Supplementary information for

Preparation and single enantiomers of chiral at metal bis-cyclometallated iridium complexes

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General information and materials

All reactions were carried out under an inert atmosphere of nitrogen and under microwave irradiation unless stated otherwise. After work up all the complexes were air stable. Microwave reactions were carried out in a CEM-Discover commercial microwave reactor. $^1$H, and $^{13}$C–{[$^1$H]} NMR spectra were obtained using a DRX 400 MHz spectrometer. Chemical shifts were recorded in ppm (on δ scale with tetramethylsilane as internal reference), and coupling constants are reported in Hz. FAB mass spectra were obtained on a Kratos concept mass spectrometer using NOBA as matrix. The electrospray (ES) mass spectra were recorded using a micromass Quattra LC mass spectrometer in HPLC grade acetonitrile except methanol for 2.6d. UV – Vis absorption measurements were carried out on a Shimadzu UV – 1600 series spectrometer in dry DCM. Cyclic voltammetry measurements were performed with an Eco Chemie Autolab using a one-compartment cell under N$_2$ gas, equipped with a Pt disc working electrode, a Pt gauze counter electrode and a silver wire reference electrode. The supporting electrolyte was Et$_4$NClO$_4$ (0.1 mol L$^{-1}$) in acetonitrile. Elemental analyses were performed at London Metropolitan University. All starting materials were obtained from Aldrich or Alfa Aesar.

General preparative procedure

The general procedure was as follows a mixture of the chiral ligand (X^Y = (S)-HL1, (S)-HL2), (2.2–2.4 equiv) and an equimolar amount of NaOMe in methanol (3 ml) was warmed gently at 40 °C for 15 mins. A solution of the appropriate dimer [Ir(C^N)$_2$Cl]$_2$ 1a,b (1 equiv) in DCM (6 ml) was added and the mixture was stirred for 2-4 hrs at room temperature. After this time the solvent was removed in vacuo and the residue was dissolved in DCM (15 ml) and passed through celite. The filtrate was reduced in volume and hexane was added slowly to induce precipitation. The precipitate was isolated, washed with hexane and dried in vacuo.

Synthesis of $\Delta S/$ΛS-1a

This was prepared from [Ir(ppz)$_2$Cl]$_2$ a (140 mg, 0.136 mmol), (S)-HL1 (61.3 mg, 0.299 mmol), and NaOMe (16.2 mg, 0.299 mmol) and after work up gave $\Delta S/$ΛS-1a as a grey solid (combined yield 157 mg, 85%). Slow diffusion of hexane into a DCM solution of 1a afforded selectively crystals of the ΛS isomer (63 mg, 34%), the ΔS isomer (40 mg, 21%) was obtained from the mother liquor, by recrystallisation from methanol/diethylether. Anal.Calcd for C$_{30}$H$_{28}$IrN$_5$O$_2$: C, 52.77, H, 4.13, N, 10.26. Found (ΛS): C, 52.68, H, 4.12, N, 10.17%.
^1H NMR (CDCl₃) δ: 8.05, 8.03 (2H, 2 X d, J = 2.7, H₃, e), 7.63 (1H, d, J = 2.3, H₄), 7.60 – 7.57 (2H, m, H₅, g), 7.17 – 7.09 (3H, m, H₂, d, d'), 6.84 (1H, td, J = 7.4, 1.2, H₆), 6.80 (1H, td, J = 7.8, 1.2, H₅), 6.67 (1H, d, J = 7.8, H₇), 6.64 – 6.58 (3H, m, H₆, b, f'), 6.52 (1H, t, J = 2.7, H₄), 6.37 (1H, dd, J = 7.8, 1.6, H₆), 6.33 (1H, ddd, J = 7.8, 6.7, 1.2, H₇), 6.21 (1H, dd, J = 7.4, 1.2, H₆), 4.18 (1H, ddd, J = 8.9, 3.9, H₃), 3.76 (1H, t, J = 8.9, H₉), 3.04 (1H, ddd, J = 9.4, 3.5, 1.9, H₇), 2.01 (1H, septd, J = 7.0, 1.9, H₆), 0.89 (3H, d, J = 7.0, Me₆a), 0.33 (3H, d, J = 7.0, Me₇b). ^13C NMR: 169.82 (C₈), 161.58 (C₁₁), 144.06 (C₉), 143.87 (C₈), 139.13 (C₉), 138.26 (C₁₀), 135.89 (C₉), 134.84 (C₈), 134.28 (C₄), 132.96 (C₂), 130.23 (C₇), 129.39 (C₇), 125.77 (C₆), 125.62 (C₁), 125.23 (C₂, e'), 124.76 (C₁), 121.52 (C₁), 120.78 (C₄), 112.33 (C₆), 110.59, 110.43 (C₄, d'), 110.25 (C₁₀), 107.07 (C₁), 106.84 (C₇), 70.74 (C₁), 66.41 (C₅, b'), 28.89 (C₈), 19.21 (Me₆a), 14.37 (Me₇b).

[α]D -593° in CHCl₃.

^1H NMR (CDCl₃) δ: 8.07 (1H, d, J = 2.9, H₆), 7.99 (1H, d, J = 2.9, H₇), 7.80 (1H, d, J = 2.1, H₈), 7.62 (1H, dd, J = 7.9, 1.8, H₃), 7.43 (1H, d, J = 2.3, H₈), 7.15 – 7.09 (3H, m, H₂, d, d'), 6.84 (1H, td, J = 7.6, 1.5, H₆), 6.80 (1H, td, J = 7.6, 1.5, H₆), 6.73 – 6.67 (2H, m, H₅, b), 6.63 (1H, t, J = 2.3, H₇), 6.61 (1H, td, J = 7.3, 1.2, H₉), 6.52 (1H, t, J = 2.3, H₉), 6.34 (1H, ddd, J = 7.8, 6.7, 0.8, H₈), 6.29 (1H, dd, J = 7.6, 1.5, H₆), 6.18 (1H, dd, J = 7.6, 1.5, H₆), 4.29 – 4.18 (2H, m, H₂, d), 3.93 (1H, ddd, J = 8.8, 4.4, 3.2, H₃), 0.53 (1H, septd, J = 7.0, 3.1, H₆), 0.28 (3H, d, J = 7.0, Me₇b), 0.20 (3H, d, J = 6.7, Me₆a). ^13C NMR: 170.08 (C₈), 161.66 (C₁₁), 144.60 (C₁), 143.89 (C₁₀), 138.19 (C₉), 137.01 (C₉), 135.14 (C₇), 134.25 (C₉), 133.83 (C₆), 133.16 (C₇), 129.95 (C₁), 129.61 (C₁), 125.78, 125.75 (C₁, b), 125.49 (C₁), 125.27 (C₄), 124.55 (C₄), 121.55 (C₆), 120.91 (C₆), 112.42 (C₁), 110.54 (C₆), 110.36 (C₁₀), 110.21 (C₁), 107.04 (C₁), 106.73 (C₄), 71.75 (C₆), 66.51 (C₅, b'), 28.42 (C₈), 18.58 (Me₆a), 12.87 (Me₆a). [α]D +582° in CHCl₃. MS (FAB): m/z 683 [M⁺].

**Synthesis of ΔS/ΔS-1b**

This was prepared from [Ir(ppy)₂Cl₂]b (70 mg, 0.065 mmol), (S)-HL₁ (29.3 mg, 0.143 mmol), and NaOMe (7.7 mg, 0.143 mmol) and after work up gave ΔS/ΔS-1b as a yellow solid (combined yield 68 mg, 75%). Both isomers crystallised out together in DCM/hexane or DCM/diethyl ether solvent mixtures but they could be separated by hand picking due to significant variation in colour and shape of the crystals. Anal.Calcd for C₃₉H₃₀IrN₃O₂NaCl: C, 53.50, H, 3.96, N, 5.51. Found (ΔS): C, 54.69, H, 3.35, N, 5.40%.

^1H NMR (CDCl₃) δ: 8.87 (1H, ddd, J = 5.4, 1.6, 0.8, H₃), 8.59 (1H, ddd, J = 5.8, 1.6, 0.8, H₄), 7.85 – 7.82 (2H, m, H₆, e'), 7.72 (1H, td, J = 7.4, 1.6, H₃), 7.65 (1H, td, J = 7.4, 1.6, H₃), 7.58 – 7.53 (3H, m, H₄, d, d'), 7.13 – 7.07 (2H, m, H₅, g), 6.92
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0.003(7).

values were 0.0390 (all data). The final

Crystal data for \( \Lambda-1b \): \( \text{C}_{34}\text{H}_{30}\text{IrN}_{3}\text{O}_{2}\cdot\text{CHCl}_{3}, M = 824.18 \), orthorhombic, \( a = 9.355(5) \) Å, \( b = 14.083(8) \) Å, \( c = 24.255(13) \) Å, \( \alpha = 90.0^\circ \), \( \beta = 90.0^\circ \), \( \gamma = 90.0^\circ \), \( V = 3196(3) \) Å\(^3\), \( T = 150(2) \) K, space group \( P2(1)2(1)2(1) \), \( Z = 4 \), 26714 reflections measured, 6950 independent reflections (\( R_{int} = 0.0665 \)). The final \( R_I \) values were 0.0348 (> 2\( \sigma(I) \)). The final \( wR(F^2) \) values were 0.0676 (> 2\( \sigma(I) \)). The final \( R_I \) values were 0.0390 (all data). The final \( wR(F^2) \) values were 0.0688 (all data). Flack parameter = -0.003(7).
Synthesis of ΔS/ΔS-2a

This was prepared from [Ir(ppy)2Cl]2·a (70 mg, 0.068 mmol), (S)-HL2 (36.8 mg, 0.164 mmol), and NaOMe (8.8 mg, 0.164 mmol) and after work up gave ΔS/ΔS-2a as a yellow solid (combined yield 71 mg, 75%). ΔS isomer was selectively crystallised from methanol, hence, the two isomers were separated via fractional crystallisation from methanol until a ratio of 1:10 was attained for ΔS:ΔS. Anal. Calcd for C35H38IrN4O·CH3OH: C, 56.39, H, 4.02, N, 9.96. Found (ΔS): C, 56.28, H, 3.98, N, 9.87%.

1H NMR (CDCl3) ΔS: δ 8.06 (1H, s, H3), 8.02 (1H, d, J = 3.1, H5), 7.66 (1H, d, J = 3.5, H1), 7.65 (1H, d, J = 2.3, H4), 7.52 (1H, d, J = 2.3, H6), 7.19 (1H, dd, J = 8.6, 6.7, 1.6, H2), 7.12 (1H, d, J = 7.4, H8), 7.05 (1H, dd, J = 7.8, 1.6, H4), 7.01 – 6.92 (3H, m, H8,9,10), 6.82 (1H, td, J = 7.4, 0.8, H3), 6.77 (1H, dd, J = 7.8, 1.2, H7), 6.73 – 6.66 (3H, m, H2a,b,c), 6.61 (1H, td, J = 7.8, 1.6, H5), 6.53 (1H, t, J = 2.7, H6), 6.49 (1H, t, J = 2.7, H7), 6.39 – 6.34 (3H, m, H3,8,9), 6.27 (1H, dd, J = 7.4, 1.2, H7), 6.13 (1H, dd, J = 7.4, 1.2, H5), 4.94 (1H, q, J = 7.0, H6), 1.51 (3H, d, J = 7.0, Me). 13C NMR: 166.41 (C11), 161.08 (C7), 144.24 (C5), 143.88 (C6), 141.99 (C1), 137.87 (C4), 137.81 (C9), 135.21 (C8), 134.63 (C2), 134.39 (C3), 134.17 (C4), 133.70 (C2), 131.10 (C5), 127.92 (C9,10), 126.19 (C10), 125.96 (C8,9), 125.85 (C5), 125.63 (C6), 125.43 (C7), 125.23 (C6), 123.71 (C1), 121.68 (C2), 121.42 (C12), 120.75 (C3), 112.89 (C9), 110.54 (C6), 110.47 (C2), 106.87 (C1), 106.71 (C13), 66.97 (C2), 22.81 (Me). [α]D -631° in CHCl3.

1H NMR (CDCl3) ΔS: δ 8.11 (1H, d, J = 2.7, H5), 7.97 (1H, d, J = 2.7, H6), 7.96 (1H, s, H3), 7.83 (1H, d, J = 2.3, H4), 7.36 – 7.22 (5H, m, H8,9,10), 7.20 (1H, dd, J = 7.8, 0.8, H6), 7.18 (1H, d, J = 2.3, H8), 7.14 – 7.10 (2H, m, H2a,d), 6.89 (1H, dd, J = 7.8, 1.9, H7), 6.87 – 6.81 (2H, m, H2b,c), 6.72 – 6.68 (2H, m, H2a,b), 6.67 (1H, t, J = 2.3, H6), 6.61 (1H, d, J = 8.2, H3), 6.42 (1H, dd, J = 7.4, 1.6, H2), 6.38 (1H, t, J = 2.3, H6), 6.30 (1H, ddd, J = 7.8, 6.7, 1.2, H2), 6.22 (1H, dd, J = 7.4, 1.6, H6), 4.80 (1H, q, J = 7.0, H1), 0.82 (3H, d, J = 7.0, Me). 13C NMR: 166.69 (C11), 162.25 (C6), 144.31 (C5), 143.93 (C1), 142.04 (C4), 138.78 (C9), 138.27 (C8), 135.21 (C2), 134.88 (C4), 134.27 (C5), 134.17 (C3), 133.58 (C2), 133.70 (C7), 128.60 (C9,10), 127.97 (C8,9), 124.8 (C5), 125.93 (C6), 125.61 (C8,9), 125.45 (C7), 123.66 (C6), 121.97 (C12), 121.72 (C6), 121.06 (C5), 112.76 (C3), 110.66 (C4), 110.47 (C6), 107.16 (C13), 106.61 (C7), 64.93 (C6), 20.33 (Me). [α]D +480° (for ΔS:ΔS 1:10) in CHCl3. MS (FAB): m/z 703 [M]+.

Crystal data for Δ-2a: C33H38IrN4O·CH3OH, M = 734.85, orthorhombic, α = 8.794(4) Å, β = 11.361(5) Å, c = 29.429(12) Å, β = 90.00°, γ = 90.00°, V = 2940(2) Å3, T = 150(2) K, space group P21/a, Z = 4, 23226 reflections measured, 5780 independent reflections (Rint = 0.1160). The
final $R_1$ values were 0.0457 ($>2\sigma(I)$). The final $wR(F^2)$ values were 0.0660 ($>2\sigma(I)$). The final $R_1$ values were 0.0602 (all data). The final $wR(F^2)$ values were 0.0696 (all data). Flack parameter = 0.005(10).

**Synthesis of $\Delta S$/AS-2b**

This was prepared from [Ir(ppy)$_2$Cl]$_2$, b (70 mg, 0.065 mmol), (S)-HL$_2$ (35.1 mg, 0.156 mmol), and NaOMe (8.4 mg, 0.156 mmol) and after work up gave $\Delta S$/AS-2b as a yellow solid (combined yield 74 mg, 79%). Both isomers crystallised out together in methanol but they could be separated by hand picking due to significant variation in colour and shape of the crystals. Anal.Calcd for C$_{39}$H$_{33}$IrN$_2$O: C, 61.27, H, 4.17, N, 5.80. Found ($\Delta S$): C, 61.37, H, 4.23, N, 5.83%.

$^1$H NMR (CDCl$_3$) $\Delta S$: $\delta$ 8.90 (1H, dt, $J = 5.5$, 1.2, H$_b$), 8.53 (1H, d, $J = 5.5$, H$_a$), 8.03 (1H, s, H$_3$), 7.83 (1H, d, $J = 8.2$, H$_d$), 7.65 (1H, td, $J = 7.4$, 1.6, H$_i$), 7.62 – 7.59 (2H, m, H$_{e',r}$), 7.53 (1H, dd, $J = 7.8$, 1.2, H$_c$), 7.39 (1H, dd, $J = 7.8$, 1.2, H$_c$), 7.12 (1H, ddd, $J = 8.2$, 7.1, 1.2, H$_d$), 7.10 (1H, ddd, $J = 8.6$, 5.8, 2.7, H$_d$), 7.02 – 6.91 (5H, m, H$_{4,9,9',10,10}$), 6.81 (1H, td, $J = 7.4$, 1.2, H$_c$), 6.78 (1H, td, $J = 7.8$, 1.2, H$_c$), 6.72 – 6.66 (2H, m, H$_{b,b'}$), 6.60 (1H, d, $J = 7.8$, H$_i$), 6.42 (1H, ddd, $J = 7.4$, 0.8, H$_d$), 6.35 – 6.31 (3H, m, H$_{3,8,8'}$), 6.13 (1H, dd, $J = 7.4$, 0.8, H$_a$), 4.70 (1H, q, $J = 7.0$, H$_b$), 1.45 (3H, d, $J = 7.0$, Me). $^{13}$C NMR: 169.08 (C$_a$), 168.34 (C$_b$), 166.17 (C$_{11}$), 161.13 (C$_s$), 153.09 (C$_i$), 150.93 (C$_j$), 148.95 (C$_n$), 148.58 (C$_o$), 144.73 (C$_r$), 144.46 (C$_l$), 142.12 (C$_l$), 136.50 (C$_l$), 136.46 (C$_l$), 134.96 (C$_l$), 133.56 (C$_l$), 133.13 (C$_l$), 131.91 (C$_j$), 129.27 (C$_{b,b'}$), 127.90 (C$_{9,9'}$), 126.79 (C$_{8,8'}$), 126.63 (C$_{10}$), 124.40 (C$_{i}$), 124.16 (C$_{d}$), 123.63 (C$_{d}$), 121.50 (C$_{12}$), 121.45 (C$_{g'}$), 121.33 (C$_{g'}$), 121.14 (C$_{e'}$), 120.12 (C$_{e'}$), 118.87 (C$_{d}$), 118.25 (C$_{b'}$), 112.83 (C$_{b'}$), 65.84 (C$_{d}$), 22.15 (Me). $\left[\alpha\right]_D^{535°}$ in DCM.

$^1$H NMR (CDCl$_3$) AS: $\delta$ 9.02 (1H, ddd, $J = 5.8$, 1.4, 0.8, H$_a$), 8.19 (1H, ddd, $J = 5.8$, 1.4, 0.8, H$_a$), 8.11 (1H, s, H$_3$), 7.93 (1H, d, $J = 8.2$, H$_d$), 7.80 – 7.75 (2H, m, H$_{e',r}$), 7.63 (1H, dd, $J = 7.6$, 1.2, H$_d$), 7.60 – 7.52 (2H, m, H$_{4,9,9',10,10}$), 7.35 – 7.27 (3H, m, H$_{9,9',10}$), 7.22 – 7.11 (3H, m, H$_{2,8,8',9'}$), 6.92 (1H, dd, $J = 7.8$, 1.8, H$_d$), 6.86 – 6.81 (2H, m, H$_{c,c}$), 6.78 – 6.69 (3H, m, H$_{b,b',g'}$), 6.58 (1H, d, $J = 8.5$, H$_d$), 6.47 (1H, dd, $J = 7.6$, 1.2, H$_d$), 6.30 (1H, ddd, $J = 8.2$, 6.7, 0.8, H$_a$), 6.22 (1H, dd, $J = 7.6$, 1.2, H$_a$), 4.73 (1H, q, $J = 7.0$, H$_b$), 0.73 (3H, d, $J = 7.0$, Me). $^{13}$C NMR: 169.79 (C$_{k,k}$), 167.13 (C$_{11}$), 163.03 (C$_{d}$), 154.10 (C$_{d}$), 152.97 (C$_{d}$), 151.35 (C$_{d}$), 150.09 (C$_{d}$), 146.45, 146.35 (C$_{b,b'}$), 143.22 (C$_{b}$), 138.58 (C$_{d}$), 138.11 (C$_{d}$), 136.56 (C$_{d}$), 135.02 (C$_{d}$), 134.77 (C$_{d}$), 133.29 (C$_{d}$), 131.01 (C$_{e'}$), 130.18 (C$_{d}$), 129.91 (C$_{9,9'}$), 129.43 (C$_{8,8'}$), 129.08 (C$_{10}$), 125.90 (C$_{d}$), 125.14
(C\textsubscript{d}, 124.69 (C\textsubscript{i}), 123.40 (C\textsubscript{g}), 123.18 (C\textsubscript{12}), 122.77 (C\textsubscript{e}), 121.90 (C\textsubscript{c}, C\textsubscript{g}), 120.27 (C\textsubscript{e}), 119.82 (C\textsubscript{c}), 114.18 (C\textsubscript{3}), 65.71 (C\textsubscript{6}), 22.49 (Me). [\(\alpha\])\textsubscript{D} +654° in DCM. MS (FAB): \(m/z\) 725 [M]+.

**Synthesis of \(\Delta\Delta\)-3a**

TFA (162 mg, 109.7 µL, 1.423 mmol) was added to a solution of \(\Delta S\)-2a (50 mg, 0.071 mmol) in DCM (2 ml). \(\text{H}_2\text{O}\) (2 ml) was added to this reaction mixture after stirring it for an hour. The deep yellow colour changed successively to pale yellow and colourless after stirring for 48 hrs at room temperature. After this time, the aqueous layer was separated and the organic layer was passed through celite. The filtrate was reduced in volume and hexane was added slowly to induce precipitation. The precipitate was isolated, washed with hexane and dried \textit{in vacuo} to give \(\Delta\Delta\)-3a as a grey solid (34 mg, 81%). \(^1\text{H} \text{NMR (CDCl}_3\]): \(\delta\) 8.10 (4H, d, \(J = 2.3,\) H\textsubscript{e}), 7.88 (4H, d, \(J = 2.0,\) H\textsubscript{g}), 7.13 (4H, dd, \(J = 7.8, 1.2,\) H\textsubscript{d}), 6.85 (4H, td, \(J = 7.4, 1.2,\) H\textsubscript{c}), 6.75 (4H, t, \(J = 2.7,\) H\textsubscript{f}), 6.63 (4H, td, \(J = 7.4, 1.2,\) H\textsubscript{b}), 6.10 (4H, dd, \(J = 7.8, 1.2,\) H\textsubscript{a}). MS (FAB): \(m/z\) 1071 [M-CF\textsubscript{3}CO\textsubscript{2}]\textsuperscript{+}. MS (ES): \(m/z\) 561 [Ir(ppz)\textsubscript{2}(MeCN)\textsubscript{2}]\textsuperscript{+}.

**Synthesis of \(\Delta\)-4a**

TFA (40.5 mg, 27.4 µL, 0.356 mmol) was added to a solution of \(\Delta S\)-2a (50 mg, 0.071 mmol) and bipy (12.2 mg, 0.078 mmol) in DCM (2 ml). The reaction mixture was stirred for an hour and after that the reaction mixture was washed with water (3 × 5 ml). The organic layer was separated and washed and dried with anhydrous MgSO\textsubscript{4}. The volume of filtrate was reduced and hexane was added slowly to induce precipitation. The precipitate was isolated, washed with hexane and dried \textit{in vacuo} to give \(\Delta\)-4a as a yellow solid (38 mg, 72%). Using a similar procedure \(\Lambda\)-4a was synthesised from \(\Lambda S\)-1a via \(\Lambda\Lambda\)-3a. \(^1\text{H} \text{NMR (CDCl}_3\): \(\delta\) 9.23 (2H, d, \(J = 8.2,\) H\textsubscript{4}), 8.23 (2H, td, \(J = 8.2, 0.8,\) H\textsubscript{3}), 8.11 (2H, d, \(J = 2.7,\) H\textsubscript{e}), 8.07 (2H, dd, \(J = 5.4, 1.2,\) H\textsubscript{1}), 7.40 (2H, dd, \(J = 7.0, 5.8,\) H\textsubscript{2}), 7.29 (2H, dd, \(J = 7.8, 0.8,\) H\textsubscript{5}), 7.05 (2H, td, \(J = 7.8, 1.2,\) H\textsubscript{3}), 6.87 (2H, td, \(J = 7.4, 1.2,\) H\textsubscript{5}), 6.84 (2H, d, \(J = 2.0,\) H\textsubscript{6}), 6.54 (2H, t, \(J = 2.7,\) H\textsubscript{1}), 6.31 (2H, dd, \(J = 7.4, 1.2,\) H\textsubscript{6}). [\(\alpha\)]\textsubscript{D} -471° for \(\Delta\)-4a and +473° for \(\Lambda\)-4a in DCM. MS (FAB): \(m/z\) 635 [M]\textsuperscript{+}. rotation, -471° in DCM.

**Measurement of enantiopurity by \(^1\text{H} \text{NMR}**

A sample of 4a (3.74 mg, \(5 \times 10^{-3}\) mmol) was dissolved in 0.5 mL of CD\textsubscript{2}Cl\textsubscript{2}. 1 equiv. of \(\Delta\)-[Bu\textsubscript{4}N][trisphat] (5.06 mg, \(5 \times 10^{-3}\) mmol) was then added [in small portions].
**Fig. S1:** Wireframe crystal structures showing key NOEs of $\Lambda S$-1a (left) and $\Delta S$-1a (right). Phenyl ring with primes is trans to O while with non-primes is trans to imine N for both the isomers.

**Fig. S2:** X-ray crystal structure of $\Lambda S$-1b. Selected bond lengths (Å) and bond angles (*°*):
- Ir(1)–N(1), 2.033(4);
- Ir(1)–N(2), 2.042(5);
- Ir(1)–N(3), 2.142(5);
- Ir(1)–O(1), 2.123(4);
- Ir(1)–C(11), 1.994(5);
- Ir(1)–C(22), 2.002(5);
- N(1)–Ir(1)–N(2), 172.84(18);
- N(1)–Ir(1)–C(11), 80.4(2);
- N(2)–Ir(1)–C(22), 80.5(2);
- N(3)–Ir(1)–O(1), 85.98(17).
**Fig. S3:** X-ray crystal structure of $\Delta S\text{-}2a$. Selected bond lengths (Å) and bond angles (°): Ir(1)—N(1), 1.997(6); Ir(1)—N(3), 2.012(6); Ir(1)—N(5), 2.139(7); Ir(1)—O(1), 2.120(5); Ir(1)—C(9), 2.000(8); Ir(1)—C(18), 2.001(8); N(1)—Ir(1)—N(3), 173.5(3); N(1)—Ir(1)—C(9), 80.4(3); N(3)—Ir(1)—C(18), 79.8(3); N(5)—Ir(1)—O(1), 88.6(3).

**Fig S4** CD spectra of $\Delta S\text{-}2b$ and $\Lambda S\text{-}2b$
Figure S5

Racemic mixture

Lambda

delta
**Fig S6** CD spectra of ∆S and ΛS-4a

**CHIRALPAK® AD-H (250mmL x 4.6 ID) / 5µm**
Eluent: n-Heptane / EtOH / TEA / TFA 90:10:0.3:0.1
Flow Rate: 1.0mL/min
Temperature: 25°C
Detection: UV 250 nm

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**Totals**

|               | 44978399 | 100.00  |

Fig S7a
**Fig S7b**

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**Totals**

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As mentioned in the paper to check the enantiopurity of $\Delta\Delta$-3a it was reacted separately with L1 and L2. In each case this gave only 1 diastereomer. Relevant parts of the NMR spectra are shown below.

Figure S8: (a) Selected part of the crude $^1$H NMR spectrum of the reaction of $\Delta\Delta$-3a with (S)-Na(L1). $\Delta S$-$1a:\Lambda S$-$1a$ ratio is 53:1; (b) Selected part of the crude NMR spectrum of the 50:50 mixture of $\Delta S$-$1a:\Lambda S$-$1a$ formed from the reaction of racemic $[\text{Ir}(ppz)_2\text{Cl}]_2$ with (S)-Na(L1).

Figure S9: (a) Selected part of the crude $^1$H NMR spectrum of the reaction of $\Delta\Delta$-3a with (S)-Na(L2). Only $\Delta S$-$2a$ is observed; (b) Selected part of the crude NMR spectrum of the 50:50 mixture of $\Delta S$-$1a:\Lambda S$-$1a$ formed from the reaction of racemic $[\text{Ir}(ppz)_2\text{Cl}]_2$ with (S)-Na(L2).