Divergent approach for tris-heteroleptic cyclometalated iridium complexes using triisopropylsilylethynyl substituted synthons

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S1. Synthesis

General Details

Nuclear magnetic resonance (NMR) spectra were recorded in deuterated solvent solutions on a VNMRS-600 and VNMRS-700 spectrometer (Varian Technologies, Palo Alto, CA, USA), and were referenced against solvent resonances \((^1\text{H}, ^{13}\text{C}[^1\text{H}])\). Electrospray mass spectra (ESMS) data were recorded on a TQD mass spectrometer (Waters Ltd, UK) in acetonitrile, MALDI–TOF MS data were recorded on an Autoflex II TOF/TOF (Bruker Daltonics, Inc, Billerica, MA, USA). ASAP data were recorded on a Xevo Q-TOF (Waters) high resolution, an accurate mass tandem mass spectrometer equipped with Atmospheric Pressure Gas Chromatography (APGC) and Atmospheric Solids Analysis Probe (ASAP). Microanalyses were performed by Elemental Analysis Service, London Metropolitan University or Durham University Elemental Analysis Service, UK. 2-Phenyl-4-((triisopropylsilyl)ethynyl)pyridine (Hppy≡-TIPS)\(^1\) and [Ir(ppy≡-TIPS)\(_2\)(acac)\(^1\)] \(^1\) (1) were synthesized according to literature methods. All other chemicals were sourced from standard suppliers.

\[[\text{Ir}(\text{ppy}≡-\text{TIPS})(\text{ppy})(\text{acac})] \ (2)\]

Three compounds, Hppy≡-TIPS (678 mg, 0.79 mmol), 2-phenylpyridine (0.28 mL, 305 mg, 2.0 mmol), and IrCl\(_3\)·3H\(_2\)O (715 mg, 2.0 mmol), were suspended in a 3:1 (v/v) mixture of 2-ethoxyethanol and water (8 mL), and heated at 110 °C for 16 h. During this time, the solution turned from a pale yellow to a dark orange colour. The solution was allowed to cool to room temperature, and water (30 mL) was added, precipitating a bright orange solid, which was filtered, washed with water (2 × 10 mL), and dissolved in CH\(_2\)Cl\(_2\) (4 × 20 mL). The CH\(_2\)Cl\(_2\) solution was washed with water (10 mL), separated, dried over MgSO\(_4\), filtered and reduced \textit{in vacuo} to an orange, oily solid. The crude material was triturated with hexanes (5 mL), yielding a mixture of \(\mu\)-dichloro-bridged diiridium dimers that appeared as an orange solid. This crude
mixture was dissolved in a 1:1 (v/v) mixture of acetone:EtOH (30 mL) with acetylacetone (0.5 mL, excess) and K₂CO₃ (250 mg) was suspended in the mixture. The mixture was heated at 60 °C for 4 h. Solvents were removed in vacuo, and the residual orange solid was purified by column chromatography (SiO₂, 2:1 (v/v) CH₂Cl₂:hexanes to CH₂Cl₂), yielding the compound 1 as the fore-running fraction (152 mg, 40%), which appeared as a bright orange solid. The second fraction yielded the title product, also appearing as a bright orange solid. **Yield:** 136 mg (22%). **¹H NMR** (700 MHz; CDCl₃): δH/ppm 8.49 (d, 3J_HA,HB = 5.4 Hz, 1H, HA), 8.46 (d, 3J_HA',HB' = 5.9 Hz, 1H, HA'), 7.85 (2 H, m), 7.72 (t, 3J_HC',HB',HD' = 7.6 Hz, 1H, HC'), 7.55 (m, 2H, HE+ε'), 7.11-7.16 (m, 2H, HB+D'), 6.81 (m, 2H, HF+F'), 6.70 (m, 2H, HG+G'), 6.30 (d, 3J_HH,HG = 7.6 Hz, 1H, HH), 6.26 (d, 3J_HH',HG' = 7.6 Hz, 1H, HH'), 5.20 (s, 1H, HI), 1.78 (s, 6H, HJ), 1.19 (m, 21H, HK+L). For information on atom labels, see Figure S1. **¹³C{¹H} NMR** (176 MHz; CDCl₃): δC/ppm 184.8, 168.7, 168.6, 148.2, 148.1, 147.8, 147.6, 144.8, 144.2, 137.0, 133.2, 132.1, 129.5, 129.3, 124.1, 124.0, 121.6, 121.0, 120.9, 120.8, 118.5, 104.1, 100.5, 98.8, 29.6, 28.9, 18.8, 17.9, 12.4, 11.4. **Acc. MS** (ASAP⁺): m/z 778.2726 (M⁺), calcd. for C₃₈H₄₃N₂O₂Si¹⁹¹Ir 778.2700 ([Δm/z] = 3.3 ppm). **Elemental Anal.** Calcd. for C₃₈H₄₄IrN₂O₂Si: C, 58.43; 5.68; N, 3.59%. Found: C, 58.79; 5.67; N, 3.53%. 

**General method for Sonogashira coupling with 1**

Tetrahydrofuran (50 mL) was added to a suspension containing Et₃N (5 mL), 1 (0.10 mmol), ArI (0.25 mmol), Pd(PPh₃)₄ (23 mg, 0.04 mmol), and CuI (4 mg, 0.04 mmol). The solution was degassed via three freeze–pump–thaw cycles, before tetrabutylammonium fluoride (1.0 M in THF, 0.50 mL, 0.50 mmol) was added. The resultant solution was then stirred at room temperature for 12 h before the solvent was removed. The residue was purified by silica chromatography, eluted by dichloromethane (DCM) or a solvent gradient of neat DCM to 1:10 acetone:DCM, and the emissive band was collected. The solvent was removed to yield an orange-red solid.
Ir(PPy≡C₆H₄-CN)₂(acac) (3)

**Yield:** 41 mg (49%).

**¹H NMR (700 MHz, CDCl₃):** δ_H/ppm 8.51 (d, 3_J HA,HB = 5.9 Hz, 2H, H_A), 7.94 (s, 2H, H_C), 7.71-7.68 (m, 8H, H_H+I), 7.57 (dd, 3_J HG,HF = 7.9 Hz, 4_J HG,HE = 1.4 Hz), 2H, H_G), 7.20 (dd, 3_J HB,HA = 5.9 Hz, 4_J HB,HC = 1.8 Hz, 2H, H_B), 6.83 (td, 3_J HF,HE,HG = 7.5 Hz, 4_J HF,HD = 1.2 Hz, 2H, H_F), 6.72 (td, 3_J HE,HG,HF = 7.4 Hz, 4_J HE,HG = 1.3 Hz, 2H, H_E), 6.28 (dd (4_J HD,HE = 7.7 Hz, 4_J HD,HF = 1.2 Hz, 2H, H_D), 5.23 (s, 1H, H_J), 1.80 (s, 6H, H_K). For information on atom labels, see Figure S3.

**¹³C{¹H} NMR (176 MHz; CDCl₃):** δ_C/ppm 184.9, 168.6, 147.8, 147.6, 143.6, 133.0, 132.4, 132.2, 131.0, 129.5, 126.7, 124.1, 123.3, 121.0, 120.4, 118.1, 112.7, 100.5, 93.3, 90.3, 28.7. **Acc. MS (ASAP⁺):** m/z 849.1947 [M]+, calcd. for C₄₅H₃₀N₄O₂Ir 849.1975 (|Δm/z| = 3.3 ppm).

Ir(PPy≡C₆H₄-SMe)₂(acac) (4)

**Yield:** 60 mg (65%).

**¹H NMR (600 MHz, TCE-d₂):** δ_H/ppm 8.45 (d, 3_J HA,HB = 5.9 Hz, 2H, H_A), 7.95 (s, 2H, H_C), 7.64 (dd, 3_J HG,HF = 7.4 Hz, 4_J HG,HE = 1.5 Hz, 2H, H_G), 7.57 (d, 4_J HLHH = 8.3 Hz, 4H, H_I), 7.29-7.28 (m, 6H, H_B+H), 6.95 (td, 3_J HF,HE,HG = 7.4 Hz, 4_J HF,HD = 1.5 Hz, 2H, H_F), 6.78 (td, 3_J HE,HG,HF = 7.4 Hz, 4_J HE,HG = 1.5 Hz, 2H, H_E), 6.32 (dd, 3_J HD,HE,HG = 7.7 Hz, 4_J HD,HF = 1.2 Hz, 2H, H_D), 5.30 (s, 1H, H_J), 2.55 (s, 6H, H_L), 1.86 (s, 6H, H_K). For information on atom labels, see Figure S5.

**¹³C{¹H} NMR (150 MHz, CDCl₃):** δ_C/ppm 184.8, 168.3, 147.6, 147.9, 144.0, 141.1, 133.0, 132.2, 132.1, 129.3, 125.7, 123.9, 123.2, 120.9, 120.2, 117.9, 100.4, 95.6, 86.8.
28.7, 15.1.\(^1\) **MS-MALDI**: \(m/z\) 829.1 [M\(^+\)]. **Elemental Anal.** Calcd. for C\(_{45}\)H\(_{35}\)IrN\(_2\)O\(_2\)S\(_2\): C, 60.59; H, 3.95; N, 3.14%. Found: C, 60.53; H, 3.96; N, 3.11%.

**General method for Sonogashira coupling with 2**

Tetrahydrofuran (50 mL) was added to a suspension containing Et\(_3\)N (5 mL), 3 (0.10 mmol), ArI (0.15 mmol), Pd(PPh\(_3\))\(_4\) (11 mg, 0.01 mmol), and CuI (1.9 mg, 0.01 mmol). The resultant solution was degassed by three freeze–pump–thaw cycles, before tetrabutylammonium fluoride (1.0 M in THF, 0.25 mL, 0.25 mmol) was added. The solution was then stirred at room temperature for 12 h before the solvent was removed. The residue was purified by silica chromatography eluted by either 1:2 hexane:DCM or neat DCM, collecting the emissive band. The solvent was removed to yield an orange solid.

**Ir(ppy)(ppy=\(-C\(_6\)H\(_5\))(acac)** (5)

\[
\text{Yield: 38 mg (55%).} \quad \text{\(^1\)H NMR (700 MHz; CDCl}_3\):} \quad \delta_H/\text{ppm} \quad 8.50-8.47 (m, 2H, H\(_A\)+A’), \quad 7.93 \quad (d, \quad 4J_{HD,HB} = 1.9 \quad \text{Hz, 1H, H}\_D), \quad 7.84 \quad (dd, \quad 3J_{HD',HC'} = 8.3 \quad \text{Hz, 4J_{HD',HB'} = 1.1 \quad \text{Hz, 1H, H'}D}, \quad 7.72 \quad (td, \quad 3J_{HC',HB';HD'} = 8.2 \quad \text{Hz, 4J_{HC',HA'} = 1.6 \quad \text{Hz, 1H, H'C}}, \quad 7.62-7.60 \quad (m, 2H, H\_K), \quad 7.56 \quad (dd, \quad 3J_{HE,HE'} = 7.7 \quad \text{Hz, 4J_{HE,HE} = 1.3 \quad \text{Hz, 1H, H'E}}, \quad 7.43-7.40 \quad (m, 3H, H\_L+M), \quad 7.18 \quad (dd, \quad 3J_{HB,HA} = 5.9 \quad \text{Hz, 4J_{HB,HD} = 1.8 \quad \text{Hz, 1H, H'B}}, \quad 7.13 \quad (td, \quad 3J_{HB',HA',HC'} = 7.3 \quad \text{Hz, 4J_{HB',HD'} = 1.4 \quad \text{Hz, 1H, H'B'}}, \quad 6.83-6.78 \quad (m, 2H, H\_E=F), \quad 6.73-6.68 \quad (m, 2H, H\_G+G'), \quad 6.30 \quad (dd, \quad 3J_{HH,HH} = 7.7 \quad \text{Hz, 4J_{HH,HF} = 1.2 \quad \text{Hz, 1H, H'}H}), \quad 6.27 \quad (dd, \quad 3J_{HH',HG'} = 7.7, \quad 4J_{HH',HF'} = 1.1 \quad \text{Hz, 1H, H'F'}), \quad 5.21 \quad (s, \quad 1H, H\_i), \quad 1.79 \quad (s, 6H, H\_j). \quad \text{For information on atom labels, see Figure S8.} \quad \text{\(^{13}\)C\{(\text{\(^1\)H})\} NMR (176 MHz; CDCl}_3\):} \quad \delta_C/\text{ppm} \quad 184.6, \quad 168.5, \quad 168.4, \quad 148.0, \quad 147.9, \quad 147.4, \quad 147.4, \quad 144.6, \quad 144.0, \quad 136.8, \quad 133.0, \quad 132.0, \quad 131.9, \quad 129.3, \quad 129.1, \quad 128.5, \quad 123.9, \quad 123.7, \quad 123.7,
\]

\(^1\) Limited solubility of the compound gave poor \(^{13}\)C NMR data.
Yield: 42 mg (59%). ¹H NMR (700 MHz; TCE-d₂): δ_H/ppm 8.50 (d, ^3J_HA,HB = 5.9 Hz, 1H, H_A), 8.46 (d, ^3J_HA',HB' = 5.9 Hz, 1H, H_A'), 7.95 (d, ^3J_HD,HB = 1.8 Hz, 1H, H_D), 7.86 (dd, ^3J_HD,HC' = 8.2 Hz, ^4J_HD,HB' = 1.2 Hz, 1H, H_D'), 7.79 (td, ^3J_HC',HB',HD' = 7.9 Hz, ^4J_HC',HA' = 1.6 Hz, 1H, H_C'), 7.75-7.72 (m, 4H, H_K+L), 7.63 (dd, ^3J_HE,HE' = 7.7 Hz, ^4J_HE,HE' = 1.3 Hz, 1H, H_E), 7.60 (dd, ^3J_HE',HF' = 7.7 Hz, ^4J_HE',HF' = 1.3 Hz, 1H, H_E'), 7.28 (dd, ^3J_HB,HA = 5.9 Hz, ^4J_HB,HD = 1.8 Hz, 1H, H_B), 7.32 (ddd, ^3J_HB',HC = 7.2 Hz, ^3J_HB',HA' = 5.7 Hz, ^4J_HB',HD' = 1.4 Hz, 1H, H_B'), 6.95-6.92 (m, 2H, H_F+F'), 6.78-6.74 (m, 2H, H_G+G'), 6.27 (dd, ^3J_HH',HG' = 7.7 Hz, ^4J_HH',HG' = 1.2 Hz, 2H, H_H+H'), 5.28 (s, 1H, H_I), 1.84 (s, 6H, H_J). For information on atom labels, see Figure S10. ¹³C{¹H} NMR (176 MHz; TCE-d₂): δ_C/ppm 185.0, 184.9, 168.4, 167.8, 148.1, 148.0, 147.6, 146.7, 145.3, 144.5, 137.4, 133.7, 133.5, 132.6, 132.3, 131.0, 129.2, 128.8, 126.7, 124.3, 124.0, 123.9, 122.0, 120.9, 120.5, 118.6, 112.5, 101.1, 93.7, 90.4, 29.0. Acc. MS (ASAP⁺): m/z 723.1624 [M]^+ calcd. for C₃₆H₂₆N₃O₂ Ir 723.1631 (|Δm/z| = 1.5 ppm).

Yield: 30 mg (41%). ¹H NMR (700 MHz; CDCl₃): δ_H/ppm 8.49 (d, ^3J_HA,HB = 5.73 Hz, 1H, H_A), 8.47 (d, ^3J_HA',HB' = 5.9 Hz, 1H, H_A'), 7.90 (d, ^4J_HD,HB = 1.6 Hz, 1H, H_D), 7.84 (d, ^3J_HD,HC' = 8.0 Hz, 1H, H_D'), 7.72 (td, ^3J_HC',HB' = 7.8 Hz, ^4J_HC',HA' = 1.6 Hz, 1H, H_C'). 7.56-
7.50 (m, 6H), 7.16 (dd, $^3J_{HH,HA} = 5.9$ Hz, $^4J_{HH,HD} = 1.8$ Hz, 1H, H$_B$), 7.13 (td, $^3J_{HH',HA',HC'} = 7.2$ Hz, $^4J_{HH',HD'} = 1.4$ Hz, 1H, H$_B'$), 6.82-6.79 (m, 2H, H$_{F+F'}$), 6.70-6.68 (m, 2H, H$_{G+G'}$), 6.29 (d, $^3J_{HH,HC} = 7.6$ Hz, 1H, H$_I$), 6.26 (d, $^3J_{HH',HC'} = 7.6$ Hz, 1H, H$_{I'}$), 5.20 (s, 1H, H$_I$), 2.52 (s, 3H, H$_M$), 1.78 (pseudo doublet, 6H, H$_J$). For information on atom labels, see Figure S12.

$^{13}$C{$^1$H} NMR (176 MHz; CDCl$_3$): $\delta/$ppm 184.9, 168.4, 167.8, 148.0, 147.6, 146.7, 145.3, 144.5, 137.4, 133.7, 133.5, 132.6, 132.3, 131.0, 129.2, 128.8, 126.7, 124.3, 124.0, 123.9, 122.0, 120.9, 120.5, 118.6, 112.5, 101.1, 93.7, 90.4, 28.7. Acc-MS (ASAP$^+$): $m/z$ 745.1661 [M]$^+$, calcd. for C$_{36}$H$_{29}$N$_2$O$_2$S$^{191}$Ir 745.1634 ($|\Delta m/z| = 3.6$ ppm). $^+$: $m/z$ 645.1115 [M–acac]$^+$, calcd. for C$_{31}$H$_{23}$N$_2$S$^{191}$Ir 645.1110 ($|\Delta m/z| = 0.8$ ppm).
S2. NMR spectra of reported compounds

Figure S1. $^1$H NMR spectrum of 2, recorded in CDCl$_3$.

Figure S2. $^{13}$C($^1$H) NMR spectrum of 2, recorded in CDCl$_3$.  

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Figure S3. $^1$H NMR spectrum of 3, recorded in CDCl$_3$.

Figure S4. $^{13}$C($^1$H) NMR spectrum of 3, recorded in CDCl$_3$. 
Figure S5. $^1$H NMR spectrum of 4, recorded in TCE-d$_2$.

Figure S6. $^1$H NMR spectrum of 4, recorded in CDCl$_3$. 
Figure S7. $^{13}$C{^1}H NMR spectrum of 4, recorded in CDCl$_3$.

Figure S8. $^1$H NMR spectrum of 5, recorded in CDCl$_3$. 
Figure S9. $^{13}$C\{$^1$H\} NMR spectrum of 5, recorded in CDCl$_3$.

Figure S10. $^1$H NMR spectrum of 6, recorded in TCE-d$_2$. 
Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 6, recorded in TCE-d$_2$.

Figure S12. $^1\text{H}$ NMR spectrum of 7, recorded in CDCl$_3$.
Figure S13. $^{13}$C{$^1$H} NMR spectrum of 7, recorded in CDCl$_3$. 
S3. Crystallographic data

The X-ray single crystal data have been collected using $\lambda_{\text{MoK}\alpha}$ radiation ($\lambda = 0.71073 \ \text{Å}$) on a Bruker D8 Venture (Photon100 CMOS detector, IµS-microsource, focusing mirrors) diffractometer equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostats at the temperature 120.0(2) K. The structure was solved by direct method and refined by full-matrix least squares on $F^2$ for all data using Olex2 and SHELXTL software. All non-hydrogen atoms were refined in anisotropic approximation; hydrogen atoms were placed in the calculated positions and refined in riding mode. The structure of 6 contains several severely disordered solvent molecules, most probably three DMF molecules, which could not be modelled and refined reliably. The contribution of disordered solvent molecules into diffraction intensities was taken into account by application of the MASK procedure of the Olex2 program package.

Crystal data and parameters of refinement are listed in Table S1. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-2169136.
Table S1. Crystal and Refinement Data for 6

| Compound | 6 |
|----------|---|
| Empirical formula | C_{36}H_{26}IrN_{3}O_{2} |
| Formula weight | 724.80 |
| Temperature/K | 120.0 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 9.7255(5) |
| b/Å | 11.4855(6) |
| c/Å | 14.8982(8) |
| α° | 103.6151(19) |
| β° | 92.9966(19) |
| γ° | 94.0713(19) |
| Volume/Å³ | 1609.23(15) |
| Z | 2 |
| ρcalc g/cm³ | 1.496 |
| μ/mm⁻¹ | 4.183 |
| F(000) | 712.0 |
| Crystal size/mm³ | 0.27 × 0.13 × 0.03 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.21 to 57.998 |
| Index ranges | -13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20 |
| Reflections collected | 33240 |
| Independent reflections | 8560 [R_int = 0.0447, Rsigma = 0.0475] |
| Data/restraints/parameters | 8560/0/381 |
| Goodness-of-fit on F² | 1.028 |
| Final R indexes [I ≥ 2σ(I)] | R₁ = 0.0338, wR₂ = 0.0731 |
| Final R indexes [all data] | R₁ = 0.0455, wR₂ = 0.0768 |
| Largest diff. peak/hole / e Å⁻³ | 2.35/–0.78 |
Table S2. Selected bond lengths for 6.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| Ir1  | O1   | 2.164(2) | C13  | C14  | 1.396(6) |
| Ir1  | O2   | 2.142(2) | C14  | C15  | 1.393(5) |
| Ir1  | N1   | 2.034(3) | C14  | C23  | 1.427(5) |
| Ir1  | N2   | 2.024(3) | C15  | C16  | 1.389(5) |
| Ir1  | C7   | 1.993(3) | C16  | C17  | 1.456(5) |
| Ir1  | C18  | 1.981(4) | C17  | C18  | 1.419(5) |
| C18  | C33  | 1.267(4) | C17  | C22  | 1.393(5) |
| C18  | C35  | 1.266(4) | C18  | C19  | 1.397(5) |
| N1   | C1   | 1.351(4) | C19  | C20  | 1.389(5) |
| N1   | C5   | 1.362(4) | C20  | C21  | 1.397(6) |
| N2   | C12  | 1.346(4) | C21  | C22  | 1.387(5) |
| N2   | C16  | 1.372(5) | C23  | C24  | 1.188(5) |
| N3   | C31  | 1.119(6) | C24  | C25  | 1.442(5) |
| C1   | C2   | 1.363(5) | C25  | C26  | 1.387(5) |
| C2   | C3   | 1.392(5) | C25  | C30  | 1.391(6) |
| C3   | C4   | 1.371(5) | C26  | C27  | 1.367(5) |
| C4   | C5   | 1.390(5) | C27  | C28  | 1.390(6) |
| C5   | C6   | 1.456(5) | C28  | C29  | 1.394(6) |
| C6   | C7   | 1.416(5) | C28  | C31  | 1.444(6) |
| C6   | C11  | 1.396(5) | C29  | C30  | 1.375(6) |
| C7   | C8   | 1.403(5) | C32  | C33  | 1.509(5) |
| C8   | C9   | 1.382(5) | C33  | C34  | 1.402(5) |
| C9   | C10  | 1.378(6) | C34  | C35  | 1.389(5) |
| C10  | C11  | 1.390(5) | C35  | C36  | 1.496(5) |
| C12  | C13  | 1.368(5) |      |      |          |
Table S3. Selected bond angles for 6.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| O2   | Ir1  | O1   | 88.42(9) | N2   | C12  | C13  | 122.7(4) |
| N1   | Ir1  | O1   | 89.86(10) | C12  | C13  | C14  | 119.3(3) |
| N1   | Ir1  | O2   | 95.55(10) | C13  | C14  | C23  | 119.2(4) |
| N2   | Ir1  | O1   | 94.38(11) | C15  | C14  | C13  | 118.3(3) |
| N2   | Ir1  | O2   | 87.87(10) | C15  | C14  | C23  | 122.4(4) |
| N2   | Ir1  | N1   | 174.64(10) | C16  | C15  | C14  | 120.3(4) |
| C7   | Ir1  | O1   | 90.54(11) | N2   | C16  | C15  | 120.1(3) |
| C7   | Ir1  | N1   | 80.62(13) | C15  | C16  | C17  | 113.7(3) |
| C7   | Ir1  | N2   | 96.03(13) | C18  | C17  | C16  | 114.6(3) |
| C18  | Ir1  | O1   | 174.63(11) | C22  | C17  | C16  | 123.3(3) |
| C18  | Ir1  | O2   | 88.58(11) | C22  | C17  | C18  | 122.0(3) |
| C18  | Ir1  | N1   | 94.86(13) | C17  | C18  | Ir1  | 114.6(3) |
| C18  | Ir1  | N2   | 81.07(13) | C20  | C18  | Ir1  | 128.9(3) |
| C18  | Ir1  | C7   | 92.75(13) | C20  | C19  | C18  | 116.4(3) |
| C33  | O1   | Ir1  | 124.0(2)  | C20  | C19  | C18  | 121.9(3) |
| C35  | O2   | Ir1  | 125.5(2)  | C21  | C20  | C21  | 120.5(4) |
| C1   | N1   | Ir1  | 124.3(2)  | C22  | C21  | C20  | 119.2(4) |
| C1   | N1   | C5   | 119.6(3)  | C21  | C22  | C17  | 119.9(4) |
| C5   | N1   | Ir1  | 116.1(2)  | C24  | C23  | C14  | 175.3(4) |
| C12  | N2   | Ir1  | 125.1(2)  | C23  | C24  | C25  | 174.9(4) |
| C12  | N2   | C16  | 119.2(3)  | C26  | C25  | C24  | 119.2(4) |
| C16  | N2   | Ir1  | 115.6(2)  | C26  | C25  | C30  | 119.8(4) |
| N1   | C1   | C2   | 122.2(3)  | C30  | C25  | C24  | 121.0(4) |
| C1   | C2   | C3   | 119.0(4)  | C27  | C26  | C25  | 120.6(4) |
| C4   | C3   | C2   | 119.1(3)  | C26  | C27  | C28  | 119.8(4) |
| C3   | C4   | C5   | 120.4(3)  | C27  | C28  | C29  | 119.9(4) |
| N1   | C5   | C4   | 119.7(3)  | C27  | C28  | C31  | 120.1(4) |
| N1   | C5   | C6   | 113.6(3)  | C29  | C28  | C31  | 120.0(4) |
| C4   | C5   | C6   | 126.7(3)  | C30  | C29  | C28  | 120.0(4) |
| C7   | C6   | C5   | 115.2(3)  | C29  | C30  | C25  | 119.8(4) |
| C11  | C6   | C5   | 123.8(3)  | N3   | C31  | C28  | 179.0(6) |
| C11  | C6   | C7   | 120.9(3)  | O1   | C33  | C32  | 114.8(3) |
| C6   | C7   | Ir1  | 114.4(2)  | O1   | C33  | C34  | 126.9(3) |
| C8   | C7   | Ir1  | 128.4(3)  | C34  | C33  | C32  | 118.3(3) |
| C8   | C7   | C6   | 117.1(3)  | C35  | C34  | C33  | 128.9(3) |
| C9   | C8   | C7   | 121.3(4)  | O2   | C35  | C34  | 126.2(3) |
| C10  | C9   | C8   | 121.1(4)  | O2   | C35  | C36  | 116.0(3) |
| C9   | C10  | C11  | 119.4(3)  | C34  | C35  | C36  | 117.8(3) |
| C10  | C11  | C6   | 120.2(3)  |
S4. Electrochemistry

Electrochemical analyses of the iridium complexes were carried out using an EmStat\textsuperscript{2} potentiometer (PalmSens Instruments, West Lafayette, IN, USA), with platinum working, platinum counter and platinum pseudo-reference electrodes. Analyses were performed at a scan rate of 100 mV s\textsuperscript{-1}. The ferrocene/ferrocenium (Fc/Fc\textsuperscript{+}) or decamethylferrocene/decamethylferrocenium (Fc\textsuperscript{*}/Fc\textsuperscript{*+}) couple was used as the internal reference where the Fc/Fc\textsuperscript{+} couple is at 0.0 V. Analytical grade solvents were used.

| Complex | $E_{1/2}$ Ox (V\textsubscript{Fc/Fc}+) | $E_{1/2}$ Red (V\textsubscript{Fc/Fc}+) | HLG (eV) |
|---------|---------------------------------|---------------------------------|----------|
| 1\textsuperscript{1} | 0.39 | - | 2.69 |
| 2 | 0.36 | -2.33 | 2.42 |
| 3 | 0.40 | -2.02 | 2.36 |
| 4 | 0.36\textsuperscript{a} | - | 2.59 |
| 5 | 0.36 | -2.23 | 2.59 |
| 6 | 0.39 | -1.97 | 2.36 |
| 7 | 0.36 | -2.23 | 2.59 |

\textsuperscript{a} Recorded in DCM
Figure S14. Cyclic voltammogram of complex 2 recorded with scan rate of 100 mV s$^{-1}$.

Figure S15. Cyclic voltammogram of complex 3 recorded with scan rate of 100 mV s$^{-1}$.
Figure S16. Cyclic voltammogram of complex 4 recorded with scan rate of 100 mV s\(^{-1}\).

Figure S17. Cyclic voltammogram of complex 5 recorded with scan rate of 100 mV s\(^{-1}\).

Note: the minor signal at ca. -1.5 V is attributed to the presence of trace oxygen.
Figure S18. Cyclic voltammogram of complex 6 recorded with scan rate of 100 mV s$^{-1}$. Note: the minor signal at ca. -1.5 V is attributed to the presence of trace oxygen.

Figure S19. Cyclic voltammogram of complex 7 recorded with scan rate of 100 mV s$^{-1}$. 
S5. Photophysical measurements

All photophysical measurements of iridium complexes (except solvatochromism) were performed using DCM as the solvent. The ultraviolet (UV)-visible spectra were measured on a UV2-100 spectrometer operated with Vison software (Unicam Digital, Leeds, UK). Samples were held in quartz cuvettes, with path length \( l = 1 \text{ cm} \). Excitation and emission photoluminescence spectra were recorded on a Spex\textsuperscript{®} Fluorolog\textsuperscript{®} 3-22 spectrofluorometer (Horiba Scientific, Irvine, CA, USA). Samples were degassed in quartz cuvettes of \( l = 1 \text{ cm} \) fitted with Teflon J Young taps by repeated freeze–pump–thaw cycles using a turbomolecular pump until the pressure was stable. The solutions’ absorbance was < 0.15 to minimize inner filter effects.

Photoluminescence quantum yields (PLQYs) were measured following our previously reported method (see below).\textsuperscript{4} Quinine sulfate in 0.1 M H\textsubscript{2}SO\textsubscript{4} (\( \Phi_F: 0.546 \))\textsuperscript{5} or rhodamine 101 in ethanol (\( \Phi_F: 1.00 \))\textsuperscript{6} as the references, the emission spectra of quinine sulfate were collected by exciting the samples at 360 nm. The PLQY of each complex was measured in duplicate and determined by the following method:

1. The UV–vis absorbance spectrum was recorded in quartz cuvette with path length \( l = 2 \text{ cm} \) (to improve spectrum signal-to-noise), recording the absorbance at the excitation wavelength.

2. The same sample solution was transferred to the quartz fluorescence cell (a standard 1 cm cell modified with a Teflon Young’s tap) degassed via repeated freeze-pump-thaw cycles before the emission spectrum was recorded.

3. The fully corrected fluorescence spectrum was integrated and the integrated intensity (the area of the fluorescence spectrum) was recorded.

4. Steps 1 to 3 were repeated for five additional solutions with increasing concentrations (with absorbance ranging from 0.02 to 0.1).

5. The integrated fluorescence intensity was plotted verse absorbance, which resulted a linear plot with gradient X (\( \text{Grad}_X \)).
6. Steps 1, 3, 4 and 5 were repeated for the chosen standard (quinine sulfate).

7. Fluorescence quantum yield for each complex was calculated using the following equation

\[ \Phi_X = \Phi_{ST} \left( \frac{Grad_X}{Grad_{ST}} \right) \frac{\eta^2_X}{\eta^2_{ST}} \]

Where ST and X denote standard and the measured complex, \( \Phi \) is the fluorescence quantum yield, Grad the gradient from the plot of integrated fluorescence intensity vs. absorbance, and \( \eta \) the refractive index of the solvent.

Emission lifetimes were measured using a custom spectrometer by time-correlated single photon counting (TCSPC) using a pulsed diode laser (371 nm), made by IBH Ltd, running at 1 MHz. The fluorescence emission was collected at right angles to the excitation source. The emission wavelength was selected using a Horiba Jobin Yvon Triax 190 monochromator and was detected by using a cooled IBH TBX-04 photomultiplier (PMT). Timing was achieved using a 567 time-to-amplitude converter (Ortec, Melbourne, AU) and a pulse-height analyzer (PHA; E. G. & G. Trumpcard, Carlsbad, CA, USA). Data were recorded using Maestro (version 510) software. The data were transferred to a personal computer (PC) and analysed using non-linear regression to a single exponential decay, and the quality of fit was established by reduced \( \chi^2 \) and random residuals. The decay data were fitted to a single exponential function.
Electronic absorption spectra

Figure S20. Electronic absorption spectra of complexes 3 and 4 recorded in DCM solution.

Figure S21. Electronic absorbance spectra of complexes 2, 5, 6, and 7 recorded in DCM solution.
Photostability

Figure S22. Photostability of complex 3 recorded in DCM solution.

Figure S23. Photostability of complex 6 recorded in DCM solution.
Solvatochromism

Figure S24. Emission of complex 1 recorded in cyclohexane (Cyc), toluene (Tol), dichloromethane (DCM), and acetonitrile (MeCN).

Figure S25. Emission of complex 2 recorded in cyclohexane (Cyc), toluene (Tol), dichloromethane (DCM), and acetonitrile (MeCN).
Figure S26. Emission of complex 3 recorded in cyclohexane (Cyc), toluene (Tol), dichloromethane (DCM), and acetonitrile (MeCN).

Figure S27. Emission of complex 4 recorded in cyclohexane (Cyc), toluene (Tol), dichloromethane (DCM), and acetonitrile (MeCN).
Figure S28. Emission of complex 5 recorded in cyclohexane (Cyc), toluene (Tol),
dichloromethane (DCM), and acetonitrile (MeCN).

Figure S29. Emission of complex 6 recorded in cyclohexane (Cyc), toluene (Tol),
dichloromethane (DCM), and acetonitrile (MeCN).
Figure S30. Emission of complex 7 recorded in cyclohexane (Cyc), toluene (Tol),
dichloromethane (DCM), and acetonitrile (MeCN).
Lifetime Traces

Figure S31. Lifetime trace for complex 2 recorded in DCM excited at 488 nm.

Figure S32. Lifetime trace for complex 3 recorded in DCM excited at 488 nm.
Figure S33. Lifetime trace for complex 4 recorded in DCM excited at 488 nm.

Figure S34. Lifetime trace for complex 5 recorded in DCM excited at 488 nm.
Figure S35. Lifetime trace for complex 6 recorded in DCM excited at 488 nm.

Figure S36. Lifetime trace for complex 7 recorded in DCM excited at 488 nm.
PLQY Measurements

Figure S37. Integrated Intensity vs. Absorbance for a) 2 and b) quinine sulfate.
Figure S38. Integrated Intensity vs. Absorbance for a) 3 and b) quinine sulfate.
Figure S39. Integrated Intensity vs. Absorbance for a) 4 and b) rhodamine 101.
Figure S40. Integrated Intensity vs. Absorbance for a) 5 and b) quinine sulfate.
Figure S41. Integrated Intensity vs. Absorbance for a) 6 and b) quinine sulfate.
Figure S42. Integrated Intensity vs. Absorbance for a) 7 and b) quinine sulfate.
### S6. Calculations

Hybrid density functional theory (DFT) calculations were performed using the Gaussian16 package (Gaussian, Inc)\(^7\) All calculations used the B3LYP\(^8\) functional with a mixed basis set LANL2DZ/3-21G* where the pseudopotential LANL2DZ\(^9,10\) was applied to iridium and the 3-21G* basis set\(^11,12\) for all other atoms. The fully optimised geometries were confirmed as true minima with no imaginary frequencies found from frequency calculations. The rotational barriers were estimated from constrained geometries with fixed torsional angles so that the two rings attached to the ethynyl bridge are perpendicular to each other. A frequency calculation on each constrained geometry showed one imaginary frequency indicating a rotation barrier transition state. Orbital figures were drawn using GabEdit\(^13\) and the group contributions to each orbital were estimated as a percentage (%) with GaussSum\(^14\).

**Table S5.** Comparison of calculated and experimental bond lengths in angstroms for fully optimised and X-ray geometries of 6.

| Bond length | Calculated | Experimental | Difference |
|-------------|------------|--------------|------------|
| Ir-O        | 2.168      | 2.164(2)     | 0.004      |
| Ir-O        | 2.168      | 2.142(2)     | 0.026      |
| Ir-N        | 2.051      | 2.034(3)     | 0.017      |
| Ir-N        | 2.041      | 2.024(3)     | 0.017      |
| Ir-C        | 2.011      | 1.993(3)     | 0.018      |
| Ir-C        | 2.009      | 1.981(4)     | 0.028      |
**Table S6. Total and relative energy data**

| Complex | Electronic Energy (au) | Relative Electronic Energy (kJ mol\(^{-1}\)) | Gibbs Free Energy (au) | Relative Gibbs Free Energy (kJ mol\(^{-1}\)) |
|---------|------------------------|---------------------------------------------|------------------------|---------------------------------------------|
| 1       | -2834.195469           |                                             | -2833.287705           |                                             |
| 2       | -2117.296306           |                                             | -2116.652848           |                                             |
| 3       | -2194.899904           | 0.00                                        | -2194.36803            | 0.00                                        |
| 3 (90°,90°) | -2194.896722     | 8.37                                        | -2194.360057           | 20.92                                       |
| 4       | -2882.141402           | 0.00                                        | -2881.55536            | 0.00                                        |
| 4 (90°,90°) | -2882.138160     | 8.49                                        | -2881.547061           | 21.80                                       |
| 5       | -1705.917279           | 0.00                                        | -1705.457135           | 0.00                                        |
| 5 (90°) | -1705.915704           | 4.14                                        | -1705.453432           | 9.71                                        |
| 6       | -1797.647989           | 0.00                                        | -1797.191808           | 0.00                                        |
| 6 (90°) | -1797.646393           | 4.18                                        | -1797.188056           | 9.83                                        |
| 7       | -2141.268611           | 0.00                                        | -2140.785541           | 0.00                                        |
| 7 (90°) | -2141.267023           | 4.18                                        | -2140.781504           | 10.59                                       |
Electronic structure data

**Table S7.** Comparison of calculated HOMO and LUMO energies in eV with observed electrochemical data.

| Complex | Calculated HOMO | Calculated LUMO | Calculated HLG | Observed HOMO | Observed LUMO | Observed HLG |
|---------|-----------------|-----------------|----------------|---------------|--------------|--------------|
| 1       | -4.79           | -1.73           | 3.06           | -4.79         | -            | -            |
| 2       | -4.77           | -1.70           | 3.07           | -4.76         | -2.07        | 2.69         |
| 3       | -5.05           | -2.53           | 2.52           | -4.80         | -2.38        | 2.42         |
| 3 (90°,90°) | -5.04       | -2.03           | 3.01           |               |              |              |
| 4       | -4.86           | -2.10           | 2.76           | -4.76         | -            | -            |
| 4 (90°,90°) | -4.87       | -1.77           | 3.10           |               |              |              |
| 5       | -4.77           | -1.91           | 2.86           | -4.76         | -2.17        | 2.59         |
| 5 (90°) | -4.78           | -1.66           | 3.12           |               |              |              |
| 6       | -4.91           | -2.44           | 2.47           | -4.79         | -2.43        | 2.36         |
| 6 (90°) | -4.90           | -1.97           | 2.93           |               |              |              |
| 7       | -4.81           | -2.06           | 2.75           | -4.76         | -2.17        | 2.59         |
| 7 (90°) | -4.81           | -1.72           | 3.09           |               |              |              |

*a* Observed potential values in V converted to \( E(\text{HOMO/LUMO}) = -4.4 - E_{1/2}(\text{Ox/Red}) \) V for comparison with calculated \( E(\text{HOMO/LUMO}) \) values.
Figure S43. Frontier molecular orbitals for 1 and 2. Isocontours drawn at 0.04 and 0.055 e bohr $^{-3/2}$ for 1 and 2 respectively.

Figure S44. Frontier molecular orbitals for the fully optimised geometry 3 where the phenylene rings attached to the ethynyl bridge are coplanar to each other and the constrained geometry 3 (90°, 90°) where the phenylene rings attached to the ethynyl bridge are constrained to be perpendicular to each other. Isocontours are at 0.04 e bohr $^{-3/2}$. 
Figure S45. Frontier molecular orbitals for the fully optimised geometry 4 and the constrained geometry 4 (90°, 90°). Isocontours at 0.04 e bohr$^{-3/2}$.

Figure S46. Frontier molecular orbitals for the fully optimised geometry 5 and the constrained geometry 5 (90°). Isocontours at 0.055 e bohr$^{-3/2}$.
Figure S47. Frontier molecular orbitals for the fully optimised geometry 6 and the constrained geometry 6 (90°). Isocontours at 0.055 e bohr$^{-3/2}$.

Figure S48. Frontier molecular orbitals for the fully optimised geometry 7 and the constrained geometry 7 (90°). Isocontours at 0.055 e bohr$^{-3/2}$. 

S46
Time-dependent density functional theory (TD-DFT) data

Table S8. Comparison of calculated $S_0 \rightarrow T_1$ values and observed emission maxima in nm.

| Complex | Calculated $S_0 \rightarrow T_1$ | Calculated $S_0 \leftarrow T_1$ adjusted$^a$ | Observed emission |
|---------|----------------------------------|-----------------------------------------------|-------------------|
| 1       | 560                              | 593                                           | 580               |
| 2       | 560                              | 593                                           | 588               |
| 3       | 653                              | 643$^b$                                       | 639               |
| 3 (90°,90°) | 568                            |                                                |                   |
| 4       | 606                              | 614$^b$                                       | 600               |
| 4 (90°,90°) | 557                            |                                                |                   |
| 5       | 589                              | 604$^b$                                       | 603               |
| 5 (90°) | 553                              |                                                |                   |
| 6       | 669                              | 654$^b$                                       | 646               |
| 6 (90°) | 575                              |                                                |                   |
| 7       | 609                              | 617$^b$                                       | 608               |
| 7 (90°) | 559                              |                                                |                   |

$^a$ Energy scaling factor of 0.945 applied – see reference$^{15}$.

$^b$ Energies averaged from two conformers.
Figure S49. Natural transition orbitals (yellow = hole, purple = particle) involved in the NTOs involved in the S₀ ← T₁ emission for 1. The table lists the % group contribution to each NTO. Isocontours drawn at 0.04 e bohr⁻³/².

| NTO   | Ir | phenylene | acac | pyridyl | -C=C- | -Si/Pr₃ |
|-------|----|-----------|------|---------|-------|---------|
| Particle | 4  | 8         | 1    | 66      | 17    | 4       |
| Hole   | 46 | 42        | 6    | 6       | 0     | 0       |

Figure S50. NTOs involved in the S₀−T₁ emission for 2. Isocontours at 0.055 e bohr⁻³/².

| NTO   | Ir | phenylene | acac | pyridyl | -C=C- | -Si/Pr₃ |
|-------|----|-----------|------|---------|-------|---------|
| Particle | 5  | 8         | 1    | 65      | 17    | 4       |
| Hole   | 46 | 42        | 6    | 6       | 0     | 0       |
**Figure S51.** NTOs involved in the $S_0 \leftrightarrow T_1$ emissions for the fully optimised geometry $3$ where the phenylene rings attached to the ethynyl bridge are coplanar to each other and the constrained geometry $3$ (90°, 90°) where the phenylene rings attached to the ethynyl bridge are constrained to be perpendicular to each other. Isocontours at 0.04 e bohr$^{-3/2}$. 

| NTO  | Ir | phenylene | acac | pyridyl | $\text{-C=C-}$ | $\text{-C_3H_2CN}$ |
|------|----|-----------|------|---------|----------------|-----------------|
| Particle | 3  | 3         | 1    | 34      | 16             | 43              |
| Hole   | 45 | 43        | 6    | 6       | 0              | 0               |

| NTO  | Ir | phenylene | acac | pyridyl | $\text{-C=C-}$ | $\text{-C_3H_2CN}$ |
|------|----|-----------|------|---------|----------------|-----------------|
| Particle | 4  | 8         | 1    | 66      | 16             | 5               |
| Hole   | 45 | 43        | 6    | 6       | 0              | 0               |
Figure S52. NTOs involved in the $S_0 \leftrightarrow T_1$ emissions for the fully optimised geometry 4 and the constrained geometry 4 (90°, 90°). Isocontours at 0.04 e bohr$^{-3/2}$. 
Figure S53. NTOs involved in the $S_0 \rightarrow T_1$ emissions for the fully optimised geometry 5 and the constrained geometry 5 (90°). Isocontours at 0.055 e bohr$^{-3/2}$. 
Figure S54. NTOs involved in the $S_0$–$T_1$ emissions for the fully optimised geometry 6 and the constrained geometry 6 (90°). Isocontours at 0.055 e bohr$^{-3/2}$. 
Figure S55. NTOs involved in the S₀←T₁ emissions for the fully optimised geometry 7 and the constrained geometry 7 (90°). Isocontours at 0.055 e bohr⁻³/₂.
S8. References

1. Davidson, R.; Hsu, Y.-T.; Griffiths, G. C.; Li, C.; Yufit, D.; Pal, R.; Beeby, A. Highly Linearized Twisted Iridium(III) Complexes. *Inorganic Chemistry* **2018**, 57 (22), 14450-14462 DOI: 10.1021/acs.inorgchem.8b02818.

2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *Journal of Applied Crystallography* **2009**, 42, 339-341 DOI: 10.1107/s0021889808042726.

3. Sheldrick, G. A short history of SHELX. *Acta Crystallogr., Sect. A* **2008**, 64 (1), 112-122 DOI: doi:10.1107/S0108767307043930.

4. Davidson, R.; Hsu, Y.-T.; Batchelor, T.; Yufit, D.; Beeby, A. The use of organolithium reagents for the synthesis of 4-aryl-2-phenylpyridines and their corresponding iridium(iii) complexes. *Dalton Trans.* **2016**, 45 (28), 11496-11507 DOI: 10.1039/C6DT01461E.

5. Melhuish, W. H. Quantum efficiencies of fluorescence of organic substances: effect of solvent and concentration of the fluorescent solute. *J. Phys. Chem.* **1961**, 65 (2), 229-235 DOI: 10.1021/j100820a009.

6. Karstens, T.; Kobs, K. Rhodamine B and rhodamine 101 as reference substances for fluorescence quantum yield measurements. *The Journal of Physical Chemistry* **1980**, 84 (14), 1871-1872 DOI: 10.1021/j100451a030.

7. M. J. Frisch; G. W. Trucks; H. B. Schlegel; G. E. Scuseria; M. A. Robb; J. R. Cheeseman; G. Scalmani; V. Barone; B. Mennucci; G. A. Petersson; H. Nakatsuji; M. Caricato; X. Li; H. P. Hratchian; A. F. Izmaylov; J. Bloino; G. Zheng; J. L. Sonnenberg; M. Hada; M. Ehara; K. Toyota; R. Fukuda; J. Hasegawa; M. Ishida; T. Nakajima; Y. Honda; O. Kitao; H. Nakai; T. Vreven; J. A. Montgomery, J., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A.
8. Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Physical Review B 1988, 37 (2), 785-789 DOI: 10.1103/PhysRevB.37.785.

9. Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. The Journal of Chemical Physics 1985, 82 (1), 299-310 DOI: 10.1063/1.448975.

10. Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. The Journal of Chemical Physics 1985, 82 (1), 270-283 DOI: 10.1063/1.448799.

11. Petersson, G. A.; Al-Laham, M. A. A complete basis set model chemistry. II. Open-shell systems and the total energies of the first-row atoms. The Journal of Chemical Physics 1991, 94 (9), 6081-6090 DOI: 10.1063/1.460447.

12. Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. A complete basis set model chemistry. I. The total energies of closed-shell atoms and hydrides of the first-row elements. The Journal of Chemical Physics 1988, 89 (4), 2193-2218 DOI: 10.1063/1.455064.
13. Allouche, A.-R. Gabedit—A graphical user interface for computational chemistry softwares. *Journal of Computational Chemistry* 2011, 32 (1), 174-182 DOI: https://doi.org/10.1002/jcc.21600.

14. O'Boyle, N. M.; Tenderholt, A. L.; Langner, K. M. cclib: A library for package-independent computational chemistry algorithms. *Journal of Computational Chemistry* 2008, 29 (5), 839-845 DOI: https://doi.org/10.1002/jcc.20823.

15. Benjamin, H.; Fox, M. A.; Batsanov, A. S.; Al-Attar, H. A.; Li, C.; Ren, Z.; Monkman, A. P.; Bryce, M. R. Pyridylpyrazole N^N ligands combined with sulfonyl-functionalised cyclometalating ligands for blue-emitting iridium(III) complexes and solution-processable PhOLEDs. *Dalton Transactions* 2017, 46 (33), 10996-11007 DOI: 10.1039/C7DT02289A.