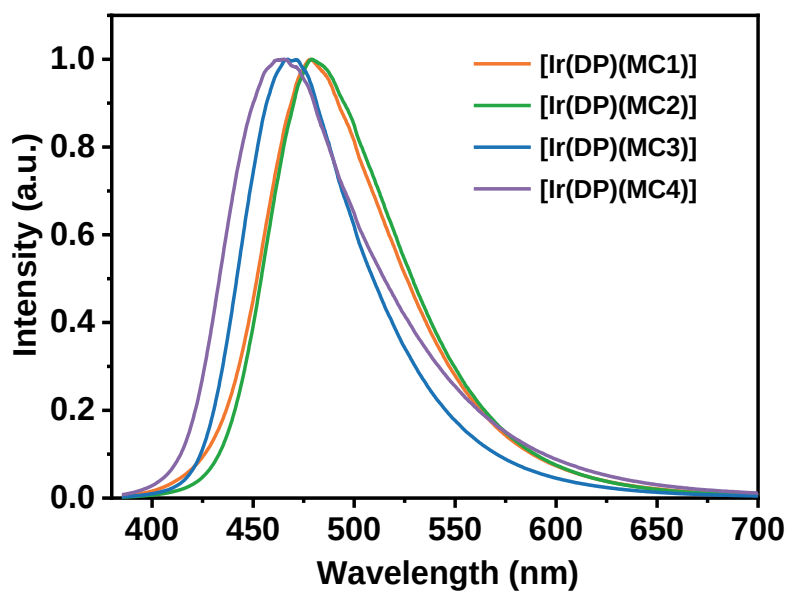


Figure S11. Room temperature emission spectra of studied Ir(III) complexes at 10 wt% deposited in a 65:35 mixture of SiCzCz : SiTrzCz2.

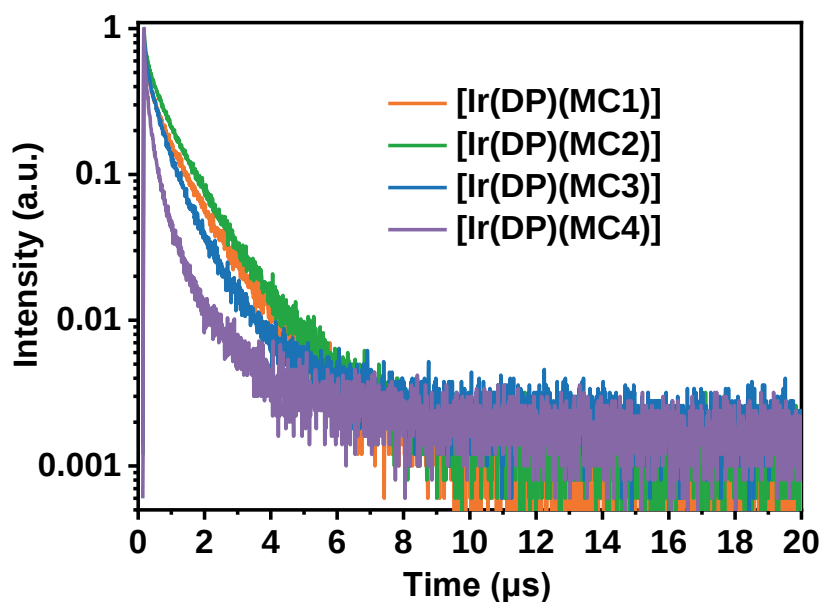


Figure S12. Transient decay curves of Ir(III) emitters deposited in a 65:35 mixture of SiCzCz : SiTrzCz2 at RT (10 wt%).

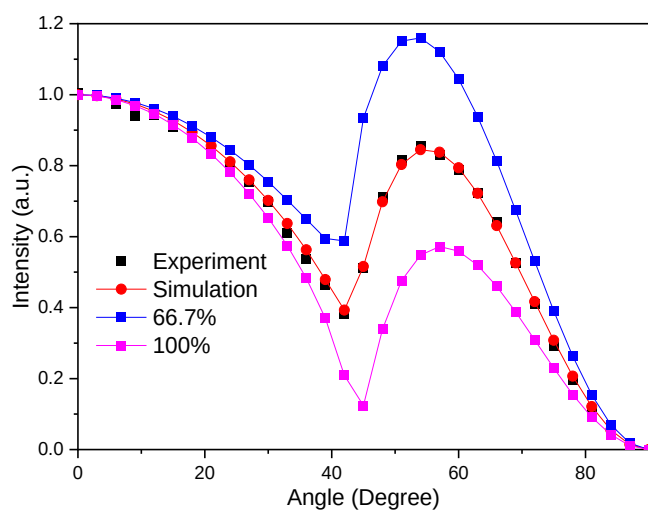


Figure S13. The experimentally measured angle-dependent *p*-polarized PL intensities composed of [Ir(DP)(MC3)] on a quartz substrate and simulated profiles.

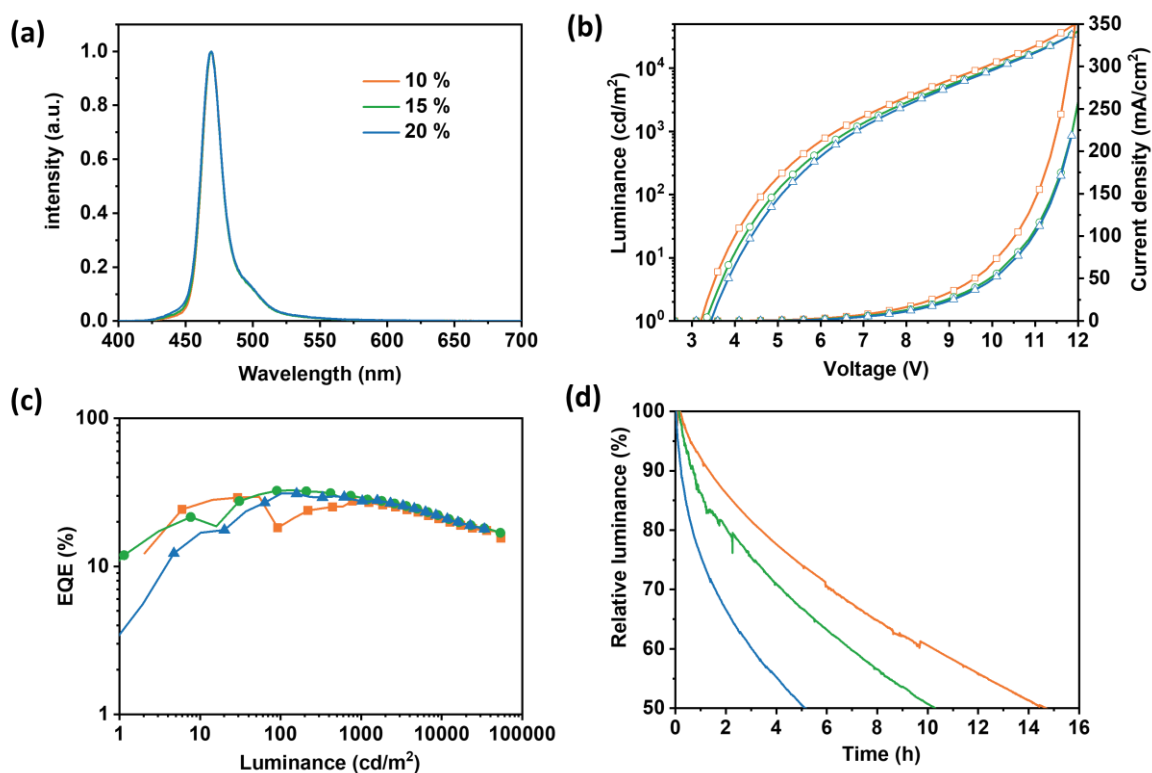


Figure S14. Hyper-OLED bearing $[\text{Ir}(\text{DP})(\text{MC3})]$ as sensitizer with different doping ratios from 10 wt% to 20 wt% and 1 wt% of ν -DABNA terminal emitter co-deposited in a 65:35 mixture of SiCzCz: SiTrzCz2. (a) EL spectra; (b) Current density-voltage-luminance (J - V - L) curves; (c) External quantum efficiency (EQE) versus luminance. (d) Relative luminance as a function of operational time of OLED with $L_0 = 1000 \text{ cd}\cdot\text{m}^{-2}$.

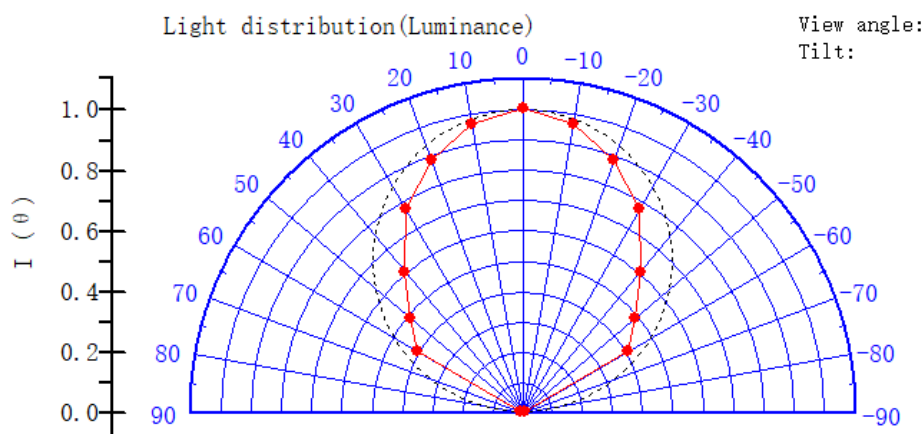


Figure S15. Angle-dependent EL patterns of the $[\text{Ir}(\text{DP})(\text{MC3})]$ based hyper-OLED device.

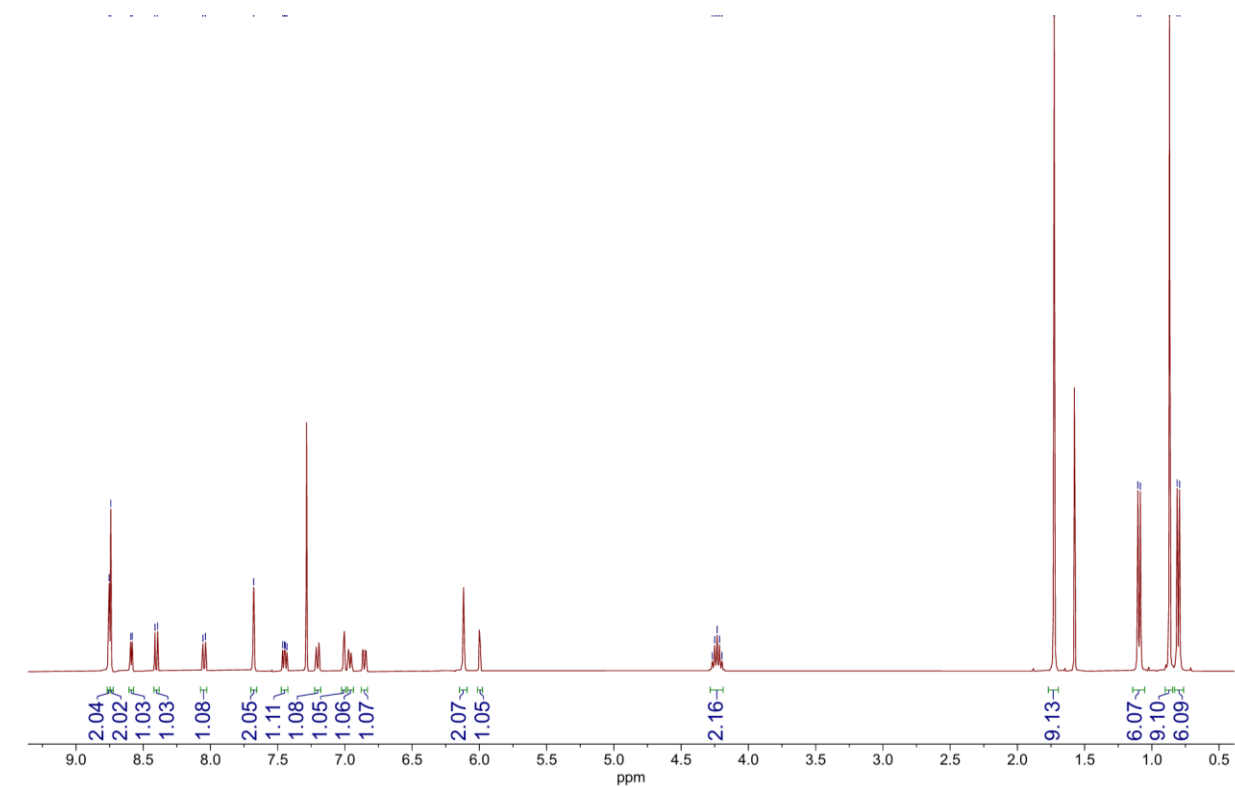


Figure S16. ¹H NMR (400 MHz) spectrum of [Ir(DP)(MC1)] recorded in CDCl₃ solution at RT.

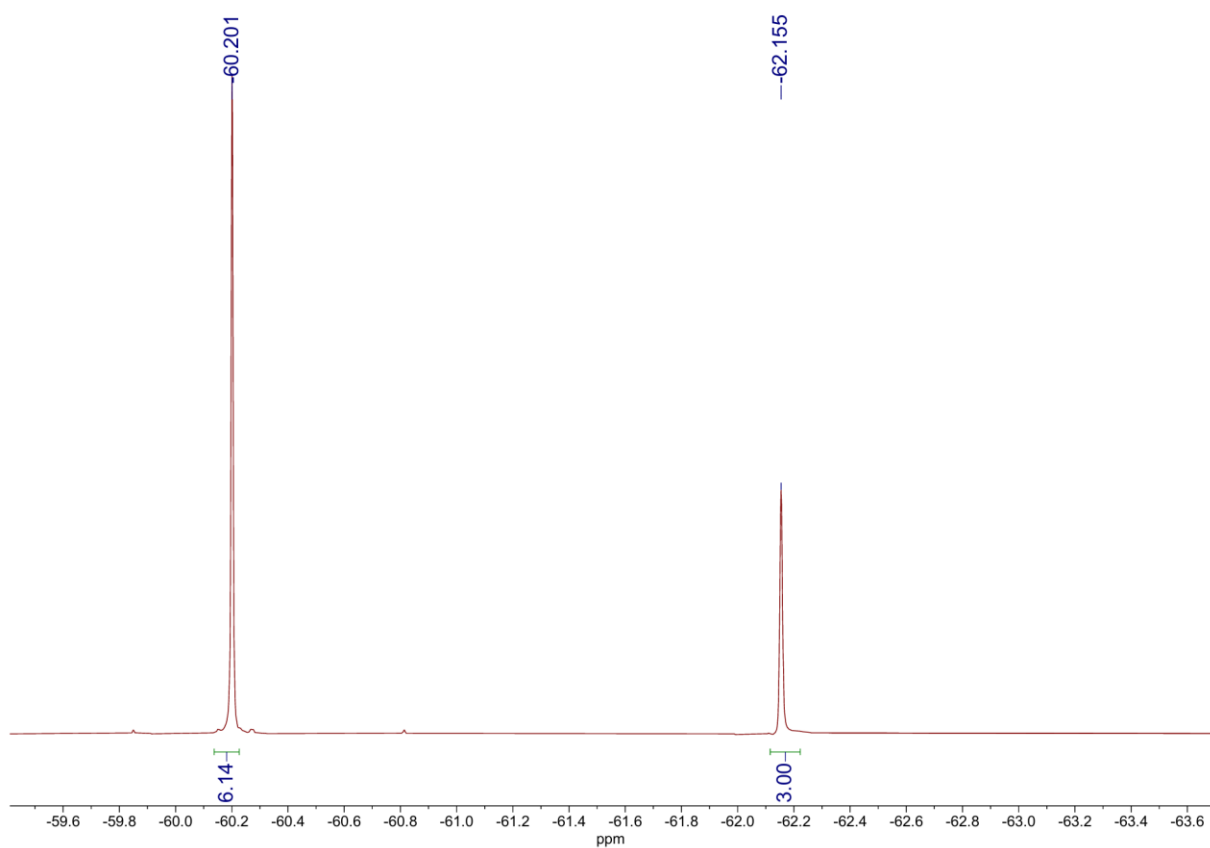


Figure S17. ¹⁹F NMR (376 MHz) spectrum of [Ir(DP)(MC1)] recorded in CDCl₃ solution at RT.

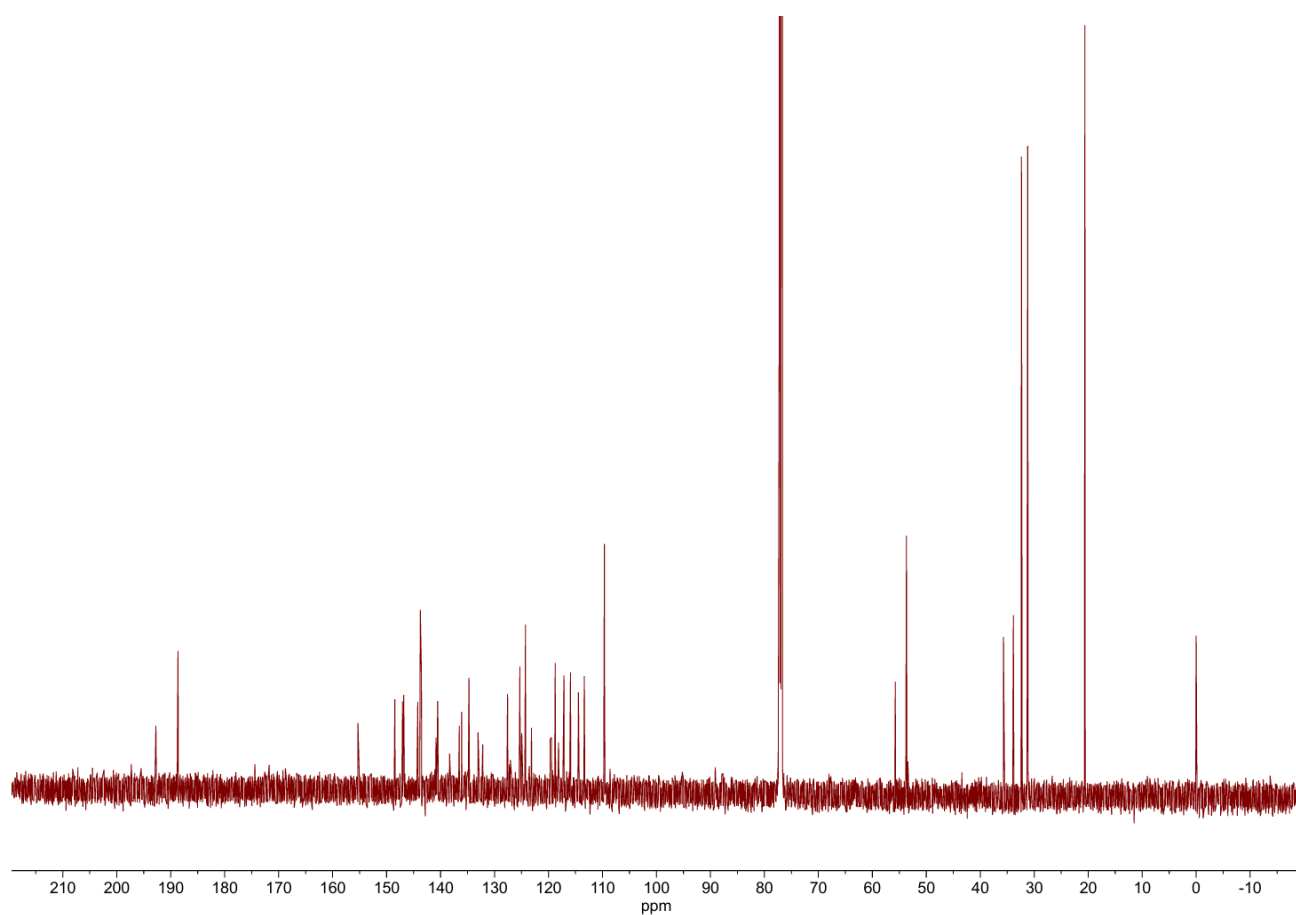


Figure S18. ¹³C NMR (100 MHz) spectrum of [Ir(DP)(MC1)] recorded in CDCl₃ solution at RT.

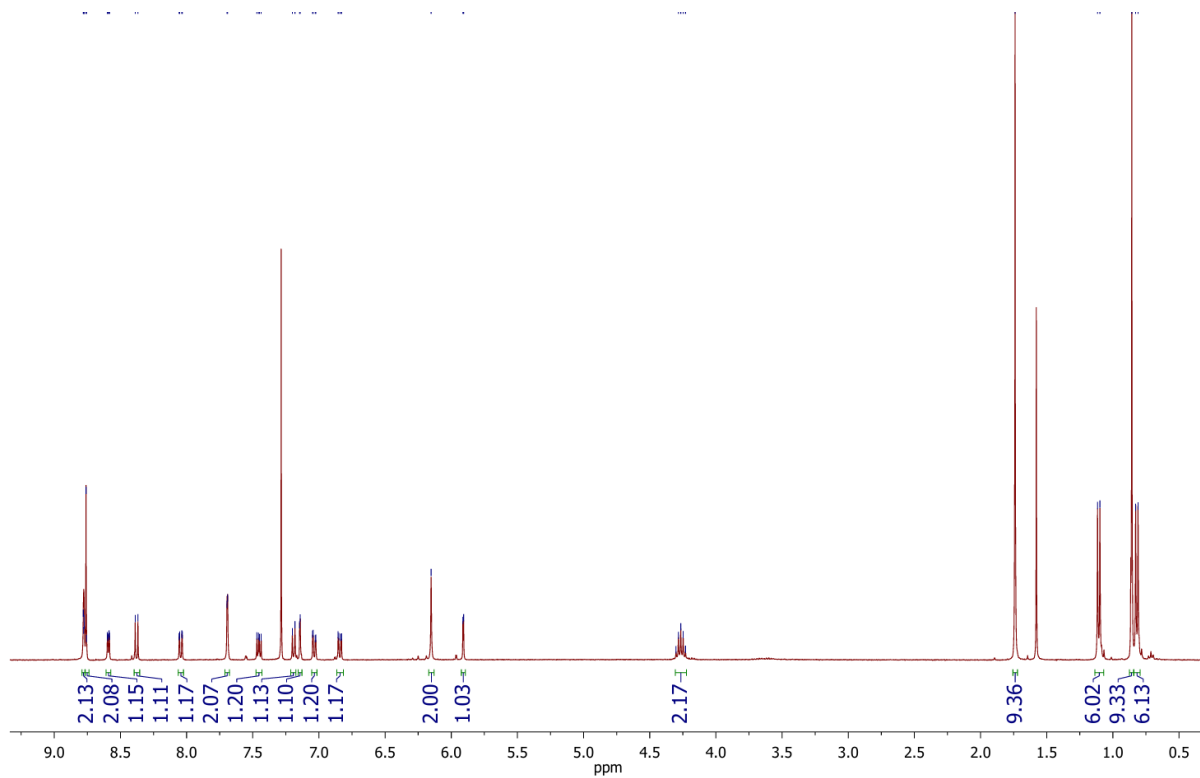


Figure S19. ¹H NMR (400 MHz) spectrum of [Ir(DP)(MC2)] recorded in CDCl₃ solution at RT.

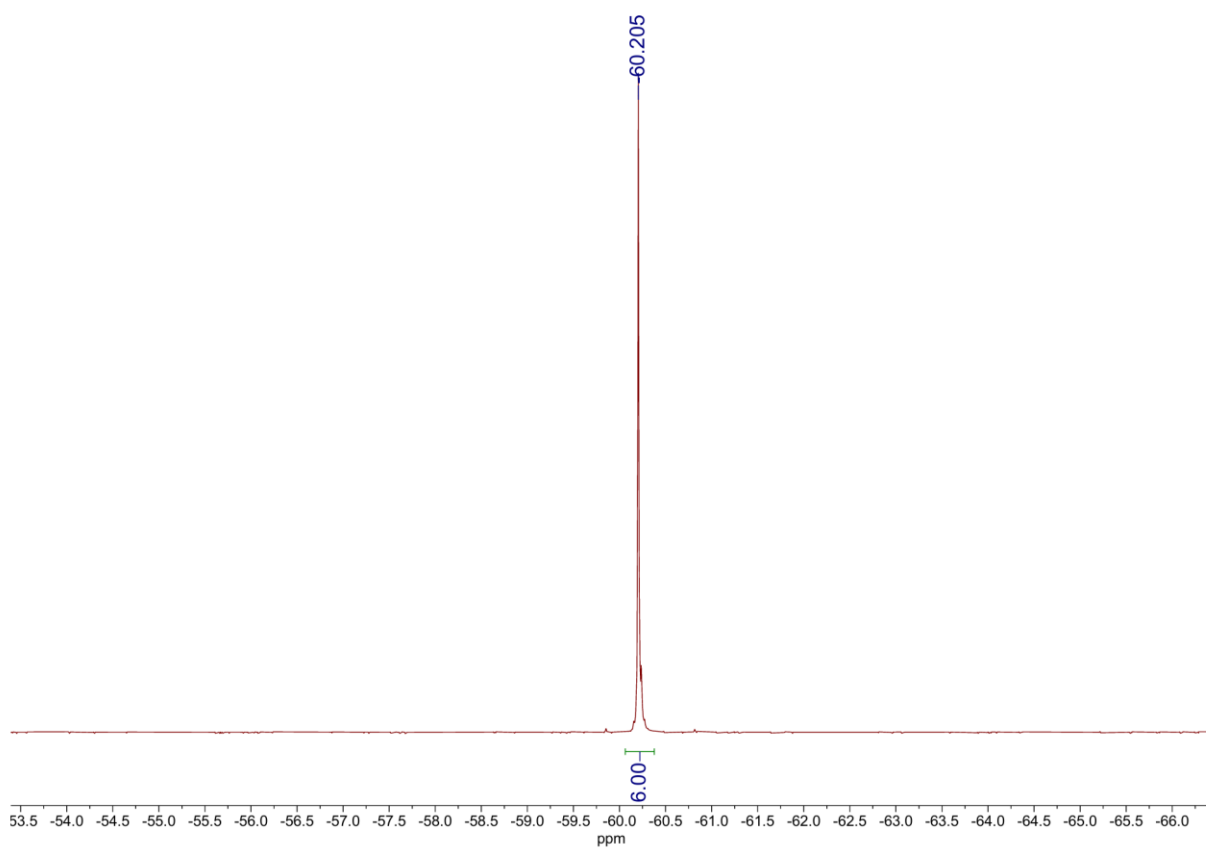


Figure S20. ^{19}F NMR (376 MHz) spectrum of **[Ir(DP)(MC2)]** recorded in CDCl_3 solution at RT.

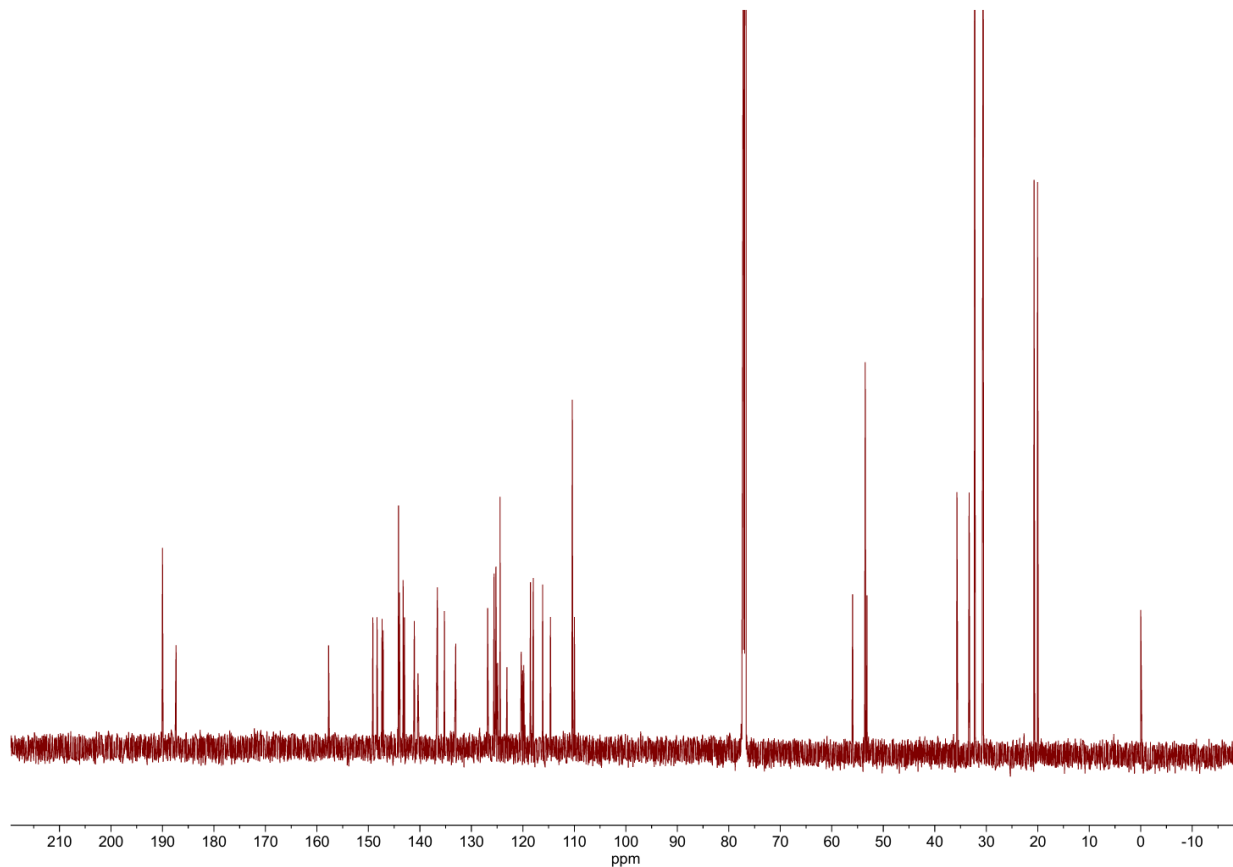


Figure S21. ^{13}C NMR (100 MHz) spectrum of **[Ir(DP)(MC2)]** recorded in CDCl_3 solution at RT.

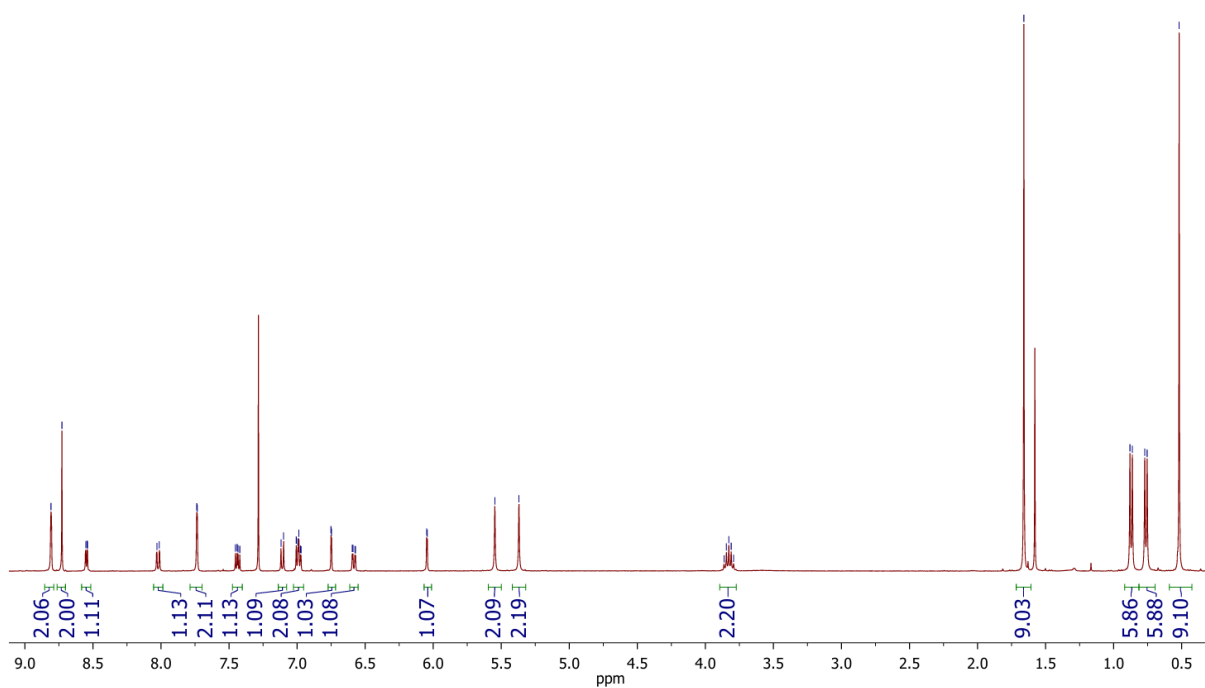


Figure S22. ¹H NMR (400 MHz) spectrum of [Ir(DP)(MC3)] recorded in CDCl₃ solution at RT.

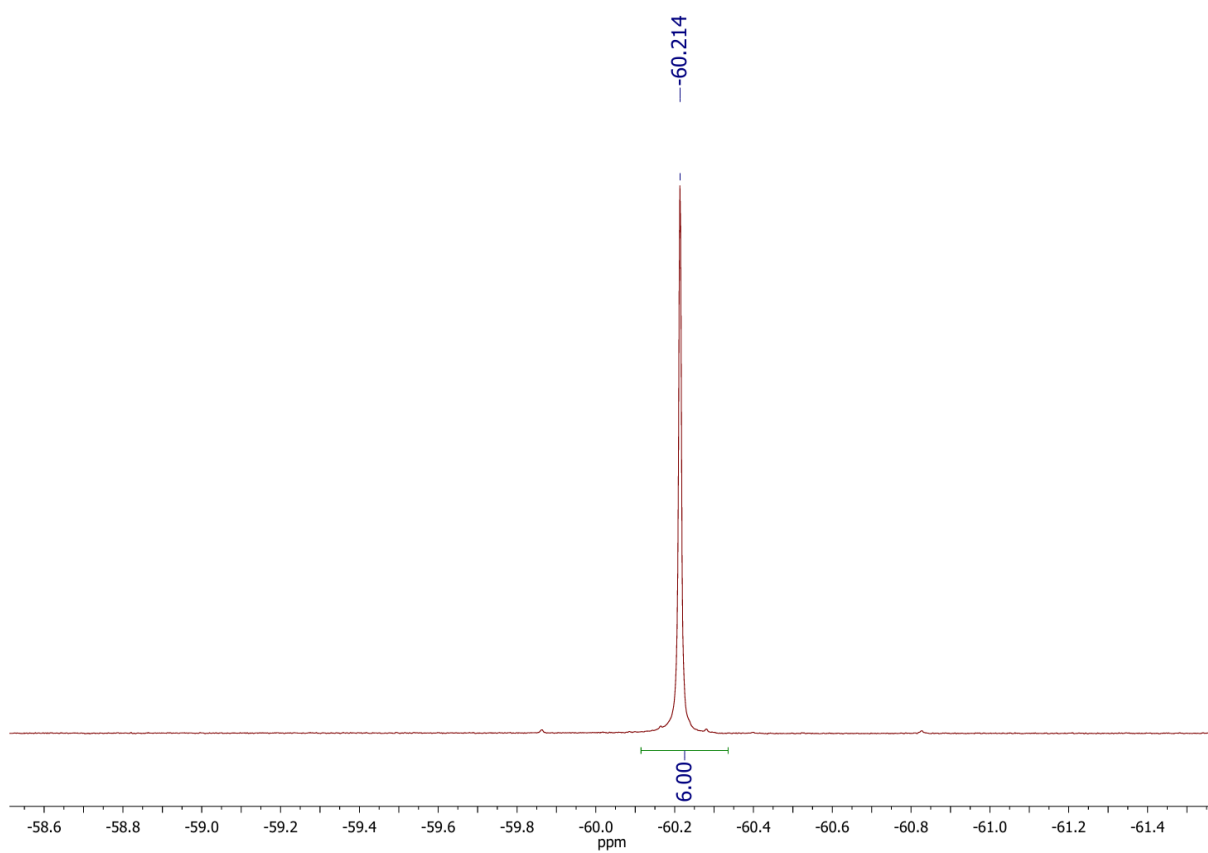


Figure S23. ¹⁹F NMR (376 MHz) spectrum of [Ir(DP)(MC3)] recorded in CDCl₃ solution at RT.

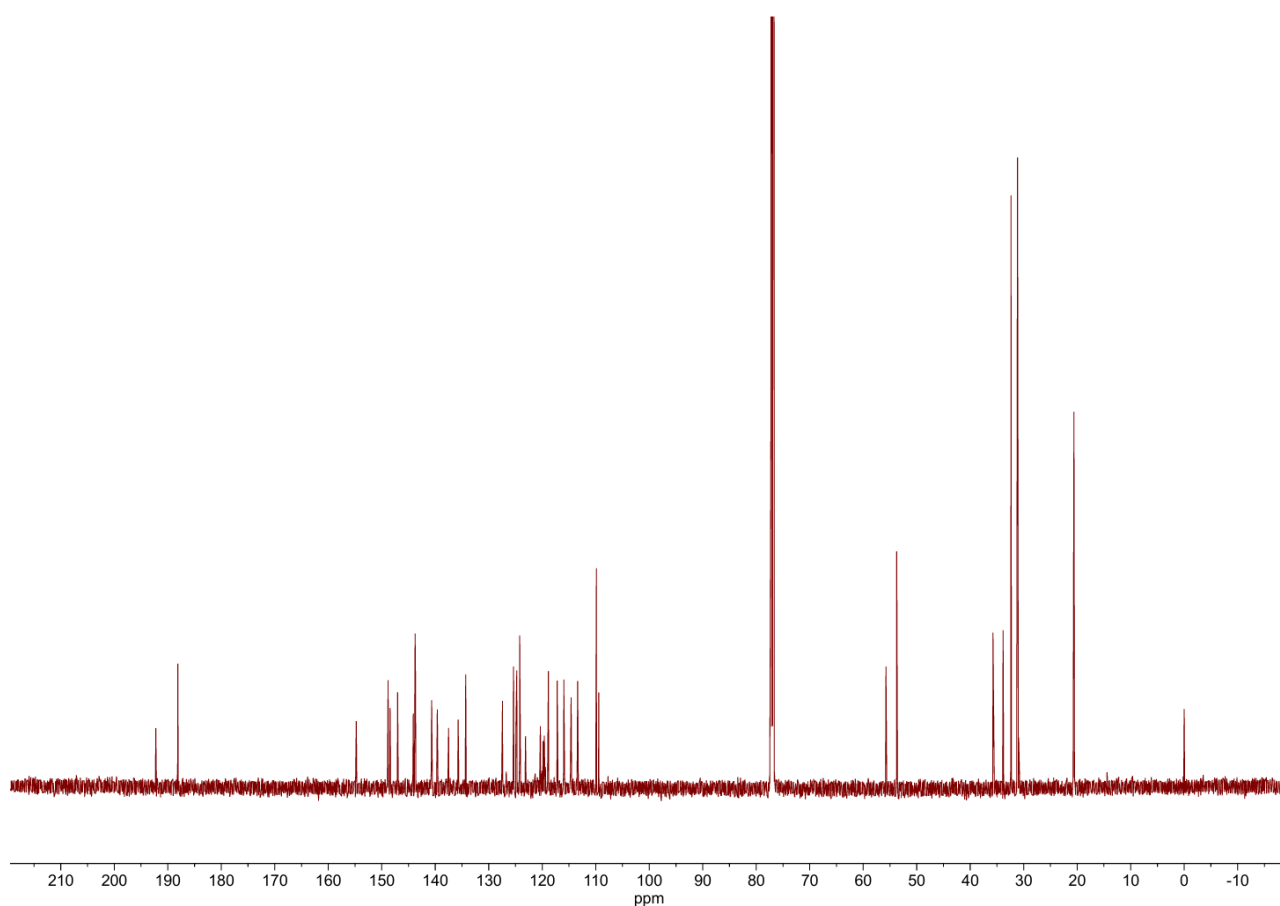


Figure S24. ¹³C NMR (100 MHz) spectrum of [Ir(DP)(MC3)] recorded in CDCl₃ solution at RT.

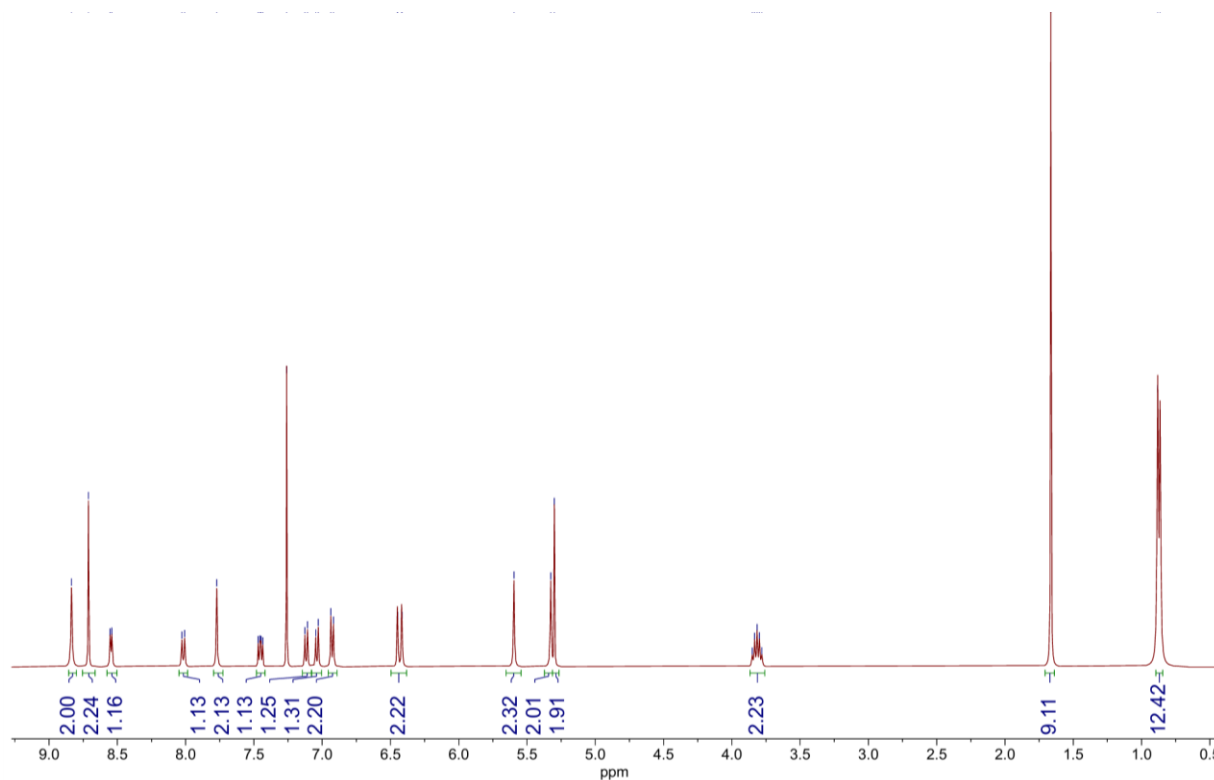


Figure S25. ¹H NMR (400 MHz) spectrum of [Ir(DP)(MC4)] recorded in CDCl₃ solution at RT.

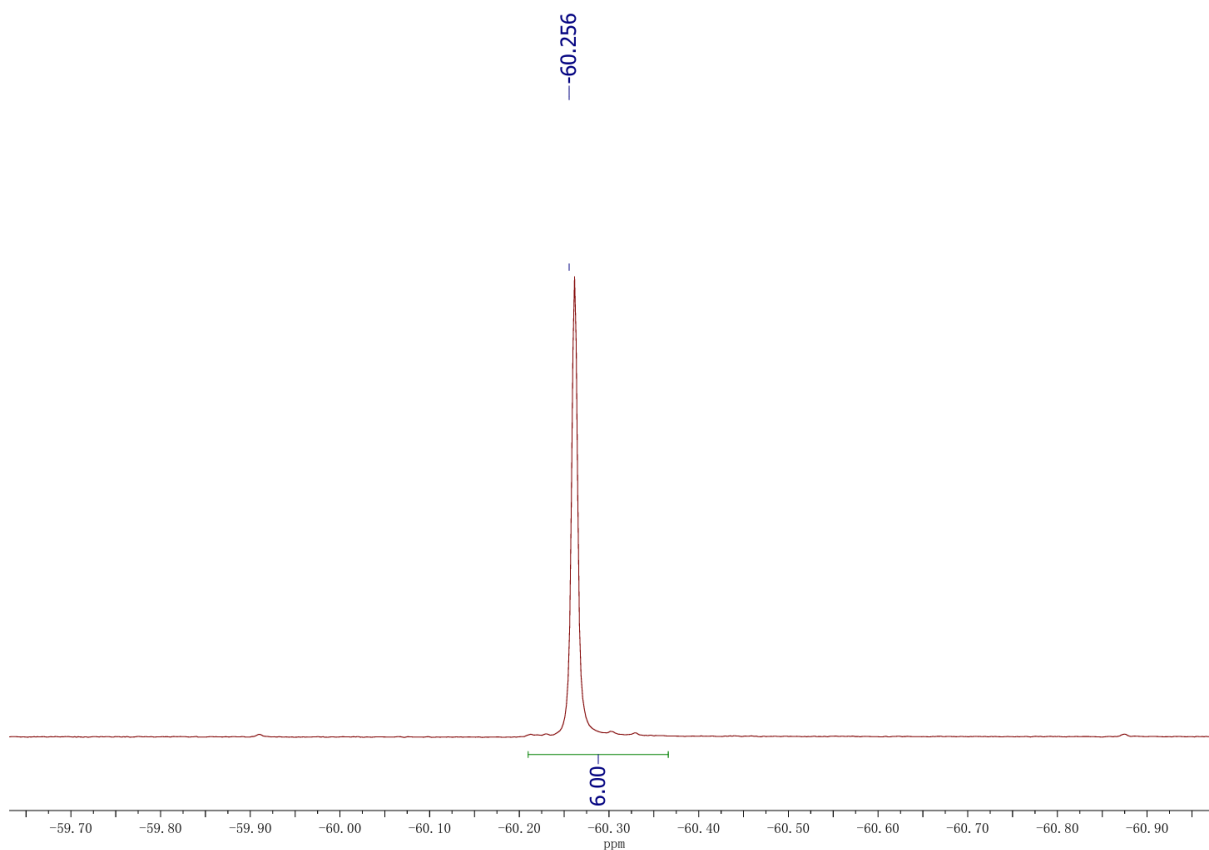


Figure S26. ^{19}F NMR (376 MHz) spectrum of **[Ir(DP)(MC4)]** recorded in CDCl_3 solution at RT.

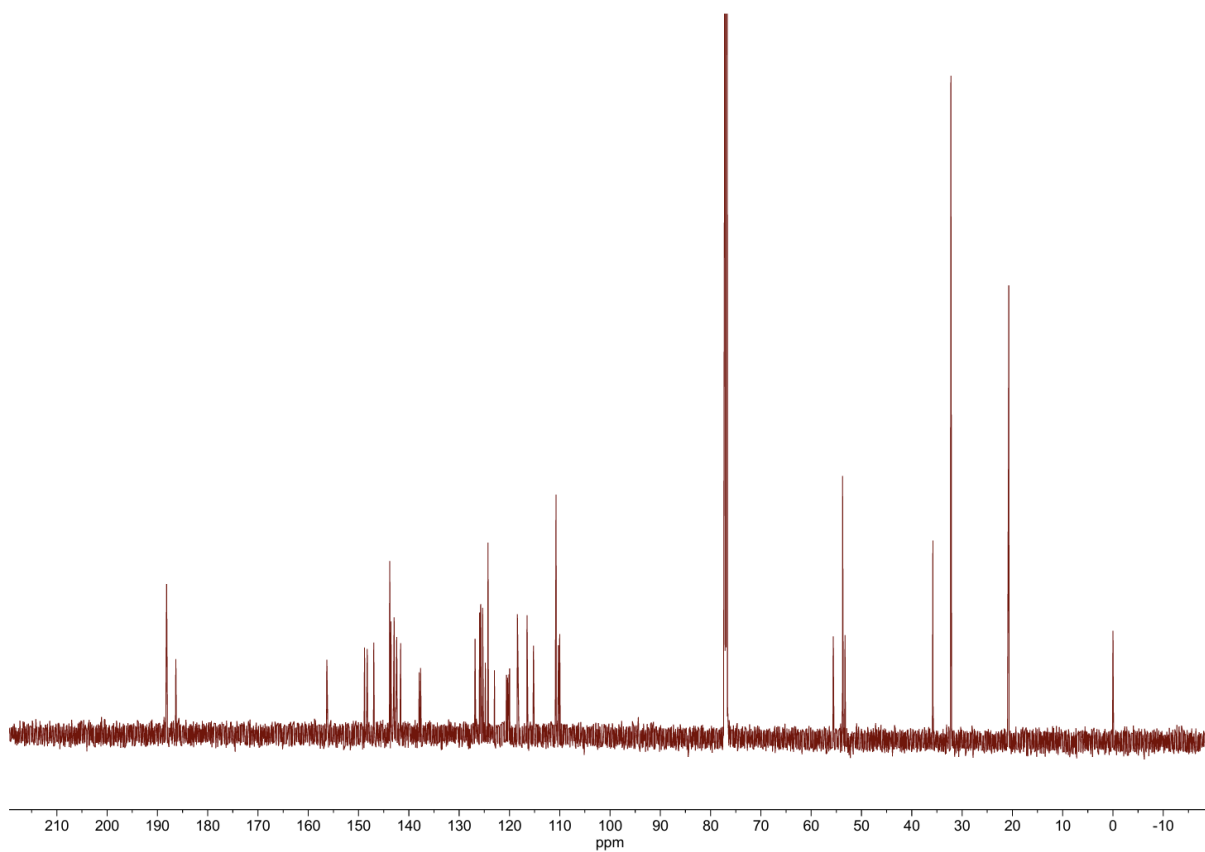


Figure S27. ^{13}C NMR (100 MHz) spectrum of **[Ir(DP)(MC4)]** recorded in CDCl_3 solution at RT.

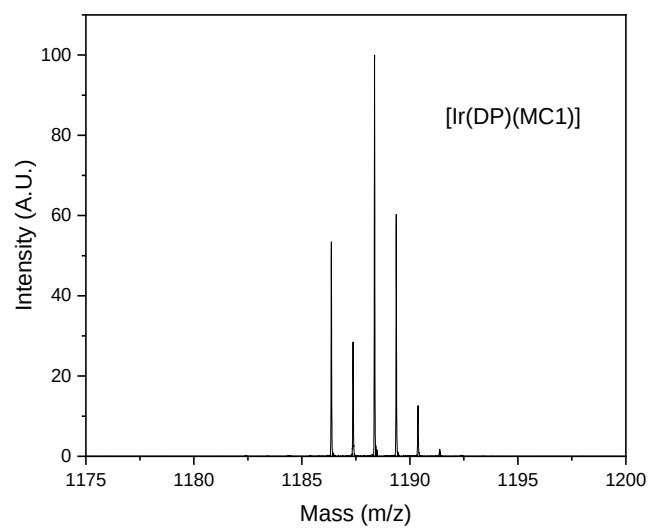


Figure S28. HRMS spectrum of $[\text{Ir}(\text{DP})(\text{MC1})]$.

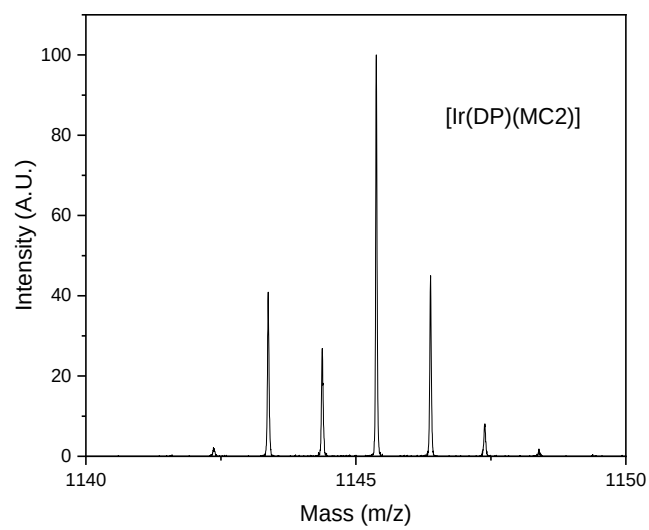


Figure S29. HRMS spectrum of $[\text{Ir}(\text{DP})(\text{MC2})]$.

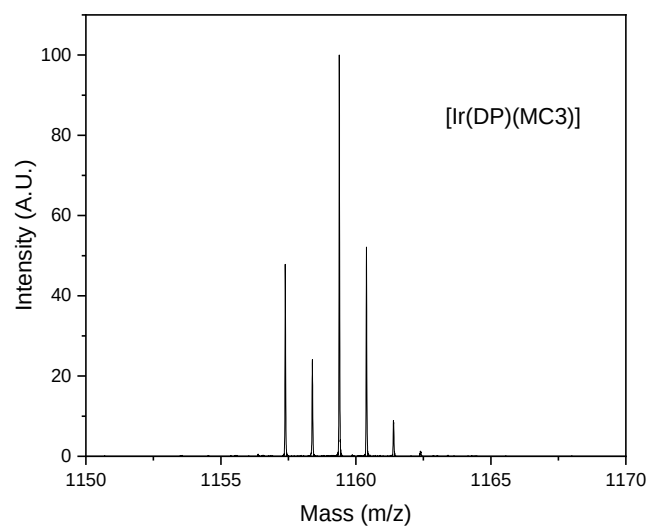


Figure S30. HRMS spectrum of $[\text{Ir}(\text{DP})(\text{MC3})]$.

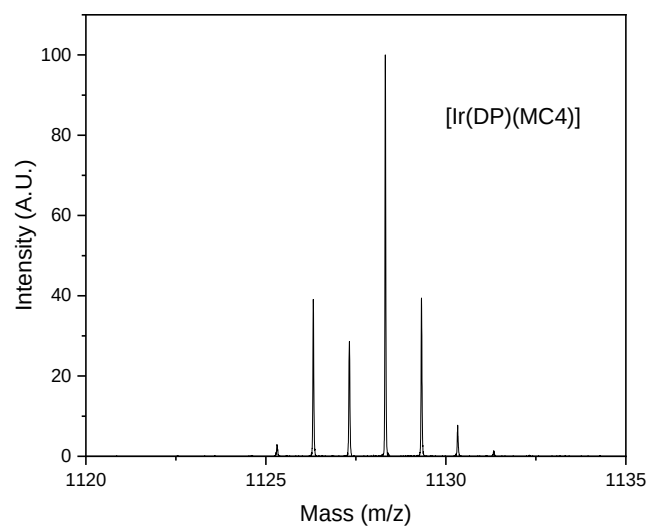


Figure S31. HRMS spectrum of $[\text{Ir}(\text{DP})(\text{MC4})]$.

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