Supporting Information

Highly Potent Extranuclear-targeted Luminiscent Iridium(III) Antitumor Agents Containing Benzimidazole-based Ligands with a Handle for Functionalization

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Table of Contents

The C, H, and N analyses were performed with a Carlo Erba model EA 1108 microanalyzer. The ^{1}H and ^{13}C spectra were recorded on a Bruker AC 300E, Bruker AV 400, or Bruker AV 600 NMR spectrometer. Chemical shifts are cited relative to $SiMe_4$ (^{1}H and ^{13}C, external). ESI mass (positive mode) analyses were performed on a HPLC/MS TOF 6220. The isotopic distribution of the heaviest set of peaks matched very closely that calculated for the formulation of the complex cation in every case. UV/vis spectroscopy was carried out on a PerkinElmer Lambda 750 S spectrometer with operating software. Fluorescence measurements were carried out with a PerkinElmer LS 55 50 Hz fluorescence spectrometer.

Starting materials and reagents:

All synthetic manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried by the usual methods.

Substituted benzaldehydes, trifluoroacetic acid, magnesium sulfate, sodium sulfate, phen, bipy, and 2-(2-pyridyl)benzimidazole were obtained from Sigma-Aldrich (Madrid, Spain) and iridium chloride from Johnson Matthey. CDDP [purity ≥ 99.9% based on elemental and inductively coupled plasma mass spectroscopy (ICP-MS) trace analysis] and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich (Prague, Czech Republic). Stock solutions for cellular studies were prepared by dissolving the iridium compounds in DMSO to a final concentration of 5.10^{-3} M and serially diluted prior to testing in DMSO. To avoid DMSO toxicity, the final DMSO concentration in culture medium didn't exceed 0.4 % (v/v). CDDP stock solution was prepared by dissolving CDDP in ultrapure water (Milli-Q®, Merck Millipore) to a final concentration of 3.10^{-3} M.
Deuterated solvents were obtained from Euriso-top. Methyl 3-amino-4-(butylamino)benzoate was prepared as reported elsewhere.[1,2] The purity of all biologically evaluated molecules, based on elemental analysis, is >95%.

Synthesis and characterization of N^N ligands a and b: Methyl 3-amino-4-(butylamino)benzoate (1 mmol) was dissolved in ethanol (10 mL) in a round-bottom flask equipped with stirrer and nitrogen atmosphere. Respective benzaldehyde (1.2 mmol) was added at room temperature with constant stirring followed by addition of trifluoroacetic acid (0.1 mmol) and magnesium sulfate (5 mmol). The reaction mixture was stirred at room temperature for 24 h, and the progress of reaction was monitored by TLC. After complete conversion, reaction was filtered to remove magnesium sulfate. Filtrate was concentrated and then dissolved in dichloromethane. Dichloromethane was washed with water (2 × 10 mL) and brine (10 mL), dried on sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate−hexane (1:3) as eluent to obtain respective ligands (**a** and **b**) with good yield.

Methyl 1-butyl-2-(pyridin-2-yl)-1H-benzo[d]imidazole-5-carboxylate, a. Reported.[3] Anal. Calcd for $C_{18}H_{19}N_3O_2$: C, 69.88; H, 6.19; N, 13.58; Found: C, 70.12; H, 6.56; N, 12.87 (%).

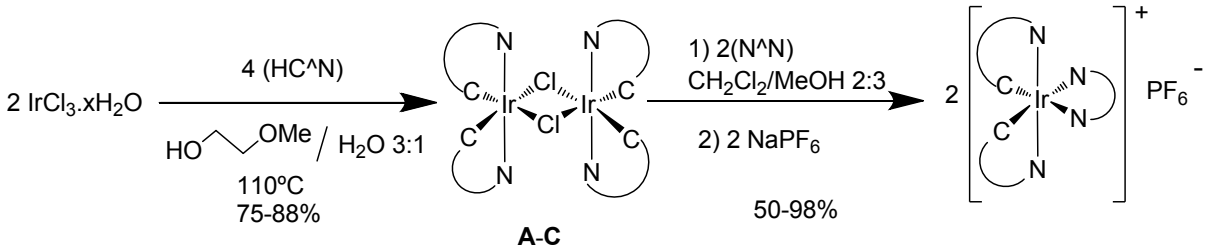
Methyl 1-butyl-2-(isoquinolin-3-yl)-1H-benzo[d]imidazole-5-carboxylate, b. White solid. Yield: 46%. Anal. Calcd for e $C_{22}H_{21}N_3O_2$: C, 73.52; H, 5.89; N, 11.69. Found: C, 73.25; H, 5.80; N, 11.60 (%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.57 (d, 1H, J = 1.2 Hz), 8.56 (d, 1H, J = 8.4 Hz), 8.28 (d, 1H, J = 8.5 Hz), 8.10 (d, 1H, J = 8.4 Hz), 8.06 (dd, 1H, J = 8.4, 1.4 Hz), 7.86 (dd, 1H, J = 8.2, 1.2 Hz), 7.75 (ddd, 1H, J = 8.2, 6.9, 1.2 Hz), 7.59 (ddd, J = 8.2, 6.9, 1.2, Hz, 1H), 7.48 (dd, J = 8.5, 0.4 Hz, 1H), 5.00 (m, 2H), 3.95 (s, 3H), 1.99 (m, 2H), 1.49 (m, 2H), 0.97 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 151.2, 149.8, 147.3, 141.8, 139.9, 136.7, 129.9, 129.6, 127.9, 127.8, 127.5, 125.0, 122.6, 121.9, 110.0, 52.1, 46.1, 32.3, 29.7, 20.3, 13.9. ESI-MS (pos ion mode, CH_2Cl_2): m/z 360.1764 ($[M + H]^+$).

Synthesis and characterization of Proligand HL^2: The *N*-benzylation was performed by reaction of 2-phenyl benzimidazole HL^1 (185 mg, 0.92 mmol) dissolved in acetonitrile (1 mL/ 0.1 mM benzimidazole) in a round-bottom flask equipped with stirrer and nitrogen atmosphere. Caesium carbonate (1.5 eq) and the 1-(bromomethyl)-4-(trifluoromethyl)benzene (1.05 eq) was added. The reaction mixture was stirred at room temperature for 3 h, and the progress of reaction was monitored by TLC. After completion of the reaction, reaction mixture was concentrated *in vacuo*. The residue was suspended in a mixture of CH_2Cl_2 and sat. $NaHCO_3$ (vol % 50:50, 10 mL/0.1 mmol benzimidazole). The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL/0.1 mmol benzimidazole). The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography using

cyclohexane: ethyl acetate to get pure 2-phenyl-1-(4-(trifluoromethyl)benzyl)-1H-benzo[d]imidazole (HL^2).

2-Phenyl-1-(4-(trifluoromethyl)benzyl)-1H-benzo[d]imidazole, HL^2. White solid. Yield: 94%. Anal. Calcd for HL^2 $C_{21}H_{15}F_3N_2$: C, 71.58; H, 4.29; N, 7.95. Found: C, 71.25; H, 4.52; N, 7.74 (%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, 1H, J = 8.0 Hz), 7.69 (d, 2H, J = 6.4 Hz), 7.63 (d, 2H, J = 8.4 Hz), 7.53 (m, 3H), 7.40 (m, 1H), 7.32 (m, 1H), 7.23 (m, 3H), 5.54 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 154.08, 143.21, 140.38, 135.76, 130.08, 129.80, 129.13, 128.85, 126.28, 126.12, 126.04, 123.27, 122.93, 120.20, 110.17, 76.99, 47.96. ESI-MS (pos ion mode, CH_2Cl_2): m/z = 353.12 ($[M + H]^+$).

Synthesis of dimer complexes $[(C\text{^}N)_2Ir(\mu\text{-}Cl)]_2$ A-C:



Scheme S1. Synthesis of dimer and momomer iridium(III) compounds.

2-Phenyl-1-(4-(trifluoromethyl)benzyl)-1H-benzo[d]imidazole (2.2 mmol) and iridium(III) chloride (1 mmol) was dissolved in a 2-ethoxyethanol/deionized H_2O (3:1) in a round bottom flask. The reaction was allowed to heat to reflux overnight under nitrogen protection. The mixture was cooled to ambient temperature and the resultant solid was collected by filtration. The solid was washed with water and ethanol. After drying we get the powdered iridium dimer **B**. The iridium dimers containing 2-phenyl benzimidazole (**A**) and 1-phenylpyrazole (**C)** were prepared in a similar way.
Dimer A. Reported.[4]

Dimer B. ESI-MS (pos ion mode, CH_2Cl_2): m/z = 895.18 ($[M/2\text{-}Cl_2]^+$). Anal. Calcd for $C_{84}H_{56}Cl_2F_{12}Ir_2N_8$: C, 54.22; H, 3.03; N, 6.02. Found: C, 54.11; H, 2.95; N, 6.11 (%). ^{1}H NMR (400 MHz, acetonitrile-d_3): δ 7.67 (m, 4H), 7.43 (m, 4H), 7.37 (m, 2H), 6.65 (m, 1H), 6.58 (m, 1H), 6.25 (brs, 1H), 6.15 (m, 1 H).

Dimer C. Reported.[5]

Synthesis and characterization of the final complexes 1a-c, 2a-c and 3a-c:

The corresponding iridium dimer (1.0 mmol) and respective N^N ligand (2.0 mmol) was dissolved in dichloromethane: methanol (2:3 vol) in round bottom flask equipped with stirrer and nitrogen atmosphere. Reaction was refluxed at 65 °C for 24 h. After completion of 24 h reaction was cooled to room temperature. And then sodium hexaflurophoshate ($NaPF_6$) (2.0 mmol) was added at room temperature and stir for 30 min. The solvent was concentrated under reduced pressure on rota vap. And then product was recrystallized using dichloromethane and ether with good 54-98 % yield.

Compound 1a. Orange solid. Yield: 89%. Anal. Calcd for $C_{44}H_{37}F_6IrN_7O_2P$: C, 51.16; H, 3.61; N, 9.49. Found: C, 51.02; H, 3.43; N, 9.21 (%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 14.02 (s, NH, 1H), 13.84 (s, NH, 1H), 8.73 (d, J = 8.4 Hz, 1H), 8.27 (td, J = 8.0, 1.2 Hz, 1H), 8.26 (d, J = 5.2 Hz, 1H), 8.09 (d, J = 8.8 Hz, 1H), 7.98 (dd, J = 8.4, 1.2 Hz, 1H), 7.93 (d, J = 6.8 Hz, 1H), 7.86 (d, J = 6.8 Hz, 1H), 7.79 (m, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.15 (m, 3H), 7.06 (m, 2H), 6.86 (m, 2H), 6.73 (t, J = 7.6 Hz, 1H), 6.36 (d, J = 7.6 Hz, 1H), 6.27 (d, J = 7.2 Hz, 1H), 5.58 (d, J = 8.4 Hz, 1H), 5.58 (d, J = 8.4 Hz, 1H), 5.01 (m, 2H), 3.68 (s, 3H), 1.67 (m, 2H), 0.98 (m, 2H), 0.63 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100.5 MHz, DMSO-d_6): δ 166.60, 165.60, 165.53, 155.66, 153.79, 152.33, 148.46, 148.05, 141.12, 140.60 (2C), 140.57, 140.36, 140.32, 135.89, 135.61, 134.68, 134.48, 133.42, 133.82, 131.71, 131.25, 130.15, 127.55, 127.34, 127.09, 125.84, 125.57, 124.61, 124.57, 124.48, 124.35, 123.30, 123.25, 121.40, 114.40 (3C), 114.28, 113.96, 53.19, 46.76, 32.88, 20.34, 16.49. ESI-MS (pos ion mode, CH_2Cl_2): m/z = 888.2706 $[M - PF_6]^+$.

Compound 1b. Reddish solid. Yield: 88%. Anal. Calcd for $C_{48}H_{39}F_6IrN_7O_2P$: C, 53.23; H, 3.63; N, 9.05. Found: C, 52.78; H, 3.57; N, 8,98 (%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.96 (s, NH, 1H), 13.83 (s, NH, 1H), 8.90 (d, J = 8.8 Hz, 1H), 8.71 (d, J = 8.8 Hz, 1H), 8.29 (d, J = 8.8 Hz, 1H), 8.15 (t, J = 7.2 Hz, 2H), 7.97 (dd, J = 8.8, 1.2 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.15 (m, 4H), 7.01 (t, J = 7.6 Hz, 1H), 6.85 (m, 3H), 6.75 (t, J = 8.0 Hz, 2H), 6.33 (d, J = 7.6 Hz, 1H), 6.15 (d, J = 7.6 Hz, 1H), 5.91 (d, J = 8.0 Hz, 1H), 5.67 (d, J = 7.6 Hz, 1H), 5.09 (m, 2H), 3.70 (s, 3H), 1.71 (m, 2H), 0.98 (m, 2H), 0.66 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100.5 MHz, DMSO-d_6): δ 166.73, 165.83, 165.03, 161.99, 157.58, 150.91, 149.91, 149.81, 147.87, 144.36, 143.61, 142.81, 140.76, 140.68, 140.54, 135.76, 135.45, 135.30, 134.43, 133.27, 133.56, 133.53, 132.78, 131.73, 131.39, 130.80, 130.29 (2C), 127.63, 127.48, 125.89, 125.62, 124.58 (2C), 124.53, 123.10, 123.01, 121.98, 121.74, 114.74, 114.57, 114.38, 114.14, 66.13, 53.12, 20.35, 16.50, 14.83. ESI-MS (pos ion mode, CH_2Cl_2): m/z = 938.2894 $[M - PF_6]^+$.

Compound 1c. Light orange yellow solid. Yield: 67%. Anal. Calcd for $C_{38}H_{27}F_6IrN_7P$: C, 49.67; H, 2.96; N, 10.67. Found: C, 49.43; H, 2.87; N, 10.51 (%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 14.04 (s, 1H), 13.92 (s, 1H), 8.73 (d, J = 7.6 Hz, 1H), 8.33 (m, 1H), 8.11 (d, 1H, J = 5.6 Hz), 7.93 (d, J = 7.5 Hz, 1H), 7.90 (d, J = 7.5 Hz, 1H), 7.72 (m, 2H), 7.57 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 8.2 Hz, 1H), 7.36 (m, 1H), 7.18 (m, 2H), 7.03 (m, 3H), 6.89 (m, 1H), 6.84 (m, 2H), 6.74 (m, 1H), 6.39 (d, J = 7.5 Hz, 1H), 6.30 (d, J = 7.5 Hz, 1H), 6.26 (d, J = 8.2 Hz, 1H), 5.75 (d, J = 8.2 Hz, 1H), 5.62 (d, J = 8.2 Hz, 1H). ^{13}C NMR (100.5 MHz, DMSO-d_6): δ 164.35, 164.28, 153.58, 151.46, 150.71, 148.39, 146.85, 140.97, 139.66, 139.37, 139.18, 134.85, 134.53, 133.99 (4C), 133.43, 133.16, 132.63, 130.21, 129.55, 128.92, 128.22, 126.52, 125.51, 124.45, 124.08, 123.79, 123.26, 123.01, 121.75(2C), 116.95, 113.82, 112.98(2C), 112.55. ESI-MS (pos ion mode, CH_2Cl_2): m/z = 774.1992 $[M - PF_6]^+$.

Compound 2a. Orangish yellow solid. Yield: 96%. Anal. Calcd for $C_{60}H_{47}F_{12}IrN_7O_2P$: C, 53.41; H, 3.51; N, 7.27. Found: C, 53.27; H, 3.45; N, 7.24 (%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.76 (d, J = 8.0 Hz, 1H), 8.39 (m, 1H), 8.20 (d, J = 4.8 Hz, 1H), 8.13 (d, J = 8.8 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.82 (m, 3H), 7.76 (m, 4H), 7.32 (m, 4H), 7.23 (m, 2H), 6.80 (m, 10H), 6.41 (m, 2H), 6.34 (brs, NCH_2Ar, 2H), 6.24 (m, , NCH_2Ar, 2H), 5.94 (d, J = 8.4 Hz, 1H), 5.71 (d, J = 8.4 Hz, 1H), 5.04 (m, 2H), 3.52 (s, 3H), 1.64 (m, 2H), 0.98 (m, 2H), 0.53 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100.5 MHz, DMSO-d_6): δ 166.35, 164.20, 164.03,

155.65, 154.33, 153.42, 150.07, 148.40, 142.28, 142.10, 141.49, 140.50, 139.99, 139.80, 139.26, 136.57, 136.42, 135.24, 134.79, 134.71, 134.41, 131.82, 131.42, 131.19, 130.29, 128.11 (2C), 127.64, 127.54 (2C), 127.49, 127.33, 127.29, 127.21, 127.15, 127.01, 126.72, 126.68, 126.64, 126.55, 125.69, 125.22, 125.04, 124.03, 123.85, 123.58, 121.14, 115.01, 114.55, 114.51, 114.37, 113.20, 113.11, 52.83, 48.27, 47.94, 46.78, 32.76, 20.17, 14.69. ESI-MS (pos ion mode, CH_2Cl_2): *m/z* = 1204.3510 $[M - PF_6]^+$. λ_{em} = 578 nm (in CH_2Cl_2); Emission lifetime (τ) = 1.31 μs.

Compound 2b. Red solid. Yield: 92%. Anal. Calcd for $C_{64}H_{49}F_{12}IrN_7O_2P$: C, 54.93; H, 3.53; N, 7.01. Found: C, 54.78; H, 3.39; N, 6.89 (%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.93 (d, *J* = 8.8 Hz, 1H), 8.70 (d, *J* = 8.8 Hz, 1H), 8.21 (m, 2H), 8.07 (d, *J* = 8.8 Hz, 1H), 8.01 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.77 (m, 3H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.20 (m, 2H), 7.08 (m, 2H), 6.97 (m, 5H), 6.86 (m, 4H), 6.74 (d, *J* = 1.2 Hz, 1H), 6.43 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.27 (m, 6H), 5.93 (d, *J* = 8.0 Hz, 1H), 5.14 (m, 1H), 5.02 (m, 1H), 3.52 (s, 3H), 1.72 (m, 1H), 1.61 (m, 1H), 0.89 (m, 1H), 0.77 (m, 1H), 0.57 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (50 MHz, DMSO-d_6) δ 165.45, 163.19, 162.47, 156.66 (2C), 154.52, 149.96, 148.47, 145.33 (2C), 142.02, 141.19 (2C), 139.73, 139.23, 138.74, 138.61, 135.37, 135.26, 133.77, 133.71, 133.02, 132.78, 131.78, 130.91, 130.67, 129.71, 129.42, 129.38, 128.81, 128.74, 128.38, 128.31, 127.90, 127.95, 126.78 (2C), 126.70, 126.51, 126.37, 126.09 (2C), 125.84, 125.79, 124.72, 124.31, 124.14, 123.09, 122.58, 122.48, 122.36, 121.20, 120.37, 114.34, 113.85, 113.74, 112.19, 51.81, 47.00, 46.39, 32.11, 31.05, 19.22, 13.68. ESI-MS (pos ion mode, CH_2Cl_2): *m/z* = 1254.3390 $[M - PF_6]^+$.

Compound 2c. Orangish yellow solid. Yield: 85%. Anal. Calcd for $C_{54}H_{37}F_{12}IrN_7P$: C, 52.51; H, 3.02; N, 7.94. Found: C, 51.98; H, 2.97; N, 7.73 (%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.67 (d, *J* = 8.4 Hz, 1H), 8.34 (m, 1H), 8.03 (d, *J* = 5.6 Hz, 1H), 7.76 (m, 8H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.37 (m, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.22 (m, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.92 (m, 4H), 6.87 (m, 3H), 6.40 (m, 2H), 6.28 (brs, NC*H*$_2$Ar, 2H), 6.22 (brs, NC*H*$_2$Ar, 2H), 6.09 (d, *J* = 8.1 Hz, 1H), 5.84 (d, *J* = 8.1 Hz, 1H), 5.67 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 164.32, 164.20, 142.33, 142.23, 142.09 (4C), 141.50, 139.85, 139.60, 136.58 , 136.49, 135.37 (2C), 134.95 (2C), 134.40, 131.77, 131.71, 131.18, 129.59 (4C), 128.03 (4C), 127.82 (6C), 127.32, 127.28, 127.04 (2C), 126.74, 126.63, 125.73 (2C), 125.12, 125.01, 123.39 (2C), 117.95, 114.92, 114.38, 113.30, 113.15, 48.21, 47.97. ESI-MS (pos ion mode, CH_2Cl_2): *m/z* = 1090.2647 $[M - PF_6]^+$.

Compound 3a. Bright yellow solid. Yield: 95 %. Anal. Calcd for $C_{36}H_{33}F_6IrN_7O_2P$: C, 46.35 H, 3.57; N, 10.51. Found: C, 46.21; H, 3.49; N, 3.48 (%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.88 (d, *J* = 2.8 Hz, 1H), 8.79 (d, *J* = 2.8 Hz, 1H), 8.61 (d, *J* = 8.4 Hz, 1H), 8.32 (td, *J* = 7.5, 1.6 Hz, 1H), 8.15 (dd, *J* = 5.2, 1.2 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.97 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.70 (m, 3H), 7.20 (m, 2H), 7.10 (m, 3H), 6.85 (m, 2H), 6.62 (m, 2H), 6.23 (d, *J* = 7.6 Hz, 2H), 4.95 (m, 2H), 3.69 (s, 3H), 1.92 (m, 2H), 1.41 (m, 2H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100.5 MHz, DMSO-d_6): δ 13.71, 19.34, 31.41, 45.69, 51.92, 108.33, 108.46, 112.10, 112.24, 112.91, 119.52, 122.86, 123.01, 125.82, 125.97, 126.23, 126.41, 128.36, 128.70, 132.59, 133.29, 133.41, 138.72, 139.10, 139.20, 139.48, 140.17 (2C), 143.31, 146.64, 151.86 (2C), 154.55, 165.44. ESI-MS (pos ion mode, CH_2Cl_2): *m/z* = 788.2355 $[M - PF_6]^+$. λ_{em} = 563 nm (in CH_2Cl_2); Emission lifetime (τ) = 0.97 μs.

Compound 3b. Brown solid. Yield: 98 %. Anal. Calcd for $C_{40}H_{35}F_6IrN_7O_2P$: C, 48.88 H, 3.59; N, 9.97. Found: C, 48.75; H, 3.48; N, 9.92 (%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.96 (d, *J* = 8.4 Hz, 1H), 8.88 (d, *J* = 2.8 Hz, 1H), 8.75 (d, *J* = 2.8 Hz, 1H), 8.68 (d, *J* = 8.4 Hz,

1H), 8.36 (d, J = 8.8 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.8 Hz, 1H), 7.98 (dd, J = 8.4, 1.2 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.65 (dd, J = 7.2 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 2.4 Hz, 1H), 7.29 (m, 1H), 7.19 (d, J = 2.4 Hz, 1H), 7.18 (t, J = 7.2 Hz, 1H), 7.00 (m, 1H), 6.92 (d, J = 1.2 Hz, 1H), 6.89 (m, 2H), 6.64 (t, J = 2.4 Hz, 1H), 6.55 (t, J = 2.4 Hz, 1H), 6.25 (dd, J = 7.6, 1.2 Hz, 1H), 6.03 (dd, J = 7.6, 1.2 Hz, 1H), 4.95 (m, 2H), 3.68 (s, 3H), 1.92 (m, 2H), 1.41 (m, 2H), 0.87 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100.5 MHz, DMSO-d_6): δ 13.96, 19.70, 31.06, 46.55, 52.19, 108.57, 108.91, 112.59 (4C), 113.37, 120.03, 121.44, 122.95, 123.60, 126.29, 126.39 (2C), 126.52,126.76, 128.55, 128.84, 128.91, 129.12, 129.38, 129.67, 131.96, 133.06, 133.22, 134.88, 139.21, 139.55, 139.77, 141.87, 143.05, 143.15, 148.86, 149.56, 156.48, 165.78. ESI-MS (pos ion mode, CH_2Cl_2): m/z = 838.2554; ESI-MS (pos ion mode, CH_2Cl_2): m/z = 838.2554 $[M - PF_6]^+$.

Compound 3c. Light yellow solid. Yield: 94 %. Anal. Calcd for $C_{30}H_{23}F_6IrN_7P$: C, 44.01 H, 2.83; N, 11.98. Found: C, 43.88; H, 2.87; N, 11.85 (%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 14.90 (brs, 1H), 8.86 (d, J = 2.8 Hz, 1H), 8.80 (d, J = 2.8 Hz, 2H), 8.66 (d, J = 7.6 Hz, 1H), 8.32 (m, 1H), 7.99 (d, J = 5.2 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.61 (m, 3H), 7.35 (t, J = 8.0Hz, 1H), 7.20 (d, J = 2.4 Hz, 1H), 7.04 (m, 3H), 6.62 (m, 2H), 6.58 (m, 2H), 6.29 (d, J = 7.6 Hz, 3H). ^{13}C NMR (100.5 MHz, DMSO-d_6): δ 153.96, 150.66, 147.99, 143.47, 143.39, 140.77, 139.79, 139.13, 138.62, 134. 48, 133.33, 133.01, 132.61, 128.81, 128.50, 128.17, 128.05, 126.21, 125.59, 125.13, 124.13(2C), 122.77, 122.68, 116.32, 113.81, 112.04, 11.78, 108.36, 108.22. ESI-MS (pos ion mode, CH_2Cl_2): m/z = 674.16 $[M - PF_6]^+$.

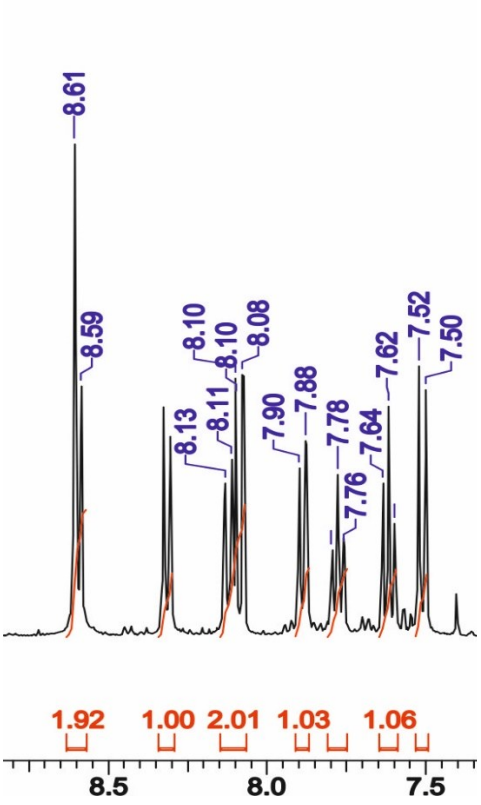


Figure S1. Aromatic region of the ^{1}H NMR spectrum of ligand **b** (300 MHz, $CDCl_3$).

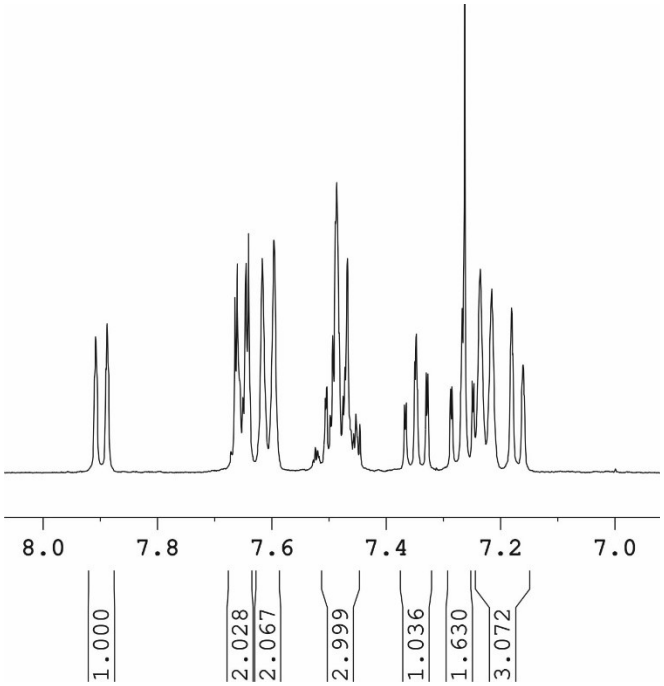


Figure S2. Aromatic region of the ^{1}H NMR spectrum of proligand **HL²** in $CDCl_3$.

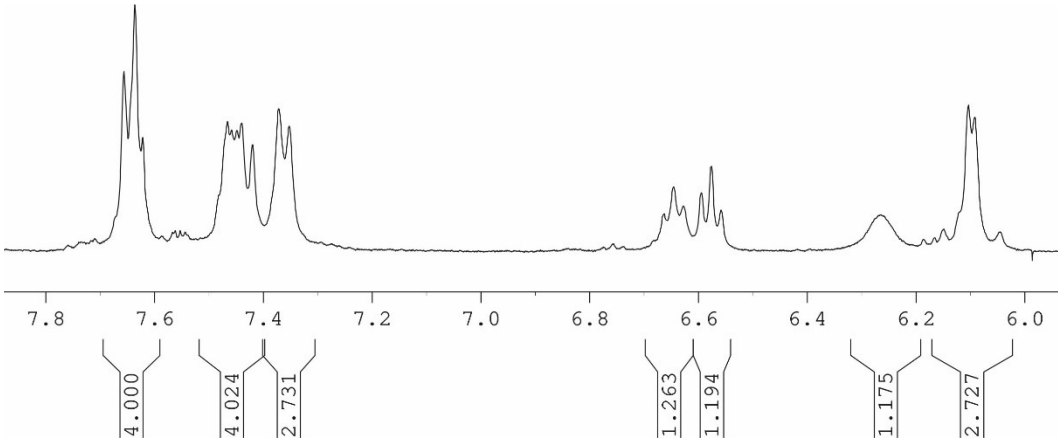


Figure S3. Aromatic region of the ^{1}H NMR spectrum of iridium dimer **B** in acetonitrile-d_3

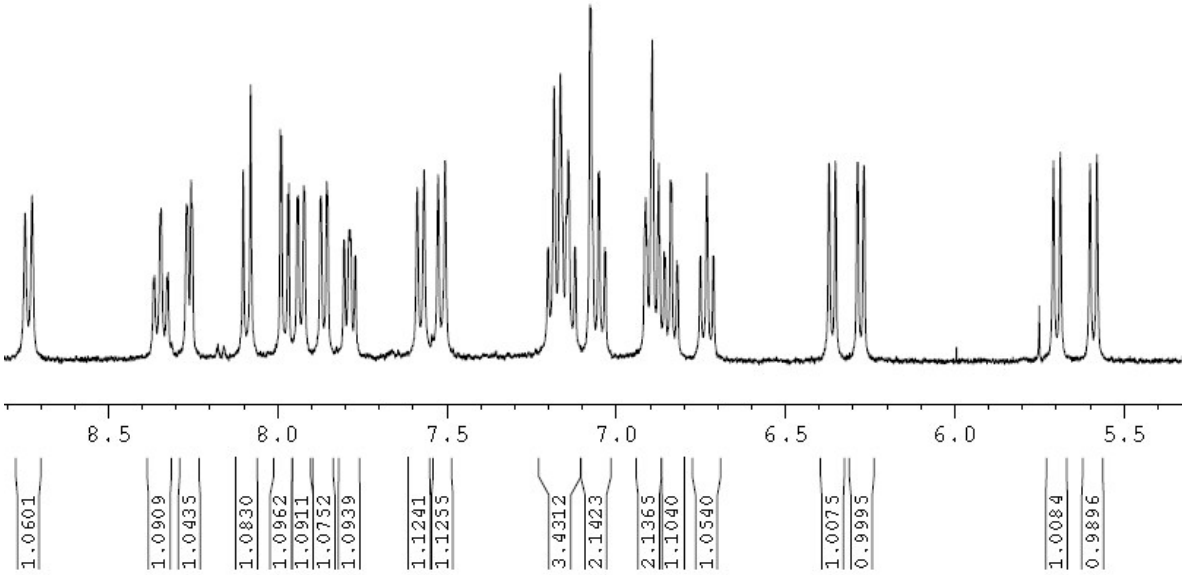


Figure S4. Aromatic region of the ^{1}H NMR spectrum of complex **1a** (400 MHz, DMSO-d_6).

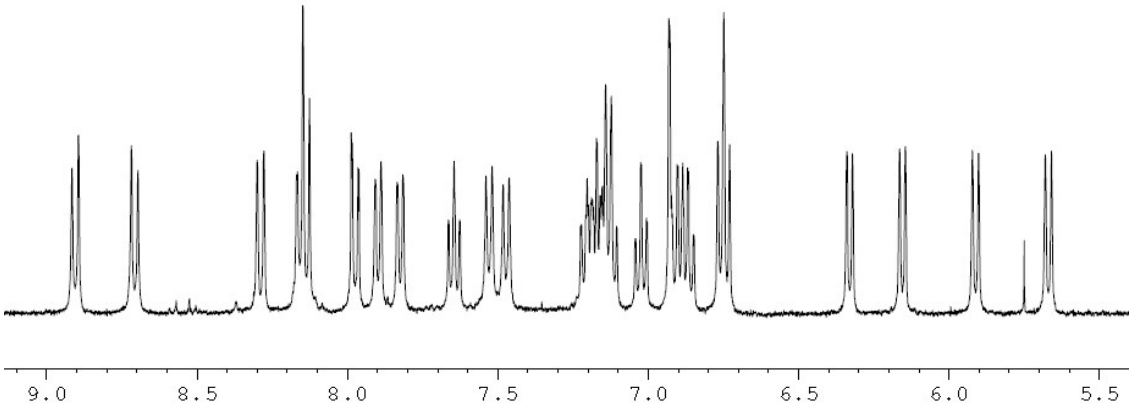


Figure S5. Aromatic region of the ^{1}H NMR spectrum of complex **1b** (400 MHz, DMSO-d_6).

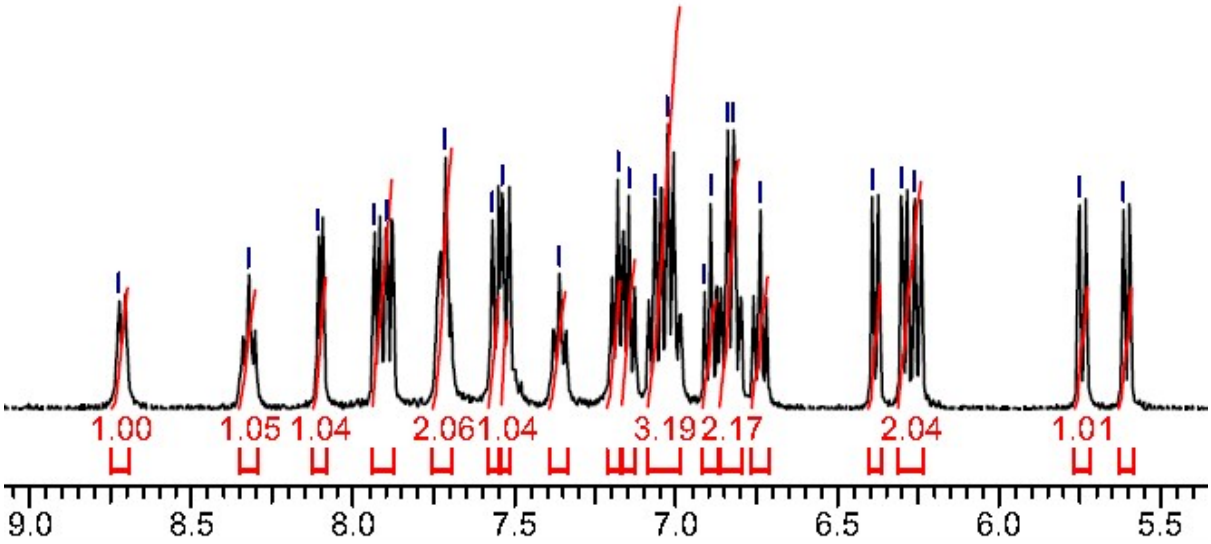


Figure S6. Aromatic region of the ^{1}H NMR spectrum of complex **1c** (400 MHz, DMSO-d_6).

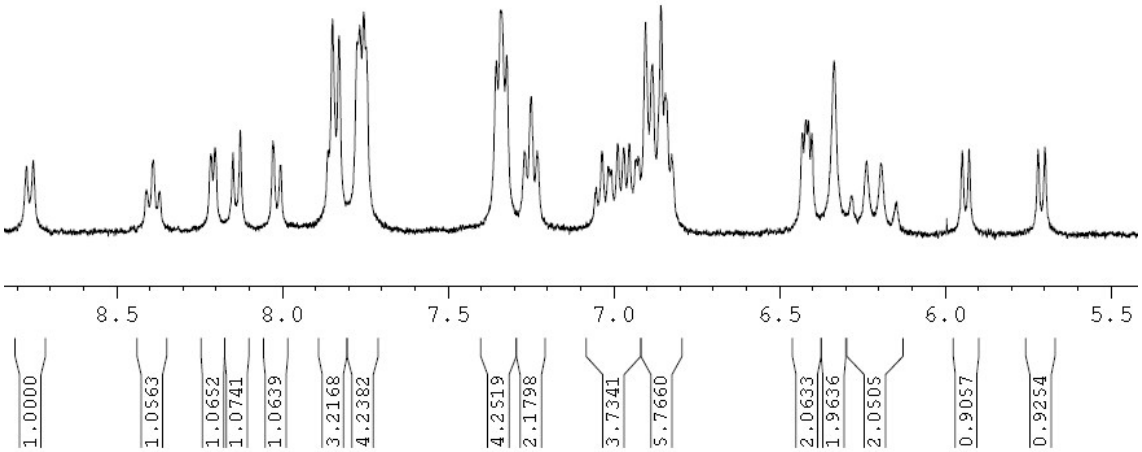


Figure S7. Aromatic region of the ^{1}H NMR spectrum of complex **2a** (400 MHz, DMSO-d_6).

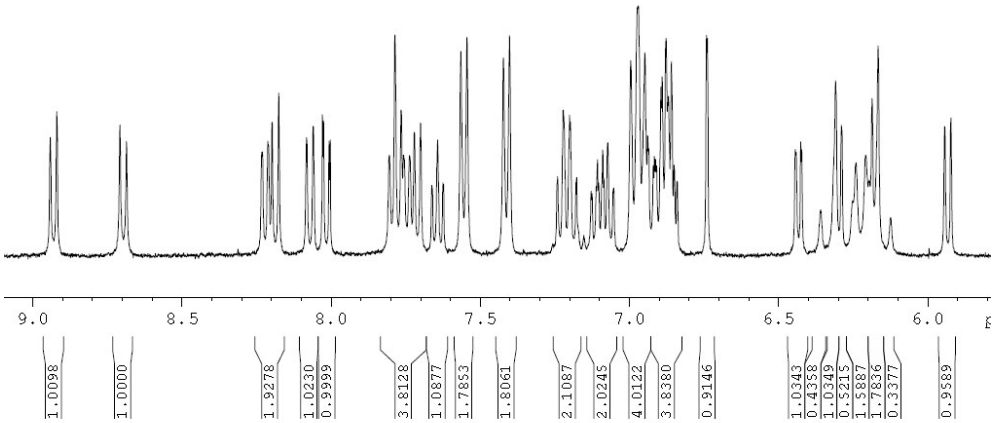


Figure S8. Aromatic region of the ^{1}H NMR spectrum of complex **2b** (400 MHz, DMSO-d_6).

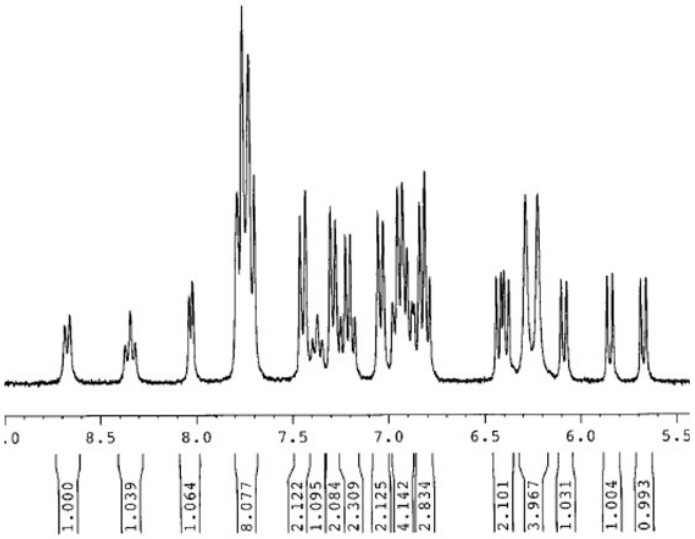


Figure S9. Aromatic region of the ^{1}H NMR spectrum of complex **2c** (300 MHz, DMSO-d_6).

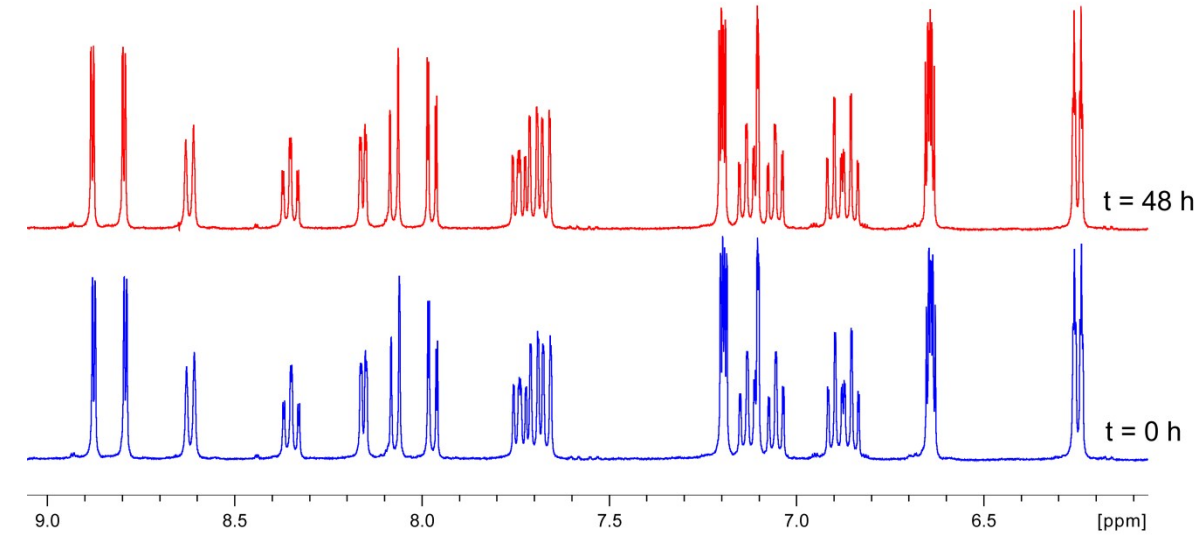


Figure S10. Aromatic region of the ^{1}H-NMR spectra of **3a** measured after dissolving immediately in DMSO-d_6 (bottom) and after 48 h (top) at RT.

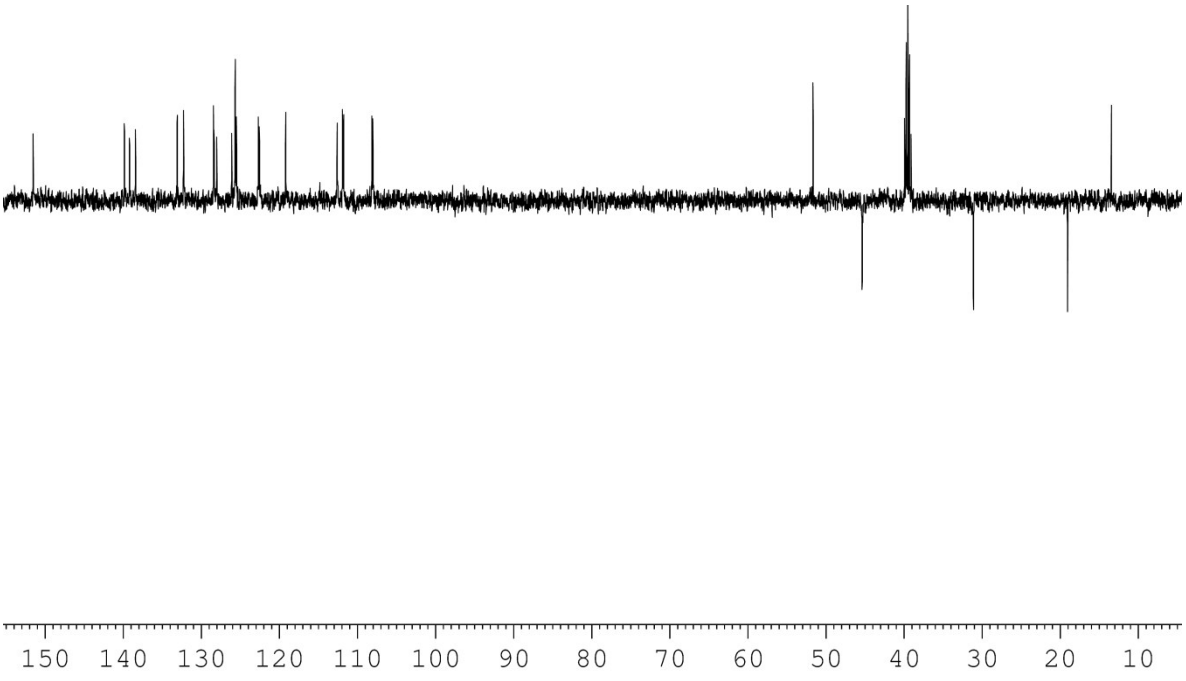


Figure S11. DEPT spectrum of complex **3a** in DMSO-d_6.

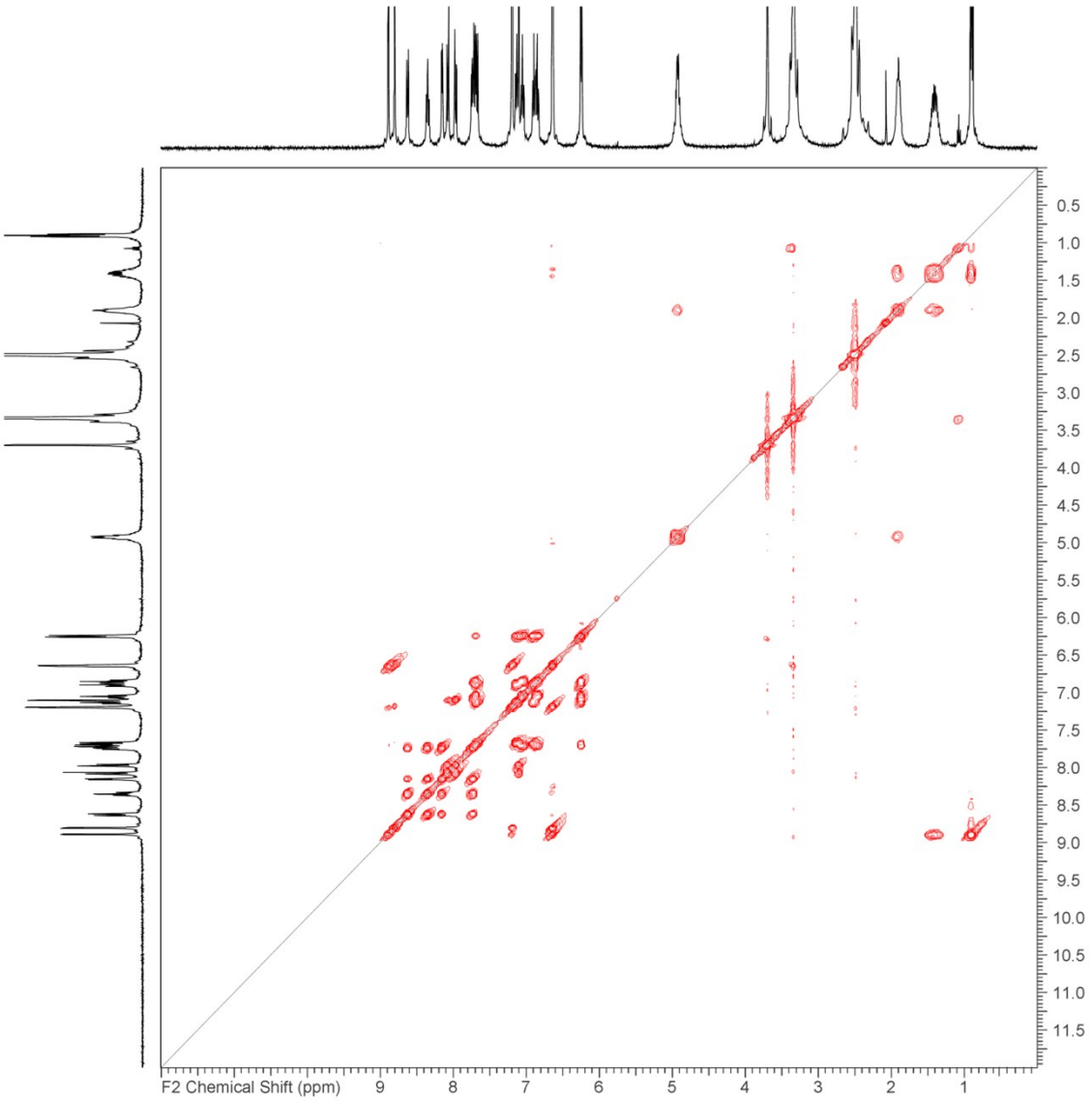


Figure S12. ^{1}H-^{1}H-COSY spectrum of **3a** (400 MHz, DMSO-d_6).

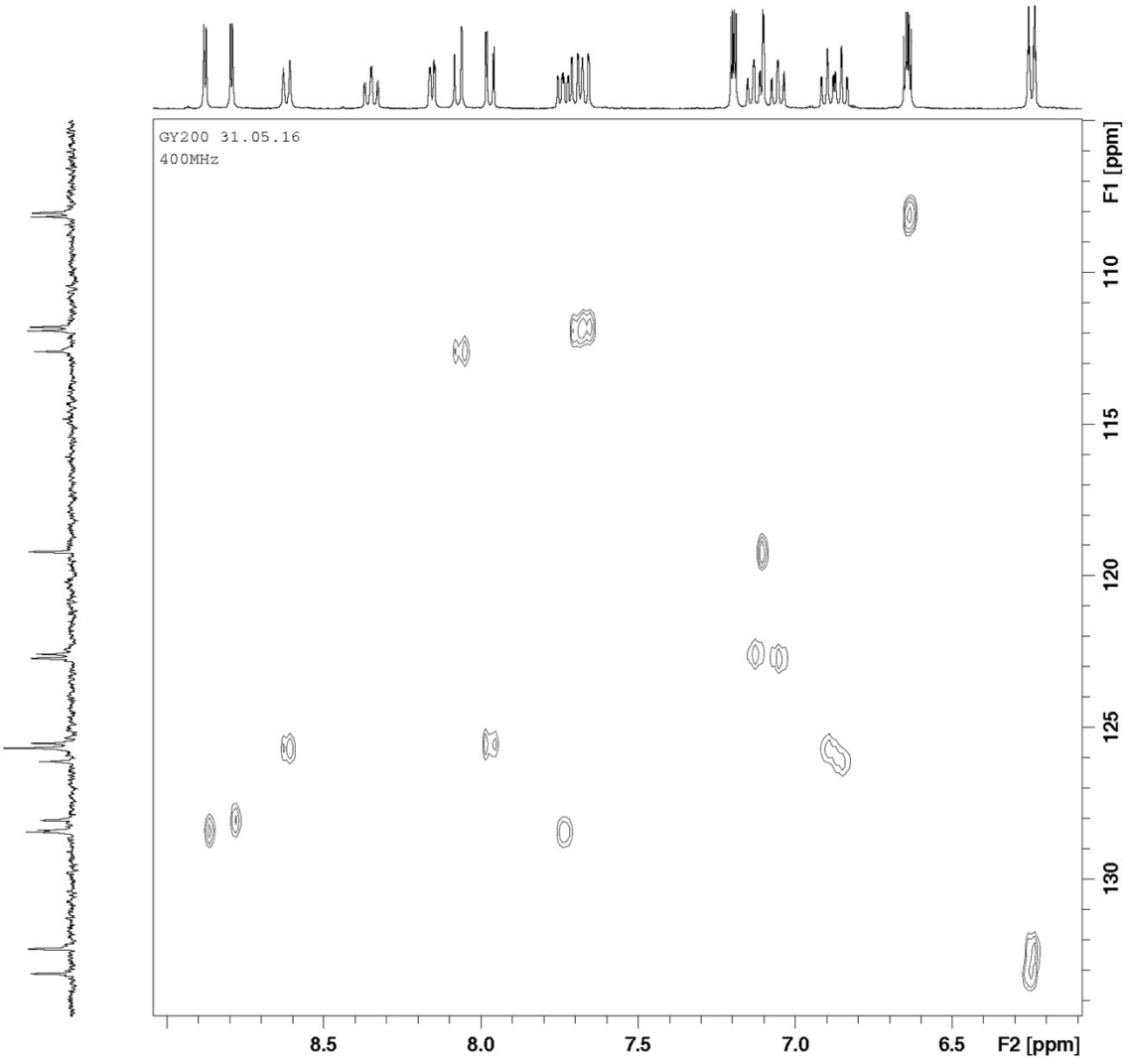


Figure S13. HSQC spectrum (aromatic region) of **3a** (400 MHz, DMSO-d_6).

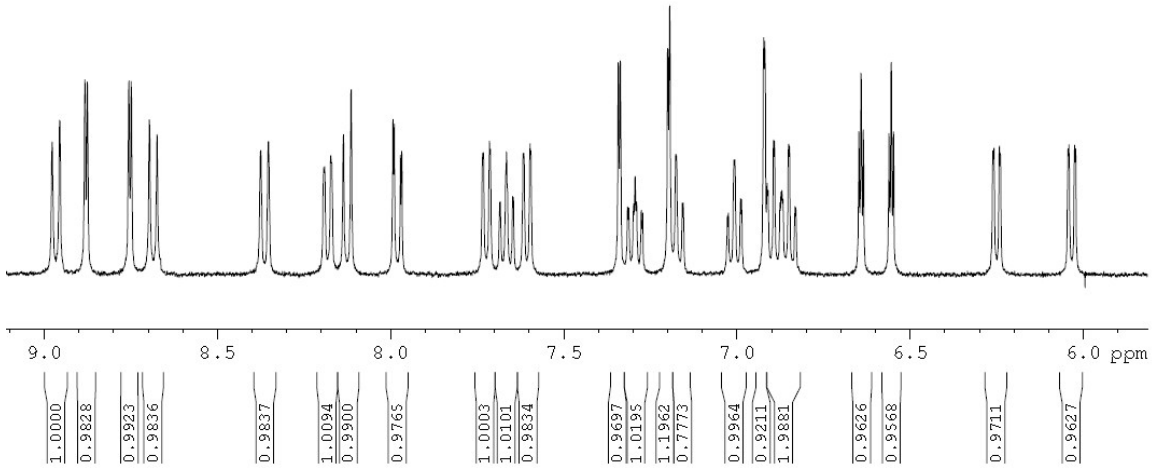


Figure S14. Aromatic region of the ^{1}H NMR spectrum of complex **3b** (400 MHz, DMSO-d_6).

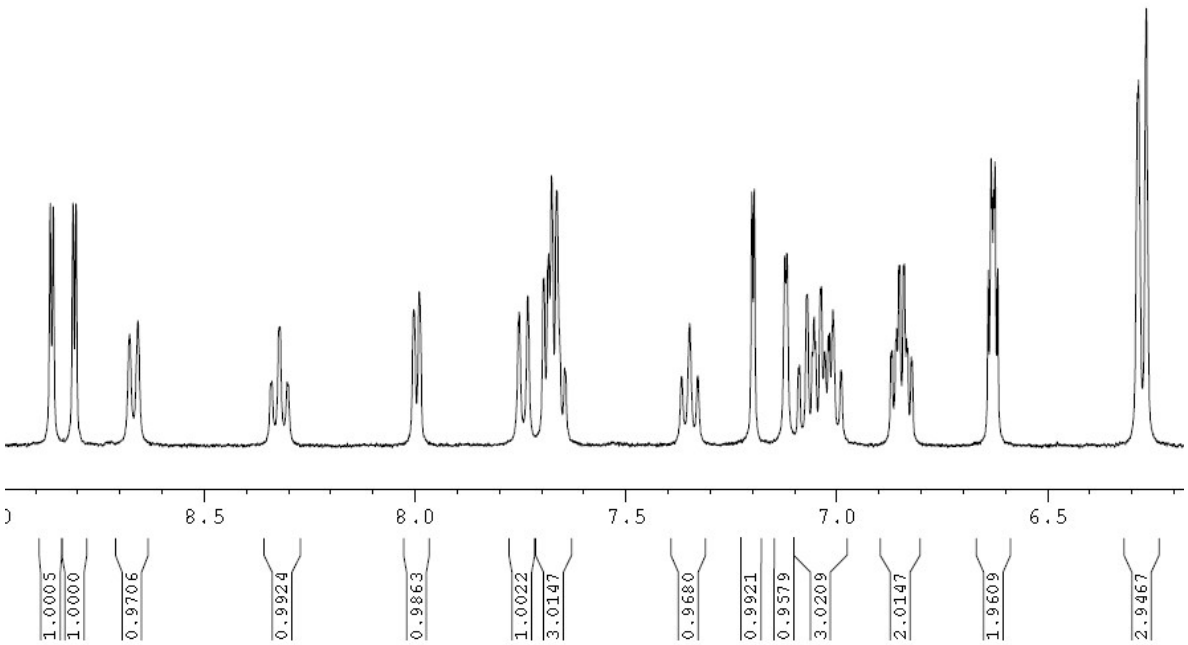


Figure S15. Aromatic region of the ^{1}H NMR spectrum of complex **3c** (400 MHz, DMSO-d_6).

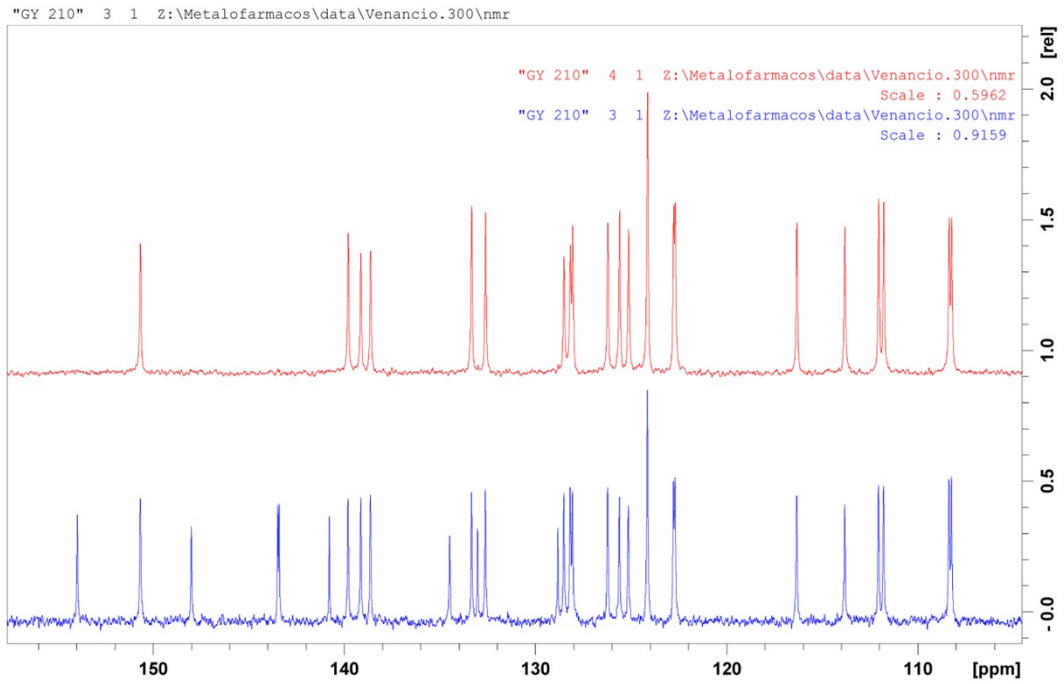


Figure S16. DEPT and ^{13}C NMR spectra (aromatic region) of complex **3c** in DMSO-d_6.

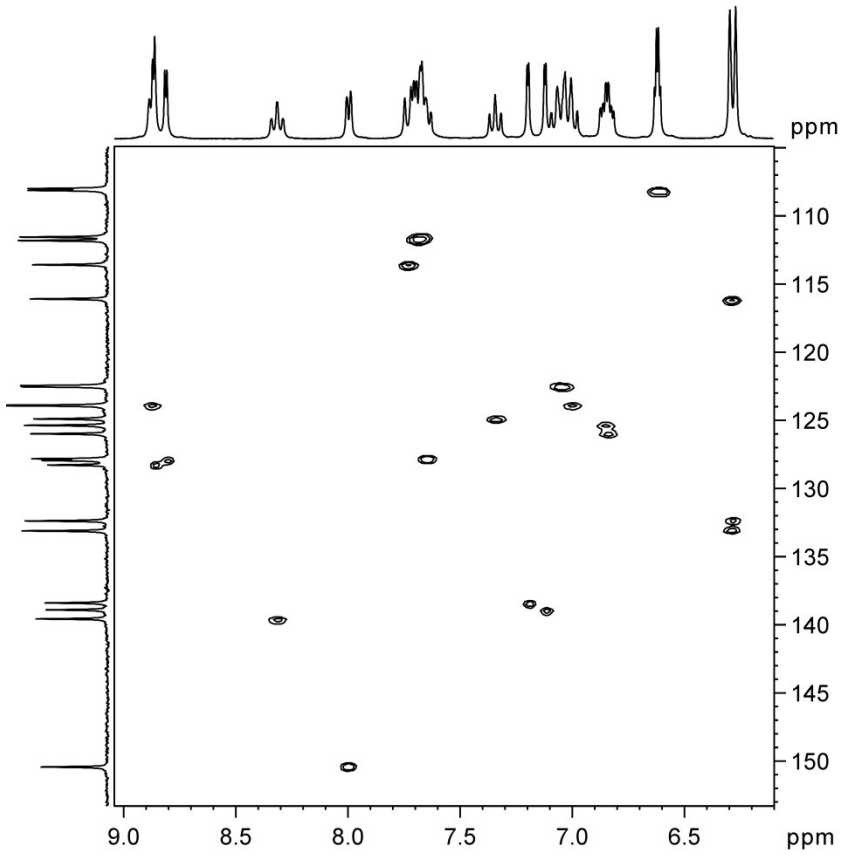


Figure S17. HSQC spectrum (aromatic region) of **3c** (400 MHz, DMSO-d_6).

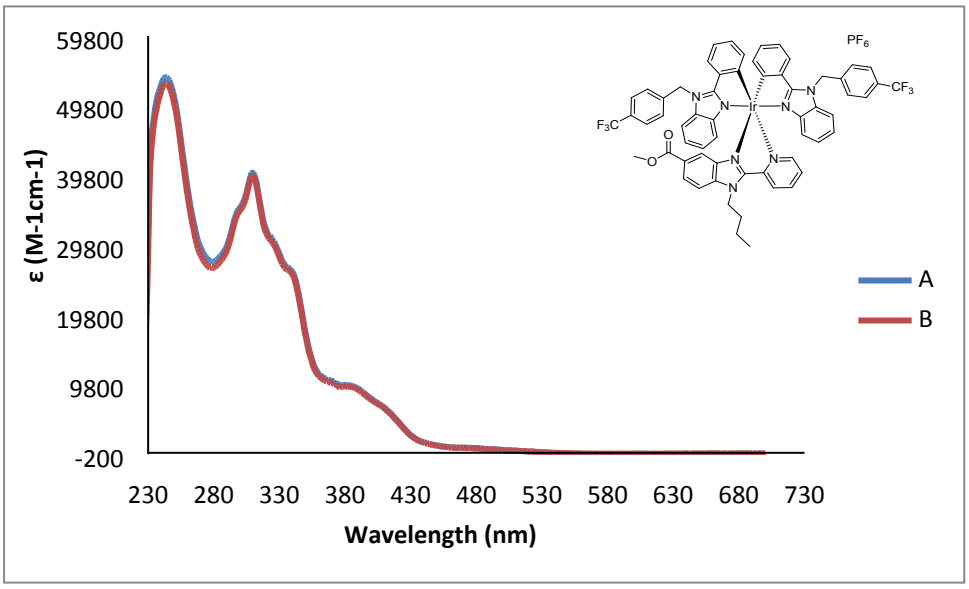


Figure S18. UV/Vis absorption spectra of complex **2a** in water/DMSO (99:1) at room temperature at t = 0. A and B mean two independent measurements.

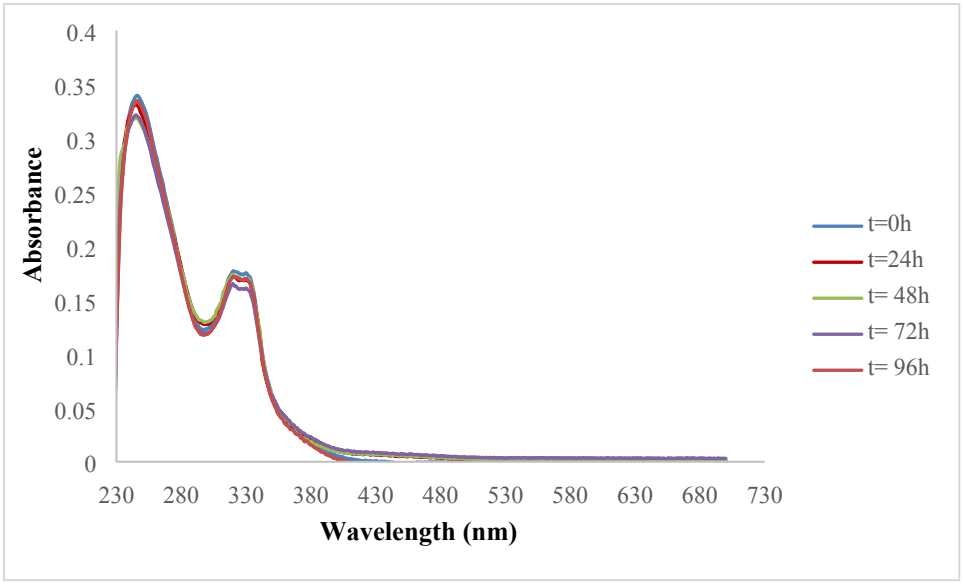


Figure S19. UV-Vis absorption spectra of **3a** in water/DMSO (99:1) at room temperature over 5 days.

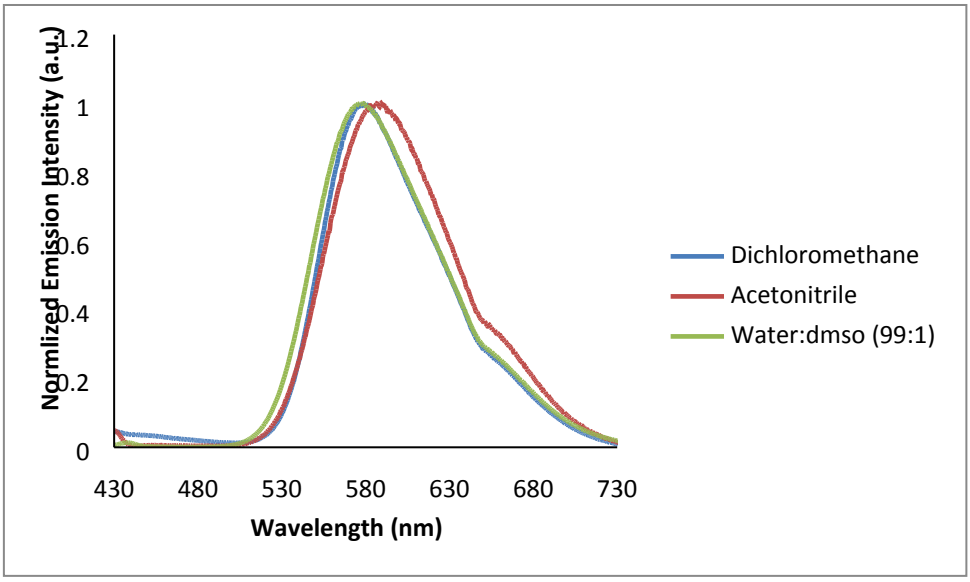


Figure S20. The emission spectra of complex **2a** in different solvents at room temperature (Exc. at 381 nm).

RP-HPLC purity analyses: The purity of Ir(III) complexes was analyzed using a RP-HPLC/MS TOF 6220 equipped with a double binary pump (model G1312A), degasser, autosampler (model G1329A), diode array detector (model G1315D) and mass detector in series Agilent Technologies 1200. Chromatographic analyses were carried out on a Brisa C18 column (150 mm × 4.6 mm, 5 μm particle size). The mobile phase was a mixture of (A) H_2O/HCOOH 0.1% and (B) acetonitrile/HCOOH 0.1%. The flow rate was 0.6 mL min^{-1} in a linear gradient starting with 10% B at 0–13 min, reaching 90% B at 14–20 min, and 10% B at 21–25 min. Chromatograms were recorded at 280 nm. The HPLC system was controlled by a ChemStation software (MASS HUNTER.). Samples were dissolved in acetonitrile (1 mg/mL final concentration).

Table S1. HPLC method.

Time (min)	0.1% formic acid in dH_2O	0.1% formic acid in CH_3CN
0	90	10
14	10	90
18	10	90
18.1	90	10
25	90	10

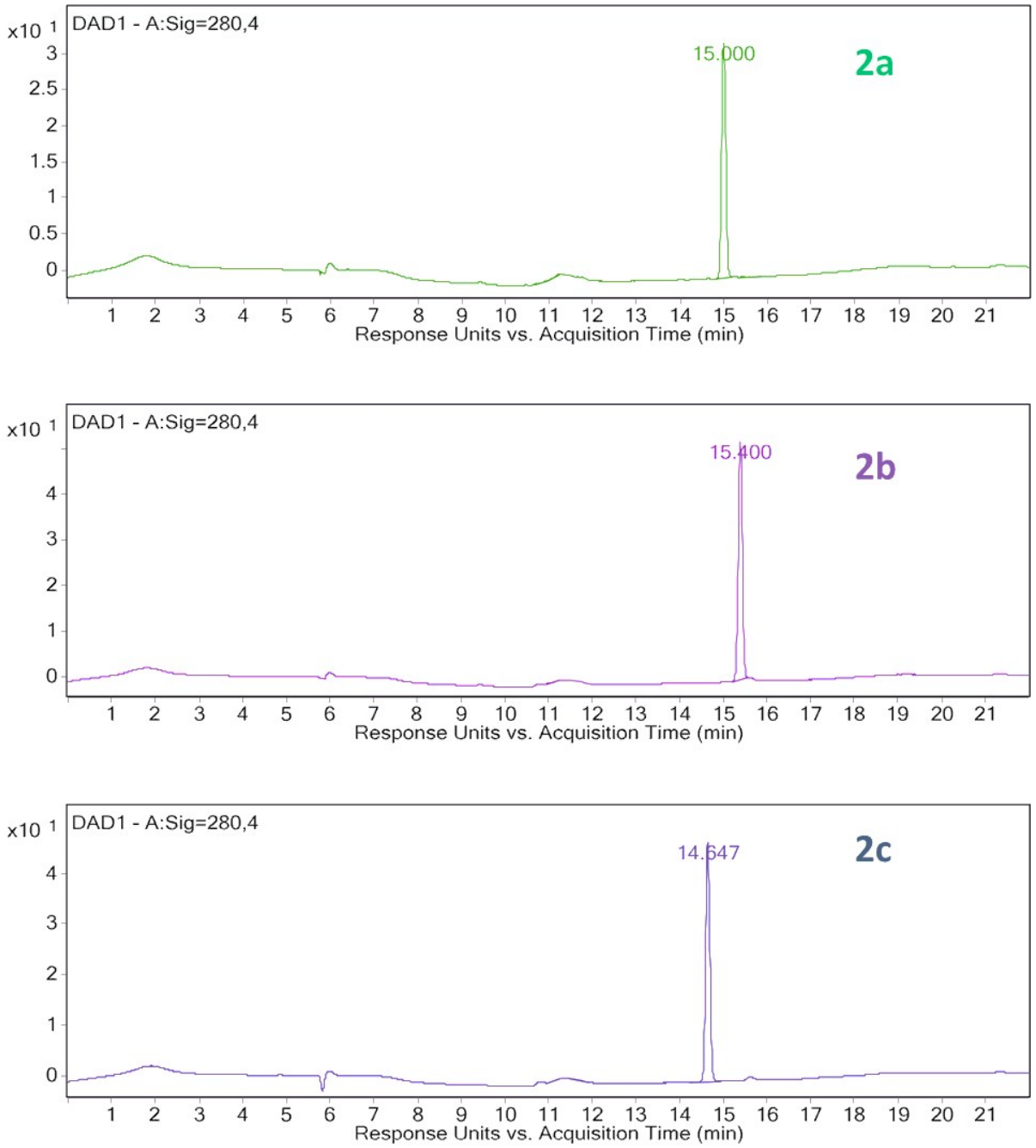


Figure S21. RP-HPLC chromatograms (0.1% HCOOH H_2O/ 0.1% HCOOH MeCN) traces of complexes **2a**-**2c** (in acetonitrile/, λ = 280 nm). Curves were obtained within 30 min after preparation of the **2a**-**2c** solutions at room temperature.

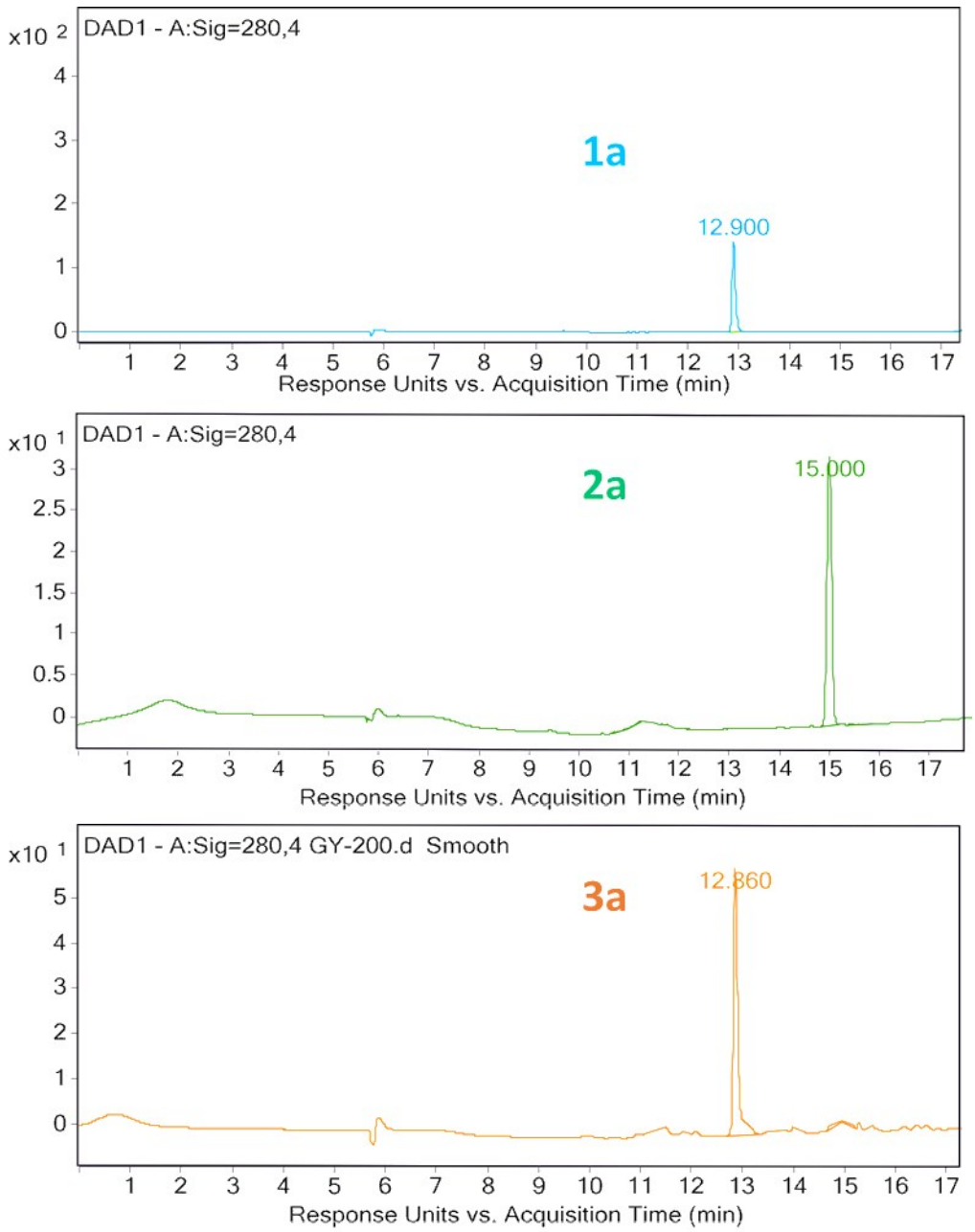


Figure S22. RP-HPLC chromatograms (0.1% HCOOH H_2O/ 0.1% HCOOH MeCN) traces of complexes **1a, 2a** and **3a** (in acetonitrile / λ = 280 nm). Curves were obtained within 30 min after preparation of the sample solutions at room temperature.

X-ray Crystallographic Analysis: Single crystals suitable for X-ray diffraction analysis were obtained for complexes **1a** and **3a** from CH_2Cl_2/hexane. A summary of crystal data collection and refinement parameters for all compounds are given in Tables S2-S6 in the Supporting Information. Crystals were mounted on glass fibers and transferred to the cold gas stream of the diffractometer Bruker Smart APEX. Data were recorded with Mo Kα radiation (λ = 0.71073 Å) in ω scan mode. Absorption correction for the compound was based on multi-scans. Both structures were solved by direct methods (SHELXS-97);[6] refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite;[6] empirical (multi-scan) absorption correction with SADABS (Bruker).[7] All non-hydrogen positions were refined with anisotropic temperature factors. Hydrogen atoms for aromatic CH, aliphatic CH_2 and CH_3 groups were positioned geometrically (C–H = 0.95 Å for aromatic CH, C–H = 0.99 Å for CH_2, C–H = 0.98 Å for CH_3) and refined using a riding model (AFIX 43 for aromatic CH, AFIX 23 for CH_2, AFIX 137 for CH_3), with $U_{iso}(H) = 1.2U_{eq}(CH, CH_2)$ and $U_{iso}(H) = 1.5U_{eq}(CH_3)$. Graphics were drawn with DIAMOND (Version 3.2).[8]

Special feature for 3a: The R-values appear good, and the structure of the iridium cation could be unequivocally defined together with hexafluorophosphate anion. Yet the structure suffers from orientational ligand disorder together with its surrounding solvent molecules, an incompletely found disordered butyl group and ill-defined solvent molecules of crystallization. Evidence for this orientational ligand disorder are the thermal ellipsoids and two or more orientations of the ligands as illustrated in the Supporting Information (Figures S20a). Only one CH_2Cl_2 molecule could be reasonably refined. Additional solvent molecules, most likely also CH_2Cl_2 because of the associated electron density were strongly disordered and the associated electron density was removed by using the option SQUEEZE built in PLATON.[9] The singly refined CH_2Cl_2 molecule has 50% occupancy and essentially shares a position with the fully found n-butyl group which also has 50% occupancy (Figure S20b). Because of the strong disorder in the iridium cation we refrained from an analysis of supramolecular packing interactions.

bis-(2-phenyl-1H-benzo[d]imidazole-κ^2N,C)- {methyl 1-butyl-2-(pyridin-2-yl)-1H-benzo[d]imidazole-5- carboxyl-ate-κ^2N,N'}iridium(III) hexafluorophosphate tris(dichloromethane) solvate, 1a

Table S2. Crystal data and structure refinement for **1a**.

Crystal data

$C_{44}H_{37}IrN_7O_2 \cdot F_6P \cdot 3(CH_2Cl_2)$	D_x = 1.662 Mg m^{-3}
M_r = 1287.75	Mo $K\alpha$ radiation, λ = 0.71073 Å
Orthorhombic, *Pbca*	Cell parameters from 9634 reflections
a = 22.1254 (11) Å	θ = 2.5–28.3°
b = 16.4448 (9) Å	μ = 3.01 mm^{-1}
c = 28.2843 (15) Å	T = 100 K
V = 10291.2 (9) Å^3	Prism, orange
Z = 8	0.27 × 0.11 × 0.03 mm
F(000) = 5104	CCDC no. 1483570

Data collection

Bruker D8 Quest CCD diffractometer	9542 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.075
ω and ϕ scans	θ_{max} = 26.4°, θ_{min} = 2.1°
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	h = -27→27
T_{min} = 0.555, T_{max} = 0.746	k = -20→19
230408 measured reflections	l = -35→35
10495 independent reflections	

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)]$ = 0.062	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.127	$w = 1/[\sigma^2(F_o^2) + (0.0163P)^2 + 179.5196P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.15	$(\Delta/\sigma)_{max}$ = 0.001
10495 reflections	$\Delta\rangle_{max}$ = 2.31 e Å^{-3}
639 parameters	$\Delta\rangle_{min}$ = -3.62 e Å^{-3}

Special details

Refinement. Hydrogen atoms for aromatic CH, aliphatic CH, CH_2 and methyl groups were positioned geometrically (C—H = 0.95 Å for aromatic CH, C—H = 1-00 Å for aliphatic CH, C—H = 0.99 Å for CH_2, C—H = 0.98 Å for CH_3) and refined using a riding model (AFIX 43 for aromatic CH, AFIX 23 for CH_2, AFIX 137 for rotating group for CH_3), with $U_{iso}(H) = 1.2U_{eq}(CH)$ and $U_{iso}(H) = 1.5U_{eq}(CH_3)$.
The two protic H atoms on the two imidazole N atoms were found and refined with $U_{iso}(H) = 1.5U_{eq}(N)$.
The largest residual electron density peak of 2.31 e Å^{-3} is within 1.00 Å from H42A or 1.92 Å from C42 (the chain end of the n-butyl group). The second largest electron density peak of 2.22 e Å^{-3} is within 0.39 Å from Cl3 of a CH_2Cl_2 solvent molecule.
Possible disordered solvent residues in what would be otherwise voids were tried to remove with the option SQUEEZE by PLATON. In four voids in the unit cell of 98 Å^3 each 19 electrons each were removed. Total potential solvent accessible void volume per unit cell is 392.4 Å^3 (3.8%) with a total electron count/cell of 77.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for ***1a***

	x	*y*	*z*	U_{iso}*/U_{eq}
Ir	0.45436 (2)	0.40610 (2)	0.18904 (2)	0.01467 (8)
N1	0.3842 (2)	0.4367 (3)	0.2330 (2)	0.0160 (12)
N2	0.3495 (3)	0.4548 (4)	0.3052 (2)	0.0222 (13)
H2	0.348 (4)	0.457 (6)	0.333 (3)	0.033*
N3	0.5270 (3)	0.3600 (3)	0.1525 (2)	0.0181 (12)
N4	0.5760 (3)	0.2531 (4)	0.1251 (2)	0.0220 (13)
H4	0.581 (4)	0.206 (6)	0.117 (3)	0.033*
N5	0.4126 (3)	0.4414 (4)	0.1248 (2)	0.0193 (12)
N6	0.3836 (3)	0.5377 (4)	0.0741 (2)	0.0296 (15)
N7	0.4752 (2)	0.5332 (3)	0.1827 (2)	0.0172 (12)
C1	0.3230 (3)	0.4542 (4)	0.2294 (3)	0.0196 (15)
C2	0.2844 (3)	0.4597 (4)	0.1908 (3)	0.0224 (15)
H2A	0.2988	0.4524	0.1595	0.027*
C3	0.2239 (3)	0.4762 (5)	0.1998 (3)	0.0293 (18)
H3	0.1964	0.4800	0.1741	0.035*
C4	0.2031 (3)	0.4874 (4)	0.2453 (3)	0.0281 (17)
H4A	0.1614	0.4988	0.2499	0.034*
C5	0.2404 (3)	0.4827 (4)	0.2845 (3)	0.0254 (17)
H5	0.2256	0.4905	0.3157	0.030*
C6	0.3010 (3)	0.4657 (4)	0.2754 (3)	0.0217 (15)
C7	0.3984 (3)	0.4375 (4)	0.2785 (3)	0.0180 (14)
C8	0.4598 (3)	0.4177 (4)	0.2919 (3)	0.0183 (14)

C9	0.4949 (3)	0.3929 (4)	0.2527 (3)	0.0161 (14)
C10	0.5544 (3)	0.3716 (5)	0.2622 (3)	0.0232 (15)
H10	0.5801	0.3554	0.2370	0.028*
C11	0.5773 (3)	0.3737 (4)	0.3080 (3)	0.0260 (16)
H11	0.6175	0.3559	0.3137	0.031*
C12	0.5422 (4)	0.4014 (5)	0.3458 (3)	0.0276 (16)
H12	0.5592	0.4061	0.3765	0.033*
C13	0.4833 (3)	0.4216 (5)	0.3380 (3)	0.0242 (16)
H13	0.4583	0.4382	0.3635	0.029*
C14	0.5795 (3)	0.3880 (4)	0.1315 (2)	0.0172 (14)
C15	0.6027 (3)	0.4652 (5)	0.1258 (3)	0.0226 (15)
H15	0.5820	0.5115	0.1376	0.027*
C16	0.6573 (4)	0.4730 (5)	0.1022 (3)	0.0275 (17)
H16	0.6740	0.5257	0.0977	0.033*
C17	0.6886 (3)	0.4051 (5)	0.0849 (3)	0.0269 (16)
H17	0.7261	0.4126	0.0692	0.032*
C18	0.6658 (3)	0.3275 (5)	0.0901 (3)	0.0277 (17)
H18	0.6864	0.2813	0.0781	0.033*
C19	0.6107 (3)	0.3204 (4)	0.1140 (3)	0.0209 (15)
C20	0.5265 (3)	0.2790 (4)	0.1478 (3)	0.0194 (14)
C21	0.4748 (3)	0.2349 (4)	0.1660 (3)	0.0182 (14)
C22	0.4320 (3)	0.2875 (4)	0.1883 (2)	0.0175 (13)
C23	0.3792 (3)	0.2497 (4)	0.2047 (3)	0.0202 (15)
H23	0.3495	0.2817	0.2204	0.024*
C24	0.3690 (3)	0.1677 (4)	0.1989 (3)	0.0243 (16)
H24	0.3320	0.1448	0.2096	0.029*
C25	0.4118 (4)	0.1178 (4)	0.1776 (3)	0.0257 (17)
H25	0.4046	0.0611	0.1745	0.031*
C26	0.4656 (3)	0.1516 (4)	0.1609 (3)	0.0211 (15)
H26	0.4953	0.1184	0.1463	0.025*
C27	0.3783 (3)	0.4046 (5)	0.0895 (3)	0.0217 (15)
C28	0.3627 (3)	0.3236 (5)	0.0826 (3)	0.0246 (16)
H28	0.3762	0.2820	0.1034	0.030*
C29	0.3267 (4)	0.3067 (5)	0.0441 (3)	0.0272 (17)
C30	0.3067 (4)	0.3678 (6)	0.0131 (3)	0.037 (2)
H30	0.2814	0.3536	-0.0128	0.044*
C31	0.3230 (4)	0.4475 (6)	0.0193 (3)	0.036 (2)
H31	0.3100	0.4889	-0.0018	0.044*
C32	0.3595 (4)	0.4648 (5)	0.0582 (3)	0.0295 (17)
C33	0.4161 (3)	0.5201 (4)	0.1142 (3)	0.0218 (15)

C34	0.4516 (3)	0.5737 (4)	0.1451 (3)	0.0205 (15)
C35	0.5084 (3)	0.5738 (4)	0.2140 (3)	0.0197 (15)
H35	0.5244	0.5454	0.2404	0.024*
C36	0.5207 (4)	0.6568 (5)	0.2094 (3)	0.0263 (17)
H36	0.5442	0.6846	0.2324	0.032*
C37	0.4979 (4)	0.6968 (5)	0.1709 (3)	0.0289 (18)
H37	0.5062	0.7530	0.1666	0.035*
C38	0.4629 (4)	0.6557 (5)	0.1386 (3)	0.0299 (18)
H38	0.4466	0.6835	0.1120	0.036*
C39	0.3796 (5)	0.6157 (5)	0.0486 (3)	0.040 (2)
H39A	0.3737	0.6607	0.0714	0.048*
H39B	0.3447	0.6148	0.0267	0.048*
C40	0.4405 (6)	0.6293 (7)	0.0198 (4)	0.061 (3)
H40A	0.4755	0.6144	0.0398	0.074*
H40B	0.4407	0.5936	-0.0084	0.074*
C41	0.4463 (7)	0.7182 (9)	0.0043 (5)	0.083 (4)
H41A	0.4108	0.7337	-0.0150	0.100*
H41B	0.4474	0.7538	0.0325	0.100*
C42	0.5039 (6)	0.7297 (15)	-0.0246 (5)	0.124 (8)
H42A	0.5120	0.7880	-0.0284	0.185*
H42B	0.4988	0.7046	-0.0558	0.185*
H42C	0.5379	0.7041	-0.0081	0.185*
C43	0.3067 (4)	0.2204 (6)	0.0341 (3)	0.037 (2)
C44	0.3117 (6)	0.0828 (6)	0.0603 (5)	0.071 (4)
H44A	0.3257	0.0515	0.0877	0.106*
H44B	0.3318	0.0628	0.0317	0.106*
H44C	0.2679	0.0764	0.0569	0.106*
O1	0.2772 (3)	0.2004 (4)	0.0005 (2)	0.0493 (18)
O2	0.3263 (4)	0.1693 (4)	0.0672 (3)	0.0524 (19)
P	0.65419 (10)	0.05754 (13)	0.07261 (8)	0.0292 (5)
F1	0.6583 (5)	-0.0306 (4)	0.0948 (3)	0.119 (4)
F2	0.7032 (4)	0.0871 (8)	0.1072 (4)	0.146 (5)
F3	0.6046 (4)	0.0254 (7)	0.0388 (4)	0.119 (4)
F4	0.6470 (5)	0.1442 (4)	0.0513 (3)	0.100 (3)
F5	0.7037 (3)	0.0336 (4)	0.0353 (2)	0.0601 (17)
F6	0.6056 (3)	0.0800 (3)	0.1128 (2)	0.0624 (19)
C45	0.1901 (4)	0.1786 (5)	0.2841 (4)	0.042 (2)
H45A	0.1964	0.1628	0.3176	0.051*
H45B	0.2186	0.1466	0.2645	0.051*
Cl1	0.11552 (10)	0.15496 (13)	0.26745 (8)	0.0374 (5)

Cl2	0.20634 (11)	0.28248 (15)	0.27759 (10)	0.0492 (6)
C46	0.6692 (8)	0.7569 (13)	0.1088 (6)	0.127 (8)
H46A	0.7016	0.7350	0.0883	0.153*
H46B	0.6795	0.8139	0.1166	0.153*
Cl3	0.6659 (2)	0.7028 (6)	0.1582 (2)	0.192 (4)
Cl4	0.6019 (3)	0.7548 (7)	0.0786 (2)	0.223 (5)
C47	0.2279 (5)	0.2654 (6)	0.1476 (4)	0.048 (2)
H47A	0.2214	0.2964	0.1771	0.058*
H47B	0.2716	0.2672	0.1402	0.058*
Cl5	0.18769 (11)	0.31217 (16)	0.10153 (9)	0.0492 (6)
Cl6	0.20591 (13)	0.16307 (16)	0.15667 (10)	0.0538 (6)

*Atomic displacement parameters (Å²) for **1a**.*

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ir	0.01124 (12)	0.01152 (12)	0.02126 (13)	0.00064 (10)	-0.00125 (10)	-0.00117 (11)
N1	0.013 (3)	0.011 (3)	0.024 (3)	0.004 (2)	-0.003 (2)	-0.001 (2)
N2	0.020 (3)	0.021 (3)	0.025 (3)	0.002 (2)	0.003 (3)	-0.005 (3)
N3	0.012 (3)	0.013 (3)	0.029 (3)	-0.002 (2)	0.003 (2)	-0.003 (2)
N4	0.021 (3)	0.014 (3)	0.031 (3)	0.004 (3)	0.010 (3)	0.001 (3)
N5	0.019 (3)	0.016 (3)	0.024 (3)	-0.001 (2)	-0.001 (2)	0.000 (2)
N6	0.038 (4)	0.024 (3)	0.027 (3)	-0.002 (3)	-0.010 (3)	0.005 (3)
N7	0.013 (3)	0.014 (3)	0.024 (3)	-0.001 (2)	0.004 (2)	-0.003 (2)
C1	0.015 (3)	0.010 (3)	0.034 (4)	0.000 (3)	0.005 (3)	-0.001 (3)
C2	0.021 (4)	0.016 (3)	0.031 (4)	0.003 (3)	-0.002 (3)	0.000 (3)
C3	0.015 (3)	0.029 (4)	0.044 (5)	0.002 (3)	-0.008 (3)	0.003 (4)
C4	0.016 (3)	0.018 (4)	0.050 (5)	0.005 (3)	0.006 (3)	0.003 (4)
C5	0.020 (4)	0.013 (3)	0.044 (5)	0.003 (3)	0.009 (3)	0.000 (3)
C6	0.017 (3)	0.016 (3)	0.033 (4)	0.000 (3)	0.001 (3)	0.002 (3)
C7	0.019 (3)	0.010 (3)	0.025 (4)	0.001 (3)	0.003 (3)	-0.003 (3)
C8	0.016 (3)	0.011 (3)	0.028 (4)	0.002 (3)	-0.001 (3)	-0.002 (3)
C9	0.016 (3)	0.007 (3)	0.026 (3)	-0.003 (2)	-0.002 (3)	0.001 (3)
C10	0.016 (4)	0.025 (4)	0.028 (4)	0.002 (3)	-0.001 (3)	0.000 (3)
C11	0.021 (4)	0.018 (3)	0.039 (4)	0.003 (3)	-0.009 (3)	0.001 (3)
C12	0.032 (4)	0.025 (4)	0.025 (4)	0.001 (4)	-0.012 (3)	-0.007 (3)
C13	0.025 (4)	0.025 (4)	0.023 (4)	0.003 (3)	-0.002 (3)	-0.004 (3)
C14	0.015 (3)	0.018 (4)	0.019 (3)	0.000 (3)	0.001 (3)	0.000 (3)
C15	0.017 (3)	0.022 (4)	0.029 (4)	-0.002 (3)	-0.001 (3)	0.003 (3)
C16	0.026 (4)	0.029 (4)	0.027 (4)	-0.011 (3)	0.001 (3)	0.002 (3)
C17	0.015 (3)	0.039 (4)	0.026 (4)	-0.004 (3)	0.006 (3)	0.001 (4)

C18	0.015 (3)	0.033 (4)	0.036 (4)	0.005 (3)	0.008 (3)	0.002 (4)
C19	0.021 (4)	0.016 (3)	0.026 (4)	0.000 (3)	0.003 (3)	0.003 (3)
C20	0.015 (3)	0.020 (3)	0.023 (4)	-0.001 (3)	0.001 (3)	0.001 (3)
C21	0.015 (3)	0.017 (3)	0.023 (4)	-0.002 (3)	0.002 (3)	0.003 (3)
C22	0.020 (3)	0.013 (3)	0.020 (3)	0.001 (3)	-0.004 (3)	0.002 (3)
C23	0.014 (3)	0.014 (3)	0.033 (4)	0.002 (3)	-0.001 (3)	0.002 (3)
C24	0.018 (3)	0.019 (4)	0.036 (4)	-0.007 (3)	0.000 (3)	0.003 (3)
C25	0.030 (4)	0.011 (3)	0.036 (4)	0.000 (3)	0.000 (3)	0.003 (3)
C26	0.019 (4)	0.015 (3)	0.029 (4)	0.002 (3)	0.003 (3)	-0.004 (3)
C27	0.018 (3)	0.022 (4)	0.025 (4)	-0.001 (3)	-0.004 (3)	0.000 (3)
C28	0.023 (4)	0.023 (4)	0.028 (4)	0.000 (3)	-0.004 (3)	-0.006 (3)
C29	0.029 (4)	0.019 (4)	0.033 (4)	0.000 (3)	-0.004 (3)	-0.005 (3)
C30	0.037 (5)	0.045 (5)	0.030 (4)	-0.001 (4)	-0.016 (4)	-0.004 (4)
C31	0.040 (5)	0.036 (5)	0.033 (5)	-0.002 (4)	-0.017 (4)	0.005 (4)
C32	0.032 (4)	0.025 (4)	0.032 (4)	-0.003 (3)	-0.006 (4)	-0.001 (3)
C33	0.023 (4)	0.020 (4)	0.023 (4)	0.000 (3)	0.000 (3)	0.001 (3)
C34	0.021 (3)	0.014 (3)	0.026 (4)	0.000 (3)	0.002 (3)	-0.001 (3)
C35	0.018 (3)	0.012 (3)	0.029 (4)	-0.002 (3)	-0.005 (3)	-0.002 (3)
C36	0.024 (4)	0.022 (4)	0.033 (4)	-0.003 (3)	0.001 (3)	-0.010 (3)
C37	0.035 (4)	0.015 (4)	0.036 (4)	-0.007 (3)	0.001 (4)	-0.001 (3)
C38	0.035 (5)	0.024 (4)	0.031 (4)	-0.001 (3)	-0.001 (4)	0.005 (3)
C39	0.062 (6)	0.020 (4)	0.038 (5)	-0.006 (4)	-0.017 (4)	0.014 (4)
C40	0.073 (8)	0.060 (7)	0.051 (6)	-0.004 (6)	0.005 (6)	0.023 (6)
C41	0.085 (10)	0.098 (11)	0.066 (8)	-0.009 (9)	0.008 (7)	0.020 (8)
C42	0.047 (8)	0.26 (3)	0.066 (9)	0.008 (12)	0.003 (7)	0.005 (13)
C43	0.034 (5)	0.036 (5)	0.040 (5)	-0.006 (4)	-0.005 (4)	-0.011 (4)
C44	0.104 (10)	0.024 (5)	0.084 (9)	-0.021 (6)	-0.022 (8)	-0.014 (5)
O1	0.052 (4)	0.044 (4)	0.051 (4)	-0.004 (3)	-0.019 (3)	-0.022 (3)
O2	0.083 (5)	0.019 (3)	0.056 (4)	-0.018 (3)	-0.025 (4)	-0.009 (3)
P	0.0316 (11)	0.0261 (10)	0.0297 (11)	0.0087 (9)	0.0080 (9)	-0.0011 (9)
F1	0.235 (11)	0.058 (4)	0.064 (5)	0.082 (6)	0.080 (6)	0.028 (4)
F2	0.059 (5)	0.247 (13)	0.132 (8)	0.022 (7)	-0.032 (5)	-0.127 (9)
F3	0.065 (5)	0.146 (9)	0.146 (8)	-0.017 (6)	-0.019 (5)	-0.072 (7)
F4	0.179 (9)	0.038 (4)	0.083 (5)	0.039 (5)	0.072 (6)	0.026 (4)
F5	0.064 (4)	0.057 (4)	0.060 (4)	0.007 (3)	0.035 (3)	-0.012 (3)
F6	0.084 (5)	0.026 (3)	0.076 (4)	0.020 (3)	0.054 (4)	0.006 (3)
C45	0.032 (5)	0.028 (5)	0.066 (7)	-0.001 (4)	-0.005 (5)	0.008 (4)
Cl1	0.0295 (10)	0.0314 (11)	0.0512 (13)	-0.0011 (9)	-0.0024 (9)	-0.0013 (10)
Cl2	0.0446 (13)	0.0330 (12)	0.0702 (17)	-0.0050 (10)	-0.0037 (12)	0.0053 (12)
C46	0.124 (15)	0.170 (19)	0.087 (12)	-0.084 (14)	0.052 (11)	-0.049 (12)

Cl3	0.052 (2)	0.411 (13)	0.114 (4)	-0.016 (5)	-0.007 (3)	0.018 (6)
Cl4	0.085 (3)	0.480 (15)	0.105 (4)	0.015 (6)	0.035 (3)	0.057 (7)
C47	0.040 (5)	0.037 (5)	0.068 (7)	0.000 (4)	0.003 (5)	0.001 (5)
Cl5	0.0406 (13)	0.0516 (14)	0.0555 (15)	0.0074 (11)	0.0053 (11)	0.0078 (12)
Cl6	0.0536 (15)	0.0437 (14)	0.0641 (16)	-0.0052 (12)	-0.0023 (13)	0.0075 (13)

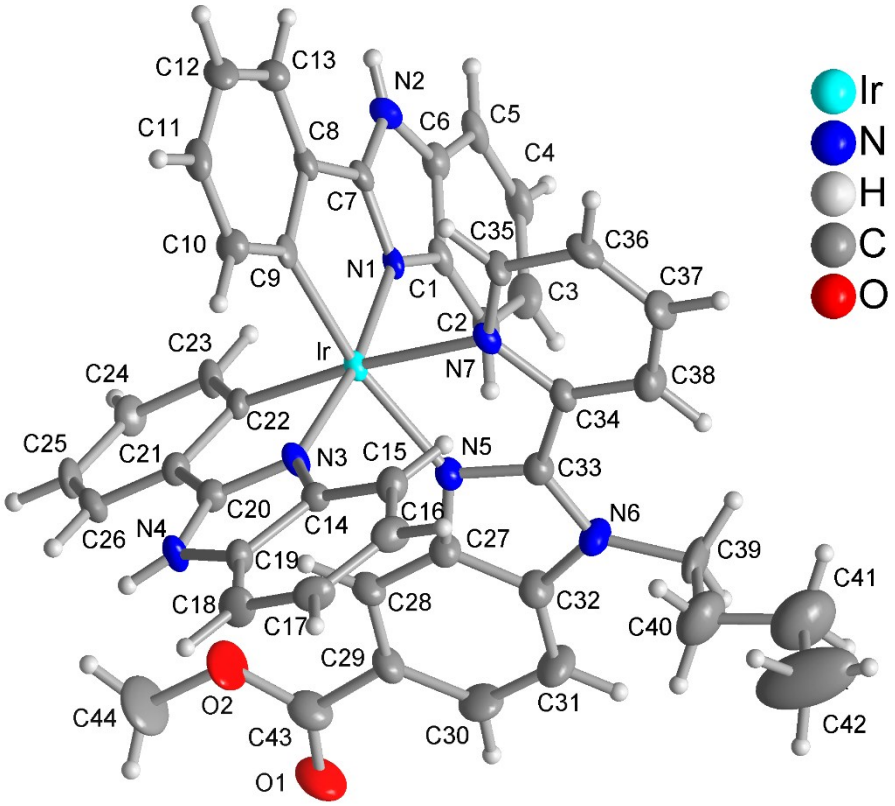


Figure S23. Iridium cation in the structure of **1a** with 50% thermal ellipsoids. The larger thermal ellipsoids of the butyl chain are indicative of some orientational disorder.

Table S3. Bond lengths [Å] and angles [°] for **1a**.

Ir—C22	2.012 (7)	C24—C25	1.391 (11)
Ir—C9	2.023 (7)	C24—H24	0.9500
Ir—N1	2.051 (6)	C25—C26	1.395 (10)
Ir—N3	2.055 (6)	C25—H25	0.9500
Ir—N5	2.119 (6)	C26—H26	0.9500
Ir—N7	2.149 (6)	C27—C28	1.390 (10)
N1—C7	1.325 (9)	C27—C32	1.392 (11)
N1—C1	1.390 (9)	C28—C29	1.378 (11)
N2—C7	1.348 (9)	C28—H28	0.9500
N2—C6	1.377 (10)	C29—C30	1.406 (12)
N2—H2	0.79 (9)	C29—C43	1.514 (11)

N3—C20	1.337 (9)	C30—C31	1.370 (12)
N3—C14	1.385 (9)	C30—H30	0.9500
N4—C20	1.341 (9)	C31—C32	1.393 (11)
N4—C19	1.383 (9)	C31—H31	0.9500
N4—H4	0.82 (9)	C33—C34	1.468 (10)
N5—C33	1.330 (9)	C34—C38	1.384 (10)
N5—C27	1.392 (9)	C35—C36	1.397 (10)
N6—C33	1.374 (10)	C35—H35	0.9500
N6—C32	1.388 (10)	C36—C37	1.368 (12)
N6—C39	1.473 (10)	C36—H36	0.9500
N7—C35	1.330 (9)	C37—C38	1.377 (11)
N7—C34	1.359 (9)	C37—H37	0.9500
C1—C2	1.388 (10)	C38—H38	0.9500
C1—C6	1.401 (10)	C39—C40	1.591 (15)
C2—C3	1.387 (10)	C39—H39A	0.9900
C2—H2A	0.9500	C39—H39B	0.9900
C3—C4	1.379 (12)	C40—C41	1.532 (18)
C3—H3	0.9500	C40—H40A	0.9900
C4—C5	1.385 (12)	C40—H40B	0.9900
C4—H4A	0.9500	C41—C42	1.525 (18)
C5—C6	1.394 (10)	C41—H41A	0.9900
C5—H5	0.9500	C41—H41B	0.9900
C7—C8	1.447 (10)	C42—H42A	0.9800
C8—C13	1.405 (10)	C42—H42B	0.9800
C8—C9	1.414 (10)	C42—H42C	0.9800
C9—C10	1.390 (10)	C43—O1	1.200 (10)
C10—C11	1.390 (11)	C43—O2	1.330 (11)
C10—H10	0.9500	C44—O2	1.473 (10)
C11—C12	1.396 (11)	C44—H44A	0.9800
C11—H11	0.9500	C44—H44B	0.9800
C12—C13	1.364 (11)	C44—H44C	0.9800
C12—H12	0.9500	P—F2	1.540 (8)
C13—H13	0.9500	P—F3	1.549 (8)
C14—C15	1.378 (10)	P—F4	1.555 (6)
C14—C19	1.400 (10)	P—F5	1.570 (6)
C15—C16	1.385 (10)	P—F1	1.582 (7)
C15—H15	0.9500	P—F6	1.609 (5)
C16—C17	1.402 (11)	C45—Cl2	1.755 (9)
C16—H16	0.9500	C45—Cl1	1.761 (9)
C17—C18	1.379 (11)	C45—H45A	0.9900

C17—H17	0.9500	C45—H45B	0.9900
C18—C19	1.397 (10)	C46—Cl3	1.66 (2)
C18—H18	0.9500	C46—Cl4	1.72 (2)
C20—C21	1.450 (9)	C46—H46A	0.9900
C21—C26	1.392 (10)	C46—H46B	0.9900
C21—C22	1.429 (10)	C47—Cl5	1.755 (11)
C22—C23	1.404 (10)	C47—Cl6	1.771 (10)
C23—C24	1.378 (10)	C47—H47A	0.9900
C23—H23	0.9500	C47—H47B	0.9900
C22—Ir—C9	90.8 (3)	C24—C25—H25	120.2
C22—Ir—N1	93.3 (3)	C26—C25—H25	120.2
C9—Ir—N1	79.7 (2)	C21—C26—C25	118.8 (7)
C22—Ir—N3	80.2 (3)	C21—C26—H26	120.6
C9—Ir—N3	93.5 (3)	C25—C26—H26	120.6
N1—Ir—N3	170.6 (2)	C28—C27—C32	121.2 (7)
C22—Ir—N5	98.6 (2)	C28—C27—N5	130.7 (7)
C9—Ir—N5	170.2 (2)	C32—C27—N5	108.1 (7)
N1—Ir—N5	97.1 (2)	C29—C28—C27	116.6 (7)
N3—Ir—N5	90.6 (2)	C29—C28—H28	121.7
C22—Ir—N7	174.3 (3)	C27—C28—H28	121.7
C9—Ir—N7	94.8 (2)	C28—C29—C30	122.2 (7)
N1—Ir—N7	88.6 (2)	C28—C29—C43	120.3 (7)
N3—Ir—N7	98.6 (2)	C30—C29—C43	117.5 (7)
N5—Ir—N7	75.8 (2)	C31—C30—C29	121.3 (8)
C7—N1—C1	107.5 (6)	C31—C30—H30	119.4
C7—N1—Ir	114.4 (4)	C29—C30—H30	119.4
C1—N1—Ir	138.1 (5)	C30—C31—C32	116.8 (8)
C7—N2—C6	108.1 (6)	C30—C31—H31	121.6
C7—N2—H2	127 (7)	C32—C31—H31	121.6
C6—N2—H2	125 (7)	N6—C32—C27	107.0 (7)
C20—N3—C14	107.2 (6)	N6—C32—C31	131.0 (8)
C20—N3—Ir	114.3 (5)	C27—C32—C31	122.0 (8)
C14—N3—Ir	138.5 (5)	N5—C33—N6	111.1 (6)
C20—N4—C19	108.0 (6)	N5—C33—C34	118.8 (7)
C20—N4—H4	124 (6)	N6—C33—C34	130.0 (7)
C19—N4—H4	128 (6)	N7—C34—C38	120.8 (7)
C33—N5—C27	107.1 (6)	N7—C34—C33	112.1 (6)
C33—N5—Ir	115.7 (5)	C38—C34—C33	127.1 (7)
C27—N5—Ir	137.1 (5)	N7—C35—C36	122.4 (7)

C33—N6—C32	106.7 (6)	N7—C35—H35	118.8
C33—N6—C39	128.3 (7)	C36—C35—H35	118.8
C32—N6—C39	124.7 (7)	C37—C36—C35	118.1 (7)
C35—N7—C34	119.1 (6)	C37—C36—H36	120.9
C35—N7—Ir	123.5 (5)	C35—C36—H36	120.9
C34—N7—Ir	117.4 (4)	C36—C37—C38	120.0 (7)
C2—C1—N1	132.2 (7)	C36—C37—H37	120.0
C2—C1—C6	120.5 (7)	C38—C37—H37	120.0
N1—C1—C6	107.3 (6)	C37—C38—C34	119.4 (8)
C3—C2—C1	117.5 (7)	C37—C38—H38	120.3
C3—C2—H2A	121.2	C34—C38—H38	120.3
C1—C2—H2A	121.2	N6—C39—C40	108.8 (8)
C4—C3—C2	121.2 (8)	N6—C39—H39A	109.9
C4—C3—H3	119.4	C40—C39—H39A	109.9
C2—C3—H3	119.4	N6—C39—H39B	109.9
C3—C4—C5	122.7 (7)	C40—C39—H39B	109.9
C3—C4—H4A	118.6	H39A—C39—H39B	108.3
C5—C4—H4A	118.6	C41—C40—C39	110.6 (10)
C4—C5—C6	115.8 (7)	C41—C40—H40A	109.5
C4—C5—H5	122.1	C39—C40—H40A	109.5
C6—C5—H5	122.1	C41—C40—H40B	109.5
N2—C6—C5	131.5 (7)	C39—C40—H40B	109.5
N2—C6—C1	106.3 (6)	H40A—C40—H40B	108.1
C5—C6—C1	122.2 (7)	C42—C41—C40	110.0 (14)
N1—C7—N2	110.8 (6)	C42—C41—H41A	109.7
N1—C7—C8	118.2 (6)	C40—C41—H41A	109.7
N2—C7—C8	130.9 (7)	C42—C41—H41B	109.7
C13—C8—C9	122.5 (6)	C40—C41—H41B	109.7
C13—C8—C7	125.4 (6)	H41A—C41—H41B	108.2
C9—C8—C7	112.1 (6)	C41—C42—H42A	109.5
C10—C9—C8	116.2 (7)	C41—C42—H42B	109.5
C10—C9—Ir	128.3 (6)	H42A—C42—H42B	109.5
C8—C9—Ir	115.0 (5)	C41—C42—H42C	109.5
C9—C10—C11	121.3 (7)	H42A—C42—H42C	109.5
C9—C10—H10	119.4	H42B—C42—H42C	109.5
C11—C10—H10	119.4	O1—C43—O2	124.3 (9)
C10—C11—C12	121.2 (7)	O1—C43—C29	124.3 (9)
C10—C11—H11	119.4	O2—C43—C29	111.4 (7)
C12—C11—H11	119.4	O2—C44—H44A	109.5
C13—C12—C11	119.2 (7)	O2—C44—H44B	109.5

C13—C12—H12	120.4	H44A—C44—H44B	109.5
C11—C12—H12	120.4	O2—C44—H44C	109.5
C12—C13—C8	119.5 (7)	H44A—C44—H44C	109.5
C12—C13—H13	120.2	H44B—C44—H44C	109.5
C8—C13—H13	120.2	C43—O2—C44	116.4 (8)
C15—C14—N3	132.1 (6)	F2—P—F3	178.2 (8)
C15—C14—C19	120.4 (6)	F2—P—F4	91.6 (7)
N3—C14—C19	107.5 (6)	F3—P—F4	90.1 (6)
C14—C15—C16	117.8 (7)	F2—P—F5	90.9 (4)
C14—C15—H15	121.1	F3—P—F5	89.6 (4)
C16—C15—H15	121.1	F4—P—F5	92.4 (4)
C15—C16—C17	121.6 (7)	F2—P—F1	89.8 (7)
C15—C16—H16	119.2	F3—P—F1	88.4 (6)
C17—C16—H16	119.2	F4—P—F1	177.4 (5)
C18—C17—C16	121.2 (7)	F5—P—F1	89.8 (4)
C18—C17—H17	119.4	F2—P—F6	87.1 (4)
C16—C17—H17	119.4	F3—P—F6	92.4 (5)
C17—C18—C19	116.6 (7)	F4—P—F6	89.7 (3)
C17—C18—H18	121.7	F5—P—F6	177.1 (4)
C19—C18—H18	121.7	F1—P—F6	88.2 (3)
N4—C19—C18	131.3 (7)	Cl2—C45—Cl1	112.2 (5)
N4—C19—C14	106.3 (6)	Cl2—C45—H45A	109.2
C18—C19—C14	122.3 (7)	Cl1—C45—H45A	109.2
N3—C20—N4	111.0 (6)	Cl2—C45—H45B	109.2
N3—C20—C21	118.0 (6)	Cl1—C45—H45B	109.2
N4—C20—C21	131.1 (7)	H45A—C45—H45B	107.9
C26—C21—C22	123.0 (6)	Cl3—C46—Cl4	111.8 (9)
C26—C21—C20	124.8 (7)	Cl3—C46—H46A	109.3
C22—C21—C20	112.1 (6)	Cl4—C46—H46A	109.3
C23—C22—C21	115.4 (6)	Cl3—C46—H46B	109.3
C23—C22—Ir	129.1 (5)	Cl4—C46—H46B	109.3
C21—C22—Ir	115.4 (5)	H46A—C46—H46B	107.9
C24—C23—C22	122.0 (7)	Cl5—C47—Cl6	112.6 (6)
C24—C23—H23	119.0	Cl5—C47—H47A	109.1
C22—C23—H23	119.0	Cl6—C47—H47A	109.1
C23—C24—C25	121.2 (7)	Cl5—C47—H47B	109.1
C23—C24—H24	119.4	Cl6—C47—H47B	109.1
C25—C24—H24	119.4	H47A—C47—H47B	107.8
C24—C25—C26	119.5 (7)		

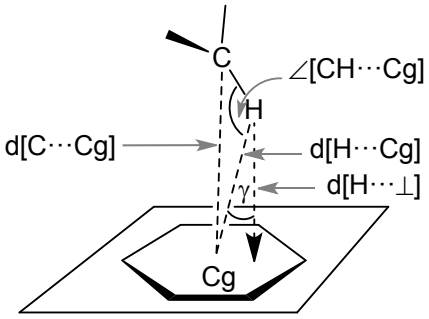
The packing in the structure of **1d** is organized (according to the analysis by PLATON[i] by intermolecular N-H···F, C-H···F (Table S3a),[10,11,12] and C-H···π interactions[13] (Table S3b) but not by C-H···Cl,[14] or π-π interactions.[15]

The listed "Analysis of Short Ring-Interactions" for possible π-stacking interactions yielded rather long centroid-centroid distances (>4.0 Å) together with non-parallel ring planes (alpha >> 0°) and large slip angles (β, γ >30°).
In comparison, significant π-stacking show rather short centroid-centroid contacts (<3.8 Å), near parallel ring planes (alpha < 10° to ~0° or even exactly 0° by symmetry), small slip angles (β, γ <25°) and vertical displacements (slippage <1.5 Å) which translate into a sizable overlap of the aryl-plane areas.[16]
Significant intermolecular C-H···π contacts start below around 2.7 Å for the (C-)H···ring centroid distances with H-perp also starting at below 2.6-2.7 Å and C-H··Cg > 145°.

Table S4a. Hydrogen bonds [Å and °] for **1a**.[a]

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···F1^{i}	0.79 (9)	2.06 (9)	2.846 (10)	176 (10)
N4—H4···F6	0.82 (9)	2.14 (9)	2.941 (8)	167 (9)
C18—H18···F4	0.95	2.53	3.235 (11)	131
C31—H31···F5^{ii}	0.95	2.56	3.075 (10)	114
C39—H39*A*···Cl5^{iii}	0.99	2.96	3.860 (10)	151
C39—H39*A*···Cl6^{iii}	0.99	2.99	3.677 (11)	128
C44—H44*B*···F5^{iv}	0.98	2.59	3.330 (13)	132
C45—H45*A*···F2^{v}	0.99	2.47	3.433 (13)	165
C47—H47*A*···Cl2	0.99	2.87	3.719 (12)	144

[a] For found and refined H atoms the standard deviations are given for their hydrogen bond distances and angles.
Symmetry codes: (i) -*x*+1, *y*+1/2, -*z*+1/2; (ii) *x*-1/2, -*y*+1/2, -*z*; (iii) -*x*+1/2, *y*+1/2, *z*; (iv) -*x*+1, -*y*, -*z*; (v) *x*-1/2, *y*, -*z*+1/2.



Scheme S2. Graphical presentation of the parameters used for the description of CH-π interactions.

Table S4b. Analysis of intermolecular X-H...Cg(Pi-Ring) Interactions (H..Cg < 3.0 Ang. - Gamma < 30.0 Deg) in **1a**

==========

Cg(J) = Center of gravity of ring J (Plane number above)
- H-Perp = Perpendicular distance of H to ring plane J
- Gamma = Angle between Cg-H vector and ring J normal
- C-H..Cg = C-H-Cg angle (degrees)
- C..Cg = Distance of X to Cg (Angstrom)
- C-H, Pi = Angle of the X-H bond with the Pi-plane (i.e.' Perpendicular = 90 degrees, Parallel = 0 degrees)

X--H(I)	Res(I)	Cg(J) [ARU(J)]		H..Cg	H-Perp	Gamma	C-H..Cg	C..Cg	C-H,Pi
C(36) -H(36)	[1]	-> Cg(11) [4655.01]		2.53	2.50	9.24	150	3.384(9)	67
C(37) -H(37)	[1]	-> Cg(9) [4655.01]		2.60	2.54	12.81	143	3.407(9)	58
C(42) -H(42B)	[1]	-> Cg(5) [5665.01]		2.65	2.57	14.28	151	3.540(15)	53
		Min or Max	2.530	2.648	9.2	162	3.152	67	

[4655] = 1-X,1/2+Y,1/2-Z
[5665] = 1-X,1-Y,-Z

The Cg(I) refer to the Ring Centre-of-Gravity numbers given in

Ring 5: N3-N4-C14-C19-C20
Ring 9: C8-C9-C10-C11-C12-C13
Ring 11: C21-C22-C23-C24-C25-C26

bis(1-phenyl-1H-pyrazole-k^{2}N,C)-{methyl 1-butyl-2-(pyridin-2-yl)-1H-benzo[d]imidazole-5-carboxylate-k^{2}N,N'}iridium(III) hexafluorophosphate dichloromethane solvate, 3a

Table S5. Crystal data and structure refinement for **3a**.

Crystal data

$C_{35}H_{29.50}IrN_7O_2 \cdot F_6P \cdot 0.5(CH_2Cl_2)$	$F(000) = 3772$
$M_r = 959.79$	$D_x = 1.477$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 24.4157$ (10) Å	Cell parameters from 9344 reflections
$b = 16.5559$ (7) Å	$\theta = 2.6–30.5°$
$c = 23.3462$ (9) Å	$\mu = 3.25$ mm^{-1}
$\beta = 113.7896$ (14)°	$T = 100$ K
$V = 8635.2$ (6) Å^3	Prism, yellow
$Z = 8$	0.19 × 0.17 × 0.16 mm
	CCDC no. 1483571

Data collection

Bruker D8 Quest CCD diffractometer	$R_{int} = 0.044$
Radiation source: fine-focus sealed tube	$\theta_{max} = 26.1°$, $\theta_{min} = 2.0°$
ω and ϕ scans	$h = -30 \rightarrow 30$
260552 measured reflections	$k = -20 \rightarrow 20$
8538 independent reflections	$l = -28 \rightarrow 28$
8151 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.034$	H-atom parameters constrained
$wR(F^2) = 0.082$	$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2 + 58.2454P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} = 0.001$
8538 reflections	$\Delta\rangle_{max} = 1.65$ e Å^{-3}
676 parameters	$\Delta\rangle_{min} = -2.13$ e Å^{-3}

Special details

Refinement. Hydrogen atoms for aromatic CH, aliphatic CH_2 and methyl groups were positioned geometrically (C—H = 0.95 Å for aromatic CH, C—H = 0.99 Å for CH_2, C—H = 0.98 Å for CH_3) and refined using a riding model (AFIX 43 for aromatic CH, AFIX 23 for CH_2, AFIX 137 for rotating group for CH_3), with $U_{iso}(H) = 1.2U_{eq}(CH)$ and $U_{iso}(H) = 1.5U_{eq}(CH_3)$. The Ir molecule suffers from a mobility disorder together with surrounding disordered solvent molecules. One half-occupied CH_2Cl_2 molecule could be reasonably refined. Additional solvent molecules, most likely also CH_2Cl_2 because of the associated electron density were strongly disordered and the associated electron density was removed by using the option SQUEEZE built in PLATON.
The largest residual electron density peak of 1.65 e $Å^{-3}$ is within 1.00 Å from P1 and F6 of one of the PF_6 anions. The second largest electron density peak of 1.40 e $Å^{-3}$ is within 1.00 Å from F3 of the same PF_6 anion, which indicates some unresolved disorder of this PF_6 anion. The deepest hole of -2.13 e $Å^{-3}$ is 0.80 Å from Ir.
Possible disordered solvent residues in what would be otherwise voids were tried to remove with the option SQUEEZE by Platon. In two voids of 735 $Å^3$ each, in the unit cell, 176 electrons each, were removed. Total potential solvent accessible void volume per unit cell is 1468.2 $Å^3$ (17%) with a total electron count/cell of 358. The total electron count for the potential solvent molecules is: hexane = 48, CH_2Cl_2 = 48. The structure has Z = 8. Thus, a half-occupied CH_2Cl_2 or hexane molecule with Z = 8 would give 24 x 8 = 192 electrons per void in the unit cell. With two voids of the same electron count, overall the approximate equivalent of a full hexane or CH_2Cl_2 molecule could be present per formula unit.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for ***3a***

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ir	0.18028 (2)	0.92390 (2)	0.16476 (2)	0.02794 (6)	
N1	0.24232 (17)	0.9188 (3)	0.12866 (17)	0.0490 (11)	
C1A	0.2462 (8)	0.9399 (7)	0.0733 (8)	0.028 (3)	0.4
H1A	0.2124	0.9517	0.0359	0.033*	0.4
C2A	0.3063 (9)	0.9424 (8)	0.0780 (10)	0.037 (3)	0.4
H2A	0.3203	0.9461	0.0456	0.045*	0.4
C3A	0.3393 (13)	0.9379 (10)	0.1433 (14)	0.036 (4)	0.4
H3A	0.3813	0.9458	0.1645	0.044*	0.4
C1B	0.2418 (7)	0.9023 (9)	0.0724 (6)	0.063 (4)	0.6
H1B	0.2075	0.8931	0.0348	0.076*	0.6
C2B	0.3010 (8)	0.9010 (13)	0.0796 (8)	0.104 (7)	0.6
H2B	0.3146	0.8977	0.0468	0.125*	0.6
C3B	0.3357 (9)	0.9054 (11)	0.1410 (10)	0.072 (6)	0.6
H3B	0.3780	0.8994	0.1597	0.087*	0.6
N2	0.30015 (16)	0.9198 (3)	0.17166 (18)	0.0477 (10)	
C4	0.30866 (18)	0.9221 (2)	0.23527 (19)	0.0339 (9)	

C5	0.25560 (18)	0.9261 (2)	0.24454 (18)	0.0312 (9)	
C6	0.2623 (2)	0.9301 (3)	0.3066 (2)	0.0439 (11)	
H6	0.2279	0.9337	0.3157	0.053*	
C7	0.3192 (2)	0.9289 (3)	0.3558 (2)	0.0510 (13)	
H7	0.3228	0.9315	0.3978	0.061*	
C8	0.3699 (2)	0.9240 (3)	0.3440 (2)	0.0443 (12)	
H8	0.4081	0.9227	0.3779	0.053*	
C9	0.36569 (19)	0.9208 (2)	0.2833 (2)	0.0380 (10)	
H9	0.4004	0.9179	0.2746	0.046*	
N3	0.12661 (16)	0.9402 (3)	0.21007 (16)	0.0487 (11)	
C10	0.1010 (2)	0.8935 (6)	0.2391 (2)	0.083 (2)	
H10	0.0996	0.8361	0.2386	0.099*	
C11	0.0767 (4)	0.9449 (10)	0.2704 (4)	0.147 (7)	
H11	0.0559	0.9283	0.2950	0.176*	
C12	0.0876 (4)	1.0203 (9)	0.2599 (4)	0.128 (6)	
H12	0.0760	1.0674	0.2753	0.154*	
N4	0.11866 (19)	1.0177 (4)	0.2227 (2)	0.0722 (19)	
C13	0.1440 (3)	1.0760 (4)	0.1972 (3)	0.075 (2)	
C14	0.1790 (2)	1.0452 (3)	0.1671 (2)	0.0478 (13)	
C15	0.2043 (3)	1.1028 (4)	0.1420 (3)	0.075 (2)	
H15	0.2299	1.0863	0.1224	0.090*	
C16	0.1923 (4)	1.1858 (5)	0.1452 (4)	0.111 (4)	
H16	0.2084	1.2242	0.1260	0.133*	
C17	0.1588 (7)	1.2112 (7)	0.1750 (6)	0.168 (8)	
H17	0.1528	1.2675	0.1781	0.201*	
C18	0.1336 (4)	1.1583 (6)	0.2005 (4)	0.125 (5)	
H18	0.1089	1.1766	0.2206	0.150*	
N5	0.10927 (15)	0.9056 (2)	0.07487 (16)	0.0378 (9)	
C19	0.08006 (17)	0.9512 (3)	0.02138 (18)	0.0393 (11)	
C20	0.07858 (19)	1.0329 (4)	0.0126 (2)	0.0516 (14)	
H20	0.0984	1.0690	0.0463	0.062*	
C21	0.0465 (2)	1.0607 (5)	-0.0482 (2)	0.073 (2)	
C22	0.0167 (2)	1.0058 (6)	-0.0975 (2)	0.083 (3)	
H22	-0.0050	1.0264	-0.1384	0.099*	
C23	0.0181 (3)	0.9265 (6)	-0.0885 (3)	0.093 (3)	
H23	-0.0021	0.8903	-0.1220	0.112*	
C24	0.0504 (2)	0.8990 (4)	-0.0282 (2)	0.072 (2)	
N6A	0.0718 (3)	0.8351 (5)	-0.0129 (3)	0.0291 (14)	0.5
C25A	0.1060 (4)	0.8393 (6)	0.0510 (4)	0.030 (2)	0.5
C26A	0.1353 (4)	0.7727 (6)	0.0946 (4)	0.0350 (19)	0.5

N6B	0.0503 (3)	0.8107 (4)	0.0048 (3)	0.0258 (13)	0.5
C25B	0.0886 (4)	0.8213 (5)	0.0660 (4)	0.0254 (18)	0.5
C26B	0.1149 (4)	0.7627 (5)	0.1163 (4)	0.0330 (18)	0.5
N7	0.1687 (2)	0.7958 (2)	0.1583 (2)	0.0602 (14)	
C27	0.1995 (3)	0.7447 (3)	0.2032 (3)	0.077 (2)	
H27	0.2223	0.7628	0.2447	0.092*	
C28A	0.1975 (5)	0.6648 (7)	0.1877 (5)	0.052 (3)	0.5
H28A	0.2245	0.6281	0.2168	0.063*	0.5
C29A	0.1570 (5)	0.6363 (6)	0.1305 (4)	0.054 (3)	0.5
H29A	0.1503	0.5799	0.1236	0.065*	0.5
C30A	0.1260 (4)	0.6912 (6)	0.0832 (4)	0.046 (2)	0.5
H30A	0.0987	0.6724	0.0434	0.055*	0.5
C31A	0.0635 (4)	0.7665 (5)	-0.0565 (4)	0.0358 (18)	0.5
H31A	0.0320	0.7807	-0.0978	0.043*	0.5
H31B	0.0495	0.7188	-0.0406	0.043*	0.5
C32A	0.1198 (4)	0.7447 (5)	-0.0644 (4)	0.0363 (18)	0.5
H32A	0.1502	0.7267	-0.0235	0.044*	0.5
H32B	0.1111	0.6987	-0.0938	0.044*	0.5
C33A	0.1455 (4)	0.8127 (6)	-0.0884 (4)	0.040 (2)	0.5
H33A	0.1548	0.8580	-0.0583	0.048*	0.5
H33B	0.1144	0.8317	-0.1286	0.048*	0.5
C34A	0.2011 (7)	0.7925 (10)	-0.0985 (7)	0.050 (3)	0.5
H34A	0.2333	0.7777	-0.0585	0.075*	0.5
H34B	0.2133	0.8395	-0.1160	0.075*	0.5
H34C	0.1928	0.7470	-0.1277	0.075*	0.5
C28B	0.1765 (7)	0.6640 (8)	0.2155 (6)	0.078 (5)	0.5
H28B	0.1965	0.6344	0.2531	0.094*	0.5
C29B	0.1242 (6)	0.6364 (7)	0.1677 (5)	0.073 (4)	0.5
H29B	0.1092	0.5841	0.1701	0.088*	0.5
C30B	0.0942 (5)	0.6855 (6)	0.1170 (4)	0.052 (3)	0.5
H30B	0.0597	0.6663	0.0829	0.062*	0.5
C31B	0.0253 (3)	0.7348 (5)	-0.0284 (3)	0.0282 (16)	0.5
H31C	-0.0089	0.7475	-0.0683	0.034*	0.5
H31D	0.0100	0.7019	-0.0026	0.034*	0.5
C32B	0.0715 (4)	0.6857 (6)	-0.0422 (4)	0.044 (2)	0.5
C35A	0.0362 (4)	1.1655 (6)	-0.0536 (4)	0.043 (2)	0.55
O1A	0.0101 (4)	1.1964 (6)	-0.1040 (4)	0.083 (3)	0.55
O2A	0.0617 (3)	1.2080 (4)	-0.0008 (3)	0.0526 (16)	0.55
C36A	0.0589 (6)	1.2949 (6)	-0.0062 (5)	0.069 (3)	0.55
H36A	0.0882	1.3137	-0.0221	0.104*	0.55

H36B	0.0679	1.3189	0.0350	0.104*	0.55
H36C	0.0186	1.3111	-0.0352	0.104*	0.55
C35B	0.0516 (4)	1.1288 (6)	-0.0720 (5)	0.031 (2)	0.45
O1B	0.0256 (3)	1.1526 (4)	-0.1262 (3)	0.0419 (17)	0.45
O2B	0.0830 (3)	1.1775 (4)	-0.0254 (3)	0.0366 (15)	0.45
C36B	0.0886 (5)	1.2598 (6)	-0.0409 (6)	0.053 (3)	0.45
H36D	0.1128	1.2623	-0.0658	0.079*	0.45
H36E	0.1082	1.2912	-0.0024	0.079*	0.45
H36F	0.0488	1.2822	-0.0653	0.079*	0.45
P1	0.44468 (11)	1.00333 (15)	0.04554 (11)	0.0407 (5)	0.5
F1	0.4462 (3)	1.0703 (4)	-0.0035 (3)	0.0659 (18)	0.5
F2	0.4075 (3)	1.0637 (4)	0.0691 (4)	0.073 (2)	0.5
F3	0.4455 (3)	0.9285 (6)	0.0885 (4)	0.118 (4)	0.5
F4	0.4826 (3)	0.9427 (4)	0.0243 (4)	0.0717 (19)	0.5
F5	0.5053 (3)	1.0429 (5)	0.0952 (4)	0.082 (2)	0.5
F6	0.3869 (3)	0.9664 (3)	-0.0027 (3)	0.0529 (14)	0.5
P2	0.0000	0.72597 (10)	-0.2500	0.0336 (3)	
F7	0.07048 (11)	0.7251 (2)	-0.21246 (15)	0.0663 (9)	
F8	0.01080 (15)	0.7252 (3)	-0.31138 (15)	0.1007 (16)	
F9	0.0000	0.6317 (3)	-0.2500	0.141 (4)	
F10	0.0000	0.8204 (3)	-0.2500	0.0877 (18)	
C37	0.1961 (9)	0.8243 (18)	-0.1256 (10)	0.125 (11)	0.5
H37A	0.1881	0.7655	-0.1279	0.150*	0.5
H37B	0.1853	0.8435	-0.1689	0.150*	0.5
Cl1	0.14782 (11)	0.8712 (2)	-0.09670 (11)	0.0544 (6)	0.5
Cl2	0.26751 (19)	0.8377 (5)	-0.0867 (3)	0.177 (4)	0.5

Atomic displacement parameters (Å²) for ***3a***

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ir	0.02023 (8)	0.03960 (10)	0.01524 (8)	0.01089 (6)	-0.00192 (6)	-0.00748 (6)
N1	0.0250 (18)	0.092 (3)	0.0240 (18)	0.0203 (19)	0.0035 (15)	-0.0060 (19)
C1A	0.027 (6)	0.028 (6)	0.021 (5)	-0.002 (6)	0.002 (4)	-0.008 (5)
C2A	0.029 (6)	0.041 (7)	0.043 (8)	0.002 (5)	0.015 (6)	-0.006 (6)
C3A	0.030 (7)	0.042 (8)	0.035 (7)	-0.001 (7)	0.010 (5)	-0.012 (7)
C1B	0.041 (6)	0.119 (12)	0.027 (5)	0.021 (9)	0.012 (4)	-0.009 (8)
C2B	0.052 (8)	0.23 (2)	0.042 (7)	0.025 (14)	0.027 (6)	0.025 (13)
C3B	0.029 (7)	0.133 (17)	0.051 (8)	0.022 (11)	0.012 (6)	0.004 (12)
N2	0.0227 (18)	0.083 (3)	0.0306 (19)	0.0156 (18)	0.0034 (15)	-0.0023 (19)
C4	0.027 (2)	0.039 (2)	0.026 (2)	0.0110 (16)	-0.0005 (16)	-0.0038 (16)

C5	0.0248 (19)	0.036 (2)	0.0216 (18)	0.0100 (16)	-0.0019 (15)	-0.0067 (15)
C6	0.030 (2)	0.066 (3)	0.023 (2)	0.012 (2)	-0.0030 (17)	-0.0088 (19)
C7	0.038 (3)	0.074 (4)	0.021 (2)	0.015 (2)	-0.0083 (19)	-0.009 (2)
C8	0.028 (2)	0.045 (3)	0.034 (2)	0.0092 (18)	-0.0132 (18)	-0.0072 (19)
C9	0.024 (2)	0.034 (2)	0.041 (2)	0.0073 (16)	-0.0028 (18)	-0.0025 (18)
N3	0.0237 (18)	0.098 (3)	0.0173 (16)	0.0133 (19)	0.0006 (14)	-0.0092 (19)
C10	0.026 (2)	0.189 (8)	0.024 (2)	0.008 (4)	0.000 (2)	0.016 (4)
C11	0.031 (4)	0.37 (2)	0.033 (3)	0.044 (8)	0.008 (3)	-0.018 (8)
C12	0.041 (4)	0.272 (15)	0.046 (5)	0.065 (7)	-0.009 (3)	-0.073 (8)
N4	0.030 (2)	0.128 (5)	0.039 (2)	0.035 (3)	-0.0062 (19)	-0.046 (3)
C13	0.048 (3)	0.079 (4)	0.050 (3)	0.041 (3)	-0.029 (3)	-0.045 (3)
C14	0.035 (2)	0.052 (3)	0.028 (2)	0.007 (2)	-0.0170 (19)	-0.011 (2)
C15	0.078 (4)	0.054 (3)	0.042 (3)	-0.014 (3)	-0.028 (3)	0.008 (3)
C16	0.121 (7)	0.056 (4)	0.063 (5)	-0.029 (4)	-0.059 (5)	0.009 (4)
C17	0.178 (13)	0.077 (7)	0.102 (8)	0.041 (7)	-0.096 (8)	-0.047 (6)
C18	0.090 (6)	0.103 (6)	0.094 (6)	0.057 (5)	-0.053 (5)	-0.072 (6)
N5	0.0252 (17)	0.054 (2)	0.0211 (16)	0.0174 (16)	-0.0039 (13)	-0.0122 (15)
C19	0.0172 (18)	0.082 (3)	0.0146 (17)	0.016 (2)	0.0020 (15)	-0.002 (2)
C20	0.022 (2)	0.095 (4)	0.026 (2)	-0.010 (2)	-0.0028 (17)	0.018 (2)
C21	0.022 (2)	0.143 (6)	0.039 (3)	-0.018 (3)	-0.003 (2)	0.046 (3)
C22	0.013 (2)	0.218 (9)	0.014 (2)	0.020 (4)	0.0018 (17)	0.019 (4)
C23	0.052 (4)	0.183 (9)	0.019 (2)	0.072 (5)	-0.012 (2)	-0.027 (4)
C24	0.048 (3)	0.107 (5)	0.030 (3)	0.052 (3)	-0.016 (2)	-0.035 (3)
N6A	0.026 (4)	0.038 (4)	0.016 (3)	-0.002 (3)	0.002 (3)	-0.007 (3)
C25A	0.026 (5)	0.037 (5)	0.019 (4)	0.004 (4)	0.001 (4)	0.001 (4)
C26A	0.034 (5)	0.040 (5)	0.019 (4)	-0.003 (4)	-0.002 (4)	0.000 (4)
N6B	0.019 (3)	0.031 (4)	0.019 (3)	0.004 (3)	-0.002 (3)	-0.002 (3)
C25B	0.022 (4)	0.029 (5)	0.017 (4)	-0.005 (3)	0.000 (3)	-0.003 (3)
C26B	0.031 (4)	0.033 (4)	0.024 (4)	0.001 (4)	-0.001 (4)	0.005 (3)
N7	0.053 (3)	0.032 (2)	0.050 (3)	0.0099 (18)	-0.026 (2)	-0.0124 (18)
C27	0.065 (4)	0.041 (3)	0.068 (4)	0.004 (3)	-0.032 (3)	-0.002 (3)
C28A	0.057 (7)	0.050 (6)	0.028 (5)	-0.008 (5)	-0.006 (5)	0.009 (5)
C29A	0.071 (7)	0.036 (5)	0.031 (5)	-0.011 (5)	-0.005 (5)	-0.005 (4)
C30A	0.051 (6)	0.039 (5)	0.027 (4)	-0.007 (4)	-0.006 (4)	-0.004 (4)
C31A	0.035 (4)	0.042 (5)	0.019 (4)	-0.001 (4)	0.000 (3)	-0.008 (3)
C32A	0.035 (4)	0.045 (5)	0.022 (4)	0.003 (4)	0.005 (3)	-0.006 (3)
C33A	0.045 (5)	0.034 (5)	0.037 (5)	0.004 (4)	0.013 (4)	-0.006 (4)
C34A	0.037 (7)	0.062 (7)	0.053 (9)	-0.001 (5)	0.020 (7)	-0.013 (6)
C28B	0.085 (10)	0.055 (7)	0.046 (7)	-0.020 (7)	-0.025 (7)	0.019 (6)
C29B	0.093 (9)	0.050 (6)	0.039 (6)	-0.024 (6)	-0.012 (6)	0.013 (5)

C30B	0.056 (6)	0.044 (5)	0.029 (4)	-0.018 (5)	-0.010 (4)	0.005 (4)
C31B	0.019 (3)	0.034 (4)	0.024 (4)	-0.012 (3)	0.000 (3)	-0.003 (3)
C32B	0.031 (4)	0.045 (5)	0.045 (5)	0.004 (4)	0.003 (4)	-0.017 (4)
C35A	0.030 (5)	0.056 (6)	0.033 (4)	-0.006 (4)	0.000 (4)	0.017 (4)
O1A	0.094 (6)	0.070 (6)	0.040 (4)	-0.019 (5)	-0.021 (4)	0.024 (4)
O2A	0.054 (4)	0.049 (4)	0.039 (3)	0.004 (3)	0.003 (3)	0.008 (3)
C36A	0.090 (9)	0.039 (5)	0.063 (7)	0.009 (5)	0.014 (6)	0.007 (5)
C35B	0.018 (4)	0.032 (5)	0.040 (5)	0.013 (4)	0.009 (4)	-0.010 (4)
O1B	0.051 (4)	0.028 (4)	0.032 (4)	0.007 (3)	0.002 (3)	0.008 (3)
O2B	0.044 (4)	0.028 (3)	0.035 (4)	0.000 (3)	0.013 (3)	-0.007 (3)
C36B	0.057 (7)	0.031 (5)	0.067 (8)	-0.005 (5)	0.021 (6)	-0.005 (5)
P1	0.0365 (12)	0.0404 (12)	0.0371 (12)	-0.0046 (10)	0.0063 (10)	0.0092 (10)
F1	0.089 (5)	0.054 (4)	0.062 (4)	-0.003 (3)	0.038 (4)	0.029 (3)
F2	0.076 (5)	0.068 (4)	0.083 (5)	-0.028 (4)	0.040 (4)	-0.030 (4)
F3	0.045 (4)	0.162 (8)	0.095 (6)	-0.045 (4)	-0.026 (4)	0.108 (6)
F4	0.062 (4)	0.067 (4)	0.091 (5)	-0.011 (3)	0.037 (4)	-0.013 (4)
F5	0.054 (4)	0.081 (5)	0.086 (5)	-0.030 (4)	0.003 (4)	-0.011 (4)
F6	0.075 (4)	0.046 (3)	0.043 (3)	-0.013 (3)	0.029 (3)	-0.009 (2)
P2	0.0203 (7)	0.0409 (8)	0.0362 (8)	0.000	0.0080 (6)	0.000
F7	0.0218 (13)	0.105 (3)	0.0600 (19)	0.0054 (15)	0.0042 (13)	0.0111 (18)
F8	0.0471 (19)	0.212 (5)	0.0433 (18)	-0.006 (3)	0.0189 (15)	-0.033 (2)
F9	0.088 (4)	0.044 (3)	0.315 (12)	0.000	0.108 (6)	0.000
F10	0.066 (3)	0.037 (2)	0.172 (6)	0.000	0.060 (4)	0.000
C37	0.049 (9)	0.22 (3)	0.087 (16)	0.015 (16)	0.003 (11)	-0.087 (17)
Cl1	0.0446 (13)	0.077 (2)	0.0372 (12)	0.0008 (13)	0.0116 (10)	-0.0036 (12)
Cl2	0.058 (2)	0.259 (8)	0.192 (6)	-0.008 (3)	0.029 (3)	-0.160 (6)

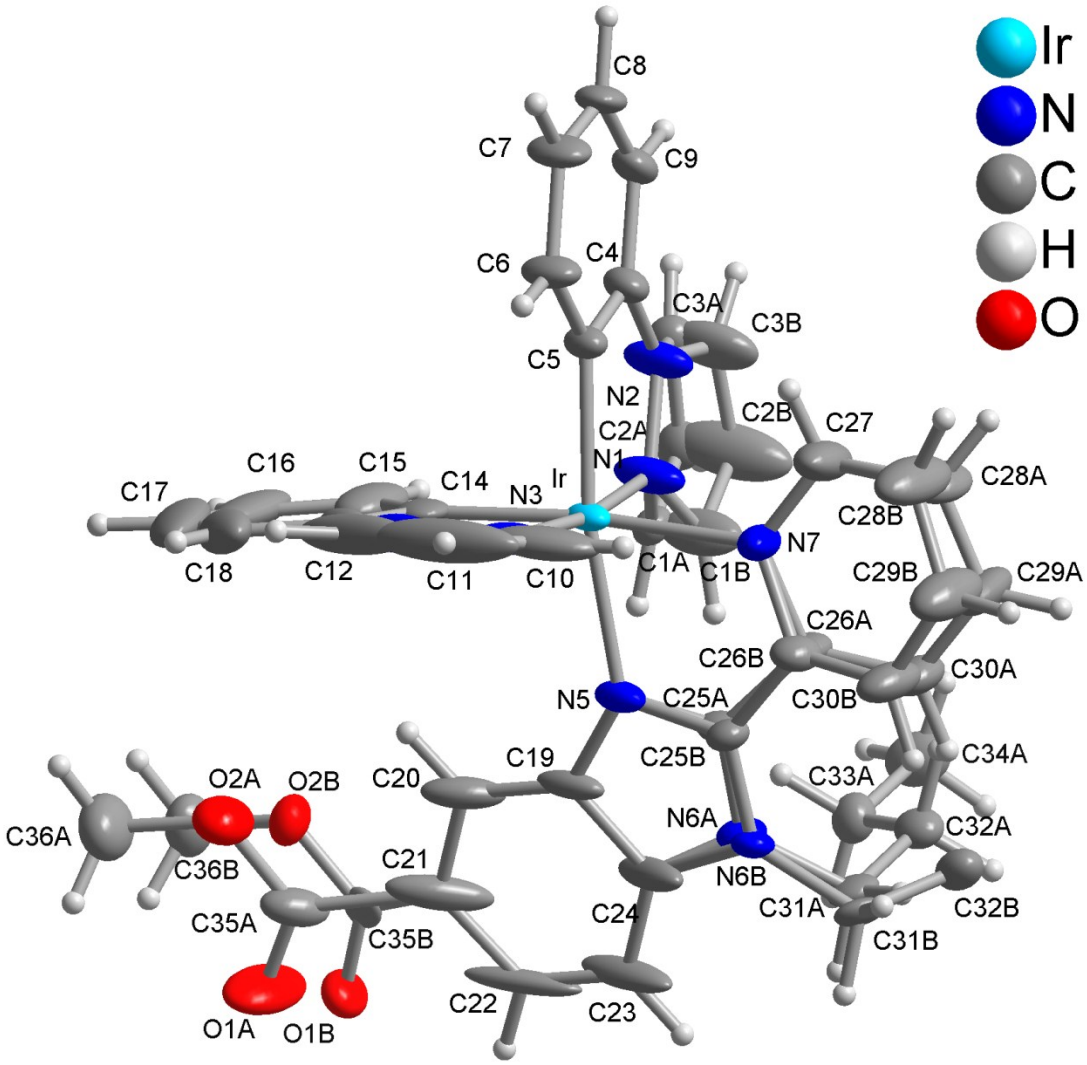


Figure S24a. Iridium cation in the structure of **3a** with 50% thermal ellipsoids and ligand disorder. The large thermal ellipsoids and two or more orientations of the ligands as illustrated in Fig. S19 are evidence of an orientational ligand disorder. There are two positions of one pyrazolyl ring, the pyridyl group, the imidazol ring, the methyl ester and the butyl chain. Only one position of the disordered butyl chain could be found, the second position remained incomplete with only the first two carbon atoms (C31B, C32B) refined. The occupation factores of the two split positions of the C, N, O atoms were refined to mostly about 50% each, for the pyrazolyl ring C atoms to 40/60 and for the methyl ester atoms to 55/45.
Once refined, the occupation factors were restrained to 0.40/0.60 and 0.55/0.45.

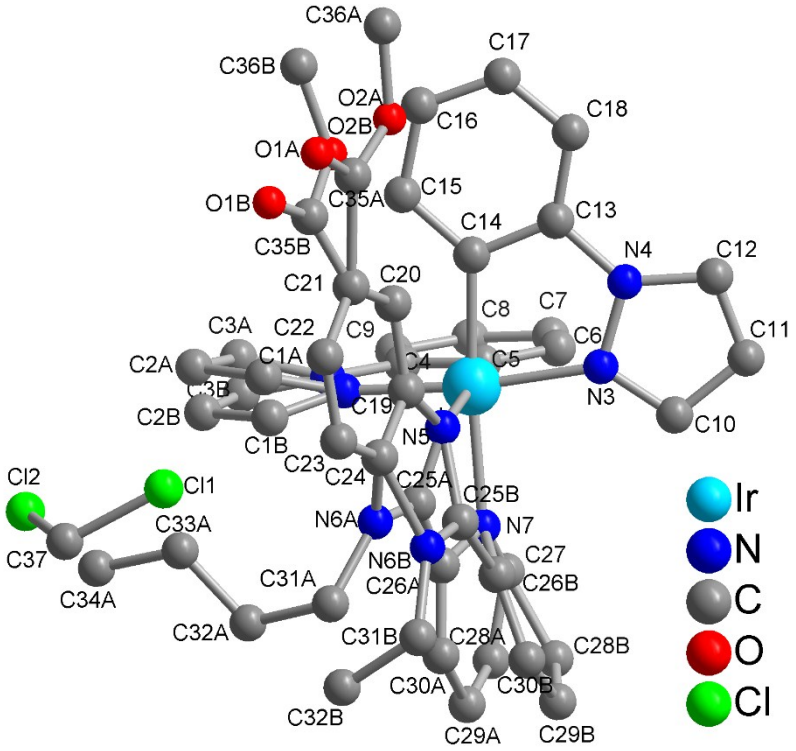


Figure S24b. The iridium cation in the structure of **3a** together with the refined methylene chloride solvent molecule. Only one half-occupied CH_2Cl_2 molecule could be reasonably refined. This singly refined CH_2Cl_2 molecule has 50% occupancy and essentially shares a position with the fully found n-butyl group, which also has 50% occupancy.
From the second position of the n-butyl group only the first two carbon atoms (C31B, C32B) could be found and refined.

Because of the strong disorder in the iridium cation and surrounding (squeezed) solvent molecules, we refrained from an analysis of supramolecular packing interactions.

Table S6. Bond lengths [Å] and angles [°] for **3a**.

Ir—N3	2.007 (4)	N6A—C25A	1.385 (11)
Ir—C14	2.010 (5)	N6A—C31A	1.483 (10)
Ir—N1	2.010 (4)	C25A—C26A	1.475 (13)
Ir—C5	2.022 (4)	C26A—C30A	1.377 (13)
Ir—N7	2.137 (4)	C26A—N7	1.430 (9)
Ir—N5	2.137 (3)	N6B—C25B	1.366 (10)
N1—C1B	1.337 (14)	N6B—C31B	1.473 (10)
N1—N2	1.363 (5)	C25B—C26B	1.458 (12)
N1—C1A	1.379 (19)	C26B—C30B	1.377 (13)
C1A—C2A	1.43 (3)	C26B—N7	1.395 (9)
C1A—H1A	0.9500	N7—C27	1.321 (7)
C2A—C3A	1.41 (4)	C27—C28A	1.366 (13)
C2A—H2A	0.9500	C27—C28B	1.522 (14)

C3A—N2	1.40 (3)	C27—H27	0.9500
C3A—H3A	0.9500	C28A—C29A	1.387 (14)
C1B—C2B	1.39 (2)	C28A—H28A	0.9500
C1B—H1B	0.9500	C29A—C30A	1.394 (13)
C2B—C3B	1.34 (3)	C29A—H29A	0.9500
C2B—H2B	0.9500	C30A—H30A	0.9500
C3B—N2	1.35 (2)	C31A—C32A	1.503 (12)
C3B—H3B	0.9500	C31A—H31A	0.9900
N2—C4	1.415 (6)	C31A—H31B	0.9900
C4—C9	1.391 (6)	C32A—C33A	1.502 (13)
C4—C5	1.398 (6)	C32A—H32A	0.9900
C5—C6	1.392 (6)	C32A—H32B	0.9900
C6—C7	1.400 (6)	C33A—C34A	1.507 (19)
C6—H6	0.9500	C33A—H33A	0.9900
C7—C8	1.375 (7)	C33A—H33B	0.9900
C7—H7	0.9500	C34A—H34A	0.9800
C8—C9	1.379 (7)	C34A—H34B	0.9800
C8—H8	0.9500	C34A—H34C	0.9800
C9—H9	0.9500	C28B—C29B	1.390 (16)
N3—C10	1.338 (8)	C28B—H28B	0.9500
N3—N4	1.347 (7)	C29B—C30B	1.378 (14)
C10—C11	1.400 (13)	C29B—H29B	0.9500
C10—H10	0.9500	C30B—H30B	0.9500
C11—C12	1.319 (17)	C31B—C32B	1.527 (12)
C11—H11	0.9500	C31B—H31C	0.9900
C12—N4	1.366 (11)	C31B—H31D	0.9900
C12—H12	0.9500	C35A—O1A	1.203 (10)
N4—C13	1.403 (10)	C35A—O2A	1.335 (12)
C13—C18	1.393 (10)	O2A—C36A	1.443 (11)
C13—C14	1.402 (9)	C36A—H36A	0.9800
C14—C15	1.389 (9)	C36A—H36B	0.9800
C15—C16	1.414 (11)	C36A—H36C	0.9800
C15—H15	0.9500	C35B—O1B	1.230 (12)
C16—C17	1.337 (19)	C35B—O2B	1.322 (12)
C16—H16	0.9500	O2B—C36B	1.432 (12)
C17—C18	1.342 (19)	C36B—H36D	0.9800
C17—H17	0.9500	C36B—H36E	0.9800
C18—H18	0.9500	C36B—H36F	0.9800
N5—C25A	1.220 (10)	P1—F6	1.533 (6)
N5—C19	1.385 (6)	P1—F4	1.574 (8)

N5—C25B	1.471 (10)	P1—F3	1.589 (6)
C19—C20	1.368 (8)	P1—F2	1.589 (8)
C19—C24	1.391 (7)	P1—F1	1.605 (6)
C19—C25A	1.989 (11)	P1—F5	1.606 (7)
C20—C21	1.393 (6)	P2—F8^{i}	1.558 (3)
C20—H20	0.9500	P2—F8	1.558 (3)
C21—C35B	1.286 (11)	P2—F9	1.561 (6)
C21—C22	1.416 (10)	P2—F10	1.563 (5)
C21—C35A	1.752 (13)	P2—F7	1.585 (3)
C22—C23	1.327 (11)	P2—F7^{i}	1.585 (3)
C22—H22	0.9500	C37—Cl2	1.62 (2)
C23—C24	1.384 (8)	C37—Cl1	1.76 (2)
C23—H23	0.9500	C37—H37A	0.9900
C24—N6A	1.170 (9)	C37—H37B	0.9900
C24—N6B	1.654 (11)		
N3—Ir—C14	80.2 (2)	N6A—C25A—C26A	128.2 (8)
N3—Ir—N1	171.58 (17)	N5—C25A—C19	43.4 (4)
C14—Ir—N1	94.4 (2)	N6A—C25A—C19	72.8 (5)
N3—Ir—C5	93.25 (15)	C26A—C25A—C19	159.0 (7)
C14—Ir—C5	88.59 (16)	C30A—C26A—N7	116.4 (8)
N1—Ir—C5	80.08 (16)	C30A—C26A—C25A	127.1 (8)
N3—Ir—N7	94.3 (2)	N7—C26A—C25A	115.6 (7)
C14—Ir—N7	172.18 (19)	C25B—N6B—C31B	128.6 (7)
N1—Ir—N7	91.7 (2)	C25B—N6B—C24	104.2 (6)
C5—Ir—N7	97.36 (15)	C31B—N6B—C24	125.9 (5)
N3—Ir—N5	95.34 (14)	N6B—C25B—C26B	130.6 (8)
C14—Ir—N5	98.80 (15)	N6B—C25B—N5	108.7 (7)
N1—Ir—N5	91.86 (14)	C26B—C25B—N5	120.2 (7)
C5—Ir—N5	169.50 (14)	C30B—C26B—N7	127.1 (7)
N7—Ir—N5	76.00 (15)	C30B—C26B—C25B	125.6 (8)
C1B—N1—N2	108.8 (7)	N7—C26B—C25B	106.8 (7)
N2—N1—C1A	104.1 (8)	C27—N7—C26B	112.3 (5)
C1B—N1—Ir	135.2 (7)	C27—N7—C26A	123.9 (5)
N2—N1—Ir	115.0 (3)	C27—N7—Ir	124.2 (3)
C1A—N1—Ir	137.0 (8)	C26B—N7—Ir	120.0 (4)
N1—C1A—C2A	113.2 (15)	C26A—N7—Ir	110.1 (5)
N1—C1A—H1A	123.4	N7—C27—C28A	117.5 (6)
C2A—C1A—H1A	123.4	N7—C27—C28B	125.2 (6)
C3A—C2A—C1A	101.7 (19)	N7—C27—H27	121.2

C3A—C2A—H2A	129.1	C28A—C27—H27	121.2
C1A—C2A—H2A	129.1	C27—C28A—C29A	121.3 (10)
N2—C3A—C2A	109 (2)	C27—C28A—H28A	119.3
N2—C3A—H3A	125.6	C29A—C28A—H28A	119.3
C2A—C3A—H3A	125.6	C28A—C29A—C30A	119.3 (9)
N1—C1B—C2B	106.7 (12)	C28A—C29A—H29A	120.3
N1—C1B—H1B	126.6	C30A—C29A—H29A	120.3
C2B—C1B—H1B	126.6	C26A—C30A—C29A	119.4 (8)
C3B—C2B—C1B	107.8 (15)	C26A—C30A—H30A	120.3
C3B—C2B—H2B	126.1	C29A—C30A—H30A	120.3
C1B—C2B—H2B	126.1	N6A—C31A—C32A	112.9 (7)
C2B—C3B—N2	108.2 (16)	N6A—C31A—H31A	109.0
C2B—C3B—H3B	125.9	C32A—C31A—H31A	109.0
N2—C3B—H3B	125.9	N6A—C31A—H31B	109.0
C3B—N2—N1	107.7 (9)	C32A—C31A—H31B	109.0
N1—N2—C3A	110.9 (13)	H31A—C31A—H31B	107.8
C3B—N2—C4	135.0 (10)	C33A—C32A—C31A	114.0 (8)
N1—N2—C4	116.3 (4)	C33A—C32A—H32A	108.7
C3A—N2—C4	130.8 (12)	C31A—C32A—H32A	108.7
C9—C4—C5	124.4 (4)	C33A—C32A—H32B	108.7
C9—C4—N2	121.4 (4)	C31A—C32A—H32B	108.7
C5—C4—N2	114.2 (3)	H32A—C32A—H32B	107.6
C6—C5—C4	115.8 (4)	C32A—C33A—C34A	115.5 (9)
C6—C5—Ir	129.9 (3)	C32A—C33A—H33A	108.4
C4—C5—Ir	114.3 (3)	C34A—C33A—H33A	108.4
C5—C6—C7	121.0 (5)	C32A—C33A—H33B	108.4
C5—C6—H6	119.5	C34A—C33A—H33B	108.4
C7—C6—H6	119.5	H33A—C33A—H33B	107.5
C8—C7—C6	120.8 (5)	C33A—C34A—H34A	109.5
C8—C7—H7	119.6	C33A—C34A—H34B	109.5
C6—C7—H7	119.6	H34A—C34A—H34B	109.5
C7—C8—C9	120.5 (4)	C33A—C34A—H34C	109.5
C7—C8—H8	119.7	H34A—C34A—H34C	109.5
C9—C8—H8	119.7	H34B—C34A—H34C	109.5
C8—C9—C4	117.5 (4)	C29B—C28B—C27	115.3 (9)
C8—C9—H9	121.2	C29B—C28B—H28B	122.3
C4—C9—H9	121.2	C27—C28B—H28B	122.3
C10—N3—N4	107.6 (5)	C30B—C29B—C28B	119.5 (10)
C10—N3—Ir	136.6 (5)	C30B—C29B—H29B	120.2
N4—N3—Ir	115.2 (4)	C28B—C29B—H29B	120.2

N3—C10—C11	107.1 (10)	C26B—C30B—C29B	119.1 (9)
N3—C10—H10	126.4	C26B—C30B—H30B	120.4
C11—C10—H10	126.4	C29B—C30B—H30B	120.4
C12—C11—C10	108.6 (9)	N6B—C31B—C32B	112.3 (6)
C12—C11—H11	125.7	N6B—C31B—H31C	109.1
C10—C11—H11	125.7	C32B—C31B—H31C	109.1
C11—C12—N4	107.0 (9)	N6B—C31B—H31D	109.1
C11—C12—H12	126.5	C32B—C31B—H31D	109.1
N4—C12—H12	126.5	H31C—C31B—H31D	107.9
N3—N4—C12	109.6 (8)	O1A—C35A—O2A	123.0 (10)
N3—N4—C13	115.8 (4)	O1A—C35A—C21	119.7 (9)
C12—N4—C13	134.6 (8)	O2A—C35A—C21	117.1 (6)
C18—C13—C14	123.1 (10)	C35A—O2A—C36A	117.1 (7)
C18—C13—N4	121.8 (9)	O2A—C36A—H36A	109.5
C14—C13—N4	115.1 (5)	O2A—C36A—H36B	109.5
C15—C14—C13	115.3 (6)	H36A—C36A—H36B	109.5
C15—C14—Ir	131.3 (5)	O2A—C36A—H36C	109.5
C13—C14—Ir	113.4 (5)	H36A—C36A—H36C	109.5
C14—C15—C16	120.5 (9)	H36B—C36A—H36C	109.5
C14—C15—H15	119.8	O1B—C35B—C21	128.8 (9)
C16—C15—H15	119.8	O1B—C35B—O2B	122.7 (9)
C17—C16—C15	121.2 (11)	C21—C35B—O2B	107.7 (8)
C17—C16—H16	119.4	C35B—O2B—C36B	117.0 (8)
C15—C16—H16	119.4	O2B—C36B—H36D	109.5
C16—C17—C18	120.8 (10)	O2B—C36B—H36E	109.5
C16—C17—H17	119.6	H36D—C36B—H36E	109.5
C18—C17—H17	119.6	O2B—C36B—H36F	109.5
C17—C18—C13	119.1 (11)	H36D—C36B—H36F	109.5
C17—C18—H18	120.5	H36E—C36B—H36F	109.5
C13—C18—H18	120.5	F6—P1—F4	89.9 (4)
C25A—N5—C19	99.3 (5)	F6—P1—F3	85.8 (4)
C19—N5—C25B	111.5 (5)	F4—P1—F3	81.0 (5)
C25A—N5—Ir	117.0 (5)	F6—P1—F2	91.2 (4)
C19—N5—Ir	136.7 (3)	F4—P1—F2	178.3 (5)
C25B—N5—Ir	111.7 (4)	F3—P1—F2	97.8 (5)
C20—C19—N5	130.3 (4)	F6—P1—F1	91.8 (4)
C20—C19—C24	121.1 (5)	F4—P1—F1	91.7 (4)
N5—C19—C24	108.6 (5)	F3—P1—F1	172.2 (6)
C20—C19—C25A	163.6 (4)	F2—P1—F1	89.6 (4)
N5—C19—C25A	37.2 (3)	F6—P1—F5	179.0 (4)

C24—C19—C25A	72.3 (4)	F4—P1—F5	90.0 (4)
C19—C20—C21	116.7 (5)	F3—P1—F5	95.1 (4)
C19—C20—H20	121.7	F2—P1—F5	89.0 (4)
C21—C20—H20	121.7	F1—P1—F5	87.3 (4)
C35B—C21—C20	128.1 (7)	F8^{i}—P2—F8	179.1 (4)
C35B—C21—C22	108.6 (6)	F8^{i}—P2—F9	89.5 (2)
C20—C21—C22	120.7 (7)	F8—P2—F9	89.5 (2)
C20—C21—C35A	113.9 (6)	F8^{i}—P2—F10	90.5 (2)
C22—C21—C35A	124.5 (5)	F8—P2—F10	90.5 (2)
C23—C22—C21	122.3 (5)	F9—P2—F10	180.0
C23—C22—H22	118.9	F8^{i}—P2—F7	92.30 (17)
C21—C22—H22	118.9	F8—P2—F7	87.70 (17)
C22—C23—C24	117.0 (6)	F9—P2—F7	89.47 (15)
C22—C23—H23	121.5	F10—P2—F7	90.53 (15)
C24—C23—H23	121.5	F8^{i}—P2—F7^{i}	87.69 (17)
N6A—C24—C23	127.6 (6)	F8—P2—F7^{i}	92.30 (17)
N6A—C24—C19	106.8 (5)	F9—P2—F7^{i}	89.47 (15)
C23—C24—C19	122.3 (7)	F10—P2—F7^{i}	90.53 (15)
C23—C24—N6B	131.2 (7)	F7—P2—F7^{i}	178.9 (3)
C19—C24—N6B	105.0 (5)	Cl2—C37—Cl1	117.5 (12)
C24—N6A—C25A	106.5 (7)	Cl2—C37—H37A	107.9
C24—N6A—C31A	124.1 (6)	Cl1—C37—H37A	107.9
C25A—N6A—C31A	129.3 (7)	Cl2—C37—H37B	107.9
N5—C25A—N6A	116.0 (8)	Cl1—C37—H37B	107.9
N5—C25A—C26A	115.7 (8)	H37A—C37—H37B	107.2

Symmetry code: (i) -*x*, *y*, -*z*-1/2.

Cell lines and culture media. Human breast cancer (MDA-MB-231 and MCF-7), BGM, cell lines were acquired from the American Type Tissue Culture Collection (ATCC, USA), while the ovarian carcinoma cell line A2780 and the CDDP-resistant A2780cis were obtained from European Collection of Animal Cell Culture (ECACC, Salisbury, U.K.). These last cell lines were cultured in the RPMI-1640 medium, the human breast cancer cells were all cultured in DMEM medium, but with a low glucose (1g/L) concentration. Finally, BGM cells were cultured in the medium M199. All media were supplemented with fetal bovine serum (FBS) 10 %, glutamine 1 mM, and penicillin and streptomycin. DMEM media was also supplemented with pyruvate 2 mM. Cells were subculture and medium change once a week, and in all case trypsine 0.12%-EDTA 0.05 mM were used.

Before and after experiments, all cell lines were mycoplasma-free, as determined the Hoechst DNA stain method.[17]

Cytotoxicity Assays. 5000 cells/well (200 μL of culture medium as described above) were seeded in a 96-well plate and left at 37 °C in a 5% or 10% CO_2 humidified atmosphere (for RPMI and DMEM, respectively) for 24 h. Independently, a solution of the iridium compound in DMSO at 12.5 mM concentration was prepared. From this, successive 1:1 dilutions were performed, obtaining a total of 8 solutions of concentrations ranging from 12.5 to 0.0976 mM, all of them in DMSO. From these, 8 solutions were prepared by diluting 50 μL of each DMSO solution in 2450 μL of the culture medium (dilution 1:50, DMSO 2%). Finally, 50 μL of these last 8 solutions were added to the 200 μL present in the wells. The highest final concentration of the wells was 50 μM (1/250 dilution from the original DMSO solution). In all cases, the wells have a concentration of 0.4% DMSO. Cells were left for 48 h in the incubator (37 °C). Then the MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay was performed. Briefly, media were removed from the wells, 250 μL of MTT (1 mg/mL final concentration) dissolved in the culture medium was added and left for 4 h. MTT was then removed and 100 μL of DMSO was added. The absorbance at 560 nm was measured in a Fluostar Omega spectrophotometer.

Absorbances at each compound concentration were translated into inhibition percentages, *I*%, according to the following equation,

$$I\% = \left[1 - \frac{A_T}{A_C}\right] x100 \qquad [1]$$

where A_T and A_C are the absorbances of treated and control cells, respectively.

IC_{50} values were obtained from a 3 parameters fitting of the semi-logarithmic curves (*I*% as a function of the logarithm of the concentration of compound), according to equation 2,

$$I\% = \frac{Imax}{1 + \left(\frac{IC_{50}}{C}\right)^n}$$

where I_{max} is the maximum inhibition observed (i.e. the inhibition observed at the highest inhibitor concentration), IC_{50} is the concentration at which 50% of the cell population is live (or death), *C* is the compound concentration at what the inhibition *I*% is observed and *n* is the slope of the curve at the IC_{50} value. The fitting was performed using Sigma Plot 11.0 software. All compounds were tested in three independent studies with quadruplicate points. The *in vitro* studies were performed in the SACE service (Support Service for Experimental Sciences, University of Murcia, Murcia, Spain).

All studies were performed with maximum DMSO concentration of 0.4% (except for CDDP, water diluted) and in all the experiments measurements were corrected with a water control. It was verified that DMSO at this concentration had no effect on cell viability.

Luminiscence Confocal Microscopy Preparations. The fluorescence signal was detected from 450 to 700 nm. A2780 cells were seeded on 35 mm glass bottom culture dishes (Mattek) at the density $0.6 \cdot 10^6$ cells/dish. After overnight incubation the cells were treated with 5 μM **2a**, imaged after 3 h. Cells were incubated in phenol red-free RPMI-1640 medium one passage before the seeding for the confocal microscopy experiment and for all the time needed for subsequent visualization. Cells were visualized under the standard cultivating conditions (5% CO_2, humidified atmosphere) with confocal microscope Olympus FV10i. Cells were illuminated with 405 nm diode laser and the fluorescence detection window was set approximately from 500 to 700 nm.

Cellular uptake. Cellular accumulations of **2a** and **3a** and CDDP were determined in MCF-7 human breast carcinoma cells. In these experiments, 2×10^6 MCF-7 cells were seeded on 100 mm Petri dishes. After overnight pre-incubation in a drug-free medium at 37 °C in a 5% CO_2 humidified atmosphere, the cells were treated with iridium compounds or CDDP and allowed further 24 h of drug exposure under similar conditions. After treatment, the cells were extensively washed with PBS (37 °C), detached using 0.25% trypsin and washed twice with ice cold PBS. The cell pellets were stored at -70 °C and digested using microwave acid (HCl) digestion system (CEM Mars®). Quantity of metal taken up by the cells was determined by ICP-MS (Agilent 7500 (Agilent, Japan)). All experiments were carried out in triplicate.

Measurement of the partition coefficients. To determine the partition coefficients (P) of **2a**, **3a** or CDDP, the "shake flask" method was used. Octanol-saturated water (OSW) and water-saturated octanol (WSO) were prepared using analytical grade octanol and ultrapure water. The metal complexes were dissolved in WSO and then mixed with OSW in volumetric

ratios of 2:1, 1:1 and 1:2. CDDP was dissolved in the OSW containing 200 mM NaCl (to suppress hydrolysis of the chlorido complex) and mixed with WSO in the same manner. Mixing was done by vortexing for 30 min at room temperature to establish the partition equilibrium. To separate the phases, centrifugation was done at 3000 g for 5 min. The aqueous layers were carefully separated from the octanol layer for metal analysis by flameless atomic absorption spectrometry (FAAS). Partition coefficients were calculated using the equation log P = log ([Ir/Pt]WSO/[Ir/Pt]OSW).

Quantification of metals bound to nucleic acids. MCF-7 cells were seeded and treated with **2a**, **3a** or C as described above. For DNA isolation, the cell pellets were stored at -70 °C and after lysed in DNAzol (DNAzol®, MRC) supplemented with RNAse A (100 µg mL^{-1}). Genomic DNA was precipitated from the lysate by 100% ethanol, washed twice with 75% ethanol and resuspended in 8 mM NaOH. Total cellular RNA was isolated by lysis of cells in RNAzol (RNAzol®RT, MRC) on Petri dishes. RNA was extracted from the lysate by centrifugation at 12000*g* for 15 min, precipitated with isopropanol, washed twice with 75% ethanol and dissolved in 1 mM NaOH. The DNA or RNA content in each sample was determined by UV spectrophotometry. Samples were digested in 30% hydrochloric acid (Suprapur®, Merck Millipore). The amount of metal bound to nucleic acids was quantified by ICP-MS. All measurements were done in triplicate.

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