Electronic Supplementary Information for Dalton Transactions

Supporting Information

Unprecedented Diastereoselective Generation of Chiral-at-Metal Half-Sandwich Ir(III) and Rh(III) Complexes via Anomeric Isomerism on "Sugar-Coated" N-Heterocyclic Carbene Ligands

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General methods

Materials: All chemicals were purchased from Aldrich and Nacalai Tesque. $[IrCp^*Cl_2]_2$[S1] and $[RhCp^*Cl_2]_2$[S1] were prepared according to the reported procedures. All reagents and solvents were used without further purification.

Measurements: ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 FT-NMR spectrometer. Chemical shifts are expressed in ppm upfield from $SiMe_4$ (^1H) and referenced to solvent peaks (^{13}C). Electrospray mass spectrometry was performed on an Applied Biosystem Mariner spectrometer using HPLC grade solvents. Elemental analyses were performed by Analytical Research Center at Osaka City University on a J-Science Lab, JM-10 elemental analyzer.

X-ray Crystallographic analyses: Data were collected on a Rigaku AFC-7/Mercury CCD area-detector diffractomer with graphite monochromated Mo-Kα radiation (λ = 0.7107 Å). The CrystalClear software[S2] was used for data collections, processing, and corrections for Lorrentzian and polarization effects. Absorption corrections were applied by the Coppen's numerical or multi scan methods. The structures were solved by using the SIR97 direct method,[S3] expanded using Fourier techniques, and refined by full matrix least-squares against F^2 using CRYSTALS software.[S4] CrystalStructure[S5] was used for a graphical interface.

DFT Calculations: DFT calculations were carried out using Gaussian03.[S6] Atomic coordinates were optimized at B3LYP/LanL2DZ (for Ir)/6-31G(d) (for others) level. Structural optimization of ***R*-[Ir4β]$^+$** was started from the structure based on the crystallographic analysis. For the other complexes, starting coordinates were generated by the modification of the structure of the optimized ***R*-[Ir4β]$^+$**.

Synthesis of 1-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)imidazole (1α) and 1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)imidazole (1β): These compounds were prepared by modified methods that previously reported.[S7] A mixture of well-grinded D-glucose (20 g, 0.11 mol), acetic anhydride (73 g, 0.72 mol), and catalytic amount of I_2 (0.25 g, 1.0 mmol) was stirred in a 300 mL flask at room temperature followed by an exothermic reaction resulting in dissolving all the solids. After 1 h, the reaction mixture was cooled in an ice bath and then a 33% HBr/CH_3COOH solution (100 mL) was added. A drying tube with $CaCl_2$ was attached to the flask, and then the mixture was stirred overnight. The resulting mixture was poured into 300 g of ice and the resulting aqueous solution was extracted with 100 mL of CH_2Cl_2 three times. The separated organic phase was washed with 300 mL of water, 10% $Na_2S_2O_3$aq., cold saturated aqueous $NaHCO_3$, and brine. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure to give a viscous solid of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide. Imidazole (17 g, 0.25 mol) and dioxane (300 mL) were added to the solid and the mixture was refluxed for 3 h. The dioxane layer was separated and the solvent was removed under reduced pressure. The residue was dissolved in $CHCl_3$ and the solution was washed with dilute aqueous ammonia, water, and brine. The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was washed with diethylether to give a mixture of anomeric isomers of 1-(2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl)imidazole (**1α** : **1β** = 1 : 3). Yield: 24 g (0.06 mol, 54%). Recrystallization from MeOH several times gave needle-shape microcrystals of pure **1β** and a mother liquor mainly containing **1α** with a small amount of **1β**. The solvent of the separated mother liquor was

evaporated and the residue was purified by silica-gel column chromatography (eluent *n*-hexane : CH_2Cl_2 : MeOH = 5 : 5 : 1) several times to give pure **1α**.

3-(2-picolyl)-1-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)imidazolium chloride (2αHCl): A mixture of **1α** (2.0 g, 5.0 mmol), 2-(bromomethyl)pyridine hydrobromide (1.4 g, 6.0 mmol), and $NaHCO_3$ (0.85 g, 10.0 mmol) in acetonitrile (100 mL) were refluxed overnight. The resulting mixture was cooled to room temperature. After insoluble solids were filtered off, the solvent was evaporated to dryness. The resulting solid was dissolved in 200 mL of H_2O and the solution was washed with $CHCl_3$ twice and then with *n*-hexane. Dowex ion-exchange resin (Cl form, 10 g) was added to the separated aqueous phase. After the mixture was stirred for 10 min, Dowex was filtered off followed by the removal of the solvent to give a yellow oily material. The material was dissolved in $CHCl_3$ and the solution was dried over $MgSO_4$. The solvent of the solution was evaporated to give a yellow hygroscopic powder. Yield 2.1 g (4.0 mmol, 80%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.46 (s, 1H, 2-imidazolium), 8.59 (d, 1H, 6-pyridine), 8.12 (d, 1H, 3-pyridine), 8.02 (s, 1H, 4-imidazolium), 7.95 (t, 1H, 4-pyridine), 7.66 (s, 1H, 3-imidazolium), 7.45 (dd, 1H, 5-pyridine), 6.64 (d, 1H, 1-glucose), 6.07 (d, 1H, py-CH_2-N), 6.05 (d, 1H, py-CH_2-N), 5.53 (dd, 1H, 2-glucose), 5.37 (t, 1H, 3-glucose), 5.10 (dd, 1H, 4-glucose), 4.44 (dd, 1H, 6-glucose), 4.33 (dd, 1H, 6-glucose), 4.25 (ddd, 1H, 5-glucose), 2.15 (s, 3H, AcO), 2.12 (s, 3H, AcO), 2.09 (s, 3H, AcO), 2.07 (s, 3H, AcO). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6 (C=O), 169.6 (C=O), 169.4 (C=O), 168.9 (C=O), 151.5 (2-pyridine), 148.1 (6-pyridine), 140.0 (4-pyridine), 138.1 (2-imidazolium), 125.7 (3-pyridine), 124.9 (5-pyridine), 123.5 (3-imidazolium), 120.3 (4-imidazolium), 81.9 (1-glucose), 73.2 (5-glucose), 68.7 (3-glucose), 67.8 (2-glucose), 67.1 (4-glucose), 61.4 (6-glucose), 53.1 (py-CH_2-N), 20.9 (CH_3-Ac), 20.8 (2C, CH_3-Ac), 20.7 (CH_3-Ac). ESI-MS: *m/z* 490 ($[M - Cl]^+$).

3-(2-picolyl)-1-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)imidazolium chloride (2βHCl): This material was synthesized in a similar manner for **2αHCl** using **1β** instead of **1α**. Yield: 2.35 g (4.5 mmol, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.47 (s, 1H, 2-imidazolium), 8.54 (d, 1H, 6-pyridine), 7.7–8.0 (m, 2H, 3,4-pyridine), 7.63 (s, 1H, 4-imidazolium), 7.46 (s, 1H, 5-imidazolium), 7.31 (m, 1H, 5-pyridine) 6.37

(d, 1H, 1-glucose), 5.81 (d, 2H, py-CH_2-N), 5.48, (t, 1H, 4-glucose) 5.26, 5.23 (t, 2H, 2,3-glucose), 4.33 (dd, 1H, 6-glucose), 4.23 (ddd, 1H, 5-glucose), 4.15 (dd, 1H, 6-glucose), 2.08, 2.06, 2.01, 2.00 (s, 12H, OAc) ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5 (C=O), 169.8 (C=O), 169.6 (C=O), 169.5 (C=O), 152.4 (2-pyridine), 150.0 (6-pyridine), 138.7 (2-imidazole), 137.9, 124.2, 124.1 (3,4,5-pyridine), 123.5 (4-imidazole), 118.7 (5-imidazole), 84.2 (1-glucose), 75.2 (5-glucose), 72.5 (4-glucose), 70.6, 67.6 (2,3-glucose), 61.4 (6-glucose), 54.4 (py-CH_2-N), 20.8 (CH_3), 20.6 (CH_3), 20.53 (CH_3), 20.51 (CH_3). ESI-MS: *m/z* 490 ($[M - Cl]^+$)

[IrCp*Cl(α-pagi)]Cl (Ir4α): A mixture of **2αHCl** (105 mg, 0.20 mmol) and Ag_2O (28 mg, 0.12 mmol) in 10 mL of $CHCl_3$ was stirred for 1 h at room temperature producing a silver NHC complex **3α** quantitatively checked by *in-situ* ^{1}H NMR measurement. $[IrCp^*Cl_2]_2$ (80 mg, 0.10 mmol) was added to the mixture and the mixture was stirred for 1h. After addition of Celite, the mixture was stirred for additional 30 min. The mixture was filtered over Celite to remove AgCl and the solvent of the filtrate was removed under reduced pressure to give a red oily material, which was dissolved in 2 mL of $CHCl_3$. The solution was added dropwise to 40 mL of *n*-hexane with stirring to afford a yellow powder of the diastereomeric mixture of the product. Diastereomeric ratio *R* : *S* = 1 : 9. The powder was collected by suction filtration and dried in *vacuo*. Yield: 164 mg (0.18 mmol, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) for the major product (*S* form): δ 8.68 (d, 1H, pyridine), 8.36 (s, 1H, 4-imidazole), 8.33 (d, 1H, 3-pyridine), 7.88 (t, 1H, 4-pyridine), 7.39 (s, 1H, 3-imidazole), 7.33 (t, 1H, 5-pyridine), 6.86 (d, 1H, CH_2N), 6.48 (d, 1H, 1-glucose), 5.60 (t, 1H, 2-glucose), 5.34 (t, 1H, 3-glucose), 5.12 (dd, 1H, 4-glucose), 4.79 (d, 1H, CH_2N), 4.44 (dt, 1H, 5-glucose), 4.25 (d, 2H, 6-glucose), 2.15 (s, 3H, AcO), 2.10 (s, 3H, AcO), 2.07 (s, 3H, AcO), 1.98 (s, 3H, AcO) 1.69 (s, 15H, Cp*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4 (C=O), 169.4 (C=O), 169.1 (C=O), 168.2 (C=O), 157.8 (2-pyridine), 155.7 (6-pyridine), 155.6 (carbene) 140.5 (4-pyridine), 127.2 (3-pyridine), 126.3 (5-pyridine), 124.6 (4-imidazole), 120.1 (3-imidazole), 91.3 ($C_5(CH_3)_5$), 81.4 (1-glucose), 71.7 (5-glucose), 70.9 (3-glucose), 69.4 (2-glucose), 68.8 (4-glucose), 62.3 (6-glucose), 54.5 (CH_2-N), 20.92 ($2CH_3$-AcO), 20.90 (CH_3-AcO), 20.73 (CH_3-AcO), 9.2 ($C_5(CH_3)$). ESI-MS: *m/z* = 852 ($[M - Cl]^+$).

[IrCp*Cl(β-pagi)]Cl (Ir4β): This complex was synthesized in a similar manner for **4α** using **2βHCl** instead of **2αHCl**. Yield: 170 mg (0.19 mmol, 96%). Diastereomeric ratio *R* : *S* = 9 : 1. ^{1}H NMR (300 MHz, $CDCl_3$) for the major product (*R* form): δ8.74 (d, 1H, 6-pyridine), 8.41 (d, 1H, 3-pyridine), 8.22 (d, 1H, 5-imidazolium), 7.93 (t, 1H, 4-pyridine), 7.36 (t, 1H, 5-pyridine), 7.32 (d, 1H, 4-imidazolium), 7.04 (d, ^{2}J = 16 Hz, CH_2N), 5.96 (d, 1H, 1-glucose), 5.43 (t, 1H, 2-glucose), 5.39 (t, 1H, 3-glucose), 5.18 (t, 1H, 4-glucose), 4.74 (d, 1H, CH_2N), 4.21 (d, 2H, 6-glucose), 3.95 (dt, 1H, 5-glucose), 2.08 (s, 3H, AcO), 2.07 (s, 3H, AcO), 2.00 (s, 3H, AcO) 1.69 (s, 15H, Cp*). ^{13}C NMR (75 MHz, $CDCl_3$): δ170.2 (C=O), 169.8 (C=O), 169.3 (C=O), 169.1 (C=O), 157.4 (2-imidazolium), 155.7 (2-pyridine), 155.3 (6-pyridine), 140.4 (4-pyridine), 127.3 (3-pyridine), 126.1 (5-pyridine), 124.4 (5-imidazolium), 119.3 (4-imidazolium), 91.1 ($C_5(CH_3)_5$), 84.5 (1-glucose), 74.2 (5-glucose), 72.8 (3-glucose), 68.9 (2-glucose), 68.2 (4-glucose), 62.4 (6-glucose), 54.5 (CH_2-N), 20.72 (CH_3-AcO), 20.56 (CH_3-AcO), 20.49 (CH_3-AcO), 20.45 (CH_3-AcO), 9.3 ($C_5(CH_3)$). ESI-MS: *m/z* = 852 ($[M - Cl]^+$).

[IrCp*Cl(β-pagi)]PF_6 (Ir4β-PF_6): A mixture of Ir**4β** and an excess amount of KPF_6 in 5 mL of CH_2Cl_2 was stirred for 1h followed by filtration to remove insoluble solids. Et_2O was slowly diffused into the filtrate gave a yellow cotton-like solid of the product. Anal. Calcd for $C_{33}H_{42}N_3O_9F_6PClIr•0.20CH_2Cl_2$: C, 39.31; H, 4.21; N, 4.14. Found: C, 39.28; H, 4.21; N, 4.30. ^{1}H NMR (300 MHz, $CDCl_3$) for the major product (*R* form): δ8.77 (d, 1H, 6-pyridine), 7.95 (t, 1H, 4-pyridine), 7.84 (d, 1H, 3-pyridine), 7.50 (d, 1H, 4-imidazole), 7.40 (t, 1H, 5-pyridine), 7.38 (d, 1H, 5-imidazole), 5.95 (m, 1H, 1-glucose), 5.58 (d, 1H, CH_2-N), 5.40 (m, 2H, 2,3-glucose), 5.17 (m, 1H, 4-glucose), 4.86 (d, 1H, CH_2-N), 4.21 (d, 2H, 6-glucose), 3.96 (dt, 1H, 5-glucose), 2.08 (s, 6H, Ac), 2.01 (s, 3H, Ac), 1.69 (s, 15H, Cp*), 1.67 (s, 3H, Ac), ^{13}C NMR (75 MHz, $CDCl_3$): δ170.3 (C=O), 169.8 (C=O), 169.5 (C=O), 158.7 (carbene), 155.9 (6-pyridine), 155.0 (2-pyridine), 140.7 (4-pyridine), 126.6, 126.4 (3,5-pyridine), 123.5 (4-imidazole), 120.1 (5-imidazole), 91.6 (Cp*), 84.8 (-glucose), 74.4 (5-glucose), 72.8, 69.4 (2,3-glucose), 68.4 (4-glucose), 62.6 (6-glucose), 55.3 (CH_2-N), 20.8 (CH_3-Ac), 20.7 (CH_3-Ac), 20.6 (CH_3-Ac), 9.3 (CH_3-Cp*).

[RhCp*Cl(α-pagi)]Cl (Rh4α): This complex was synthesized in a similar manner for **Ir4α** using $[RhCp^*Cl_2]_2$ (62 mg, 0.10 mmol) instead of $[Cp^*IrCl_2]_2$. Yield: 162 mg (0.20 mmol, >99%). Diastereomeric ratio *R* : *S* = 1 : 9. ^{1}H NMR (300 MHz, $CDCl_3$) for the major product (*S* form): δ8.76 (d, 1H, 6-pyridine), 8.37 (s, 1H, 4-imidazole), 8.23 (d, 1H, 3-pyridine), 7.92 (t, 1H, 4-pyridine), 7.42 (s, 1H, 3-imidazole), 7.40 (t, 1H, 5-pyridine), 6.86 (d, 1H, CH_2N), 6.52 (d, 1H, 1-glucose), 5.59 (t, 1H, 2-glucose), 5.35 (t, 1H, 3-glucose), 5.12 (dd, 1H, 4-glucose), 4.96 (d, 1H, CH_2N), 4.45 (dt, 1H, 5-glucose), 4.27 (d, 2H, 6-glucose), 2.16 (s, 3H, AcO), 2.11 (s, 3H, AcO), 2.08 (s, 3H, AcO), 1.96 (s, 3H, AcO) 1.68 (s, 15H, Cp*). ^{13}C NMR (75 MHz, $CDCl_3$): δ172.4 (d, ^2J = 52 Hz, carbene) 170.4 (C=O), 169.5 (C=O), 169.2 (C=O), 168.2 (C=O), 155.8 (2-pyridine), 155.3 (6-pyridine), 140.3 (4-pyridine), 127.3 (3-pyridine), 125.9 (5-pyridine), 125.7 (4-imidazole), 121.0 (3-imidazole), 98.8 ($C_5(CH_3)_5$), 81.7 (1-glucose), 71.9 (5-glucose), 70.9 (3-glucose), 69.2 (2-glucose), 68.8 (4-glucose), 62.4 (6-glucose), 54.1 (CH_2-N), 21.0 ($2CH_3$-AcO), 20.8 (CH_3-AcO), 9.6 ($C_5(CH_3)$). ESI-MS: *m/z* = 762 ($[M - Cl]^+$).

[RhCp*Cl(β-pagi)]Cl (Rh4β): This complex was synthesized in a similar manner for **Ir4β** using $[RhCp^*Cl_2]_2$ (62 mg, 0.10 mmol) instead of $[IrCp^*Cl_2]_2$. Yield: 156 mg (0.20 mmol, 98%). Diastereomeric ratio *R* : *S* = 9 : 1. ^{1}H NMR (300 MHz, $CDCl_3$) for the major product (*R* form): δ8.79 (d, 1H, 6-pyridine), 8.34 (d, 1H, 3-pyridine), 8.24 (d, 1H, 5-imidazolium), 7.94 (t, 1H, 4-pyridine), 7.39 (t, 1H, 5-pyridine), 7.32 (d, 1H, 4-imidazolium), 6.79 (d, CH_2N), 6.05 (m, 1H, 1-glucose), 5.42 (m, 2H, 2,3-glucose), 5.18 (m, 1H, 4-glucose), 4.99 (d, 1H, CH_2N), 4.21 (d, 2H, 6-glucose), 3.96 (dt, 1H, 5-glucose), 2.09 (s, 3H, AcO), 2.07 (s, 3H, AcO), 1.99 (s, 3H, AcO) 1.68 (s, 15H, Cp*), 1.61 (s, 3H, AcO).

[RhCp*Cl(β-pagi)]PF_6 (Rh4β-PF_6): This complex was synthesized in a similar manner for **Ir4β-PF_6** using **Rh4β** instead of **Ir4β**. Anal. Calcd for $C_{33}H_{42}N_3O_9F_6PClRh\bullet0.20CH_2Cl_2$: C, 43.11; H, 4.62; N, 4.54. Found: C, 43.03; H, 4.58; N, 4.65. ^{1}H NMR (300 MHz, $CDCl_3$) for the major product (*R* form): δ8.84 (d, 1H, 6-pyridine), 7.97 (t, 1H, 4-pyridine), 7.80 (d, 1H, 3-pyridine), 7.54 (d, 1H, 4-imidazole), 7.45 (t, 1H, 5-pyridine), 7.41 (d, 1H, 5-imidazole), 6.04 (m, 1H, 1-glucose), 5.58 (d, 1H, CH_2-N), 5.42 (m, 2H, 2,3-glucose), 5.20 (m, 1H, 4-glucose), 5.05 (d, 1H, CH_2-N), 4.22 (d, 2H, 6-glucose),

3.98 (dt, 1H, 5-glucose), 2.08 (s, 6H, Ac), 2.00 (s, 3H, Ac), 1.67 (s, 15H, Cp*), 1.62 (s, 3H, Ac), ^{13}C NMR (75 MHz, $CDCl_3$): δ173.8 (d, ^2J = 52 Hz, carbene), 170.4 (C=O), 169.8 (C=O), 169.59 (C=O), 169.57 (C=O), 155.4 (6-pyridine), 155.1 (2-pyridine), 140.4 (4-pyridine), 126.5 (3-pyridine), 126.0 (5-pyridine), 124.6 (4-imidazole), 120.9 (5-imidazole), 99.0 (Cp*), 84.9 (1-glucose), 74.3 (5-glucose), 72.8, (3-glucose), 69.6 (2-glucose), 68.4 (4-glucose), 62.6 (6-glucose), 54.9 (CH_2-N), 20.8 (CH_3-Ac), 20.7 (CH_3-Ac), 20.6 (CH_3-Ac), 20.5 (CH_3-Ac), 9.6 (CH_3-Cp*).

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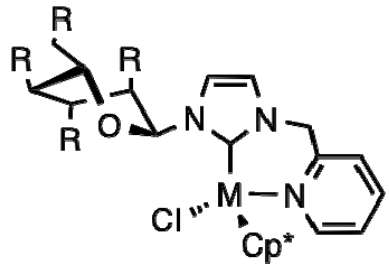

Fig. S1 Proposed Skew Structure of *S*-α-Complexes, ***S*-[M4α]$^+$,** (M = Ir, Rh; R = OAc).

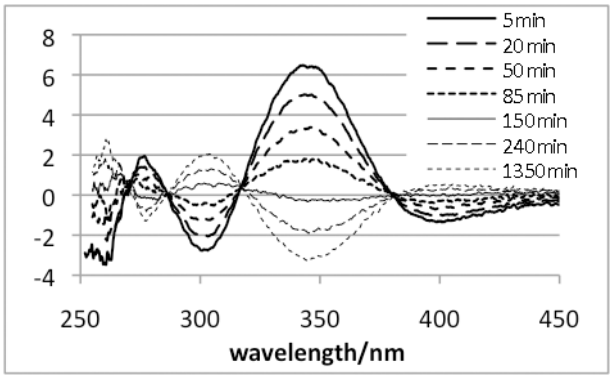

Fig. S2 CD spectra of **Rh4β** with isosbestic point.

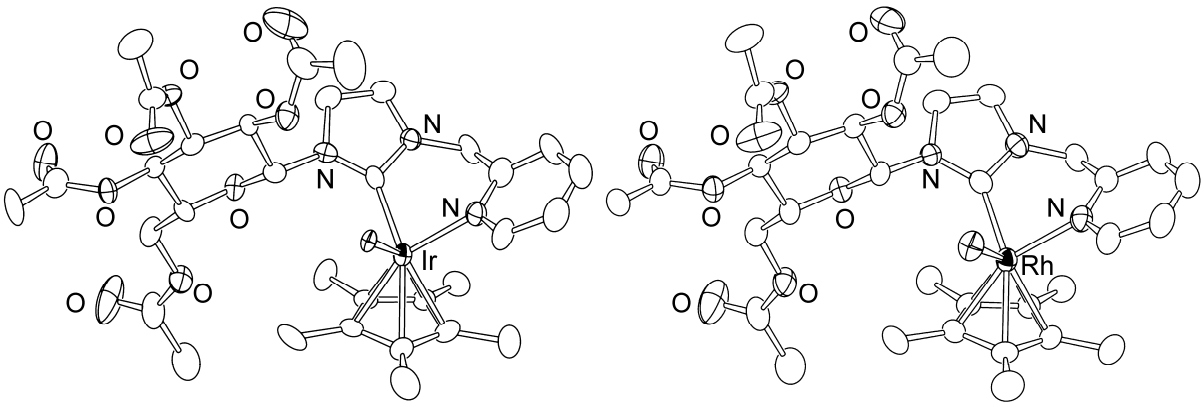

Fig. S3 ORTEP of **Ir4β-PF_6** (left) and **Rh4β-PF_6** (right) with 50% probability of thermal ellipsoids. Hydrogen atoms, counter ions, and solvent molecules were omitted for clarity.

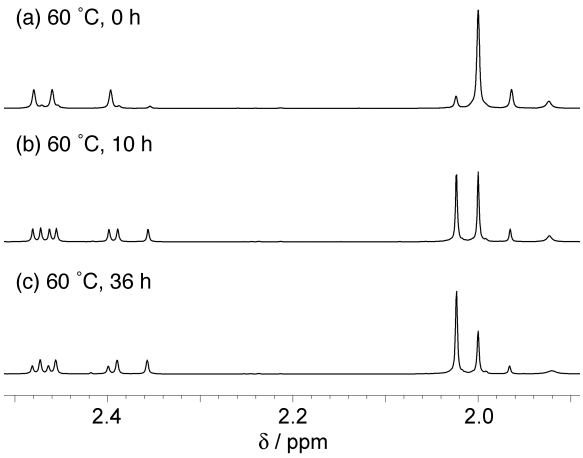

Fig. S4 ^{1}H NMR spectra of **Ir4β** in D_2O showing isomerization of the complex.

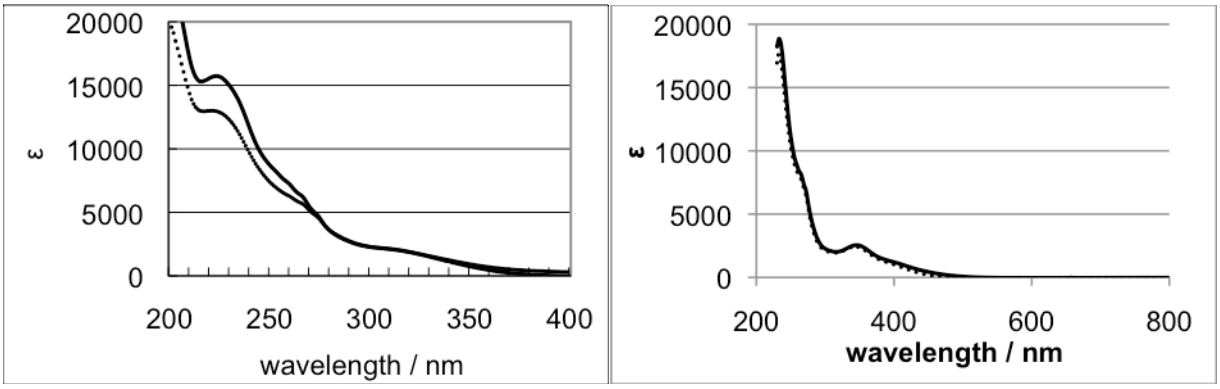

Fig. S5 Absorption spectra of the compelxes. Left: **Ir4α** (dashed line) and **Ir4β** (solid line) in H_2O. Right: **Rh4α** (dashed line) and **Rh4β** (solid line) in CH_2Cl_2. Each sample was a crude diastereomeric mixture with the ratio of the major and minor diastereomers was 9 : 1.

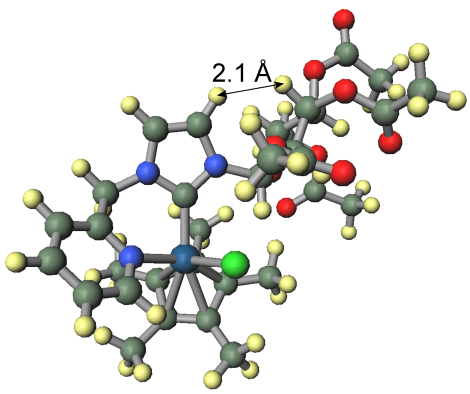

Fig. S6 Optimized structure of ***S*-[Ir4α]**

Table S1 Crystallographic Data for Complexes ***R*-Ir4β-PF_6** and ***R*-Rh4β-PF_6**

	***R*-Ir4β-PF_6•$2CH_3OH$•H_2O**	***R*-Rh4β-PF_6•CH_2Cl_2**
formula	$C_{35}H_{52}ClF_6IrN_3O_{12}P$	$C_{34}H_{44}Cl_3F_6N_3O_9PRh$
fw	1079.44	992.96
cryst system	*Orthorhombic*	*Orthorhombic*
space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a (Å)	12.6224(13)	12.5638(7)
b (Å)	15.2989(18)	15.2175(9)
c (Å)	22.254(3)	22.2295(14)
V (Å^3)	4297.4(9)	4250.0(4)
Z	4	4
D_{calcd} (g/cm^3)	1.668	1.552
diffractometer	AFC-7/Mercury CCD	AFC-7/Mercury CCD
temp (K)	193(1)	193(1)
reflcns collcd	42049	41443
indpdt reflcns	9707 (R_{int} = 0.069)	9654 (R_{int} = 0.043)
μ (mm^{-1})	3.302	0.706
T_{min}–T_{max}	0.413–0.517	0.843–0.900
data/para	9707/ 574	9654/559
R_1 [$I > 2\sigma(I)$]	0.0455	0.0454
wR_2 (all data)	0.0968	0.1062
GOF on F^2	1.002	1.021
Flack Para.	0.051(7)	0.00(2)

Table S2 Selected Bond Lengths and Angles for Optimized Structures of Ir Complexes

	***R*-[Ir4β]$^+$** (X-ray)	***R*-[Ir4β]$^+$**	***S*-[Ir4β]$^+$**	***R*-[Ir4α]$^+$**	***S*-[Ir4α]$^+$**	***R*-[Ir4α]$^+$**	***S*-[Ir4α]$^+$**
Conformation of D-Glc	Chair	Chair	Chair	Chair	Chair	Skew	Skew
Ir–Cl	2.4510(16)	2.4494	2.4524	2.4396	2.4600	2.4470	2.4470
Ir–C_{im}	2.035(7)	2.0238	2.0264	2.0370	2.0264	2.0310	2.0310
Ir–N_{py}	2.100(5)	2.1619	2.1667	2.1795	2.1684	2.1669	2.1669
Ir–C_{Cp*}	2.170(7)	2.2217	2.2244	2.2132	2.2170	2.2477	2.2251
	2.175(8)	2.2414	2.2244	2.2363	2.2326	2.2251	2.2243
	2.166(8)	2.2279	2.2105	2.2293	2.2138	2.2243	2.2936
	2.248(7)	2.3108	2.3278	2.3122	2.3178	2.2936	2.2902
	2.214(8)	2.3105	2.3224	2.3208	2.3140	2.2902	2.2477
GlcH-ImH[a]				2.06	2.08		
Ir–C_{Cp*} *av*	2.262(30)	2.2625	2.2619	2.2624	2.2590	2.2562	2.2562
C_{im}–Ir–N_{py}	85.3(2)	83.7	84.1	85.1	84.6	83.6	84.4
C_{im}–Ir–Cl	90.5(2)	92.0	90.6	90.7	89.2	89.9	89.4
Cl–Ir–N_{py}	86.52(19)	86.4	85.7	83.8	85.1	85.6	84.5
N_{im}–C_{br}–C_{py}	112.3(6)	111.7	111.7	111.9	111.8	111.2	112.1
G/Hartree		–2688.242	–2688.254	–2688.238	–2688.247	–2688.311	–2688.320
ΔG/kcal		7.53[b]	–	51.5[c]	45.8[c]	5.65[c]	–

[a]Shortest distance between methyne proton of glucopyranosyl group and imidazolylidene backbone proton

[b]Energy difference between chair ***S*-[Ir4β]$^+$**. [c]Energy difference between skew ***S*-[Ir4α]$^+$**.

Table S3 Selected Bond Lengths and Angles for Ir and Rh Complexes

	Ir4β-PF_6	**Rh4β-PF_6**	[$IrCp^*Cl(mpim)]^+$	[$RhCp^*Cl_2$(dmim)]
M–Cl	2.4510(16)	2.4003(10)	2.441(3)	2.424 (4)
M–C_{im}	2.035(7)	2.036(3)	2.02(1)	2.050(3)
M–N_{py}	2.100(5)	2.112(3)	2.10(1)	
M–C_{Cp*}	2.166(8)	2.155(3)	2.16(1)	2.139(4)
	—2.248(7)	—2.225(3)	—2.22(1)	—2.230(3)
M–C_{Cp*} *av*	2.262(30)	2.185(29)	2.19(2)	2.152(33)
C_{im}–M–N_{py}	85.3(2)	84.87(14)	85.4(5)	90.0(2)
C_{im}–M–Cl	91.55(11)	90.5(2)	88.4(4)	87.9(1)
Cl–M–N_{py}	88.56(9)	86.52(19)	84.7(3)	86.9(1)
N_{im}–C_{br}–C_{py}	113.4(3)	112.3(6)	114(1)	

DFT Calculations:

Table S4 Optimized atomic coordinates of ***R*-[Ir4α]$^+$** with chair conformation

number	atom	x	y	z
1	Ir	2.479909	-0.1017	-0.313242
2	Cl	1.248784	-2.190042	-0.586988
3	N	1.4342	0.861015	2.294007
4	N	-0.271654	0.775736	0.970936
5	N	3.35226	-1.124634	1.403437
6	C	1.084199	0.565611	1.01145
7	C	0.333067	1.231185	3.053066
8	C	-0.73255	1.180758	2.222878
9	C	2.810316	0.81304	2.781859
10	C	3.416164	-0.560986	2.629531
11	C	4.01992	-1.210491	3.70377
12	C	4.581703	-2.473095	3.514714
13	C	4.500397	-3.054938	2.252774
14	C	3.868515	-2.357866	1.22756
15	C	-1.112536	0.581051	-0.239763
16	C	2.333101	0.815385	-2.321702
17	C	3.315312	-0.260907	-2.472431
18	C	4.398766	-0.004634	-1.599671
19	C	4.139066	1.262078	-0.909342
20	C	2.902922	1.795039	-1.418729
21	C	1.148536	0.994566	-3.226868
22	C	3.146505	-1.418092	-3.405014
23	C	5.652253	-0.814494	-1.447298
24	C	5.137824	1.985467	-0.053688
25	C	2.370236	3.168378	-1.144251
26	H	0.40927	1.506402	4.093491
27	H	-1.759581	1.435676	2.410661
28	H	3.402947	1.547366	2.226314
29	H	2.804066	1.107118	3.832888
30	H	4.045816	-0.729404	4.676244
31	H	5.060502	-2.992285	4.339131
32	H	4.906063	-4.041137	2.054856
33	H	3.741368	-2.785289	0.241884
34	H	0.588421	0.060849	-3.334452
35	H	1.487495	1.293821	-4.227847
36	H	0.466999	1.770411	-2.870895
37	H	3.924232	-2.172486	-3.268093
38	H	3.197492	-1.064016	-4.442542
39	H	2.176564	-1.901379	-3.25556
40	H	5.996055	-0.840431	-0.408771
41	H	6.459887	-0.37427	-2.046423
42	H	5.516034	-1.844438	-1.785746
43	H	4.669634	2.77846	0.535973
44	H	5.903628	2.457656	-0.683264
45	H	5.655059	1.305791	0.630383

46	H	1.29736	3.238334	-1.327746
47	H	2.863533	3.883698	-1.815758
48	H	2.574535	3.488752	-0.118257
49	C	-2.326486	1.548433	-0.339482
50	C	-3.613791	1.070989	0.354005
51	C	-3.86526	-0.414662	0.098029
52	C	-2.595299	-1.207047	0.435783
53	C	-2.71152	-2.711561	0.234823
54	O	-2.072764	2.870141	0.166861
55	O	-4.669015	1.850635	-0.201032
56	O	-4.937179	-0.847144	0.945086
57	O	-1.54349	-0.732387	-0.416584
58	O	-3.247216	-3.015976	-1.059221
59	H	-0.440131	0.77648	-1.070564
60	H	-2.543401	1.620497	-1.40809
61	H	-3.549297	1.228568	1.433194
62	H	-4.13861	-0.578377	-0.945911
63	H	-2.320819	-1.050697	1.490986
64	H	-1.710653	-3.147357	0.293644
65	H	-3.354692	-3.14305	1.003817
66	C	-1.485047	3.757279	-0.684458
67	C	-5.5074	2.653957	0.539777
68	C	-6.076389	-1.321018	0.323137
69	C	-4.360151	-3.80899	-1.096471
70	C	-1.550149	5.159125	-0.141831
71	O	-0.994154	3.421001	-1.740697
72	C	-5.455296	2.557323	2.051927
73	O	-6.24964	3.384887	-0.059188
74	C	-7.040186	-1.884889	1.329392
75	O	-6.224549	-1.308326	-0.873753
76	C	-4.834634	-4.003805	-2.510882
77	O	-4.894123	-4.254673	-0.104379
78	H	-1.287875	5.180784	0.919823
79	H	-2.577603	5.52978	-0.235487
80	H	-0.885262	5.806189	-0.714749
81	H	-5.55163	1.522831	2.395766
82	H	-6.27853	3.15274	2.447253
83	H	-4.514271	2.963907	2.441115
84	H	-6.803506	-2.949102	1.448305
85	H	-8.057765	-1.798365	0.944624
86	H	-6.950871	-1.396624	2.302147
87	H	-5.502556	-3.17074	-2.759398
88	H	-5.400257	-4.934573	-2.578829
89	H	-4.001208	-4.003731	-3.216674

Table S5 Optimized atomic coordinates of ***S*-[Ir4α]$^+$** with chair conformation

number	atom	x	y	z
1	Ir	-2.330119	0.369939	-0.198442
2	Cl	-1.510489	-1.26718	-1.84255
3	N	-1.516428	-0.902457	2.361373
4	N	0.279632	-0.653614	1.187295
5	N	-3.667484	-1.213855	0.437097
6	C	-1.064168	-0.410142	1.178034
7	C	-0.483902	-1.463694	3.101741
8	C	0.640308	-1.305921	2.365359
9	C	-2.925796	-0.870707	2.743428
10	C	-3.796528	-1.58169	1.732471
11	C	-4.698586	-2.568779	2.123183
12	C	-5.492687	-3.195174	1.162816
13	C	-5.340329	-2.826043	-0.170841
14	C	-4.411618	-1.842667	-0.4959
15	C	1.180266	-0.24805	0.086119
16	C	-1.666434	2.216249	-1.22947
17	C	-2.951264	1.87041	-1.852146
18	C	-3.946929	1.892597	-0.849655
19	C	-3.315322	2.257753	0.422052
20	C	-1.92129	2.536124	0.151716
21	C	-0.400504	2.459408	-1.995072
22	C	-3.121913	1.57091	-3.309007
23	C	-5.414743	1.641253	-1.026785
24	C	-4.060563	2.606651	1.677992
25	C	-0.941489	3.127336	1.11821
26	H	-0.638913	-1.913912	4.069921
27	H	1.646413	-1.623087	2.576319
28	H	-3.239592	0.173825	2.83952
29	H	-3.021409	-1.345613	3.721405
30	H	-4.773215	-2.84247	3.170682
31	H	-6.203937	-3.962741	1.451648
32	H	-5.919491	-3.29371	-0.959617
33	H	-4.22788	-1.549171	-1.521304
34	H	-0.241294	1.681421	-2.747266
35	H	-0.466272	3.422355	-2.518907
36	H	0.47139	2.505305	-1.340112
37	H	-4.126793	1.207305	-3.536738
38	H	-2.954151	2.481322	-3.898312
39	H	-2.403	0.81539	-3.640225
40	H	-5.839845	1.102089	-0.174924
41	H	-5.950307	2.596011	-1.107529
42	H	-5.625487	1.067601	-1.932575
43	H	-3.405219	2.597446	2.553487
44	H	-4.484104	3.616962	1.601105
45	H	-4.892892	1.920054	1.861791
46	H	0.087356	2.866762	0.868282

47	H	-1.016764	4.221791	1.080798
48	H	-1.149061	2.815431	2.145916
49	C	2.158255	-1.35322	-0.380324
50	C	3.482281	-1.412886	0.399893
51	C	4.065674	-0.021492	0.700046
52	C	2.965655	0.891522	1.271963
53	C	3.438156	2.320321	1.515739
54	O	1.484108	-2.611127	-0.287415
55	O	4.398357	-2.315118	-0.246176
56	O	5.052778	-0.17951	1.719973
57	O	1.851891	0.954903	0.369225
58	O	4.016926	2.893436	0.332865
59	H	0.505494	-0.025815	-0.736352
60	H	2.385644	-1.142385	-1.42661
61	H	3.320488	-1.908139	1.361216
62	H	4.465479	0.424302	-0.206716
63	H	2.644908	0.499838	2.248705
64	H	2.604635	2.939123	1.85163
65	H	4.225724	2.313354	2.271844
66	C	1.536908	-3.440019	-1.380704
67	C	4.902027	-2.014439	-1.480253
68	C	6.395983	0.113411	1.55923
69	C	3.26001	3.770142	-0.38718
70	C	0.638143	-4.62955	-1.179198
71	O	2.206901	-3.205629	-2.357305
72	C	5.640942	-3.192015	-2.053496
73	O	4.74983	-0.939439	-2.021207
74	C	6.843385	0.781103	0.277654
75	O	7.124563	-0.157218	2.475996
76	C	4.026832	4.271267	-1.583527
77	O	2.132691	4.090802	-0.081228
78	H	-0.402804	-4.295322	-1.257481
79	H	0.780887	-5.061832	-0.184647
80	H	0.840896	-5.373562	-1.950113
81	H	6.316342	-2.850899	-2.839329
82	H	4.901123	-3.871478	-2.492205
83	H	6.188329	-3.734659	-1.27895
84	H	6.630477	0.170264	-0.604865
85	H	7.918616	0.945118	0.351967
86	H	6.336761	1.742697	0.140469
87	H	4.966071	4.733272	-1.262994
88	H	3.421687	4.998526	-2.125228
89	H	4.282241	3.434893	-2.243063

Table S6 Optimized atomic coordinates of ***R*-[Ir4α]$^+$** with skew conformation

number	atom	x	y	z
1	Ir	-2.12756	-0.431257	-0.253313
2	Cl	-0.834487	0.897062	-1.859075
3	N	-1.784845	1.090056	2.283304
4	N	0.196781	0.713395	1.539664
5	N	-3.404073	1.297426	-0.102711
6	C	-1.118217	0.46528	1.275467
7	C	-0.909896	1.747066	3.143111
8	C	0.336321	1.507979	2.674493
9	C	-3.242648	1.154173	2.333149
10	C	-3.803806	1.802109	1.087563
11	C	-4.686441	2.876588	1.162033
12	C	-5.172356	3.451411	-0.012049
13	C	-4.736451	2.94333	-1.23213
14	C	-3.845124	1.875501	-1.239228
15	C	1.320319	0.32549	0.692167
16	C	-1.596823	-2.37927	-1.269533
17	C	-2.883025	-1.935922	-1.806303
18	C	-3.813902	-1.906534	-0.730491
19	C	-3.122774	-2.267832	0.498405
20	C	-1.753994	-2.610097	0.135567
21	C	-0.39894	-2.66566	-2.119229
22	C	-3.143394	-1.673683	-3.258576
23	C	-5.271581	-1.57477	-0.829016
24	C	-3.774358	-2.590251	1.811804
25	C	-0.754659	-3.248588	1.051907
26	H	-1.250147	2.309799	3.997738
27	H	1.30366	1.829648	3.017297
28	H	-3.636541	0.139329	2.440849
29	H	-3.528591	1.727331	3.21611
30	H	-4.98307	3.259145	2.132892
31	H	-5.862984	4.287463	0.029058
32	H	-5.064268	3.368059	-2.174195
33	H	-3.441434	1.474195	-2.159689
34	H	-0.144653	-1.800109	-2.736669
35	H	-0.633577	-3.500224	-2.791469
36	H	0.476159	-2.951807	-1.53596
37	H	-4.099704	-1.16986	-3.415924
38	H	-3.171909	-2.61722	-3.816448
39	H	-2.353549	-1.052356	-3.688705
40	H	-5.640554	-1.088091	0.07692
41	H	-5.849823	-2.496541	-0.965391
42	H	-5.485799	-0.92407	-1.679073
43	H	-3.088701	-2.441503	2.649958
44	H	-4.090263	-3.640927	1.832764
45	H	-4.66734	-1.984001	1.985839
46	H	0.255586	-3.202142	0.644473

47	H	-1.00184	-4.310291	1.173067
48	H	-0.764078	-2.796101	2.047028
49	C	2.269717	-0.680664	1.34293
50	C	3.312717	-1.10495	0.279232
51	C	3.569557	0.007112	-0.749174
52	C	3.345849	1.397144	-0.125065
53	C	3.561798	2.534474	-1.113535
54	O	2.900132	-0.04892	2.472589
55	O	2.766534	-2.228186	-0.419371
56	O	4.92931	-0.130064	-1.189802
57	O	1.990373	1.518545	0.354723
58	O	3.557309	3.769555	-0.381605
59	H	0.871078	-0.149171	-0.186944
60	H	1.733631	-1.569685	1.678837
61	H	4.250459	-1.354475	0.776449
62	H	2.902753	-0.121623	-1.606529
63	H	4.030801	1.526166	0.723861
64	H	4.54137	2.439436	-1.588784
65	H	2.778177	2.545797	-1.873106
66	C	3.453787	-0.892606	3.398337
67	C	3.159233	-3.531522	-0.205193
68	C	5.151549	-0.128782	-2.549207
69	C	2.679612	4.735216	-0.782678
70	C	4.037249	-0.1251	4.553273
71	O	3.4476	-2.095753	3.267099
72	C	4.492055	-3.783155	0.454753
73	O	2.40736	-4.394549	-0.586609
74	C	6.611278	-0.351503	-2.842
75	O	4.273682	0.035695	-3.359611
76	C	2.814733	5.955104	0.095266
77	O	1.925306	4.619582	-1.718627
78	H	3.237583	0.375367	5.108603
79	H	4.71941	0.648855	4.19114
80	H	4.563189	-0.812412	5.214555
81	H	5.288398	-3.196133	-0.012144
82	H	4.715214	-4.845168	0.361516
83	H	4.444199	-3.519245	1.516213
84	H	7.218357	0.403008	-2.333624
85	H	6.774447	-0.300977	-3.917595
86	H	6.924282	-1.329873	-2.465143
87	H	2.727787	5.679411	1.149718
88	H	2.04657	6.679795	-0.172015
89	H	3.803942	6.402026	-0.044499

Table S7 Optimized atomic coordinates of ***S*-[Ir4α]$^+$** with skew conformation

number	atom	x	y	z
1	Ir	-2.368573	-0.397881	-0.28792
2	Cl	-1.562463	-0.7694	1.99065
3	N	-1.558038	2.410081	-0.793267
4	N	0.238542	1.311393	-0.335495
5	N	-3.706212	1.040348	0.637321
6	C	-1.110817	1.173714	-0.449879
7	C	-0.500719	3.303399	-0.941529
8	C	0.627434	2.608712	-0.66702
9	C	-2.971631	2.709855	-1.000366
10	C	-3.818914	2.311086	0.187468
11	C	-4.693296	3.217433	0.783453
12	C	-5.47539	2.811709	1.864316
13	C	-5.342802	1.506941	2.330323
14	C	-4.440794	0.655744	1.700542
15	C	1.186578	0.238018	0.015714
16	C	-1.609752	-2.140137	-1.427611
17	C	-2.746	-2.656068	-0.662809
18	C	-3.908803	-1.947988	-1.050247
19	C	-3.529876	-0.991304	-2.096207
20	C	-2.126596	-1.164812	-2.364252
21	C	-0.253984	-2.778342	-1.478175
22	C	-2.636011	-3.743501	0.358069
23	C	-5.311179	-2.167262	-0.565451
24	C	-4.505744	-0.198757	-2.915248
25	C	-1.337303	-0.515636	-3.461238
26	H	-0.645707	4.329827	-1.238684
27	H	1.660963	2.905692	-0.698337
28	H	-3.319765	2.184113	-1.895453
29	H	-3.066409	3.781652	-1.180022
30	H	-4.755079	4.23139	0.402813
31	H	-6.163101	3.505385	2.337172
32	H	-5.914794	1.145072	3.17724
33	H	-4.269192	-0.353747	2.050736
34	H	0.073691	-3.115539	-0.494923
35	H	-0.282462	-3.647334	-2.148407
36	H	0.505711	-2.092618	-1.860537
37	H	-3.548299	-3.845761	0.947886
38	H	-2.447989	-4.69997	-0.144266
39	H	-1.80655	-3.549532	1.042371
40	H	-5.859679	-1.225952	-0.472659
41	H	-5.863725	-2.797343	-1.273024
42	H	-5.330565	-2.666959	0.405034
43	H	-4.014446	0.597259	-3.479699
44	H	-4.998604	-0.853556	-3.644537
45	H	-5.291427	0.246988	-2.299406
46	H	-0.29944	-0.347866	-3.165405

47	H	-1.330177	-1.1674	-4.343183
48	H	-1.766078	0.442648	-3.7627
49	C	1.843629	0.452419	1.397774
50	C	3.135148	-0.389923	1.618013
51	C	3.835067	-0.788198	0.310713
52	C	3.494659	0.253623	-0.762667
53	C	4.2005	0.069604	-2.110353
54	O	2.211465	1.843799	1.516686
55	O	2.976548	-1.486874	2.537508
56	O	5.247148	-0.800518	0.578167
57	O	2.094961	0.129168	-1.062369
58	O	5.526677	0.625066	-2.09609
59	H	0.601468	-0.676344	0.088175
60	H	1.110976	0.213361	2.170023
61	H	3.822255	0.264365	2.156045
62	H	3.520275	-1.771552	-0.039288
63	H	3.713108	1.261859	-0.394558
64	H	4.326939	-0.984327	-2.358712
65	H	3.599351	0.573362	-2.87043
66	C	2.094212	2.402726	2.768944
67	C	2.144816	-2.505112	2.22252
68	C	5.979436	-1.809585	0.0144
69	C	5.604462	1.978833	-2.203662
70	C	2.474281	3.859518	2.733709
71	O	1.729065	1.777704	3.732879
72	C	2.107342	-3.535009	3.318242
73	O	1.508665	-2.545942	1.187909
74	C	7.432195	-1.679046	0.385131
75	O	5.498347	-2.665925	-0.691398
76	C	7.039272	2.43512	-2.257967
77	O	4.62799	2.697466	-2.247454
78	H	1.758872	4.412592	2.116889
79	H	3.462431	3.985983	2.283022
80	H	2.469397	4.257941	3.747412
81	H	1.627208	-4.441019	2.95016
82	H	1.532417	-3.137319	4.161051
83	H	3.11482	-3.752983	3.679382
84	H	7.846092	-0.790451	-0.101846
85	H	7.97278	-2.562564	0.048043
86	H	7.545636	-1.548703	1.464218
87	H	7.562253	2.137	-1.344214
88	H	7.07189	3.518591	-2.365235
89	H	7.553446	1.959422	-3.097884

Table S8 Optimized atomic coordinates of ***R*-[Ir4β]$^+$** with chair conformation

number	atom	x	y	z
1	Ir	2.197683	0.348436	-0.368771
2	Cl	0.993464	-1.097062	-1.935327
3	N	-1.942478	0.718762	1.117434
4	N	-1.439885	-2.755315	0.183554
5	N	-4.282859	-2.392819	-0.211314
6	C	-4.996386	0.293414	-0.89545
7	C	-2.450092	3.378444	0.618559
8	C	1.904788	-0.879559	2.310659
9	C	-0.093446	-0.609812	1.5527
10	C	3.536745	-1.318957	-0.066441
11	C	1.2205	-0.435058	1.221696
12	C	1.044197	-1.291003	3.320563
13	C	-0.210225	-1.109587	2.8489
14	C	3.36475	-0.951922	2.351338
15	C	3.921552	-1.714719	1.169492
16	C	4.802654	-2.777881	1.350594
17	C	5.306272	-3.452842	0.238497
18	C	4.893594	-3.05013	-1.02803
19	C	4.000965	-1.989007	-1.140904
20	C	-1.223315	-0.412079	0.658574
21	C	-2.171655	-1.632622	0.644523
22	C	-3.342264	-1.317096	-0.296948
23	C	-4.027847	-0.007367	0.11718
24	C	-2.981797	1.119319	0.214585
25	C	-3.524431	2.439272	0.743007
26	H	1.454871	2.256842	-1.232007
27	H	2.642127	1.904136	-2.020104
28	H	3.752055	1.873306	-1.144465
29	H	3.290537	2.203995	0.205608
30	H	1.876858	2.512528	0.11757
31	H	0.11282	2.555862	-1.827039
32	H	2.626473	1.663223	-3.498081
33	H	5.179283	1.591829	-1.508542
34	H	4.193757	2.525469	1.36165
35	H	1.013426	3.054094	1.216617
36	H	1.398189	-1.656353	4.272056
37	H	-1.163921	-1.263068	3.325748
38	H	3.769975	0.064144	2.37052
39	H	3.648712	-1.44817	3.281074
40	H	5.085879	-3.074486	2.355307
41	H	5.994628	-4.282826	0.363507
42	H	5.239443	-3.552137	-1.924974
43	H	3.615535	-1.66678	-2.099564
44	H	-0.807047	-0.258547	-0.341077
45	H	-2.563903	-1.791229	1.653526
46	H	-2.985011	-1.245903	-1.328633

47	H	-4.536516	-0.130001	1.077692
48	H	-2.556247	1.290417	-0.784802
49	C	-3.831427	2.325821	1.787806
50	C	-4.38826	2.756369	0.153554
51	C	-0.218263	1.745878	-2.48414
52	C	0.177214	3.470519	-2.431331
53	C	-0.638869	2.73144	-1.055232
54	O	3.589973	1.2982	-3.862099
55	O	2.402361	2.59804	-4.027366
56	O	1.85998	0.928978	-3.765094
57	O	5.689363	1.012582	-0.732991
58	O	5.727977	2.535252	-1.625924
59	H	5.260067	1.043792	-2.450346
60	H	3.669428	2.461758	2.319276
61	H	4.57452	3.551535	1.270656
62	H	5.063797	1.862313	1.398566
63	H	0.017966	2.606416	1.210291
64	H	0.870328	4.133166	1.083643
65	H	1.463962	2.887558	2.198877
66	C	-1.495838	-4.005424	0.762378
67	C	-4.755292	-2.91116	-1.401148
68	C	-6.206131	0.785031	-0.483424
69	C	-2.549239	4.674854	1.04985
70	C	-2.465324	-4.237637	1.904881
71	O	-0.760347	-4.850812	0.327242
72	C	-5.699318	-4.054372	-1.132504
73	O	-4.427832	-2.491625	-2.481217
74	C	-7.151657	0.905087	-1.648885
75	O	-6.438193	1.08187	0.666423
76	C	-3.877171	5.135401	1.607067
77	O	-1.568733	5.372062	0.955426
78	H	-2.153207	-3.694235	2.804744
79	H	-2.455992	-5.304273	2.130587
80	H	-3.479275	-3.919899	1.648654
81	H	-6.435585	-3.780647	-0.37112
82	H	-5.136514	-4.915954	-0.755467
83	H	-6.198464	-4.334419	-2.060572
84	H	-6.735974	1.584439	-2.400694
85	H	-8.113773	1.280744	-1.300038
86	H	-7.277709	-0.068698	-2.132635
87	H	-4.682672	5.010962	0.87486
88	H	-3.790337	6.189366	1.870979
89	H	-4.154085	4.562822	2.49953

Table S9 Optimized atomic coordinates of ***S*-[Ir4β]$^+$** with chair conformation

number	atom	x	y	z
1	Ir	2.321991	-0.183014	-0.432809
2	Cl	0.988889	1.473114	-1.65566
3	N	1.897491	0.590686	2.40673
4	N	-0.051138	0.228195	1.56769
5	N	3.53766	1.50393	0.184125
6	C	1.278043	0.21426	1.258955
7	C	0.976053	0.858658	3.415915
8	C	-0.247675	0.631879	2.88677
9	C	3.346288	0.742111	2.503406
10	C	3.875488	1.71868	1.476851
11	C	4.683367	2.790737	1.848815
12	C	5.162372	3.664217	0.872547
13	C	4.798421	3.445533	-0.453185
14	C	3.977073	2.364531	-0.756642
15	C	-1.132389	0.067583	0.606743
16	C	1.697483	-2.001013	-1.522214
17	C	2.721176	-1.390535	-2.379917
18	C	3.930698	-1.330402	-1.652191
19	C	3.704729	-1.923359	-0.329862
20	C	2.344033	-2.404806	-0.297445
21	C	0.330671	-2.400853	-1.995698
22	C	2.471016	-0.929759	-3.781808
23	C	5.25363	-0.811907	-2.132456
24	C	4.790566	-2.255007	0.652441
25	C	1.728017	-3.239571	0.783193
26	H	1.273587	1.167689	4.405721
27	H	-1.228142	0.700762	3.327876
28	H	3.812725	-0.237999	2.361424
29	H	3.583993	1.089476	3.510254
30	H	4.929743	2.938128	2.895331
31	H	5.795291	4.502527	1.146564
32	H	5.129458	4.103354	-1.249391
33	H	3.632913	2.176358	-1.765356
34	H	-0.129562	-1.603606	-2.586708
35	H	0.399759	-3.289532	-2.63697
36	H	-0.33916	-2.649114	-1.168617
37	H	3.330996	-0.400075	-4.197882
38	H	2.265378	-1.794291	-4.425611
39	H	1.606774	-0.259813	-3.824003
40	H	5.782617	-0.262201	-1.347943
41	H	5.897736	-1.647271	-2.436099
42	H	5.143837	-0.150544	-2.995085
43	H	4.390623	-2.455862	1.650354
44	H	5.328957	-3.156811	0.331718
45	H	5.527755	-1.450239	0.731903
46	H	0.655698	-3.053789	0.867614

47	H	1.868388	-4.302473	0.546841
48	H	2.190226	-3.052376	1.756556
49	C	-2.241085	-0.893616	1.065241
50	C	-3.265442	-0.985488	-0.072257
51	C	-3.79998	0.407682	-0.426519
52	C	-2.639531	1.396687	-0.653419
53	C	-3.098609	2.842492	-0.767458
54	O	-1.739077	-2.210881	1.33301
55	O	-4.36211	-1.799925	0.34703
56	O	-4.523086	0.326669	-1.664187
57	O	-1.718135	1.337854	0.439367
58	O	-3.790098	3.172756	0.435269
59	H	-0.668034	-0.280333	-0.320685
60	H	-2.716878	-0.505786	1.967895
61	H	-2.805096	-1.447705	-0.950691
62	H	-4.463263	0.766637	0.363193
63	H	-2.114378	1.135306	-1.584373
64	H	-2.216842	3.47883	-0.90071
65	H	-3.747143	2.939459	-1.645663
66	C	-1.839467	-2.659708	2.629395
67	C	-4.478039	-3.045928	-0.208639
68	C	-5.89762	0.324385	-1.60293
69	C	-4.352923	4.407417	0.636512
70	C	-1.514248	-4.128719	2.718133
71	O	-2.138576	-1.944754	3.555436
72	C	-5.726617	-3.72051	0.297335
73	O	-3.679793	-3.506553	-0.991915
74	C	-6.475699	0.199623	-2.990405
75	O	-6.52012	0.408266	-0.574439
76	C	-4.306695	5.397445	-0.509264
77	O	-4.857142	4.632382	1.705833
78	H	-1.930699	-4.673479	1.867106
79	H	-1.903572	-4.523355	3.657729
80	H	-0.427208	-4.268903	2.708818
81	H	-5.68824	-3.81587	1.387603
82	H	-5.822111	-4.705385	-0.160479
83	H	-6.601716	-3.106236	0.061528
84	H	-6.090044	0.992974	-3.638617
85	H	-7.563007	0.257872	-2.935458
86	H	-6.177648	-0.756308	-3.434417
87	H	-4.785715	6.319526	-0.180055
88	H	-4.837315	5.012491	-1.387676
89	H	-3.276732	5.614486	-0.813722