Supplementary Material (ESI) for Chemical Communications


**Supporting Information for**

# Efficient Formation of Organoiridium Macrocycles via C-H Activation Directed Self-Assembly

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## Materials and instrumentations

All reactions and manipulations were performed under a nitrogen atmosphere, using standard Schlenk techniques. However, once the reactions were completed, subsequent workups were done without precaution, as the compounds are air-stable. Solvents were purified by standard methods prior to use. $[Cp^*IrCl_2]_2$ was prepared according to the reported procedures.[1] The $^1$H-NMR spectra were measured on a VAVCE-DMX 400 Spectrometer in $CD_3OD$, $CDCl_3$ or $CD_3CN$. Elemental analysis was performed on Elementar vario EL III Analyzer. IR (KBr) spectra were recorded on the Nicolet FT-IR spectrophotometer.

The terephthal-bis-imine ligands **L1-L4** were prepared by the reactions of terephthalaldehyde with two equivalents of the corresponding amines in methanol overnight at room temperature according to known procedures.[2] *N,N'*-bisbenzylidenebenzene-1,4-diamines ligands **L5-L6** were prepared by the reactions of 1,4-phenylenediamine with two equivalents of the corresponding benzaldehydes in methaol overnight at room temperature according to known procedures.[3]

**Preparation of dinuclear complexes 3a-d**

**Preparation of 3a**: A mixture of $[Cp^*IrCl_2]_2$ (80 mg, 0.1 mmol), NaOAc (49 mg, 0.6 mmol), L1 (28 mg, 0.1 mmol), and benzaldehyde (trace) was stirred at 50°C in 20 mL of dichloromethane for 6 h. The mixture was filtered through Celite and evaporated to afford dark solid which was further purified by silica gel column chromatography to afford pure cyclometalated compound **3a** (77 mg, 76%). Anal. Calcd for $C_{40}H_{44}Cl_2Ir_2N_2$: C 47.66, H 4.40, N 2.78; found: C 47.58, H 4.37, N 2.83. $^1$H-NMR (400MHz, $CDCl_3$, ppm): $\delta$ = 8.42 (s, 2H, HC=N); 8.10 (s, 2H); 7.58 (d, 4H); 7.42 (m, 4H); 7.31 (m, 2H); 1.45 (s, 30H, $C_5Me_5$). $^{13}$C-NMR ($CDCl_3$, ppm): $\delta$ = 175.78 (Ir-C), 159.60 (HC=N), 152.03, 151.50, 135.38, 128.97, 127.35, 122.60, 88.97 ($C_5Me_5$), 8.85 ($C_5Me_5$). IR(KBr): $\nu_{C=N}$ = 1551 cm$^{-1}$.

**Preparation of 3b**: A mixture of $[Cp^*IrCl_2]_2$ (80 mg, 0.1 mmol), NaOAc (49 mg, 0.6 mmol), L2 (34 mg, 0.1 mmol), and benzaldehyde (trace) was stirred at 50°C in 20 mL of dichloromethane for 6 h. The mixture was filtered through Celite and evaporated to afford dark solid which was further purified by

silica gel column chromatography to afford pure cyclometalated compound **3b** (80 mg, 75%). Anal. Calcd for $C_{42}H_{48}Cl_2Ir_2N_2O_2$: C 47.23, H 4.53, N 2.62; found: C 47.16, H 4.24, N 2.72. $^1$H-NMR (400MHz, $CDCl_3$, ppm): δ = 8.36 (s, 2H, HC=N); 8.06 (s, 2H); 7.52 (d, 4H); 6.92 (d, 4H); 3.86 (s, 6H, OMe); 1.46 (s, 30H, $C_5Me_5$). $^{13}$C-NMR (400 MHz, $CDCl_3$/$CD_3OD$ 4:1, 50$^o$C): δ = 174.86 (Ir-C), 158.99 (HC=N), 158.74, 151.37, 145.28, 135.03, 123.46, 113.85, 88.88 ($C_5Me_5$), 55.39 (OMe), 8.58 ($C_5Me_5$). IR(KBr): $\nu_{C=N}$ = 1534 cm$^{-1}$.

**Preparation of 3c**: A mixture of $[Cp^*IrCl_2]_2$ (80 mg, 0.1 mmol), NaOAc (49 mg, 0.6 mmol), L3 (31 mg, 0.1 mmol), and benzaldehyde (trace) was stirred at 50°C in 20 mL of dichloromethane for 6 h. The mixture was filtered through Celite and evaporated to afford dark solid which was further purified by silica gel column chromatography to afford pure cyclometalated compound **3c** (81 mg, 78%). Anal. Calcd for $C_{42}H_{48}Cl_2Ir_2N_2$: C 48.68, H 4.67, N 2.70; found: C 48.45, H 4.39, N 2.83. $^1$H-NMR (400MHz, $CDCl_3$, ppm): δ = 8.37 (s, 2H, HC=N); 8.07 (s, 2H); 7.45 (d, 4H); 7.20 (d, 4H); 2.41 (s, 6H, Me);1.48 (s, 30H, $C_5Me_5$). IR(KBr): $\nu_{C=N}$ = 1560 cm$^{-1}$.

**Preparation of 3d**: A mixture of $[Cp^*IrCl_2]_2$ (80 mg, 0.1 mmol), NaOAc (49 mg, 0.6 mmol), L4 (35 mg, 0.1 mmol), and benzaldehyde (trace) was stirred at 50°C in 20 mL of dichloromethane for 6 h. The mixture was filtered through Celite and evaporated to afford dark solid which was further purified by silica gel column chromatography to afford pure cyclometalated compound **3d** (75 mg, 70%). Anal. Calcd for $C_{40}H_{42}Cl_4Ir_2N_2$: C 44.61, H 3.93, N 2.60; found: C 44.29, H 3.57, N 2.66. $^1$H-NMR (400MHz, $CDCl_3$, ppm): δ = 8.39 (s, 2H, HC=N); 8.10 (s, 2H); 7.54 (d, 4H); 7.40 (d, 4H); 1.50 (s, 30H, $C_5Me_5$). $^{13}$C-NMR ($CDCl_3$, ppm): δ = 176.07 (Ir-C), 160.09 (HC=N), 151.48, 150.56, 135.62, 132.93, 129.11, 123.93, 89.10 ($C_5Me_5$), 8.92 ($C_5Me_5$). IR(KBr): $\nu_{C=N}$ = 1556 cm$^{-1}$.

**Preparation of dinuclear complexes 4a,b**

**Preparation of 4a**: A mixture of $[Cp^*IrCl_2]_2$ (80 mg, 0.1 mmol), NaOAc (49 mg, 0.6 mmol), L5 (28 mg, 0.1 mmol), and benzaldehyde (trace) was stirred at 50°C in 20 mL of dichloromethane for 6 h. The

mixture was filtered through Celite and evaporated to afford dark solid which was further purified by silica gel column chromatography to afford pure cyclometalated compound **4a** (82 mg, 82%). Anal. Calcd for $C_{40}H_{44}Cl_2Ir_2N_2$: C 47.66, H 4.40, N 2.78; found: C 47.37, H 4.25, N 2.71. $^1$H-NMR (400MHz, $CDCl_3$, ppm): δ = 8.52 (s, 2H, HC=N); 8.28 (d, 2H); 7.92 (d, 2H); 7.53-7.73 (m, 4H); 7.29 (m, 2H); 7.10 (m, 2H); 1.44 (s, 30H, $C_5Me_5$). IR(KBr): $\nu_{C=N}$ = 1586 cm$^{-1}$.

**Preparation of 4b**: A mixture of $[Cp^*IrCl_2]_2$ (80 mg, 0.1 mmol), NaOAc (49 mg, 0.6 mmol), L6 (34 mg, 0.1 mmol), and benzaldehyde (trace) was stirred at 50°C in 20 mL of dichloromethane for 6 h. The mixture was filtered through Celite and evaporated to afford dark solid which was further purified by silica gel column chromatography to afford pure cyclometalated compound **4b** (98 mg, 92%). Anal. Calcd for $C_{42}H_{48}Cl_2Ir_2N_2O_2$: C 47.23, H 4.53, N 2.62; found: C 47.36, H 4.26, N 2.52. $^1$H-NMR (400MHz, $CDCl_3$, ppm): δ = 8.25 (s, 2H, HC=N); 7.60-7.63 (m, 6H); 7.39 (d, 2H); 6.61-6.64 (m, 2H); 3.93 (s, 6H, OMe); 1.51 (s, 30H, $C_5Me_5$). $^{13}$C-NMR ($CDCl_3$, ppm): δ = 174.00, 173.68 (Ir-C); 162.77, 162.73 (HC=N); 150.56, 150.53; 140.54, 140.47; 131.54, 131.47; 123.25, 123.22; 108.96, 108.94; 89.15, 89.04 ($C_5Me_5$); 55.17 (OMe); 9.01, 8.94 ($C_5Me_5$). IR(KBr): $\nu_{C=N}$ = 1588 cm$^{-1}$.

**Preparation of tetra-nuclear complexes 1a-d**

**Preparation of 1a**: The first method: Pyrazine (8 mg, 0.1 mmol) was added to a suspension of $[Cp^*IrCl_2]_2$ (80 mg, 0.1 mmol) in $CH_3OH$ at room temperature and stirred for 5 h. $Ag(CF_3SO_3)$ (102 mg, 0.4 mmol) was added to the resulting yellow precipitate and stirred for 2 h. NaOAc (49 mg, 0.6 mmol) and L1 (28 mg, 0.1 mmol) were added and keep stirring for additional 12 h. The solvent was removed and the residue was extracted with $CH_2Cl_2$, followed by filtration through a glass filter (G5) to remove insoluble compounds. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give **1a** as a red solid in 56% yield.

The second method: $Ag(CF_3SO_3)$ (51 mg, 0.2 mmol) was added to a solution of **3a** (101 mg, 0.1 mmol) in $CH_3OH$ (20 mL) at room temperature and stirred for 3 h, followed by filtration to remove insoluble materials. Pyrazine (8 mg, 0.1 mmol) was added to the filtrate and stirred for 12 h. The solvent was

removed and the residue was extracted with $CH_2Cl_2$, followed by filtration through a glass filter (G5) to remove insoluble compounds. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give **1a** as a red solid in 72% yield. Anal. Calcd. for $C_{92}H_{96}F_{12}Ir_4N_8O_{12}S_4$: C 42.00, H 3.68, N 4.26; found: C 41.82, H 3.63, N 4.09. $^1$H-NMR (400MHz, $CD_3OD$, ppm): δ = 8.86, 8.84 (s, 4H, HC=N); 8.31, 8.28 (s, 8H, pyrazine); 8.24 (d, 4H, Ar-H); 7.49-7.58 (m, 12H, Ar-H); 7.28-7.30 (m, 8H, Ar-H); 1.52, 1.63 (s, 60H, $C_5Me_5$). IR(KBr): $\nu_{C=N}$ = 1555 cm$^{-1}$.

**Preparation of 1b**: This complex was obtained in 58% yield by a procedure similar to that the first method described for **1a** when L2 used. And this complex also could be obtained from **3b** and pyrazine by a procedure similar to that the second method described for **1a** as a red solid in 75% yield. Anal. Calcd. for $C_{96}H_{104}F_{12}Ir_4N_8O_{16}S_4$: C 41.91, H 3.81, N 4.07; found: C 41.78, H 3.54, N 4.33. $^1$H-NMR (400MHz, $CDCl_3$, ppm): δ = 8.62 (s, 4H, HC=N); 8.40 (s, 8H, pyrazine); 8.14 (s, 4H, Ar-H); 7.36 (d, 8H, Ar-H); 7.14 (d, 8H, Ar-H); 3.91 (s, 12H, $OCH_3$); 1.57 (s, 60H, $C_5Me_5$). IR(KBr): $\nu_{C=N}$ = 1556 cm$^{-1}$.

**Preparation of 1c**: This complex was obtained in 54% yield by a procedure similar to that the first method described for **1a** when L3 used. And this complex also could be obtained from **3c** and pyrazine by a procedure similar to that the second method described for **1a** as a red solid in 63% yield. Anal. Calcd. for $C_{96}H_{104}F_{12}Ir_4N_8O_{12}S_4$: C 42.91, H 3.90, N 4.17; found: C 42.73, H 3.71, N 4.26. $^1$H-NMR (400MHz, $CDCl_3$, ppm): δ = 8.69 (s, 4H, HC=N); 8.43 (s, 8H, pyrazine); 8.28 (s, 4H, Ar-H); 7.39 (d, 8H, Ar-H); 7.06 (d, 8H, Ar-H); 2.42 (s, 12H, $CH_3$); 1.54 (s, 60H, $C_5Me_5$). IR(KBr): $\nu_{C=N}$ = 1555 cm$^{-1}$.

**Preparation of 1d**: This complex was obtained in 54% yield by a procedure similar to that the first method described for **1a** when L4 used. And this complex also could be obtained from **3d** and pyrazine by a procedure similar to that the second method described for **1a** as a red solid in 60% yield. Anal. Calcd. for $C_{92}H_{92}Cl_4F_{12}Ir_4N_8O_{12}S_4$: C 39.91, H 3.35, N 4.05; found: C 39.65, H 3.04, N 4.02. $^1$H-NMR (400MHz, $CD_3OD$, ppm): δ = 8.85 (s, 4H, HC=N); 8.23-8.25 (m, 12H, pyrazine and Ar-H); 7.59 (d, 8H, Ar-H); 7.32 (d, 8H, Ar-H); 1.67 (s, 60H, $C_5Me_5$). IR(KBr): $\nu_{C=N}$ = 1551 cm$^{-1}$.

**Preparation of tetra-nuclear complexes 2a and 2b**

**Preparation of 2a**:

The first method: Pyrazine (8 mg, 0.1 mmol) was added to a suspension of $[Cp^*IrCl_2]_2$ (80 mg, 0.1 mmol) in $CH_3OH$ at room temperature and stirred for 5 h. $Ag(CF_3SO_3)$ (102 mg, 0.4 mmol) was added to the resulting yellow precipitate and stirred for 2 h. NaOAc (49 mg, 0.6 mmol) and L5 (28 mg, 0.1 mmol) were added and keep stirring for additional 12 h. The solvent was removed and the residue was extracted with $CH_2Cl_2$, followed by filtration through a glass filter (G5) to remove insoluble compounds. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give **2a** as a red solid in 68% yield.

The second method: $Ag(CF_3SO_3)$ (51 mg, 0.2 mmol) was added to a solution of **4a** (101 mg, 0.1 mmol) in $CH_3OH$ (20 mL) at room temperature and stirred for 3 h, followed by filtration to remove insoluble materials. Pyrazine (8 mg, 0.1 mmol) was added to the filtrate and stirred for 12 h. The solvent was removed and the residue was extracted with $CH_2Cl_2$, followed by filtration through a glass filter (G5) to remove insoluble compounds. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give **2a** as a red solid in 75% yield. Anal. Calcd. for $C_{92}H_{96}F_{12}Ir_4N_8O_{12}S_4$: C 42.00, H 3.68, N 4.26; found: C 41.79, H 3.31, N 4.17. $^1$H-NMR (400MHz, $CD_3OD$, ppm): $\delta$ = 8.56 (s, 4H, HC=N); 8.44 (s, 8H, pyrazine); 7.89 (m, 4H, Ar-H); 7.89 (s, 8H, Ar-H); 7.56 (d, 4H, Ar-H); 7.37 (m, 4H, Ar-H); 7.00-7.05 (m, 4H, Ar-H); 1.59 (s, 60H, $C_5Me_5$). IR(KBr): $\nu_{C=N}$ = 1584 cm$^{-1}$.

**Preparation of 2b**: This complex was obtained in 71% yield by a procedure similar to that the first method described for **2a** when L6 used. And this complex also could be obtained from **4b** and pyrazine by a procedure similar to that the second method described for **1a** as a red solid in 78% yield. Anal. Calcd. for $C_{96}H_{104}F_{12}Ir_4N_8O_{16}S_4$: C 41.91, H 3.81, N 4.07; found: C 41.63, H 3.66, N 3.98. $^1$H-NMR (400MHz, $CD_3OD$, ppm): $\delta$ = 8.64 (s, 4H, HC=N); 8.21 (s, 8H, pyrazine); 7.68 (s, 8H, Ar-H); 7.67 (s, 4H, Ar-H); 7.15 (d, 4H, Ar-H); 6.65-6.67 (dd, 4H, Ar-H); 3.87 (s, 12H, $OCH_3$); 1.61 (s, 60H, $C_5Me_5$). IR(KBr): $\nu_{C=N}$ = 1586 cm$^{-1}$.

**Preparation of tetra-nuclear complexes 5a and 5b**

**Preparation of 5a**: A mixture of **1a** (132 mg, 0.05 mmol) and DMAD (28 *u*L, 0.22 mmol) in 20 mL methanol was stirred at room temperature for 12 h. The solution was evaporated to dryness, and the solid was washed with hexane and dimethyl ether to remove execss DMAD. **5a** was obtained as a red solid (125 mg, 78%). Anal. Calcd. for $C_{116}H_{120}F_{12}Ir_4N_8O_{28}S_4$: C 43.55, H 3.78, N 3.50; found: C 43.39, H 3.66, N 3.21. $^1$H-NMR (400MHz, $CD_3CN$, ppm): $\delta$ = 8.93 (s, 4H, HC=N); 7.62 (s, 8H, pyrazine); 7.53-7.58 (m, 12H, Ar-H); 7.43 (m, 4H, Ar-H); 7.09 (d, 8H, Ar-H); 3.70 (s, 12H, $COOCH_3$); 3.64 (s, 12H, $COOCH_3$); 1.52 (s, 60H, $C_5Me_5$). IR(KBr): $\nu$ = 1556 (C=N), 1710 (C=O) $cm^{-1}$.

**Preparation of 5b**: A mixture of **1b** (138 mg, 0.05 mmol) and DMAD (28 *u*L, 0.22 mmol) in 20 mL methanol was stirred at room temperature for 12 h. The solution was evaporated to dryness, and the solid was washed with hexane and dimethyl ether to remove execss DMAD. **5b** was obtained as a red solid (134 mg, 81%). Anal. Calcd. for $C_{120}H_{128}F_{12}Ir_4N_8O_{32}S_4$: C 43.42, H 3.89, N 3.38; found: C 43.25, H 3.57, N 3.16. $^1$H-NMR (400MHz, $CD_3CN$, ppm): $\delta$ = 8.63 (s, 4H, HC=N); 8.40 (d, 8H, pyrazine); 8.14 (d, 4H, Ar-H); 7.35 (d, 8H, Ar-H); 7.14 (d, 8H, Ar-H); 3.91 (s, 12H, $OCH_3$); 3.89 (s, 12H, $COOCH_3$); 3.85 (s, 12H, $COOCH_3$); 1.57 (s, 60H, $C_5Me_5$). IR(KBr): 1553 (C=N), 1732 (C=O) $cm^{-1}$.

## Single-Crystal Structure Determination.

All the determinations of unit cell and intensity data were performed with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All the data were collected at room temperature using the $\omega$ scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on $F^2$ by a full-matrix least-squares method. All the calculations were carried out with the SHELXTL[4] program. In complex **1b**, **1c**, **2a**, **3a**, **3b**, **4a** and **4b**, all non-hydrogen atoms were refined anisotropically.

In complex **1a**, all atoms of two triflate anions were refined isotropically because of non-positive definition and other non-hydrogen atoms were refined anisotropically. Two of the four triflate anions and some unknown solvents are strongly disordered and cannot be refined properly, as a result, the SQUEEZE[5] algorithm was used to omit all of these disordered fragments. Three pair of atoms (O2, S1, F2, and O2' S1', F2') with C45/S1 triflate anion and all O and F atoms with C46/S2 were treated using disorder mode. All 67 restraints were used to restrain the geometry of both triflate anions (C45/S1, C45'/S1', and C46/S2) to get the better result.

Because the diffraction point is not very perfect and there some trailing, the error of refinement of complex **1b** is slightly larger, as a result, the reported su parameters on the unit cell axes are also large.

In complex **1c**, the bond distance of C47-F2 was restrained so that the geometry of the triflate anion looks better, the thermal ellipsoid of atom N1 was restrained, 13 least-squares restraints were used, of which 12 thermal parameters of C47 and N1, and 1 bond distance C47-F2 were restrained. Some unknown solvents are strongly disordered and cannot be refined properly, as a result, the SQUEEZE[5] algorithm was used to omit all of these disordered fragments.

In the asymmetric unit of complex **2a**, two of the four triflate anions and some unknown solvents are strongly disordered and cannot be refined properly, as a result, the SQUEEZE[5] algorithm was used to omit all of these disordered fragments. The H atoms of the water molecule couldn't restrainted and deleted. 8 least-squares restraints were used, which are corresponding to 6 thermal parameters of C46

and 2 bond distances of S2-C46. The cell contents (C 368, H 392, N 32, O 52, F48, S16, Ir 16) include the atoms in absence of two triflate anions.

The pentamethylcyclopentadienyl ligand of complex **4a** was strongly disordered because of rotation in room temperature, and it was also refined to two idealized positions (68:32). The 120 thermal parameters of 20 atoms, which are C11 C12 C13 C14 C15 C16 C17 C18 C19 C20 C11' C12' C13' C14' C15' C16' C17' C18' C19' C20', were restrained. Some unknown solvents are strongly disordered and cannot be refined properly, as a result, the SQUEEZE[5] algorithm was used to omit all of these disordered fragments.

In Complex **4b**, the 2 restraints were used to restrain both bond distance of C22- Cl2 and angle distance of Cl2 Cl2_#1 ( symmetry code #1: 2-x, y, 3/2-z).

In all complexes, hydrogen atoms which could be found were placed in the geometrically calculated positions with fixed isotropic thermal parameters.

Crystal data for **1a**·unknown solvent: $C_{92}H_{96}F_{12}Ir_4N_8O_{12}S_4$, $M$ = 2630.81, monoclinic, $a$ = 33.826(15), $b$ = 18.632(8), $c$ = 19.427(9) Å, $\beta$ = 109.080(7)°, $V$ = 11571(9) Å$^3$, $T$ = 293 K, space group $C2/c$, $Z$ = 4, 23505 reflections measured, 10174 unique ($R_{int}$ = 0.0982) which were used in all calculations. The final $wR(F_2)$ was 0.1379 (all data).

Crystal data for **1b**·2$CH_3OH$: $C_{98}H_{112}F_{12}Ir_4N_8O_{18}S_4$, $M$ = 2815.00, monoclinic, $a$ = 17.03(3) Å, $b$ = 18.63(3) Å, $c$ = 17.40(3) Å, $\beta$ = 114.60(2)°, $V$ = 5020(14) Å$^3$, $T$ = 293 K, space group $P2_1/n$, $Z$ = 2, 20681 reflections measured, 8812 unique ($R_{int}$ = 0.1283) which were used in all calculations. The final $wR(F_2)$ was 0.1194 (all data).

Crystal data for **1c**·2$CH_2Cl_2$·unknown solvent: $C_{98}H_{106}Cl_4F_{12}Ir_4N_8O_{12}S_4$, $M$ = 2854.75, monoclinic, $a$ = 16.551(10) Å, $b$ = 34.96(2) Å, $c$ = 21.073(13) Å, $\beta$ = 106.644(9)°, $V$ = 11684(12) Å$^3$, $T$ = 293 K, space group $C2/c$, $Z$ = 4, 22373 reflections measured, 10252 unique ($R_{int}$ = 0.0775) which were used in all calculations. The final $wR(F_2)$ was 0.0908 (all data).

Crystal data for **2a**·$H_2O$·unknown solvent: $C_{92}H_{98}F_{12}Ir_4N_8O_{13}S_4$, $M$ = 2648.82, monoclinic, $a$ =

27.719(12) Å, $b$ = 22.208(12) Å, $c$ = 20.173(10) Å, $\beta$ = 119.209(9)°, $V$ = 10840(9) Å$^3$, $T$ = 293 K, space group $C2/m$, $Z$ = 4, 25942 reflections measured, 11808 unique ($R_{int}$ = 0.0699) which were used in all calculations. The final $wR(F_2)$ was 0.1359 (all data).

Crystal data for **3a**: $C_{40}H_{44}Cl_2Ir_2N_2$, $M$ = 1008.07, monoclinic, $a$ = 7.468(3) Å, $b$ = 18.049(7) Å, $c$ = 13.623(6) Å, $\beta$ = 101.915(5)°, $V$ = 1796.8(13) Å$^3$, $T$ = 293 K, space group $P2_1/n$, $Z$ = 2, 8531 reflections measured, 3824 unique ($R_{int}$ = 0.0390) which were used in all calculations. The final $wR(F_2)$ was 0.0471 (all data).

Crystal data for **3b**·2$CH_2Cl_2$: $C_{44}H_{52}Cl_6Ir_2N_2O_2$, $M$ = 1237.98, monoclinic, $a$ =16.338(7) Å, $b$ = 10.244(5) Å, $c$ = 13.969(6) Å, $\beta$ = 105.319(6)°, $V$ = 2255.0(18) Å$^3$, $T$ = 293 K, space group $P2_1/c$, $Z$ = 2, 10451 reflections measured, 4818 unique ($R_{int}$ = 0.0500) which were used in all calculations. The final $wR(F_2)$ was 0.0723 (all data).

Crystal data for **4a**·unknown solvent: $C_{40}H_{44}Cl_2Ir_2N_2$, $M$ = 1008.07, monoclinic, $a$ =22.261(12) Å, $b$ = 8.705(5) Å, $c$ = 22.589(12) Å, $\beta$ = 90.839(7)°, $V$ = 4377(4) Å$^3$, $T$ = 293 K, space group $C2/c$, $Z$ = 4, 10280 reflections measured, 4686 unique ($R_{int}$ = 0.0531) which were used in all calculations. The final $wR(F_2)$ was 0.0705 (all data).

Crystal data for **4b**·$CH_2Cl_2$: $C_{43}H_{50}Cl_4Ir_2N_2O_2$, $M$ = 1153.05, monoclinic, $a$ = 27.594(9) Å, $b$ = 12.355(4) Å, $c$ = 12.452(4) Å, $\beta$ = 96.464(4)°, $V$ = 4218(2) Å$^3$, $T$ = 293 K, space group $C2/c$, $Z$ = 4, 9875 reflections measured, 4462 unique ($R_{int}$ = 0.0337) which were used in all calculations. The final $wR(F_2)$ was 0.0765 (all data).

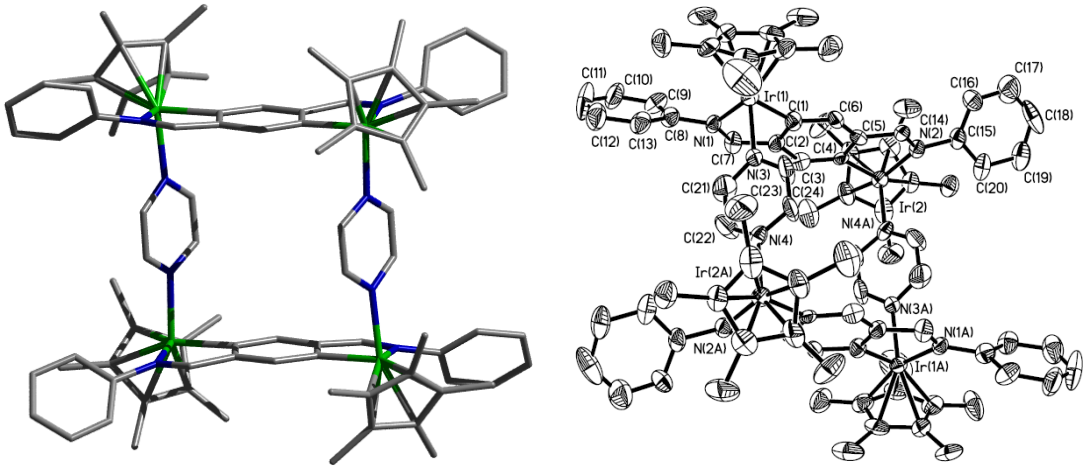



***Figure S1***. Left: Side view of the cation of **1a** in stick mode. All hydrogen atoms, anions, and solvent molecules are omitted for clarity. Right: ORTEP view of **1a** (ellipsoids at the 30% probability level). All hydrogen atoms, anions, and solvent molecules are omitted for clarity.

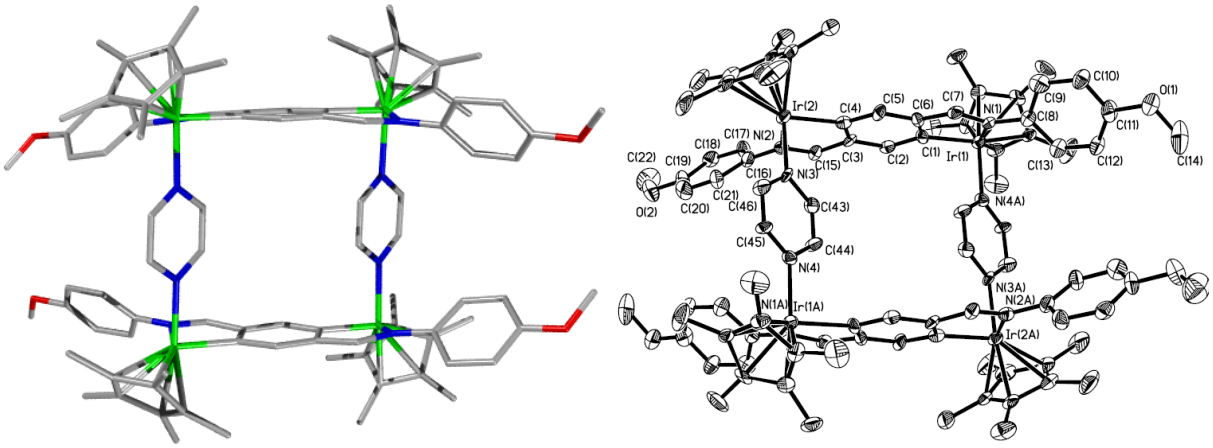
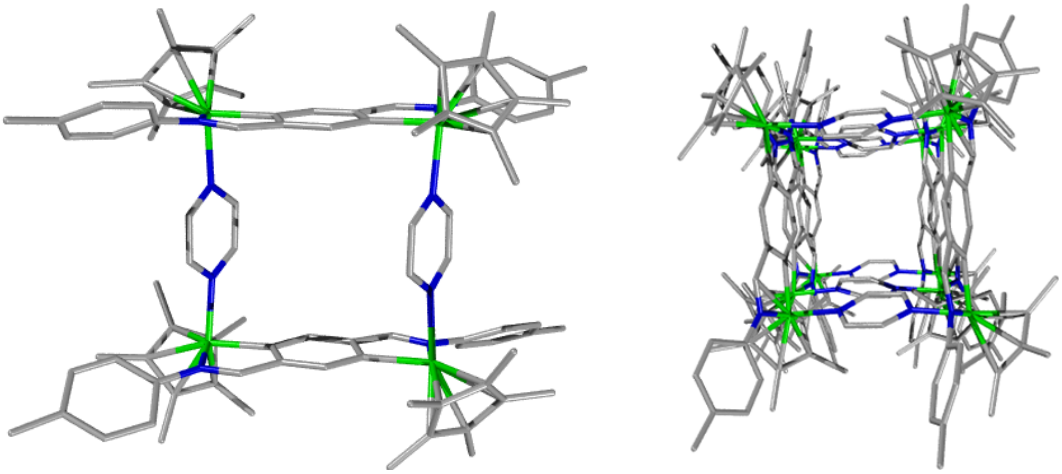
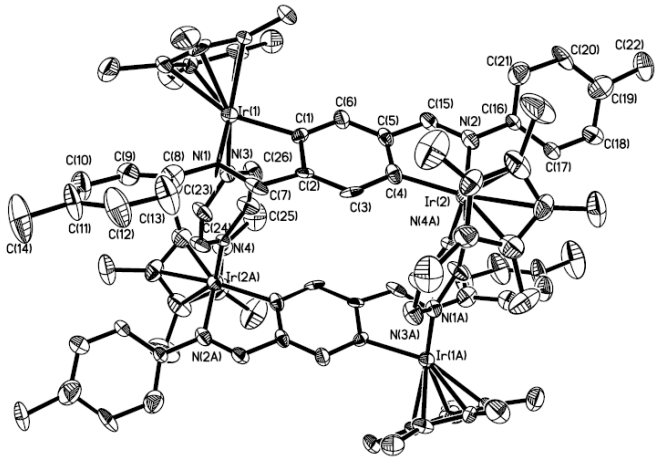



***Figure S2***. Left: Side view of the cation of **1b** in stick mode. Ir (green), N (blue), C (dark gray), O (red). Right: ORTEP view of **1b** (ellipsoids at the 30% probability level). All hydrogen atoms, anions, and solvent molecules are omitted for clarity.



(a) (b)




(c)

***Figure S3***. (a) Side view of the cation of **1c** in stick mode. (b) The crystal packing of **1c** in the solid states. Ir (green), N (blue), C (dark gray). (c) ORTEP view of **1c** (ellipsoids at the 30% probability level). All hydrogen atoms, anions, and solvent molecules are omitted for clarity.

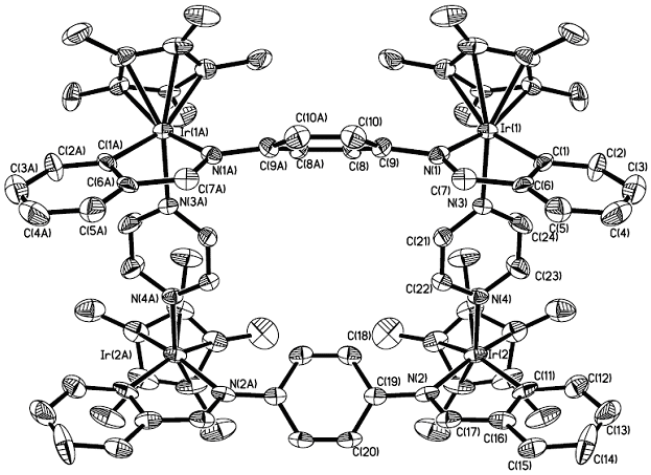



***Figure S4***. ORTEP view of the cationic part of **2a** (ellipsoids at the 30% probability level). Selected bond lengths [Å] and angles [°]: Ir(1)-C(1) 2.045(9), Ir(1)-N(1) 2.119(8), Ir(1)-N(3) 2.121(7); C(1)-Ir(1)-N(1) 77.9(3), C(1)-Ir(1)-N(3) 84.2(3), N(1)-Ir(1)-N(3) 88.6(3).

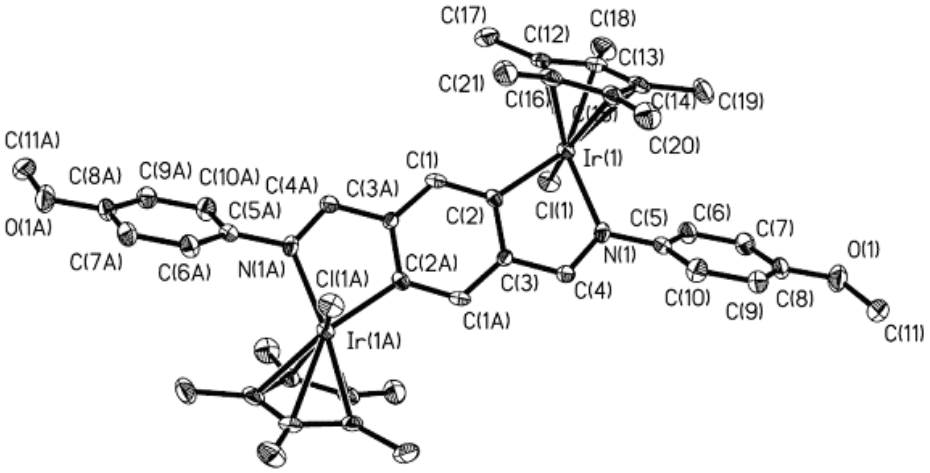



***Figure S5***. ORTEP view of **3b** (ellipsoids at the 30% probability level). All hydrogen atoms and solvent molecules are omitted for clarity.

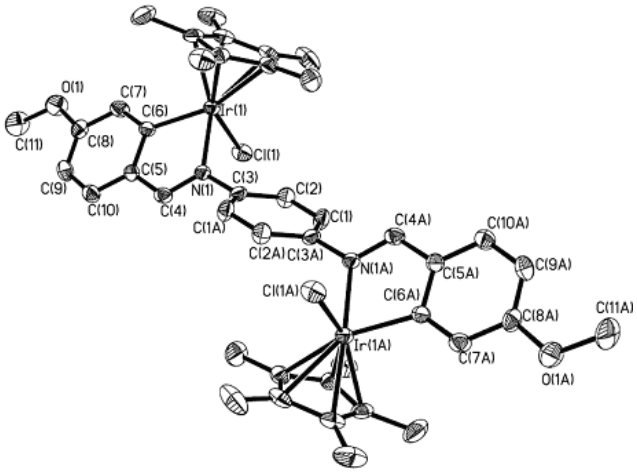



***Figure S6***. ORTEP view of **4b** (ellipsoids at the 30% probability level). All hydrogen atoms and solvent molecules are omitted for clarity.

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