Emission tuning of Ir(N^C)$_2$(pic) based complexes via torsional twisting of picolinate substituents

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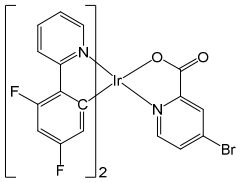
S1. Synthesis of reported compounds

General details. NMR spectra were recorded in deuterated solvent solutions on Varian VNMRS-600 spectrometer and referenced against solvent resonances (^{1}H, ^{13}C). Electrospray mass spectra (ESMS) data were recorded on a TQD mass spectrometer (Waters Ltd, UK) in acetonitrile or MALDI TOF MS data were recorded on an Bruker Autoflex II ToF/ToF. Purity of compounds (**Ir(F_2PPy)$_2$(Pic-Br)**, **1**-**3** and **5**-**7**) were determined using microanalyses, performed by Elemental Analysis Service, London Metropolitan University, UK. Where insufficient sample was available to analyse purity was established by NMR and high resolution mass-spectrometry.

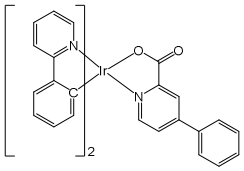
Analytical grades of solvents were used. [Ir(F_2PPy)$_2$Cl]$_2$ and Ir(PPy)$_2$(Pic-Br) were synthesised according to literature methods. All other chemicals were sourced from standard suppliers.

Ir(F_2PPy)$_2$(Pic-Br). 4-bromopicolinic acid (pic-Br, 198 mg, 0.98 mmol) was added to a suspension of [Ir(F_2PPy)$_2$Cl]$_2$ (400 mg, 0.32 mmol) and K_2CO_3 (135 mg, 0.98 mmol) in acetone (50 mL). The solution was heated to reflux overnight under nitrogen. The solvent was removed under *vaccuo* leaving a yellow solid, this was dissolved in dichloromethane (DCM) and filtered. The yellow filtrate was purified by column chromatography on silica eluted using a gradient from dichloromethane to acetone affording a yellow-orange solid, crystals were grown by layer diffusion of methanol into a dichloromethane solution. Yield: 335 mg (68 %). ^{1}H-NMR ($CDCl_3$): δ 8.69 (dd, *J* = 5.8, 1.7 Hz, 1H), 8.47 (d, *J* = 1.8 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.78 (tt, *J* = 7.9, 1.8 Hz, 1H), 7.57-7.55 (m, 2H), 7.45 (dd, *J* = 5.6, 1.6 Hz, 1H), 7.20 (td, *J* = 7.3, 5.8 Hz, 1H), 7.00 (td, *J* = 7.3, 5.8 Hz, 1H), 6.47 (td, *J* = 9.2, 2.4 Hz, 1H), 6.39 (td, *J* = 9.2, 2.4 Hz, 1H), 5.79 (dd, *J* = 8.6, 2.4 Hz, 1H), 5.54 (dd, *J* = 8.6, 2.4 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ: 171.3, 165.6, 164.2, 164.1, 163.9, 162.4, 162.2, 160.0, 160.7, 152.5, 151.8, 150.3, 148.6, 148.5, 147.8, 138.4, 135.7, 132.2, 131.8, 128.0, 123.4, 122.9, 122.5, 114.5, 114.4, 98.2, 97.9 ppm. ^{19}F-NMR ($CDCl_3$) δ: -106.8 (d, *J* = 10.4 Hz, 1F), -107.8 (d, *J* = 10.4 Hz, 1F), -109.5 (d, *J* = 10.5 Hz, 1F), -110.2 (d, *J* = 10.5 Hz, 1F) ppm. MS-MALDI: m/z 772.7 $[M]^+$. Anal. Calc. for: C, 55.90; H, 3.40; N, 5.67 %. Found: C, 55.68; H, 3.55; N, 5.48 %.



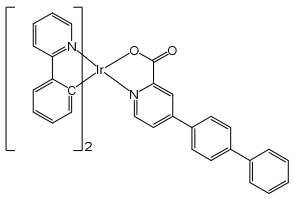
General Suzuki-Miyaura coupling. $Pd(PPh_3)_4$ (10 %) was added to a solution containing $Ir(X_2PPy)_2$(Pic-Br) (1 eq), arylboronic acid (1.1 eq) and K_2CO_3 (2 eq) in dry DMF (20 mL) the solution was degassed by 3 freeze-pump-thaw cycles be it was heated to 90°C for 16 hours before being cooled to room temperature. The solution was poured into water forming a precipitate that was collected by filtration. The yellow solid was purified via column chromatography on silica eluted by a solvent gradient of neat DCM to DCM:acetone (95:5).

$Ir(PPy)_2$(Pic-Ph) (1). Yield: 74 mg (75 %). ^{1}H-NMR ($CDCl_3$): δ 8.81 (d, *J* = 5.7 Hz, 1H), 8.57 (d, *J* = 2.1 Hz, 1H), 7.88 (dd, *J* = 8.2, 1.3, 1H), 7.84 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.77 (d, *J* = 5.6 Hz, 1H), 7.71-7.67 (m, 4H), 7.61 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.59-7.75 (m, 2H), 7.52 (dd, *J* = 5.6, 2.0 Hz, 1H), 7.49-7.45 (m, 3H), 7.13 (td, *J* = 7.4, 1.3 Hz, 1H), 6.94-6.91 (m, 2H), 6.86 (td, *J* = 7.4, 1.3 Hz, 1H), 6.80 (td, *J* = 7.4, 1.3 Hz, 1H), 6.75 (td, *J* = 7.4, 1.3 Hz, 1H), 6.42 (d, *J* = 8.4 Hz, 1H), 6.20 (d, *J* = 8.3 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ: 169.2, 167.6, 149.6, 149.4, 148.9, 148.5, 148.0, 147.3, 144.1, 144.0, 137.1, 137.0, 136.1, 132.5, 132.4, 130.1, 129.9, 129.5, 129.3, 126.9, 125.7, 125.2, 124.3, 124.0, 122.1, 121.9, 121.5, 120.9, 119.0, 118.4 ppm. MS-MALDI: m/z 699.1 $[M]^+$. Anal. Calc. for $C_{34}H_{24}IrN_3O_2 \cdot ½CH_2Cl_2$: C, 55.90; H, 3.40; N, 5.67 %. Found: C, 55.68; H, 3.55; N, 5.48 %.

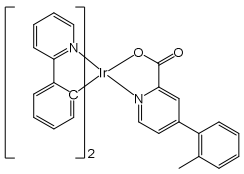


$Ir(PPy)_2$(Pic-Biphen) (2).Yield: 66 mg (60 %). ^{1}H-NMR ($CDCl_3$) δ: 8.83 (dd, *J* = 5.8, 1.5 Hz, 1H), 8.62 (dd, *J* = 2.2, 0.7 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.79-7.77 (m, 3H), 7.72-7.69 (m, 4H), 7.63-7.62 (m, 3H), 7.59-7.56 (m, 3H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.14 (ddd, *J* = 7.3, 5.8, 1.4 Hz, 1H), 6.94 (td, *J* = 7.4, 1.3 Hz, 2H), 6.86 (td, *J* = 7.6, 1.2 Hz, 1H), 6.82 (td, *J* = 7.6, 1.2 Hz, 1H), 6.75 (td, *J* = 7.6, 1.2 Hz, 1H), 6.44 (d, *J* = 7.4 Hz, 1H), 6.20 (d, *J* = 7.4 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ: 172.9, 162.2, 167.6, 152.4, 149.4, 149.1, 149.0, 148.5, 148.0, 147.4, 144.1, 144.0, 142.9, 139.7, 137.0, 134.8, 132.5, 132.4, 129.9, 129.5, 128.9, 128.0, 127.3, 127.0, 125.5, 125.0,

124.3, 124.0, 122.1, 121.9, 121.5, 120.9, 119.0, 118.4 ppm. MS-MALDI: m/z 775.1 $[M]^+$. Anal. Calc. for $C_{40}H_{28}IrN_3O_2 \cdot 1.5CH_4O$: C, 60.57; H, 4.16; N, 5.11 %. Found: C, 60.63; H, 3.89; N, 4.88 %.

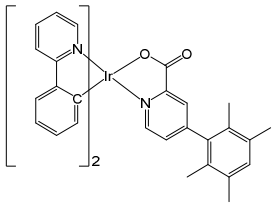


Ir(PPy)$_2$(Pic-Tol) (3). Yield: 71 mg (71%). ^{1}H-NMR ($CDCl_3$): δ 8.83 (dd, *J* = 5.7, 1.6 Hz, 1H), 8.32 (d, *J* = 2.0 Hz, 1H), 7.88 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.85 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.76 (dd, *J* = 5.4, 0.7 Hz, 1H), 7.73-7.69 (m, 2H), 7.62 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.58 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.54 (dd, *J* = 5.7, 1.6 Hz, 1H), 7.33-7.21 (m, 5H), 7.15 (td, *J* = 7.3, 1.4 Hz, 1H), 6.95-6.91 (m, 2H), 6.85 (td, *J* = 7.4, 1.3 Hz, 1H), 6.80 (td, *J* = 7.4, 1.3 Hz, 1H), 6.75 (td, *J* = 7.4, 1.3 Hz, 1H), 6.43 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.18 (dd, *J* = 7.6, 1.2 Hz, 1H), 2.28 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$) δ: 172.9, 169.2, 167.6, 151.8, 151.4, 149.3, 149.0, 148.0, 147.8, 147.4, 144.1, 144.0, 137.3, 137.1, 137.0, 134.9, 132.5, 132.4,131.0, 129.9, 129.5, 129.2, 128.6, 128.3, 126.3, 124.3, 124.0, 122.2, 121.9, 121.5, 121.0, 119.0, 118.4, 20.3 ppm. MS-MALDI: m/z 713.1 $[M]^+$. Anal. Calc. for $C_{35}H_{26}IrN_3O_2 \cdot 0.75CH_2Cl_2$: C, 55.30; H, 3.57; N, 5.41 %. Found: C, 55.06; H, 3.81; N, 5.30 %.

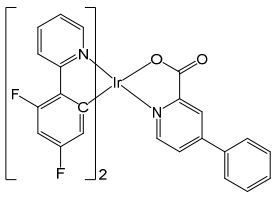


Ir(PPy)$_2$(Pic-Dur) (4). Yield: 24 mg (23 %). ^{1}H-NMR ($CDCl_3$): δ 8.86 (dd, *J* = 5.7, 1.5 Hz, 1H), 8.11 (d, *J* = 1.8 Hz, 1H), 7.89-7.85 (m, 2H), 7.79 (dd, *J* = 5.4, 0.7 Hz, 1H), 7.74-7.69 (m, 2H), 7.63 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.57 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.48 (dd, *J* = 5.7, 1.5 Hz, 1H), 7.16 (td, *J* = 7.3, 5.7 Hz, 1H), 7.09 (dd, *J* = 5.4, 1.9 Hz, 1H), 7.02 (s, 1H), 6.94-6.91 (m, 2H), 6.86 (td, *J* = 7.7, 1.2 Hz, 1H), 6.80 (td, *J* = 7.7, 1.2 Hz, 1H), 6.74 (td, *J* = 7.7, 1.2 Hz, 1H), 6.44 (dd, *J* = 7.8, 1.2 Hz,1H), 6.19 (dd, *J* = 7.9, 1.2 Hz, 1H), 2.25 (s, 3H), 2.21 (s, 3H), 1.86 (s, 3H), 1.71 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$) δ: 173.0, 169.3, 167.7, 153.0, 152.1, 149.3, 149.1, 148.1, 147.7, 147.4, 144.1, 144.0, 137.8, 137.1, 137.0, 134.1, 134.0, 132.5, 132.4, 131.7, 130.5, 130.3, 129.9, 129.5, 129.1, 124.3, 124.0, 122.1, 121.9, 121.5,

120.9, 119.0, 118.4, 20.0, 19.9, 17.1 ppm. MS-MALDI: m/z 755.1 $[M]^+$. Acc-MS ($ASAP^+$): *m/z* 754.2182 ($[M+H]^+$), calcd. for $C_{38}H_{33}N_3O_2{}^{191}Ir$ 754.2179 ($|\Delta m/z| = 0.4$ ppm).[1]



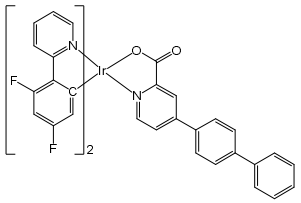
Ir(F_2PPy)$_2$(Pic-Ph) (5). Yield: 78 mg (78 %). ^{1}H-NMR ($CDCl_3$): δ 8.77 (dd, *J* = 5.7, 1.6 Hz, 1H), 8.58 (d, *J* = 2.2 Hz, 1H), 8.29 (d, *J* = 8.5 Hz, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.78-7.75 (m, 3H), 7.71-7.69 (m, 2H), 7.61 (dd, *J* = 5.6, 2.1 Hz, 1H), 7.54-7.48 (m, 4H), 7.19 (ddd, *J* = 7.3, 5.8, 1.4 Hz, 1H), 6.98 (ddd, *J* = 7.3, 5.8, 1.4 Hz, 1H), 6.48 (td, *J* = 9.0, 2.3 Hz, 1H), 6.39 (td, *J* = 9.0, 2.3 Hz, 1H), 5.84 (dd, *J* =8.6, 2.3 Hz, 1H), 5.58 (dd, *J* = 8.6, 2.3 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ: 172.7, 165.8, 164.2, 164.1, 163.8, 162.7, 162.4, 161.9, 160.4, 152.9, 151.8, 151.2, 150.5, 148.7, 148.3, 147.9, 138.1, 135.7, 132.0, 130.4, 129.4, 128.4, 127.9, 128.4, 127.9, 127.0, 126.0, 125.6, 123.3, 122.7, 122.2, 114.6, 114.3, 98.0, 97.6 ppm. ^{19}F-NMR ($CDCl_3$) δ: -107.2 (d, *J* = 10.4 Hz, 1F), -108.1 (d, *J* = 10.4 Hz, 1F), -109.8 (d, *J* = 10.4 Hz, 1F), -110.4 (d, *J* = 10.4 Hz, 1F) ppm. MS-MALDI: m/z 771.1 $[M]^+$. Anal. Calc. for $C_{34}H_{20}F_4IrN_3O_2 \cdot 0.5CH_2Cl_2$: C, 50.95; H, 2.60; N, 5.16 %. Found: C, 50.98; H, 2.58; N, 5.16 %.



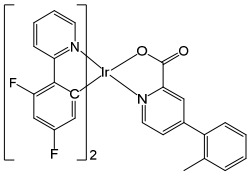
Ir(F_2PPy)$_2$(Pic-biphen) (6). Yield: 69 mg (63 %). ^{1}H-NMR ($CDCl_3$): δ 8.78 (d, *J* = 5.6 Hz, 1H), 8.62 (d, *J* = 1.7 Hz, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.80-7.76 (m, 5H), 7.71-7.72 (m, 2H), 7.66 (dd, *J* = 5.6, 2.2 Hz, 1H), 7.63-7.62 (m, 2H), 7.54 (d, *J* = 5.4 Hz, 1H), 7.46 (dd, *J* = 8.38, 7.0 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.20 (ddd, *J* = 7.3, 5.8, 1.4 Hz, 1H), 6.99 (ddd, *J* = 7.3, 5.8, 1.4 Hz, 1H), 6.48 (ddd, *J* = 11.9, 9.1, 2.3 Hz, 1H), 6.40 (ddd, *J* = 11.9, 9.1, 2.3 Hz, 1H), 5.85 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.59 (dd, *J* = 8.6, 2.3 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ: 172.7, 165.7, 164.2, 164.1, 163.8, 162.7, 162.3, 161.9, 160.4, 152.9, 151.8, 151.2, 149.9, 148.7, 148.3, 148.0, 143.3, 139.6, 138.1, 134.3, 128.9, 128.0,

[1] Insufficient sample for elemental analysis

127.4, 127.0, 125.3, 123.2, 122.6, 122.5, 122.2, 114.5, 114.4, 98.0, 97.6 ppm. ^{19}F-NMR ($CDCl_3$) δ: -107.2 (d, *J* = 10.4 Hz, 1F), -108.0 (d, *J* = 10.4 Hz, 1F), -109.8 (d, *J* = 10.4 Hz, 1F), -110.3 (d, *J* = 10.4 Hz, 1F) ppm. MS-MALDI: m/z 847.1 $[M]^+$. Anal. Calc. for $C_{40}H_{24}F_4IrN_3O_2$: C, 56.73; H, 2.86; N, 4.96 %. Found: C, 56.50; H, 2.84; N, 4.85 %.

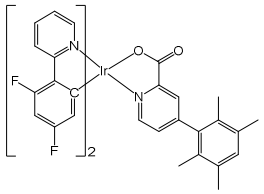


Ir(F_2PPy)$_2$(Pic-Tol) (7). Yield: 60 mg (60%). ^{1}H-NMR ($CDCl_3$): δ 8.79 (dd, J = 5.7, 1.6 Hz, 1H), 8.32 (dd, *J* = 2.0, 0.7 Hz, 1H), 8.30 (d, *J* = 8.6 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.80-7.77 (m, 3H), 7.51 (dd, *J* = 5.7, 1.6 Hz, 1H), 7.38 (dd, *J* = 5.5, 2.0 Hz, 1H), 7.35-7.33 (m, 1H), 7.30-7.27 (m, 2H), 7.23-7.20 (m, 2H), 7.00 (td, *J* = 7.3, 5.7 Hz, 1H), 6.48 (td, *J* = 9.1, 2.4 Hz, 1H), 6.40 (td, *J* = 9.1, 2.4 Hz, 1H), 5.85 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.56 (dd, *J* = 8.7, 2.3 Hz, 1H), 2.29 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$) δ: 172.6, 165.7, 164.3, 164.1, 163.8, 162.7, 162.3, 161.8, 160.5, 152.7, 152.3, 151.3, 148.8, 147.9, 147.7, 138.1, 136.9, 134.9, 131.1, 129.4, 129.2, 128.9, 128.7, 128.0, 126.4, 123.2, 122.6, 122.2, 114.6, 114.2, 98.1, 97.6, 20.3 ppm. ^{19}F-NMR ($CDCl_3$) δ: -107.2 (d, *J* = 10.4 Hz, 1F), -108.0 (d, *J* = 10.4 Hz, 1F), -109.8 (d, *J* = 10.5 Hz, 1F), -110.3 (d, *J* = 10.5 Hz, 1F) ppm. MS-MALDI: m/z 785.1 $[M]^+$. Anal. Calc. for $C_{35}H_{22}F_4IrN_3O_2 \cdot CH_2Cl_2$: C, 49.72; H, 2.78; N, 4.83 %. Found: C, 49.59; H, 2.82; N, 4.85 %.



Ir(F_2PPy)$_2$(Pic-Dur) (8). Yield: 21 mg (19 %). ^{1}H-NMR ($CDCl_3$): δ 8.83 (d, *J* = 5.4 Hz, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 8.12 (s, 1H), 7.83-7.78 (m, 3H), 7.45 (d, *J* = 5.8 Hz, 1H), 7.22 (t, *J* = 7.0 Hz, 1H), 7.20 (dd, *J* = 5.7, 1.5 Hz, 1H), 7.04 (s, 1H), 6.99 (ddd, *J* = 7.3, 5.8, 1.4 Hz, 1H), 6.48 (ddd, *J* = 11.8, 9.1, 2.3 Hz, 1H), 6.41 (ddd, *J* = 11.8, 9.1, 2.3 Hz, 1H), 5.87 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.58 (dd, *J* = 8.6, 2.3 Hz, 1H), 2.26 (s, 3H), 2.22 (s, 3H), 1.87 (s, 3H), 1.72 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$) δ: 172.7, 165.9, 164.3, 162.0, 160.3, 154.0, 152.8, 151.6, 151.3, 148.8, 148.0, 147.6, 138.2, 137.4, 134.2, 131.9, 130.4,

130.2, 129.9, 129.6, 123.4, 122.8, 122.2, 114.6, 114.3, 98.1, 97.6, 20.0, 17.1 ppm.[2] ^{9}F-NMR ($CDCl_3$) δ: -107.2 (d, *J* = 10.4 Hz, 1F), -108.0 (d, *J* = 10.4 Hz, 1F), -109.8 (d, *J* = 10.5 Hz, 1F), -110.3 (d, *J* = 10.5 Hz, 1F) ppm. MS-MALDI: m/z 827.2 $[M]^+$. Acc-MS (ASAP$^+$): *m/z* 826.1807 ($[M+H]^+$), calcd. for $C_{38}H_{29}N_3O_2F_4{}^{191}Ir$ 826.1802 ($|\Delta m/z|$ = 0.6 ppm).[3]



[2] Low concentration

[3] Insufficient sample for elemental analysis

S2. NMR spectra of reported compounds

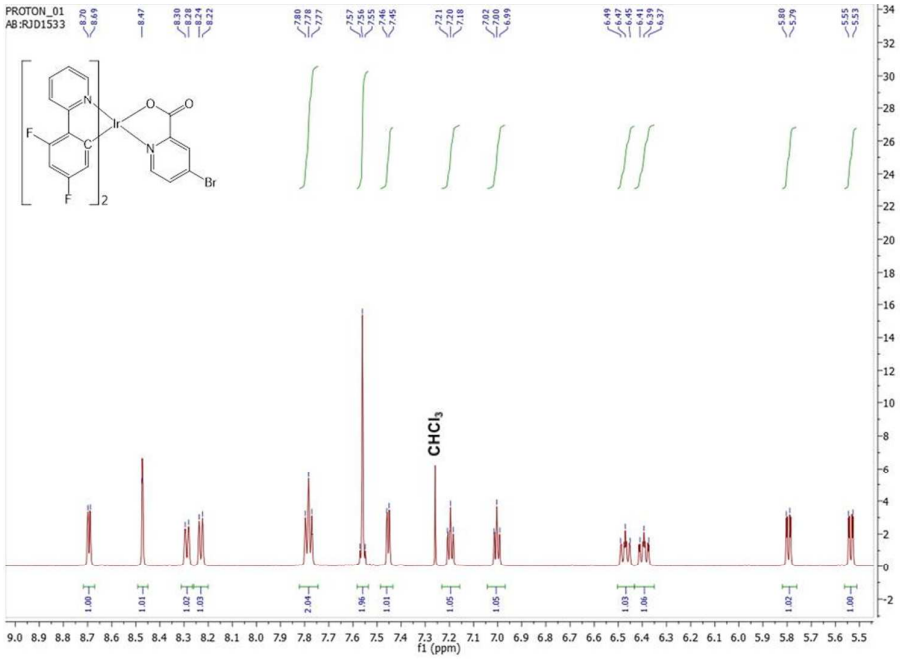


Figure S1. ^{1}H NMR spectra of Ir(F_2PPy)$_2$(pic-4-Br) recorded in $CDCl_3$.

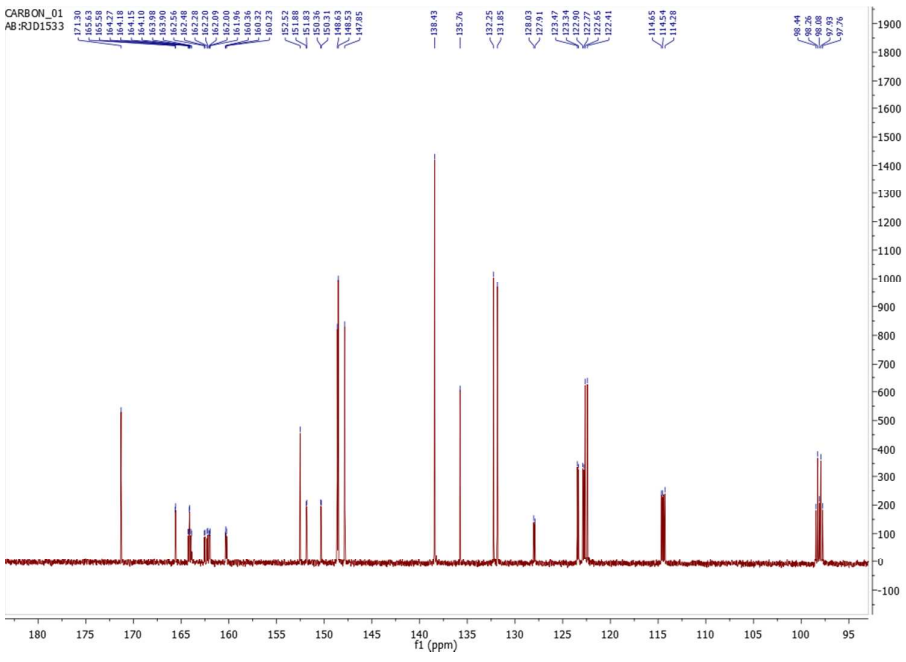


Figure S2. ^{13}C NMR spectra of Ir(F_2PPy)$_2$(pic-4-Br) recorded in $CDCl_3$.

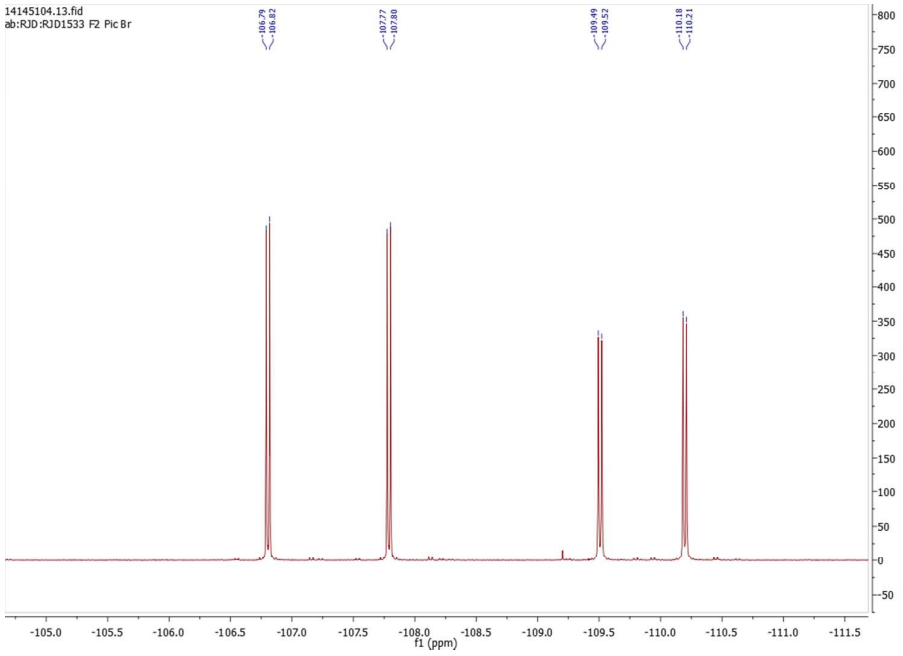


Figure S3. ^{19}F NMR spectra of $Ir(F_2PPy)_2$(pic-4-Br) recorded in $CDCl_3$.

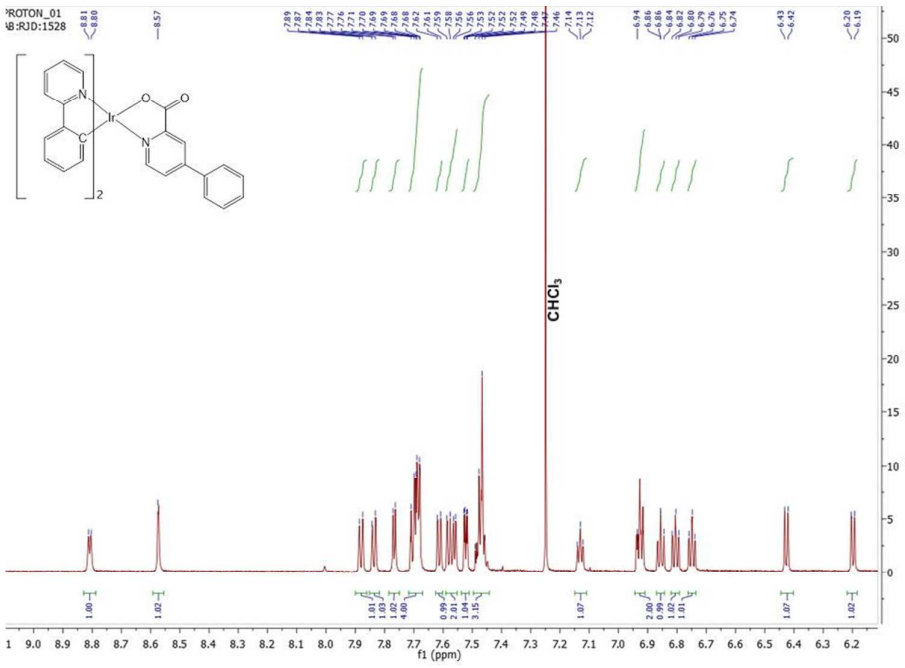


Figure S4. ^{1}H NMR spectra of **1** recorded in $CDCl_3$.

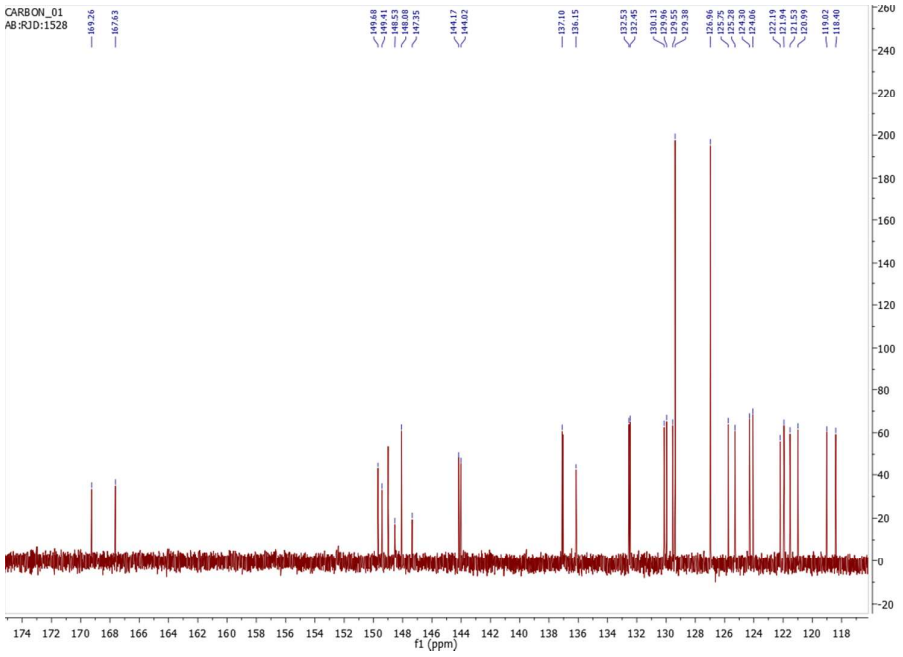


Figure S5. ^{13}C NMR spectra of **1** recorded in $CDCl_3$.

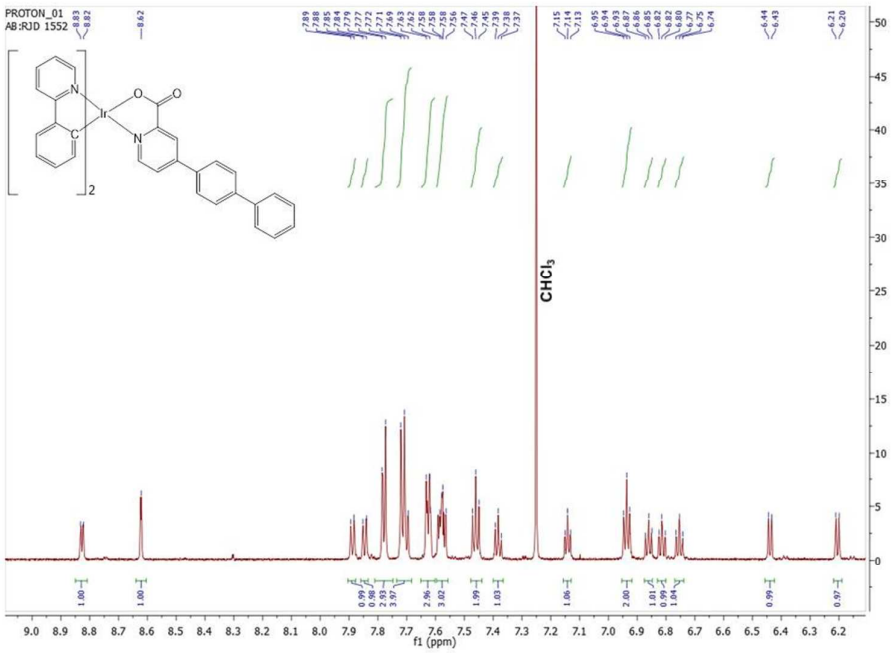


Figure S6. ^{1}H NMR spectra of **2** recorded in $CDCl_3$.

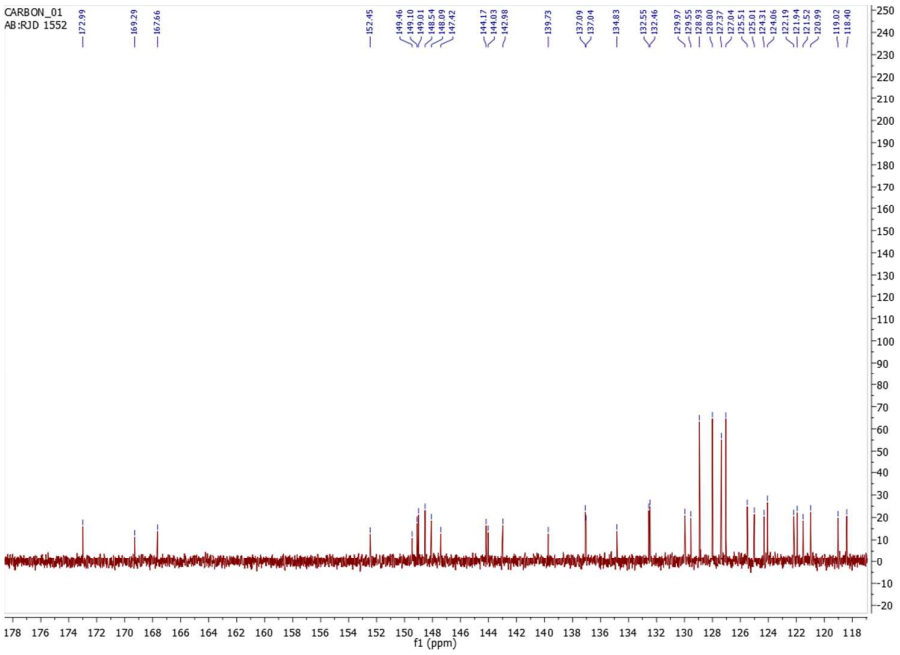


Figure S7. ^{13}C NMR spectra of **2** recorded in $CDCl_3$.

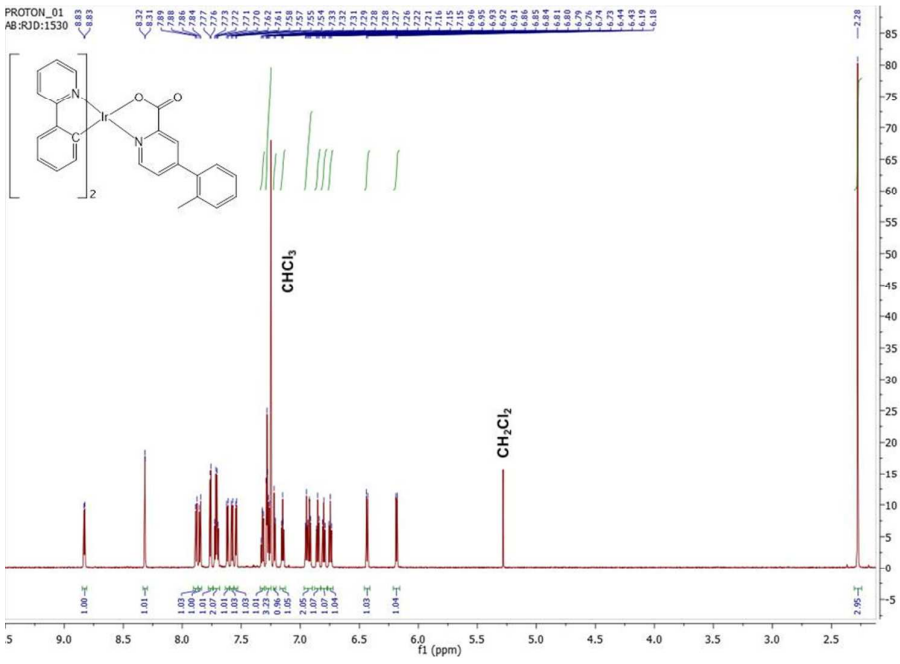


Figure S8. ^{1}H NMR spectra of **3** recorded in $CDCl_3$.

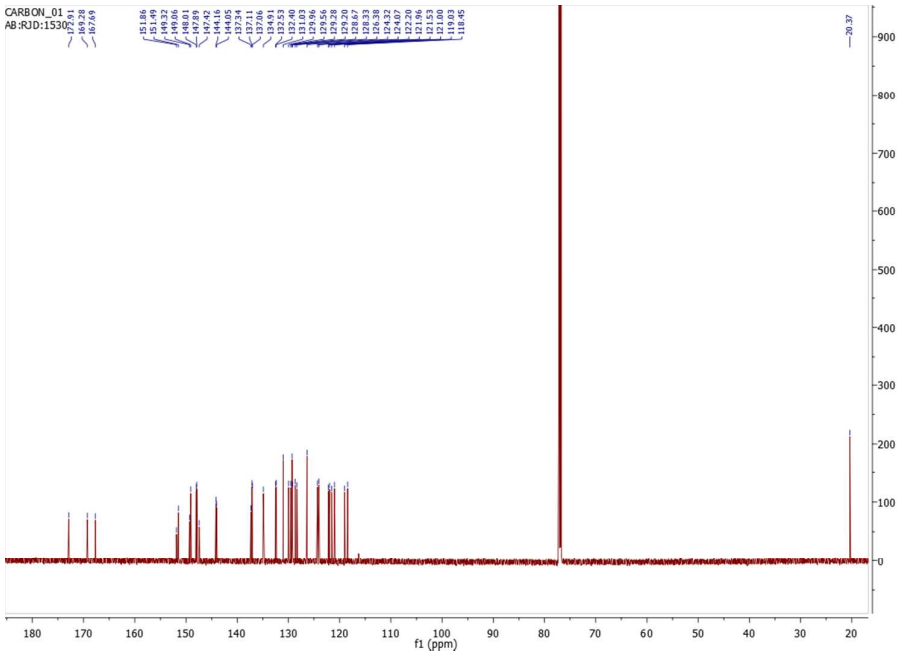


Figure S9. ^{13}C NMR spectra of **3** recorded in $CDCl_3$.

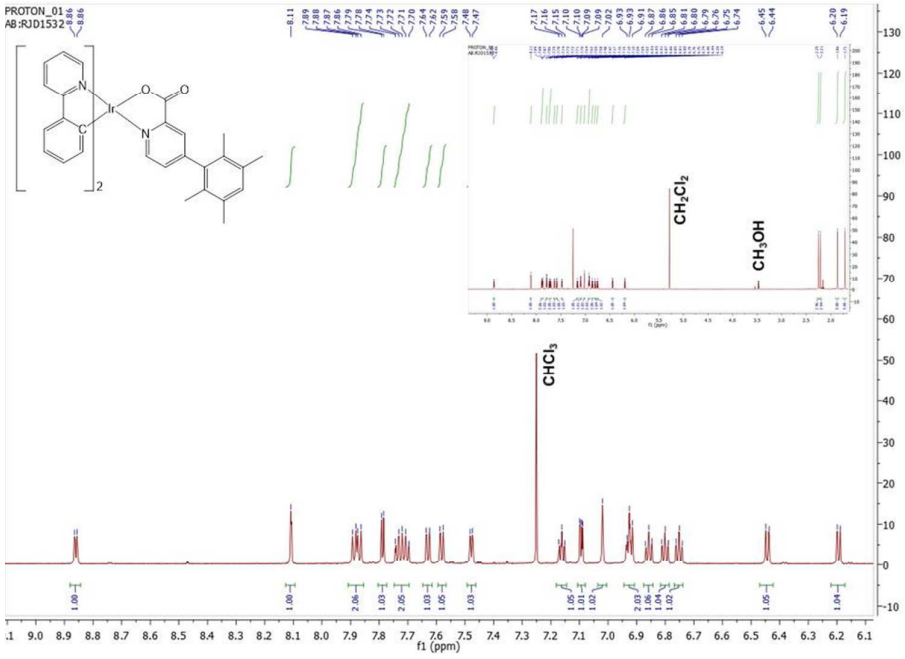


Figure S10. ^{1}H NMR spectra of **4** recorded in $CDCl_3$.

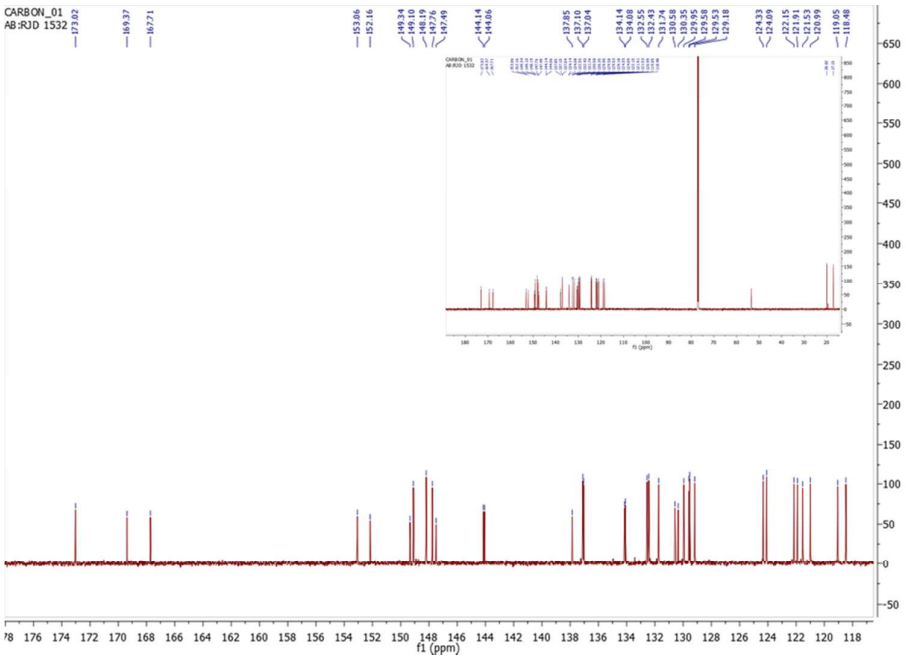


Figure S11. ^{13}C NMR spectra of **4** recorded in $CDCl_3$.

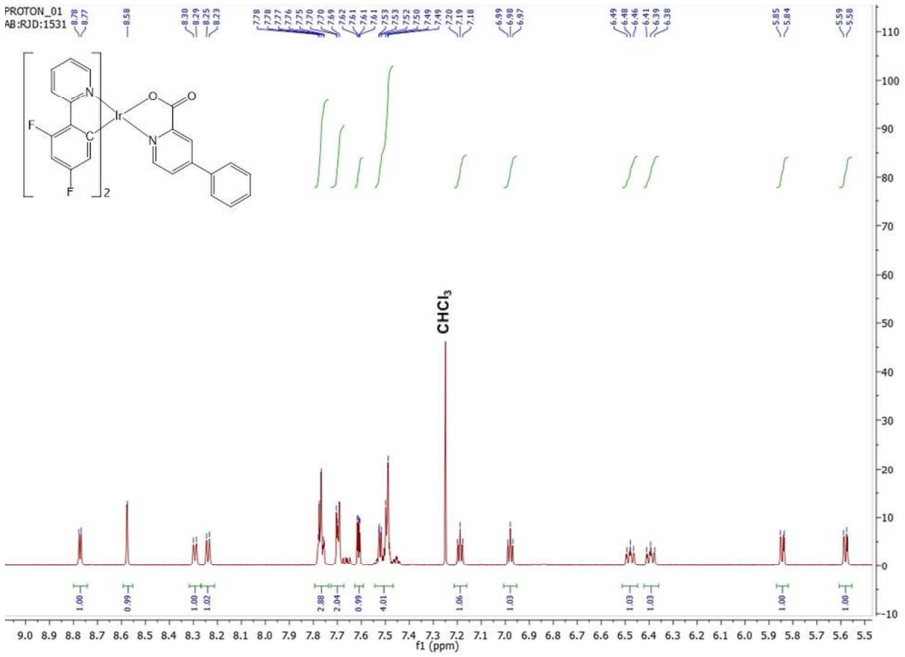


Figure S12. ^{1}H NMR spectra of **5** recorded in $CDCl_3$.

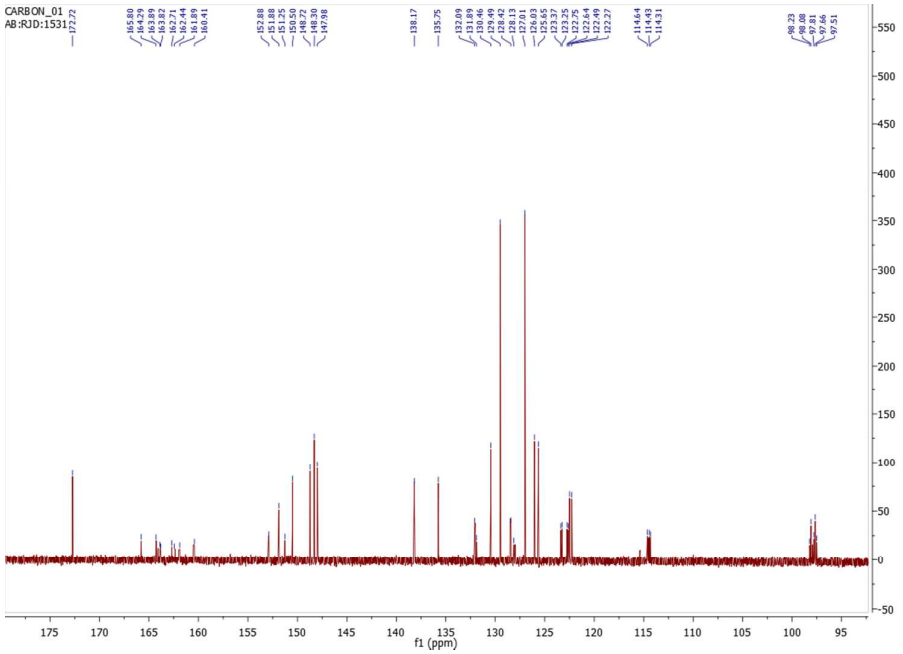


Figure S13. ^{13}C NMR spectra of **5** recorded in $CDCl_3$.

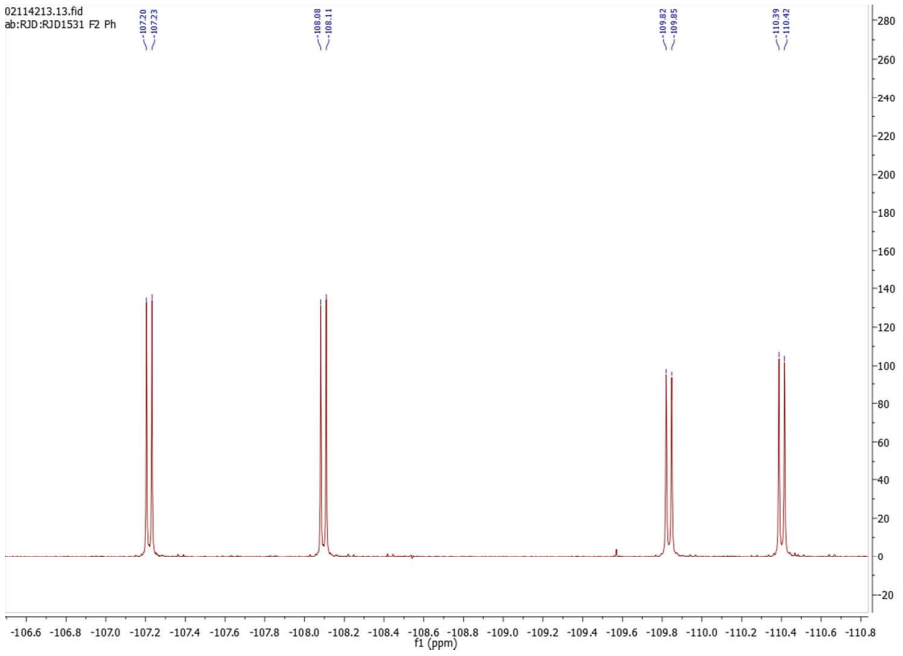


Figure S14. ^{19}F NMR spectra of **5** recorded in $CDCl_3$.

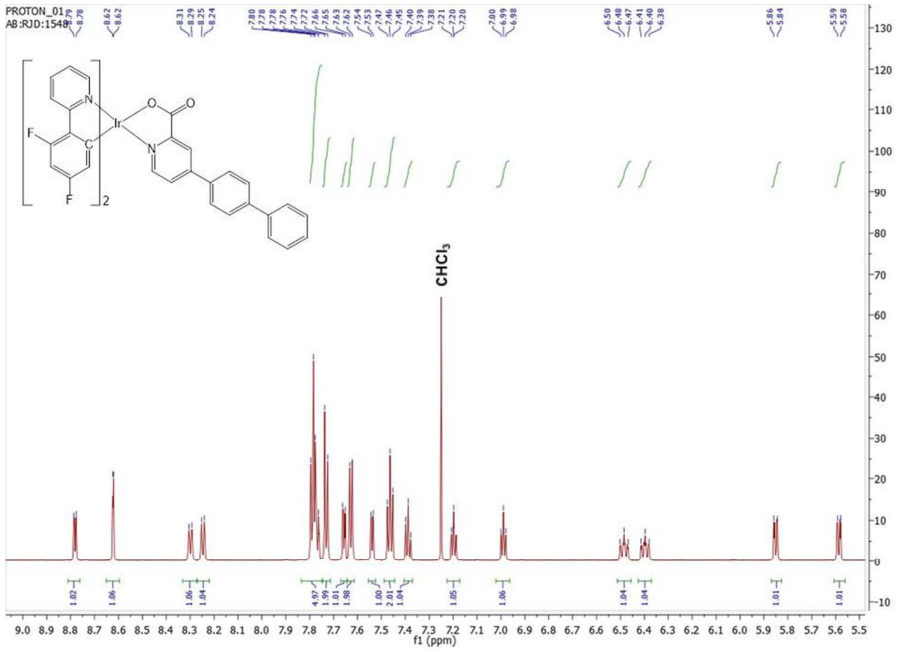


Figure S15. ^{1}H NMR spectra of **6** recorded in $CDCl_3$.

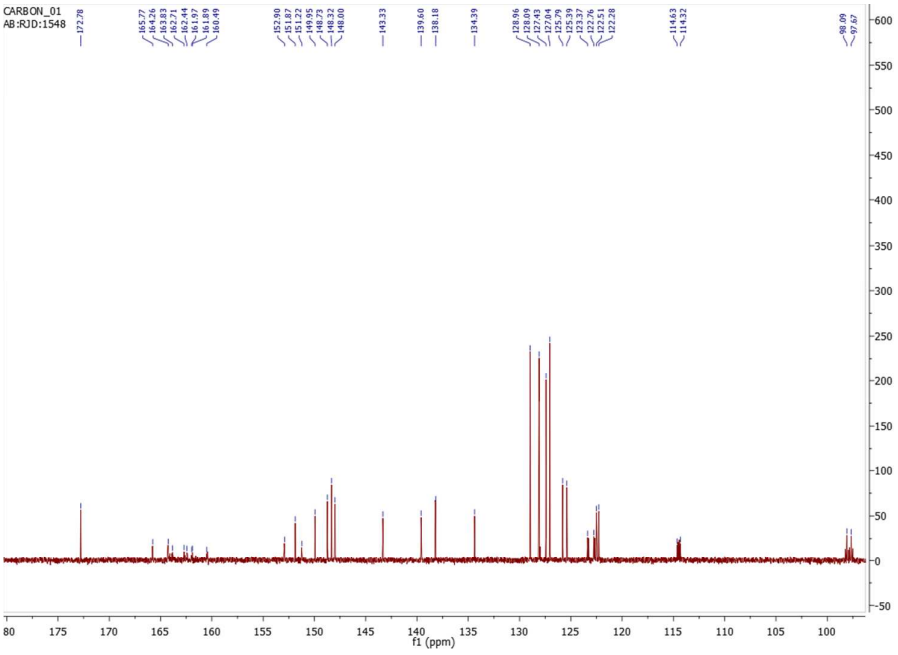


Figure S16. ^{13}C NMR spectra of **6** recorded in $CDCl_3$.

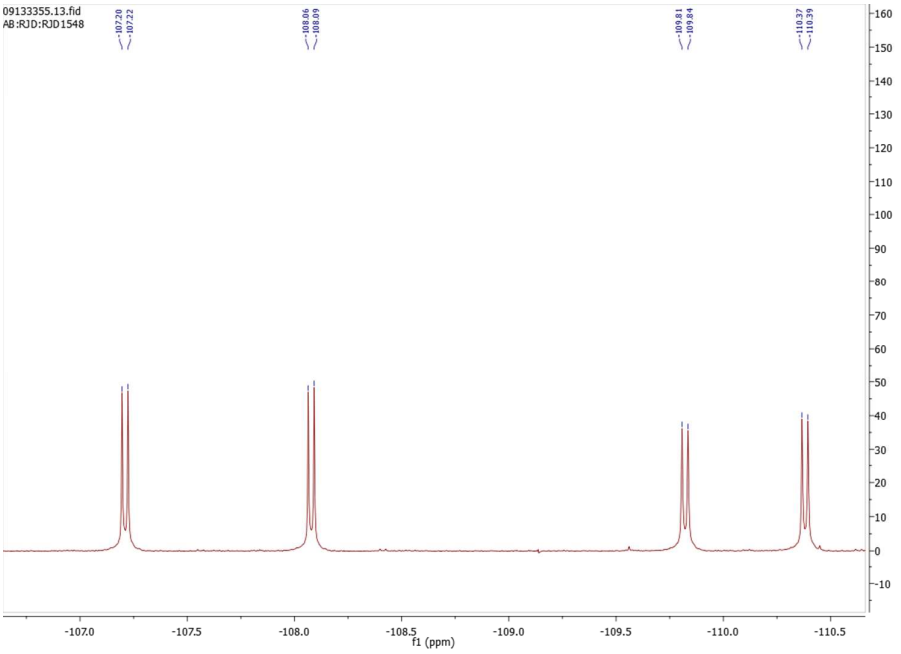


Figure S17. ^{19}F NMR spectra of **6** recorded in $CDCl_3$.

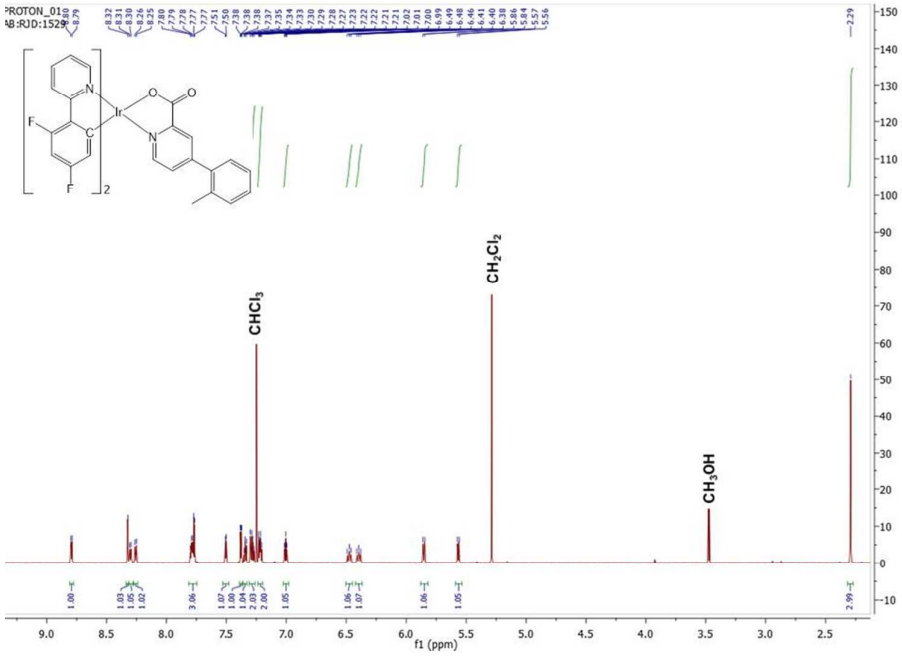


Figure S18. ^{1}H NMR spectra of **7** recorded in $CDCl_3$.

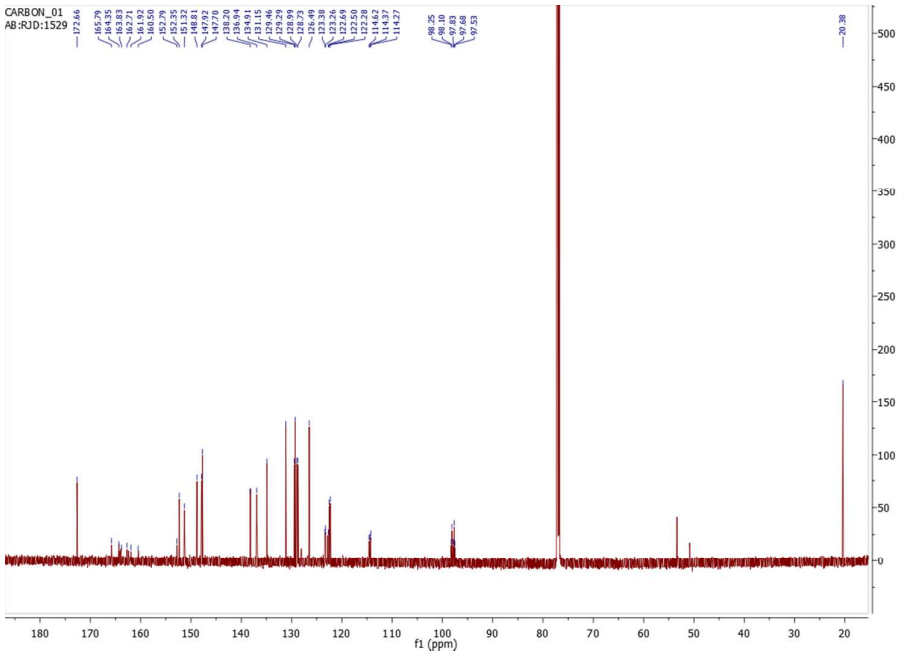


Figure S19. ^{13}C NMR spectra of **7** recorded in $CDCl_3$.

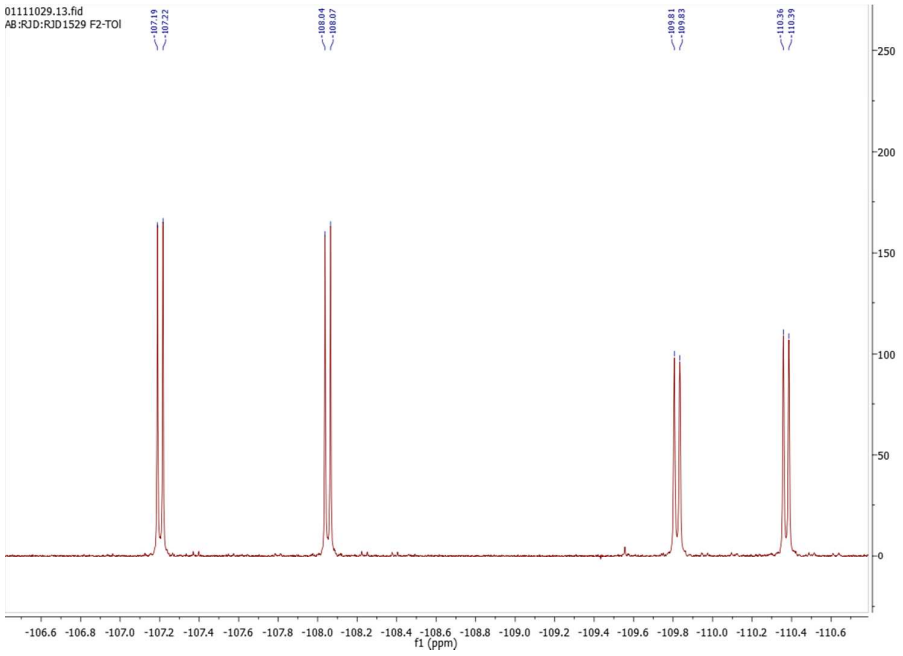


Figure S20. ^{19}F NMR spectra of **7** recorded in $CDCl_3$.

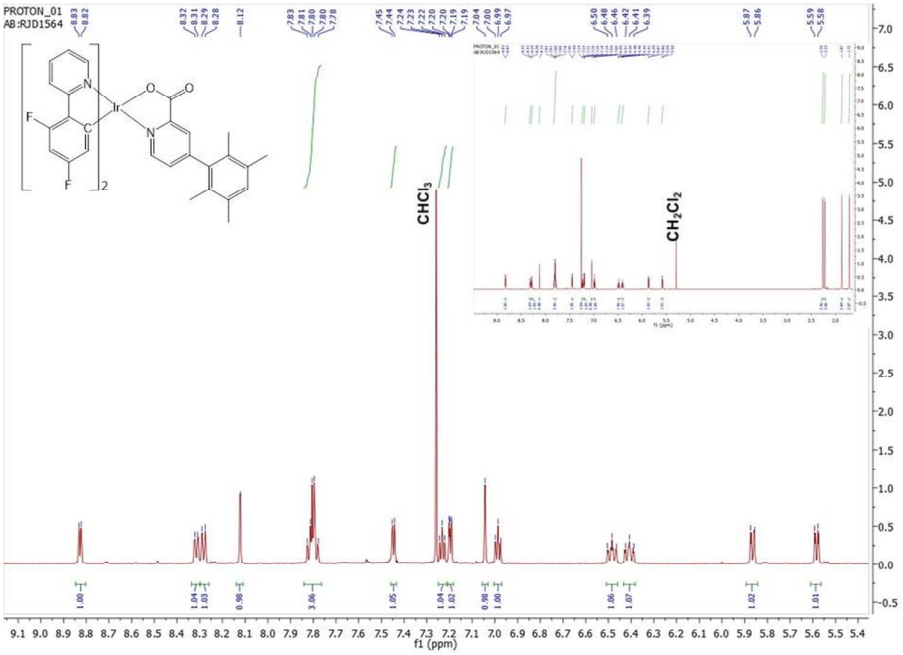


Figure S21. ^{1}H NMR spectra of **8** recorded in $CDCl_3$.

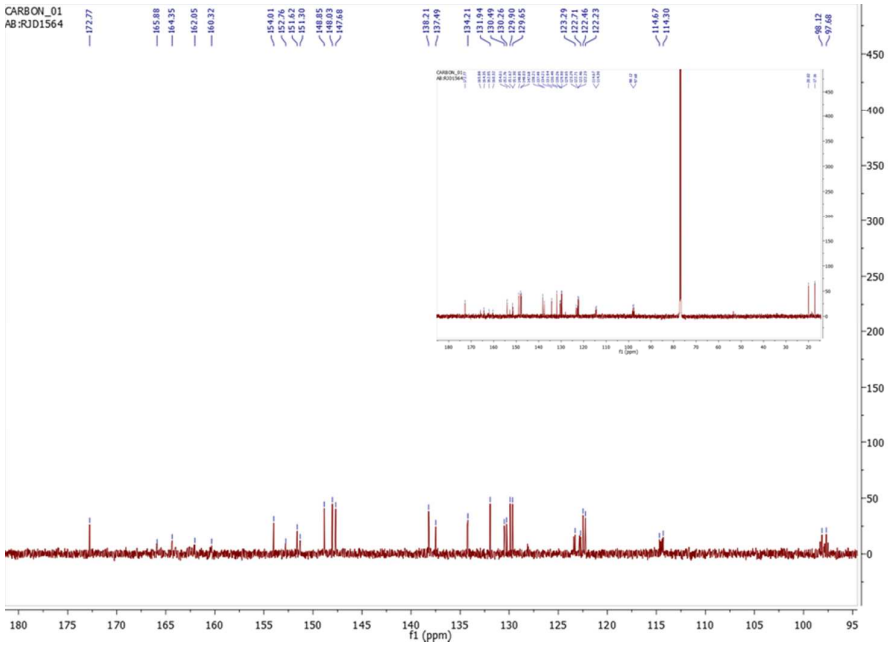


Figure S22. ^{13}C NMR spectra of **8** recorded in $CDCl_3$.

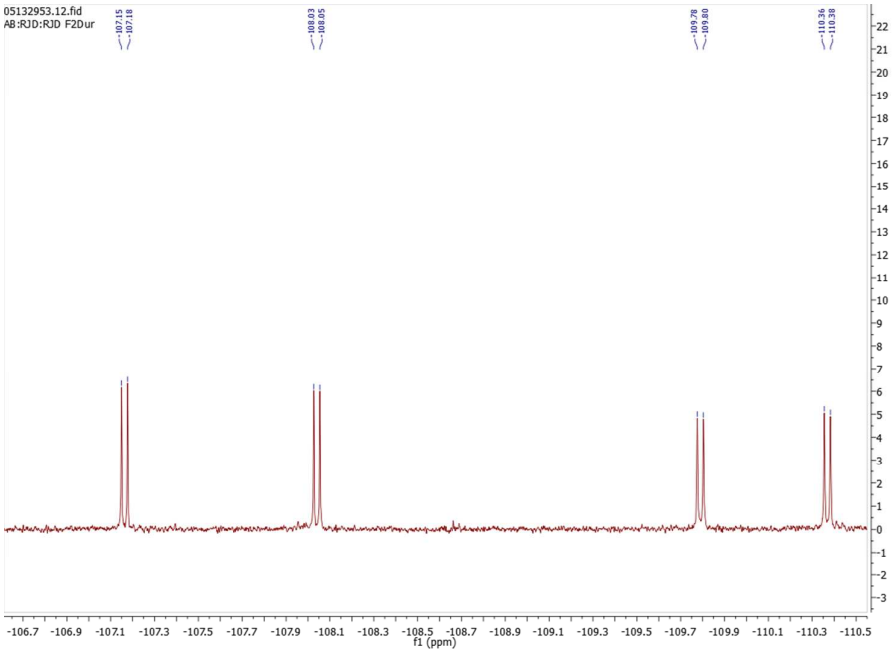


Figure S23. ^{19}F NMR spectra of **8** recorded in $CDCl_3$.

S3. X-ray Crystallography

The X-ray single crystal data have been collected using λMoKα radiation (λ =0.71073Å) on a Bruker D8Venture (compounds **1**, **5**, **6** and **8;** Photon100 CMOS detector, IμS-microsource, focusing mirrors) and Agilent XCalibur (compounds **3** and 7; Sapphire-3 CCD detector, fine-focus sealed tube, graphite monochromator) diffractometers equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostats at the temperature 120.0(2)K. All structures were solved by direct method and refined by full-matrix least squares on F^2 for all data using Olex2[1] and SHELXTL[2] software. All non-disordered non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed in the calculated positions and refined in riding mode. All studied structures (except **5**) contain various disordered solvent molecules. Disordered atoms were refined isotropically with various fixed S.O.F. Some severely disordered solvent molecules in the structures **1** and **6** could not be modelled properly and their contributions were taken into account by applying the MASK procedure of the Olex2 software package. Crystal data and parameters of refinement are listed in Table **S3.1**. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 1832981-1832986.

S3. Crystallographic data

Table S1. Crystal and Refinement Data for **1**·½CH_2Cl_2·1¼CH_3OH, **3**·CH_3CN, and 5·CH_3CN.

Identification code	**1**	**3**	**5**
Empirical formula	$C_{34}H_{24}IrN_3O_2$ x 0.5 CH_2Cl_2 x 1.25 CH_3OH	$C_{35}H_{26}IrN_3O_2$ x CH_3CN	$C_{34}H_{20}F_4IrN_3O_2$ x CH_3CN
Formula weight	781.28	753.84	811.78
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/n$	$P2_1/n$
a/Å	9.5253(4)	10.11985(14)	14.3882(7)
b/Å	17.6927(8)	9.48604(12)	10.0239(5)
c/Å	21.3093(9)	31.6584(4)	21.5425(10)
α/°	114.0251(15)	90	90
β/°	95.9517(16)	95.8281(12)	107.3648(17)
γ/°	92.9604(16)	90	90
Volume/$Å^3$	3245.0(2)	3023.41(7)	2965.4(2)
Z	4	4	4
$\rho_{calc}g/cm^3$	1.599	1.656	1.818
μ/mm^{-1}	4.237	4.457	4.570
F(000)	1542.0	1488.0	1584.0
Reflections collected	68932	44198	46609
Independent reflections, R_{int}	18075, 0.0362	7312, 0.0412	8633, 0.0344
Data/restraints/parameters	18075/2/806	7312/2/396	8633/0/425
Goodness-of-fit on F^2	1.030	1.039	1.029
Final R_1 indexes [I>=2σ (I)]	0.02772	0.0267	0.0208
Final wR_2 indexes [all data]	0.0601	0.0592	0.0427
Largest diff. peak/hole / e $Å^{-3}$	1.42/-1.16	1.49/-0.71	1.06/-0.91

Table S2. Crystal and Refinement Data for **6**·¾CH_2Cl_2, **7**·CH_2Cl_2 and **8**·CH_3OH

Identification code	**6**	**7**	**8**
Empirical formula	$C_{40}H_{24}F_4IrN_3O_2$ x 0.75 CH_2Cl_2	$C_{35}H_{22}F_4IrN_3O_2$ x CH_2Cl_2	$C_{38}H_{28}F_4IrN_3O_2$ x 2 CH_3OH
Formula weight	910.52	869.68	890.92
Temperature/K	120.0	120.0	120.0
Crystal system	monoclinic	triclinic	triclinic
Space group	C2/c	P-1	P-1
a/Å	20.1364(16)	10.0577(2)	11.8141(5)
b/Å	16.3280(13)	13.6822(5)	12.1751(6)
c/Å	23.703(2)	13.7269(4)	14.2388(7)
α/°	90	66.178(3)	83.4331(18)
β/°	109.188(3)	70.167(3)	66.2572(16)
γ/°	90	78.533(3)	68.0077(16)
Volume/$Å^3$	7360.4(10)	1621.36(10)	1736.72(14)
Z	8	2	2
$\rho_{calc}g/cm^3$	1.643	1.781	1.704
μ/mm^{-1}	3.797	4.344	3.913
F(000)	3564.0	848.0	884.0
Reflections collected	79982	24085	37388
Independent reflections, R_{int}	10716, 0.0335	8615, 0.0413	10091, 0.0282
Data/restraints/parameters	10716/6/492	8615/62/475	10091/3/474
Goodness-of-fit on F^2	1.090	1.032	1.100
Final R_1 indexes [I>=2σ (I)]	0.0273	0.0331	0.0355
Final wR_2 indexes [all data]	0.0696	0.0796	0.0848
Largest diff. peak/hole / e $Å^{-3}$	3.01/-0.93	1.37/-0.95	3.59/-1.85

Table S3. Selected bond lengths for **1**·½CH_2Cl_2·1¼CH_3OH.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.166(2)		Ir1A	N3A	2.126(2)
Ir1	N1	2.042(2)		Ir1A	C7A	1.998(3)
Ir1	N2	2.038(2)		Ir1A	C18A	2.003(3)
Ir1	N3	2.127(2)		O1A	C28A	1.280(4)
Ir1	C7	2.000(3)		O2A	C28A	1.232(3)
Ir1	C18	1.993(3)		N1A	C1A	1.342(4)
O1	C28	1.272(4)		N1A	C5A	1.367(3)
O2	C28	1.244(3)		N2A	C12A	1.343(4)
N1	C1	1.344(4)		N2A	C16A	1.367(4)
N1	C5	1.363(4)		N3A	C23A	1.347(4)
N2	C12	1.345(4)		N3A	C27A	1.348(3)
N2	C16	1.363(4)		C1A	C2A	1.376(4)
N3	C23	1.345(4)		C2A	C3A	1.385(4)
N3	C27	1.351(4)		C3A	C4A	1.372(4)
C1	C2	1.375(4)		C4A	C5A	1.392(4)
C2	C3	1.381(5)		C5A	C6A	1.467(4)
C3	C4	1.377(5)		C6A	C7A	1.413(4)
C4	C5	1.396(4)		C6A	C11A	1.395(4)
C5	C6	1.469(4)		C7A	C8A	1.392(4)
C6	C7	1.415(4)		C8A	C9A	1.395(4)
C6	C11	1.390(4)		C9A	C10A	1.377(5)
C7	C8	1.400(4)		C10A	C11A	1.387(4)
C8	C9	1.387(4)		C12A	C13A	1.379(4)
C9	C10	1.390(4)		C13A	C14A	1.373(5)
C10	C11	1.383(5)		C14A	C15A	1.370(5)
C12	C13	1.371(4)		C15A	C16A	1.386(4)
C13	C14	1.388(4)		C16A	C17A	1.465(4)
C14	C15	1.374(4)		C17A	C18A	1.405(4)
C15	C16	1.391(4)		C17A	C22A	1.401(4)
C16	C17	1.468(4)		C18A	C19A	1.406(4)
C17	C18	1.415(4)		C19A	C20A	1.387(5)
C17	C22	1.398(4)		C20A	C21A	1.384(5)
C18	C19	1.397(4)		C21A	C22A	1.383(5)
C19	C20	1.395(4)		C23A	C24A	1.378(4)
C20	C21	1.383(4)		C24A	C25A	1.392(4)
C21	C22	1.381(4)		C25A	C26A	1.395(4)
C23	C24	1.373(4)		C25A	C29A	1.485(4)
C24	C25	1.393(4)		C26A	C27A	1.382(4)
C25	C26	1.399(4)		C27A	C28A	1.512(4)
C25	C29	1.480(4)		C29A	C30A	1.392(4)
C26	C27	1.377(4)		C29A	C34A	1.392(4)
C27	C28	1.514(4)		C30A	C31A	1.380(5)
C29	C30	1.391(5)		C31A	C32A	1.383(5)
C29	C34	1.399(5)		C32A	C33A	1.382(5)
C30	C31	1.391(5)		C33A	C34A	1.385(5)
C31	C32	1.373(7)		Cl1	C1S	1.759(3)
C32	C33	1.382(7)		Cl2	C1S	1.761(3)
C33	C34	1.380(5)		O1S	C2S	1.417(4)
Ir1A	O1A	2.170(2)		O2S	C3S	1.413(5)
Ir1A	N1A	2.037(2)		O2SA	C3S	1.406(5)
Ir1A	N2A	2.040(2)		O3S	C4S	1.416(10)

Table S4. Selected bond angles for **1**·½CH_2Cl_2·1¼CH_3OH.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	Ir1	O1	89.24(8)		N1A	Ir1A	N2A	174.34(9)
N1	Ir1	N3	95.55(9)		N1A	Ir1A	N3A	90.80(9)
N2	Ir1	O1	94.16(8)		N2A	Ir1A	O1A	90.86(9)
N2	Ir1	N1	175.50(9)		N2A	Ir1A	N3A	94.27(10)
N2	Ir1	N3	88.10(9)		N3A	Ir1A	O1A	76.83(8)
N3	Ir1	O1	76.71(8)		C7A	Ir1A	O1A	171.03(10)
C7	Ir1	O1	98.07(10)		C7A	Ir1A	N1A	81.01(11)
C7	Ir1	N1	80.61(10)		C7A	Ir1A	N2A	95.87(11)
C7	Ir1	N2	95.97(10)		C7A	Ir1A	N3A	96.71(10)
C7	Ir1	N3	173.63(10)		C7A	Ir1A	C18A	89.81(11)
C18	Ir1	O1	172.47(9)		C18A	Ir1A	O1A	97.16(10)
C18	Ir1	N1	95.97(10)		C18A	Ir1A	N1A	94.59(11)
C18	Ir1	N2	80.94(10)		C18A	Ir1A	N2A	80.62(11)
C18	Ir1	N3	97.31(10)		C18A	Ir1A	N3A	172.13(10)
C18	Ir1	C7	88.18(11)		C28A	O1A	Ir1A	115.92(18)
C28	O1	Ir1	116.18(18)		C1A	N1A	Ir1A	124.7(2)
C1	N1	Ir1	124.6(2)		C1A	N1A	C5A	119.5(2)
C1	N1	C5	119.6(2)		C5A	N1A	Ir1A	115.69(18)
C5	N1	Ir1	115.78(19)		C12A	N2A	Ir1A	125.4(2)
C12	N2	Ir1	124.64(19)		C12A	N2A	C16A	118.9(3)
C12	N2	C16	119.5(2)		C16A	N2A	Ir1A	115.7(2)
C16	N2	Ir1	115.81(18)		C23A	N3A	Ir1A	126.60(19)
C23	N3	Ir1	126.73(19)		C23A	N3A	C27A	118.5(3)
C23	N3	C27	118.1(2)		C27A	N3A	Ir1A	114.86(19)
C27	N3	Ir1	115.14(19)		N1A	C1A	C2A	122.1(3)
N1	C1	C2	122.0(3)		C1A	C2A	C3A	119.1(3)
C1	C2	C3	119.4(3)		C4A	C3A	C2A	119.1(3)
C4	C3	C2	118.9(3)		C3A	C4A	C5A	120.3(3)
C3	C4	C5	120.3(3)		N1A	C5A	C4A	119.8(3)
N1	C5	C4	119.7(3)		N1A	C5A	C6A	113.7(2)
N1	C5	C6	114.1(2)		C4A	C5A	C6A	126.5(3)
C4	C5	C6	126.1(3)		C7A	C6A	C5A	115.3(2)
C7	C6	C5	114.5(3)		C11A	C6A	C5A	123.1(3)
C11	C6	C5	123.8(3)		C11A	C6A	C7A	121.6(3)
C11	C6	C7	121.6(3)		C6A	C7A	Ir1A	114.2(2)
C6	C7	Ir1	114.8(2)		C8A	C7A	Ir1A	128.5(2)
C8	C7	Ir1	128.6(2)		C8A	C7A	C6A	117.2(3)
C8	C7	C6	116.5(3)		C7A	C8A	C9A	121.0(3)
C9	C8	C7	121.5(3)		C10A	C9A	C8A	120.9(3)
C8	C9	C10	120.9(3)		C9A	C10A	C11A	119.7(3)
C11	C10	C9	118.9(3)		C10A	C11A	C6A	119.5(3)
C10	C11	C6	120.4(3)		N2A	C12A	C13A	122.9(3)
N2	C12	C13	122.2(3)		C14A	C13A	C12A	118.5(3)
C12	C13	C14	118.8(3)		C15A	C14A	C13A	119.2(3)
C15	C14	C13	119.4(3)		C14A	C15A	C16A	120.9(3)
C14	C15	C16	119.8(3)		N2A	C16A	C15A	119.5(3)
N2	C16	C15	120.1(3)		N2A	C16A	C17A	113.8(3)
N2	C16	C17	113.7(2)		C15A	C16A	C17A	126.6(3)
C15	C16	C17	126.2(3)		C18A	C17A	C16A	115.2(3)
C18	C17	C16	115.1(2)		C22A	C17A	C16A	123.0(3)
C22	C17	C16	123.4(3)		C22A	C17A	C18A	121.9(3)
C22	C17	C18	121.6(3)		C17A	C18A	Ir1A	114.7(2)
C17	C18	Ir1	114.4(2)		C17A	C18A	C19A	116.5(3)
C19	C18	Ir1	128.5(2)		C19A	C18A	Ir1A	128.8(2)

Table S4 continued. Selected bond angles for **1**·½CH_2Cl_2·1¼CH_3OH.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
C19	C18	C17	117.0(3)		C20A	C19A	C18A	121.6(3)
C20	C19	C18	121.1(3)		C21A	C20A	C19A	120.6(3)
C21	C20	C19	120.9(3)		C22A	C21A	C20A	119.6(3)
C22	C21	C20	119.6(3)		C21A	C22A	C17A	119.7(3)
C21	C22	C17	119.9(3)		N3A	C23A	C24A	122.4(3)
N3	C23	C24	122.6(3)		C23A	C24A	C25A	120.1(3)
C23	C24	C25	120.3(3)		C24A	C25A	C26A	116.7(3)
C24	C25	C26	116.7(3)		C24A	C25A	C29A	121.4(3)
C24	C25	C29	121.5(3)		C26A	C25A	C29A	121.8(3)
C26	C25	C29	121.8(3)		C27A	C26A	C25A	120.8(3)
C27	C26	C25	120.4(3)		N3A	C27A	C26A	121.4(3)
N3	C27	C26	121.9(3)		N3A	C27A	C28A	116.1(3)
N3	C27	C28	115.4(2)		C26A	C27A	C28A	122.4(3)
C26	C27	C28	122.7(3)		O1A	C28A	C27A	116.2(2)
O1	C28	C27	116.6(3)		O2A	C28A	O1A	124.9(3)
O2	C28	O1	125.6(3)		O2A	C28A	C27A	119.0(3)
O2	C28	C27	117.8(3)		C30A	C29A	C25A	120.0(3)
C30	C29	C25	120.5(3)		C30A	C29A	C34A	118.8(3)
C30	C29	C34	119.4(3)		C34A	C29A	C25A	121.2(3)
C34	C29	C25	120.1(3)		C31A	C30A	C29A	120.6(3)
C29	C30	C31	119.7(4)		C30A	C31A	C32A	120.3(3)
C32	C31	C30	120.6(4)		C33A	C32A	C31A	119.5(3)
C31	C32	C33	119.7(4)		C32A	C33A	C34A	120.4(3)
C34	C33	C32	120.7(4)		C33A	C34A	C29A	120.3(3)
C33	C34	C29	119.8(4)		Cl1	C1S	Cl2	111.9(3)
N1A	Ir1A	O1A	92.75(8)					

Table S5. Selected bond lengths for **3**·CH_3CN.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.168(2)		C14	C15	1.369(5)
Ir1	N1	2.037(2)		C15	C16	1.386(4)
Ir1	N2	2.042(3)		C16	C17	1.463(4)
Ir1	N3	2.133(3)		C17	C18	1.417(4)
Ir1	C7	2.007(3)		C17	C22	1.396(4)
Ir1	C18	1.994(3)		C18	C19	1.404(4)
O1	C28	1.285(4)		C19	C20	1.382(4)
O2	C28	1.232(3)		C20	C21	1.387(5)
N1	C1	1.339(4)		C21	C22	1.378(5)
N1	C5	1.367(4)		C23	C24	1.383(4)
N2	C12	1.347(4)		C24	C25	1.395(4)
N2	C16	1.369(4)		C25	C26	1.392(4)
N3	C23	1.343(4)		C25	C29	1.486(4)
N3	C27	1.352(4)		C26	C27	1.378(4)
C1	C2	1.367(4)		C27	C28	1.526(4)
C2	C3	1.391(5)		C29	C30	1.415(4)
C3	C4	1.375(5)		C29	C34	1.380(4)
C4	C5	1.397(4)		C30	C31	1.394(5)
C5	C6	1.469(4)		C30	C35	1.516(4)
C6	C7	1.414(4)		C31	C32	1.380(5)
C6	C11	1.393(4)		C32	C33	1.382(5)
C7	C8	1.401(4)		C33	C34	1.396(5)
C8	C9	1.385(4)		N4	C1S	1.151(6)
C9	C10	1.392(5)		N4A	C1SB	1.146(6)
C10	C11	1.381(4)		C1S	C2S	1.449(6)
C12	C13	1.369(4)		C1SB	C2S	1.438(6)
C13	C14	1.387(5)				

Table S5. Selected bond angles for **3**·CH_3CN.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	Ir1	O1	89.04(8)		N2	C12	C13	122.1(3)
N1	Ir1	N2	174.80(10)		C12	C13	C14	119.6(3)
N1	Ir1	N3	96.46(10)		C15	C14	C13	118.4(3)
N2	Ir1	O1	95.04(9)		C14	C15	C16	120.9(3)
N2	Ir1	N3	87.65(10)		N2	C16	C15	119.9(3)
N3	Ir1	O1	76.48(9)		N2	C16	C17	113.7(3)
C7	Ir1	O1	99.06(10)		C15	C16	C17	126.5(3)
C7	Ir1	N1	80.71(12)		C18	C17	C16	115.2(3)
C7	Ir1	N2	95.43(11)		C22	C17	C16	123.4(3)
C7	Ir1	N3	174.82(10)		C22	C17	C18	121.4(3)
C18	Ir1	O1	172.57(10)		C17	C18	Ir1	114.5(2)
C18	Ir1	N1	95.52(11)		C19	C18	Ir1	128.8(2)
C18	Ir1	N2	80.77(12)		C19	C18	C17	116.7(3)
C18	Ir1	N3	97.13(11)		C20	C19	C18	121.5(3)
C18	Ir1	C7	87.49(12)		C19	C20	C21	120.7(3)
C28	O1	Ir1	116.74(19)		C22	C21	C20	119.7(3)
C1	N1	Ir1	124.6(2)		C21	C22	C17	120.0(3)
C1	N1	C5	119.5(3)		N3	C23	C24	122.0(3)
C5	N1	Ir1	115.9(2)		C23	C24	C25	120.3(3)
C12	N2	Ir1	125.1(2)		C24	C25	C29	122.2(3)
C12	N2	C16	119.2(3)		C26	C25	C24	116.6(3)
C16	N2	Ir1	115.7(2)		C26	C25	C29	121.1(3)
C23	N3	Ir1	126.0(2)		C27	C26	C25	120.6(3)
C23	N3	C27	118.4(3)		N3	C27	C26	121.8(3)
C27	N3	Ir1	115.3(2)		N3	C27	C28	115.3(3)
N1	C1	C2	122.5(3)		C26	C27	C28	122.9(3)
C1	C2	C3	119.3(3)		O1	C28	C27	115.6(3)
C4	C3	C2	118.7(3)		O2	C28	O1	126.1(3)
C3	C4	C5	120.2(3)		O2	C28	C27	118.3(3)
N1	C5	C4	119.8(3)		C30	C29	C25	122.1(3)
N1	C5	C6	114.1(3)		C34	C29	C25	118.0(3)
C4	C5	C6	126.2(3)		C34	C29	C30	120.0(3)
C7	C6	C5	114.7(3)		C29	C30	C35	124.3(3)
C11	C6	C5	123.2(3)		C31	C30	C29	117.4(3)
C11	C6	C7	122.0(3)		C31	C30	C35	118.2(3)
C6	C7	Ir1	114.6(2)		C32	C31	C30	122.4(3)
C8	C7	Ir1	128.8(2)		C31	C32	C33	119.7(3)
C8	C7	C6	116.6(3)		C32	C33	C34	119.2(3)
C9	C8	C7	121.6(3)		C29	C34	C33	121.3(3)
C8	C9	C10	120.4(3)		N4	C1S	C2S	169.5(11)
C11	C10	C9	119.9(3)		N4A	C1SB	C2S	171.9(10)
C10	C11	C6	119.5(3)					

Table S6. Selected bond lengths for **5**·CH_3CN.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.1423(14)		C9	C10	1.378(3)
Ir1	N1	2.0407(17)		C10	C11	1.373(3)
Ir1	N2	2.0424(17)		C12	C13	1.381(3)
Ir1	N3	2.1304(17)		C13	C14	1.382(3)
Ir1	C7	2.004(2)		C14	C15	1.384(3)
Ir1	C18	1.988(2)		C15	C16	1.398(3)
F1	C11	1.360(3)		C16	C17	1.461(3)
F2	C9	1.364(3)		C17	C18	1.425(3)
F3	C20	1.360(3)		C17	C22	1.391(3)
F4	C22	1.355(2)		C18	C19	1.401(3)
O1	C28	1.289(2)		C19	C20	1.371(3)
O2	C28	1.224(2)		C20	C21	1.385(3)
N1	C1	1.350(3)		C21	C22	1.377(3)
N1	C5	1.366(3)		C23	C24	1.377(3)
N2	C12	1.346(3)		C24	C25	1.393(3)
N2	C16	1.370(3)		C25	C26	1.396(3)
N3	C23	1.344(3)		C25	C29	1.476(3)
N3	C27	1.348(3)		C26	C27	1.380(3)
C1	C2	1.384(3)		C27	C28	1.520(3)
C2	C3	1.381(3)		C29	C30	1.403(3)
C3	C4	1.382(3)		C29	C34	1.396(3)
C4	C5	1.399(3)		C30	C31	1.383(3)
C5	C6	1.463(3)		C31	C32	1.388(4)
C6	C7	1.422(3)		C32	C33	1.384(4)
C6	C11	1.391(3)		C33	C34	1.391(3)
C7	C8	1.400(3)		N4	C1S	1.133(4)
C8	C9	1.379(3)		C1S	C2S	1.452(4)

Table S6. Selected bond angles for **5**·CH_3CN.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	Ir1	O1	89.30(6)		F1	C11	C10	116.5(2)
N1	Ir1	N2	173.43(7)		C10	C11	C6	123.4(2)
N1	Ir1	N3	98.15(7)		N2	C12	C13	122.6(2)
N2	Ir1	O1	95.41(6)		C12	C13	C14	118.4(2)
N2	Ir1	N3	87.40(7)		C13	C14	C15	119.9(2)
N3	Ir1	O1	76.92(6)		C14	C15	C16	119.7(2)
C7	Ir1	O1	97.69(7)		N2	C16	C15	119.84(19)
C7	Ir1	N1	80.30(8)		N2	C16	C17	113.15(18)
C7	Ir1	N2	94.50(8)		C15	C16	C17	126.82(19)
C7	Ir1	N3	174.45(7)		C18	C17	C16	115.30(18)
C18	Ir1	O1	174.64(7)		C22	C17	C16	126.17(19)
C18	Ir1	N1	94.90(8)		C22	C17	C18	118.40(19)
C18	Ir1	N2	80.68(8)		C17	C18	Ir1	114.23(15)
C18	Ir1	N3	99.14(7)		C19	C18	Ir1	127.36(15)
C18	Ir1	C7	86.32(8)		C19	C18	C17	118.41(19)
C28	O1	Ir1	116.50(13)		C20	C19	C18	119.7(2)
C1	N1	Ir1	124.14(14)		F3	C20	C19	119.0(2)
C1	N1	C5	119.46(18)		F3	C20	C21	117.5(2)
C5	N1	Ir1	116.40(14)		C19	C20	C21	123.6(2)
C12	N2	Ir1	124.55(14)		C22	C21	C20	116.3(2)
C12	N2	C16	119.53(18)		F4	C22	C17	120.1(2)
C16	N2	Ir1	115.92(14)		F4	C22	C21	116.4(2)
C23	N3	Ir1	127.15(14)		C21	C22	C17	123.5(2)
C23	N3	C27	118.35(18)		N3	C23	C24	122.2(2)
C27	N3	Ir1	114.20(14)		C23	C24	C25	120.3(2)
N1	C1	C2	122.3(2)		C24	C25	C26	116.88(19)
C3	C2	C1	118.9(2)		C24	C25	C29	121.5(2)
C2	C3	C4	119.3(2)		C26	C25	C29	121.67(19)
C3	C4	C5	120.2(2)		C27	C26	C25	120.07(19)
N1	C5	C4	119.8(2)		N3	C27	C26	122.13(19)
N1	C5	C6	113.10(18)		N3	C27	C28	115.78(18)
C4	C5	C6	127.0(2)		C26	C27	C28	122.07(18)
C7	C6	C5	115.35(18)		O1	C28	C27	115.28(18)
C11	C6	C5	126.1(2)		O2	C28	O1	125.5(2)
C11	C6	C7	118.5(2)		O2	C28	C27	119.18(18)
C6	C7	Ir1	114.15(15)		C30	C29	C25	120.3(2)
C8	C7	Ir1	126.96(16)		C34	C29	C25	120.68(19)
C8	C7	C6	118.88(19)		C34	C29	C30	119.0(2)
C9	C8	C7	118.7(2)		C31	C30	C29	120.5(2)
F2	C9	C8	117.9(2)		C30	C31	C32	120.2(2)
F2	C9	C10	117.9(2)		C33	C32	C31	119.8(2)
C10	C9	C8	124.2(2)		C32	C33	C34	120.5(2)
C11	C10	C9	116.3(2)		C33	C34	C29	120.0(2)
F1	C11	C6	120.1(2)		N4	C1S	C2S	178.1(3)

Table S7. Selected bond lengths for **6**·¾CH_2Cl_2.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.1619(19)		C24	C25	1.394(4)
Ir1	N1	2.034(2)		C25	C26	1.462(5)
Ir1	N2	2.045(2)		C26	C27	1.420(4)
Ir1	N3	2.123(2)		C26	C31	1.394(4)
Ir1	C7	1.989(3)		C27	C28	1.398(4)
Ir1	C27	2.001(3)		C28	C29	1.376(5)
F1	C11	1.353(3)		C29	C30	1.375(5)
F2	C9	1.358(3)		C30	C31	1.374(5)
F3	C31	1.361(4)		C32	C33	1.381(4)
F4	C29	1.364(4)		C33	C34	1.403(4)
O1	C37	1.277(3)		C34	C35	1.400(4)
O2	C37	1.233(3)		C34	C38	1.481(4)
N1	C1	1.351(4)		C35	C36	1.386(4)
N1	C5	1.373(4)		C36	C37	1.521(4)
N2	C21	1.344(4)		C38	C39	1.399(4)
N2	C25	1.370(4)		C38	C43	1.399(4)
N3	C32	1.340(4)		C39	C40	1.386(4)
N3	C36	1.348(3)		C40	C41	1.400(4)
C1	C2	1.380(5)		C41	C42	1.399(4)
C2	C3	1.391(5)		C41	C44	1.480(4)
C3	C4	1.385(5)		C42	C43	1.385(4)
C4	C5	1.398(4)		C44	C45	1.397(4)
C5	C6	1.455(4)		C44	C49	1.398(4)
C6	C7	1.426(4)		C45	C46	1.393(5)
C6	C11	1.398(4)		C46	C47	1.384(5)
C7	C8	1.398(4)		C47	C48	1.388(5)
C8	C9	1.382(4)		C48	C49	1.392(5)
C9	C10	1.375(4)		Cl1	C1S	1.779(8)
C10	C11	1.376(4)		Cl2	C1S	1.736(9)
C21	C22	1.381(4)		Cl3	C2S	1.804(7)
C22	C23	1.391(5)		C2S	$Cl3^1$	1.804(7)
C23	C24	1.374(5)				

Table S8. Selected bond angles for **6**·¾CH_2Cl_2.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	Ir1	O1	95.65(9)		N2	C25	C24	120.0(3)
N1	Ir1	N2	171.31(10)		N2	C25	C26	113.4(3)
N1	Ir1	N3	90.13(10)		C24	C25	C26	126.6(3)
N2	Ir1	O1	90.80(8)		C27	C26	C25	115.2(3)
N2	Ir1	N3	97.05(10)		C31	C26	C25	126.6(3)
N3	Ir1	O1	76.61(8)		C31	C26	C27	118.2(3)
C7	Ir1	O1	172.93(9)		C26	C27	Ir1	114.7(2)
C7	Ir1	N1	80.93(11)		C28	C27	Ir1	126.6(2)
C7	Ir1	N2	93.27(10)		C28	C27	C26	118.8(3)
C7	Ir1	N3	97.13(10)		C29	C28	C27	119.2(3)
C7	Ir1	C27	87.97(11)		F4	C29	C28	118.2(3)
C27	Ir1	O1	98.42(9)		F4	C29	C30	117.7(3)
C27	Ir1	N1	92.83(11)		C30	C29	C28	124.1(3)
C27	Ir1	N2	80.44(11)		C31	C30	C29	116.0(3)
C27	Ir1	N3	174.46(10)		F3	C31	C26	119.7(3)
C37	O1	Ir1	116.37(17)		F3	C31	C30	116.7(3)
C1	N1	Ir1	123.9(2)		C30	C31	C26	123.7(3)
C1	N1	C5	119.9(3)		N3	C32	C33	122.4(3)
C5	N1	Ir1	116.00(19)		C32	C33	C34	120.2(3)
C21	N2	Ir1	124.0(2)		C33	C34	C38	121.1(3)
C21	N2	C25	119.6(3)		C35	C34	C33	116.7(3)
C25	N2	Ir1	116.1(2)		C35	C34	C38	122.2(3)
C32	N3	Ir1	126.16(19)		C36	C35	C34	119.9(3)
C32	N3	C36	118.4(2)		N3	C36	C35	122.4(3)
C36	N3	Ir1	115.44(18)		N3	C36	C37	115.3(2)
N1	C1	C2	122.3(3)		C35	C36	C37	122.3(2)
C1	C2	C3	118.7(3)		O1	C37	C36	115.9(2)
C4	C3	C2	119.4(3)		O2	C37	O1	125.4(3)
C3	C4	C5	120.2(3)		O2	C37	C36	118.7(3)
N1	C5	C4	119.5(3)		C39	C38	C34	120.9(3)
N1	C5	C6	113.0(3)		C39	C38	C43	118.2(3)
C4	C5	C6	127.5(3)		C43	C38	C34	120.9(3)
C7	C6	C5	115.7(2)		C40	C39	C38	121.1(3)
C11	C6	C5	126.7(3)		C39	C40	C41	120.8(3)
C11	C6	C7	117.7(3)		C40	C41	C44	121.1(3)
C6	C7	Ir1	114.1(2)		C42	C41	C40	117.9(3)
C8	C7	Ir1	126.6(2)		C42	C41	C44	120.9(3)
C8	C7	C6	119.3(2)		C43	C42	C41	121.4(3)
C9	C8	C7	119.0(3)		C42	C43	C38	120.6(3)
F2	C9	C8	118.4(3)		C45	C44	C41	121.3(3)
F2	C9	C10	117.9(3)		C45	C44	C49	118.8(3)
C10	C9	C8	123.7(3)		C49	C44	C41	119.9(3)
C9	C10	C11	116.6(3)		C46	C45	C44	120.5(3)
F1	C11	C6	119.5(3)		C47	C46	C45	120.0(3)
F1	C11	C10	116.9(3)		C46	C47	C48	120.1(3)
C10	C11	C6	123.6(3)		C47	C48	C49	120.0(3)
N2	C21	C22	122.3(3)		C48	C49	C44	120.5(3)
C21	C22	C23	118.6(3)		Cl2	C1S	Cl1	111.7(5)
C24	C23	C22	119.5(3)		Cl3	C2S	$Cl3^1$	103.1(6)
C23	C24	C25	120.1(3)					

Table S9. Selected bond lengths for **7**·CH_2Cl_2.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.160(2)		C16	C17	1.465(5)
Ir1	N1	2.039(3)		C17	C18	1.428(5)
Ir1	N2	2.029(3)		C17	C22	1.388(5)
Ir1	N3	2.135(3)		C18	C19	1.400(5)
Ir1	C7	2.004(4)		C19	C20	1.382(5)
Ir1	C18	1.993(3)		C20	C21	1.376(6)
F1	C9	1.356(5)		C21	C22	1.366(6)
F2	C11	1.362(5)		C23	C24	1.380(6)
F3	C20	1.365(4)		C24	C25	1.399(5)
F4	C22	1.358(4)		C25	C26	1.396(5)
O1	C28	1.281(5)		C25	C29	1.505(5)
O2	C28	1.232(4)		C25	C29A	1.470(10)
N1	C1	1.347(4)		C26	C27	1.380(5)
N1	C5	1.379(5)		C27	C28	1.519(5)
N2	C12	1.340(5)		C29	C30	1.3900
N2	C16	1.370(5)		C29	C34	1.3900
N3	C23	1.341(4)		C30	C31	1.3900
N3	C27	1.353(4)		C30	C35	1.514(7)
C1	C2	1.382(5)		C31	C32	1.3900
C2	C3	1.381(6)		C32	C33	1.3900
C3	C4	1.382(6)		C33	C34	1.3900
C4	C5	1.397(5)		C29A	C30A	1.3900
C5	C6	1.457(5)		C29A	C34A	1.3900
C6	C7	1.411(6)		C30A	C31A	1.3900
C6	C11	1.389(6)		C30A	C35A	1.512(9)
C7	C8	1.412(5)		C31A	C32A	1.3900
C8	C9	1.377(6)		C32A	C33A	1.3900
C9	C10	1.370(7)		C33A	C34A	1.3900
C10	C11	1.373(6)		Cl1	C2S	1.765(5)
C12	C13	1.379(6)		Cl2	C2S	1.779(5)
C13	C14	1.375(7)		Cl3	C1S	1.764(4)
C14	C15	1.379(6)		Cl4	C1S	1.760(4)
C15	C16	1.387(5)		Cl5	C1S	1.764(4)

Table S10. Selected bond angles for **7**·CH_2Cl_2.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	Ir1	O1	86.47(10)		C18	C17	C16	115.4(3)
N1	Ir1	N3	96.72(11)		C22	C17	C16	126.2(3)
N2	Ir1	O1	96.64(11)		C22	C17	C18	118.4(4)
N2	Ir1	N1	173.37(12)		C17	C18	Ir1	114.4(3)
N2	Ir1	N3	89.70(13)		C19	C18	Ir1	126.6(3)
N3	Ir1	O1	76.75(10)		C19	C18	C17	119.0(3)
C7	Ir1	O1	97.53(13)		C20	C19	C18	118.5(4)
C7	Ir1	N1	80.25(14)		F3	C20	C19	117.9(4)
C7	Ir1	N2	93.52(15)		F3	C20	C21	118.2(3)
C7	Ir1	N3	173.74(12)		C21	C20	C19	123.9(4)
C18	Ir1	O1	175.10(12)		C22	C21	C20	116.9(3)
C18	Ir1	N1	96.79(13)		F4	C22	C17	120.0(4)
C18	Ir1	N2	80.50(14)		F4	C22	C21	116.7(3)
C18	Ir1	N3	99.19(12)		C21	C22	C17	123.3(4)
C18	Ir1	C7	86.64(14)		N3	C23	C24	122.5(3)
C28	O1	Ir1	116.0(2)		C23	C24	C25	120.8(4)
C1	N1	Ir1	124.3(3)		C24	C25	C29	124.3(4)
C1	N1	C5	119.3(3)		C24	C25	C29A	116.9(7)
C5	N1	Ir1	116.4(2)		C26	C25	C24	115.8(4)
C12	N2	Ir1	122.9(3)		C26	C25	C29	119.8(4)
C12	N2	C16	119.6(3)		C26	C25	C29A	127.1(7)
C16	N2	Ir1	117.2(3)		C27	C26	C25	121.0(3)
C23	N3	Ir1	127.3(2)		N3	C27	C26	122.1(3)
C23	N3	C27	117.8(3)		N3	C27	C28	115.3(3)
C27	N3	Ir1	114.8(2)		C26	C27	C28	122.5(3)
N1	C1	C2	122.5(4)		O1	C28	C27	116.1(3)
C3	C2	C1	119.2(4)		O2	C28	O1	124.8(4)
C2	C3	C4	118.9(4)		O2	C28	C27	119.1(4)
C3	C4	C5	120.8(4)		C30	C29	C25	122.3(3)
N1	C5	C4	119.3(3)		C30	C29	C34	120.0
N1	C5	C6	112.9(3)		C34	C29	C25	117.5(3)
C4	C5	C6	127.7(4)		C29	C30	C35	123.5(4)
C7	C6	C5	115.7(3)		C31	C30	C29	120.0
C11	C6	C5	125.8(4)		C31	C30	C35	116.3(4)
C11	C6	C7	118.5(4)		C30	C31	C32	120.0
C6	C7	Ir1	114.7(3)		C33	C32	C31	120.0
C6	C7	C8	118.8(4)		C32	C33	C34	120.0
C8	C7	Ir1	126.5(3)		C33	C34	C29	120.0
C9	C8	C7	118.8(4)		C30A	C29A	C25	121.3(9)
F1	C9	C8	118.1(4)		C30A	C29A	C34A	120.0
F1	C9	C10	118.2(4)		C34A	C29A	C25	118.6(9)
C10	C9	C8	123.7(4)		C29A	C30A	C35A	122.0(12)
C9	C10	C11	116.8(4)		C31A	C30A	C29A	120.0
F2	C11	C6	120.3(4)		C31A	C30A	C35A	117.9(12)
F2	C11	C10	116.3(4)		C30A	C31A	C32A	120.0
C10	C11	C6	123.4(4)		C33A	C32A	C31A	120.0
N2	C12	C13	122.0(4)		C32A	C33A	C34A	120.0
C14	C13	C12	119.2(4)		C33A	C34A	C29A	120.0
C13	C14	C15	119.1(4)		Cl4	C1S	Cl3	107.1(4)
C14	C15	C16	120.4(4)		Cl4	C1S	Cl5	110.3(4)
N2	C16	C15	119.6(4)		Cl5	C1S	Cl3	111.8(4)
N2	C16	C17	112.3(3)		Cl1	C2S	Cl2	109.1(4)
C15	C16	C17	128.1(3)					

Table S11. Selected bond lengths for **8**·CH_3OH.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.152(3)		C22	C23	1.380(8)
Ir1	N1	2.037(3)		C23	C24	1.370(8)
Ir1	N2	2.029(3)		C24	C25	1.400(6)
Ir1	N3	2.135(3)		C25	C26	1.459(6)
Ir1	C7	2.001(4)		C26	C27	1.429(5)
Ir1	C27	1.987(4)		C26	C31	1.389(6)
F1	C11	1.370(5)		C27	C28	1.383(6)
F2	C9	1.353(5)		C28	C29	1.383(6)
F3	C31	1.372(5)		C29	C30	1.373(7)
F4	C29	1.349(6)		C30	C31	1.376(7)
O1	C37	1.277(4)		C32	C33	1.386(5)
O2	C37	1.235(5)		C33	C34	1.392(5)
N1	C1	1.335(5)		C34	C35	1.389(5)
N1	C5	1.381(5)		C34	C38	1.500(5)
N2	C21	1.339(6)		C35	C36	1.380(5)
N2	C25	1.368(5)		C36	C37	1.514(5)
N3	C32	1.336(5)		C38	C39	1.359(6)
N3	C36	1.353(5)		C38	C43	1.411(6)
C1	C2	1.384(6)		C39	C40	1.440(6)
C2	C3	1.373(7)		C39	C44	1.489(6)
C3	C4	1.377(7)		C40	C41	1.386(7)
C4	C5	1.394(6)		C40	C45	1.512(6)
C5	C6	1.460(6)		C41	C42	1.385(6)
C6	C7	1.419(5)		C42	C43	1.402(6)
C6	C11	1.395(6)		C42	C46	1.503(7)
C7	C8	1.398(6)		C43	C47	1.505(6)
C8	C9	1.383(6)		O1S	C1S	1.409(6)
C9	C10	1.375(7)		O2SA	C2S	1.403(6)
C10	C11	1.362(7)		O2SB	C2S	1.400(7)
C21	C22	1.386(6)				

Table S12. Selected bond angles for **8**·CH_3OH.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	Ir1	O1	87.39(11)		C24	C23	C22	119.8(4)
N1	Ir1	N3	97.24(12)		C23	C24	C25	120.0(5)
N2	Ir1	O1	95.73(12)		N2	C25	C24	119.6(4)
N2	Ir1	N1	174.04(12)		N2	C25	C26	112.6(4)
N2	Ir1	N3	88.42(12)		C24	C25	C26	127.8(4)
N3	Ir1	O1	77.02(11)		C27	C26	C25	115.8(4)
C7	Ir1	O1	95.30(13)		C31	C26	C25	126.2(4)
C7	Ir1	N1	80.98(14)		C31	C26	C27	118.0(4)
C7	Ir1	N2	93.65(14)		C26	C27	Ir1	113.7(3)
C7	Ir1	N3	172.21(14)		C28	C27	Ir1	127.1(3)
C27	Ir1	O1	172.35(12)		C28	C27	C26	118.8(4)
C27	Ir1	N1	96.52(14)		C27	C28	C29	119.6(4)
C27	Ir1	N2	80.98(15)		F4	C29	C28	118.7(4)
C27	Ir1	N3	95.93(13)		F4	C29	C30	117.6(4)
C27	Ir1	C7	91.81(15)		C30	C29	C28	123.7(5)
C37	O1	Ir1	116.6(2)		C29	C30	C31	116.2(4)
C1	N1	Ir1	124.6(3)		F3	C31	C26	118.7(4)
C1	N1	C5	120.0(3)		F3	C31	C30	117.5(4)
C5	N1	Ir1	115.4(3)		C30	C31	C26	123.8(4)
C21	N2	Ir1	123.5(3)		N3	C32	C33	122.8(4)
C21	N2	C25	119.7(4)		C32	C33	C34	119.8(4)
C25	N2	Ir1	116.6(3)		C33	C34	C38	122.8(3)
C32	N3	Ir1	127.9(3)		C35	C34	C33	117.1(3)
C32	N3	C36	117.7(3)		C35	C34	C38	120.1(3)
C36	N3	Ir1	114.2(2)		C36	C35	C34	120.1(3)
N1	C1	C2	122.3(4)		N3	C36	C35	122.5(3)
C3	C2	C1	118.4(4)		N3	C36	C37	116.0(3)
C2	C3	C4	120.2(4)		C35	C36	C37	121.4(3)
C3	C4	C5	120.0(4)		O1	C37	C36	116.0(3)
N1	C5	C4	119.0(4)		O2	C37	O1	125.9(3)
N1	C5	C6	113.8(3)		O2	C37	C36	118.0(3)
C4	C5	C6	127.3(4)		C39	C38	C34	117.3(4)
C7	C6	C5	115.2(3)		C39	C38	C43	123.3(4)
C11	C6	C5	127.1(4)		C43	C38	C34	119.3(4)
C11	C6	C7	117.6(4)		C38	C39	C40	117.7(4)
C6	C7	Ir1	114.3(3)		C38	C39	C44	124.6(4)
C8	C7	Ir1	126.4(3)		C40	C39	C44	117.7(4)
C8	C7	C6	119.2(4)		C39	C40	C45	121.4(4)
C9	C8	C7	119.2(4)		C41	C40	C39	119.0(4)
F2	C9	C8	118.6(5)		C41	C40	C45	119.6(4)
F2	C9	C10	118.2(4)		C42	C41	C40	122.6(4)
C10	C9	C8	123.2(4)		C41	C42	C43	118.6(4)
C11	C10	C9	116.8(4)		C41	C42	C46	118.8(4)
F1	C11	C6	119.2(4)		C43	C42	C46	122.6(4)
C10	C11	F1	116.8(4)		C38	C43	C47	121.7(4)
C10	C11	C6	124.0(4)		C42	C43	C38	118.7(4)
N2	C21	C22	122.3(5)		C42	C43	C47	119.6(4)
C23	C22	C21	118.5(5)					

S4 Orbital Contributions

Density functional theory (DFT) calculations were carried out using the Gaussian 09 package (Gaussian, Inc)[3], all results were displayed using GaussView[4] and GaussSum[5]. All calculations used the B3LYP level set employing a 3-21G*/LANL2DZ basis set, geometrically optimised in a DCM solvent field using the SCRF-PCM method.

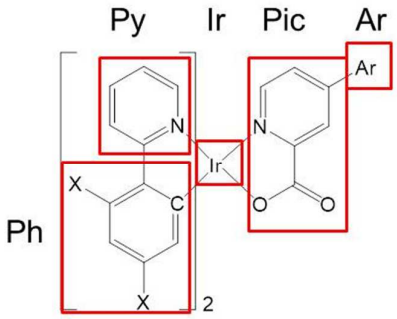


Figure S24. Molecular components of complexes **1-8**;where Ar = -Ph, -Biphen, -*o*Tol, or -Dur and x = -H or -F.

Table S13. Orbital contributions for $Ir(ppy)_2(pic)$

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)				
			Ir	Py	Ph	Pic	Ar
127	L+5	-0.91	2	55	9	34	N/A
126	L+4	-0.92	2	86	11	1	N/A
125	L+3	-1.18	1	31	4	64	N/A
124	L+2	-1.51	5	70	24	1	N/A
123	L+1	-1.57	5	59	25	11	N/A
122	LUMO	-1.73	2	8	3	87	N/A
121	HOMO	-5.29	45	6	43	5	N/A
120	H-1	-5.77	59	10	7	24	N/A
119	H-2	-6.11	61	16	17	6	N/A
118	H-3	-6.23	8	18	65	8	N/A
117	H-4	-6.5	4	21	70	5	N/A
116	H-5	-6.59	5	13	42	41	N/A

Table S14. Orbital contributions for $Ir(F_2ppy)_2(pic)$

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)				
			Ir	Py	Ph	Pic	Ar
143	L+5	-0.98	2	67	10	21	N/A
142	L+4	-0.99	2	81	10	7	N/A
141	L+3	-1.26	1	25	4	71	N/A
140	L+2	-1.65	5	70	25	1	N/A
139	L+1	-1.7	5	59	25	11	N/A
138	LUMO	-1.83	2	9	4	86	N/A
137	HOMO	-5.65	46	7	41	6	N/A
136	H-1	-5.98	55	10	8	27	N/A
135	H-2	-6.34	48	19	28	5	N/A
134	H-3	-6.46	10	26	57	7	N/A
133	H-4	-6.6	18	21	57	4	N/A
132	H-5	-6.72	3	3	32	62	N/A

Table S15. Orbital contributions for complex **1**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)				
			Ir	Py	Ph	Pic	Ar
147	L+5	-0.92	2	87	11	0	0
146	L+4	-0.94	2	68	11	18	2
145	L+3	-1.26	1	18	2	74	5
144	L+2	-1.51	5	70	24	1	0
143	L+1	-1.58	5	65	28	2	0
142	LUMO	-1.95	2	2	0	76	20
141	HOMO	-5.29	45	6	43	5	0
140	H-1	-5.77	59	10	7	24	0
139	H-2	-6.08	61	14	14	7	3
138	H-3	-6.23	6	19	68	8	0
137	H-4	-6.5	4	22	69	5	0
136	H-5	-6.59	3	13	45	39	1

Table S16. Orbital contributions for complex **2**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)				
			Ir	Py	Ph	Pic	Ar
167	L+5	-0.92	2	87	11	0	0
166	L+4	-0.96	2	70	11	11	6
165	L+3	-1.29	1	14	1	75	9
164	L+2	-1.51	5	70	24	1	0
163	L+1	-1.58	4	65	28	1	1
162	LUMO	-2.03	2	1	0	68	29
161	HOMO	-5.29	45	6	43	5	0
160	H-1	-5.77	59	10	7	24	0
139	H-2	-6.08	61	14	14	7	3
138	H-3	-6.23	6	19	68	8	0
137	H-4	-6.5	4	22	69	5	0
136	H-5	-6.59	3	13	45	39	1

Table S17. Orbital contributions for complex **3**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)				
			Ir	Py	Ph	Pic	Ar
151	L+5	-0.92	1	67	10	21	2
150	L+4	-0.93	2	78	9	10	1
149	L+3	-1.18	1	30	3	62	4
148	L+2	-1.5	5	70	25	1	0
147	L+1	-1.58	5	64	28	3	1
146	LUMO	-1.77	2	3	1	79	16
145	HOMO	-5.29	45	6	44	5	0
144	H-1	-5.85	59	9	7	25	0
143	H-2	-6.14	64	14	14	6	3
142	H-3	-6.25	5	18	62	14	0
141	H-4	-6.49	2	12	39	47	0
140	H-5	-6.53	5	20	51	23	1

Table S18. Orbital contributions for complex **4**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)				
			Ir	Py	Ph	Pic	Ar
163	L+5	-0.92	2	81	11	5	0
162	L+4	-0.92	2	65	9	22	1
161	L+3	-1.2	1	25	3	68	2
160	L+2	-1.51	5	70	24	1	0
159	L+1	-1.57	5	60	25	9	0
158	LUMO	-1.73	2	7	3	86	2
157	HOMO	-5.29	45	6	43	5	0
156	H-1	-5.76	59	10	7	24	0
155	H-2	-6.11	62	16	16	6	0
154	H-3	-6.23	7	19	66	8	0
153	H-4	-6.31	0	0	0	0	100
152	H-5	-6.5	4	21	70	5	0

Table S19. Orbital contributions for complex **5**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)				
			Ir	Py	Ph	Pic	Ar
163	L+5	-0.98	2	86	11	1	0
162	L+4	-1	2	72	11	14	2
161	L+3	-1.34	1	15	2	77	5
160	L+2	-1.64	5	70	25	1	0
159	L+1	-1.71	5	65	28	2	0
158	LUMO	-2.05	2	2	1	77	19
157	HOMO	-5.65	46	7	41	6	0
156	H-1	-5.98	55	10	8	27	0
155	H-2	-6.3	53	16	20	7	4
154	H-3	-6.45	6	27	59	7	1
153	H-4	-6.58	10	22	62	4	2
152	H-5	-6.72	2	2	35	60	0

Table S20. Orbital contributions for complex **6**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)				
			Ir	Py	Ph	Pic	Ar
183	L+5	-0.98	2	87	11	0	0
182	L+4	-1.01	2	72	12	10	5
181	L+3	-1.37	1	12	1	77	9
180	L+2	-1.64	5	70	25	1	0
179	L+1	-1.71	4	66	28	1	0
178	LUMO	-2.12	2	1	0	70	27
177	HOMO	-5.65	46	7	41	6	0
176	H-1	-5.98	55	10	8	27	0
175	H-2	-6.25	45	11	12	9	24
174	H-3	-6.44	2	27	57	6	9
173	H-4	-6.52	4	14	46	4	31
172	H-5	-6.64	23	13	29	5	29

Table S21. Orbital contributions for complex **7**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)				
			Ir	Py	Ph	Pic	Ar
167	L+5	-0.98	2	85	11	2	0
166	L+4	-1	2	69	10	17	2
165	L+3	-1.31	1	18	2	74	5
164	L+2	-1.64	5	70	25	1	0
163	L+1	-1.71	5	65	27	3	0
162	LUMO	-1.95	2	3	1	82	12
161	HOMO	-5.65	46	7	41	6	0
160	H-1	-5.98	55	10	8	27	0
159	H-2	-6.31	52	16	22	7	3
158	H-3	-6.45	7	27	59	7	1
157	H-4	-6.59	12	21	61	4	3
156	H-5	-6.72	2	3	34	61	0

Table S22. Orbital contributions for complex **8**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)				
			Ir	Py	Ph	Pic	Ar
179	L+5	-0.98	1	79	11	8	0
178	L+4	-0.99	2	72	10	16	1
177	L+3	-1.28	1	21	3	72	2
176	L+2	-1.65	5	70	24	1	0
175	L+1	-1.7	5	59	25	10	0
174	LUMO	-1.83	2	8	3	85	2
173	HOMO	-5.65	46	7	41	6	0
172	H-1	-5.98	55	10	8	27	0
171	H-2	-6.33	0	0	0	0	100
170	H-3	-6.33	49	18	26	6	0
169	H-4	-6.46	9	26	57	8	0
168	H-5	-6.6	16	21	58	4	0

S5. Physical Measurements

Instrumentation. All the photophysical measurements of iridium complexes were performed using DCM as the solvent.

The UV-Visible spectra were measured on a Unicam UV2-100 spectrometer operated with the Unicam Vison software in quartz cuvettes with path length l = 1 cm.

Excitation and emission photoluminescence spectra were recorded on a Horiba Jobin Yvon SPEX Fluorolog 3-22 spectrofluorometer. Samples were degassed by repeated freeze-pump-thaw cycles using a turbomolecular pump until the pressure was stable in quartz cuvettes, l = 1 cm. The solutions had absorbance below 0.15 to minimise inner filter effects. PLQYs were measured following our previously reported method.[6]

Emission lifetimes were determined by using a custom spectrometer; measured by time-correlated single photon counting (TCSPC) using a pulsed diode laser (371 nm), made by IBH Ltd, running at 1 MHz. The fluorescence emission was collected at right angles to the excitation source. The emission wavelength was selected using a Horiba Jobin Yvon Triax 190 monochromator and detected by a cooled IBH TBX-04 PMT. Timing was achieved using an Ortec 567 time-to-amplitude converter and an E. G. & G Trumpcard pulse height analyser (PHA), and data was recorded using Maestro (ver.510) software. The data were transferred to a PC and analysed using non-linear regression to a single exponential decay, and the quality of fit established by reduced χ^2 and random residuals. The samples were degassed by repeated freeze-pump-thaw cycles in duplicates. The decay data were fitted to a single exponential function. Low temperature emission spectra and lifetime data were measured in a DN1704 optical cryostat (Oxford Instruments) with a ITC601 temperature controller (Oxford Instruments).

Electrochemical analyses of the iridium complexes were carried out using a PalmSens EmStat^2 potentiometer, with platinum working, platinum counter and platinum pseudo reference electrodes, from solutions in DCM containing 0.1 M supporting electrolyte (tetrabutylammonium hexafluorophospate, $TBAPF_6$), scan rate = 100 mV s^{-1}. The ferrocene/ferrocinium couple was used as the internal reference.

Low temperature emission

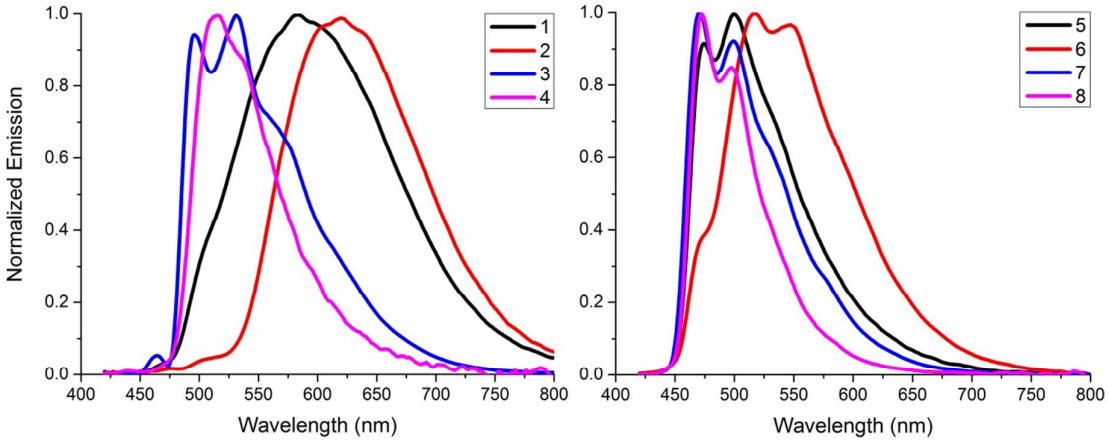


Figure S25. Emission spectra of complexes **1-8** recorded at 298K in methyl-tetrahydrofuran.

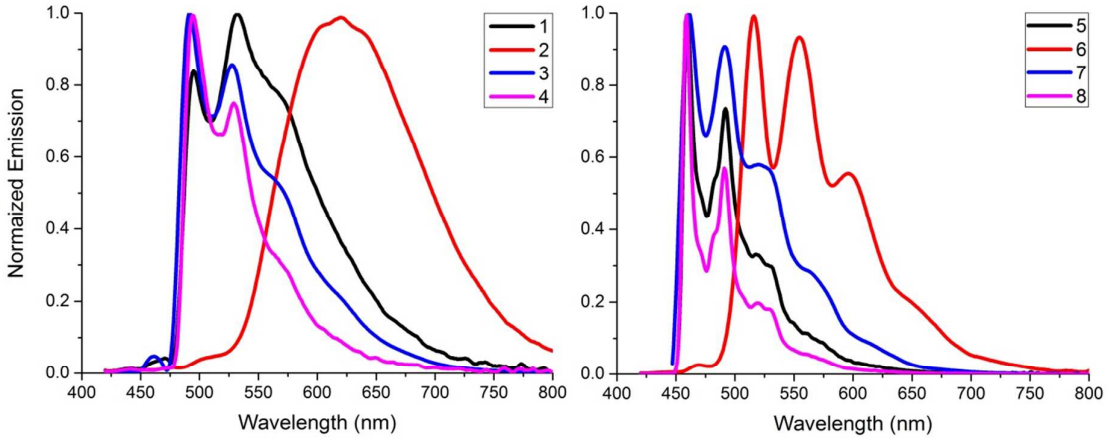


Figure S26. Emission spectra of complexes **1-8** recorded at 77K in methyl-tetrahydrofuran.

Lifetime

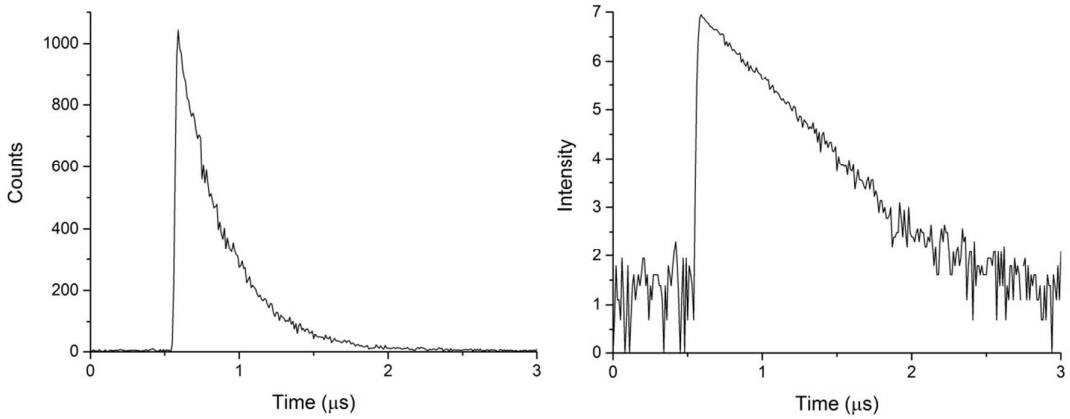


Figure S27. Lifetime traces for **1**, recorded in DCM.

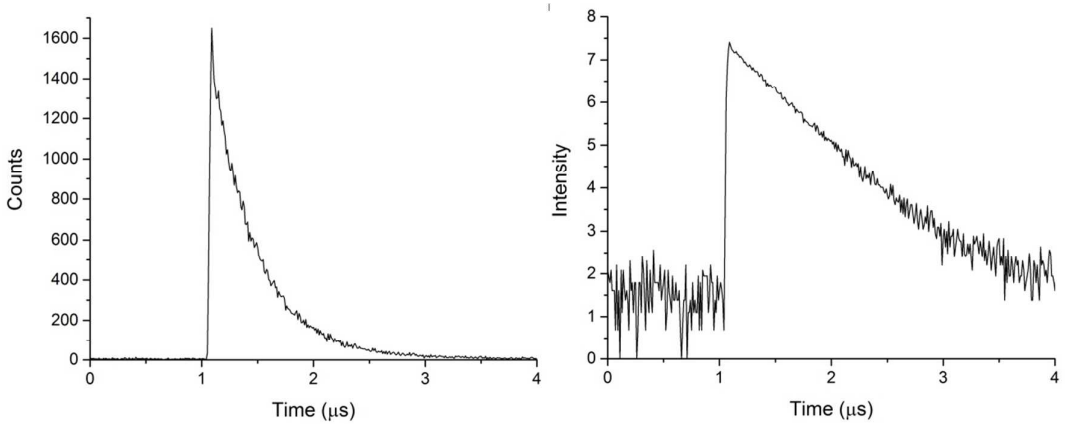


Figure S28. Lifetime traces for **2**, recorded in DCM.

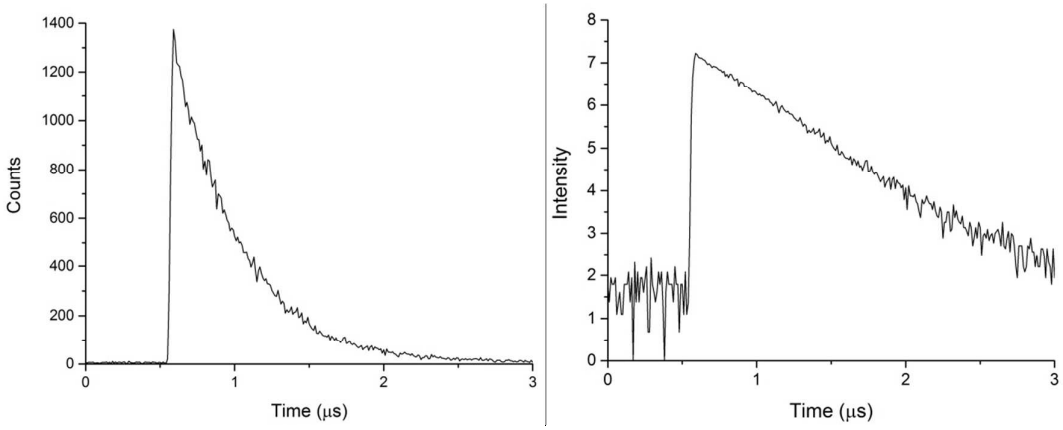


Figure S29. Lifetime traces for **3**, recorded in DCM.

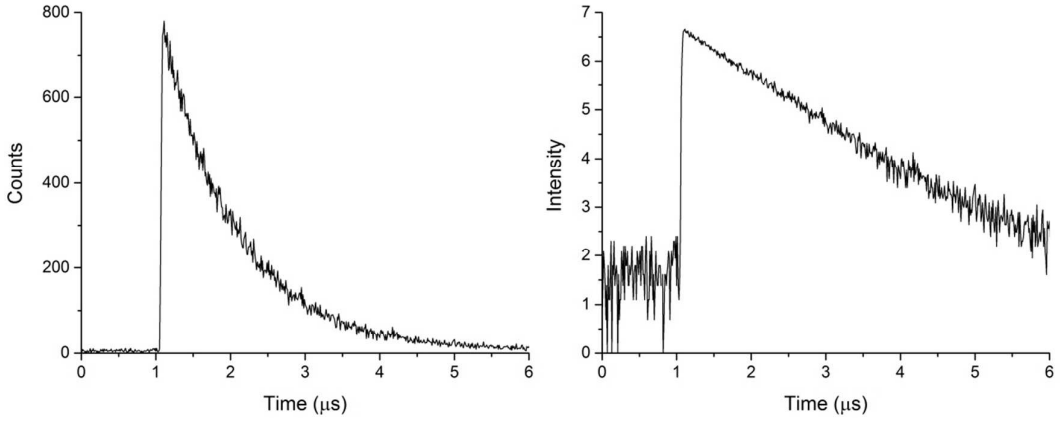


Figure S5.6. Lifetime traces for **4**, recorded in DCM.

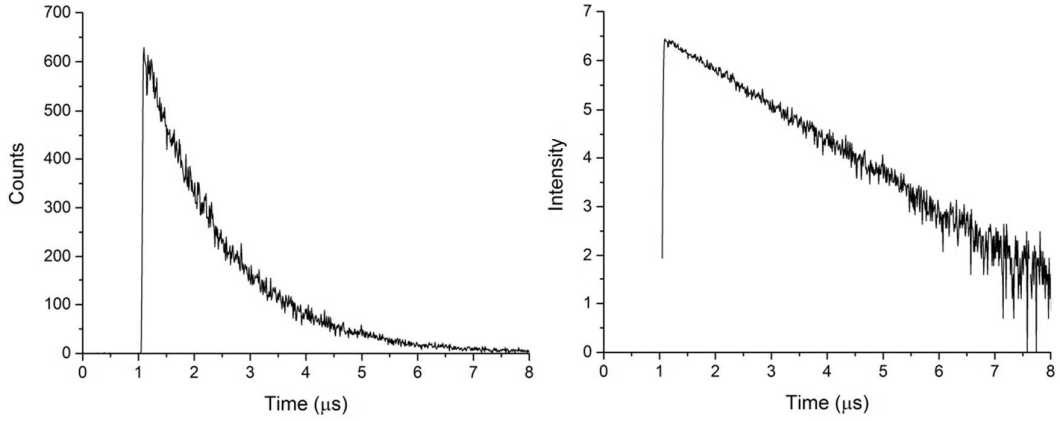


Figure S30. Lifetime traces for **5**, recorded in DCM.

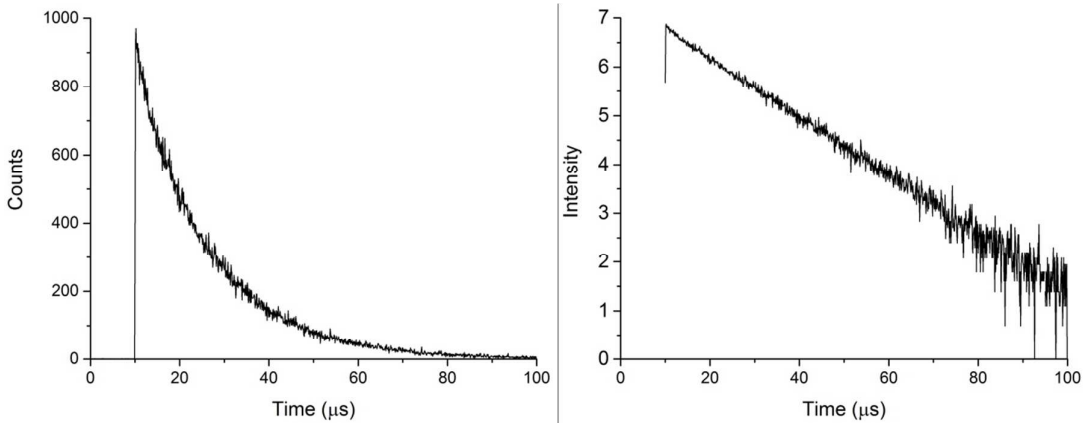


Figure S31. Lifetime traces for **6**, recorded in DCM.

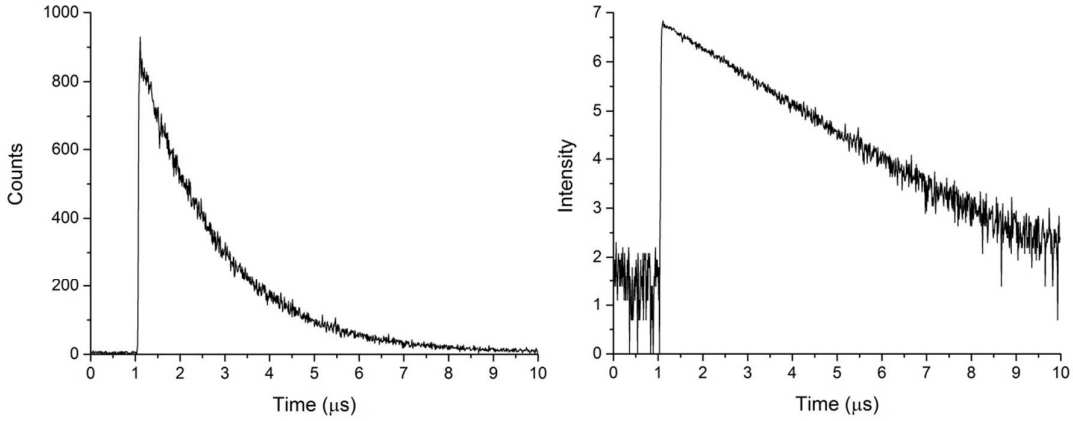


Figure S32. Lifetime traces for **7**, recorded in DCM.

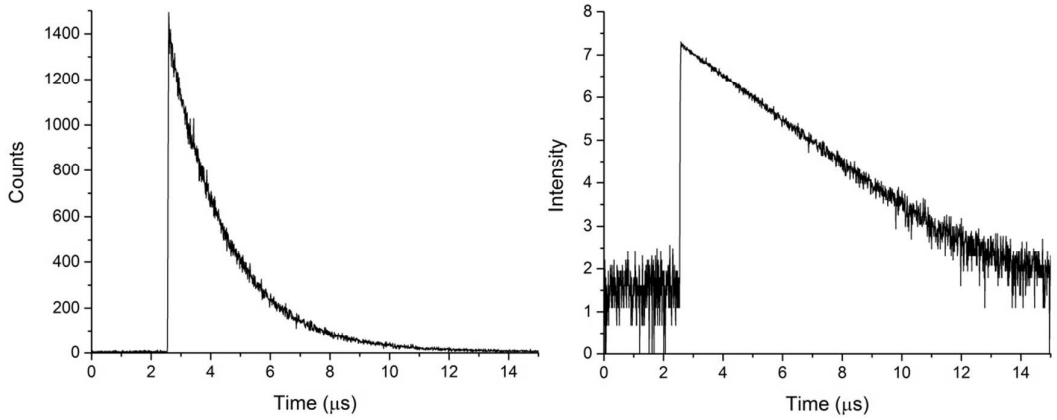


Figure S33. Lifetime traces for **8**, recorded in DCM.

Electrochemical data

Table 23. Electrochemical data for the iridium complexes **1**-**8**.

Complex	$E_{1/2}$ ($V_{Fc/Fc+}$)[1]	HOMO (eV)[2]	LUMO (eV)[3]
1	0.499	-4.824	-2.228
2	0.493	-4.820	-2.299
3	0.512	-4.839	-2.140
4	0.512	-4.840	-2.028
5	0.834	-5.145	-2.367
6	0.830	-5.154	-2.425
7	0.840	-5.154	-2.286
8	0.850	-5.181	-2.182

[1]Recorded in 1.0 M $TBAPF_6$ in DCM, [2]determind electrochemically, [3]determined by DFT.

S6. References

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