

SUPPORTING INFORMATION

Room-Temperature Synthesis of Cyclometalated Iridium(III) Complexes: Kinetic Isomers and Reactive Functionalities

Ayan Maity, Bryce Lane Anderson, Nihal Deligonal, and Thomas G. Gray*

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Experimental Details

General Information. All synthetic procedures involving moisture-sensitive or air-sensitive substances were performed under an inert N₂ or argon atmosphere and anhydrous conditions. Anhydrous solvents were used directly from MBraun solvent purification system or were purchased from Sigma Aldrich. NMR spectra were recorded on a Varian AS-400 spectrometer. High-resolution mass spectrometry was carried out on a Bruker BioTOF II or Bruker microTOFQ mass spectrometer at the University of Cincinnati.

IrCl₃·H₂O, palladium(II) acetate and silver(I) triflate (AgOTf) were purchased from Strem Chemicals. The ligands 2-phenylpyridine (ppy), *p*-tolylpyridine (tpy) and 2-acetylphenylboronic acid (**4**) were purchased from Acros; 2,4-difluorophenylpyridine (F₂ppy), 2-phenylquinoline (pq), 2-(2'-benzothienyl)pyridine (btp), *n*-butyllithium (1.6 M in hexanes) were purchased from Sigma-Aldrich. 2-Formylphenyl boronic acid (**5**) and 2-formyl-5-methylphenylboronic acid (**6**) were purchased from Frontier Scientific.

A heavy-walled high pressure vessel (catalog no. CG-1880-05, Chemglass) was used for bromination reactions. N-bromosuccinamide (NBS) (Alfa Aesar), 2-isopropoxy-4,4,5,5,-tetramethyl-[1,3,2]-dioxaborolane (Acros) were used as they received.

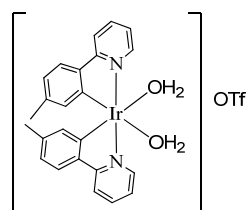
Cyclometalated Ir(III) μ -chloro-bridged dimers, (C[^]N)₂Ir(μ -Cl)₂Ir(C[^]N)₂, (abbreviated as [{Ir(C[^]N)₂(μ -Cl)}₂]) were synthesized via the method reported by Nonoyama;^[1] IrCl₃·3H₂O was refluxed with 2-2.5 equiv cyclometalating ligand in a 3:1 mixture of 2-ethoxyethanol (Acros) and water.

Syntheses of [{Ir(ppy)₂(μ -Cl)}₂],^[2] [{Ir(tpy)₂(μ -Cl)}₂],^[3] [{Ir(pq)₂(μ -Cl)}₂],^[4] [{Ir(btp)₂(μ -Cl)}₂],^[5] [{Ir(F₂ppy)₂(μ -Cl)}₂],^[6] have been reported.

Synthesis of bis-aquo complexes [L₂Ir(H₂O)₂]⁺ (a-e). General procedure. The bis(aquo) iridium(III) complexes were prepared in a similar fashion to the synthesis employed by McDaniel *et al.*^[7] To the solid chloro-bridged dimer was added a 9:1 (v/v) mixture of ethanol and water and 2.2 equiv silver trifluoromethanesulfonate (AgOTf). The reaction mixture was then refluxed for 24 hours at 100 °C. After this time period the reaction mixture was passed through celite to remove AgCl. Solvent was removed by rotary evaporation, and the reaction mixture was dissolved in methylene chloride. After washing with water and drying over anhydrous Na₂SO₄, the volume of solvent was reduced, and pentane was added with precipitation of a yellow solid. The precipitate was collected, washed with ether and pentane,

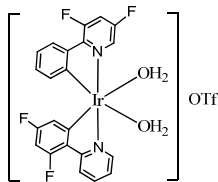
and dried overnight. Characterization of $[\text{Ir}(\text{ppy})_2(\text{H}_2\text{O})_2]\text{OTf}^{[7]}$ (**a**) and $[\text{Ir}(\text{pq})_2(\text{H}_2\text{O})_2]\text{OTf}^{[8]}$ (**c**) has been reported elsewhere.

$[\text{Ir}(\text{tpy})_2(\text{H}_2\text{O})_2]\text{OTf}$ (b): Orange-colored solid. Yield 75%. ^1H NMR (400 MHz, CD_2Cl_2), δ



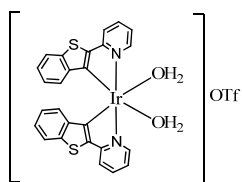
(ppm): 8.96 (d, 2H, $J = 4.8$ Hz), 7.89-7.88 (dd, 2H, $J = 3.8, 1.7$ Hz), 7.87 (d, 2H, $J = 1.1$ Hz), 7.45 (d, 2H, $J = 7.9$ Hz), 7.36-7.33 (m, 2H), 6.72 (d, 2H, $J = 9.5$ Hz), 5.92 (s, 2H), 2.05 (s, 6H). HRMS: Calcd. for $\text{C}_{24}\text{H}_{20}\text{IrN}_2$ $[\text{M}-2\text{H}_2\text{O}]^+$: 529.1256 Found: 529.1267.

$[\text{Ir}(\text{F}_2\text{ppy})_2(\text{H}_2\text{O})_2]\text{OTf}$ (d): Bright orange-colored solid. Yield 79%. ^1H NMR (400 MHz, D_2O),



δ (ppm): 8.89 (d, 2H, $J = 5.3$ Hz), 8.34 (d, 2H, $J = 8.2$ Hz), 8.04 (t, 2H, $J = 7.1$ Hz), 7.51 (t, 2H, $J = 7.2$ Hz), 6.53 (t, 2H, $J = 8.9$ Hz), 5.67 (d, 2H, $J = 7.9$ Hz). HRMS: Calcd. for $\text{C}_{22}\text{H}_{12}\text{F}_4\text{IrN}_2$ $[\text{M}-2\text{H}_2\text{O}]^+$: 573.0566 Found: 573.0581.

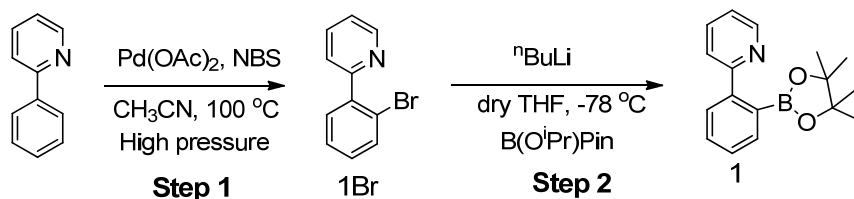
$[\text{Ir}(\text{btp})_2(\text{H}_2\text{O})_2]\text{OTf}$ (e): Brick red-colored solid. Yield 66%. ^1H NMR (400 MHz, Acetone- d_6),



δ (ppm): 9.33-9.02 (m, 2H), 8.23-8.14 (m, 2H), 7.90-7.85 (m, 2H), 7.75-7.71 (m, 2H), 7.57-7.46 (m, 2H), 7.18-7.11 (m, 2H), 6.89-6.84 (m, 2H), 6.24-6.07 (m, 2H). HRMS: Calcd. for $\text{C}_{26}\text{H}_{16}\text{IrN}_2\text{S}_2$ $[\text{M}-2\text{H}_2\text{O}]^+$: 613.0384 Found: 613.0454.

Synthesis of ligand precursors 1-3. The borylated ligands **1-3** have been synthesized by borylation via lithiation of their brominated precursors.

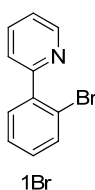
Synthetic scheme for obtaining boronic esters of the cyclometalating ligands.



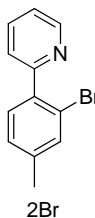
Similar schemes have been applied to obtain the ligands **1-3**.

Step 1. Bromination of free ligands. General procedure. Bromination followed the procedure of Sanford *et. al.*^[9] To a solution of ligand (1.0 equiv), dissolved in dry CH₃CN in a high pressure tube, was added N-bromosuccinimide (NBS) (1.1 equiv) and Pd(OAc)₂ (10 mol%). The reaction vessel was evacuated and back-filled with Ar. The reaction mixture was heated to 100 °C for 24 h, after which time the mixture was cooled to room temperature and solvent was removed under vacuum. The residue was purified by chromatography. Yields, eluting solvents, and characterization data for **1Br–3Br** are as follows:

2-(2-Bromophenyl)pyridine (1Br):^[9] Product was purified by silica gel column chromatography eluted with ether/hexane (1:4 v/v). A transparent liquid was obtained. Yield 58%. ¹H NMR (400 MHz, CDCl₃), δ: 8.71 (d, 1H, *J* = 5.5 Hz), 7.76 (td, 1H, *J* = 7.8, 1.8 Hz), 7.67 (dd, 1H, *J* = 7.8, 1.2 Hz), 7.59 (d, 1H, *J* = 7.8 Hz), 7.53 (dd, 1H, *J* = 7.6, 1.2 Hz), 7.40 (td, 1H, *J* = 7.4, 1.2 Hz), 7.31-7.23 (m, 2H). HRMS: Calcd. for C₁₁H₉BrN [MH]⁺: 233.9918 Found: 233.9912.

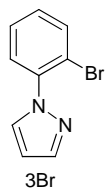


2-(2-Bromo-4-methylphenyl)pyridine (2Br):^[10]



Product was purified by silica gel column chromatography eluted with ether/hexane (1:5 v/v). An oily liquid was collected. Yield 62%. ¹H NMR (400 MHz, CDCl₃), δ: 8.70 (d, 1H, *J* = 4.9 Hz), 7.74 (td, 1H, *J* = 7.8, 1.8 Hz), 7.59 (d, 1H, *J* = 7.8 Hz), 7.50 (s, 1H), 7.43 (d, 1H, *J* = 7.8 Hz), 7.29-7.27 (m, 1H), 7.21 (d, 1H, *J* = 7.8 Hz), 2.38 (s, 3H). HRMS: Calcd. for C₁₂H₁₁BrN [MH]⁺: 248.0075 Found: 248.0123.

1-(2-bromophenyl)-1H-pyrazole (3Br):

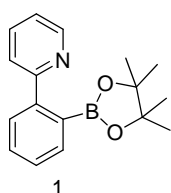


Product was purified by silica gel column chromatography eluted with ether/hexanes (1:5 v/v) to recover a liquid product. Yield 40%. ¹H NMR (400 MHz, CDCl₃), δ: 7.82 (dd, 1H, *J* = 1.8 Hz), 7.75 (d, 1H, *J* = 1.7 Hz), 7.70 (m, 1H), 7.51 (m, 1H), 7.43 (m, 1H), 7.28 (m, 1H), 6.47 (m, 1H). HRMS: Calcd. for C₉H₈BrN₂ [MH]⁺: 222.9871 Found: 222.9825.

Step 2. Borylation via lithiation of brominated ligands. Synthesis of ligand precursor 1-3.

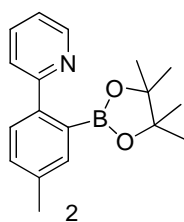
General procedure. 1.6 M *n*-butyllithium (1.5 equiv) was slowly added to brominated ligand (1 equiv) in THF at $-78\text{ }^{\circ}\text{C}$. The mixture was stirred for 30 min at $-78\text{ }^{\circ}\text{C}$. 2-Isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (1.5 equiv) was added dropwise, and the mixture was stirred at room temperature overnight. The reaction was quenched by the addition of water, and the mixture was extracted with methylene chloride. The volume of solvent was reduced, and the crude product was purified by recrystallization from methylene chloride with pentane. In each case, an off-white solid was obtained.

2-[2-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-pyridine (1):



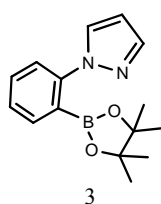
Yield 68%. Compound **1** has been reported elsewhere.^[3]

2-[4-methyl-2-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-pyridine (2):



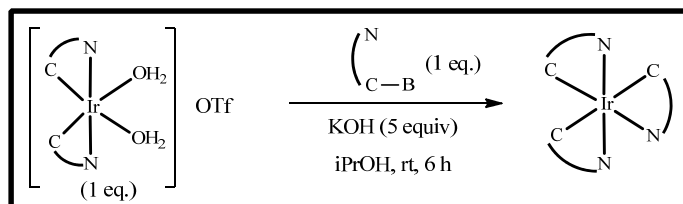
Following the general procedure afforded **2**. Yield 63%. ^1H NMR (400 MHz, CDCl_3), δ : 8.61 (d, 1H, $J = 5.6$ Hz), 7.90 (t, 1H, $J = 7.7$ Hz), 7.72 (d, 1H, $J = 8.9$ Hz), 7.51 (t, 2H, $J = 8.6$ Hz), 7.29 (t, 1H, $J = 7.3$ Hz), 7.07 (d, 1H, $J = 7.8$ Hz), 2.37 (s, 3H), 1.41 (s, 12H). HRMS: Calcd. for $\text{C}_{18}\text{H}_{22}\text{BNNaO}_2$ $[\text{MNa}]^+$: 318.1641 Found: 318.1647.

2-[2-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-pyridine (3):

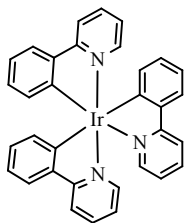


The general procedure afforded the desired product as a solid. Yield 40%. This compound has been described elsewhere.^[11]

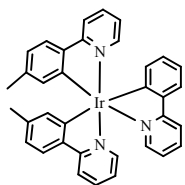
Base promoted transmetalation reactions. Synthesis of Iridium complexes with C^N chelating ligands.



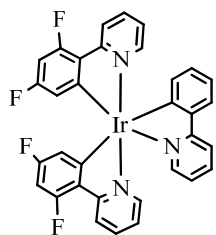
[Ir(ppy)₃]. In 7 mL 2-propanol were suspended [Ir(ppy)₂(H₂O)₂]OTf, **a** (100 mg, 0.146 mmol) and compound **1** (41 mg, 0.146 mmol). To this suspension was added KOH (40.9 mg, 0.729 mmol), and the mixture was stirred at room temperature for 6 h. After 6 h the boronic ester was consumed as observed by TLC. Evaporation of solvent under reduced pressure yielded a dark orange-colored residue that was dissolved in 10 mL methylene chloride. The methylene chloride layer was washed twice with water followed by brine, and was passed through anhydrous Na₂SO₄. The volume of solvent was reduced, and sufficient pentane was added to precipitate a dark-orange solid. The precipitate was collected and dried. Yield: 87 mg (91%). ¹H NMR (400 MHz, CDCl₃), δ: 8.10 (d, 1H, *J* = 5.5 Hz), 7.92 (d, 2H, *J* = 7.9 Hz), 7.79 (d, 2H, *J* = 8.0 Hz), 7.74 (d, 1H, *J* = 7.3 Hz), 7.69-7.59 (m, 4H), 7.52 (t, 1H, *J* = 8.0 Hz), 7.46 (t, 1H, *J* = 7.6 Hz), 6.97-6.92 (m, 5H), 6.88 (t, 2H, *J* = 7.0 Hz), 6.83 (t, 1H, *J* = 8.3 Hz), 6.72 (dd, 2H, *J* = 6.2 Hz), 6.61 (d, 1H, *J* = 5.9 Hz), 6.46 (d, 1H, *J* = 9.0 Hz). HRMS: Calcd. For C₃₃H₂₅IrN₃ [MH]⁺: 656.1678 Found: 656.1653 Anal. Calcd. For C₃₃H₂₄IrN₃: C, 60.53; H, 3.69; N, 6.42. Found: C, 60.63; H, 3.98; N, 6.55.



[Ir(tpy)₂ppy]. In 5 mL 2-propanol were suspended [Ir(tpy)₂(H₂O)₂]OTf, **b** (91.2 mg, 0.128 mmol) and compound **1** (35.9 mg, 0.128 mmol). To this suspension was added KOH (35.8 mg, 0.638 mmol), and the mixture was stirred at room temperature for 6 h. Starting material was consumed after 6 h, as indicated by TLC. Evaporation of solvent under reduced pressure yielded a dark orange-colored residue that was dissolved in 10 mL methylene chloride. The methylene chloride layer was washed twice with water followed by brine, and was passed through anhydrous Na₂SO₄. The volume of solvent was reduced to 0.5 mL, and sufficient pentane was added to afford a dark orange precipitate. The precipitate was collected and dried. Yield: 76 mg (87%). ¹H NMR (400 MHz, CD₂Cl₂), δ: 8.04 (d, 1H, *J* = 5.6 Hz), 7.95 (d, 2H, *J* = 7.6 Hz), 7.78 (t, 3H, *J* = 3.8 Hz), 7.63-7.46 (m, 5H), 6.97-6.79 (m, 6H), 6.72-6.69 (m, 3H), 6.39 (s, 1H), 6.23 (s, 1H), 2.14 (s, 3H), 2.13 (s, 3H). HRMS: Calcd. For C₃₅H₂₉IrN₃ [MH]⁺: 684.1991 Found: 684.1988 Anal. Calcd. For C₃₅H₂₈IrN₃: C, 61.56; H, 4.13; N, 6.15. Found: C, 61.85; H, 4.35; N, 5.90.

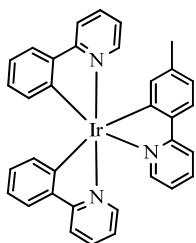


[Ir(F₂ppy)₂ppy]. In 5 mL 2-propanol were suspended [Ir(F₂ppy)₂(H₂O)₂]OTf, **d** (106 mg, 0.139 mmol) and compound **1** (39.3 mg, 0.139 mmol). To this suspension was added KOH (39.2 mg,

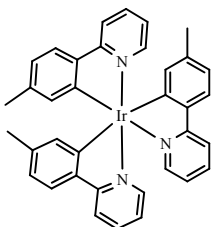


0.699 mmol), and the mixture was stirred at room temperature for 6 h. After 6 h the boronic ester was consumed as observed by TLC. Evaporation of solvent under reduced pressure yielded a dark orange-colored residue that was dissolved in 10 mL methylene chloride. The methylene chloride layer was washed twice with water followed by brine, and was passed through anhydrous Na_2SO_4 . The volume of solvent was reduced to 1 mL and sufficient pentane was added to precipitate an orange solid. The precipitate was collected and dried. Yield: 93.6 mg (92%). ^1H NMR (400 MHz, CD_2Cl_2), δ : 8.21 (d, 1H, $J = 8.4$ Hz), 8.08 (d, 1H, $J = 5.9$ Hz), 7.95 (d, 1H, $J = 8.3$ Hz), 7.87 (d, 1H, $J = 5.5$ Hz), 7.75 (d, 1H, $J = 6.7$ Hz), 7.67 (td, 1H, $J = 8.2, 1.6$ Hz), 7.59 (t, 1H, $J = 7.24$), 7.49 (t, 1H, $J = 7.4$ Hz), 7.03-6.99 (m, 3H), 6.95 (t, 1H, $J = 6.0$ Hz), 6.90 (d, 1H, $J = 8.1$ Hz), 6.75 (q, 2H, $J = 5.8$ Hz), 6.47-6.37 (m, 3H), 6.02 (dd, 1H, $J = 7.4, 2.3$ Hz), 5.82 (dd, 1H, $J = 9.2, 2.3$ Hz). HRMS: Calcd. For $\text{C}_{33}\text{H}_{21}\text{F}_4\text{IrN}_3$ $[\text{MH}]^+$: 728.1301 Found: 728.1372 Anal. Calcd. For $\text{C}_{33}\text{H}_{20}\text{F}_4\text{IrN}_3$: C, 54.54; H, 2.77; N, 5.78. Found: C, 54.61; H, 3.06; N, 5.93.

[Ir(ppy)₂tpy]. In 8 mL 2-propanol were suspended $[\text{Ir}(\text{ppy})_2(\text{H}_2\text{O})_2]\text{OTf}$, **a** (100 mg, 0.146 mmol) and compound **2** (43.0 mg, 0.146 mmol). To this suspension was added KOH (40.9 mg, 0.729 mmol), and the mixture was stirred at room temperature for 6 h. After 6 h the boronic ester **2** was consumed as observed by TLC. Evaporation of solvent under reduced pressure yielded a dark orange-colored residue that was dissolved in 20 mL methylene chloride. The methylene chloride layer was washed twice with water followed by brine, and was passed through anhydrous Na_2SO_4 . The volume of solvent was reduced to 0.5 mL and pentane was added to precipitate a bright orange solid. The precipitate was collected and dried. Yield: 85.8 mg (88%). ^1H NMR (400 MHz, CD_2Cl_2), δ : 8.12 (d, 1H, $J = 5.7$ Hz), 7.89 (t, 2H, $J = 8.3$ Hz), 7.84 (d, 1H, $J = 3.8$ Hz), 7.82 (d, 1H, $J = 3.6$ Hz), 7.71 (d, 1H, $J = 7.6$ Hz), 7.67 (d, 2H, $J = 7.8$ Hz), 7.64-7.51 (m, 4H), 6.97-6.75 (m, 8H), 6.69 (s, 1H), 6.56 (d, 1H, $J = 7.1$ Hz), 6.41 (d, 1H, $J = 7.4$ Hz), 2.11 (s, 3H). HRMS: Calcd. For $\text{C}_{34}\text{H}_{27}\text{IrN}_3$ $[\text{MH}]^+$: 670.1834 Found: 670.1876 Anal. Calcd. For $\text{C}_{34}\text{H}_{26}\text{IrN}_3$: C, 61.06; H, 3.92; N, 6.28. Found: C, 61.25; H, 4.11; N, 5.98.

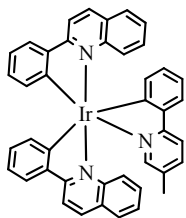


[Ir(tpy)₃]. In 7 mL 2-propanol were suspended [Ir(tpy)₂(H₂O)₂]OTf, **b** (91.2 mg, 0.128 mmol) and compound **2** (37.7 mg, 0.128 mmol). To this suspension was added KOH



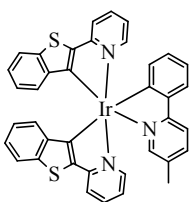
(35.8 mg, 0.638 mmol), and the mixture was stirred at room temperature for 6 h. Evaporation of solvent under reduced pressure yielded a dark orange-colored residue that was dissolved in 10 mL methylene chloride. The methylene chloride layer was washed twice with water followed by brine, and was passed through anhydrous Na₂SO₄. The volume of solvent was reduced, and pentane was added to get bright yellow precipitate. The precipitate was collected and dried. Yield: 74.8 mg (84%). ¹H NMR (400 MHz, CD₂Cl₂), δ: 8.07 (d, 1H, *J* = 6.2 Hz), 7.90-7.88 (m, 2H), 7.79-7.76 (dd, 2H, *J* = 8.0, 4.2 Hz), 7.65-7.48 (m, 8H), 6.86 (t, 1H, *J* = 6.3 Hz), 6.80 (t, 2H, *J* = 6.1 Hz), 6.72 (t, 3H, *J* = 6.8 Hz), 6.36 (s, 1H), 6.21 (s, 1H), 2.13 (s, 6H), 2.12 (s, 3H). HRMS: Calcd. For C₃₆H₃₁IrN₃ [MH]⁺: 698.2147 Found: 698.2144 Anal. Calcd. For C₃₆H₃₀IrN₃: C, 62.05; H, 4.34; N, 6.03. Found: C, 62.25; H, 4.14; N, 5.88.

[Ir(pq)₂tpy]. In 10 mL 2-propanol were suspended [Ir(pq)₂(H₂O)₂]OTf, **c** (100 mg, 0.127 mmol) and compound **2** (37.6 mg, 0.127 mmol). To this suspension was added KOH



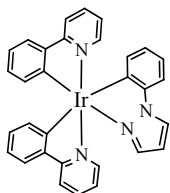
(35.7 mg, 0.636 mmol), and the mixture was stirred at room temperature for 16 h. Evaporation of solvent under reduced pressure yielded a dark orange-colored residue that was dissolved in 15 mL methylene chloride. The methylene chloride layer was washed twice with water followed by brine, and was passed through anhydrous Na₂SO₄. The volume of solvent was reduced, and pentane was added with precipitation of a dark red solid. The precipitate was recrystallized from methylene chloride and pentane one more time to obtain, after drying, an analytically pure product. Yield: 62.6 mg (64%). ¹H NMR (400 MHz, CD₂Cl₂), δ: 8.26 (s, 2H), 8.00 (d, 1H, *J* = 8.1 Hz), 7.92-7.83 (m, 3H), 7.71 (t, 2H, *J* = 7.6 Hz), 7.61 (d, 1H, *J* = 5.4 Hz), 7.51-7.44 (m, 3H), 7.36-7.32 (m, 4H), 7.21 (t, 1H, *J* = 7.1 Hz), 7.02 (d, 1H, *J* = 7.7 Hz), 6.99-6.92 (m, 2H), 6.86 (t, 1H, *J* = 7.4 Hz), 6.63 (t, 1H, *J* = 7.4 Hz), 6.58 (t, 2H, *J* = 7.2 Hz), 6.23 (d, 1H, *J* = 8.0 Hz), 5.99 (d, 1H, *J* = 7.8 Hz), 5.74 (d, 1H, *J* = 7.8 Hz), 1.92 (s, 3H). HRMS: Calcd. For C₄₂H₃₁IrN₃ [MH]⁺: 770.2147 Found: 770.2148 Anal. Calcd. For C₄₂H₃₀IrN₃: C, 65.60; H, 3.93; N, 5.46. Found: C, 65.81; H, 4.28; N, 5.67.

[Ir(btp)₂tpy]. In 10 mL 2-propanol were suspended [Ir(btp)₂(H₂O)₂]OTf, **e** (100 mg, 0.125 mmol) and compound **2** (36.9 mg, 0.125 mmol). To this suspension was added



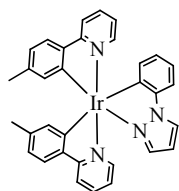
KOH (35.0 mg, 0.626 mmol), and the mixture was stirred at room temperature for 16 h. Evaporation of solvent under reduced pressure yielded a dark orange-colored residue that was dissolved in 15 mL methylene chloride. The methylene chloride layer was washed twice with water followed by brine, and was passed through anhydrous Na₂SO₄. The volume of solvent was reduced, and sufficient pentane was added to precipitate a bright red solid. The precipitate was collected and dried. Yield: 56.8 mg (58%). ¹H NMR (400 MHz, CDCl₃), δ: 9.12 (d, 1H, *J* = 6.0 Hz), 8.08 (d, 1H, *J* = 5.6 Hz), 7.81-7.65 (m, 7H), 7.59 (t, 1H, *J* = 7.4 Hz), 7.50 (d, 1H, *J* = 7.5 Hz), 7.24 (d, 1H, *J* = 8.2 Hz), 7.11-7.06 (m, 2H), 6.98 (t, 1H, *J* = 7.1 Hz), 6.83-6.77 (m, 2H), 6.73 (t, 1H, *J* = 5.7 Hz), 6.59 (t, 1H, *J* = 6.4 Hz), 6.33 (d, 1H, *J* = 7.6 Hz), 6.28 (d, 1H, *J* = 7.9 Hz), 6.21 (s, 1H), 6.02 (d, 1H, *J* = 7.9 Hz), 2.02 (s, 3H). HRMS: Calcd. For C₃₈H₂₇IrN₃S₂ [MH]⁺: 782.1276 Found: 782.1263 Anal. Calcd. For C₃₈H₂₆IrN₃S₂: C, 58.44; H, 3.36; N, 5.38. Found: C, 58.66; H, 3.29; N, 5.41.

[Ir(ppy)₂ppz]. In 8 mL 2-propanol were suspended [Ir(ppy)₂(H₂O)₂]OTf, **a** (100 mg, 0.146 mmol) and compound **3** (39.4 mg, 0.146 mmol). To this suspension was added



KOH (40.9 mg, 0.729 mmol), and the mixture was stirred at room temperature for 6 h. After 6 h the boronic ester was consumed as observed by TLC. Evaporation of solvent under reduced pressure yielded a dark orange-colored residue that was dissolved in 10 mL methylene chloride. The methylene chloride layer was washed twice with water followed by brine, and was passed through anhydrous Na₂SO₄. The volume of solvent was reduced, and sufficient pentane was added to precipitate a dark orange solid. The precipitate was collected and dried. Yield: 76.0 mg (81%). ¹H NMR (400 MHz, CDCl₃), δ: 9.05 (d, 1H, *J* = 5.8 Hz), 8.01 (dd, 1H, *J* = 7.6, 1.1 Hz), 7.88-7.83 (m, 2H), 7.78 (t, 1H, *J* = 7.3 Hz), 7.52-7.43 (m, 4H), 7.37 (t, 2H, *J* = 6.2 Hz), 7.29 (dd, 1H, *J* = 7.8, 4.0 Hz), 7.12 (t, 1H, *J* = 7.6 Hz), 6.93 (td, 1H, *J* = 7.6, 1.6 Hz), 6.79-6.72 (m, 3H), 6.59 (t, 1H, *J* = 7.6 Hz), 6.38 (t, 1H, *J* = 6.0 Hz), 6.34-6.31 (m, 2H), 6.27 (t, 1H, *J* = 2.5 Hz), 6.01 (d, 1H, *J* = 7.5 Hz). HRMS: Calcd. For C₃₁H₂₄IrN₄ [MH]⁺: 645.1630 Found: 645.1639 Anal. Calcd. For C₃₁H₂₃IrN₄: C, 57.84; H, 3.60; N, 8.70. Found: C, 57.91; H, 3.77; N, 8.71.

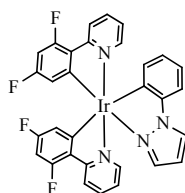
[Ir(tpy)₂ppz]. In 5 mL 2-propanol were suspended [Ir(tpy)₂(H₂O)₂]OTf, **b** (105.6 mg, 0.148 mmol) and compound **3** (39.9 mg, 0.148 mmol). To this suspension was added



KOH (41.5 mg, 0.739 mmol), and the mixture was stirred at room temperature for 6 h. After 6 h the boronic ester was consumed as observed by TLC.

Evaporation of solvent under reduced pressure yielded a dark orange-colored residue that was dissolved in methylene chloride. The methylene chloride layer was washed twice with water followed by brine, and was passed through anhydrous Na₂SO₄. The volume of solvent was reduced, and pentane was added. A bright yellow precipitate was collected and dried. Yield: 84.5 mg (85%). ¹H NMR (400 MHz, CDCl₃), δ: 8.95 (d, 1H, *J* = 5.6 Hz), 7.99 (d, 1H, *J* = 7.6 Hz), 7.82 (d, 1H, *J* = 5.5 Hz), 7.76 (t, 2H, *J* = 8.4 Hz), 7.48 (s, 1H), 7.42-7.33 (m, 5H), 7.16 (d, 1H, *J* = 7.7 Hz), 7.07 (t, 1H, *J* = 7.6 Hz), 6.92 (t, 1H, *J* = 7.8 Hz), 6.58 (d, 1H, 8.6 Hz), 6.55 (d, 1H, *J* = 7.8 Hz), 6.32 (t, 2H, *J* = 7.8 Hz), 6.26 (s, 1H), 6.11 (s, 1H), 5.81 (s, 1H), 2.07 (s, 3H), 1.92 (s, 3H). HRMS: Calcd. For C₃₃H₂₈IrN₄ [MH]⁺: 673.1943 Found: 673.1941 Anal. Calcd. For C₃₃H₂₇IrN₄: C, 59.00; H, 4.05; N, 8.34. Found: C, 59.11; H, 4.13; N, 8.36.

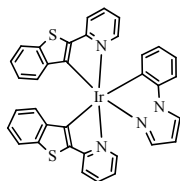
[Ir(F₂ppy)₂ppz]. In 5 mL 2-propanol were suspended [Ir(F₂ppy)₂(H₂O)₂]OTf, **d** (120 mg, 0.158 mmol) and compound **3** (42.7 mg, 0.158 mmol). To this suspension was added



KOH (44.4 mg, 0.792 mmol), and the mixture was stirred at room temperature for 6 h. After 6 h the boronic ester was consumed as observed by TLC.

Evaporation of solvent under reduced pressure yielded a dark orange-colored residue that was dissolved in 20 mL methylene chloride. The methylene chloride layer was washed twice with water followed by brine, and was passed through anhydrous Na₂SO₄. The volume of solvent was reduced, and sufficient pentane was added to precipitate a bright orange solid. The precipitate was collected and dried. Yield: 102.0 mg (90%). ¹H NMR (400 MHz, CDCl₃), δ: 9.05 (d, 1H, *J* = 6.6 Hz), 8.31 (d, 1H, *J* = 9.0 Hz), 8.13 (d, 1H, *J* = 8.5 Hz), 7.96 (d, 1H, *J* = 2.7 Hz), 7.94 (d, 1H, *J* = 5.8 Hz), 7.78 (t, 1H, *J* = 7.6 Hz), 7.57 (t, 1H, *J* = 8.3 Hz), 7.12-7.06 (m, 2H), 6.85 (td, 1H, *J* = 7.1, 1.6 Hz), 6.75 (d, 1H, *J* = 2.3 Hz), 6.66 (t, 1H, *J* = 6.7 Hz), 6.54-6.47 (m, 2H), 6.43-6.31 (m, 3H), 5.91 (dd, 1H, *J* = 8.5, 2.5 Hz), 5.55 (dd, 1H, *J* = 8.8, 2.3 Hz). HRMS: Calcd. For C₃₁H₂₀F₄IrN₄ [MH]⁺: 717.1253 Found: 717.1281 Anal. Calcd. For C₃₁H₁₉F₄IrN₄: C, 52.02; H, 2.68; N, 7.83. Found: C, 52.39; H, 2.92; N, 8.11.

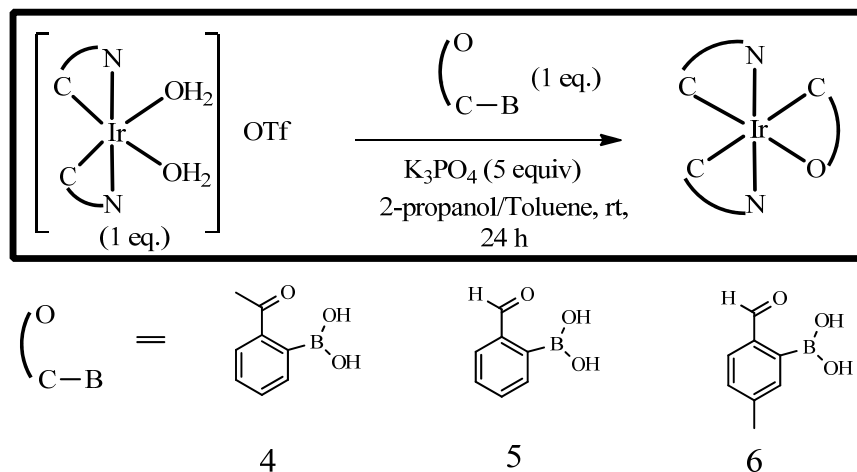
[Ir(btp)₂ppz]. In 5 mL 2-propanol were suspended [Ir(btp)₂(H₂O)₂]OTf, **e** (120 mg, 0.150 mmol) and compound **3** (40.6 mg, 0.150 mmol). To this suspension was added KOH



(42.2 mg, 0.752 mmol), and the mixture was stirred at room temperature for 6 h. After 6 h the boronic ester was consumed as observed by TLC. Evaporation of solvent under reduced pressure yielded a dark orange-colored residue that was

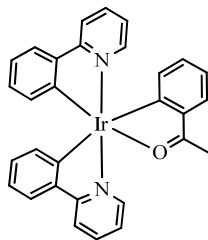
dissolved in methylene chloride. The methylene chloride layer was washed twice with water followed by brine, and was passed through anhydrous Na₂SO₄. The volume of solvent was reduced to 0.5 mL and sufficient pentane was added to precipitate a dark red solid. The precipitate was collected and dried. Yield: 89.8 mg (79%). ¹H NMR (400 MHz, CDCl₃), δ: 9.11 (d, 1H, *J* = 5.5 Hz), 7.96 (d, 1H, *J* = 2.2 Hz), 7.93 (d, 1H, *J* = 5.4 Hz), 7.78-7.68 (m, 4H), 7.64 (d, 1H, *J* = 8.0 Hz), 7.56-7.43 (m, 2H), 7.10-7.02 (m, 2H), 6.95 (t, 1H, *J* = 5.8, 1.5 Hz), 6.87-6.74 (m, 4H), 6.59 (dd, 1H, *J* = 8.3, 1.3 Hz), 6.52-6.46 (m, 2H), 6.32 (d, 1H, *J* = 8.1 Hz), 6.27 (t, 1H, *J* = 2.5 Hz), 6.10 (d, 1H, *J* = 8.1 Hz). HRMS: Calcd. For C₃₅H₂₄IrN₄S₂ [MH]⁺: 757.1072 Found: 757.1097 Anal. Calcd. For C₃₅H₂₃IrN₄S₂: C, 55.61; H, 3.07; N, 7.41. Found: C, 55.83; H, 3.23; N, 7.77.

Synthesis of Iridium complexes with C[^]O chelating ligands.



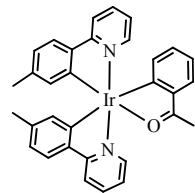
Synthesis of Ir(III) acetyl and formyl complexes.

[Ir(ppy)₂AcPh]. In 5 mL 2-propanol were suspended [Ir(ppy)₂(H₂O)₂]OTf, **a** (100 mg, 0.146 mmol) and compound **4** (23.9 mg, 0.146 mmol). To this suspension was added



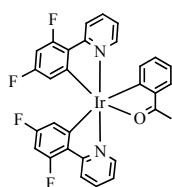
K₃PO₄ (154.8 mg, 0.729 mmol), and the mixture was stirred at room temperature for 24 h. Evaporation of solvent under reduced pressure yielded a dark red-colored residue that was dissolved in methylene chloride. The methylene chloride layer was washed twice with water followed by brine, and was passed through anhydrous Na₂SO₄. Deep red crystals were collected after crystallization from methylene chloride and pentane, and were dried. Yield: 77.7 mg (86%). ¹H NMR (400 MHz, CD₂Cl₂), δ: 8.12 (d, 1H, *J* = 6.1 Hz), 7.92-7.82 (m, 4H), 7.72-7.57 (m, 5H), 7.07-6.81 (m, 7H), 6.75 (t, 1H, *J* = 8.3 Hz), 6.49 (d, 1H, *J* = 6.9 Hz), 6.38 (d, 1H, *J* = 7.9 Hz), 2.83 (s, 3H). IR (KBr): □ = 1573 (s) cm⁻¹ (C=O). HRMS: Calcd. For C₃₀H₂₄IrN₂O [MH]⁺: 620.1440 Found: 620.1445 Anal. Calcd. For C₃₀H₂₃IrN₂O: C, 58.14; H, 3.74; N, 4.52. Found: C, 58.44; H, 4.01; N, 4.32.

[Ir(tpy)₂AcPh]. In 7 mL 2-propanol were suspended [Ir(tpy)₂(H₂O)₂]OTf, **b** (100 mg, 0.140 mmol) and compound **4** (22.9 mg, 0.140 mmol). To this solution was added



K₃PO₄ (148 mg, 0.700 mmol), and the mixture was stirred at room temperature for 22 h. After 22 h the compound **4** was consumed as observed by TLC. Evaporation of solvent under reduced pressure yielded a dark red-colored residue that was dissolved in 10 mL methylene chloride. After washing twice with water followed by brine, the resulting red liquid was passed through anhydrous Na₂SO₄. The volume of solvent was reduced, and sufficient pentane was added to precipitate a dark red solid. The precipitate was collected and dried. Yield: 73.5 mg (81%). ¹H NMR (400 MHz, CD₂Cl₂), δ: 8.03 (dd, 1H, *J* = 5.8, 0.7 Hz), 7.78 (dd, 1H, *J* = 5.9, 0.9 Hz), 7.73 (dd, 2H, *J* = 8.0, 3.5 Hz), 7.66 (d, 1H, *J* = 8.0 Hz), 7.52 (d, 1H, *J* = 7.9 Hz), 7.51 (td, 1H, *J* = 7.3, 1.6 Hz), 7.42 (td, 1H, 7.4, 1.6 Hz), 7.41 (d, 1H, *J* = 7.8 Hz), 6.99 (td, 1H, *J* = 7.1, 1.2 Hz), 6.92 (dd, 1H, *J* = 7.3, 0.9 Hz), 6.85 (ddd, 1H, *J* = 7.8, 7.8, 1.4 Hz), 6.82 (ddd, 1H, *J* = 5.9, 5.9, 1.4 Hz), 6.66-6.64 (m, 2H), 6.59 (dd, 1H, *J* = 7.8, 1.3 Hz), 6.28 (s, 1H), 6.14 (s, 1H), 2.73 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H). IR (KBr): □ = 1589 (s) cm⁻¹ (C=O). HRMS: Calcd. For C₃₂H₂₈IrN₂O [MH]⁺: 649.1831 Found: 649.1835 Anal. Calcd. For C₃₂H₂₇IrN₂O: C, 59.33; H, 4.20; N, 4.32. Found: C, 59.09; H, 4.26; N, 4.66.

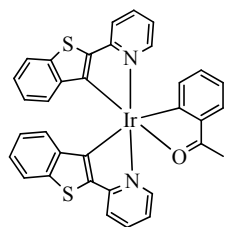
[Ir(F₂ppy)₂AcPh]. In 10 mL 2-propanol were suspended [Ir(F₂ppy)₂(H₂O)₂]OTf, **d** (100 mg,



0.132 mmol) and compound **4** (21.6 mg, 0.132 mmol). To this suspension was added K₃PO₄ (140 mg, 0.659 mmol), and the mixture was stirred at room temperature for 24 h. After 24 h compound **4** was consumed as observed by TLC. Solvent was evaporated under reduced pressure, and the residue was dissolved in

10 mL methylene chloride which was washed twice with water followed by brine, and was passed through anhydrous Na₂SO₄. The volume of solvent was reduced to 0.5 mL and sufficient pentane was added precipitate a red solid. The precipitate was collected and dried. Yield: 74.8 mg (82%). ¹H NMR (400 MHz, CDCl₃), δ: 8.28 (dd, 1H, *J* = 8.2, 2.5 Hz), 8.18 (d, 1H, *J* = 8.2 Hz), 8.07 (dd, 1H, *J* = 5.8, 0.8 Hz), 7.85 (d, 1H, *J* = 5.8 Hz), 7.83 (d, 1H, *J* = 7.4 Hz), 7.67 (t, 1H, *J* = 7.5 Hz), 7.59 (t, 1H, 7.5 Hz), 7.13 (t, 1H, *J* = 6.0 Hz), 7.01-6.97 (m, 3H), 6.82 (td, 1H, *J* = 5.8, 1.4 Hz), 6.43-6.36 (m, 2H), 5.95 (dd, 1H, *J* = 7.5, 2.4 Hz), 5.78 (dd, 1H, *J* = 9.5, 2.3 Hz), 2.85 (s, 3H). IR (KBr): ν = 1589 (s) cm⁻¹ (C=O). HRMS: Calcd. For C₃₀H₂₀F₄IrN₂O [MH]⁺: 693.1141 Found: 693.1172 Anal. Calcd. For C₃₀H₁₉F₄IrN₂O: C, 52.09; H, 2.77; N, 4.05. Found: C, 52.42; H, 2.81; N, 3.88.

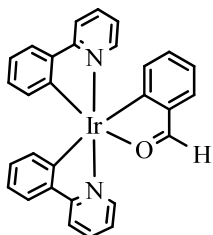
[Ir(btp)₂AcPh]. In 5 mL 2-propanol were suspended [Ir(btp)₂(H₂O)₂]OTf, **e** (50 mg, 0.063



mmol) and compound **4** (10.3 mg, 0.063 mmol). To this suspension was added K₃PO₄ (66.5 mg, 0.313 mmol), and the mixture was stirred at room temperature for 24 h. After 24 h compound **4** was consumed as observed by TLC. Solvent was evaporated under reduced pressure, and the residue was dissolved in 15 mL methylene chloride, which was washed twice with water

followed by brine, and then passed through anhydrous Na₂SO₄. The volume of solvent was reduced, and pentane was added to precipitate a brick-red solid. The precipitate was collected and dried. Yield: 33.0 mg (72%). ¹H NMR (400 MHz, CD₂Cl₂), δ: 8.26 (d, 1H, *J* = 5.8 Hz), 7.84 (d, 1H, *J* = 8.4 Hz), 7.80-7.60 (m, 6H), 7.15-7.07 (m, 3H), 7.03-7.95 (m, 2H), 6.89-6.80 (m, 3H), 6.77-6.71 (m, 2H), 6.24 (d, 1H, *J* = 7.7 Hz), 7.19 (d, 1H, *J* = 7.6 Hz), 2.87 (s, 3H). IR (KBr): ν = 1589 (s) cm⁻¹ (C=O). HRMS: Calcd. For C₃₄H₂₄IrN₂OS₂ [MH]⁺: 733.0959 Found: 733.0949 Anal. Calcd. For C₃₄H₂₃IrN₂OS₂: C, 55.79; H, 3.17; N, 3.83. Found: C, 55.88; H, 3.25; N, 4.01.

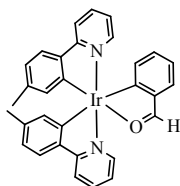
[Ir(ppy)₂FoPh]. In 10 mL dry toluene were suspended [Ir(ppy)₂(H₂O)₂]OTf, **a** (100 mg, 0.146 mmol) and compound **5** (21.8 mg, 0.146 mmol). To this suspension was



added K₃PO₄ (155 mg, 0.729 mmol), and the mixture was stirred at room temperature for 24 h. After 24 h compound **5** was consumed as observed by TLC. Solvent was evaporated under reduced pressure, and the residue was

dissolved in 10 mL methylene chloride which was washed twice with water followed by brine, and was passed through anhydrous Na₂SO₄. The volume of solvent was reduced, and sufficient pentane was added to precipitate a brick-red solid. The precipitate was collected and dried. Yield: 74.8 mg (79%). ¹H NMR (400 MHz, CDCl₃), δ: 9.96 (s, 1H), 8.17 (d, 1H, *J* = 5.3 Hz), 7.90 (dd, 1H, *J* = 6.2, 0.9 Hz), 7.86 (t, 2H, *J* = 6.4 Hz), 7.80 (d, 1H, *J* = 8.3 Hz), 7.71-7.68 (m, 1H), 7.64-7.59 (m, 2H), 7.54 (td, 1H, *J* = 7.2, 1.2 Hz), 7.09-6.93 (m, 6H), 6.86 (td, 1H, *J* = 7.1, 0.9 Hz), 6.81-6.76 (m, 2H), 6.57-6.55 (m, 1H), 6.46 (dd, 1H, *J* = 7.7, 1.1 Hz). IR (KBr): ν = 1582 (s) cm⁻¹ (C=O). HRMS: Calcd. For C₂₉H₂₂IrN₂O [MH]⁺: 607.1361 Found: 607.1363 Anal. Calcd. For C₂₉H₂₁IrN₂O: C, 57.50; H, 3.49; N, 4.62. Found: C, 57.77; H, 3.61; N, 4.78.

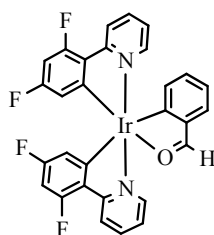
[Ir(tpy)₂FoPh]. In 5 mL dry toluene were suspended [Ir(tpy)₂(H₂O)₂]OTf, **b** (100 mg, 0.140 mmol) and compound **5** (21 mg, 0.140 mmol). To this suspension was



K₃PO₄ (148 mg, 0.700 mmol), and the mixture was stirred at room temperature for 24 h. After 24 h compound **5** was consumed as observed by TLC. Solvent was evaporated under reduced pressure, and the residue was dissolved in 10 mL

methylene chloride, which was washed twice with water followed by brine, and then passed through anhydrous Na₂SO₄. The volume of solvent was reduced to 0.5 mL and sufficient pentane was added to precipitate a deep red solid. The precipitate was collected and dried. Yield: 75.5 mg (85%). ¹H NMR (400 MHz, CDCl₃), δ: 9.93 (s, 1H), 8.11 (d, 1H, *J* = 5.9 Hz), 7.86 (dd, 2H, *J* = 6.4, 6.3 Hz), 7.80 (d, 1H, *J* = 8.0 Hz), 7.74 (d, 1H, *J* = 8.4 Hz), 7.61-7.57 (m, 2H), 7.54-7.48 (m, 2H), 7.08-7.01 (m, 2H), 6.97 (td, 1H, *J* = 6.7, 1.4 Hz), 6.91 (td, 1H, *J* = 5.9, 1.4 Hz), 6.76-6.73 (m, 2H), 6.67 (dd, 1H, *J* = 8.1, 0.9 Hz), 6.36 (s, 1H), 6.25 (s, 1H), 2.13 (s, 3H), 2.11 (s, 3H). IR (KBr): ν = 1582 (s) cm⁻¹ (C=O). HRMS: Calcd. For C₃₁H₂₆IrN₂O [MH]⁺: 635.1674 Found: 635.1643 Anal. Calcd. For C₃₁H₂₅IrN₂O: C, 58.75; H, 3.98; N, 4.42. Found: C, 58.82; H, 4.33; N, 4.78.

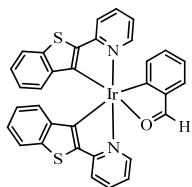
[Ir(F₂ppy)₂FoPh]. In 7 mL dry toluene were suspended [Ir(F₂ppy)₂(H₂O)₂]OTf, **d** (120 mg, 0.158 mmol) and compound **5** (23.7 mg, 0.158 mmol). To this suspension



was added K₃PO₄ (168 mg, 0.792 mmol), and the mixture was stirred at room temperature for 24 h. Evaporation of solvent under reduced pressure yielded a dark red-colored residue that was dissolved in methylene chloride. The methylene chloride layer was washed twice with water followed by brine, and

was passed through anhydrous Na₂SO₄. Deep red crystals were collected after crystallization from methylene chloride and pentane, and were dried. Yield: 94.4 mg (88%). ¹H NMR (400 MHz, CDCl₃), δ: 9.96 (s, 1H), 8.28 (dd, 1H, *J* = 7.8, 2.4 Hz), 8.19 (d, 1H, *J* = 8.2 Hz), 8.09 (dd, 1H, *J* = 5.8, 0.8 Hz), 7.89 (dd, 1H, *J* = 8.1, 0.7 Hz), 7.86 (dd, 1H, *J* = 5.8, 2.3 Hz), 7.69 (t, 1H, 7.5 Hz), 7.61 (t, 1H, *J* = 7.4 Hz), 7.14 (t, 1H, *J* = 7.4, 1.3 Hz), 7.07-6.99 (m, 3H), 6.84 (ddd, 1H, *J* = 5.8, 5.8, 1.4 Hz), 6.41 (ddd, 2H, *J* = 11.6, 1.1 Hz), 5.96 (dd, 1H, *J* = 7.9, 2.4 Hz), 5.80 (dd, 1H, *J* = 9.4, 2.4 Hz). IR (KBr): ν = 1585 (s) cm⁻¹ (C=O). HRMS: Calcd. For C₂₉H₁₈F₄IrN₂O [MH]⁺: 679.0985 Found: 679.0983 Anal. Calcd. For C₂₉H₁₇F₄IrN₂O: C, 51.40; H, 2.53; N, 4.13. Found: C, 51.71; H, 2.46; N, 4.54.

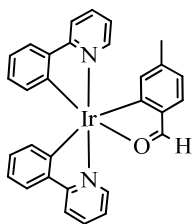
[Ir(btp)₂FoPh]. In 5 mL dry toluene were suspended [Ir(btp)₂(H₂O)₂]OTf, **e** (50 mg, 0.063 mmol) and compound **5** (9.4 mg, 0.063 mmol). To this suspension was added



K₃PO₄ (66.5 mg, 0.313 mmol), and the mixture was stirred at room temperature for 24 h. Evaporation of solvent under reduced pressure yielded a dark red-colored residue that was dissolved in methylene chloride. The methylene

chloride layer was washed twice with water followed by brine, and was passed through anhydrous Na₂SO₄. Deep red crystals were collected after crystallization from methylene chloride and pentane, and were dried. Yield: 29.2 mg (65%). ¹H NMR (400 MHz, CD₂Cl₂), δ: 9.93 (s, 1H), 8.29 (d, 1H, *J* = 5.9 Hz), 7.92 (dd, 1H, *J* = 3.4, 2.6 Hz), 7.78-7.61 (m, 6H), 7.16-7.01 (m, 5H), 6.89-6.78 (m, 5H), 6.74 (t, 1H, *J* = 8.2 Hz), 6.18 (d, 1H, *J* = 8.2 Hz). HRMS: Calcd. For C₃₃H₂₂IrN₂OS₂ [MH]⁺: 719.0803 Found: 719.0815 Anal. Calcd. For C₃₃H₂₁IrN₂OS₂: C, 55.21; H, 2.95; N, 3.90. Found: C, 55.44; H, 3.29; N, 4.13.

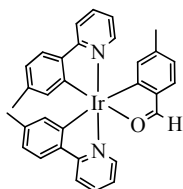
[Ir(ppy)₂FoTol]. In 5 mL dry toluene were suspended [Ir(ppy)₂(H₂O)₂]OTf, **a** (100 mg, 0.146 mmol) and compound **6** (23.9 mg, 0.146 mmol). To this suspension was added



K₃PO₄ (158 mg, 0.729 mmol), and the mixture was stirred at room temperature for 24 h. After 24 h compound **6** was consumed as observed by TLC. Solvent was evaporated under reduced pressure, and the residue was dissolved in 10 mL methylene chloride, which was washed twice with water

followed by brine, and then passed through anhydrous Na₂SO₄. The volume of solvent was reduced, and sufficient pentane was added to yield a brick red precipitate. The precipitate was collected and dried. Yield: 76.8 mg (85%). ¹H NMR (400 MHz, CDCl₃), δ: 9.86 (s, 1H), 8.16 (d, 1H, *J* = 5.7 Hz), 7.93 (d, 1H, *J* = 5.8 Hz), 7.82 (dd, 2H, *J* = 8.0, 7.8 Hz), 7.75 (d, 1H, *J* = 7.8 Hz), 7.68 (dd, 1H, *J* = 4.0, 2.1 Hz), 7.64-7.52 (m, 3H), 6.97-6.91 (m, 3H), 6.87-6.75 (m, 5H), 6.52 (dd, 1H, *J* = 3.5, 2.0 Hz), 6.45 (dd, 1H, *J* = 7.8, 0.8 Hz), 2.20 (s, 3H). IR (KBr): ν = 1584 (s) cm⁻¹ (C=O). HRMS: Calcd. For C₃₀H₂₄IrN₂O [MH]⁺: 621.1518 Found: 621.1511 Anal. Calcd. For C₃₀H₂₃IrN₂O: C, 58.14; H, 3.74; N, 4.52. Found: C, 58.34; H, 4.06; N, 4.67.

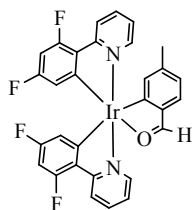
[Ir(tpy)₂FoTol]. In 5 mL dry toluene were suspended [Ir(tpy)₂(H₂O)₂]OTf, **b** (100 mg, 0.140 mmol) and compound **6** (22.9 mg, 0.140 mmol). To this suspension was added



K₃PO₄ (148 mg, 0.700 mmol), and the mixture was stirred at room temperature for 24 h. Evaporation of solvent under reduced pressure yielded a dark red-colored residue that was dissolved in methylene chloride. The methylene chloride layer was washed twice with water followed by brine, and was passed

through anhydrous Na₂SO₄. Deep red crystals were collected after crystallization from methylene chloride and pentane, and were dried. Yield: 72.0 mg (70%). ¹H NMR (400 MHz, CDCl₃), δ: 9.84 (s, 1H), 8.12 (d, 1H, *J* = 5.3 Hz), 7.90 (d, 1H, *J* = 5.8 Hz), 7.79 (d, 1H, *J* = 8.1 Hz), 7.74 (d, 1H, *J* = 8.0 Hz), 7.73 (d, 1H, *J* = 7.7 Hz), 7.60-7.56 (m, 2H), 7.51 (t, 1H, *J* = 7.1 Hz), 7.49 (d, 1H, *J* = 7.9 Hz), 6.90 (td, 1H, *J* = 6.0, 1.3 Hz), 6.84 (s, 1H), 6.80-6.73 (m, 3H), 6.66 (dd, 1H, *J* = 7.9, 1.3 Hz), 6.33 (s, 1H), 6.25 (s, 1H), 2.21 (s, 3H), 2.14 (s, 3H), 2.10 (s, 3H). IR (KBr): ν = 1583 (s) cm⁻¹ (C=O). HRMS: Calcd. For C₃₂H₂₈IrN₂O [MH]⁺: 649.1831 Found: 649.1853 Anal. Calcd. For C₃₂H₂₇IrN₂O: C, 59.33; H, 4.20; N, 4.32. Found: C, 59.13; H, 4.56; N, 4.38.

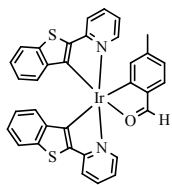
[Ir(F₂ppy)₂FoTol]. In 5 mL dry toluene were suspended [Ir(F₂ppy)₂(H₂O)₂]OTf, **d** (120 mg,



0.158 mmol) and compound **6** (25.9 mg, 0.158 mmol). To this suspension was added K₃PO₄ (168 mg, 0.792 mmol), and the mixture was stirred at room temperature for 24 h. After 24 h compound **6** was consumed as observed by TLC. Solvent was evaporated under reduced pressure, and the residue was dissolved in 10 mL methylene chloride, which was washed twice with water

followed by brine, and then passed through anhydrous Na₂SO₄. The volume of solvent was reduced, and sufficient pentane was added to precipitate a brick-red solid. The precipitate was collected and dried. Yield: 95.0 mg (87%). ¹H NMR (400 MHz, CDCl₃), δ: 9.84 (s, 1H), 8.27 (dd, 1H, *J* = 7.6, 2.6 Hz), 8.20 (d, 1H, *J* = 8.3 Hz), 8.10 (dd, 1H, *J* = 5.8, 0.8 Hz), 7.89 (dd, 1H, *J* = 5.8, 1.0 Hz), 7.78 (d, 1H, *J* = 7.7 Hz), 7.68 (t, 1H, *J* = 8.1 Hz), 7.61 (t, 1H, *J* = 8.5 Hz), 7.00 (ddd, 1H, *J* = 5.9, 5.9, 1.4 Hz), 6.87-6.83 (m, 2H), 6.80 (s, 1H), 6.44-6.37 (m, 2H), 5.93 (dd, 1H, *J* = 7.5, 2.4 Hz), 5.82 (dd, 1H, *J* = 9.5, 2.4 Hz), 2.25 (s, 3H). IR (KBr): ν = 1585 (s) cm⁻¹ (C=O). HRMS: Calcd. For C₃₀H₂₀F₄IrN₂O [MH]⁺: 693.1141 Found: 693.1157 Anal. Calcd. For C₃₀H₁₉F₄IrN₂O: C, 52.09; H, 2.77; N, 4.05. Found: : C, 52.39; H, 3.03; N, 4.28.

[Ir(btp)₂FoTol]. In 5 mL dry toluene were suspended [Ir(btp)₂(H₂O)₂]OTf, **e** (50 mg, 0.063

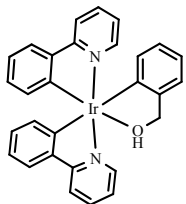


mmol) and compound **6** (10.3 mg, 0.063 mmol). To this suspension was added K₃PO₄ (66.5 mg, 0.313 mmol), and the mixture was stirred at room temperature for 24 h. Evaporation of solvent under reduced pressure yielded a dark red-colored residue that was dissolved in methylene chloride. The methylene chloride

layer was washed twice with water followed by brine, and was passed through anhydrous Na₂SO₄. Deep red crystals were collected after crystallization from methylene chloride and pentane, and were dried. Yield: 28.0 mg (61%). ¹H NMR (400 MHz, CDCl₃), δ: 9.82 (s, 1H), 8.28 (dd, 1H, *J* = 6.5, 1.6 Hz), 7.84-7.60 (m, 8H), 7.13 (t, 1H, *J* = 7.8 Hz), 7.09 (t, 1H, *J* = 7.9 Hz), 6.89-6.79 (m, 4H), 6.74 (t, 1H, *J* = 6.9 Hz), 6.64 (s, 1H), 6.26 (d, 1H, *J* = 7.9 Hz), 6.16 (d, 1H, *J* = 8.5 Hz), 2.15 (s, 3H). HRMS: Calcd. For C₃₄H₂₄IrN₂OS₂ [MH]⁺: 733.0959 Found: 733.0961 Anal. Calcd. For C₃₄H₂₃IrN₂OS₂: C, 55.79; H, 3.17; N, 3.83. Found: C, 55.88; H, 3.34; N, 4.14.

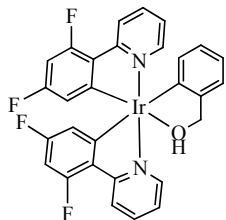
Synthesis of Ir(III) alcohol complexes.

[Ir(ppy)₂PhMeOH]. In 5 mL 2-propanol were suspended [Ir(ppy)₂(H₂O)₂]OTf, **a** (100 mg, 0.146 mmol) and compound **5** (21.8 mg, 0.146 mmol). To this suspension was added K₃PO₄ (155 mg, 0.729 mmol), and the mixture was stirred at room temperature for 24 h. After 24 h compound **5** was consumed as observed by TLC. Solvent was evaporated under reduced pressure, and the residue was



dissolved in 10 mL methylene chloride, which was washed twice with water followed by brine, and then passed through anhydrous Na₂SO₄. The volume of solvent was reduced to 0.5 mL and sufficient pentane was added to precipitate an orange solid. The precipitate was collected and dried. Yield: 73.5 mg (83%). ¹H NMR (400 MHz, CDCl₃), δ: 8.64 (d, 1H, *J* = 5.8 Hz), 8.41 (dd, 1H, *J* = 5.8, 1.2 Hz), 7.85 (d, 1H, *J* = 8.0 Hz), 7.80 (d, 1H, *J* = 8.2 Hz), 7.66 (td, 2H, *J* = 7.6, 1.7 Hz), 7.57 (dd, 1H, *J* = 7.8, 1.4 Hz), 7.51 (td, 1H, *J* = 7.1, 1.1 Hz), 6.98 (d, 1H, *J* = 7.1 Hz), 6.94-6.73 (m, 7H), 6.67 (td, 1H, *J* = 7.6, 1.1 Hz), 6.59 (dd, 1H, *J* = 6.7, 1.9 Hz), 6.52 (dd, 1H, *J* = 7.1, 1.4 Hz), 6.31 (dd, 1H, *J* = 7.8, 1.1 Hz), 5.04 (dd, 1H, *J* = 11.7 Hz), 4.86 (dd, 1H, *J* = 11.5 Hz), 3.60 (s, 1H, alcoholic broad peak). IR (KBr): $\tilde{\nu}$ = 3422 (s) cm⁻¹ (O-H br singlet). HRMS: Calcd. For C₂₉H₂₄IrN₂O [MH]⁺: 609.1518 Found: 609.1554 Anal. Calcd. For C₂₉H₂₃IrN₂O: C, 57.31; H, 3.81; N, 4.61. Found: C, 57.43; H, 4.04; N, 4.81.

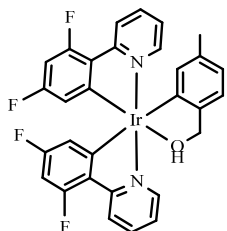
[Ir(F₂ppy)₂PhMeOH]. In 5 mL 2-propanol were suspended [Ir(F₂ppy)₂(H₂O)₂]OTf, **d** (120 mg, 0.158 mmol) and compound **5** (23.7 mg, 0.158 mmol). To this suspension was added K₃PO₄ (168 mg, 0.792 mmol), and the mixture was stirred at room temperature for 24 h. Evaporation of solvent under reduced pressure yielded a dark red-colored residue that was dissolved in methylene chloride.



The methylene chloride layer was washed twice with water followed by brine, and was passed through anhydrous Na₂SO₄. Deep red crystals were collected after crystallization from methylene chloride and pentane, and were dried. Yield: 96 mg (89%). ¹H NMR (400 MHz, CDCl₃), δ: 8.63 (d, 1H, *J* = 6.7 Hz), 8.41 (d, 1H, *J* = 5.8 Hz), 8.30 (d, 1H, *J* = 8.8 Hz), 8.21 (d, 1H, *J* = 6.8 Hz), 7.75 (td, 1H, *J* = 7.5, 1.5 Hz), 7.60 (td, 1H, *J* = 7.5, 1.5 Hz), 7.04 (d, 1H, *J* = 6.8 Hz), 7.01 (t, 1H, *J* = 5.9 Hz), 6.94 (t, 1H, *J* = 5.9 Hz), 6.87 (t, 1H, *J* = 7.3 Hz), 6.81 (t, 1H, *J* = 6.6 Hz), 6.53 (d, 1H, *J* = 7.12), 6.40-6.34 (m, 2H), 5.98 (dd, 1H, *J* = 7.3, 2.4 Hz), 5.67 (dd, 1H, *J* = 9.6, 2.3 Hz), 5.28 (d, 1H, *J* = 11.3 Hz), 5.04 (d, 1H, *J* = 11.6 Hz), 3.58 (s,

1H, alcoholic broad). IR (KBr): $\nu = 3419$ (s) cm^{-1} (O-H br singlet). HRMS: Calcd. For $\text{C}_{29}\text{H}_{20}\text{F}_4\text{IrN}_2\text{O}$ $[\text{MH}]^+$: 681.1141 Found: 681.1162 Anal. Calcd. For $\text{C}_{29}\text{H}_{19}\text{F}_4\text{IrN}_2\text{O}$: C, 51.25; H, 2.82; N, 4.12. Found: C, 51.30; H, 2.88; N, 4.23.

[Ir(F₂ppy)₂TolMeOH]. In 5 mL 2-propanol were suspended $[\text{Ir}(\text{F}_2\text{ppy})_2(\text{H}_2\text{O})_2]\text{OTf}$, **d** (120 mg,



0.158 mmol) and compound **6** (25.9 mg, 0.158 mmol). To this suspension was added K_3PO_4 (168 mg, 0.792 mmol), and the mixture was stirred at room temperature for 24 h. After 24 h compound **6** was consumed as observed by TLC. Solvent was evaporated under reduced pressure, and the residue was dissolved in 10 mL methylene chloride, which was washed twice with water

followed by brine, and was passed through anhydrous Na_2SO_4 . The volume of solvent was reduced, and sufficient pentane was added to get brick red precipitate. The precipitate was collected and dried. Yield: 88.0 mg (80%). ^1H NMR (400 MHz, CDCl_3), δ : 8.60 (d, 1H, $J = 5.8$ Hz), 8.41 (d, 1H, $J = 5.8$ Hz), 8.25 (d, 1H, $J = 8.9$ Hz), 8.20 (d, 1H, $J = 8.5$ Hz), 7.72 (t, 1H, $J = 8.3$ Hz), 7.58 (t, 1H, $J = 7.9$ Hz), 6.98 (t, 1H, $J = 7.2$ Hz), 6.91 (d, 2H, $J = 7.9$ Hz), 6.66 (d, 1H, $J = 7.68$ Hz), 6.34-6.30 (m, 3H), 5.94 (dd, 1H, $J = 7.5, 2.4$ Hz), 5.64 (dd, 1H, $J = 9.7, 2.3$ Hz), 5.16 (d, 1H, $J = 11.5$ Hz), 4.92 (d, 1H, $J = 11.3$ Hz), 4.04 (s, 1H, broad signal), 2.05 (s, 3H). IR (KBr): $\nu = 3429$ (s) cm^{-1} (O-H br singlet). HRMS: Calcd. For $\text{C}_{30}\text{H}_{22}\text{F}_4\text{IrN}_2\text{O}$ $[\text{MH}]^+$: 695.1298 Found: 695.1231 Anal. Calcd. For $\text{C}_{30}\text{H}_{21}\text{F}_4\text{IrN}_2\text{O}$: C, 51.94; H, 3.05; N, 4.04. Found: C, 52.11; H, 3.19; N, 4.12.

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Luminescence Measurements. Steady state emission spectra were recorded at room temperature on a Cary Eclipse fluorescence spectrophotometer. Time resolved phosphorescence lifetime data were collected on a nanosecond laser system. Excitation wavelengths were generated as described previously.¹ The emitted light passed through a Triax 320 spectrometer, was dispersed by a blazed grating and detected with a Hamamatsu R928 photomultiplier tube (PMT). The PMT outputs were collected and averaged with a 1 GHz oscilloscope (LeCroy 9382CM). Samples for these measurements were prepared in a glovebox containing a dinitrogen atmosphere and housed in sealable quartz EPR tubes. For lifetime measurements at 77 K, the EPR tube was immersed in liquid nitrogen in a quartz finger dewar.

Calculations. Spin-restricted density-functional theory calculations were performed within the program Gaussian 09.² Calculations used the PBE0 exchange and correlation functionals,³ and the TZVP basis set for nonmetal atoms.⁴ Calculations on iridium employ the SDD effective core potential and basis,⁵ scalar relativistic effects are included implicitly. Harmonic vibrational frequency calculations confirm all vibrational frequencies to be real. All geometry optimizations proceeded with continuum solvation in methylene chloride ($\epsilon = 8.93$). The solvation model was the integral equation formalism of Tomasi's polarizable continuum model (IEFPCM).⁶⁻⁹ Population analyses¹⁰ were performed with the AOMIX-CDA software of Gorelsky.^{11,12} Results

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³ Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158–6170.

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⁶ S. Miertus, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117–129.

⁷ J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999–3093.

⁸ E. Cancès, B. Mennucci, and J. Tomasi, *J. Chem. Phys.* **1997**, *107*, 3032–3041.

⁹ B. Mennucci, E. Cancès, J. Tomasi, *J. Phys. Chem. B* **1997**, *101*, 10506–10517.

¹⁰ R. S. Mulliken, *J. Chem. Phys.* **1955**, *23*, 1833–1840.

¹¹ S. I. Gorelsky, AOMix: Program for Molecular Orbital Analysis; York University: Toronto, 1997, <http://www.sg-chem.net>.

¹² S. I. Gorelsky, A. B. P. Lever, *J. Organomet. Chem.* **2001**, *635*, 187–196.

of time-dependent DFT calculations were parsed with the program SWizard;¹³ outputs appear as Tables S1 and S2 of this Supporting Information.

X-ray Crystallography. Single crystal X-ray data were collected on a Bruker AXS SMART APEXII CCD diffractometer using monochromatic Mo K α radiation with the omega scan technique. The unit cell was determined using the APEX2 Crystallographic Suite. All structures were solved by direct methods and refined by full matrix least squares against F^2 with all reflections using SHELXTL. Refinement of extinction coefficients was found to be insignificant. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and were refined with an isotropic displacement parameter 1.5 (CH₃) or 1.2 (all others) times that of the adjacent carbon atom.

¹³ S.I. Gorelsky, SWizard program, <http://www.sg-chem.net/>

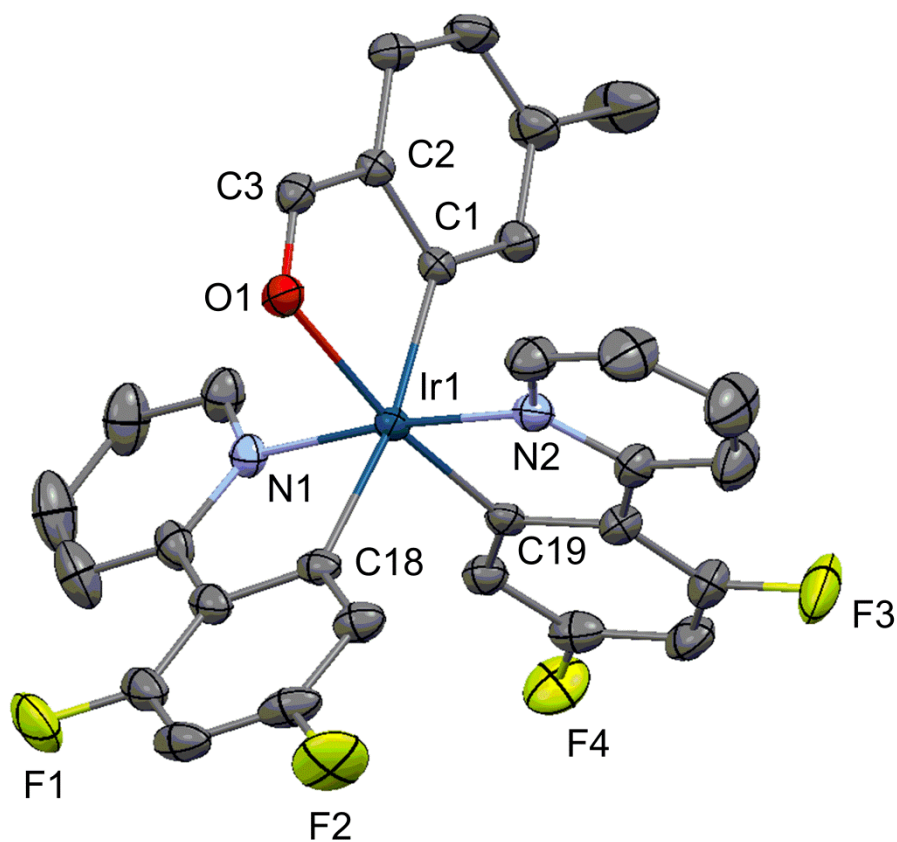
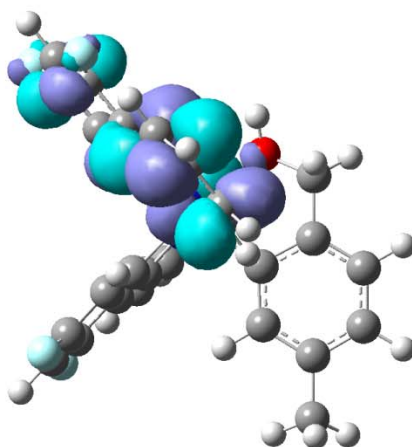
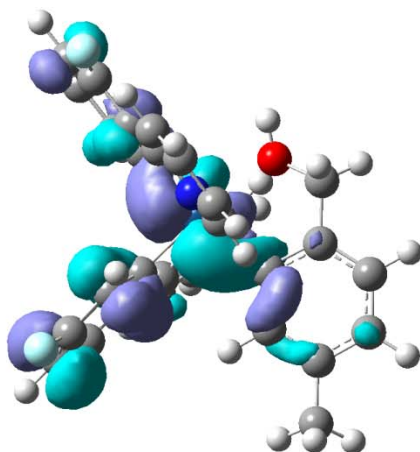


Figure S1. Crystal structure of the aldehyde complex $[(F_2ppy)_2Ir(FoTol)]$ showing ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Unlabeled atoms are carbon. Selected interatomic distances (Å): Ir1–C1: 2.0746(18); Ir1–C18: 2.0672(18); Ir1–C19: 1.9760(18); Ir1–N1: 2.0539(15); Ir1–N2: 2.0241(16); Ir1–O1: 2.2143(13); C3–O1: 1.247(2). Selected angles (°): C19–Ir1–N2: 80.83(7); C19–Ir1–N1: 96.60(7); N2–Ir1–N1: 173.65(6); C19–Ir1–C18: 94.57(7); N2–Ir1–C18: 94.73(7); N1–Ir1–C18: 79.63(7); C19–Ir1–C1: 94.93(7); N2–Ir1–C1: 90.68(7); N1–Ir1–C1: 95.34(7); C18–Ir1–C1: 169.71(7); C19–Ir1–O1: 171.68(6); N2–Ir1–O1: 95.25(6); N1–Ir1–O1: 88.03(6); C18–Ir1–O1: 93.06(6); C1–Ir1–O1: 77.72(6); O1–C3–C2: 121.44(17).



LUMO
3% Ir



HOMO
37% Ir

Figure S2. Frontier Kohn-Sham orbitals of the alcohol $[(F_2ppy)_2Ir(TolMeOH)]$ (isodensity level is 0.03 a.u.). Implicit methylene chloride solvation is included.

Table S1. Franck-Condon excited states of the aldehyde [(F₂ppy)₂Ir(FoTol)] calculated on the optimized ground-state geometry, with continuum (IEFPCM) methylene chloride solvation; *f* = oscillator strength.

FIRST 12 SINGLET STATES

#	(nm)	1000 cm ⁻¹	eV	(f)	(Assignment; H=HOMO, L=LUMO, L+1=LUMO+1, etc.)
1	432.8	23.1	2.86	0.0021	S H-0->L+0(+97%)
2	387.7	25.8	3.20	0.0540	S H-0->L+1(+94%)
3	384.9	26.0	3.22	0.0299	S H-1->L+0(+93%)
4	374.4	26.7	3.31	0.0213	S H-0->L+2(+91%)
5	343.9	29.1	3.61	0.0016	S H-1->L+1(+91%)
6	343.5	29.1	3.61	0.0125	S H-3->L+0(+63%) H-2->L+0(17%) H-5->L+0(7%)
7	337.9	29.6	3.67	0.0873	S H-2->L+0(+48%) H-3->L+0(+23%) H-5->L+0(+12%) H-4->L+0(+7%) H-1->L+2(6%)
8	327.1	30.6	3.79	0.0731	S H-1->L+2(+82%)
9	320.4	31.2	3.87	0.0255	S H-0->L+3(+96%)
10	313.0	31.9	3.96	0.0298	S H-2->L+1(+65%) H-0->L+4(16%) H-5->L+1(+7%)
11	309.8	32.3	4.00	0.0128	S H-0->L+4(+72%) H-2->L+1(+10%) H-3->L+1(6%) H-2->L+2(6%)
12	306.3	32.6	4.05	0.0115	S H-4->L+0(+29%) H-2->L+2(17%) H-5->L+0(+16%) H-2->L+0(16%) H-3->L+2(7%) H-5->L+2(5%)

FIRST SIX TRIPLET STATES

#	(nm)	1000 cm ⁻¹	eV	(f)	(Assignment; H=HOMO, L=LUMO, L+1=LUMO+1, etc.)
1	456.0	21.9	2.72	0.0000	S H-1->L+0(+48%) H-0->L+0(27%) H-7->L+0(10%) H-3->L+0(+7%)
2	442.1	22.6	2.80	0.0000	S H-0->L+0(+57%) H-1->L+0(+20%)
3	434.5	23.0	2.85	0.0000	S H-0->L+1(+41%) H-2->L+1(25%) H-0->L+0(9%)
4	430.5	23.2	2.88	0.0000	S H-0->L+2(+44%) H-4->L+2(14%) H-1->L+2(11%) H-2->L+1(+7%)
5	398.4	25.1	3.11	0.0000	S H-7->L+0(+33%) H-1->L+0(+16%) H-3->L+0(16%) H-5->L+0(9%)
6	395.1	25.3	3.14	0.0000	S H-0->L+2(+42%) H-1->L+2(+29%)

Table S2. Franck-Condon excited states of the alcohol [(F₂ppy)₂Ir(TolMeOH)] calculated on the optimized ground-state geometry, with continuum (IEFPCM) methylene chloride solvation; *f* = oscillator strength.

FIRST 12 SINGLET STATES

#	(nm	1000 cm ⁻¹	eV)	(<i>f</i>)	(Assignment; H=HOMO, L=LUMO, L+1=LUMO+1, etc.)
1	404.6	24.7	3.06	0.0348	S H-0->L+0(+96%)
2	379.4	26.4	3.27	0.0236	S H-0->L+1(+88%)
3	377.1	26.5	3.29	0.0092	S H-1->L+0(+91%)
4	346.9	28.8	3.57	0.0915	S H-1->L+1(+92%)
5	333.5	30.0	3.72	0.0291	S H-2->L+0(+85%) H-3->L+0(5%)
6	329.1	30.4	3.77	0.0097	S H-0->L+2(+97%)
7	316.2	31.6	3.92	0.0002	S H-0->L+3(+63%) H-2->L+1(+25%)
8	315.2	31.7	3.93	0.0191	S H-2->L+1(+47%) H-0->L+3(31%) H-5->L+1(+7%)
9	311.6	32.1	3.98	0.0430	S H-1->L+2(+72%) H-5->L+0(12%) H-4->L+0(9%)
10	306.6	32.6	4.04	0.0433	S H-4->L+0(+35%) H-5->L+0(+29%) H-1->L+2(+22%)
11	300.4	33.3	4.13	0.0267	S H-1->L+3(+85%) H-4->L+1(+6%)
12	295.3	33.9	4.20	0.0535	S H-3->L+0(+65%) H-6->L+0(+8%) H-4->L+0(7%)

FIRST SIX TRIPLET STATES

#	(nm	1000 cm ⁻¹	eV)	(<i>f</i>)	(Assignment; H=HOMO, L=LUMO, L+1=LUMO+1, etc.)
1	443.5	22.5	2.80	0.0000	S H-0->L+0(+53%) H-2->L+0(15%) H-3->L+0(+10%)
2	432.8	23.1	2.86	0.0000	S H-0->L+1(+42%) H-4->L+1(+10%) H-1->L+1(+9%) H-3->L+1(6%)
3	408.2	24.5	3.04	0.0000	S H-0->L+0(+34%) H-2->L+0(+17%) H-3->L+0(8%) H-0->L+1(7%) H-1->L+0(+7%) H-5->L+0(+5%)
4	405.8	24.6	3.06	0.0000	S H-1->L+1(+38%) H-0->L+1(35%)
5	386.2	25.9	3.21	0.0000	S H-1->L+0(+82%) H-2->L+0(6%)
6	357.6	28.0	3.47	0.0000	S H-1->L+1(+25%) H-4->L+1(16%) H-0->L+1(+10%) H-5->L+1(+5%)

Table S3. Optimized Cartesian coordinates (Å) of the aldehyde complex [(F₂ppy)₂Ir(FoTol)].

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	77	0	0.840804	9.439771	3.985788
2	7	0	1.842462	7.862922	3.162226
3	6	0	3.167034	7.698540	3.258934
4	6	0	3.823521	6.628892	2.688533
5	6	0	3.074446	5.690826	1.990924
6	6	0	1.707612	5.857268	1.884304
7	6	0	1.089875	6.961670	2.475918
8	6	0	-0.321800	7.304321	2.444410
9	6	0	-1.333208	6.565194	1.832401
10	6	0	-2.655972	6.947748	1.836145
11	6	0	-2.955492	8.130246	2.491591
12	6	0	-2.009920	8.910422	3.118492
13	6	0	-0.670348	8.509414	3.115534
14	1	0	3.696897	8.463275	3.811827
15	1	0	4.897115	6.540888	2.792143
16	1	0	3.552885	4.834630	1.529934
17	1	0	1.112206	5.140000	1.341276
18	1	0	-3.416191	6.351349	1.350132
19	1	0	-2.327547	9.822033	3.608624
20	9	0	-1.038678	5.414665	1.195420
21	9	0	-4.241601	8.527739	2.507620
22	7	0	-0.226826	11.096685	4.608644
23	6	0	-0.888138	11.151086	5.771836
24	6	0	-1.587058	12.266201	6.184239
25	6	0	-1.599434	13.376828	5.354678
26	6	0	-0.920084	13.330570	4.152794
27	6	0	-0.230534	12.175284	3.776847
28	6	0	0.509891	11.978861	2.533146
29	6	0	0.663125	12.927753	1.521882
30	6	0	1.365084	12.682332	0.361121
31	6	0	1.927440	11.426340	0.227323
32	6	0	1.813964	10.446886	1.191892
33	6	0	1.104928	10.703201	2.365168
34	1	0	-0.844004	10.255824	6.377020
35	1	0	-2.106973	12.252868	7.133278
36	1	0	-2.134959	14.275123	5.639227
37	1	0	-0.923081	14.186168	3.496606
38	1	0	1.464382	13.440597	-0.404032
39	1	0	2.282628	9.485302	1.012084
40	9	0	0.119627	14.157539	1.639049
41	9	0	2.613670	11.162561	-0.901437
42	6	0	0.736707	8.423875	5.811376
43	6	0	-0.154108	7.450785	6.272068
44	6	0	-0.066779	6.889706	7.546176

45	6	0	0.951448	7.307170	8.420156
46	6	0	1.856707	8.260536	8.014988
47	6	0	1.751235	8.807230	6.726389
48	6	0	2.666942	9.798900	6.257231
49	1	0	-0.955599	7.112372	5.620150
50	1	0	1.017416	6.873711	9.412722
51	1	0	2.647691	8.589565	8.683240
52	1	0	3.474457	10.156400	6.910258
53	6	0	-1.039824	5.841259	7.990265
54	1	0	-1.830744	5.693202	7.254000
55	1	0	-1.500821	6.111369	8.944247
56	1	0	-0.533502	4.882919	8.141386
57	8	0	2.584727	10.276381	5.112414

Table S4. Optimized Cartesian coordinates (Å) of the alcohol complex [(F₂ppy)₂Ir(TolMeOH)].

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	77	0	0.866910	9.434409	3.977410
2	7	0	1.816893	7.809051	3.202017
3	6	0	3.132802	7.596459	3.320798
4	6	0	3.754412	6.490977	2.780666
5	6	0	2.979241	5.566180	2.093105
6	6	0	1.620156	5.778680	1.970700
7	6	0	1.038055	6.917764	2.532406
8	6	0	-0.360916	7.306866	2.488993
9	6	0	-1.395474	6.589738	1.889888
10	6	0	-2.705377	7.013917	1.885402
11	6	0	-2.966831	8.217411	2.519172
12	6	0	-1.997669	8.979595	3.131058
13	6	0	-0.670977	8.535276	3.138237
14	1	0	3.678872	8.349991	3.873655
15	1	0	4.822380	6.363463	2.901186
16	1	0	3.430859	4.683546	1.655499
17	1	0	1.002872	5.070862	1.439803
18	1	0	-3.484556	6.432910	1.410966
19	1	0	-2.286826	9.909535	3.603949
20	9	0	-1.137124	5.418932	1.273723
21	9	0	-4.240386	8.655259	2.527683
22	7	0	-0.155978	11.122439	4.592061
23	6	0	-0.829838	11.189945	5.747822
24	6	0	-1.515330	12.317629	6.148631
25	6	0	-1.503843	13.424482	5.313496
26	6	0	-0.816624	13.362290	4.116375
27	6	0	-0.141166	12.195008	3.752177
28	6	0	0.594374	11.974422	2.507728
29	6	0	0.771976	12.916927	1.494128
30	6	0	1.451132	12.644849	0.325717
31	6	0	1.966141	11.368996	0.186483
32	6	0	1.831429	10.396231	1.155184
33	6	0	1.143005	10.677358	2.335796
34	1	0	-0.799934	10.292919	6.352506
35	1	0	-2.044737	12.316951	7.092540
36	1	0	-2.029831	14.331365	5.588497
37	1	0	-0.806177	14.213126	3.453987
38	1	0	1.568885	13.398303	-0.441629
39	1	0	2.264354	9.418184	0.973100
40	9	0	0.278061	14.167034	1.617532
41	9	0	2.628209	11.080320	-0.950407
42	6	0	0.780998	8.458942	5.839342
43	6	0	0.006573	7.352103	6.203186
44	6	0	0.086997	6.738261	7.454119
45	6	0	1.001903	7.237549	8.379853

46	6	0	1.799326	8.325265	8.054462
47	6	0	1.685327	8.934074	6.808170
48	6	0	2.511925	10.143018	6.492179
49	1	0	-0.696034	6.940884	5.480938
50	1	0	1.099533	6.766850	9.353666
51	1	0	2.521696	8.696226	8.777617
52	1	0	2.006166	11.061666	6.812482
53	1	0	3.492922	10.106052	6.973626
54	6	0	-0.798128	5.575627	7.801168
55	1	0	-1.694964	5.908152	8.334566
56	1	0	-0.284469	4.860702	8.448358
57	1	0	-1.129925	5.048583	6.904212
58	8	0	2.695828	10.200609	5.059844
59	1	0	2.980429	11.085020	4.805942
