Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Metal-Templated Enantioselective Enamine/H-Bonding Dual Activation Catalysis

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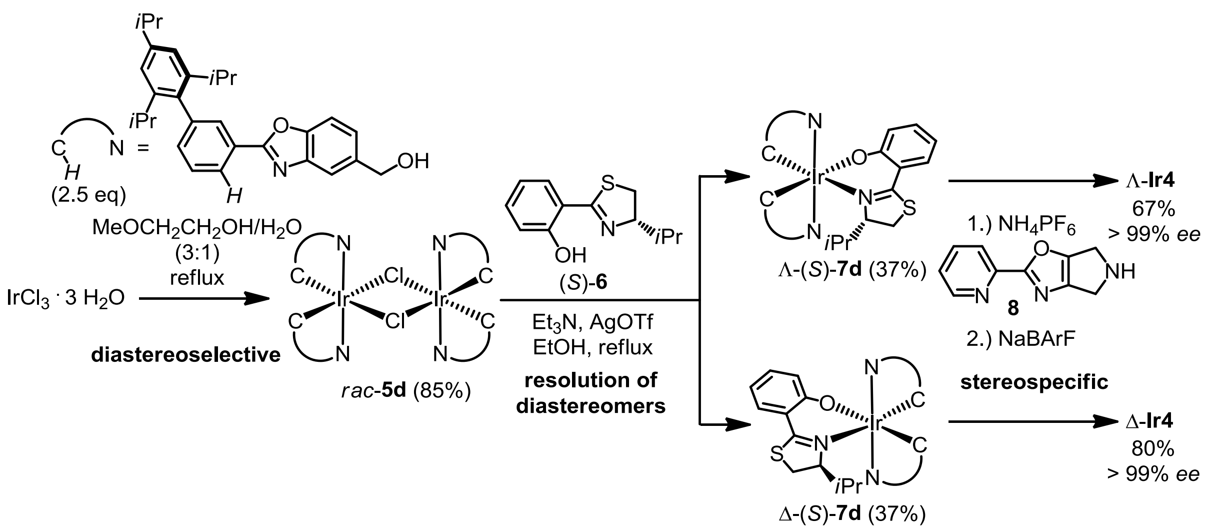
Contents

1. General Information

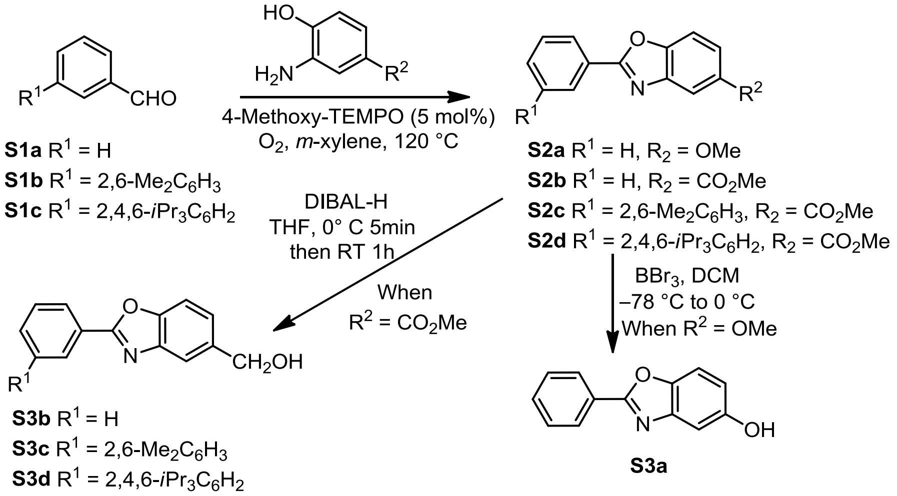
All reactions were carried out under an atmosphere of argon with magnetic stirring. Catalysis reactions were performed in a brown glass vial in the dark. Solvents were distilled under nitrogen from calcium hydride (CH_3CN, CH_2Cl_2, $CHCl_3$), sodium/benzophenone (Et_2O, THF, toluene), or magnesium turnings/iodine (MeOH). The aldehydes **1a-h** were freshly distilled. The chiral auxiliary ligand (*S*)-4-isopropyl-2-(2'-hydroxyphenyl)-2-thiazoline was prepared according to published procedures.[S1] All other reagents were purchased from commercial suppliers and used without further purification. Flash column chromatography was performed with silica gel 60 M from Macherey–Nagel (irregular shaped, 230–400 mesh, pH 6.8, pore volume: 0.81 mLg^{-1}, mean pore size: 66 Å, specific surface: 492 m^2 g^{-1}, particle size distribution: 0.5% < 25 μm and 1.7% > 71 μm, water content: 1.6%). ^1H- and ^{13}C-NMR spectra were recorded with Bruker Avance 300 (300 mHz), Bruker DRX-400 (400 MHz), Bruker AM (400 MHz), Bruker Avance 500 (500 MHz) or Bruker DRX-500 (500 MHz) spectrometers at ambient temperature. NMR standards were used as follows: ^1H NMR spectroscopy: δ = 7.26 ppm ($CDCl_3$), δ = 5.32 ppm (CD_2Cl_2), δ = 2.50 ppm (DMSO-d_6), δ = 3.31 ppm (methanol-d_4). ^{13}C NMR spectroscopy: δ = 77.0 ppm ($CDCl_3$), δ = 53.8 ppm (CD_2Cl_2), δ = 39.5 ppm (DMSO-d_6), δ = 49.0 ppm (methanol-d_4). IR spectra were recorded on a Bruker Alpha FT-IR spectrophotometer. CD spectra were recorded on a JASCO J-810 CD spectropolarimeter (600-200 nm, 1 nm bandwidth, 50 nm/min scanning speed, accumulation of 5 scans). High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0 TFT-MS instrument using ESI technique. Chiral HPLC chromatograms were obtained from an Agilent 1200 HPLC system. The optical rotations were measured on a Perkin-Elmer 241 polarimeter at concentrations of 1.0 g /100 mL.

2. Synthesis of the Iridium Catalysts Λ-Ir1-5 and Δ-Ir4



Scheme S1. Outline of the exemplary synthesis of the enantiomerically pure catalysts Λ-**Ir4** and Δ-**Ir4**. NaBArF = sodium tetrakis[(3,5-di-trifluoromethyl)phenyl]borate.

2.1. Synthesis of Benzoxazole Ligands

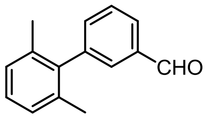


Scheme S2. Synthesis route to the benzoxazole ligands. Benzoxazole **S2b**, **S3b**[S2] and **S3a**[S3] were synthesized according to published procedures.

General procedure for synthesis of methyl 2-phenylbenzo[d]oxazole-5-carboxylates (condensation/oxidation procedure):[S4] A solution of 2-aminophenol (5.0 mmol) and benzaldehyde or substituted benzaldehyde (5.0 mmol) in *m*-xylene (25 mL) was stirred at 120 °C for 0.5 h. Then 4-methoxy-TEMPO (5 mol% in 0.5 mL *m*-xylene) was added to the mixture which was stirred at 120 °C for additional 5 h under an oxygen atmosphere. The reaction mixture was cooled and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/ hexane = 1:20).

General procedure for synthesis of 5-hydroxymethyl-2-phenylbenzo[d]oxazoles (reduction procedure):[S2] To a solution of methyl 2-phenylbenzo[*d*]oxazole-5-carboxylate (4.0 mmol) in THF (20 mL) at 0 °C was added a solution of DIBAL-H (1.0 M in hexane, 10.0 mL, 10.0 mmol) dropwise. After being stirred at 0 °C for 5 min, the reaction was quenched with a saturated aqueous solution of sodium tartrate and stirred vigorously for 1 h at room temperature. The reaction mixture was extracted with EtOAc (4 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: $MeOH/CH_2Cl_2$ = 1:50).

2',6'-Dimethylbiphenyl-3-carbaldehyde (S1b)

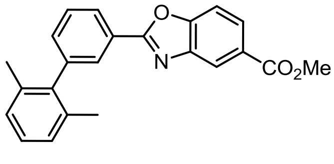


3-Bromobenzaldehyde (2.775 g, 15 mmol) and (2,6-dimethylphenyl)boronic acid (3.150 g, 21 mmol) were dissolved in a mixture of 1 M aqueous sodium carbonate solution (30 mL), toluene (30 mL), and EtOH (15 mL). After degassing with argon for 30 min, $Pd(PPh_3)_4$ (0.0867 g, 0.75 mmol) was added. The reaction mixture was stirred under argon atmosphere at 80 °C for 20 h. The reaction mixture was cooled to room temperature and water was added to the reaction mixture. The mixture was diluted with EtOAc and the insoluble material was filtered through celite. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/hexane = 1:20) to give compound **S1b** (2.961 g, yield: 94%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.97–7.88 (m, 1H), 7.76–7.70 (m, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.52–7.43 (m, 1H), 7.31–7.08 (m, 3H), 2.06 (s, 6H).

All spectroscopic data were in agreement with the literature.[S5]

Methyl 2-(2',6'-dimethylbiphenyl-3-yl)benzo[*d*]oxazole-5-carboxylate (S2c)



According to the general condensation/oxidation procedure, **S2c** (1.767 g, yield: 99%) was obtained as a white solid.

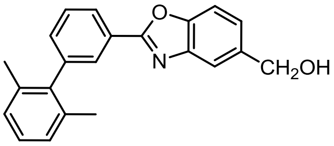
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (dd, J = 1.2, 0.5 Hz, 1H), 8.28 (dt, J = 7.8, 1.4 Hz, 1H), 8.19–8.08 (m, 2H), 7.68–7.54 (m, 2H), 7.40 (dt, J = 7.6, 1.4 Hz, 1H), 7.27–7.12 (m, 3H), 3.98 (s, 3H), 2.10 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 164.3, 153.6, 142.2, 142.1, 140.5, 135.8, 132.8, 129.2, 128.4, 127.5, 127.4, 127.1, 126.9, 126.2, 122.0, 110.3, 52.2, 20.8.

IR (film) ν_{max}: 3064, 2952, 2917, 1716, 1618, 1545, 1461, 1431, 1284, 1213, 1188, 1082, 978, 918, 901, 834, 811, 772, 742, 704 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{20}NO_3$ $[M+H]^+$: 358.1438, found: 358.1438.

(2-(2',6'-Dimethylbiphenyl-3-yl)benzo[*d*]oxazol-5-yl)methanol (S3c)



According to the general reduction procedure, **S3c** (1.223 g, yield: 93%) was obtained as a white solid.

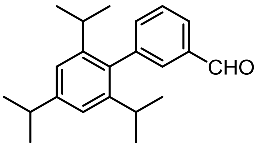
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (dt, J = 7.8, 1.4 Hz, 1H), 8.07 (t, J = 1.5 Hz, 1H), 7.74 (d, J = 0.6 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.51 (d, J = 8.3 Hz, 1H), 7.39–7.31 (m, 2H), 7.24–7.08 (m, 3H), 4.80 (s, 2H), 2.53 (br s, 1H), 2.08 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 150.2, 142.1, 142.0, 140.6, 137.9, 135.9, 132.4, 129.2, 128.3, 127.42, 127.39, 127.3, 126.0, 124.4, 118.4, 110.4, 77.4, 77.0, 76.6, 65.2, 20.8.

IR (film) ν_{max}: 3422, 3063, 3024, 2931, 2862, 1543, 1456, 1438, 1375, 1324, 1263, 1189, 1051, 979, 905, 801, 761, 726, 702 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{20}NO_2$ $[M+H]^+$: 330.1489, found: 330.1490.

2',4',6'-Triisopropylbiphenyl-3-carbaldehyde (S1c)



Synthesized according to a reported method with some mofidications.[S6] Accordingly, 2,4,6-triisopropylphenylboronic acid (1.488 g, 6.0 mmol), 3-bromobenzaldehyde (0.0736 g, 4.0 mmol), anhydrous K_3PO_4 (2.544 g, 12.0 mmol) and dicyclohexyl(2',6'-dimethoxybiphenyl-2-yl) phosphine (Sphos, 0.0164 g, 0.4 mmol) were mixed in toluene (40.0 mL). After degassing with argon for 30 min, $Pd(OAc)_2$ (0.0450 g, 0.2

mmol) was added. The reaction mixture was stirred under argon atmosphere at 110 °C for 24 h. The reaction mixture was cooled to room temperature, diluted with EtOAc, and the insoluble material was filtered through Celite. The combined organic layers were concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/hexane = 1:30) to give compound **S1c** (1.158 g, yield: 94%) as a white solid.

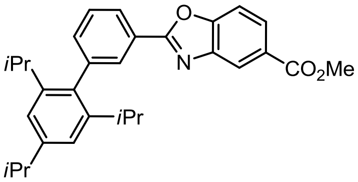
^{1}H NMR (300 MHz, CDCl$_3$) δ 10.05 (s, 1H), 7.89 (dt, J = 7.6, 1.3 Hz, 1H), 7.71 (s, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.48 (dt, J = 7.5, 1.3 Hz, 1H), 7.08 (s, 2H), 2.96 (hept, J = 6.9 Hz, 1H), 2.52 (hept, J = 6.9 Hz, 2H), 1.33 (s, 3H), 1.31 (s, 3H), 1.10 (s, 3H), 1.09 (s, 3H), 1.08 (s, 3H), 1.07 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 192.4, 148.6, 146.4, 142.0, 136.3, 135.9, 135.5, 131.3, 128.7, 127.7, 120.7, 34.3, 30.4, 24.09, 24.05, 24.0.

IR (film) ν_{max}: 2959, 2926, 2868, 1690, 1604, 1572, 1459, 1372, 1282, 1250, 1164, 878, 802, 729, 705, 652 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{28}ONa$ [M+Na]$^+$: 331.2032, found: 331.2033.

Methyl 2-(2',4',6'-triisopropylbiphenyl-3-yl)benzo[*d*]oxazole-5-carboxylate (S2d)



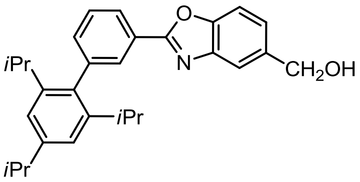
According to the general condensation/oxidation procedure, **S2d** (2.048 g, yield: 90%) was obtained as a white solid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.56–8.42 (m, 1H), 8.37–8.22 (m, 1H), 8.14 (t, J = 1.5 Hz, 1H), 8.11 (dd, J = 8.6, 1.7 Hz, 1H), 7.64–7.55 (m, 2H), 7.49–7.38 (m, 1H), 7.11 (s, 2H), 3.97 (s, 3H), 2.98 (hept, J = 6.9 Hz, 1H), 2.64 (hept, J = 6.8 Hz, 2H), 1.34 (d, J = 6.9 Hz, 6H), 1.14 (d, J = 6.5 Hz, 6H), 1.11 (d, J = 6.5 Hz, 6H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 166.7, 164.4, 153.7, 148.5, 146.4, 142.3, 141.9, 135.8, 133.4, 129.1, 128.7, 127.0, 126.5, 126.1, 122.0, 120.7, 110.3, 77.4, 77.0, 76.6, 52.2, 34.3, 30.4, 24.2, 24.13, 24.07. IR (film) ν_{max}: 2958, 2869, 1722, 1624, 1557, 1460, 1437, 1358, 1294, 1209, 1125, 1085, 1054, 841, 810, 756, 702 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{34}NO_3$ [M+H]$^+$: 456.2533, found: 456.2529.

(2-(2',4',6'-Triisopropylbiphenyl-3-yl)benzo[*d*]oxazol-5-yl)methanol (S3d)



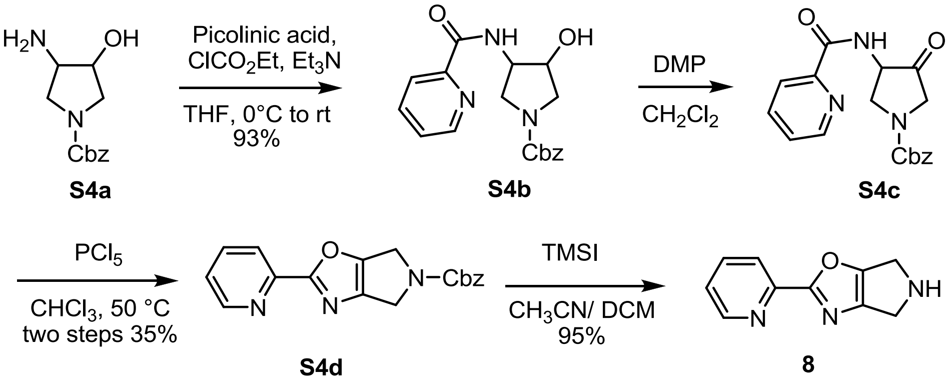
According to the general reduction procedure, **S3d** (1.674 g, yield: 98%) was obtained as a white solid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.26 (dt, J = 7.8, 1.4 Hz, 1H), 8.11 (t, J = 1.5 Hz, 1H), 7.75 (d, J = 0.9 Hz, 1H), 7.57 (t, J = 7.7 Hz, 1H), 7.49 (d, J = 8.3 Hz, 1H), 7.40 (dt, J = 7.6, 1.3 Hz, 1H), 7.34 (dd, J = 8.4, 1.6 Hz, 1H), 7.11 (s, 2H), 4.80 (s, 2H), 2.98 (hept, J = 6.9 Hz, 1H), 2.64 (hept, J = 6.8 Hz, 2H), 2.52 (br s, 1H), 1.34 (d, J = 6.9 Hz, 6H), 1.14 (d, J = 6.6 Hz, 6H), 1.11 (d, J = 6.6 Hz, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 163.6, 150.2, 148.4, 146.4, 142.2, 141.8, 137.9, 135.9, 133.1, 128.9, 128.6, 126.8, 125.9, 124.4, 120.6, 118.4, 110.4, 65.2, 34.3, 30.4, 24.2, 24.13, 24.08.

IR (film) ν_{max}: 3277, 2958, 2929, 2869, 1609, 1554, 1460, 1433, 1257, 1190, 1051, 1022, 877, 810, 781, 704 cm^{-1}.

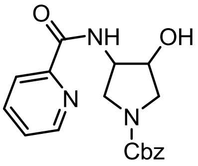
HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{34}NO_2$ [M+H]$^+$: 428.2584, found: 428.2583.

2.2. Synthesis of the Secondary Amine Ligand



Scheme S3. Synthesis route to the ligand **8**. Synthesized according to a reported method with some modifications.[S7]

Benzyl 3-hydroxy-4-(picolinamido)pyrrolidine-1-carboxylate (S4b)



To a solution of picolinic acid (4.0 g, 32.8 mmol) in THF (120 mL) at 0 °C was added successively Et_3N (9.1 mL, 65.6 mmol) and ethyl chloroformate (3.1 mL, 32.8 mmol). After being stirred at 0 °C for 1 h, a solution of **S4a**[S8] (7.1 g, 30.0 mmol) in THF (30 mL) was added. After being stirred at room temperature for overnight, the reaction was quenched with a saturated aqueous solution of NH_4Cl and extracted with CH_2Cl_2 (4 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: $MeOH/CH_2Cl_2$ = 1:50) to give compound **S4b** (9.5 g, yield: 93%) as a white solid.

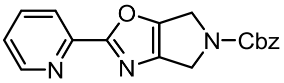
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (d, J = 4.5 Hz, 1H), 8.21 (t, J = 6.0 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 7.81 (td, J = 7.7, 1.7 Hz, 1H), 7.45–7.27 (m, 5H), 5.15 (s, 2H), 4.80 (br, 1H), 4.60–4.45 (m, 1H), 4.40 (s, 1H), 4.11–3.91 (m, 1H), 3.76 (td, J = 11.4, 5.2 Hz, 1H), 3.53 (ddd, J = 15.3, 11.8, 3.2 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 164.9, 154.9, 148.8, 148.1, 137.5, 136.5, 128.4, 127.9, 127.82, 127.79, 126.6, 122.2, 74.5, 73.6, 67.0, 56.4, 56.0, 51.7, 51.4, 49.1.

IR (film) ν_{max}: 3346, 3056, 2952, 2884, 1672, 1516, 1426, 1349, 1192, 1108, 738, 695, 595 cm^{-1}.

HRMS (ESI, m/z) calcd for $C_{18}H_{20}N_3O_4$ $[M+H]^+$: 342.1448, found: 342.1446.

Benzyl 2-(pyridin-2-yl)-4*H*-pyrrolo[3,4-*d*]oxazole-5(6*H*)-carboxylate (S4d)



To a solution of **S4b** (2.0 g, 5.9 mmol) in CH_2Cl_2 (59 mL) at 0 °C was added Dess-Martin reagent (6.1 g, 14.4 mmol). After being stirred at room temperature for overnight, the reaction mixture was diluted with CH_2Cl_2 and washed with NaOH (0.5 M, 3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product of **S4c** was used for next step without further purification. The crude **S4c** (5.9 mmol estimated on the theoretical yield) was dissolved in $CHCl_3$ (59 mL). PCl_5 (3.7 g, 17.7 mmol) was added at 50 °C and stirring was continued for an additional 3 h. The reaction was quenched with a saturated aqueous solution of Na_2CO_3 and extracted with CH_2Cl_2 (4 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was passed through a short column of silica gel (eluent: MeOH/CH_2Cl_2 = 1:50) to afford the crude product as a black solid. The crude product was washed with MeOH (3 × 3 mL) and centrifuged to afford the **S4d** (663 mg, 35% in two steps) as a white solid.

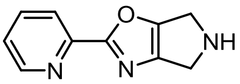
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70–8.54 (m, 1H), 8.09–7.92 (m, 1H), 7.72 (tt, J = 7.9, 1.5 Hz, 1H), 7.40–7.22 (m, 6H), 5.13 (d, J = 0.8 Hz, 2H), 4.63–4.50 (m, 2H), 4.50–4.36 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5, 154.7, 154.6, 149.9, 149.8, 149.4, 149.3, 145.7, 140.3, 140.2, 137.0, 136.9, 136.24, 136.21, 128.4, 128.1, 128.07, 128.02, 127.9, 124.7, 121.7, 121.6, 67.22, 67.20, 45.5, 45.4, 44.9, 44.7.

IR (film) ν_{max}: 3053, 2938, 2882, 1696, 1413, 1362, 1295, 1095, 942, 797, 745, 695, 614 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{16}N_3O_3$ [M+H]$^+$: 322.1186, found: 188.0814.

2-(Pyridin-2-yl)-5,6-dihydro-4*H*-pyrrolo[3,4-*d*]oxazole (8)



To a solution of **S4d** (96.3 mg, 0.3 mmol) in CH_3CN/CH_2Cl_2 (3 mL/1mL) at 0 °C was added TMSI (0.12 mL, 0.9 mmol). After being stirred at room temperature for 1 h, the reaction was quenched with dry MeOH (0.5 mL). The solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: MeOH/CH_2Cl_2 = 1:10) to give compound **8** (53.0 mg, yield: 95%) as a white solid.

^{1}H NMR (300 MHz, MeOD) δ 8.68 (d, J = 4.6 Hz, 1H), 8.11 (d, J = 7.9 Hz, 1H), 8.03 (td, J =

7.8, 1.6 Hz, 1H), 7.70–7.47 (m, 1H), 4.33–4.20 (m, 2H), 4.19–4.02 (m, 2H).

^{13}C NMR (75 MHz, MeOD) δ 167.0, 154.7, 151.0, 146.3, 145.0, 139.4, 126.8, 123.0, 44.4, 43.8.

IR (film) ν_{max}: 3036, 2934, 2882, 1423, 1363, 1296, 1209, 1153, 1095, 956, 738, 696 cm^{-1}.

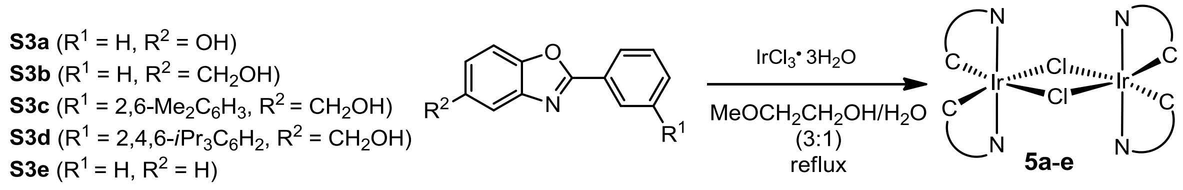
HRMS (ESI, *m*/*z*) calcd for $C_{10}H_{10}N_3O$ [M+H]$^+$: 188.0818, found: 188.0816.

2.3. Synthesis of Iridium Complexes

Our developed synthetic strategy[S2,S8] for the generation of enantiomerically pure iridium(III) complexes relies on the use of (*S*)-4-isopropyl-2-(2'-hydroxyphenyl)-2-thiazoline[S2] as a chiral auxiliary. As described in detail below, racemic iridium(III) precursor complexes were converted to diastereomeric phenolato complexes, then resolved into single diastereomers by flash silica gel column chromatography, and followed by an acid-induced substitution of the auxiliary under complete retention of configuration to afford the enantiomerically pure iridium complexes.

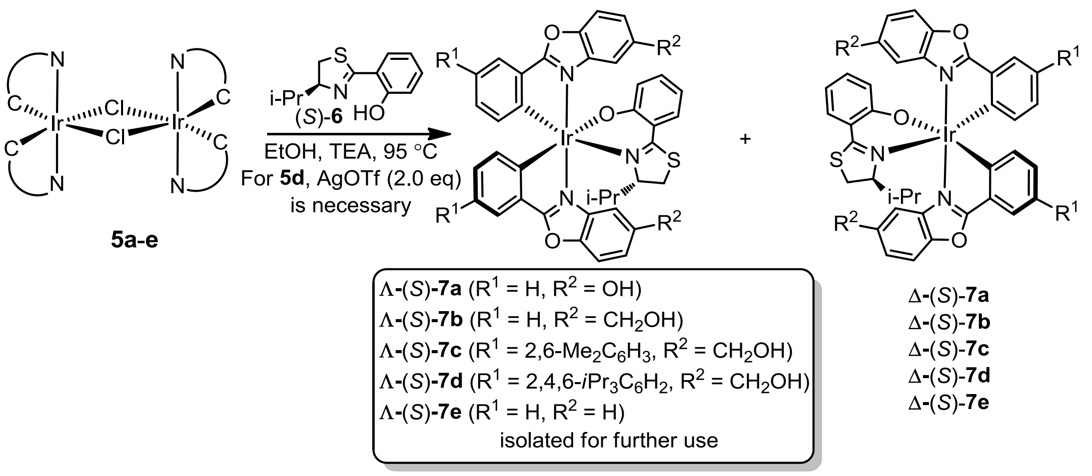
2.3.1. Synthesis of Iridium Precursor Complexes

Cyclometalated iridium(III) μ-chloro-bridged dimers of the general formula $[(C^\wedge N)_2Ir(\mu\text{-}Cl)Ir(C^\wedge N)_2]$ (C^N = (2-phenylbenzo[*d*]oxazol-5-yl)methanol and its derivatives were synthesized according to a method reported by Nonoyama,[S9] which involves refluxing $IrCl_3{\bullet}nH_2O$ with 2.0–2.5 equiv of cyclometalating ligand in a 3:1 mixture of 2-methoxyethanol and water. Accordingly, (2-phenylbenzo[*d*]oxazol-5-yl)methanol or its derivatives (2.0 mmol) were added to iridium chloride (1.0 mmol) in a mixture of methoxyethanol/water (3:1, 44 mL). The reaction mixture was heated at reflux (120 °C) with constant stirring for 24 h. The resulting precipitate was collected by centrifugation, washed with diethyl ether and dried to yield the product as a yellow powder (60-89%), which was used without further purification.



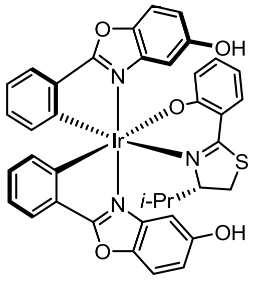
Scheme S4. Synthesis of cyclometalated Ir(III) μ-chloro-bridged dimers **5a**-**e**.

2.3.2. Preparation of Iridium Auxiliary Complexes[S2]



Scheme S5. Preparation of iridium precursor complexes Λ-(*S*)-**7a-e**. The complexes Λ-(*S*)-**7b**, Λ-(*S*)-**7e** were synthesized according to published procedures.[S2]

Preparation of iridium auxiliary complex Λ-(*S*)-7a. A mixture of iridium(III) dimer complex **5a** (259.0 mg, 0.20 mmol), (*S*)-4-isopropyl-2-(2'-hydroxyphenyl)-2-thiazoline (*S*)-**6** (110.5 mg, 0.50 mmol), and triethylamine (0.28 mL, 2.0 mmol) in ethanol (20 mL) was purged with argon for 5 min and then heated at reflux overnight. The reaction mixture was cooled to room temperature and concentrated to dryness. The residue was subjected to a flash silica gel chromatography (eluent: EtOAc/CH_2Cl_2 = 1:10) to separate the two diastereomers. Only the first eluting diastereomer (yellow solid, 127.0 mg, 38%) was characterized and used for the synthesis of enantiopure iridium catalyst, which was assigned as Λ-configuration by CD spectroscopy in analogy to reported complexes.[S2]



Λ-(*S*)-**7a**

^{1}H NMR (500 MHz, DMSO) δ 9.86 (s, 1H), 9.78 (s, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.69 (d, J = 9.0 Hz, 1H), 7.66 (d, J = 6.9 Hz, 1H), 7.56 (d, J = 6.7 Hz, 1H), 7.33 (dd, J = 8.2, 1.7 Hz, 1H), 7.10 (d, J = 2.5 Hz, 1H), 7.07 (ddd, J = 8.6, 6.8, 1.7 Hz, 1H), 6.97 (dd, J = 3.4, 2.6 Hz, 1H), 6.96 (dd, J = 3.4, 2.6 Hz, 1H), 6.90 (t, J = 7.4 Hz, 2H), 6.79 (dtd, J = 8.7, 7.5, 1.3 Hz, 2H), 6.71 (d, J = 2.3 Hz, 1H), 6.52 (d, J = 7.6 Hz, 2H), 6.29–6.21 (m, 1H), 6.18 (d, J = 7.6

Hz, 1H), 4.57 (d, *J* = 9.8 Hz, 1H), 3.47 (dd, *J* = 11.8, 10.1 Hz, 1H), 3.17 (d, *J* = 5.2 Hz, 1H), 0.83–0.70 (m, 1H), 0.21 (d, *J* = 2.4 Hz, 3H), 0.19 (d, *J* = 2.4 Hz, 3H).

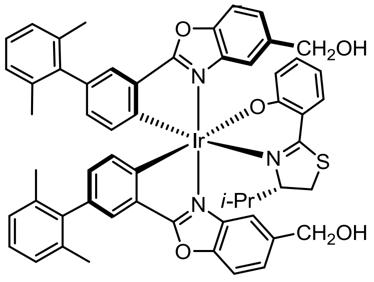
^{13}C NMR (125 MHz, DMSO) δ 177.7, 177.1, 167.4, 166.9, 156.2, 155.9, 150.6, 148.9, 143.4, 143.0, 138.9, 138.7, 134.3, 133.02, 132.98, 131.6, 131.3, 131.0, 130.6, 130.2, 125.5, 125.0, 123.6, 121.5, 120.6, 117.7, 113.8, 113.7, 112.8, 112.3, 112.0, 102.8, 101.0, 84.1, 31.0, 26.8, 18.6, 13.9.

IR (film) ν_{max}: 2958, 2925, 2867, 1592, 1561, 1530, 1440, 1388, 1355, 1299, 1160, 1028, 1003, 944, 816, 741 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{38}H_{30}IrN_3O_5SNa$ [M+Na]$^+$: 856.1428, found: 856.1422.

CD (MeOH): λ, nm (Δε, M^{-1}cm^{-1}) 356 (+40), 289 (–28), 221 (–47).

Preparation of iridium auxiliary complex Λ-(*S*)-7c A mixture of iridium(III) dimer complex **5c** (265.0 mg, 0.15 mmol), (*S*)-4-isopropyl-2-(2'-hydroxyphenyl)-2-thiazoline (*S*)-**6** (83.0 mg, 0.38 mmol), and triethylamine (0.21 mL, 1.5 mmol) in ethanol (15 mL) was purged with argon for 5 min and then heated at reflux overnight. The reaction mixture was cooled to room temperature and concentrated to dryness. The residue was subjected to a flash silica gel chromatography (eluent: EtOAc/CH_2Cl_2 = 1:10) to separate the two diastereomers. Only the first eluting diastereomer (orange solid, 120.0 mg, 37%) was characterized and used for the synthesis of enantiopure iridium catalyst, which was assigned as Λ-configuration by CD spectroscopy in analogy to reported complexes.[S2]



Λ-(*S*)-**7c**

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.52–7.39 (m, 5H), 7.25–6.98 (m, 8H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.68–6.56 (m, 2H), 6.53 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.41 (d, *J* = 7.8 Hz, 1H), 6.35 (t, *J* = 7.1 Hz, 1H), 4.96 (d, *J* = 9.7 Hz, 1H), 4.68–4.40 (m, 4H), 3.57–3.43 (m, 1H), 3.37 (t, *J* = 5.6 Hz, 1H), 2.79 (d, *J* = 11.3 Hz, 1H), 2.53 (t, *J* = 6.1 Hz, 1H), 2.09 (s, 3H), 1.99 (s, 3H), 1.75 (s, 3H), 1.72 (s, 3H), 0.26 (d, *J* = 6.4 Hz, 3H), 0.24 (d, *J* = 6.4 Hz, 3H).

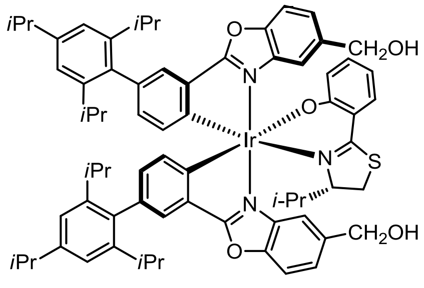
^{13}C NMR (75 MHz, $CDCl_3$) δ 178.5, 178.3, 167.67, 166.73, 149.4, 149.2, 147.9, 147.2, 141.5, 141.4, 139.8, 139.7, 138.8, 138.3, 136.6, 136.4, 136.2, 135.8, 134.1, 133.6, 133.3, 133.2, 133.1, 132.6, 132.5, 131.6, 130.9, 130.2, 127.2, 127.1, 127.03, 126.98, 126.8, 126.7, 126.0, 125.9, 124.1, 124.0, 123.5, 118.7, 116.0, 113.6, 113.4, 111.3, 111.0, 86.0, 64.7, 64.4, 31.0, 27.4, 21.0, 20.9, 20.2, 20.1, 18.7, 14.0.

IR (film) ν_{max}: 2958, 2924, 2869, 1598, 1560, 1524, 1463, 1436, 1364, 1253, 1191, 1148, 1031, 1014, 941, 836, 766, 742 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{56}H_{51}IrN_3O_5S$ $[M+H]^+$: 1070.3176, found: 1070.3189.

CD (MeOH): λ, nm (Δε, $M^{-1}cm^{-1}$) 366 (+26), 328 (+30), 306 (–28), 298 (–28), 230 (–26).

Preparation of iridium auxiliary complex Λ-(*S*)-7d and Δ-(*S*)-7d: A mixture of iridium(III) dimer complex **5d** (324.0 mg, 0.15 mmol), (*S*)-4-isopropyl-2-(2'-hydroxyphenyl)-2-thiazoline (*S*)-**6** (83.0 mg, 0.38 mmol), silver triflate (77.1 mg, 0.30 mmol), and triethylamine (0.21 mL, 1.5 mmol) in ethanol (15 mL) was purged with argon for 5 min and then heated at reflux overnight. The reaction mixture was cooled to room temperature and concentrated to dryness. The residue was subjected to a flash silica gel chromatography (eluent: EtOAc/CH_2Cl_2 = 1:30) to separate the two diastereomers. Two eluting diastereomers was characterized and can be used for the synthesis of enantiopure iridium catalyst. The first eluting diastereomer (orange solid, 140.0 mg, 37%) was assigned as Λ-configuration by CD spectroscopy in analogy to reported complexes.[S2] The second eluting diastereomer (orange solid, 140.0 mg, 37%) was assigned accordingly as Δ-configuration.



Λ-(*S*)-**7d**

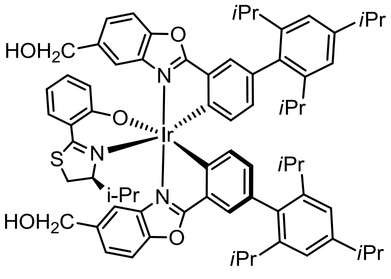
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.42–7.28 (m, 4H), 7.28–7.17 (m, 3H), 7.05 (dd, *J* = 8.6, 1.4 Hz, 1H), 6.97 (ddd, *J* = 8.6, 6.8, 1.7 Hz, 1H), 6.85–6.73 (m, 4H), 6.63 (d, *J* = 8.5 Hz, 1H), 6.49–6.35 (m, 3H), 6.21 (d, *J* = 7.8 Hz, 1H), 6.17–6.05 (m, 1H), 4.74 (d, *J* = 10.3 Hz, 1H), 4.61 (s, 2H), 4.40 (s, 2H), 3.39 (t, *J* = 10.8 Hz, 1H), 2.86–2.61 (m, 3H), 2.61–2.40 (m, 2H), 2.29–2.14 (m, 2H), 2.06 (s, 1H), 1.68 (br s, 2H), 1.08 (d, *J* = 3.7 Hz, 6H), 1.06 (d, *J* = 3.7 Hz, 6H), 0.88 (d, *J* = 5.3 Hz, 3H), 0.86 (d, *J* = 5.4 Hz, 3H), 0.80 (dd, *J* = 6.9, 1.5 Hz, 6H), 0.75 (d, *J* = 6.9 Hz, 6H), 0.71 (dd, *J* = 6.8, 1.8 Hz, 6H), 0.13 (d, *J* = 6.9 Hz, 3H), 0.01 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 178.6, 167.9, 167.4, 149.6, 149.4, 147.7, 147.6, 147.1, 147.0, 146.8, 146.7, 139.6, 139.3, 139.1, 138.6, 136.8, 134.0, 133.5, 133.4, 133.2, 133.1, 132.7, 131.4, 130.6, 129.7, 126.9, 126.6, 124.3, 124.1, 123.0, 120.6, 120.5, 120.4, 120.3, 118.7, 116.1, 113.4, 113.2, 111.5, 111.2, 85.8, 65.0, 64.9, 34.2, 31.2, 30.2, 30.1, 30.0, 27.4, 24.7, 24.4, 24.3, 24.13, 24.05, 24.0, 23.9, 18.6, 14.1.

IR (film) ν_{max}: 2958, 2926, 2867, 1599, 1562, 1531, 1464, 1436, 1363, 1334, 1256, 1191, 1155, 1059, 1031, 1012, 942, 788, 748 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{70}H_{79}IrN_3O_5S$ $[M+H]^+$: 1266.5368, found: 1266.5361.

CD (MeOH): λ, nm (Δε, M^{-1}cm^{-1}) 368 (+33), 329 (+41), 306 (–35), 295 (–35), 231 (–26).



Δ-(*S*)-**7d**

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.94 (s, 1H), 7.62–7.58 (m, 2H), 7.56–7.39 (m, 4H), 7.31 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 1H), 7.12–6.96 (m, 4H), 6.88 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.65 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.62–6.52 (m, 2H), 6.48 (d, *J* = 7.8 Hz, 1H), 6.34–6.21 (m, 1H), 4.75–4.44 (m, 4H), 3.76 (d, *J* = 9.5 Hz, 1H), 3.07 (d, *J* = 11.4 Hz, 1H), 3.01–2.69 (m, 6H), 2.59–2.33 (m, 2H), 2.29–2.10 (m, 1H), 2.02 (t, *J* = 5.6 Hz, 1H), 1.32 (d, *J* = 3.3 Hz, 6H), 1.30 (d, *J* = 3.3 Hz, 6H), 1.17 (d, *J* = 6.7 Hz, 3H), 1.11 (d, *J* = 6.9 Hz, 3H), 1.08 (d, *J* = 6.9 Hz, 3H), 1.06–0.97 (m, 12H), 0.94 (d, *J* = 4.3 Hz, 3H), 0.92 (d, *J* = 4.3 Hz, 3H), 0.34 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) *δ* 179.1, 168.8, 168.5, 149.7, 149.1, 147.9, 147.7, 147.5, 147.2, 147.0, 146.8, 146.5, 146.3, 140.1, 139.4, 138.5, 138.4, 136.7, 135.2, 133.6, 133.4, 133.1, 132.7, 132.6, 132.0, 129.6, 129.5, 129.3, 127.2, 126.5, 124.6, 124.0, 123.7, 121.8, 120.6, 120.5, 120.4, 120.3, 116.0, 115.2, 113.3, 111.3, 111.0, 80.9, 64.9, 64.6, 34.19, 34.17, 31.6, 30.8, 30.1, 30.02, 29.95, 29.86, 24.7, 24.5, 24.4, 24.2, 24.03, 23.96, 23.9, 20.2, 16.4.

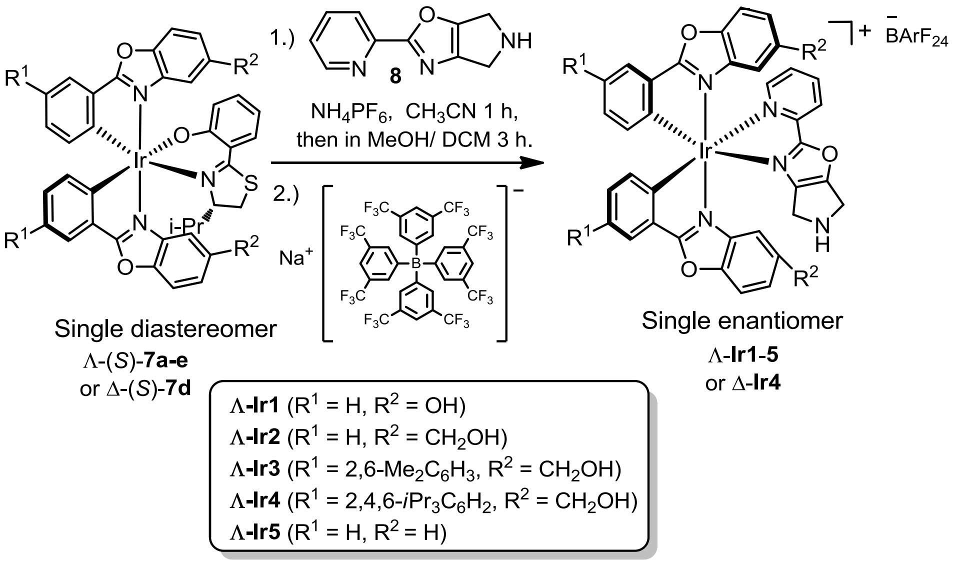
IR (film) ν_{max}: 2958, 2868, 1599, 1564, 1530, 1437, 1365, 1319, 1252, 1199, 1147, 1028, 942, 877, 816, 749 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{70}H_{79}IrN_3O_5S$ $[M+H]^+$: 1266.5369, found: 1266.5336.

CD (MeOH): λ, nm (Δε, M^{-1}cm^{-1}) 328 (–28), 304 (+24), 288 (+32).

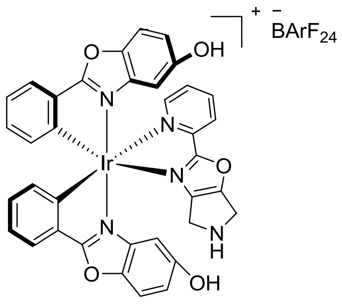
2.3.3. Synthesis of Enantiopure Iridium Catalysts

The enantiopure iridium catalysts were prepared according to a reported method with some modifications,[S2] which relies on the acid-induced substitution of the coordinated phenolato ligand against 2-(pyridin-2-yl)-5,6-dihydro-4*H*-pyrrolo[3,4-*d*]oxazole under retention of configuration and is analogous to previously reported auxiliary-mediated ruthenium(II) chemistry by Meggers et al.[S10] The absolute configurations of the obtained Λ-configured iridium(III) complexes were verified by CD spectroscopy in analogy to reported complexes.[S2] The enantiomeric purities were verified by chiral HPLC analysis.



Scheme S6. Synthesis of enantiopure iridium catalysts Λ-**Ir1**-**5** and Δ-**Ir4**.

General procedure: A suspension of the iridium auxiliary complexes Λ-(*S*)-**7a-e** or Δ-(*S*)-**7d** (1.0 eq), ligand **8** (2.0 eq), and NH_4PF_6 (5.0 eq) in acetonitrile (10 mM) was stirred at room temperature for 1 h under argon in the dark. Then, the reaction mixture was concentrated to dryness and dissolved in MeOH/CH_2Cl_2 (3:1, 10 mM). After being stirred at room temperature for 3 h, the reaction mixture was concentrated to dryness and subjected to a flash silica gel chromatography (eluent: MeOH/CH_2Cl_2 = 1:30) to give the pure yellow solid as a hexafluorophosphate salt. The product was directly suspended in CH_2Cl_2. Sodium tetrakis[(3,5-di-trifluoromethyl)phenyl]borate ($NaBArF_{24}$) (0.95 eq) was added in one portion and the mixture was stirred at room temperature for 10 min. After removal of the CH_2Cl_2 in vacuo, the residue was taken up in Et_2O (about 2.0 mL) twice and centrifuged. The combined organic layers were dried and concentrated in vacuo to give the pure product as the borate salt.



Λ-**Ir1**

Following the general procedure, Λ-(*S*)-**7a** (83.3 mg, 0.10 mmol) was converted to Λ-**Ir1** (109.7 mg, yield: 66%) as an orange solid.

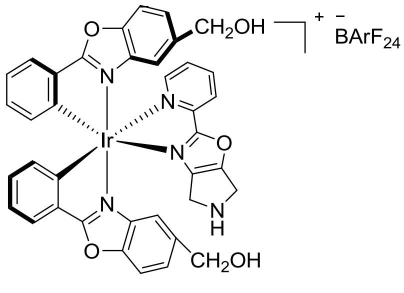
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 5.2 Hz, 1H), 7.85 (t, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.71 (s, 8H), 7.56–7.46 (m, 1H), 7.41 (s, 4H), 7.29 (d, *J* = 8.9 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.10–6.99 (m, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.82 (dd, *J* = 9.0, 2.2 Hz, 1H), 6.67 (dd, *J* = 9.0, 2.3 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 5.78 (d, *J* = 2.1 Hz, 1H), 5.08 (d, *J* = 2.3 Hz, 1H), 4.01 (d, *J* = 13.9 Hz, 1H), 3.92 (d, *J* = 14.7 Hz, 1H), 3.54 (d, *J* = 14.2 Hz, 1H), 3.25 (d, *J* = 13.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.01, 177.96, 169.9, 162.6, 162.0, 161.3, 160.7, 157.7, 155.4, 154.4, 152.9, 146.1, 144.6, 144.4, 144.0, 143.3, 141.5, 139.7, 138.0, 134.8, 133.5, 133.3, 132.9, 129.8, 129.5, 129.1, 129.0, 128.9, 128.7, 128.3, 126.8, 126.4, 126.2, 123.8, 123.7, 123.4, 122.6, 119.0, 117.5, 114.4, 113.8, 113.2, 112.7, 100.2, 99.6, 43.0, 41.8.

IR (film) ν_{max}: 1595, 1451, 1352, 1273, 1115, 888, 831, 738, 708, 672 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{36}H_{25}IrN_5O_5$ [M–BArF$_{24}$]$^+$: 800.1481, found: 800.1489.

CD (MeOH): λ, nm (Δε, M^{-1}cm^{-1}) 337 (+40), 218 (–45).



Λ-**Ir2**

Following the general procedure, Λ-(*S*)-**7b** (43.3 mg, 0.050 mmol) was converted to Λ-**Ir2** (60.0 mg, yield: 71%) as an orange solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.28 (dt, *J* = 5.4, 1.2 Hz, 1H), 8.15–8.09 (m, 2H), 7.87 (ddd, *J* = 7.7, 1.3, 0.4 Hz, 1H), 7.81 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.72 (t, *J* = 2.3 Hz, 8H), 7.67–7.60 (m, 3H), 7.54 (s, 4H), 7.33 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.28 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.19 (td, *J* =

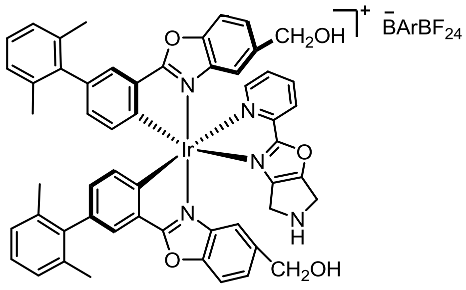
7.5, 1.0 Hz, 1H), 7.12 (td, *J* = 7.5, 1.0 Hz, 1H), 7.06 (td, *J* = 7.5, 1.4 Hz, 1H), 6.97 (td, *J* = 7.5, 1.4 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 6.58-6.50 (m, 2H), 5.83 (d, *J* = 0.8 Hz, 1H), 4.77 (d, *J* = 14.0 Hz, 1H), 4.71 (d, *J* = 14.0 Hz, 1H), 4.56 (d, *J* = 13.4 Hz, 1H), 4.52 (d, *J* = 13.4 Hz, 1H), 4.30 (ddd, *J* = 15.1, 3.9, 2.1 Hz, 1H), 4.18 (ddd, *J* = 15.0, 3.7, 2.7 Hz, 1H), 3.74 (s, 3H), 3.62 (ddd, *J* = 14.1, 3.9, 2.0 Hz, 1H), 3.22 (ddd, *J* = 14.1, 3.6, 2.6 Hz, 1H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 178.3, 177.9, 162.8, 162.4, 162.0, 161.6, 154.0, 149.9, 149.8, 147.0, 144.7, 142.2, 141.0, 140.6, 140.5, 138.1, 137.7, 135.2, 134.0, 133.73, 133.72, 133.3, 129.7, 129.44, 129.42, 129.39, 129.37, 129.19, 129.17, 129.14, 129.12, 128.94, 128.92, 128.89, 128.87, 128.3, 127.4, 127.0, 126.1, 124.8, 124.4, 124.2, 123.9, 121.8, 118.0, 117.94, 117.91, 117.88, 117.85, 112.9, 112.6, 112.2, 111.5, 64.2, 64.1, 44.2, 42.9.

IR (film) ν_{max}: 1600, 1520, 1446, 1391, 1354, 1274, 1116, 939, 888, 835, 741, 710 673 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{38}H_{29}IrN_5O_5$ [M–BArF$_{24}$]$^+$: 828.1797, found: 828.1789.

CD (MeOH): λ, nm (Δε, M^{-1}cm^{-1}) 354 (+26), 330 (+32), 261 (–9), 226 (–27).



Λ-**Ir3**

Following the general procedure, Λ-(*S*)-**7c** (64.0 mg, 0.060 mmol) was converted to Λ-**Ir3** (79.8 mg, yield: 70%) as an orange solid.

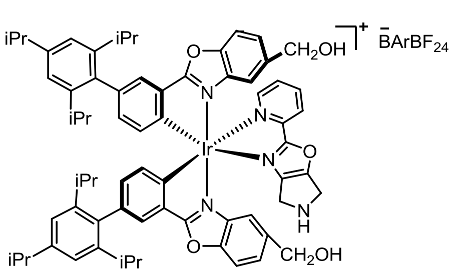
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 5.3 Hz, 1H), 7.83–7.68 (m, 2H), 7.57 (d, *J* = 1.4 Hz, 9H), 7.52 (d, *J* = 1.7 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.41–7.35 (m, 1H), 7.32 (s, 4H), 7.16–6.93 (m, 8H), 6.77 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.68 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.55-6.38 (m, 2H), 5.72 (s, 1H), 4.62 (d, *J* = 14.1 Hz, 1H), 4.54 (d, *J* = 14.1 Hz, 1H), 4.43 (d, *J* = 13.5 Hz, 1H), 4.36 (d, *J* = 13.5 Hz, 1H), 4.07 (d, *J* = 15.0 Hz, 1H), 3.88 (d, *J* = 15.1 Hz, 1H), 3.59 (d, *J* = 14.0 Hz, 1H), 3.18 (d, *J* = 14.6 Hz, 1H), 2.49 (br s, 2H), 2.00 (s, 3H), 1.93 (s, 3H), 1.81 (s, 6H), 1.56 (br s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.8, 177.5, 169.5, 162.7, 162.0, 161.3, 160.7, 160.5, 153.0, 149.3, 149.2, 145.9, 144.6, 140.6, 140.3, 140.2, 140.0, 139.7, 137.6, 137.4, 136.6, 136.5, 136.2, 135.8, 135.5, 134.7, 134.0, 133.4, 129.9, 129.3, 129.2, 128.6, 127.6, 127.5, 126.9, 126.3, 124.3, 123.8, 123.3, 122.7, 119.0, 117.4, 112.3, 111.5, 110.9, 63.7, 63.4, 43.6, 42.5, 20.9, 20.8, 20.6.

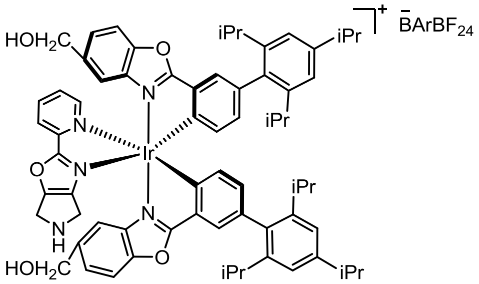
IR (film) ν_{max}: 1608, 1446, 1354, 1272, 1116, 1042, 943, 889, 837, 711, 673, 643 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{54}H_{45}IrN_5O_5$ $[M–BArF_{24}]^+$: 1036.3048, found: 1036.3053.

CD (MeOH): λ, nm (Δε, $M^{-1}cm^{-1}$) 360 (+31), 332 (+33), 274 (–15), 241 (–18).



Λ-**Ir4**



Δ-**Ir4**

Following the general procedure, Λ-(*S*)-**7d** (140.0 mg, 0.11 mmol) was converted to Λ-**Ir4** (154.4 mg, yield: 67%) and Δ-(*S*)-**7d** (140.0 mg, 0.11 mmol) to Δ-**Ir4** (185.5 mg, yield: 80%). Both complexes are orange solids.

NMR spectra of Λ-**Ir4** and Δ-**Ir4** are identical:

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.39 (d, *J* = 5.3 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.87 (td, *J* = 7.8, 1.4 Hz, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.70 (s, 9H), 7.61-7.49 (m, 3H), 7.44 (s, 4H), 7.25 (d, *J* = 8.7 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 1H), 7.12 (d, *J* = 1.6 Hz, 1H), 7.09–7.05 (m, 3H), 6.95 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.87 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.54 (s, 1H), 5.85 (s, 1H), 4.73 (d, *J* = 14.1 Hz, 1H), 4.67 (d, *J* = 14.1 Hz, 1H), 4.58 (d, *J* = 13.5 Hz, 1H), 4.50 (d, *J* = 13.5 Hz, 1H), 4.26 (d, *J* = 15.2 Hz, 1H), 4.05 (d, *J* = 15.3 Hz, 1H), 3.76 (d, *J* = 14.8 Hz, 1H), 3.33 (d, *J* = 14.0 Hz, 1H), 2.97 (hept, *J* = 6.8 Hz, 1H), 2.96 (hept, *J* = 6.8 Hz, 1H), 2.78 (hept, *J* = 6.9 Hz, 1H), 2.65 (hept, *J* = 6.9 Hz, 1H), 2.51 (hept, *J* = 6.9 Hz, 1H), 2.46 (hept, *J* = 6.8 Hz, 1H), 1.33 (d, *J* = 6.8 Hz, 6H), 1.31 (d, *J* = 6.2 Hz, 6H), 1.19 (d, *J* = 6.8 Hz, 3H), 1.17 (d, *J* = 6.9 Hz, 3H), 1.14 (d, *J* = 6.9 Hz, 3H), 1.07 (dd, *J* = 6.9, 1.9 Hz, 6H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 177.9, 177.5, 169.9, 162.3, 161.9, 161.5, 161.1, 159.5, 153.2, 149.3, 149.2, 148.6, 148.5, 146.7, 146.6, 146.3, 146.0, 145.2, 144.4, 144.2, 140.4, 140.1, 139.7, 139.5, 137.7, 137.4, 136.3, 135.61, 135.56, 135.5, 134.7, 132.9, 132.7, 129.3, 129.1, 128.9, 128.8, 128.7, 128.6, 128.0, 127.7, 127.6, 125.5, 124.3, 123.8, 123.5, 123.4, 121.2, 120.9, 120.8, 120.7, 120.5, 117.48, 117.45, 117. 42, 112.4, 112.3, 111.5, 110.6, 63.7, 63.5, 43.7, 42.6, 34.3, 30.60, 30.56, 30.33, 30.26, 24.24, 24.15, 24.10, 24.02, 23.99, 23.96.

Λ-**Ir4**:

IR (film) ν_{max}: 2963, 1606, 1527, 1445, 1354, 1272, 1118, 1040, 886, 836, 711, 673, 640 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{68}H_{73}IrN_5O_5$ [M–BArF$_{24}$]$^+$: 1232.5242, found: 1232.5234.

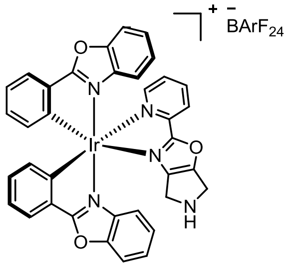
CD (MeOH): λ, nm (Δε, M^{-1}cm^{-1}) 361 (+36), 334 (+37), 269 (–22), 238 (–23).

Δ-**Ir4**:

IR (film) ν_{max}: 2961, 2912, 2872, 1606, 1525, 1445, 1353, 1274, 1119, 886, 835, 711, 673 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{68}H_{73}IrN_5O_5$ [M–BArF$_{24}$]$^+$: 1232.5242, found: 1232.5239.

CD (MeOH): λ, nm (Δε, M^{-1}cm^{-1}) 361 (–37), 335 (–37), 272 (+21), 241 (+16).



Λ-**Ir5**

Following the general procedure, Λ-(*S*)-**7e** (40.1 mg, 0.050 mmol) was converted to Λ-**Ir5** (38.0 mg, yield: 46%) as an orange solid.

^{1}H NMR (500 MHz, CD_2Cl_2) *δ* 8.20 (dt, *J* = 5.4, 1.2 Hz, 1H), 8.11–8.06 (m, 2H), 7.88 (ddd, *J* = 7.7, 1.4, 0.5 Hz, 1H), 7.83 (ddd, *J* = 7.7, 1.4, 0.5 Hz, 1H), 7.74–7.71 (m, 9H), 7.71–7.69 (m, 1H), 7.59–7.56 (m, 1H), 7.55 (s, 4H), 7.46 (ddd, *J* = 8.5, 7.6, 1.2 Hz, 1H), 7.42 (ddd, *J* = 8.5, 7.6, 1.1 Hz, 1H), 7.35–7.30 (m, 1H), 7.18 (td, *J* = 7.5, 1.0 Hz, 1H), 7.16–7.11 (m, 2H), 7.04 (td, *J* = 7.5, 1.4 Hz, 1H), 6.98 (td, *J* = 7.5, 1.4 Hz, 1H), 6.70–6.64 (m, 1H), 6.62–6.57 (m, 1H), 6.49 (ddd, *J* = 8.1, 1.1, 0.6 Hz, 1H), 5.81 (ddd, *J* = 8.1, 1.0, 0.6 Hz, 1H), 4.25 (ddd, *J* = 15.2, 4.3, 2.5 Hz, 1H), 4.04 (ddd, *J* = 15.2, 4.4, 2.6 Hz, 1H), 3.50 (ddd, *J* = 14.2, 4.4, 2.5 Hz, 1H), 3.02 (ddd, *J* = 14.2, 4.3, 2.6 Hz, 1H), 1.95 (s, 1H).

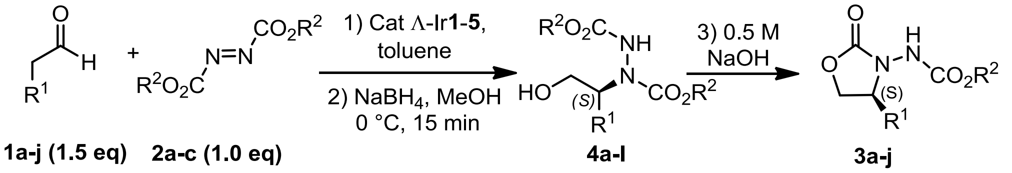
^{13}C NMR (125 MHz, CD_2Cl_2) *δ* 178.0, 177.8, 169.9, 162.8, 162.4, 162.0, 161.6, 161.0, 153.5, 150.71, 150.68, 147.4, 146.0, 145.0, 142.6, 140.4, 137.7, 137.5, 135.2, 134.0, 133.8, 133.7, 133.3, 129.7, 129.5, 129.48, 129.46, 129.43, 129.41, 129.39, 129.3, 129.21, 129.18, 129.16, 129.1, 128.9, 128.3, 127.4, 127.3, 127.05, 126.95, 126.7, 126.6, 126.1, 124.1, 124.01, 123.92, 123.7, 121.8, 117.93, 117.90, 117.87, 114.6, 114.5, 113.05, 113.00, 44.2, 42.5.

IR (film) ν_{max}: 1673, 1601, 1521, 1453, 1353, 1273, 1116, 937, 889, 743, 711, 673 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{36}H_{25}IrN_5O_3$ [M–BArF$_{24}$]$^+$: 768.1583, found: 768.1591.

CD (MeOH): λ, nm (Δε, M^{-1}cm^{-1}) 354 (+25), 328 (+30), 263 (–10), 227 (–25).

3. Iridium-Catalyzed Reactions



Scheme S7. Iridium-catalyzed asymmetric α-amination of aldehydes.

General procedure for catalytic reactions of Table 1:

To a solution of dibenzyl azodicarboxylate **2a** (0.2 mmol) and Λ-**Ir1**-**5** (0.1-4 mol%) in anhydrous toluene (2.0 mL, 0.1 M for entries 1-5, 9 or 200.0 µL, 1.0 M for entries 6-8) at 0 °C was added the 3,3-dimethylbutyraldehyde **1a** (0.30 mmol). After being stirred at 0 °C (entries 1-4, 5) or RT (entries 5-8) for 1.5 to 36 h under argon atmosphere, MeOH (2.0 mL for entries 1-5, 9 or 200.0 µL for entries 6-8) was added followed by careful addition of $NaBH_4$ (10.0 mg, 0.26 mmol) at 0 °C. After 15 min, NaOH (0.5 M, 0.52 mL) was added and after an additional 2 h the mixtures were diluted with water. The aqueous phase was extracted with EtOAc (4 × 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/hexane = 1:4) to give compound **3a**.

General procedure for catalytic reactions of Table 2:

Azodicarboxylates **2a-c** (0.2 mmol) and Λ-**Ir4** (1 mol%) were mixed in a brown glass vial with anhydrous toluene (200.0 µL, 1.0 M), and the corresponding aldehyde **1a-j** (0.30 mmol) was added at 0 °C. While being stirred at room temperature under argon atmosphere for 12-15 h, the amination products precipitated. MeOH (200.0 µL) was added followed by a careful addition of $NaBH_4$ (10.0 mg, 0.26 mmol) at 0 °C. After 15 min, NaOH (0.5 M, 0.52 mL) was added and after an additional 2 h the mixtures were diluted with water (exception for entries 11-12: this NaOH step was skipped). The aqueous phase was extracted with EtOAc (4 × 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc:hexane = 1:4→1:1) to give compounds **4k-l** and **3a-j**.

Catalysis with the PF_6 salt of Λ-Ir4 (in analogy to entry 1 of Table 2):

To a solution of Λ-**Ir4/PF_6** (2.8 mg, 0.002 mmol) in anhydrous toluene (200.0 μL) was added sodium tetrakis[(3,5-di-trifluoromethyl)phenyl]borate ($NaBArF_{24}$) (1.8 mg, 0.002 mmol) in one portion and the mixture was stirred at room temperature for 15 min. Then, dibenzyl azodicarboxylate **2a** (60.0 mg, 0.20 mmol) and 3,3-dimethylbutyraldehyde **1a** (37.6 μL, 0.30 mmol) were added successively at 0 °C. After being stirred at room temperature for 15 h under argon atmosphere, MeOH (200.0 μL) was added followed by a careful addition of $NaBH_4$ (10.0 mg, 0.26 mmol) at 0 °C. After 15 min, NaOH (0.5 M, 0.52 mL) was added and after an additional 2 h the mixtures were diluted with water. The aqueous phase was extracted with EtOAc (4 × 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/hexane = 1:4) to give compound **3a** (50.0 mg, yield: 85%, ee: 96%) as a white solid.

Recycling experiments of catalyst Λ-Ir4 (catalysis in analogy to entry 1 of Table 2).

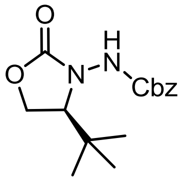
Cycle 1: Dibenzyl azodicarboxylate **2a** (298.3 mg, 1.0 mmol) and Λ-**Ir4** (20.9 mg, 0.01 mmol) were mixed in a centrifuge tube with anhydrous toluene (1.0 mL), followed by the addition of 3,3-dimethylbutyraldehyde **1a** (188.0 μL, 1.5 mmol) at 0 °C. After being stirred at room temperature for 15 h under argon atmosphere, n-hexane (300.0 μL) was added followed by centrifugation at 4 °C. The mother liquor was transferred out and concentrated under reduced pressure. The residue (TLC showed it contained the catalyst along with a minor amount of amination product) was purified by flash chromatography on silica gel (eluent: $MeOH/CH_2Cl_2$ = 1:10) to give the pure catalyst Λ-**Ir4** (17.0 mg, recovery yield: 81%). MeOH (1.0 mL) was added to the solid in the centrifuge tube followed by careful addition of $NaBH_4$ (49.4 mg, 1.3 mmol) at 0 °C. After 15 min, NaOH (0.5 M, 2.6 mL) was added and after an additional 2 h the mixtures were diluted with water. The aqueous phase was extracted with EtOAc (4 × 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude compound **3a** was purified by flash chromatography on silica gel (eluent: EtOAc/hexane = 1:4) to give compound **3a** (222.3 mg, yield: 76%, ee: 97%) as a white solid. The recycled catalyst Λ-**Ir4** was used for another catalysis reaction (cycle 2).

Cycle 2: Dibenzyl azodicarboxylate **2a** (242.1 mg, 0.81 mmol) and the recycled catalyst Λ-**Ir4** (17.0 mg, 0.0081 mmol) were mixed in a centrifuge tube with anhydrous toluene

(811.0 μL), followed by the addition of 3,3-dimethylbutyraldehyde **1a** (152.0 μL, 1.22 mmol) at 0 °C. After being stirred at room temperature for 15 h under argon atmosphere, n-hexane (250.0 μL) was added followed by centrifugation at 4 °C. The mother liquor was transferred out and concentrated under reduced pressure. The residue (TLC showed it contained the catalyst along with a minor amount of amination product) was purified by flash chromatography on silica gel (eluent: MeOH/CH_2Cl_2 = 1:10) to give the pure catalyst Λ-**Ir4** (13.2 mg, recovery yield: 78%). MeOH (811.0 μL) was added to the solid in the centrifuge tube followed by a careful addition of $NaBH_4$ (40.0 mg, 1.05 mmol) at 0 °C. After 15 min, NaOH (0.5 M, 2.1 mL) was added and after an additional 2 h the mixtures were diluted with water. The aqueous phase extracted with EtOAc (4 × 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude compound **3a** was purified by flash chromatography on silica gel (eluent: EtOAc/hexane = 1:4) to give compound **3a** (168.0 mg, yield: 71%, ee: 95%) as a white solid. The twice recycled catalyst Λ-**Ir4** was used for another catalysis reaction (cycle 3).

Cycle 3: Dibenzyl azodicarboxylate **2a** (188.0 mg, 0.63 mmol) and the twice recycled catalyst Λ-**Ir4** (13.2 mg, 0.0063 mmol) were mixed in a centrifuge tube with anhydrous toluene (630.0 μL), followed by the addition of 3,3-dimethylbutyraldehyde **1a** (118.0 μL, 0.95 mmol) at 0 °C. After being stirred at room temperature for 15 h under argon atmosphere, n-hexane (200.0 μL) was added followed by centrifugation at 4 °C. The mother liquor was transferred out and concentrated under reduced pressure. The residue (TLC showed that it contained the catalyst along with a minor amount of amination product) was purified by flash chromatography on silica gel (eluent: MeOH/CH_2Cl_2 = 1:10) to give the pure catalyst Λ-**Ir4** (MeOH/CH_2Cl_2 = 1:10) (10.0 mg, recovery yield: 76%). MeOH (630.0 μL) was added to the solid in the centrifuge tube followed by a careful addition of $NaBH_4$ (31.0 mg, 0.82 mmol) at 0 °C. After 15 min, NaOH (0.5 M, 1.7 mL) was added and after an additional 2 h the mixtures were diluted with water. The aqueous phase extracted with EtOAc (4 × 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude compound **3a** was purified by flash chromatography on silica gel (eluent: EtOAc/hexane = 1:4) to give compound **3a** (123.0 mg, yield: 67%, ee: 96%) as a white solid.

(*S*)-Benzyl 4-*tert*-butyl-2-oxooxazolidin-3-ylcarbamate (3a)



From dibenzyl azodicarboxylate **2a** (60.0 mg, 0.20 mmol) and 3,3-dimethylbutyraldehyde **1a** (37.6 μL, 0.30 mmol) for 12 h according to the general procedure to give **3a** (56.0 mg, yield: 96%) as a white solid. Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak IB column, ee = 97% (HPLC: IB, 254 nm, 40 °C, hexane/ isopropanol = 90/ 10, flow rate 0.5 mL/ min, t_r(major) = 25.0 min, t_r(minor)= 28.7 min); $[\alpha]_D^{20}$ –10.0 (*c* 0.2, $CHCl_3$).

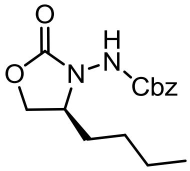
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (s, 5H), 5.15 (q, J = 12.2 Hz, 1H), 4.39 (t, J = 8.8 Hz, 1H), 4.25–3.98 (m, 1H), 3.83 (s, 1H), 0.93 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 155.0, 135.4, 128.5, 128.4, 128.0, 67.9, 64.5, 64.2, 33.3, 25.4.

IR (film) ν_{max}: 3320, 2959, 1762, 1721, 1505, 1410, 1371, 1224, 1118, 1039, 995, 744, 692 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{20}N_2O_4Na$ $[M+Na]^+$: 315.1315, found: 315.1313.

(*S*)-Benzyl 4-butyl-2-oxooxazolidin-3-ylcarbamate (3b)



From dibenzyl azodicarboxylate **2a** (60.0 mg, 0.20 mmol) and hexanal **1b** (31.8 μL, 0.30 mmol) for 15 h according to the general procedure to give **3b** (47.0 mg, yield: 81%) as a colorless oil. Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak IC column, ee = 94% (HPLC: IC, 254 nm, 40 °C, hexane/ isopropanol = 70/ 30, flow rate 0.8 mL/ min, t_r(minor) = 23.0 min, t_r(major)= 36.5 min); $[\alpha]_D^{20}$ +27.1 (*c* 1.0, $CHCl_3$).

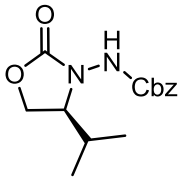
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64–6.83 (m, 6H), 5.18–4.91 (m, 2H), 4.36 (s, 1H), 4.08–3.55 (m, 2H), 1.81–1.57 (m, 1H), 1.53–1.31 (m, 1H), 1.30–1.00 (m, 4H), 0.81 (t, J = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 155.3, 135.3, 128.5, 128.3, 128.0, 67.9, 67.6, 56.7, 31.2, 26.4, 22.5, 13.8.

IR (film) ν_{max}: 3278, 2956, 2931, 2866, 1775, 1729 1503, 1458, 1420, 1227, 1118, 1049, 747, 697 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{20}N_2O_4Na$ $[M+Na]^+$: 315.1315, found: 315.1313.

(*S*)-Benzyl 4-isopropyl-2-oxooxazolidin-3-ylcarbamate (3c)



From dibenzyl azodicarboxylate **2a** (60.0 mg, 0.20 mmol) and 3-methylbutanal **1c** (32.2 μL, 0.30 mmol) for 14 h according to the general procedure to give **3c** (49.3 mg, yield: 89%) as a colorless oil. Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak IA column, ee = 95% (HPLC: IA, 254 nm, 40 °C, solvent A = 0.1% TFA, solvent B = MeCN, with a linear gradient of 30% to 50% B in 40 min, flow rate 0.5 mL/ min, t_r(major) = 27.9 min, t_r(minor)= 29.8 min); $[\alpha]_D^{20}$ +14.2 (*c* 1.0, $CHCl_3$).

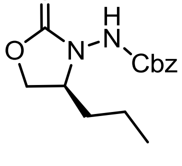
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (s, 5H), 7.14 (s, 1H), 5.16 (s, 2H), 4.36 (s, 1H), 4.12–3.66 (m, 2H), 2.07–1.90 (m, 1H), 0.90 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 155.2, 135.3, 128.6, 128.4, 128.1, 68.0, 64.0, 60.8, 28.5, 17.7, 15.8.

IR (film) ν_{max}: 3272, 2963, 1771, 1723, 1505, 1460, 1421, 1395, 1217, 1118, 1046, 744, 698 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{14}H_{18}N_2O_4Na$ $[M+Na]^+$: 301.1159, found: 301.1157.

(*S*)-Benzyl 2-oxo-4-propyloxazolidin-3-ylcarbamate (3d)



From dibenzyl azodicarboxylate **2a** (60.0 mg, 0.20 mmol) and pentanal **1d** (31.8 μL, 0.30 mmol) for 15 h according to the general procedure to give **3d** (43.2 mg, yield: 78%) as a colorless oil. Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak IA column, ee = 96% (HPLC: IA, 254 nm, 40 °C, solvent A = 0.1% TFA, solvent B = MeCN, with a linear gradient of 30% to 45% B in 40 min, flow rate 0.5 mL/ min, t_r(major) = 31.7 min, t_r(minor)= 33.8 min); $[\alpha]_D^{20}$ +23.4 (*c* 1.0, $CHCl_3$).

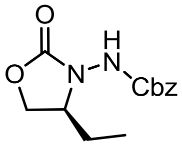
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (s, 5H), 7.21 (s, 1H), 5.15 (s, 2H), 4.43 (s, 1H), 4.06–3.80 (m, 2H), 1.86–1.61 (m, 1H), 1.56–1.37 (m, 1H), 1.36–1.18 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 157.5, 155.3, 135.3, 128.5, 128.3, 128.1, 67.9, 67.6, 56.6, 33.6, 17.8, 13.9.

IR (film) ν_{max}: 3300, 2965, 2934, 2875, 1778, 1701, 1512, 1258, 1228, 1202, 1113, 1052, 1010, 744, 694, 621, 579 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{14}H_{18}N_2O_4Na$ [M+Na]$^+$: 301.1159, found: 301.1157.

(*S*)-Benzyl 4-ethyl-2-oxooxazolidin-3-ylcarbamate (3e)



From dibenzyl azodicarboxylate **2a** (60.0 mg, 0.20 mmol) and butyraldehyde **1e** (27.0 µL, 0.30 mmol) for 15 h according to the general procedure to give **3e** (39.2 mg, yield: 73%) as a colorless oil. Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak IA column, ee = 93% (HPLC: IA, 254 nm, 40 °C, solvent A = 0.1% TFA, solvent B = MeCN, with a linear gradient of 30% to 45% B in 40 min, flow rate 0.5 mL/ min, t_r(major) = 23.8 min, t_r(minor)= 25.3 min); $[\alpha]_D^{20}$ +19.2 (*c* 1.0, CHCl$_3$).

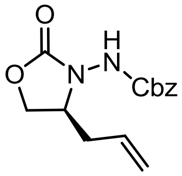
^{1}H NMR (300 MHz, CDCl$_3$) δ 7.34 (s, 5H), 7.18 (s, 1H), 5.15 (s, 2H), 4.44 (s, 1H), 4.19–3.66 (m, 2H), 1.91–1.66 (m, 1H), 1.65–1.39 (m, 1H), 0.88 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 157.5, 155.3, 135.3, 128.5, 128.4, 128.1, 68.0, 67.1, 57.6, 24.3, 8.3.

IR (film) ν_{max}: 3279, 2964, 1768, 1724, 1508, 1218, 1118, 1046, 745, 695 cm^{-1};

HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{16}N_2O_4Na$ [M+Na]$^+$: 287.1002, found: 287.1003.

(*S*)-Benzyl 4-allyl-2-oxooxazolidin-3-ylcarbamate (3f)



From dibenzyl azodicarboxylate **2a** (60.0 mg, 0.20 mmol) and pent-4-enal **1f** (29.6 µL, 0.30 mmol) for 15 h according to the general procedure to give **3f** (48.0 mg, yield: 87%) as a colorless oil. Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak IA column, ee = 92% (HPLC: IA, 254 nm, 40 °C, solvent A = 0.1% TFA, solvent B = MeCN, with a linear gradient of 30% to 45% B in 40 min, flow rate 0.5 mL/ min, t_r(major) = 28.0 min, t_r(minor)= 29.7 min); $[\alpha]_D^{20}$ +36.5 (*c* 1.0, CHCl$_3$).

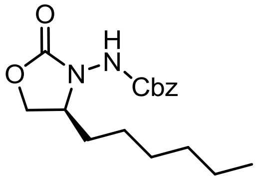
^{1}H NMR (300 MHz, CDCl$_3$) δ 7.27 (s, 5H), 7.07 (s, 1H), 5.60 (td, J = 17.0, 7.0 Hz, 1H), 5.09 (s, 3H), 5.05 (s, 1H), 4.34 (t, J = 7.5 Hz, 1H), 4.02 (s, 2H), 3.92 (t, J = 8.1 Hz, 1H), 2.54–2.34 (m, 1H), 2.23 (dt, J = 14.5, 7.3 Hz, 1H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 157.3, 155.3, 135.3, 131.2, 128.6, 128.4, 128.1, 119.4, 68.0, 66.8, 55.8, 35.7.

IR (film) ν_{max}: 3271, 2912, 1772, 1726, 1502, 1425, 1226, 1119, 1050, 924, 749, 698 cm^{-1}.

HRMS (ESI, *m/z*) calcd for $C_{14}H_{16}N_2O_4Na$ [M+Na]$^+$: 299.1002, found: 299.1000.

(*S*)-Benzyl 4-hexyl-2-oxooxazolidin-3-ylcarbamate (3g)



From dibenzyl azodicarboxylate **2a** (60.0 mg, 0.20 mmol) and octanal **1g** (31.8 μL, 0.30 mmol) for 15 h according to the general procedure to give **3g** (48.0 mg, yield: 75%) as a colorless oil. Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak IA column, ee = 95% (HPLC: IA, 254 nm, 40 °C, solvent A = 0.1% TFA, solvent B = MeCN, with a linear gradient of 30% to 60% B in 40 min, flow rate 0.5 mL/ min, t_r(major) = 33.2 min, t_r(minor)= 35.1 min); $[\alpha]_D^{20}$ +24.8 (*c* 1.0, CHCl$_3$).

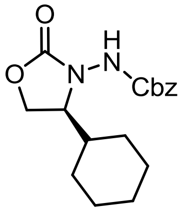
^{1}H NMR (300 MHz, CDCl$_3$) δ 7.26 (s, 6H), 5.07 (d, J = 2.0 Hz, 2H), 4.35 (s, 1H), 4.10–3.55 (m, 2H), 1.82–1.54 (m, 1H), 1.40 (s, 1H), 1.18 (s, 8H), 0.80 (t, J = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 157.5, 155.3, 135.3, 128.5, 128.3, 128.0, 67.9, 67.6, 56.7, 31.6, 31.5, 29.0, 24.3, 22.4, 13.9.

IR (film) ν_{max}: 3274, 2925, 2857, 1774, 1728, 1502, 1458, 1420, 1220, 1118, 1048, 748, 698 cm^{-1}.

HRMS (ESI, *m/z*) calcd for $C_{17}H_{24}N_2O_4Na$ [M+Na]$^+$: 343.1628, found: 343.1628.

(*S*)-Benzyl 4-cyclohexyl-2-oxooxazolidin-3-ylcarbamate (3h)



From dibenzyl azodicarboxylate **2a** (60.0 mg, 0.20 mmol) and 2-cyclohexylacetaldehyde **1h** (37.8 mg, 0.30 mmol) for 15 h according to the general procedure to give **3h** (49.0 mg, yield:

77%) as a colorless oil. Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak IC column, ee = 95% (HPLC: IC, 254 nm, 40 °C, hexane/ isopropanol = 70/ 30, flow rate 0.8 mL/ min, t_r(minor) = 23.9 min, t_r(major)= 52.3 min); $[\alpha]_D^{20}$ +24.1 (*c* 1.0, $CHCl_3$).

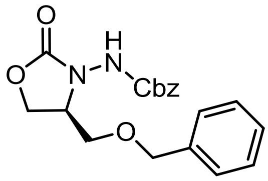
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.26 (s, 5H), 5.31–4.65 (m, 2H), 4.27 (s, 1H), 3.98 (t, *J* = 8.2 Hz, 1H), 3.85 (s, 1H), 1.88–1.32 (m, 6H), 1.32–0.61 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 155.2, 135.3, 128.5, 128.3, 128.0, 67.8, 64.6, 60.3, 38.5, 28.3, 26.3, 26.1, 25.8, 25.5.

IR (film) ν_{max}: 3265, 2925, 2854, 1771, 1722, 1504, 1449, 1419, 1213, 1121, 1047, 741, 696 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{22}N_2O_4Na$ $[M+Na]^+$: 341.1472, found: 341.1470.

(*S*)-Benzyl 4-(benzyloxymethyl)-2-oxooxazolidin-3-ylcarbamate (3i)



From dibenzyl azodicarboxylate **2a** (60.0 mg, 0.20 mmol) and 3-(benzyloxy)propanal[S12] **1i** (49.2 mg, 0.30 mmol) for 15 h according to the general procedure to give **3i** (51.2 mg, yield: 75%) as a colorless oil. Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak IC column, ee = 91% (HPLC: IC, 254 nm, 40 °C, hexane/ isopropanol = 80/ 20, flow rate 0.5 mL/ min, t_r(minor)= 27.4 min, t_r(major) = 30.6 min); $[\alpha]_D^{20}$ +13.2 (*c* 1.0, $CHCl_3$).

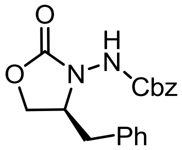
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.20 (m, 10H), 7.10 (s, 1H), 5.28–4.96 (m, 2H), 4.52 (s, 2H), 4.44 (t, *J* = 7.8 Hz, 1H), 4.30–4.00 (m, 2H), 3.59 (qd, *J* = 10.2, 3.7 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1, 155.3, 137.3, 135.2, 128.5, 128.3, 128.1, 128.0, 127.7, 73.3, 67.9, 67.7, 64.8, 55.8.

IR (film) ν_{max}: 3273, 3031, 2867, 1774, 1728, 1499, 1453, 1213, 1105, 1038, 742, 697 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{20}N_2O_5Na$ $[M+Na]^+$: 379.1264, found: 379.1262.

(*S*)-Benzyl 4-benzyl-2-oxooxazolidin-3-ylcarbamate (3j)



From dibenzyl azodicarboxylate **2a** (60.0 mg, 0.20 mmol) and 3-phenylpropanal **1j** (29.6 μL, 0.30 mmol) for 22 h (5 °C for 14 h, then up to RT for additional 8 h) according to the general procedure to give **3j** (59.2 mg, yield: 91%) as a colorless oil. Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak IC column, ee = 89% (HPLC: IC, 254 nm, 40 °C, hexane/ isopropanol = 70/ 30, flow rate 0.5 mL/ min, t_r(minor)= 40.0 min, t_r(major) = 50.5 min); $[\alpha]_D^{20}$ +23.5 (*c* 1.0, $CHCl_3$).

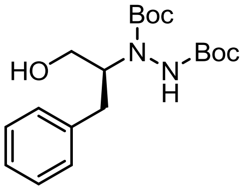
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–6.91 (m, 10H), 5.07 (s, 2H), 4.20 (s, 2H), 3.95 (s, 1H), 3.05 (dd, *J* = 13.7, 4.1 Hz, 1H), 2.91–2.12 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 155.2, 135.3, 135.1, 128.9, 128.6, 128.4, 128.2, 127.2, 68.0, 67.1, 57.7, 37.9.

IR (film) ν_{max}: 3278, 3029, 2938, 1773, 1725, 1496, 1450, 1419, 1221, 1117, 1026, 742, 698 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{18}N_2O_4Na$ $[M+Na]^+$: 349.1159, found: 349.1156.

(*S*)-Di-*tert*-butyl 1-(1-hydroxy-3-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (4k)



From di-*tert*-butyl azodicarboxylate **2b** (46.0 mg, 0.20 mmol) and 3-phenylpropanal **1j** (29.6 μL, 0.30 mmol) for 15 h according to the general procedure to give **4k** (67.0 mg, yield: 91%) as a white solid. Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak IC column, ee = 96% (HPLC: IC, 254 nm, 40 °C, hexane/ isopropanol = 80/ 20, flow rate 0.5 mL/ min, t_r(major) = 13.9 min, t_r(minor)= 16.9 min); $[\alpha]_D^{20}$ –33.7 (*c* 1.0, $CHCl_3$), (lit[S13] $[\alpha]_D^{25}$ +30.8 (*c* 0.53, $CHCl_3$) product obtained by *L*-proline catalyzed α-amination with *R*-configuration),

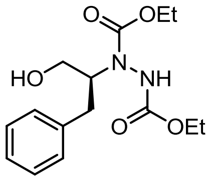
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–6.76 (m, 5H), 6.21–5.78 (m, 1H), 4.94–4.31 (m, 1H), 3.70–3.23 (m, 2H), 2.93–2.14 (m, 2H), 1.43 (s, 9H), 1.23 (m, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 155.7, 155.5, 154.7, 137.8, 128.8, 128.5, 126.5, 82.6, 82.3, 81.7, 81.3, 62.2, 61.9, 34.7, 28.1, 28.0, 27.8.

IR (film) ν_{max}: 3419, 3224, 2975, 2930, 1720, 1675, 1531, 1392, 1367, 1333, 1278, 1255, 1160, 1022, 791, 752, 701 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{30}N_2O_5Na$ $[M+Na]^+$: 389.2047, found: 389.2045.

(*S*)-Diethyl 1-(1-hydroxy-3-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (4l)



From diethyl azodicarboxylate **2c** (2.2 M in toluene, 90.9 μL, 0.20 mmol) and 3-phenylpropanal **1j** (29.6 μL, 0.30 mmol) for 15 h according to the general procedure to give **4l** (54.6 mg, yield: 88%) as a white solid. Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak IC column, ee = 95% (HPLC: IC, 254 nm, 40 °C, hexane/ isopropanol = 70/ 30, flow rate 0.5 mL/ min, t_r(minor)= 31.3 min, t_r(major) = 76.1 min); $[\alpha]_D^{20}$ –26.1 (*c* 1.0, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53–6.78 (m, 5H), 6.59–6.09 (m, 1H), 4.92–4.40 (m, 1H), 4.29–4.09 (m, 2H), 4.08–3.84 (m, 2H), 3.69–3.19 (m, 2H), 2.90–2.30 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 156.8, 137.4, 128.7, 128.6, 126.6, 62.9, 62.7, 61.9, 34.6, 14.2.

IR (film) ν_{max}: 3428, 3244, 2989, 2922, 2864, 1724, 1678, 1524, 1416, 1254, 1219, 1061, 1025, 776, 753 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{22}N_2O_5Na$ $[M+Na]^+$: 333.1421, found: 333.1417.

4. HPLC on Chiral Stationary Phase

4.1. Determination of Enantiopurities of the Iridium Catalyst Λ-Ir4 and Δ-Ir4

The analysis was performed with a Daicel Chiralpak IA (250 × 4.6 mm) HPLC column on an Agilent 1200 Series HPLC System. The column temperature was 30 °C and UV-absorption was measured at 254 nm. mobile phase: solvent A = 0.1% TFA, solvent B = MeCN, flow rate = 0.5 mL/min, column temperature = 40 °C, UV absorption = 254 nm.

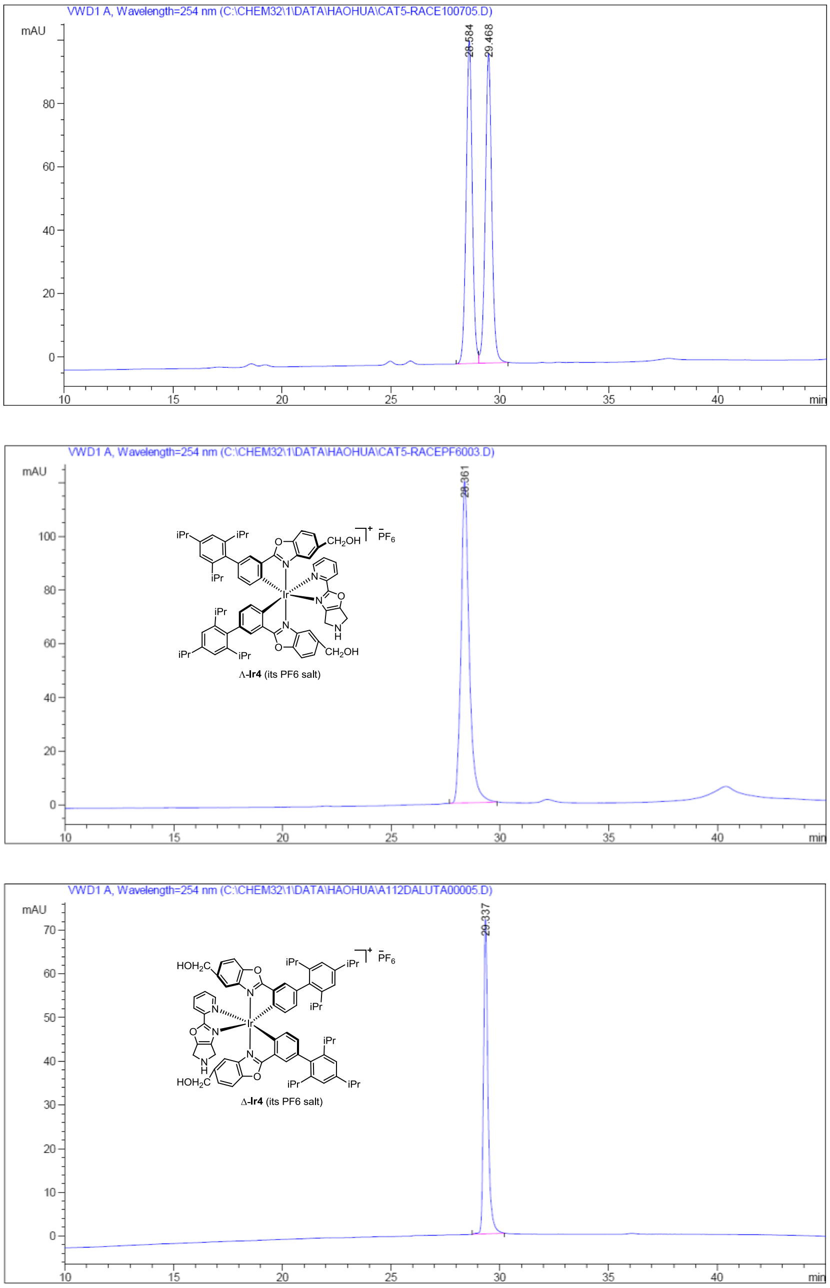
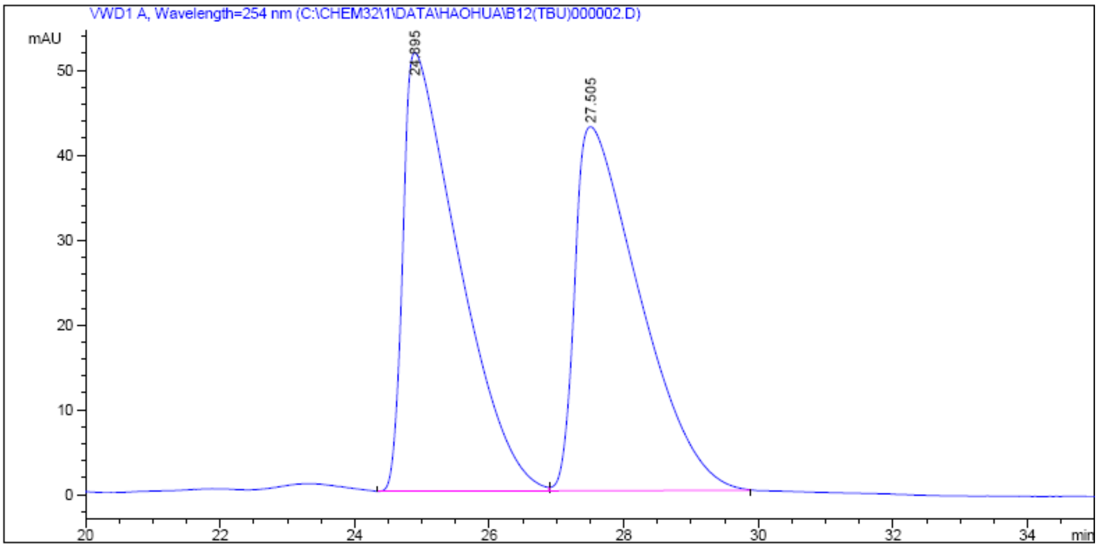


Figure S1. HPLC traces of the reference *rac*-**Ir4**, **Λ-Ir4**, and **Δ-Ir4** (all as their PF_6 salt). Integration of peak areas > 99% *ee* (Daicel Chiralpak IA, with a linear gradient of 30% to 60% B in 25 min, flow rate = 0.5 mL/min).

4.2. Determination of Enantioselectivities for the Asymmetric α-Amination Reactions

Optical purities of the compounds **3k-l** and **4a-j** were analyzed with Daicel Chiralpak IA, IB or IC (250 × 4.6 mm) HPLC columns on an Agilent 1200 Series HPLC System. Mobile phase: hexane/isopropanol or 0.1% TFA/MeCN, flow rate = 0.5 or 0.8 mL/min, column temperature = 40 °C, UV absorption = 254 nm.



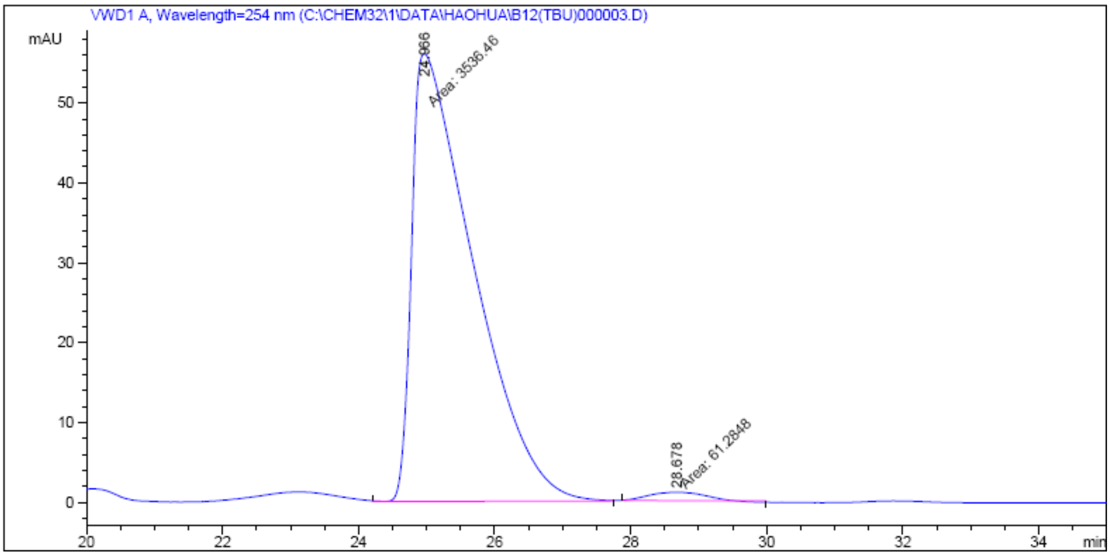


Figure S2. HPLC traces of *rac*-**3a** and (*S*)-**3a**. Area integration = 98.3:1.7 (97% ee, Daicel Chiralpak IB, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min).

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  24.966 MM    1.0509 3536.45825   56.08680  98.2966
   2  28.678 MM    0.9525   61.28478    1.07235   1.7034
```

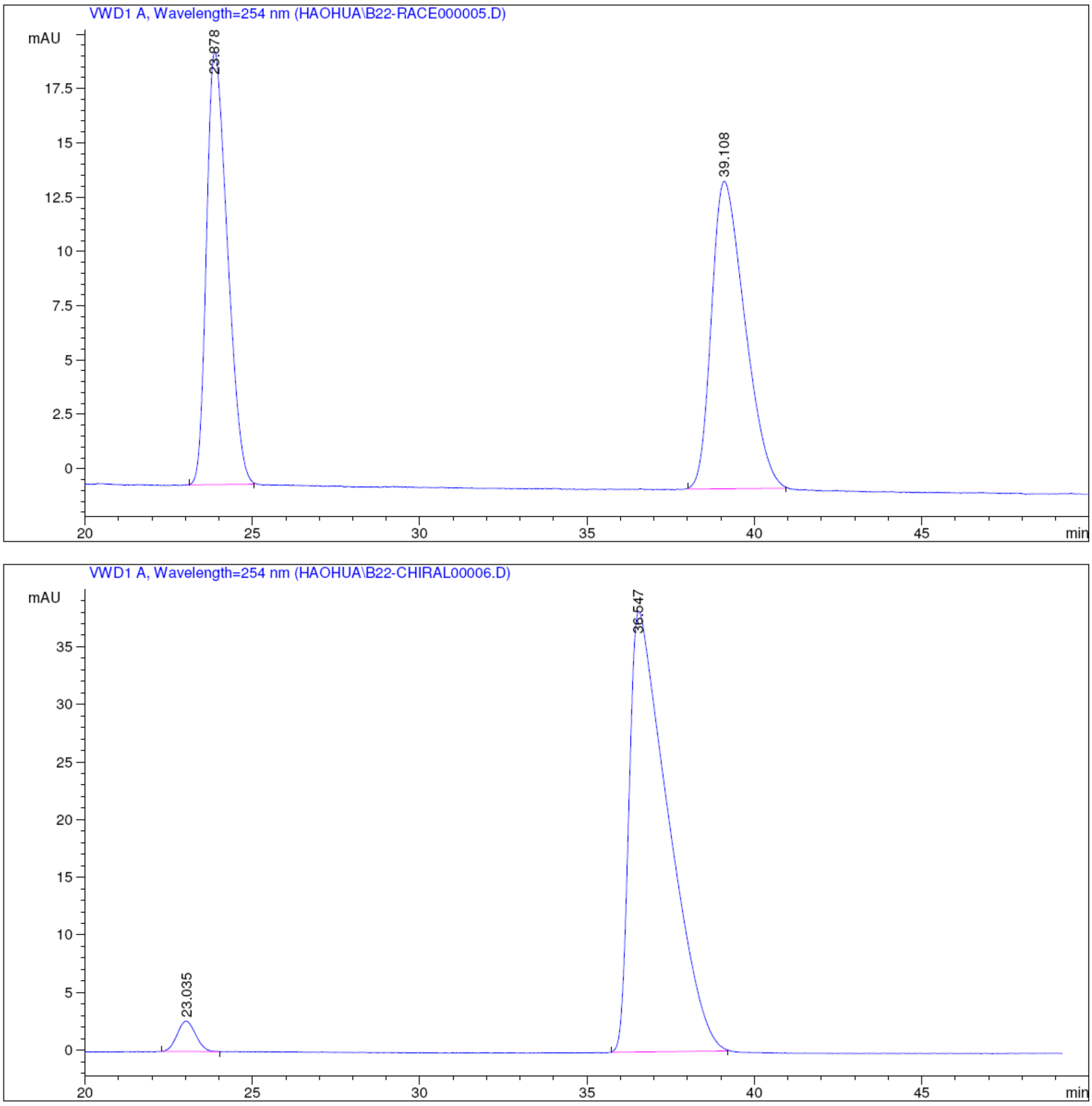
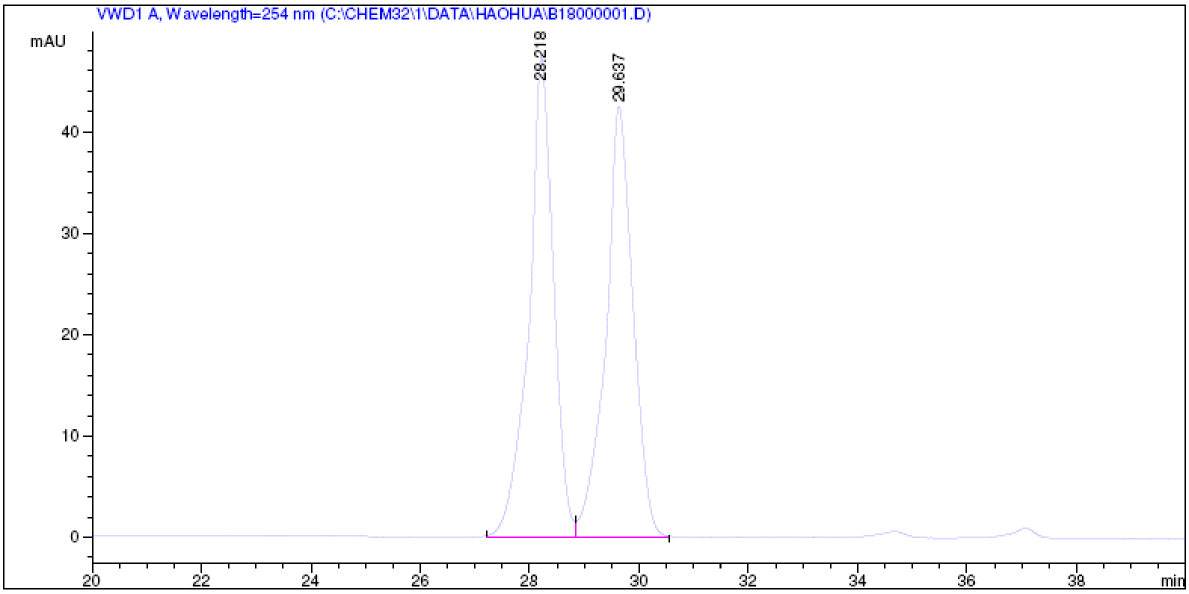


Figure S3. HPLC traces of *rac*-**3b** and (*S*)-**3b**. Area integration = 96.8: 3.2 (94% ee, Daicel Chiralpak IC, hexane/isopropanol = 70/30, flow rate = 0.8 mL/min).

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1  23.035 BB    0.4929  101.36393    2.63267   3.1877
   2  36.547 BB    1.0792 3078.53125   38.23318  96.8123
```



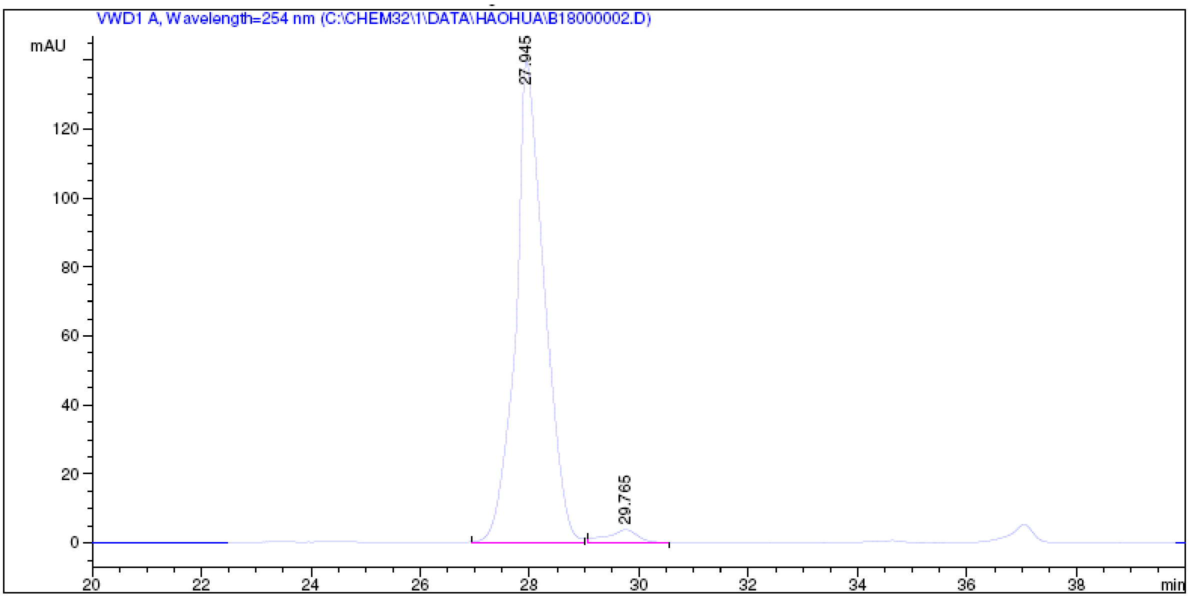


Figure S4. HPLC traces of *rac*-**3c** and (*S*)-**3c**. Area integration = 97.4: 2.6 (95% ee, Daicel Chiralpak IA, solvent A= 0.1% TFA, solvent B = MeCN, with a linear gradient of 30% to 50% B in 40 min, flow rate = 0.5 mL/min).

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s  [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1  27.945 BB    0.5279 5090.43408  139.43045  97.3738
   2  29.765 BB    0.5253  137.29082    3.68219   2.6262
```

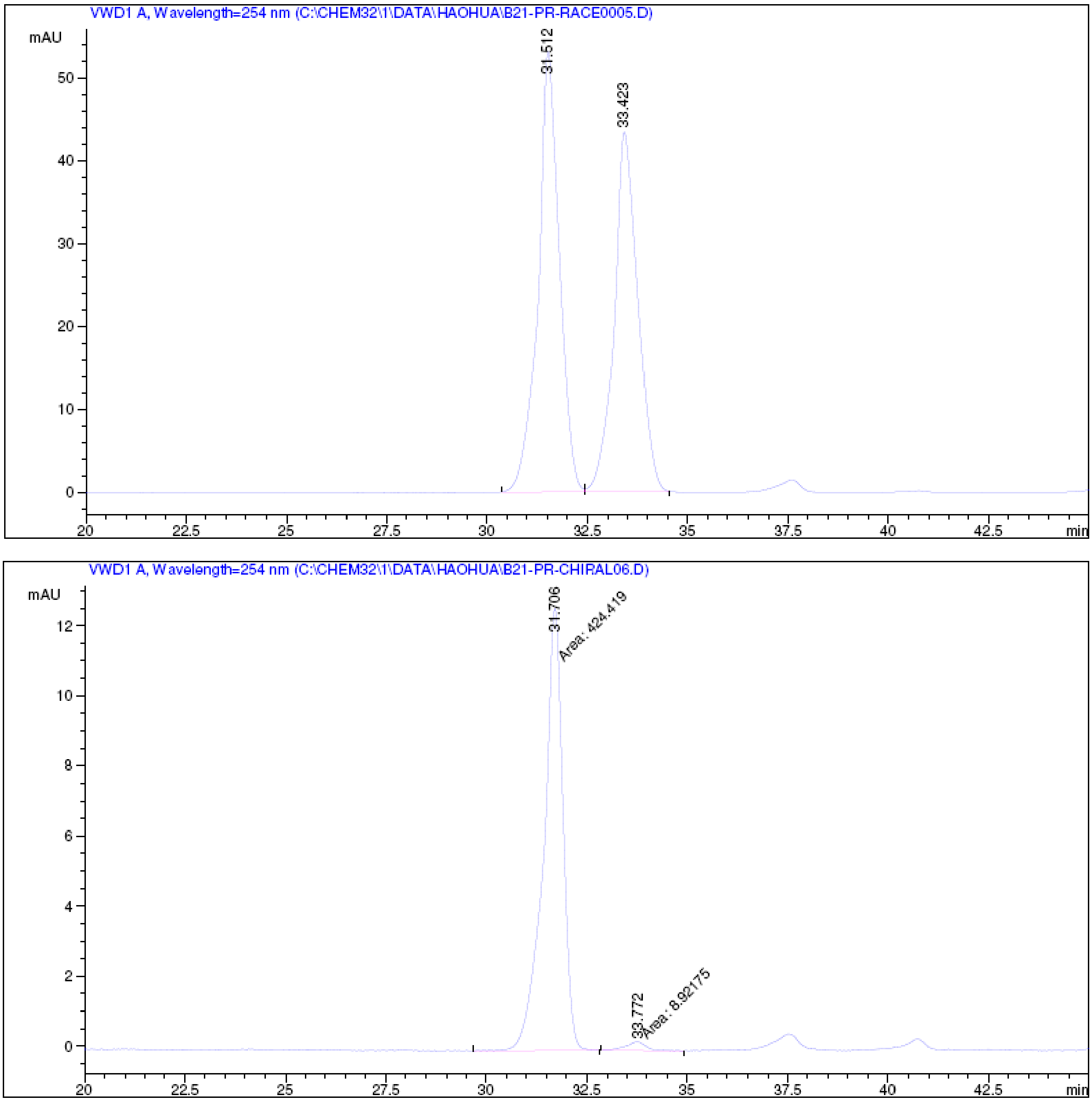


Figure S5. HPLC traces of *rac*-**3d** and (*S*)-**3d**. Area integration = 97.9: 2.1 (96% ee, Daicel Chiralpak IA, solvent A= 0.1% TFA, solvent B = MeCN, with a linear gradient of 30% to 45% B in 40 min, flow rate = 0.5 mL/min).

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1  31.706 MM    0.5609  424.41931   12.61043  97.9412
   2  33.772 MM    0.5907    8.92175 2.51743e-1   2.0588
```

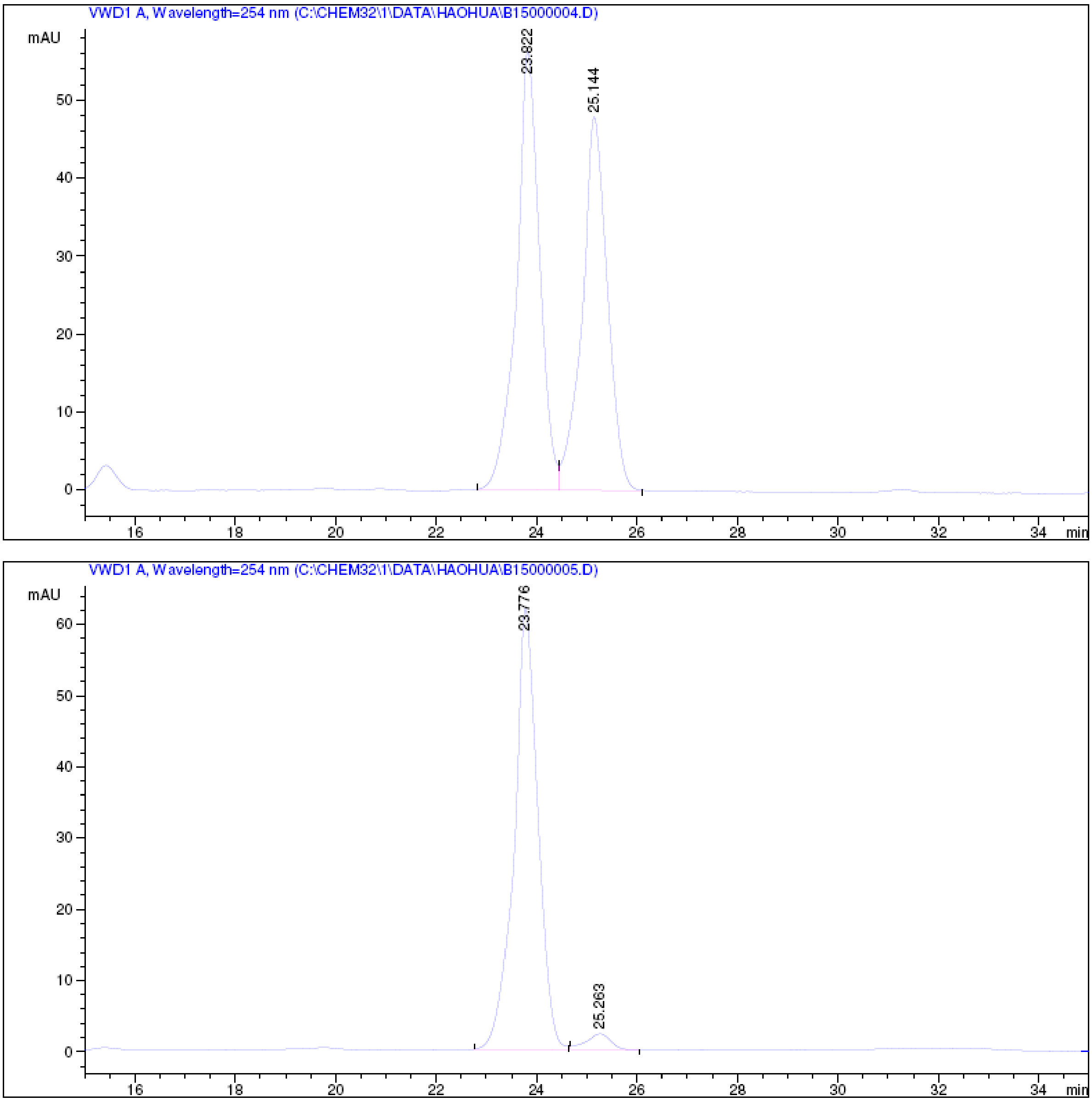


Figure S6. HPLC traces of *rac*-**3e** and (*S*)-**3e**. Area integration = 96.4: 3.6 (93% ee, Daicel Chiralpak IA, solvent A= 0.1% TFA, solvent B = MeCN, with a linear gradient of 30% to 45% B in 40 min, flow rate = 0.5 mL/min).

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU   *s   [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  23.776 BB    0.4808 2040.58545   61.88373  96.4197
   2  25.263 BB    0.4699   75.77260    2.24263   3.5803
```

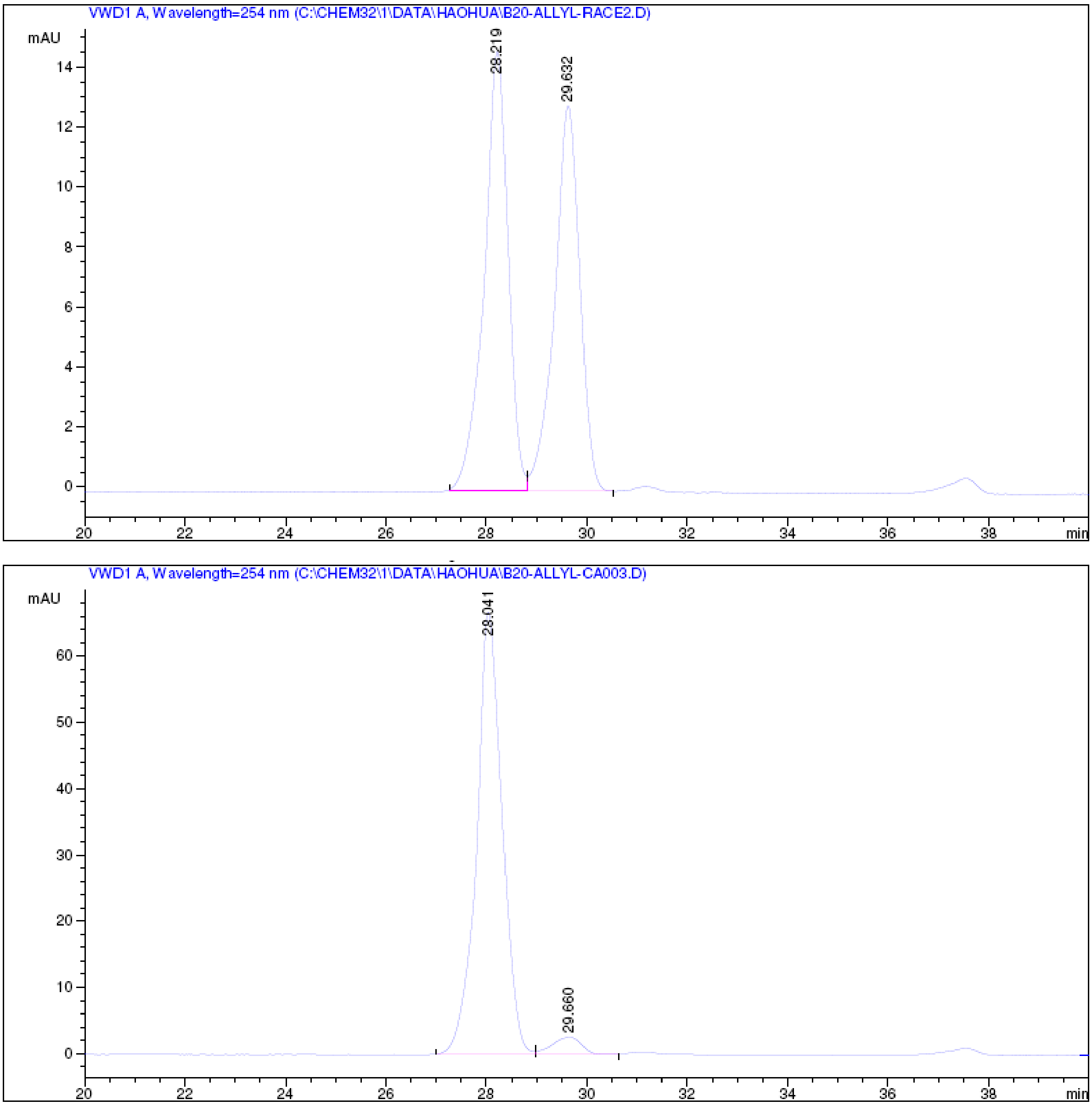


Figure S7. HPLC traces of *rac*-**3f** and (*S*)-**3f**. Area integration = 95.9: 4.1 (92% ee, Daicel Chiralpak IA, solvent A= 0.1% TFA, solvent B = MeCN, with a linear gradient of 30% to 45% B in 40 min, flow rate = 0.5 mL/min).

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  28.041 BB    0.5221 2359.26465   66.66464  95.9081
   2  29.660 BB    0.5412  100.65646    2.55497   4.0919
```

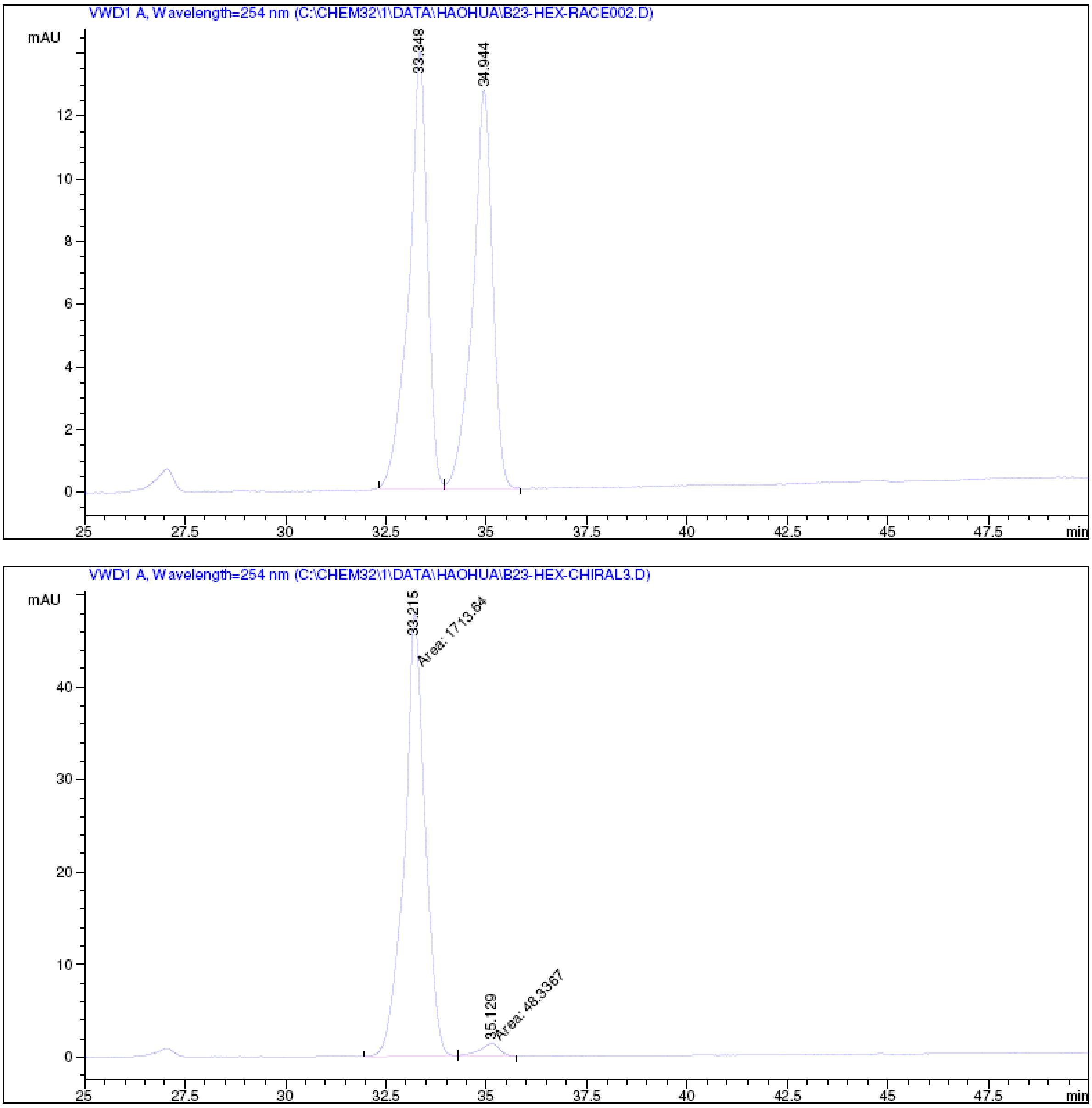


Figure S8. HPLC traces of *rac*-**3g** and (*S*)-**3g**. Area integration = 97.3: 2.7 (95% ee, Daicel Chiralpak IA, solvent A= 0.1% TFA, solvent B = MeCN, with a linear gradient of 30% to 60% B in 40 min, flow rate = 0.5 mL/min).

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1  33.215 MF    0.5966 1713.63708   47.87411  97.2567
   2  35.129 FM    0.5794   48.33672    1.39031   2.7433
```

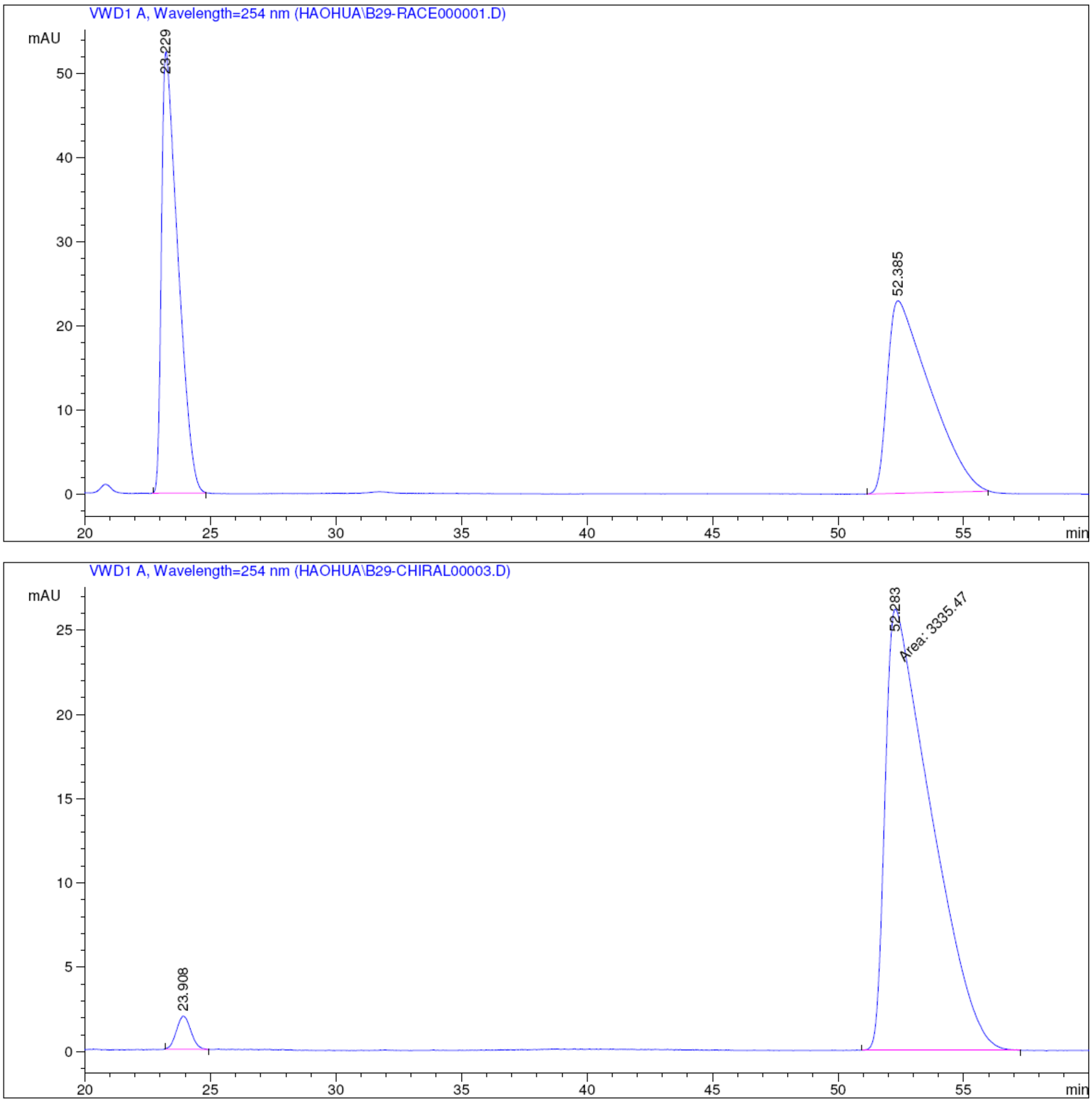


Figure S9. HPLC traces of *rac*-**3h** and (*S*)-**3h**. Area integration = 97.7: 2.3 (95% ee, Daicel Chiralpak IC, hexane/isopropanol = 70/30, flow rate = 0.8 mL/min).

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1  23.908 BB    0.4937   78.81164    1.97315   2.3083
   2  52.283 MM    2.1248 3335.46729   26.16319  97.6917
```

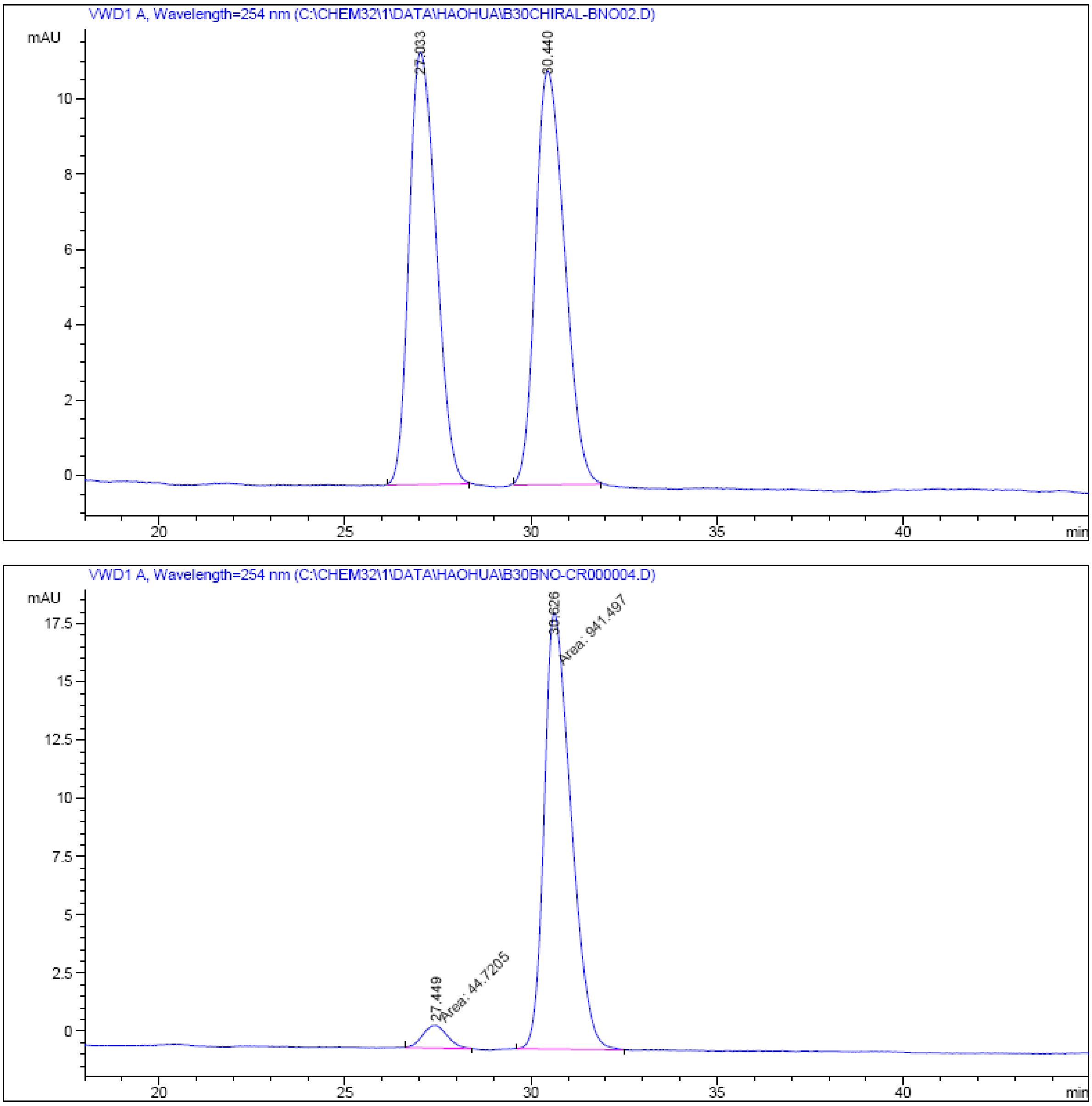


Figure S10. HPLC traces of *rac*-**3i** and (*S*)-**3i**. Area integration = 95.5: 4.5 (91% ee, Daicel Chiralpak IC, hexane/isopropanol = 80/20, flow rate = 0.5 mL/min).

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1  27.449 MM    0.7611   44.72052 9.79339e-1   4.5345
   2  30.626 MM    0.8366  941.49713   18.75706  95.4655
```

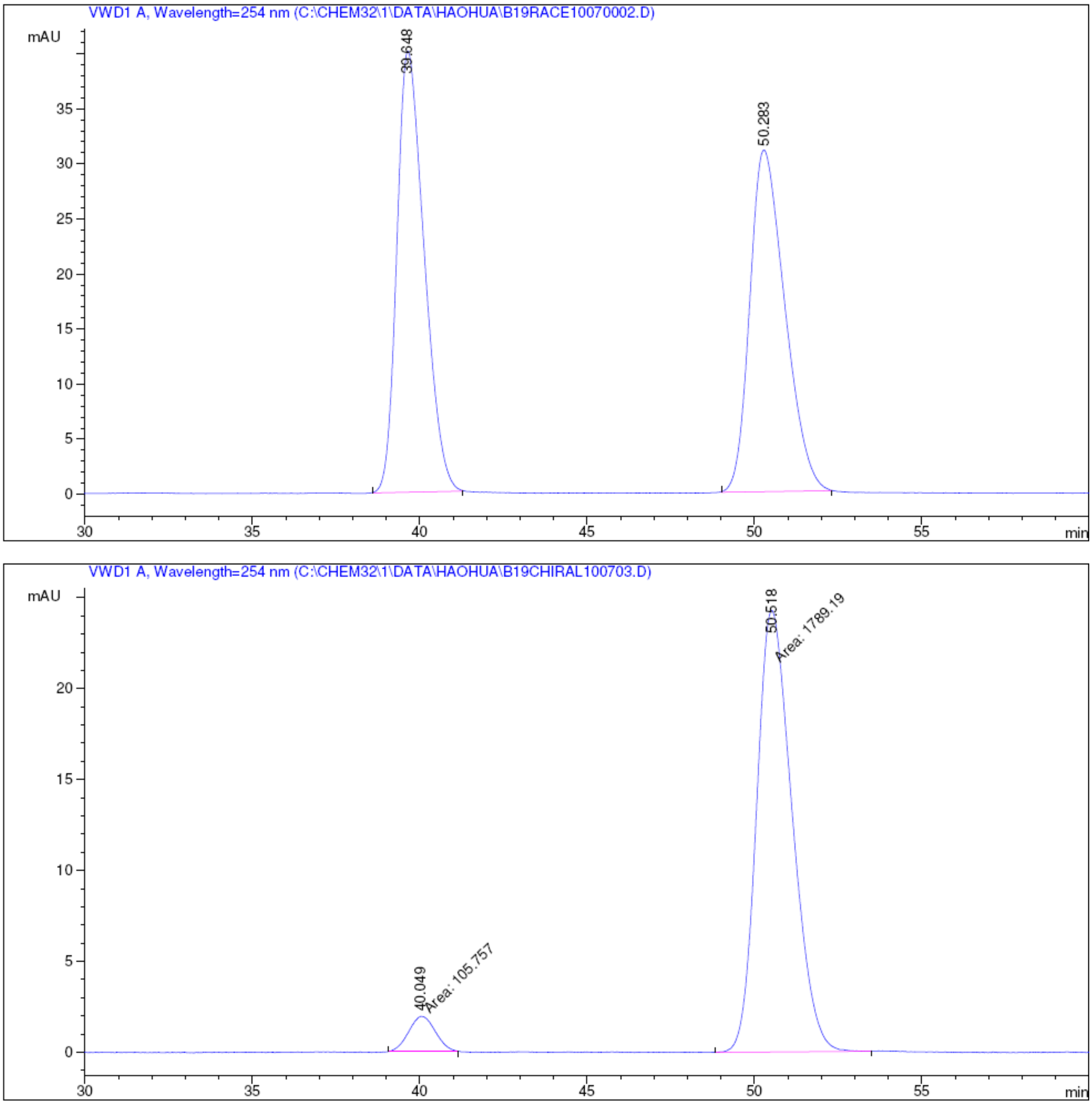


Figure S11. HPLC traces of *rac*-**3j** and (*S*)-**3j**. Area integration = 94.4: 5.6 (89% ee, Daicel Chiralpak IC, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min).

```
Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]   mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1  40.049 MM    0.9141  105.75706    1.92819   5.5810
   2  50.518 MM    1.2278 1789.18652   24.28755  94.4190
```

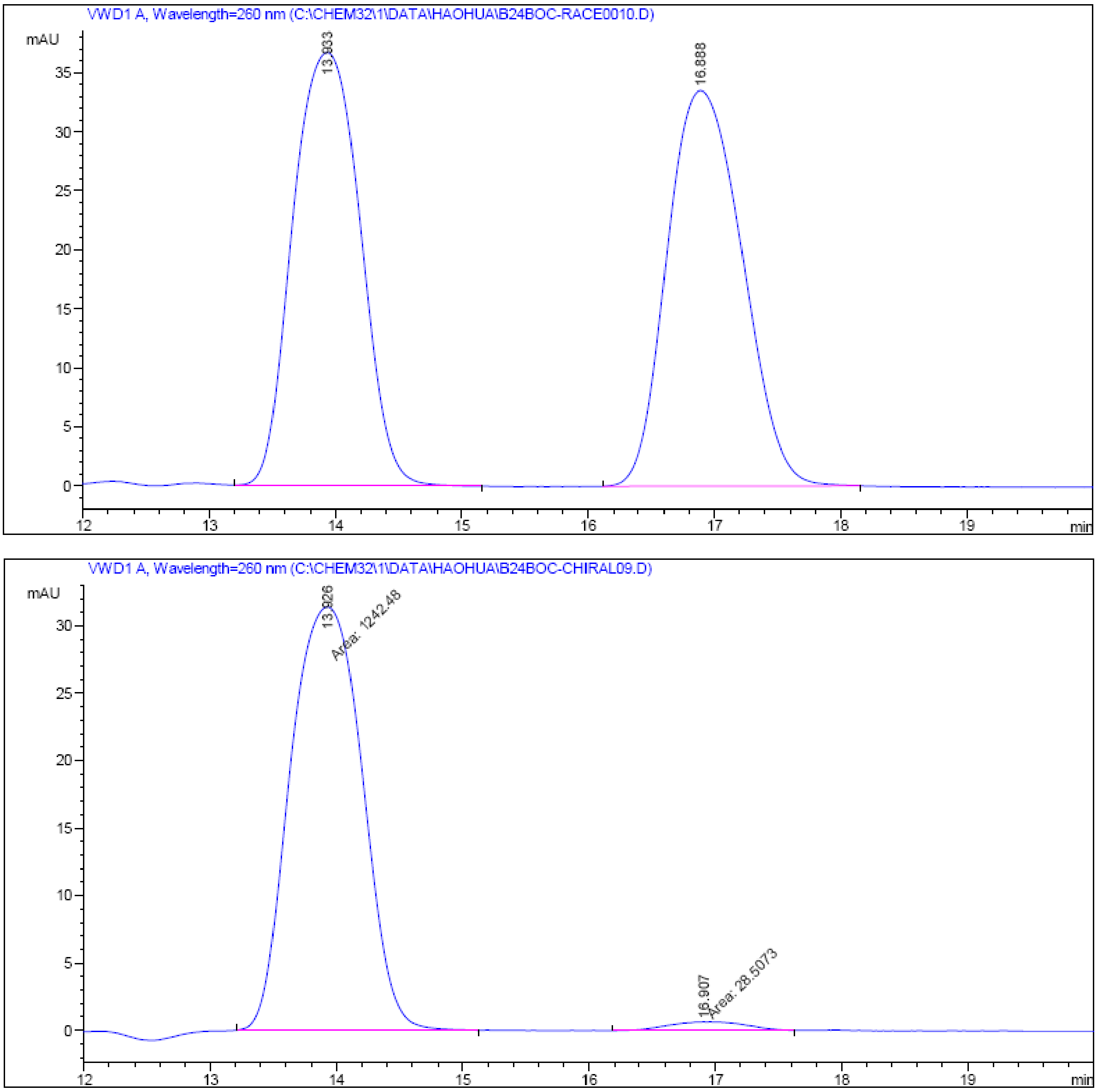


Figure S12. HPLC traces of *rac*-**4k** and (*S*)-**4k**. Area integration = 97.8: 2.2 (96% ee, Daicel Chiralpak IC, hexane/isopropanol = 80/20, flow rate = 0.5 mL/min).

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1  13.926 MM    0.6591 1242.48035   31.41781  97.7571
   2  16.907 MM    0.7234   28.50731 6.56832e-1   2.2429
```

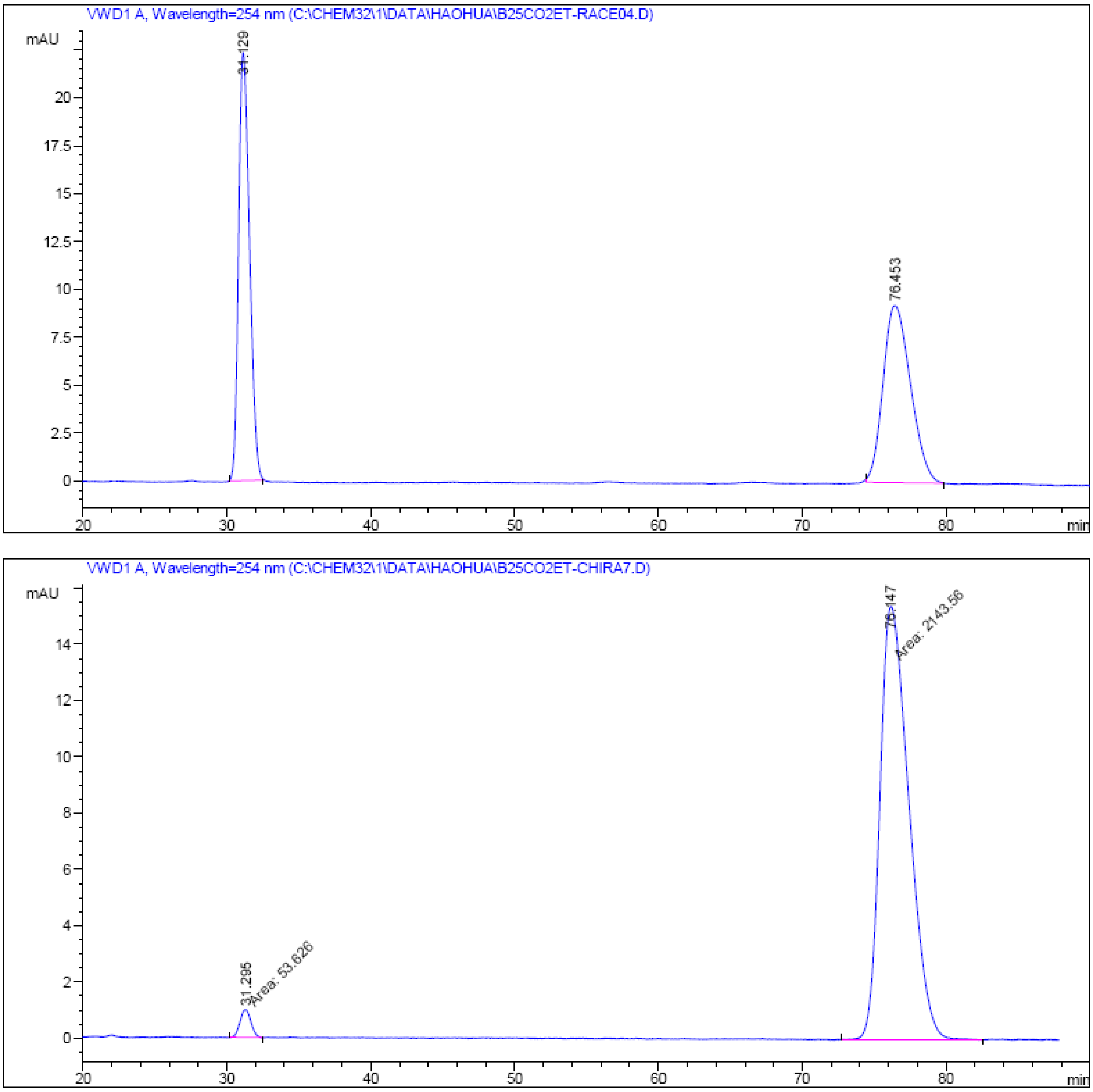


Figure S13. HPLC traces of *rac*-**4l** and (*S*)-**4l**. Area integration = 97.6: 2.4 (95% ee, Daicel Chiralpak IC, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min).

```
Peak RetTime Type  Width     Area      Height     Area  
  #   [min]        [min]  mAU    *s   [mAU    ]     %    
----|-------|----|-------|----------|----------|--------|
   1  31.295 MM    0.8908   53.62602    1.00336   2.4407
   2  76.147 MM    2.3183 2143.56348   15.41068  97.5593
```

5. CD Spectra of Chiral Iridium Complexes

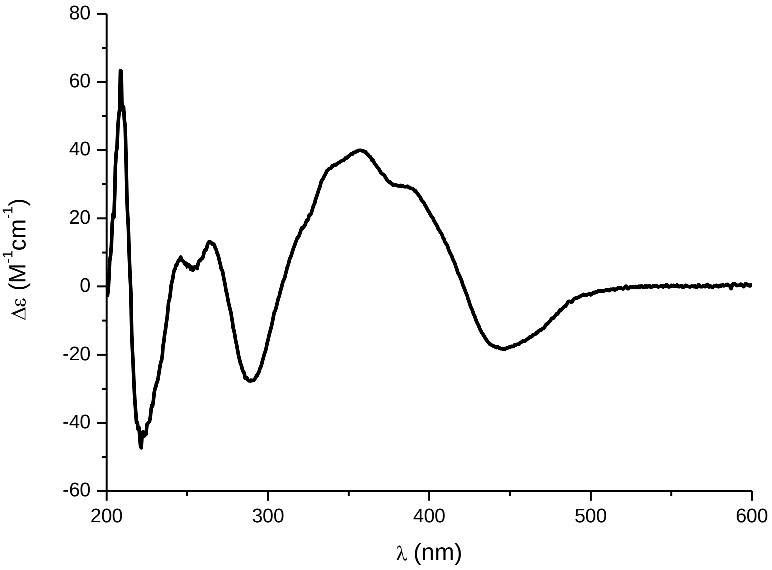


Figure S14. CD spectrum of complex Λ-(*S*)-**7a** recorded in CH_3OH (0.2 mM).

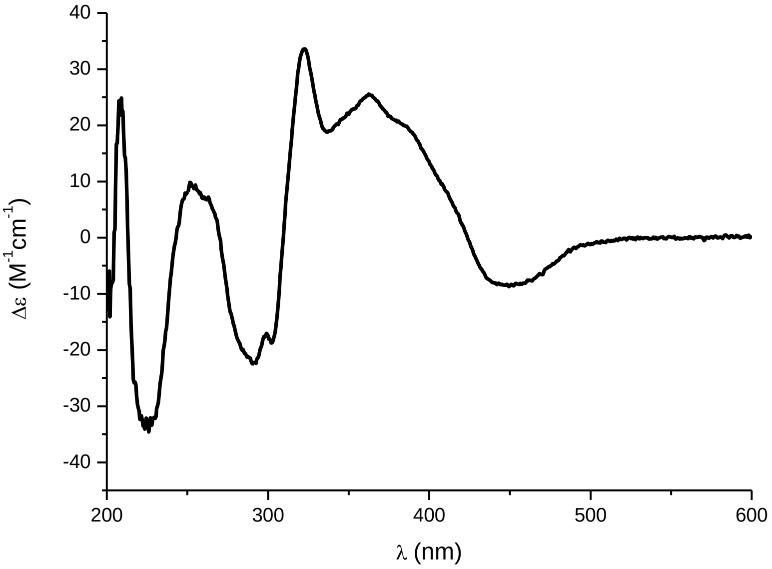


Figure S15. CD spectrum of complexΛ-(*S*)-**7b** recorded in CH_3OH (0.2 mM).

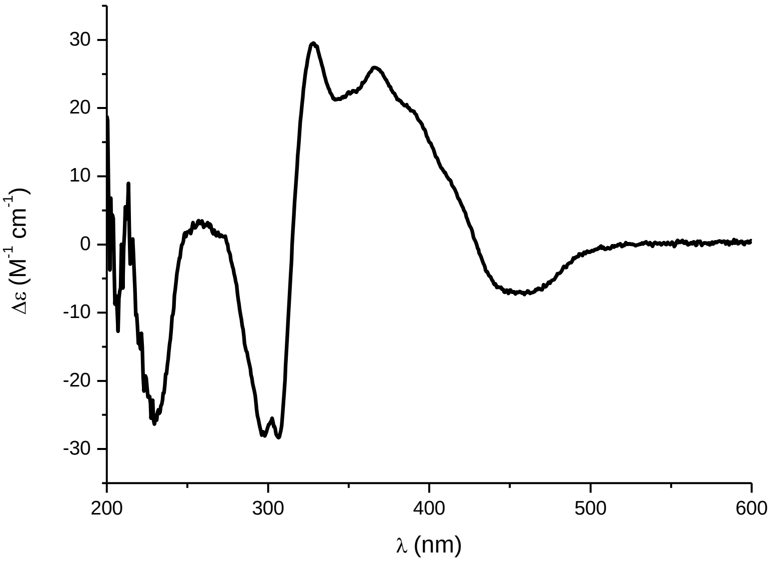


Figure S16. CD spectrum of complexΛ-(*S*)-**7c** recorded in CH_3OH (0.2 mM).

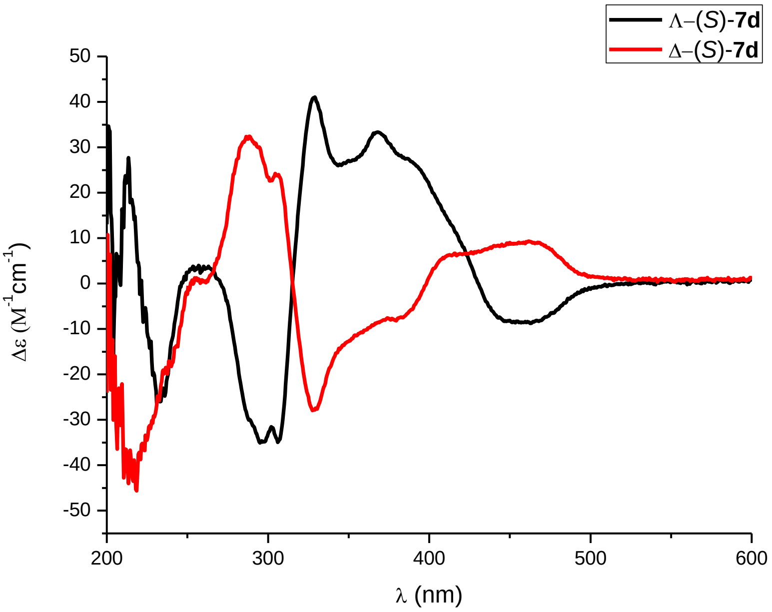


Figure S17. CD spectra of complexes Λ-(*S*)-**7d** and Δ-(*S*)-**7d** recorded in CH_3OH (0.2 mM).

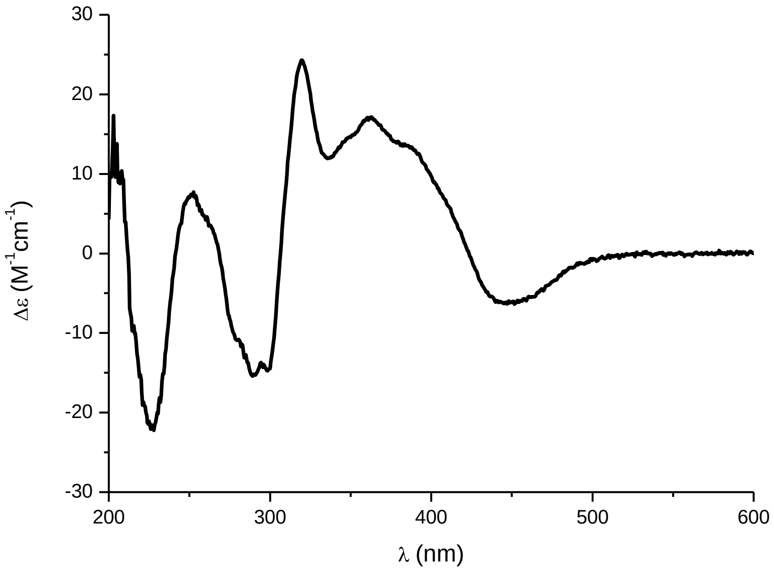


Figure S18. CD spectrum of complex Λ-(*S*)-**7e** recorded in CH_3OH (0.2 mM).

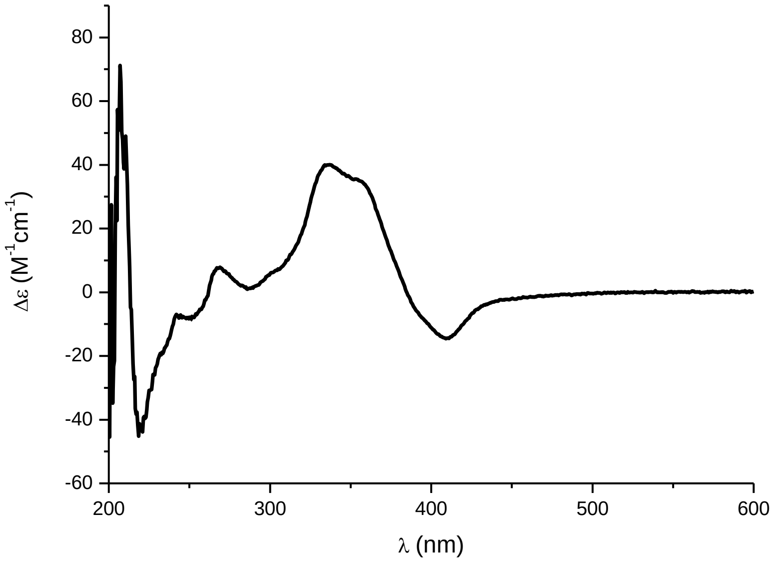


Figure S19. CD spectrum of catalyst Λ-**Ir1** recorded in CH_3OH (0.2 mM).

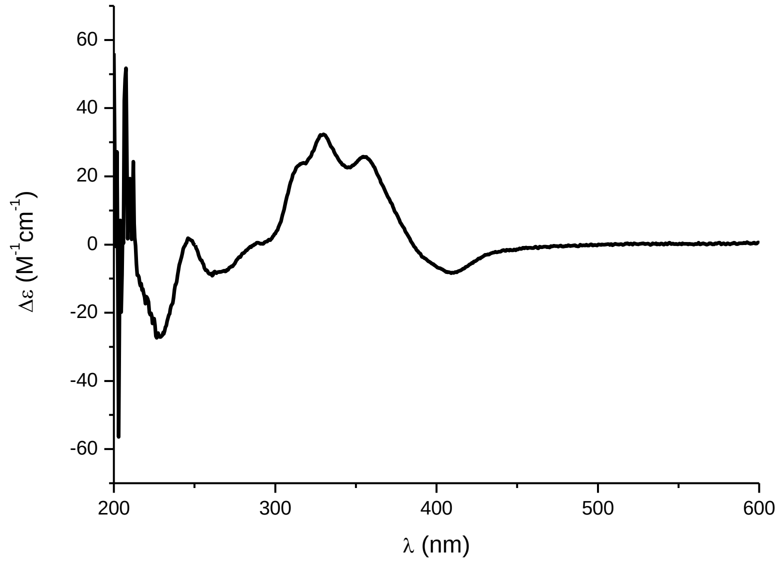


Figure S20. CD spectrum of catalyst Λ-**Ir2** recorded in CH_3OH (0.2 mM).

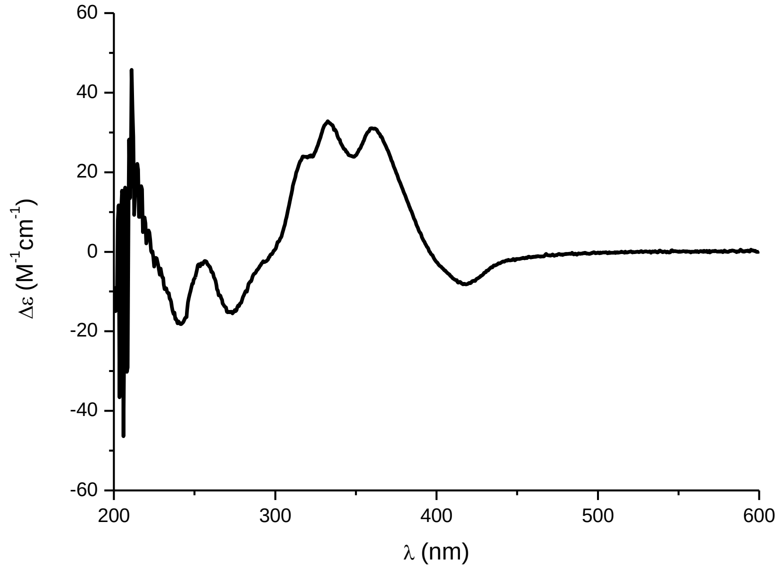


Figure S21. CD spectrum of catalyst Λ-**Ir3** recorded in CH_3OH (0.2 mM).

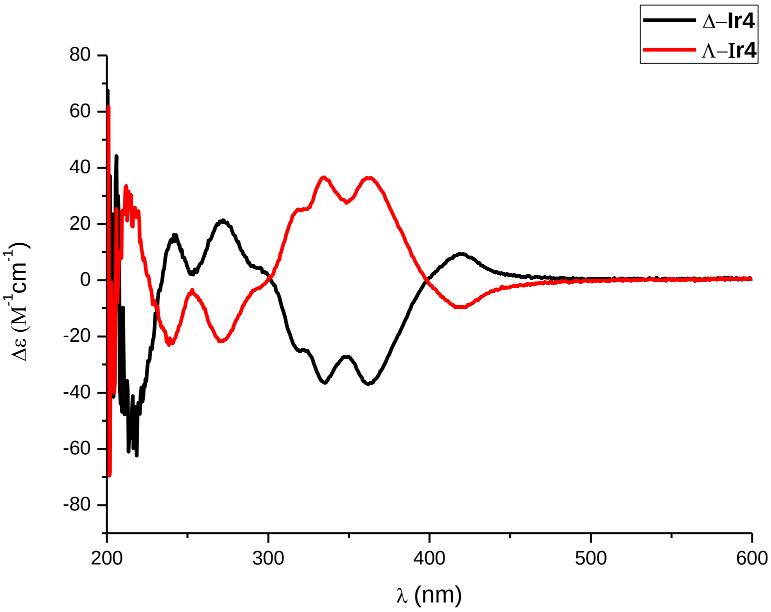


Figure S22. CD spectra of catalyst Λ-**Ir4** and Δ-**Ir4** recorded in CH$_3$OH (0.2 mM).

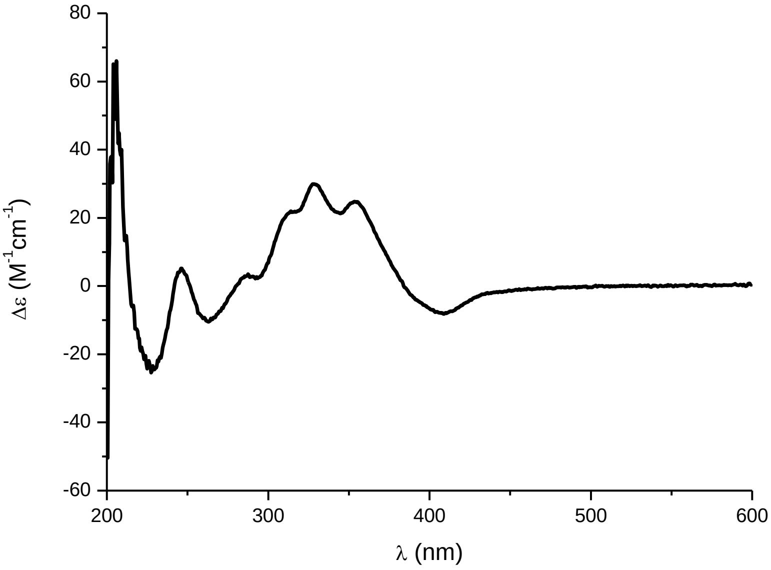


Figure S23. CD spectrum of catalyst Λ-**Ir5** recorded in CH$_3$OH (0.2 mM).

6. NMR Spectra of New Iridium Complexes

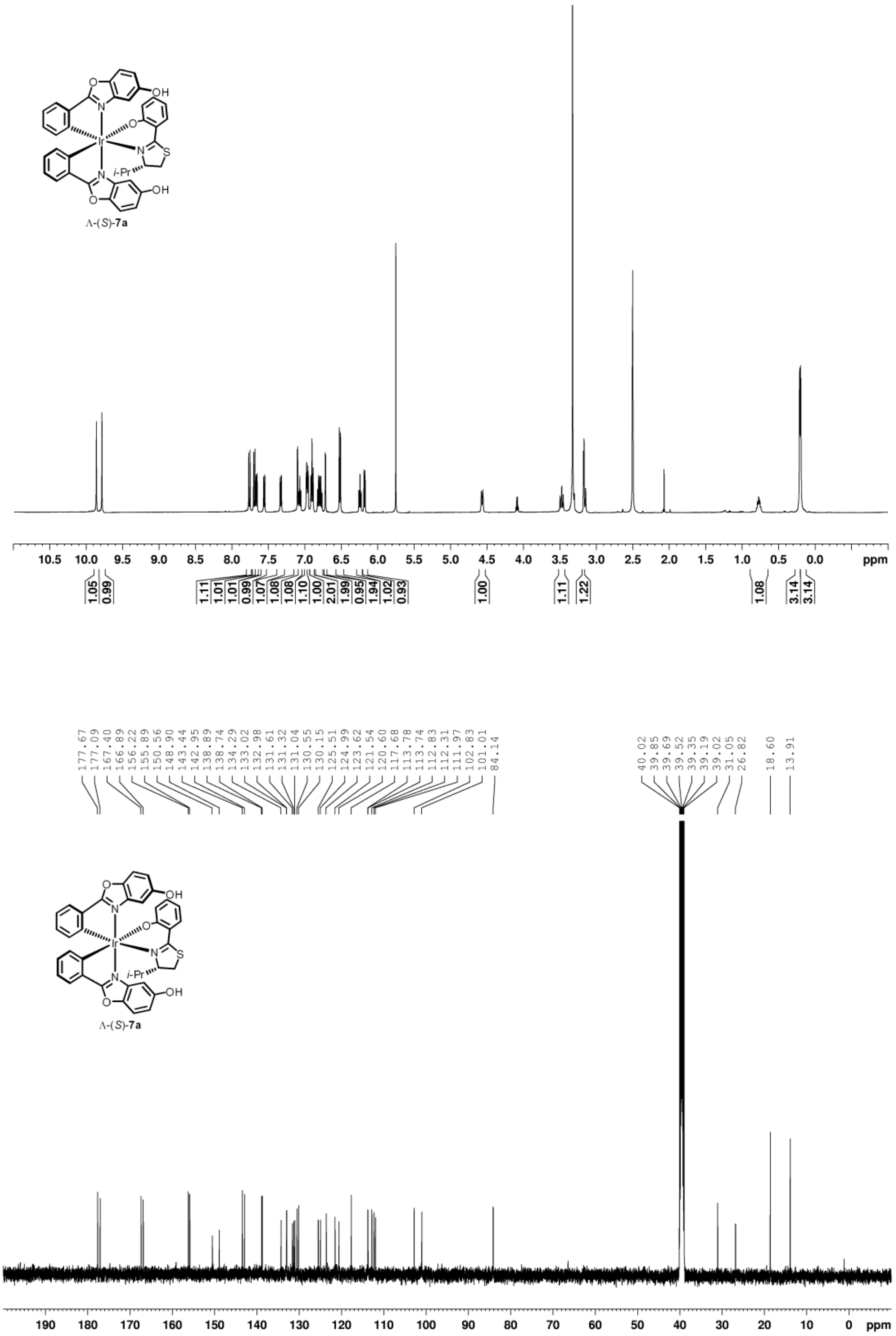


Figure S24. ^{1}H-NMR and ^{13}C-NMR spectrum of Λ-(*S*)-**7a**.

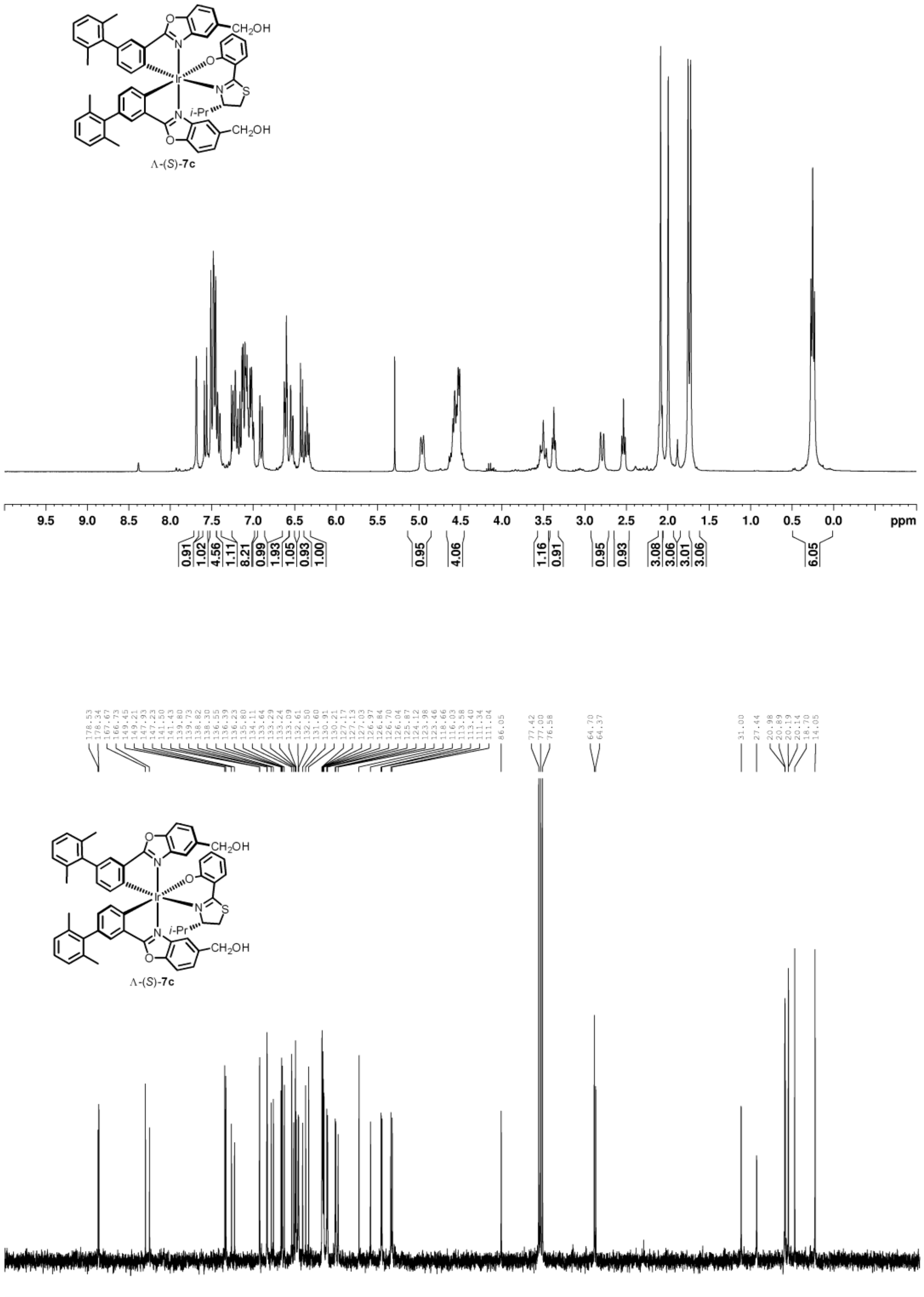


Figure S25. ^{1}H-NMR and ^{13}C-NMR spectrum of Λ-(*S*)-**7c**.

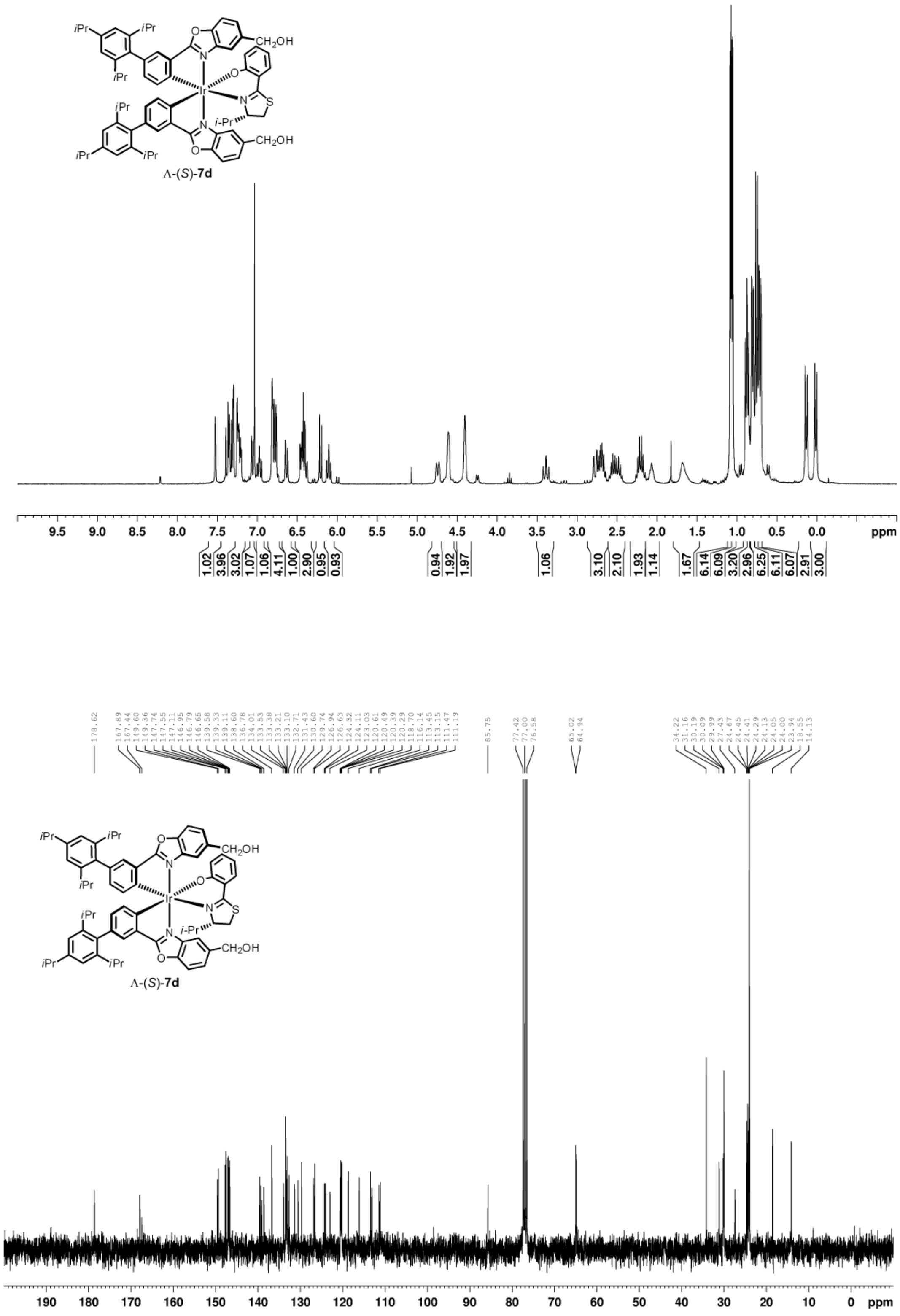


Figure S26. ^{1}H-NMR and ^{13}C-NMR spectrum of Λ-(*S*)-**7d**.

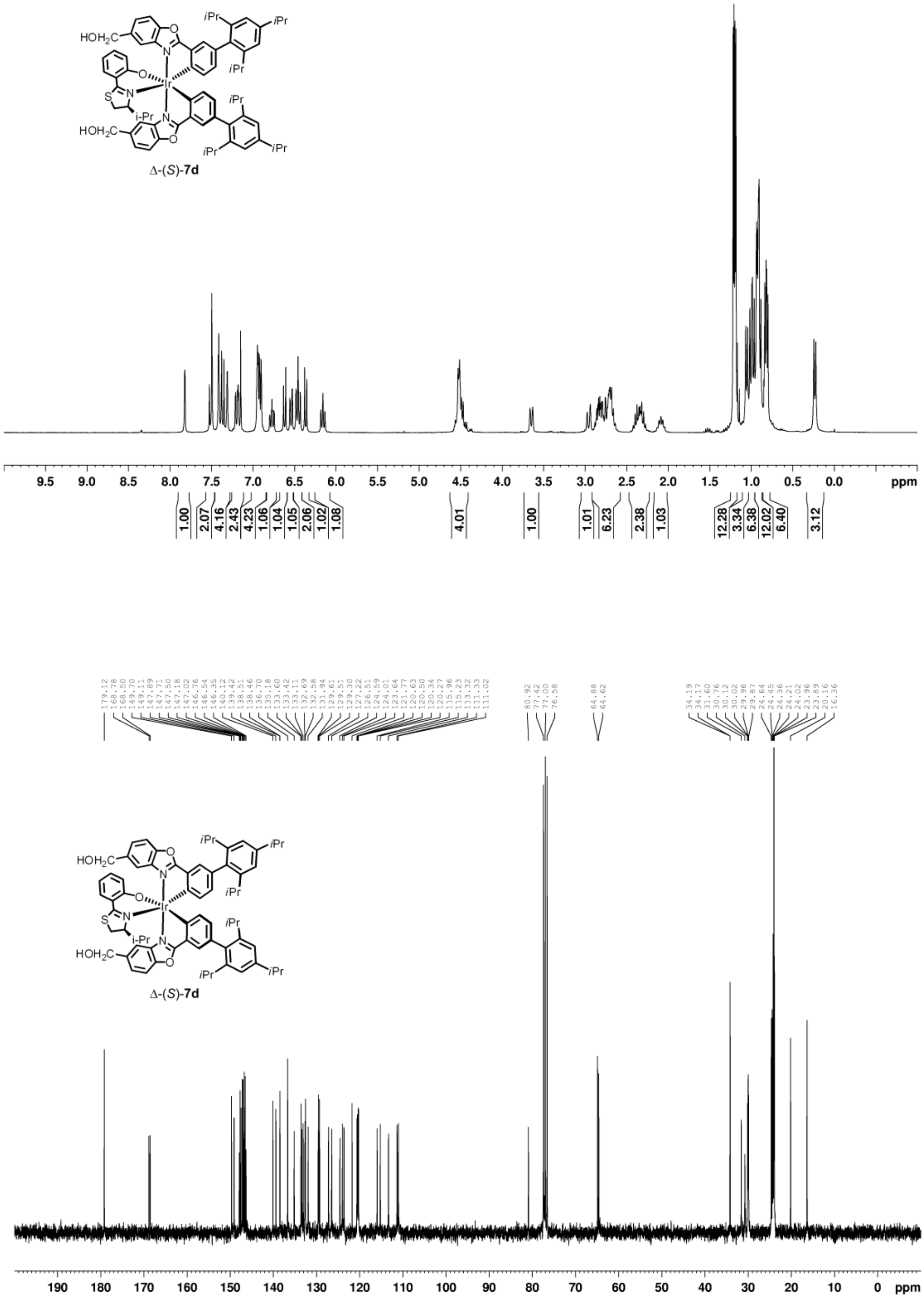


Figure S27. ^{1}H-NMR and ^{13}C-NMR spectrum of Δ-(*S*)-**7d**.

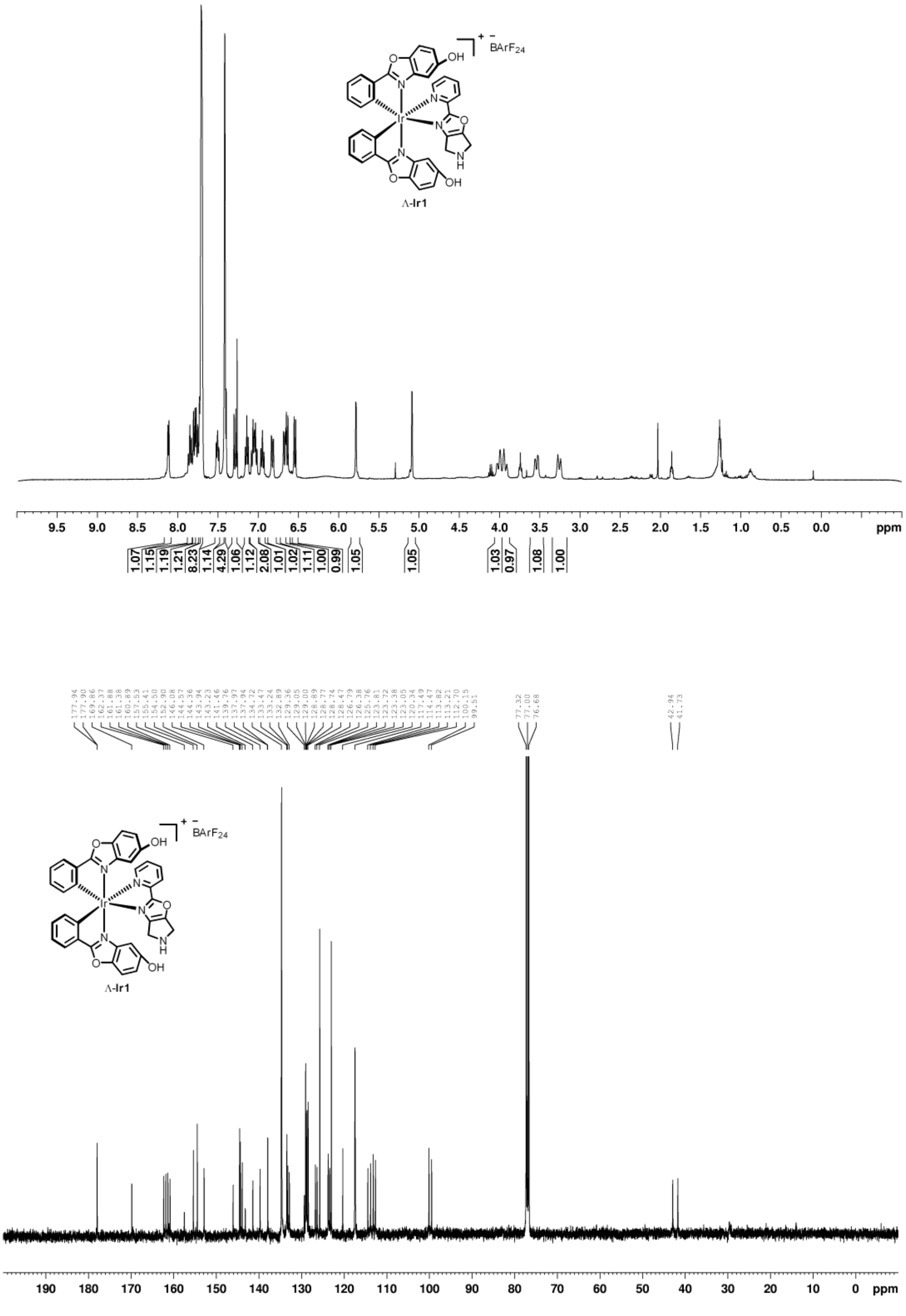


Figure S28. ^{1}H-NMR and ^{13}C-NMR spectrum of Λ-**Ir1**.

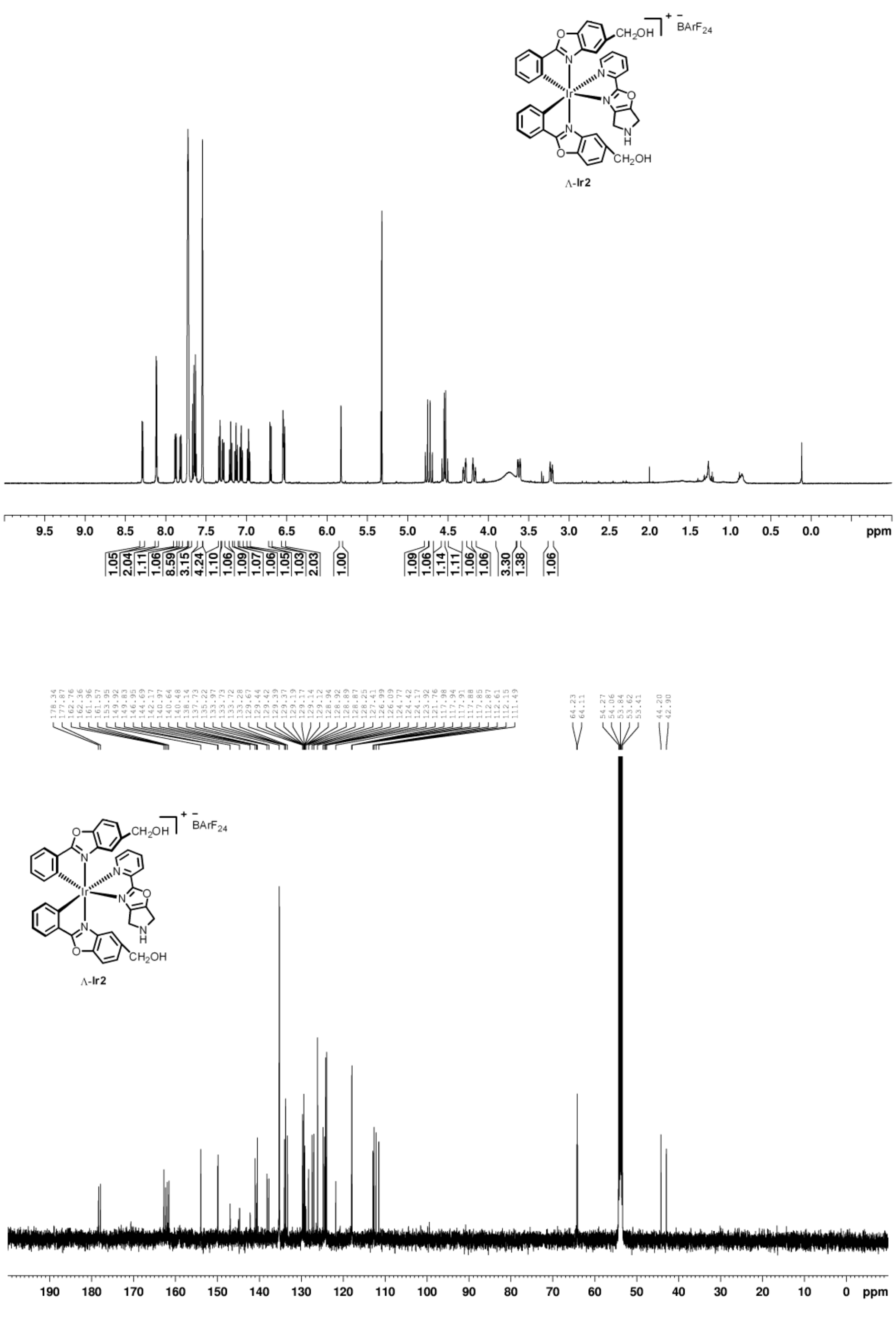


Figure S29. ^{1}H-NMR and ^{13}C-NMR spectrum of Λ-**Ir2**.

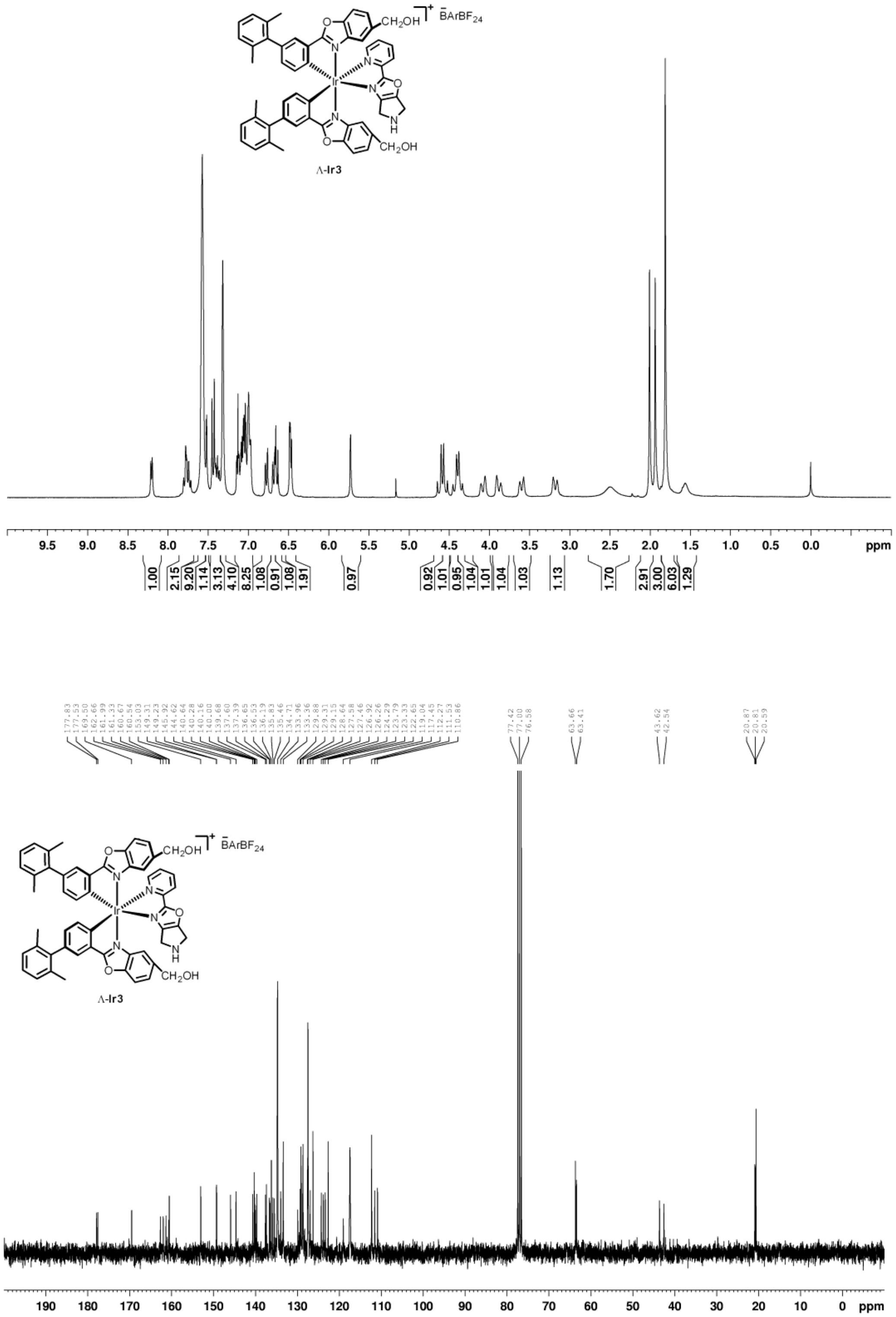


Figure S30. ^{1}H-NMR and ^{13}C-NMR spectrum of Λ-**Ir3**.

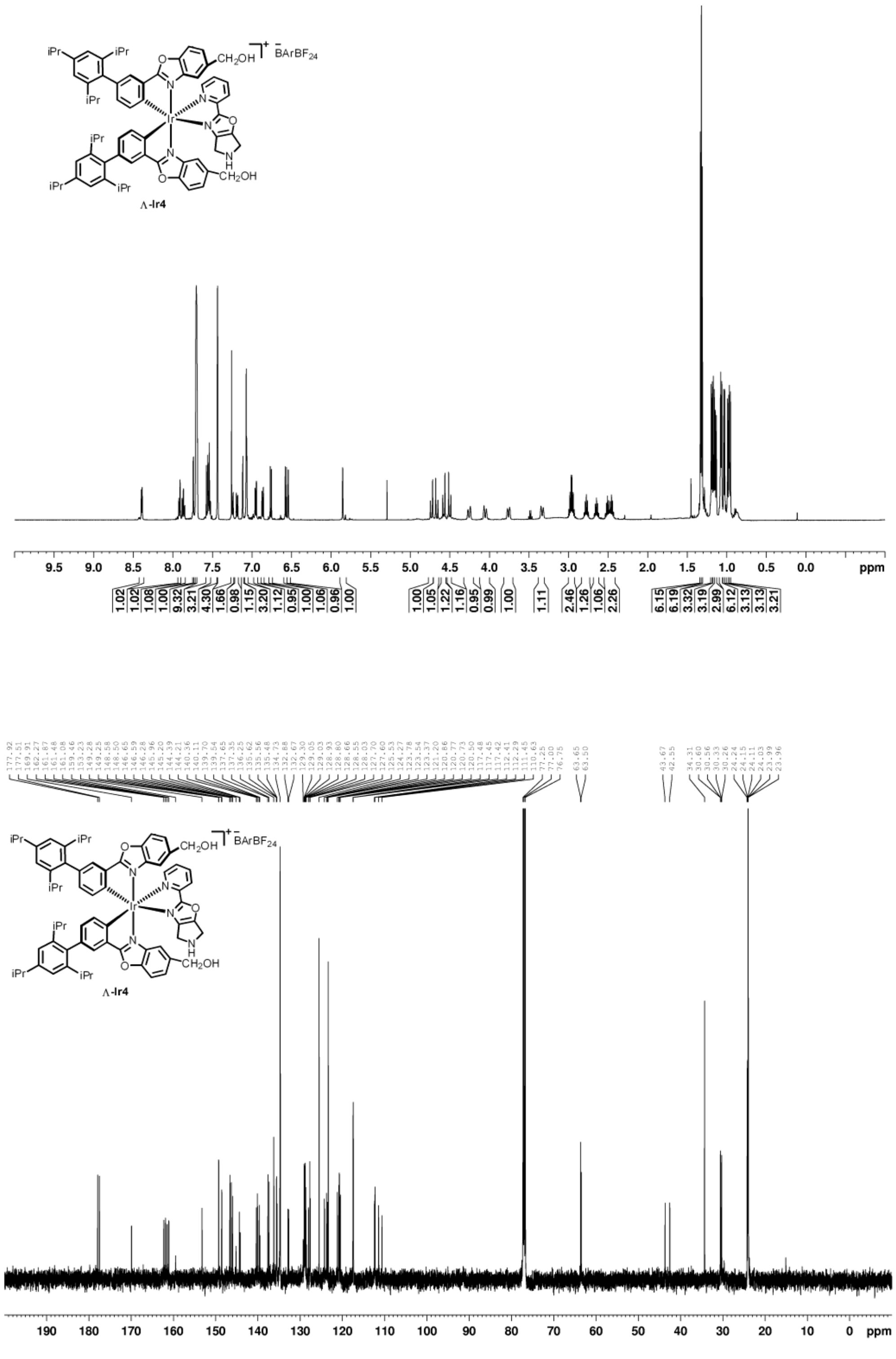


Figure S31. ^{1}H-NMR and ^{13}C-NMR spectrum of Λ-**Ir4**.

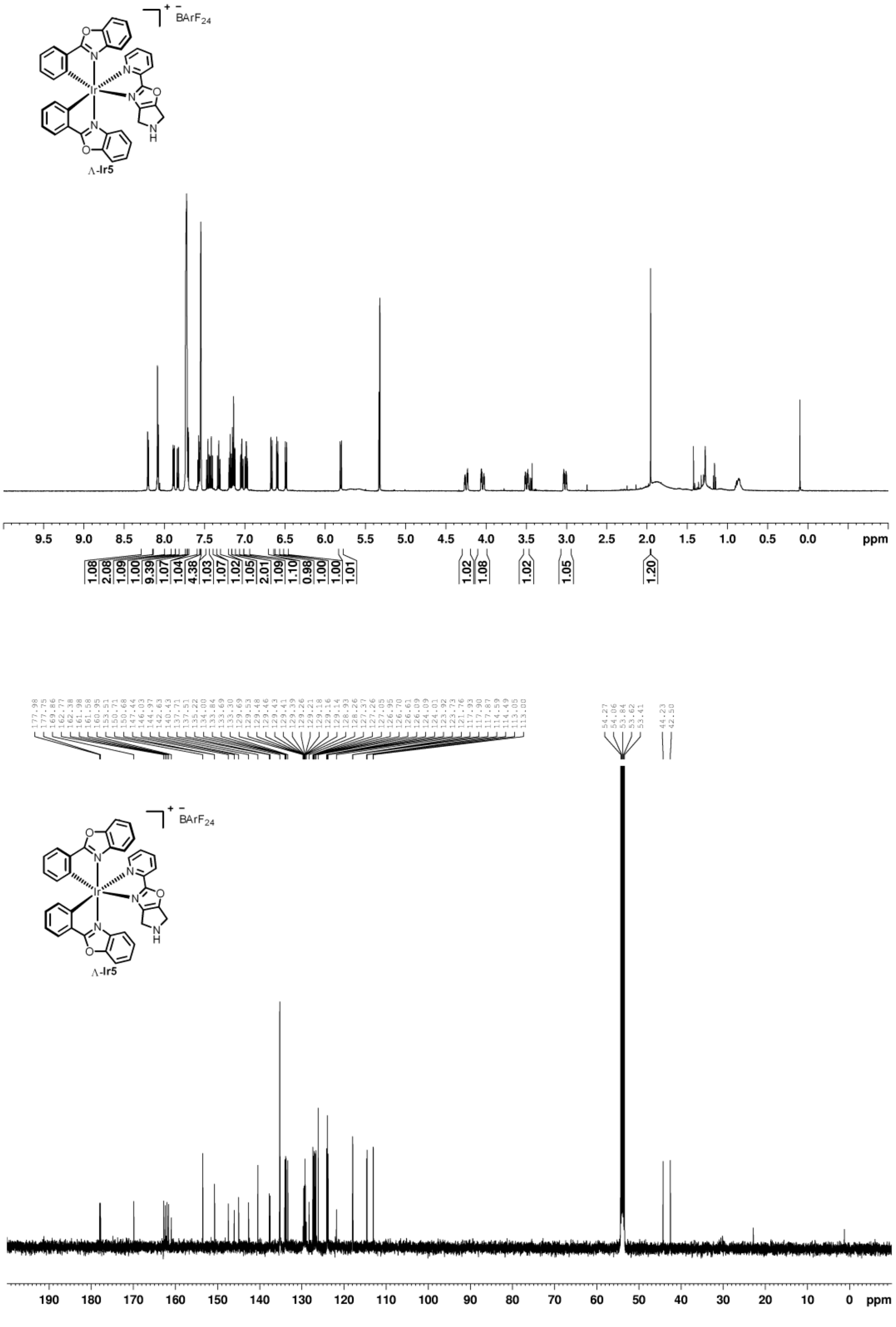


Figure S32. ^{1}H-NMR and ^{13}C-NMR spectrum of Λ-**Ir5**.

7. Single Crystal X-Ray Diffraction with Racemic Iridium Complex Λ/Δ-Ir4

An X-ray crystal structure of the racemic complex Λ/Δ-**Ir4** was obtained as an iodide salt (identification code = cat112_0m_sq). Suitable crystals were obtained by slow diffusion from a solution of Λ/Δ-**Ir4** in CH_2Cl_2/MeOH 5:1 saturated with NaI and layered with Et_2O.

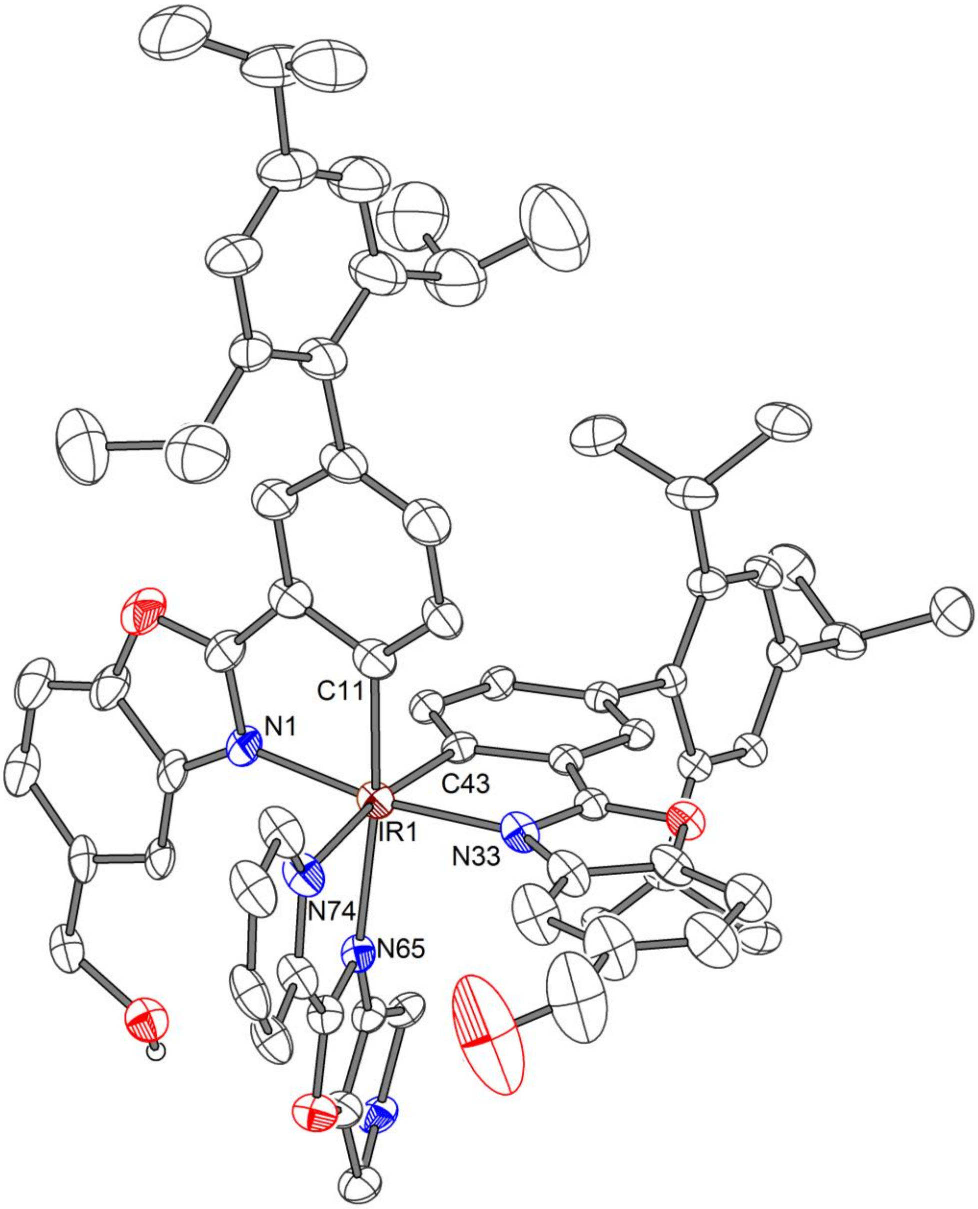


Figure S33. Crystal structure of the racemic catalyst Λ/Δ-**Ir4**. ORTEP drawing of complex 1 with 30% probability thermal ellipsoids. Iodide counterions, water molecules and CH_2Cl_2 are omitted for clarity.

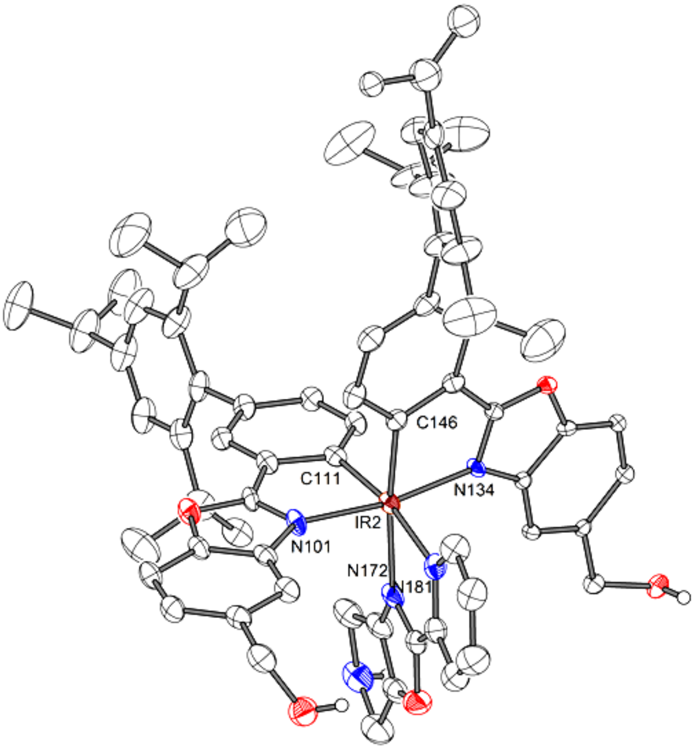


Figure S34. Crystal structure of the racemic catalyst Λ/Δ-**Ir4**. ORTEP drawing of complex 2 with 30% probability thermal ellipsoids. Iodide counterions, water molecules and CH_2Cl_2 are omitted for clarity.

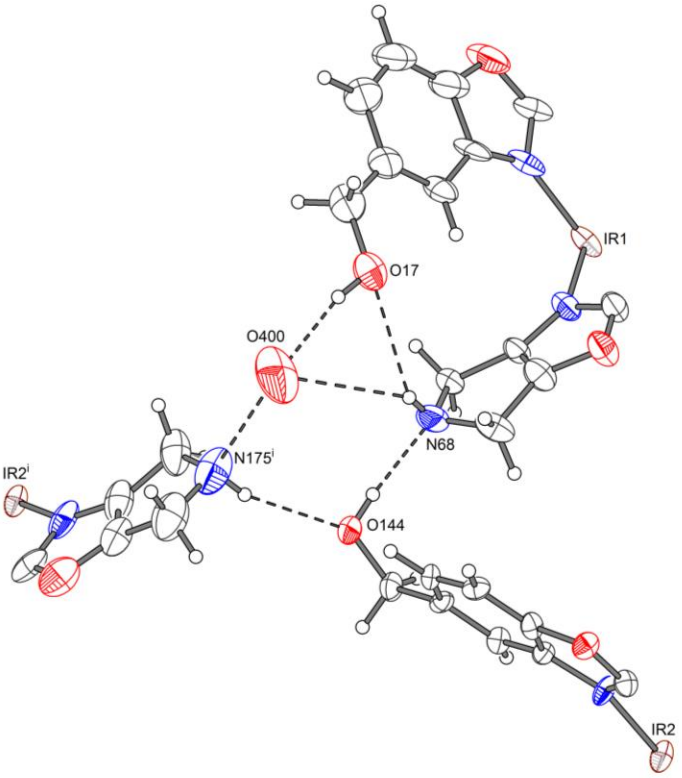


Figure S35. Hydrogen bonding network. ORTEP drawing with 50% probability thermal ellipsoids.

Table S1. Crystal data and structure refinement for cat112_0m_sq.

Crystal data		
Identification code	cat112_0m_sq	
Habitus, colour	plate, yellow	
Crystal size	0.609 x 0.209 x 0.044 mm^3	
Crystal system	Triclinic	
Space group	P -1	Z = 1
Unit cell dimensions	a = 14.9997(6) Å	α= 105.6071(19)°.
	b = 20.6925(7) Å	β= 100.893(2)°.
	c = 26.1024(10) Å	γ = 99.749(2)°.
Volume	7451.9(5) $Å^3$	
Cell determination	9717 peaks with Theta 2.5 to 27.2°.	
Empirical formula	C275 H308 Cl6 I10 Ir4 N20 O25	
Moiety formula	4[C68 H73 Ir N5 O5]+, 2(I-), I3-, I5-, 3(C H2 Cl2), 5(H2 O)	
Formula weight	6543.90	
Density (calculated)	1.458 Mg/m^3	
Absorption coefficient	2.930 mm^{-1}	
F(000)	3238	
Data collection:		
Diffractometer type	Bruker D8 QUEST area detector	
Wavelength	0.71069 Å	
Temperature	100(2) K	
Theta range for data collection	2.005 to 25.371°.	
Index ranges	-18<=h<=18, -24<=k<=24, -31<=l<=31	
Data collection software	BRUKER APEX2 2014.1-1	
Cell refinement software	SAINT V8.32B (Bruker AXS Inc., 2013)	
Data reduction software	SAINT V8.32B (Bruker AXS Inc., 2013)	
Solution and refinement:		
Reflections collected	173852	
Independent reflections	27246 [R(int) = 0.0892]	
Completeness to theta = 25.240°	99.9 %	
Observed reflections	20449[I > 2sigma(I)]	
Reflections used for refinement	27246	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.72 and 0.55	
Largest diff. peak and hole	4.544 and -2.517 $e.Å^{-3}$	
Solution	direct/ difmap	
Refinement	Full-matrix least-squares on F^2	
Treatment of hydrogen atoms	mixed, mixed	
Programs used	SHELXS-97 (Sheldrick, 2008) SHELXL-2013 (Sheldrick, 2013) DIAMOND (Crystal Impact)	
Data / restraints / parameters	27246 / 1352 / 1746	
Goodness-of-fit on F^2	1.055	
R index (all data)	wR2 = 0.1826	
R index conventional [I>2sigma(I)]	R1 = 0.0682	

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for cat112_0m_sq. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)	Occupancy
C2	0.6798(7)	0.5005(4)	0.1728(4)	0.047(2)	1
C3	0.7134(7)	0.4589(4)	0.1331(4)	0.042(2)	1
C4	0.8094(7)	0.4708(5)	0.1391(4)	0.049(2)	1
C5	0.8688(8)	0.5233(5)	0.1859(5)	0.065(3)	1
C6	0.8354(9)	0.5633(6)	0.2251(6)	0.070(3)	1
C7	0.7411(8)	0.5511(5)	0.2176(5)	0.061(3)	1
C9	0.5989(8)	0.5470(5)	0.2272(4)	0.053(2)	1
C10	0.5195(8)	0.5556(5)	0.2488(4)	0.053(2)	1
C11	0.4378(8)	0.5065(5)	0.2149(4)	0.051(2)	1
C12	0.3556(9)	0.5112(5)	0.2312(5)	0.057(2)	1
C13	0.3524(10)	0.5622(6)	0.2764(5)	0.070(3)	1
C14	0.4351(9)	0.6104(5)	0.3098(5)	0.061(2)	1
C15	0.5186(9)	0.6073(5)	0.2963(5)	0.062(3)	1
C16	0.8501(7)	0.4269(5)	0.0984(5)	0.052(2)	1
C18	0.4331(10)	0.6687(6)	0.3587(5)	0.071(3)	1
C19	0.4271(13)	0.6564(8)	0.4087(6)	0.099(4)	1
C20	0.4237(12)	0.7099(8)	0.4525(6)	0.101(5)	1
C21	0.4248(11)	0.7752(8)	0.4481(6)	0.087(4)	1
C22	0.4281(9)	0.7873(7)	0.3983(5)	0.073(3)	1
C23	0.4320(8)	0.7344(5)	0.3529(5)	0.059(3)	1
C24	0.4301(18)	0.5853(9)	0.4168(8)	0.131(6)	1
C25	0.5203(18)	0.5930(10)	0.4565(9)	0.156(7)	1
C26	0.349(2)	0.5634(15)	0.4409(12)	0.207(11)	1
C27	0.4127(12)	0.8323(9)	0.4969(6)	0.103(4)	1
C28	0.3155(13)	0.8411(10)	0.4874(7)	0.122(6)	1
C29	0.4816(16)	0.8926(11)	0.5119(9)	0.161(9)	1
C30	0.4314(10)	0.7468(6)	0.2990(5)	0.075(3)	1
C31	0.5295(13)	0.7889(9)	0.2998(9)	0.128(6)	1
C32	0.3595(13)	0.7830(8)	0.2818(7)	0.109(5)	1
C34	0.2327(7)	0.3746(5)	0.0979(4)	0.048(2)	1
C35	0.1938(8)	0.4098(7)	0.0658(6)	0.071(3)	1
C36	0.0987(9)	0.3877(8)	0.0426(6)	0.079(4)	1
C37	0.0441(8)	0.3349(7)	0.0508(5)	0.072(3)	1
C38	0.0812(7)	0.2976(6)	0.0832(5)	0.057(2)	1
C39	0.1769(7)	0.3203(5)	0.1058(4)	0.046(2)	1
C41	0.3194(6)	0.3310(4)	0.1502(3)	0.0328(16)	1
C42	0.4012(6)	0.3226(4)	0.1831(3)	0.0309(16)	1
C43	0.4816(6)	0.3740(4)	0.1889(3)	0.0334(17)	1
C44	0.5649(7)	0.3690(4)	0.2195(4)	0.0380(18)	1
C45	0.5684(6)	0.3148(4)	0.2412(3)	0.0357(18)	1
C46	0.4902(6)	0.2639(4)	0.2343(3)	0.0312(16)	1
C47	0.4053(6)	0.2682(4)	0.2056(3)	0.0310(16)	1
C48	0.0521(12)	0.4257(12)	0.0057(10)	0.144(8)	1
C50	0.5021(5)	0.2030(4)	0.2540(3)	0.0297(15)	1
C51	0.5058(7)	0.2058(5)	0.3083(4)	0.0401(19)	1
C52	0.5266(6)	0.1491(5)	0.3245(4)	0.0404(19)	1
C53	0.5421(6)	0.0916(4)	0.2889(3)	0.0355(17)	1
C54	0.5335(5)	0.0894(4)	0.2346(3)	0.0299(16)	1
C55	0.5135(5)	0.1435(4)	0.2162(3)	0.0308(16)	1
C56	0.4834(8)	0.2662(5)	0.3479(4)	0.055(2)	1
C57	0.5680(11)	0.3208(7)	0.3791(6)	0.096(5)	1
C58	0.4287(10)	0.2451(6)	0.3864(5)	0.070(3)	1
C59	0.5659(7)	0.0312(5)	0.3074(4)	0.048(2)	1
C60	0.6539(8)	0.0539(6)	0.3525(5)	0.061(3)	1
C61	0.4844(8)	-0.0051(5)	0.3226(5)	0.060(3)	1
C62	0.5020(6)	0.1365(4)	0.1550(3)	0.0354(17)	1
C63	0.4145(6)	0.0807(5)	0.1207(4)	0.047(2)	1

C64	0.5887(6)	0.1223(5)	0.1369(4)	0.0391(19)	1
C66	0.5165(6)	0.3315(4)	0.0482(4)	0.0355(17)	1
C67	0.5600(6)	0.2768(4)	0.0627(4)	0.0386(19)	1
C69	0.5352(8)	0.2650(5)	-0.0353(4)	0.051(2)	1
C70	0.5059(7)	0.3256(5)	-0.0048(4)	0.043(2)	1
C72	0.4486(6)	0.4092(4)	0.0311(4)	0.0381(18)	1
C73	0.4097(7)	0.4701(5)	0.0402(4)	0.046(2)	1
C75	0.3813(8)	0.5557(5)	0.1059(5)	0.060(3)	1
C76	0.3396(9)	0.5822(6)	0.0669(5)	0.067(3)	1
C77	0.3325(8)	0.5503(6)	0.0131(5)	0.061(3)	1
C78	0.3691(7)	0.4927(6)	-0.0013(5)	0.056(2)	1
N1	0.5898(6)	0.4991(3)	0.1796(3)	0.0441(17)	1
N33	0.3245(5)	0.3805(4)	0.1277(3)	0.0402(16)	1
N65	0.4790(5)	0.3860(3)	0.0717(3)	0.0353(15)	1
N68	0.5871(5)	0.2455(4)	0.0111(3)	0.0438(17)	1
N74	0.4154(6)	0.5001(4)	0.0934(4)	0.0480(19)	1
O8	0.6886(6)	0.5810(3)	0.2516(3)	0.0653(19)	1
O17	0.7806(5)	0.3710(4)	0.0613(3)	0.0523(16)	1
O40	0.2330(4)	0.2929(3)	0.1397(2)	0.0398(13)	1
O49	0.1041(13)	0.4588(17)	-0.0158(14)	0.218(16)	0.74(2)
O50	-0.035(2)	0.416(2)	-0.0095(18)	0.102(17)	0.26(2)
O71	0.4611(5)	0.3740(3)	-0.0173(3)	0.0470(15)	1
Ir1	0.45684(3)	0.44150(2)	0.14735(2)	0.03826(11)	1
C102	-0.1068(6)	-0.0461(5)	-0.2268(4)	0.0378(17)	1
C103	-0.1425(6)	0.0085(5)	-0.2039(4)	0.044(2)	1
C104	-0.2392(6)	-0.0065(5)	-0.2081(4)	0.043(2)	1
C105	-0.2943(6)	-0.0732(5)	-0.2346(4)	0.047(2)	1
C106	-0.2591(6)	-0.1274(5)	-0.2568(4)	0.047(2)	1
C107	-0.1633(6)	-0.1113(5)	-0.2527(4)	0.0397(18)	1
C109	-0.0235(5)	-0.1179(4)	-0.2560(4)	0.0349(17)	1
C110	0.0577(6)	-0.1415(5)	-0.2662(3)	0.0352(17)	1
C111	0.1380(5)	-0.0864(4)	-0.2458(3)	0.0323(17)	1
C112	0.2203(6)	-0.1051(5)	-0.2528(4)	0.0362(18)	1
C113	0.2226(6)	-0.1732(4)	-0.2771(3)	0.0368(18)	1
C114	0.1416(6)	-0.2264(5)	-0.2957(4)	0.0391(18)	1
C115	0.0583(6)	-0.2094(5)	-0.2906(3)	0.0369(17)	1
C116	-0.2805(7)	0.0523(6)	-0.1813(5)	0.056(3)	1
C119	0.1491(6)	-0.3005(5)	-0.3160(4)	0.047(2)	1
C120	0.1569(7)	-0.3369(5)	-0.2773(5)	0.051(2)	1
C121	0.1716(7)	-0.4035(5)	-0.2940(5)	0.062(3)	1
C122	0.1798(8)	-0.4337(6)	-0.3454(6)	0.071(3)	1
C123	0.1679(9)	-0.3989(6)	-0.3839(5)	0.076(3)	1
C124	0.1521(8)	-0.3314(6)	-0.3703(5)	0.064(3)	1
C125	0.1355(11)	-0.2932(7)	-0.4127(5)	0.087(4)	1
C126	0.2231(14)	-0.2608(11)	-0.4241(7)	0.127(6)	1
C127	0.0656(15)	-0.3392(11)	-0.4650(7)	0.143(7)	1
C128	0.2006(10)	-0.5060(6)	-0.3626(7)	0.092(4)	1
C129	0.2964(11)	-0.5028(7)	-0.3692(7)	0.103(5)	1
C130	0.1235(12)	-0.5569(7)	-0.4074(7)	0.111(6)	1
C131	0.1466(8)	-0.3066(6)	-0.2199(5)	0.058(2)	1
C132	0.0560(9)	-0.3442(9)	-0.2122(7)	0.096(5)	1
C133	0.2291(8)	-0.3057(6)	-0.1753(5)	0.056(3)	1
C135	0.3409(5)	0.0715(4)	-0.1609(3)	0.0231(14)	1
C136	0.3718(5)	0.0602(4)	-0.1114(3)	0.0228(14)	1
C137	0.4665(5)	0.0789(4)	-0.0881(3)	0.0220(14)	1
C138	0.5287(5)	0.1087(4)	-0.1137(3)	0.0242(14)	1
C139	0.4984(5)	0.1213(4)	-0.1627(3)	0.0256(15)	1
C140	0.4047(5)	0.1029(4)	-0.1848(3)	0.0240(14)	1
C142	0.2655(5)	0.0811(4)	-0.2369(3)	0.0270(15)	1
C143	0.5026(5)	0.0675(4)	-0.0335(3)	0.0300(16)	1
C145	0.1871(6)	0.0721(4)	-0.2819(3)	0.0332(17)	1
C146	0.1045(6)	0.0337(4)	-0.2758(3)	0.0333(17)	1

C147	0.0242(6)	0.0226(5)	-0.3181(4)	0.042(2)	1
C148	0.0303(7)	0.0497(5)	-0.3610(4)	0.048(2)	1
C149	0.1111(7)	0.0866(5)	-0.3656(4)	0.046(2)	1
C150	0.1923(6)	0.0988(4)	-0.3251(3)	0.0360(18)	1
C151	0.1106(9)	0.1147(6)	-0.4127(4)	0.060(3)	1
C152	0.1459(11)	0.0831(8)	-0.4546(5)	0.088(4)	1
C153	0.1142(18)	0.0863(15)	-0.5078(9)	0.068(6)	0.5
C154	0.0676(14)	0.1407(12)	-0.5118(8)	0.055(4)	0.5
C155	0.039(2)	0.1772(15)	-0.4673(10)	0.071(6)	0.5
C156	0.0701(11)	0.1724(7)	-0.4141(5)	0.081(3)	1
C157	0.1919(10)	0.0253(8)	-0.4545(4)	0.085(4)	1
C158	0.1398(13)	-0.0384(10)	-0.4988(7)	0.133(6)	1
C159	0.2932(13)	0.0406(12)	-0.4598(7)	0.131(6)	1
C160	0.0361(13)	0.1528(15)	-0.5681(11)	0.079(8)	0.5
C161	0.1047(19)	0.1717(15)	-0.5930(11)	0.077(7)	0.5
C162	-0.0605(13)	0.1310(10)	-0.5882(8)	0.048(5)	0.5
C163	0.0329(12)	0.2091(7)	-0.3678(5)	0.086(4)	1
C164	-0.0362(15)	0.2474(10)	-0.3822(8)	0.133(6)	1
C165	0.1155(16)	0.2614(9)	-0.3221(8)	0.138(7)	1
C166	0.1699(19)	0.1299(15)	-0.4942(9)	0.068(5)	0.5
C167	0.137(2)	0.1867(14)	-0.4924(9)	0.073(6)	0.5
C168	0.095(2)	0.2109(16)	-0.4525(11)	0.082(8)	0.5
C169	0.159(2)	0.2289(18)	-0.5334(14)	0.102(10)	0.5
C170	0.075(2)	0.215(2)	-0.5686(16)	0.123(12)	0.5
C171	0.249(3)	0.266(2)	-0.525(2)	0.165(18)	0.5
C173	0.1615(6)	-0.0484(6)	-0.0979(4)	0.051(2)	1
C174	0.1906(8)	-0.1141(6)	-0.1049(5)	0.060(2)	1
C176	0.1728(9)	-0.0681(7)	-0.0120(5)	0.070(3)	1
C177	0.1520(7)	-0.0232(6)	-0.0458(4)	0.051(2)	1
C179	0.1070(6)	0.0423(5)	-0.0926(4)	0.0440(18)	1
C180	0.0736(6)	0.0960(5)	-0.1073(4)	0.048(2)	1
C182	0.0522(7)	0.1472(6)	-0.1757(5)	0.058(3)	1
C183	0.0125(8)	0.1951(6)	-0.1457(5)	0.064(3)	1
C184	0.0065(8)	0.1947(7)	-0.0937(5)	0.071(3)	1
C185	0.0391(7)	0.1446(6)	-0.0751(5)	0.064(3)	1
N101	-0.0169(4)	-0.0529(4)	-0.2303(3)	0.0365(15)	1
N134	0.2516(4)	0.0578(3)	-0.1960(3)	0.0262(13)	1
N172	0.1328(5)	-0.0067(4)	-0.1272(3)	0.0425(16)	1
N175	0.2118(7)	-0.1193(6)	-0.0479(4)	0.068(2)	1
N181	0.0801(5)	0.0962(4)	-0.1577(3)	0.0425(16)	1
O108	-0.1118(4)	-0.1572(3)	-0.2721(3)	0.0420(14)	1
O117	-0.234(2)	0.0824(15)	-0.1230(9)	0.066(8)	0.25
O118	-0.2627(8)	0.1058(6)	-0.2062(4)	0.070(3)	0.75
O141	0.3543(4)	0.1090(3)	-0.2331(2)	0.0272(11)	1
O144	0.5924(4)	0.1080(3)	-0.0047(2)	0.0344(13)	1
O178	0.1150(5)	0.0336(4)	-0.0417(3)	0.0575(17)	1
Ir2	0.11712(2)	0.00684(2)	-0.20652(2)	0.03171(10)	1
I1	0.0614(3)	0.1661(3)	0.14745(18)	0.0828(18)	0.226(3)
I2	0.0955(3)	0.1076(3)	0.10795(16)	0.0807(19)	0.231(4)
I3	0.1062(4)	0.0435(3)	0.0850(2)	0.120(3)	0.243(4)
I4	0.2057(3)	0.1576(2)	0.05755(17)	0.0494(16)	0.158(3)
I5	0.30252(12)	0.1792(2)	0.02140(13)	0.0420(9)	0.566(13)
I6	0.2906(8)	0.2031(6)	0.0093(6)	0.061(3)	0.33(2)
I7	0.2969(16)	0.2079(14)	-0.0076(13)	0.071(6)	0.121(18)
I8	0.2311(4)	0.2861(3)	-0.0331(2)	0.107(3)	0.270(6)
I9	0.2739(2)	0.24756(16)	-0.06262(16)	0.1083(19)	0.502(6)
I10	0.1655(3)	0.37062(19)	-0.0884(2)	0.106(2)	0.304(5)
I11	0.2219(4)	0.3333(2)	-0.1299(2)	0.138(5)	0.284(6)
I12	0.2942(4)	0.2916(3)	-0.15887(18)	0.130(3)	0.323(5)
I13	0.2931(10)	0.2275(7)	-0.1442(6)	0.099(6)	0.085(4)
I14	0.4208(13)	0.3238(9)	-0.1603(6)	0.334(11)	0.237(6)
I15	0.2577(17)	0.2578(9)	-0.2181(8)	0.211(11)	0.114(5)

I17	0.7810(5)	0.2637(4)	-0.0660(4)	0.130(3)	0.209(5)
I18	0.76769(8)	0.25129(6)	-0.10091(9)	0.0574(6)	0.791(5)
O400	0.8232(9)	0.2435(6)	0.0252(7)	0.107(5)	0.791(5)
C300	0.770(2)	0.0537(14)	-0.3332(12)	0.122(10)	0.667
Cl1	0.7547(3)	-0.0295(3)	-0.3630(2)	0.0826(15)	0.667
Cl2	0.8041(8)	0.1157(5)	-0.3547(5)	0.173(5)	0.667
C400	0.892(3)	0.3768(16)	-0.172(2)	0.20(3)	0.5
Cl3	0.8746(5)	0.4483(4)	-0.1475(4)	0.096(2)	0.5
Cl4	0.9147(8)	0.3319(6)	-0.2271(5)	0.150(5)	0.5
C500	0.324(3)	0.226(2)	-0.4451(16)	0.077(11)	0.333
Cl5	0.2854(9)	0.2994(6)	-0.4263(7)	0.133(6)	0.333
Cl6	0.3292(9)	0.2028(8)	-0.5151(5)	0.104(4)	0.333

Table S3. Bond lengths [Å] and angles [°] for cat112_0m_sq.

C2-C7	1.385(14)	C30-H30	1.0000
C2-C3	1.389(13)	C31-H31A	0.9800
C2-N1	1.392(12)	C31-H31B	0.9800
C3-C4	1.390(13)	C31-H31C	0.9800
C3-H3	0.9500	C32-H32A	0.9800
C4-C5	1.420(15)	C32-H32B	0.9800
C4-C16	1.496(14)	C32-H32C	0.9800
C5-C6	1.363(16)	C34-C35	1.362(14)
C5-H5	0.9500	C34-C39	1.372(14)
C6-C7	1.360(16)	C34-N33	1.415(12)
C6-H6	0.9500	C35-C36	1.384(17)
C7-O8	1.387(13)	C35-H35	0.9500
C9-N1	1.331(12)	C36-C37	1.342(18)
C9-O8	1.351(13)	C36-C48	1.540(18)
C9-C10	1.428(15)	C37-C38	1.391(15)
C10-C15	1.407(14)	C37-H37	0.9500
C10-C11	1.415(15)	C38-C39	1.390(14)
C11-C12	1.389(14)	C38-H38	0.9500
C11-Ir1	2.010(9)	C39-O40	1.400(11)
C12-C13	1.370(15)	C41-N33	1.309(11)
C12-H12	0.9500	C41-O40	1.334(10)
C13-C14	1.413(18)	C41-C42	1.423(11)
C13-H13	0.9500	C42-C47	1.408(11)
C14-C15	1.370(16)	C42-C43	1.421(12)
C14-C18	1.512(14)	C43-C44	1.386(12)
C15-H15	0.9500	C43-Ir1	2.025(8)
C16-O17	1.403(12)	C44-C45	1.390(12)
C16-H16M	0.9900	C44-H44	0.9500
C16-H16N	0.9900	C45-C46	1.385(12)
C18-C19	1.409(18)	C45-H45	0.9500
C18-C23	1.410(16)	C46-C47	1.380(11)
C19-C20	1.376(19)	C46-C50	1.506(11)
C19-C24	1.55(2)	C47-H47	0.9500
C20-C21	1.38(2)	C48-O50	1.26(2)
C20-H20	0.9500	C48-O49	1.26(2)
C21-C22	1.396(19)	C48-H48A	0.9900
C21-C27	1.550(18)	C48-H48B	0.9900
C22-C23	1.398(14)	C48-H48C	0.9900
C22-H22	0.9500	C48-H48D	0.9900
C23-C30	1.496(17)	C50-C51	1.394(12)
C24-C25	1.50(3)	C50-C55	1.414(11)
C24-C26	1.53(3)	C51-C52	1.414(12)
C24-H24	1.0000	C51-C56	1.522(13)
C25-H25A	0.9800	C52-C53	1.383(12)
C25-H25B	0.9800	C52-H52	0.9500
C25-H25C	0.9800	C53-C54	1.386(11)
C26-H26A	0.9800	C53-C59	1.528(12)
C26-H26B	0.9800	C54-C55	1.388(11)
C26-H26C	0.9800	C54-H54	0.9500
C27-C29	1.39(2)	C55-C62	1.537(11)
C27-C28	1.48(2)	C56-C57	1.476(17)
C27-H27	1.0000	C56-C58	1.517(15)
C28-H28A	0.9800	C56-H56	1.0000
C28-H28B	0.9800	C57-H57A	0.9800
C28-H28C	0.9800	C57-H57B	0.9800
C29-H29A	0.9800	C57-H57C	0.9800
C29-H29B	0.9800	C58-H58A	0.9800
C29-H29C	0.9800	C58-H58B	0.9800
C30-C32	1.48(2)	C58-H58C	0.9800
C30-C31	1.57(2)	C59-C61	1.499(15)

C59-C60	1.502(14)
C59-H59	1.0000
C60-H60A	0.9800
C60-H60B	0.9800
C60-H60C	0.9800
C61-H61A	0.9800
C61-H61B	0.9800
C61-H61C	0.9800
C62-C64	1.513(12)
C62-C63	1.531(13)
C62-H62	1.0000
C63-H63A	0.9800
C63-H63B	0.9800
C63-H63C	0.9800
C64-H64A	0.9800
C64-H64B	0.9800
C64-H64C	0.9800
C66-C70	1.331(13)
C66-N65	1.393(10)
C66-C67	1.494(11)
C67-N68	1.492(11)
C67-H67A	0.9900
C67-H67B	0.9900
C69-C70	1.477(12)
C69-N68	1.500(13)
C69-H69A	0.9900
C69-H69B	0.9900
C70-O71	1.372(10)
C72-N65	1.313(11)
C72-O71	1.344(11)
C72-C73	1.458(12)
C73-N74	1.339(13)
C73-C78	1.372(14)
C75-N74	1.325(11)
C75-C76	1.379(15)
C75-H75	0.9500
C76-C77	1.357(17)
C76-H76	0.9500
C77-C78	1.385(14)
C77-H77	0.9500
C78-H78	0.9500
N1-Ir1	2.032(8)
N33-Ir1	2.053(8)
N65-Ir1	2.118(7)
N68-H68	0.781(10)
N74-Ir1	2.164(7)
O17-H17	0.8400
O49-H49	0.8400
O50-H50	0.8400
C102-C103	1.372(13)
C102-C107	1.379(13)
C102-N101	1.397(10)
C103-C104	1.406(12)
C103-H103	0.9500
C104-C105	1.396(14)
C104-C116	1.522(14)
C105-C106	1.356(14)
C105-H105	0.9500
C106-C107	1.396(12)
C106-H106	0.9500
C107-O108	1.375(11)
C109-N101	1.308(11)
C109-O108	1.355(9)
C109-C110	1.431(12)
C110-C115	1.379(12)
C110-C111	1.415(12)
C111-C112	1.385(11)
C111-Ir2	2.033(9)
C112-C113	1.390(12)
C112-H112	0.9500
C113-C114	1.400(12)
C113-H113	0.9500
C114-C115	1.375(12)
C114-C119	1.513(13)
C115-H115	0.9500
C116-O118	1.438(13)
C116-O117	1.46(2)
C116-H11A	0.9900
C116-H11B	0.9900
C116-H11C	0.9900
C116-H11D	0.9900
C119-C124	1.401(15)
C119-C120	1.412(14)
C120-C121	1.398(14)
C120-C131	1.510(16)
C121-C122	1.358(17)
C121-H121	0.9500
C122-C123	1.387(18)
C122-C128	1.545(17)
C123-C124	1.417(16)
C123-H123	0.9500
C124-C125	1.532(18)
C125-C126	1.49(2)
C125-C127	1.513(19)
C125-H125	1.0000
C126-H12A	0.9800
C126-H12B	0.9800
C126-H12C	0.9800
C127-H12D	0.9800
C127-H12E	0.9800
C127-H12F	0.9800
C128-C129	1.47(2)
C128-C130	1.493(18)
C128-H128	1.0000
C129-H12G	0.9800
C129-H12H	0.9800
C129-H12I	0.9800
C130-H13A	0.9800
C130-H13B	0.9800
C130-H13C	0.9800
C131-C133	1.523(15)
C131-C132	1.523(16)
C131-H131	1.0000
C132-H13D	0.9800
C132-H13E	0.9800
C132-H13F	0.9800
C133-H13G	0.9800
C133-H13H	0.9800
C133-H13I	0.9800
C135-C136	1.382(10)

C135-C140	1.400(10)	C163-C165	1.56(2)
C135-N134	1.408(9)	C163-H163	1.0000
C136-C137	1.377(10)	C164-H16G	0.9800
C136-H136	0.9500	C164-H16H	0.9800
C137-C138	1.401(10)	C164-H16I	0.9800
C137-C143	1.520(10)	C165-H16J	0.9800
C138-C139	1.383(10)	C165-H16K	0.9800
C138-H138	0.9500	C165-H16L	0.9800
C139-C140	1.358(10)	C166-C167	1.35(3)
C139-H139	0.9500	C166-H166	0.9500
C140-O141	1.391(8)	C167-C168	1.33(4)
C142-N134	1.321(9)	C167-C169	1.60(4)
C142-O141	1.333(9)	C168-H168	0.9500
C142-C145	1.442(11)	C169-C170	1.35(2)
C143-O144	1.407(9)	C169-C171	1.38(2)
C143-H14A	0.9900	C169-H169	1.0000
C143-H14B	0.9900	C170-H17A	0.9800
C145-C150	1.393(11)	C170-H17B	0.9800
C145-C146	1.414(12)	C170-H17C	0.9800
C146-C147	1.410(11)	C171-H17X	0.9800
C146-Ir2	2.016(8)	C171-H17Y	0.9800
C147-C148	1.392(13)	C171-H17Z	0.9800
C147-H147	0.9500	C173-C177	1.363(15)
C148-C149	1.364(14)	C173-N172	1.369(12)
C148-H148	0.9500	C173-C174	1.473(15)
C149-C150	1.388(12)	C174-N175	1.497(15)
C149-C151	1.495(14)	C174-H17D	0.9900
C150-H150	0.9500	C174-H17E	0.9900
C151-C152	1.361(16)	C176-C177	1.474(15)
C151-C156	1.434(16)	C176-N175	1.492(17)
C152-C153	1.41(2)	C176-H17F	0.9900
C152-C157	1.479(18)	C176-H17G	0.9900
C152-C166	1.64(3)	C177-O178	1.369(13)
C153-C154	1.44(3)	C179-N172	1.330(12)
C153-H153	0.9500	C179-O178	1.374(11)
C154-C155	1.39(3)	C179-C180	1.406(14)
C154-C160	1.56(3)	C180-N181	1.338(12)
C155-C156	1.41(3)	C180-C185	1.369(15)
C155-H155	0.9500	C182-N181	1.362(13)
C156-C163	1.500(18)	C182-C183	1.380(15)
C156-C168	1.50(3)	C182-H182	0.9500
C157-C158	1.47(2)	C183-C184	1.379(17)
C157-C159	1.54(2)	C183-H183	0.9500
C157-H157	1.0000	C184-C185	1.378(17)
C158-H15A	0.9800	C184-H184	0.9500
C158-H15B	0.9800	C185-H185	0.9500
C158-H15C	0.9800	N101-Ir2	2.056(6)
C159-H15D	0.9800	N134-Ir2	2.042(6)
C159-H15E	0.9800	N172-Ir2	2.138(7)
C159-H15F	0.9800	N175-H175	0.783(10)
C160-C161	1.37(2)	N181-Ir2	2.168(8)
C160-C162	1.394(19)	O117-H117	0.8400
C160-H160	1.0000	O118-H118	0.8400
C161-H16A	0.9800	O144-H144	0.8400
C161-H16B	0.9800	C300-Cl2	1.58(2)
C161-H16C	0.9800	C300-Cl1	1.64(3)
C162-H16D	0.9800	C300-H30A	0.9900
C162-H16E	0.9800	C300-H30B	0.9900
C162-H16F	0.9800	C400-Cl3	1.54(3)
C163-C164	1.46(2)	C400-Cl4	1.61(3)

C400-H40A	0.9900
C400-H40B	0.9900
C500-Cl5	1.71(4)
C500-Cl6	1.78(4)
C500-H50A	0.9900
C500-H50B	0.9900

C7-C2-C3	120.4(10)
C7-C2-N1	107.9(9)
C3-C2-N1	131.5(9)
C2-C3-C4	118.2(9)
C2-C3-H3	120.9
C4-C3-H3	120.9
C3-C4-C5	118.9(10)
C3-C4-C16	120.8(9)
C5-C4-C16	120.2(9)
C6-C5-C4	122.6(11)
C6-C5-H5	118.7
C4-C5-H5	118.7
C7-C6-C5	117.1(11)
C7-C6-H6	121.5
C5-C6-H6	121.5
C6-C7-C2	122.8(11)
C6-C7-O8	129.5(10)
C2-C7-O8	107.6(9)
N1-C9-O8	112.7(9)
N1-C9-C10	120.5(10)
O8-C9-C10	126.7(9)
C15-C10-C11	122.5(10)
C15-C10-C9	126.0(11)
C11-C10-C9	111.5(9)
C12-C11-C10	116.5(9)
C12-C11-Ir1	128.9(9)
C10-C11-Ir1	114.6(7)
C13-C12-C11	122.1(12)
C13-C12-H12	118.9
C11-C12-H12	118.9
C12-C13-C14	120.2(12)
C12-C13-H13	119.9
C14-C13-H13	119.9
C15-C14-C13	120.1(10)
C15-C14-C18	118.5(12)
C13-C14-C18	121.3(11)
C14-C15-C10	118.5(12)
C14-C15-H15	120.7
C10-C15-H15	120.7
O17-C16-C4	110.5(8)
O17-C16-H16M	109.5
C4-C16-H16M	109.5
O17-C16-H16N	109.5
C4-C16-H16N	109.5
H16M-C16-H16N	108.1
C19-C18-C23	120.4(11)
C19-C18-C14	120.2(11)
C23-C18-C14	119.3(10)
C20-C19-C18	119.4(14)
C20-C19-C24	118.7(15)
C18-C19-C24	121.8(13)
C19-C20-C21	121.2(15)
C19-C20-H20	119.4
C21-C20-H20	119.4
C20-C21-C22	119.8(12)
C20-C21-C27	119.3(14)
C22-C21-C27	120.6(14)
C21-C22-C23	120.7(13)
C21-C22-H22	119.7
C23-C22-H22	119.7
C22-C23-C18	118.5(11)
C22-C23-C30	120.5(11)
C18-C23-C30	121.0(9)
C25-C24-C26	109.3(19)
C25-C24-C19	108.2(17)
C26-C24-C19	108.8(19)
C25-C24-H24	110.2
C26-C24-H24	110.2
C19-C24-H24	110.2
C24-C25-H25A	109.5
C24-C25-H25B	109.5
H25A-C25-H25B	109.5
C24-C25-H25C	109.5
H25A-C25-H25C	109.5
H25B-C25-H25C	109.5
C24-C26-H26A	109.5
C24-C26-H26B	109.5
H26A-C26-H26B	109.5
C24-C26-H26C	109.5
H26A-C26-H26C	109.5
H26B-C26-H26C	109.5
C29-C27-C28	115.3(18)
C29-C27-C21	112.6(15)
C28-C27-C21	111.0(13)
C29-C27-H27	105.7
C28-C27-H27	105.7
C21-C27-H27	105.7
C27-C28-H28A	109.5
C27-C28-H28B	109.5
H28A-C28-H28B	109.5
C27-C28-H28C	109.5
H28A-C28-H28C	109.5
H28B-C28-H28C	109.5
C27-C29-H29A	109.5
C27-C29-H29B	109.5
H29A-C29-H29B	109.5
C27-C29-H29C	109.5
H29A-C29-H29C	109.5
H29B-C29-H29C	109.5
C32-C30-C23	114.2(11)
C32-C30-C31	108.5(12)
C23-C30-C31	110.9(13)
C32-C30-H30	107.6
C23-C30-H30	107.6
C31-C30-H30	107.6
C30-C31-H31A	109.5
C30-C31-H31B	109.5
H31A-C31-H31B	109.5
C30-C31-H31C	109.5
H31A-C31-H31C	109.5
H31B-C31-H31C	109.5
C30-C32-H32A	109.5

C30-C32-H32B	109.5
H32A-C32-H32B	109.5
C30-C32-H32C	109.5
H32A-C32-H32C	109.5
H32B-C32-H32C	109.5
C35-C34-C39	119.2(10)
C35-C34-N33	134.3(10)
C39-C34-N33	106.5(8)
C34-C35-C36	117.2(11)
C34-C35-H35	121.4
C36-C35-H35	121.4
C37-C36-C35	123.4(11)
C37-C36-C48	117.8(12)
C35-C36-C48	118.8(13)
C36-C37-C38	121.1(11)
C36-C37-H37	119.4
C38-C37-H37	119.4
C39-C38-C37	114.6(11)
C39-C38-H38	122.7
C37-C38-H38	122.7
C34-C39-C38	124.4(9)
C34-C39-O40	108.2(8)
C38-C39-O40	127.4(9)
N33-C41-O40	113.6(7)
N33-C41-C42	120.3(8)
O40-C41-C42	126.2(7)
C47-C42-C43	122.4(8)
C47-C42-C41	125.1(8)
C43-C42-C41	112.4(7)
C44-C43-C42	116.3(8)
C44-C43-Ir1	129.7(6)
C42-C43-Ir1	113.9(6)
C43-C44-C45	120.8(8)
C43-C44-H44	119.6
C45-C44-H44	119.6
C46-C45-C44	122.7(8)
C46-C45-H45	118.7
C44-C45-H45	118.7
C47-C46-C45	118.3(7)
C47-C46-C50	122.5(7)
C45-C46-C50	119.0(7)
C46-C47-C42	119.5(8)
C46-C47-H47	120.3
C42-C47-H47	120.3
O50-C48-C36	122(3)
O49-C48-C36	116.8(15)
O49-C48-H48A	108.1
C36-C48-H48A	108.1
O49-C48-H48B	108.1
C36-C48-H48B	108.1
H48A-C48-H48B	107.3
O50-C48-H48C	106.8
C36-C48-H48C	106.8
O50-C48-H48D	106.8
C36-C48-H48D	106.8
H48C-C48-H48D	106.7
C51-C50-C55	120.5(7)
C51-C50-C46	121.4(7)
C55-C50-C46	118.0(7)
C50-C51-C52	117.6(8)
C50-C51-C56	121.1(8)
C52-C51-C56	121.3(8)
C53-C52-C51	122.9(8)
C53-C52-H52	118.5
C51-C52-H52	118.5
C52-C53-C54	117.7(8)
C52-C53-C59	122.2(8)
C54-C53-C59	120.1(8)
C53-C54-C55	122.1(8)
C53-C54-H54	119.0
C55-C54-H54	119.0
C54-C55-C50	119.1(7)
C54-C55-C62	119.1(7)
C50-C55-C62	121.8(7)
C57-C56-C58	110.6(10)
C57-C56-C51	111.9(10)
C58-C56-C51	113.6(9)
C57-C56-H56	106.8
C58-C56-H56	106.8
C51-C56-H56	106.8
C56-C57-H57A	109.5
C56-C57-H57B	109.5
H57A-C57-H57B	109.5
C56-C57-H57C	109.5
H57A-C57-H57C	109.5
H57B-C57-H57C	109.5
C56-C58-H58A	109.5
C56-C58-H58B	109.5
H58A-C58-H58B	109.5
C56-C58-H58C	109.5
H58A-C58-H58C	109.5
H58B-C58-H58C	109.5
C61-C59-C60	112.9(9)
C61-C59-C53	110.3(8)
C60-C59-C53	111.4(9)
C61-C59-H59	107.3
C60-C59-H59	107.3
C53-C59-H59	107.3
C59-C60-H60A	109.5
C59-C60-H60B	109.5
H60A-C60-H60B	109.5
C59-C60-H60C	109.5
H60A-C60-H60C	109.5
H60B-C60-H60C	109.5
C59-C61-H61A	109.5
C59-C61-H61B	109.5
H61A-C61-H61B	109.5
C59-C61-H61C	109.5
H61A-C61-H61C	109.5
H61B-C61-H61C	109.5
C64-C62-C63	112.1(7)
C64-C62-C55	110.9(7)
C63-C62-C55	110.0(7)
C64-C62-H62	107.9
C63-C62-H62	107.9
C55-C62-H62	107.9
C62-C63-H63A	109.5
C62-C63-H63B	109.5
H63A-C63-H63B	109.5
C62-C63-H63C	109.5

H63A-C63-H63C	109.5
H63B-C63-H63C	109.5
C62-C64-H64A	109.5
C62-C64-H64B	109.5
H64A-C64-H64B	109.5
C62-C64-H64C	109.5
H64A-C64-H64C	109.5
H64B-C64-H64C	109.5
C70-C66-N65	107.7(7)
C70-C66-C67	111.6(7)
N65-C66-C67	140.6(8)
N68-C67-C66	101.2(7)
N68-C67-H67A	111.5
C66-C67-H67A	111.5
N68-C67-H67B	111.5
C66-C67-H67B	111.5
H67A-C67-H67B	109.3
C70-C69-N68	100.8(7)
C70-C69-H69A	111.6
N68-C69-H69A	111.6
C70-C69-H69B	111.6
N68-C69-H69B	111.6
H69A-C69-H69B	109.4
C66-C70-O71	110.2(7)
C66-C70-C69	112.7(8)
O71-C70-C69	136.7(9)
N65-C72-O71	114.0(7)
N65-C72-C73	121.3(8)
O71-C72-C73	124.6(8)
N74-C73-C78	123.9(9)
N74-C73-C72	112.4(8)
C78-C73-C72	123.7(10)
N74-C75-C76	123.0(11)
N74-C75-H75	118.5
C76-C75-H75	118.5
C77-C76-C75	119.3(10)
C77-C76-H76	120.3
C75-C76-H76	120.3
C76-C77-C78	119.1(11)
C76-C77-H77	120.5
C78-C77-H77	120.5
C73-C78-C77	117.7(11)
C73-C78-H78	121.1
C77-C78-H78	121.1
C9-N1-C2	106.0(8)
C9-N1-Ir1	112.3(7)
C2-N1-Ir1	141.0(6)
C41-N33-C34	106.4(8)
C41-N33-Ir1	113.1(6)
C34-N33-Ir1	140.5(6)
C72-N65-C66	104.7(7)
C72-N65-Ir1	113.2(5)
C66-N65-Ir1	142.1(6)
C67-N68-C69	110.1(7)
C67-N68-H68	106(9)
C69-N68-H68	109(9)
C75-N74-C73	117.0(9)
C75-N74-Ir1	126.7(7)
C73-N74-Ir1	115.3(6)
C9-O8-C7	105.8(8)
C16-O17-H17	109.5
C41-O40-C39	105.4(7)
C48-O49-H49	109.5
C48-O50-H50	109.5
C72-O71-C70	103.4(7)
C11-Ir1-C43	90.3(3)
C11-Ir1-N1	81.1(4)
C43-Ir1-N1	91.6(3)
C11-Ir1-N33	93.1(4)
C43-Ir1-N33	80.3(3)
N1-Ir1-N33	170.1(3)
C11-Ir1-N65	171.3(3)
C43-Ir1-N65	98.0(3)
N1-Ir1-N65	96.2(3)
N33-Ir1-N65	90.7(3)
C11-Ir1-N74	95.4(3)
C43-Ir1-N74	171.1(3)
N1-Ir1-N74	96.0(3)
N33-Ir1-N74	92.6(3)
N65-Ir1-N74	76.6(3)
C103-C102-C107	121.4(8)
C103-C102-N101	133.5(9)
C107-C102-N101	105.1(8)
C102-C103-C104	116.0(9)
C102-C103-H103	122.0
C104-C103-H103	122.0
C105-C104-C103	121.2(9)
C105-C104-C116	121.5(8)
C103-C104-C116	117.3(9)
C106-C105-C104	123.0(9)
C106-C105-H105	118.5
C104-C105-H105	118.5
C105-C106-C107	115.0(9)
C105-C106-H106	122.5
C107-C106-H106	122.5
O108-C107-C102	110.8(7)
O108-C107-C106	125.8(8)
C102-C107-C106	123.5(9)
N101-C109-O108	113.9(7)
N101-C109-C110	120.5(7)
O108-C109-C110	125.6(8)
C115-C110-C111	124.5(8)
C115-C110-C109	124.6(8)
C111-C110-C109	110.8(8)
C112-C111-C110	114.7(8)
C112-C111-Ir2	129.6(6)
C110-C111-Ir2	115.6(6)
C111-C112-C113	121.8(8)
C111-C112-H112	119.1
C113-C112-H112	119.1
C112-C113-C114	121.6(8)
C112-C113-H113	119.2
C114-C113-H113	119.2
C115-C114-C113	118.1(8)
C115-C114-C119	122.1(8)
C113-C114-C119	119.6(8)
C114-C115-C110	119.3(8)
C114-C115-H115	120.3
C110-C115-H115	120.3
O118-C116-C104	108.2(9)

O117-C116-C104	110.6(14)
O117-C116-H11A	109.5
C104-C116-H11A	109.5
O117-C116-H11B	109.5
C104-C116-H11B	109.5
H11A-C116-H11B	108.1
O118-C116-H11C	110.1
C104-C116-H11C	110.1
O118-C116-H11D	110.1
C104-C116-H11D	110.1
H11C-C116-H11D	108.4
C124-C119-C120	120.9(10)
C124-C119-C114	121.9(9)
C120-C119-C114	117.1(9)
C121-C120-C119	118.2(11)
C121-C120-C131	120.0(10)
C119-C120-C131	121.8(9)
C122-C121-C120	122.5(12)
C122-C121-H121	118.8
C120-C121-H121	118.8
C121-C122-C123	118.9(11)
C121-C122-C128	122.1(13)
C123-C122-C128	119.0(13)
C122-C123-C124	121.9(12)
C122-C123-H123	119.1
C124-C123-H123	119.1
C119-C124-C123	117.5(11)
C119-C124-C125	120.0(10)
C123-C124-C125	122.5(11)
C126-C125-C127	111.5(15)
C126-C125-C124	113.5(13)
C127-C125-C124	111.4(13)
C126-C125-H125	106.6
C127-C125-H125	106.6
C124-C125-H125	106.6
C125-C126-H12A	109.5
C125-C126-H12B	109.5
H12A-C126-H12B	109.5
C125-C126-H12C	109.5
H12A-C126-H12C	109.5
H12B-C126-H12C	109.5
C125-C127-H12D	109.5
C125-C127-H12E	109.5
H12D-C127-H12E	109.5
C125-C127-H12F	109.5
H12D-C127-H12F	109.5
H12E-C127-H12F	109.5
C129-C128-C130	117.3(14)
C129-C128-C122	112.2(12)
C130-C128-C122	112.3(11)
C129-C128-H128	104.5
C130-C128-H128	104.5
C122-C128-H128	104.5
C128-C129-H12G	109.5
C128-C129-H12H	109.5
H12G-C129-H12H	109.5
C128-C129-H12I	109.5
H12G-C129-H12I	109.5
H12H-C129-H12I	109.5
C128-C130-H13A	109.5
C128-C130-H13B	109.5
H13A-C130-H13B	109.5
C128-C130-H13C	109.5
H13A-C130-H13C	109.5
H13B-C130-H13C	109.5
C120-C131-C133	113.4(9)
C120-C131-C132	110.8(11)
C133-C131-C132	110.2(10)
C120-C131-H131	107.4
C133-C131-H131	107.4
C132-C131-H131	107.4
C131-C132-H13D	109.5
C131-C132-H13E	109.5
H13D-C132-H13E	109.5
C131-C132-H13F	109.5
H13D-C132-H13F	109.5
H13E-C132-H13F	109.5
C131-C133-H13G	109.5
C131-C133-H13H	109.5
H13G-C133-H13H	109.5
C131-C133-H13I	109.5
H13G-C133-H13I	109.5
H13H-C133-H13I	109.5
C136-C135-C140	120.1(7)
C136-C135-N134	132.7(7)
C140-C135-N134	107.2(6)
C137-C136-C135	117.7(7)
C137-C136-H136	121.2
C135-C136-H136	121.2
C136-C137-C138	120.8(7)
C136-C137-C143	118.9(6)
C138-C137-C143	120.3(6)
C139-C138-C137	121.9(7)
C139-C138-H138	119.0
C137-C138-H138	119.0
C140-C139-C138	116.2(7)
C140-C139-H139	121.9
C138-C139-H139	121.9
C139-C140-O141	129.2(7)
C139-C140-C135	123.2(7)
O141-C140-C135	107.6(6)
N134-C142-O141	114.8(6)
N134-C142-C145	119.2(7)
O141-C142-C145	125.9(7)
O144-C143-C137	113.9(6)
O144-C143-H14A	108.8
C137-C143-H14A	108.8
O144-C143-H14B	108.8
C137-C143-H14B	108.8
H14A-C143-H14B	107.7
C150-C145-C146	124.6(7)
C150-C145-C142	124.2(8)
C146-C145-C142	111.3(7)
C147-C146-C145	115.0(8)
C147-C146-Ir2	129.3(7)
C145-C146-Ir2	115.5(6)
C148-C147-C146	119.8(9)
C148-C147-H147	120.1
C146-C147-H147	120.1
C149-C148-C147	123.7(8)

C149-C148-H148	118.1
C147-C148-H148	118.1
C148-C149-C150	118.7(9)
C148-C149-C151	119.9(9)
C150-C149-C151	121.3(10)
C149-C150-C145	118.2(9)
C149-C150-H150	120.9
C145-C150-H150	120.9
C152-C151-C156	121.3(11)
C152-C151-C149	118.9(10)
C156-C151-C149	119.7(10)
C151-C152-C153	120.9(15)
C151-C152-C157	123.8(11)
C153-C152-C157	112.1(15)
C151-C152-C166	114.3(14)
C157-C152-C166	118.3(14)
C152-C153-C154	116(2)
C152-C153-H153	122.1
C154-C153-H153	122.1
C155-C154-C153	120(2)
C155-C154-C160	119(2)
C153-C154-C160	120(2)
C154-C155-C156	122(2)
C154-C155-H155	119.0
C156-C155-H155	119.0
C155-C156-C151	114.3(15)
C155-C156-C163	120.2(16)
C151-C156-C163	122.2(10)
C151-C156-C168	117.0(15)
C163-C156-C168	117.5(15)
C158-C157-C152	111.8(11)
C158-C157-C159	108.0(13)
C152-C157-C159	113.6(15)
C158-C157-H157	107.7
C152-C157-H157	107.7
C159-C157-H157	107.7
C157-C158-H15A	109.5
C157-C158-H15B	109.5
H15A-C158-H15B	109.5
C157-C158-H15C	109.5
H15A-C158-H15C	109.5
H15B-C158-H15C	109.5
C157-C159-H15D	109.5
C157-C159-H15E	109.5
H15D-C159-H15E	109.5
C157-C159-H15F	109.5
H15D-C159-H15F	109.5
H15E-C159-H15F	109.5
C161-C160-C162	131(3)
C161-C160-C154	117(2)
C162-C160-C154	111.1(18)
C161-C160-H160	93.2
C162-C160-H160	93.2
C154-C160-H160	93.2
C160-C161-H16A	109.5
C160-C161-H16B	109.5
H16A-C161-H16B	109.5
C160-C161-H16C	109.5
H16A-C161-H16C	109.5
H16B-C161-H16C	109.5
C160-C162-H16D	109.5
C160-C162-H16E	109.5
H16D-C162-H16E	109.5
C160-C162-H16F	109.5
H16D-C162-H16F	109.5
H16E-C162-H16F	109.5
C164-C163-C156	115.7(12)
C164-C163-C165	107.2(14)
C156-C163-C165	109.0(15)
C164-C163-H163	108.2
C156-C163-H163	108.2
C165-C163-H163	108.2
C163-C164-H16G	109.5
C163-C164-H16H	109.5
H16G-C164-H16H	109.5
C163-C164-H16I	109.5
H16G-C164-H16I	109.5
H16H-C164-H16I	109.5
C163-C165-H16J	109.5
C163-C165-H16K	109.5
H16J-C165-H16K	109.5
C163-C165-H16L	109.5
H16J-C165-H16L	109.5
H16K-C165-H16L	109.5
C167-C166-C152	121(2)
C167-C166-H166	119.6
C152-C166-H166	119.6
C168-C167-C166	119(2)
C168-C167-C169	121(3)
C166-C167-C169	119(2)
C167-C168-C156	124(2)
C167-C168-H168	118.2
C156-C168-H168	118.2
C170-C169-C171	139(4)
C170-C169-C167	102(3)
C171-C169-C167	119(3)
C170-C169-H169	90.3
C171-C169-H169	90.3
C167-C169-H169	90.3
C169-C170-H17A	109.5
C169-C170-H17B	109.5
H17A-C170-H17B	109.5
C169-C170-H17C	109.5
H17A-C170-H17C	109.5
H17B-C170-H17C	109.5
C169-C171-H17X	109.5
C169-C171-H17Y	109.5
H17X-C171-H17Y	109.5
C169-C171-H17Z	109.5
H17X-C171-H17Z	109.5
H17Y-C171-H17Z	109.5
C177-C173-N172	108.3(10)
C177-C173-C174	110.1(9)
N172-C173-C174	141.3(10)
C173-C174-N175	103.6(10)
C173-C174-H17D	111.0
N175-C174-H17D	111.0
C173-C174-H17E	111.0
N175-C174-H17E	111.0
H17D-C174-H17E	109.0

C177-C176-N175	102.2(9)
C177-C176-H17F	111.3
N175-C176-H17F	111.3
C177-C176-H17G	111.3
N175-C176-H17G	111.3
H17F-C176-H17G	109.2
C173-C177-O178	109.3(9)
C173-C177-C176	112.7(11)
O178-C177-C176	137.4(10)
N172-C179-O178	112.4(9)
N172-C179-C180	123.3(9)
O178-C179-C180	124.3(9)
N181-C180-C185	121.5(10)
N181-C180-C179	112.4(9)
C185-C180-C179	126.1(10)
N181-C182-C183	122.7(11)
N181-C182-H182	118.7
C183-C182-H182	118.7
C184-C183-C182	119.3(12)
C184-C183-H183	120.4
C182-C183-H183	120.4
C185-C184-C183	117.2(12)
C185-C184-H184	121.4
C183-C184-H184	121.4
C180-C185-C184	121.7(12)
C180-C185-H185	119.1
C184-C185-H185	119.1
C109-N101-C102	107.0(7)
C109-N101-Ir2	113.8(5)
C102-N101-Ir2	139.2(6)
C142-N134-C135	105.1(6)
C142-N134-Ir2	114.0(5)
C135-N134-Ir2	140.5(5)
C179-N172-C173	105.9(8)
C179-N172-Ir2	111.6(6)
C173-N172-Ir2	142.5(7)
C176-N175-C174	109.3(9)
C176-N175-H175	100(10)
C174-N175-H175	116(10)
C180-N181-C182	117.6(9)
C180-N181-Ir2	115.8(7)
C182-N181-Ir2	126.1(7)
C109-O108-C107	103.3(7)
C116-O117-H117	109.0
C116-O118-H118	109.5
C142-O141-C140	105.3(5)
C143-O144-H144	109.5
C177-O178-C179	104.0(8)
C146-Ir2-C111	91.1(3)
C146-Ir2-N134	79.9(3)
C111-Ir2-N134	93.8(3)
C146-Ir2-N101	93.5(3)
C111-Ir2-N101	79.2(3)
N134-Ir2-N101	170.3(3)
C146-Ir2-N172	172.0(3)
C111-Ir2-N172	96.6(3)
N134-Ir2-N172	97.4(2)
N101-Ir2-N172	90.0(3)
C146-Ir2-N181	96.5(3)
C111-Ir2-N181	169.9(3)
N134-Ir2-N181	94.0(3)
N101-Ir2-N181	93.8(3)
N172-Ir2-N181	76.1(3)
Cl2-C300-Cl1	128.8(17)
Cl2-C300-H30A	105.1
Cl1-C300-H30A	105.1
Cl2-C300-H30B	105.1
Cl1-C300-H30B	105.1
H30A-C300-H30B	105.9
Cl3-C400-Cl4	140(4)
Cl3-C400-H40A	102.0
Cl4-C400-H40A	102.0
Cl3-C400-H40B	102.0
Cl4-C400-H40B	102.0
H40A-C400-H40B	104.8
Cl5-C500-Cl6	112(2)
Cl5-C500-H50A	109.3
Cl6-C500-H50A	109.3
Cl5-C500-H50B	109.3
Cl6-C500-H50B	109.3
H50A-C500-H50B	107.9

Table S4. Anisotropic displacement parameters (Å^2) for cat112_0m_sq.
The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C2	0.059(4)	0.016(3)	0.066(5)	0.012(3)	0.023(4)	0.004(3)
C3	0.047(4)	0.021(4)	0.060(5)	0.013(3)	0.017(4)	0.005(3)
C4	0.045(4)	0.035(4)	0.072(5)	0.026(4)	0.021(4)	0.005(3)
C5	0.050(5)	0.046(5)	0.092(6)	0.017(4)	0.015(4)	0.000(4)
C6	0.064(5)	0.038(5)	0.094(7)	0.005(5)	0.017(5)	-0.001(4)
C7	0.064(4)	0.031(4)	0.077(5)	0.004(4)	0.017(4)	0.005(3)
C9	0.071(5)	0.025(4)	0.061(5)	0.005(4)	0.020(4)	0.012(3)
C10	0.082(5)	0.030(4)	0.059(5)	0.015(3)	0.031(4)	0.027(4)
C11	0.079(5)	0.034(4)	0.055(5)	0.018(4)	0.034(4)	0.027(4)
C12	0.080(6)	0.044(5)	0.064(5)	0.023(4)	0.042(5)	0.025(4)
C13	0.101(7)	0.050(5)	0.076(6)	0.020(4)	0.050(5)	0.032(5)
C14	0.097(6)	0.045(5)	0.059(5)	0.019(4)	0.044(4)	0.033(4)
C15	0.091(6)	0.040(5)	0.060(5)	0.009(4)	0.033(5)	0.022(4)
C16	0.044(5)	0.048(5)	0.075(6)	0.028(4)	0.026(4)	0.010(4)
C18	0.100(9)	0.054(5)	0.068(5)	0.009(4)	0.045(5)	0.027(5)
C19	0.150(13)	0.082(6)	0.073(6)	0.018(5)	0.054(7)	0.026(7)
C20	0.128(13)	0.098(7)	0.074(7)	0.011(5)	0.037(7)	0.037(7)
C21	0.094(9)	0.092(6)	0.064(5)	-0.001(5)	0.025(6)	0.033(6)
C22	0.081(8)	0.065(6)	0.068(5)	-0.003(4)	0.024(5)	0.034(6)
C23	0.067(7)	0.044(4)	0.063(5)	0.001(4)	0.030(5)	0.015(4)
C24	0.211(16)	0.088(8)	0.103(11)	0.039(7)	0.053(10)	0.026(9)
C25	0.227(16)	0.098(13)	0.146(15)	0.040(12)	0.040(11)	0.047(11)
C26	0.224(18)	0.23(2)	0.21(2)	0.14(2)	0.075(15)	0.031(14)
C27	0.118(10)	0.114(9)	0.066(7)	-0.006(6)	0.022(7)	0.052(7)
C28	0.132(10)	0.145(14)	0.095(11)	0.011(10)	0.049(8)	0.070(9)
C29	0.162(13)	0.137(11)	0.133(15)	-0.049(10)	0.072(11)	0.008(10)
C30	0.119(9)	0.041(5)	0.072(6)	0.009(4)	0.045(6)	0.026(5)
C31	0.135(10)	0.101(11)	0.183(17)	0.073(12)	0.075(10)	0.029(8)
C32	0.141(11)	0.084(10)	0.107(10)	0.029(8)	0.033(8)	0.040(8)
C34	0.040(4)	0.061(5)	0.065(5)	0.033(4)	0.026(3)	0.033(3)
C35	0.054(5)	0.087(7)	0.105(8)	0.064(7)	0.025(5)	0.039(5)
C36	0.051(5)	0.104(8)	0.111(9)	0.061(7)	0.024(5)	0.043(5)
C37	0.047(5)	0.108(8)	0.088(8)	0.052(6)	0.027(5)	0.045(5)
C38	0.039(4)	0.076(6)	0.070(6)	0.030(5)	0.019(4)	0.028(4)
C39	0.041(4)	0.064(5)	0.052(5)	0.027(4)	0.023(3)	0.031(3)
C41	0.035(3)	0.033(4)	0.037(4)	0.010(3)	0.018(3)	0.018(3)
C42	0.036(3)	0.028(3)	0.034(4)	0.008(3)	0.016(3)	0.015(3)
C43	0.041(4)	0.024(4)	0.037(4)	0.004(3)	0.018(3)	0.013(3)
C44	0.047(4)	0.028(4)	0.042(4)	0.007(3)	0.017(3)	0.013(3)
C45	0.038(4)	0.030(4)	0.037(4)	0.007(3)	0.007(3)	0.010(3)
C46	0.038(4)	0.028(3)	0.031(4)	0.009(3)	0.010(3)	0.014(3)
C47	0.034(4)	0.029(4)	0.033(4)	0.009(3)	0.012(3)	0.013(3)
C48	0.068(9)	0.204(18)	0.227(19)	0.166(17)	0.026(9)	0.058(10)
C50	0.025(4)	0.033(3)	0.032(3)	0.012(3)	0.004(3)	0.007(3)
C51	0.049(5)	0.040(4)	0.033(3)	0.013(3)	0.008(3)	0.016(4)
C52	0.045(5)	0.049(4)	0.033(4)	0.020(3)	0.009(4)	0.014(4)
C53	0.030(4)	0.042(4)	0.039(4)	0.016(3)	0.008(3)	0.014(3)
C54	0.026(4)	0.032(4)	0.036(3)	0.012(3)	0.009(3)	0.012(3)
C55	0.028(4)	0.034(3)	0.034(3)	0.014(3)	0.007(3)	0.014(3)
C56	0.084(7)	0.051(5)	0.037(4)	0.013(4)	0.016(4)	0.031(4)
C57	0.115(9)	0.080(7)	0.068(8)	-0.015(6)	0.036(6)	0.002(6)
C58	0.098(8)	0.069(7)	0.055(6)	0.015(5)	0.036(6)	0.040(6)
C59	0.065(5)	0.052(5)	0.042(5)	0.025(4)	0.016(4)	0.029(4)
C60	0.060(6)	0.079(7)	0.060(6)	0.041(5)	0.012(4)	0.030(5)
C61	0.070(6)	0.052(6)	0.073(7)	0.036(5)	0.022(5)	0.024(5)
C62	0.044(4)	0.039(4)	0.031(4)	0.015(3)	0.010(3)	0.021(3)
C63	0.041(5)	0.066(6)	0.032(4)	0.012(4)	0.004(3)	0.018(4)

C64	0.047(5)	0.039(5)	0.035(4)	0.010(4)	0.015(4)	0.014(4)
C66	0.034(4)	0.028(3)	0.046(4)	0.008(3)	0.012(3)	0.013(3)
C67	0.041(5)	0.027(4)	0.042(4)	0.002(3)	0.004(3)	0.014(3)
C69	0.066(6)	0.038(4)	0.049(4)	0.007(3)	0.018(4)	0.021(4)
C70	0.050(5)	0.037(4)	0.046(4)	0.011(3)	0.016(3)	0.020(4)
C72	0.038(4)	0.032(4)	0.049(4)	0.014(3)	0.013(3)	0.015(3)
C73	0.050(5)	0.046(4)	0.064(4)	0.030(3)	0.030(4)	0.029(4)
C75	0.079(7)	0.048(5)	0.087(6)	0.039(4)	0.050(5)	0.041(5)
C76	0.084(7)	0.058(6)	0.101(6)	0.054(5)	0.052(5)	0.049(6)
C77	0.063(6)	0.064(6)	0.094(6)	0.054(5)	0.047(5)	0.036(5)
C78	0.058(6)	0.062(5)	0.075(5)	0.045(4)	0.033(5)	0.030(5)
N1	0.062(4)	0.020(3)	0.054(4)	0.010(3)	0.022(3)	0.014(3)
N33	0.041(4)	0.043(4)	0.054(4)	0.022(3)	0.025(3)	0.029(3)
N65	0.037(4)	0.027(3)	0.047(3)	0.013(3)	0.016(3)	0.014(3)
N68	0.044(4)	0.032(4)	0.048(4)	-0.001(3)	0.010(3)	0.012(3)
N74	0.064(5)	0.038(4)	0.064(4)	0.028(3)	0.032(4)	0.031(4)
O8	0.076(4)	0.033(3)	0.078(5)	0.000(3)	0.021(3)	0.014(3)
O17	0.051(4)	0.051(4)	0.063(4)	0.017(3)	0.023(3)	0.021(3)
O40	0.034(3)	0.048(3)	0.045(3)	0.019(3)	0.014(2)	0.018(2)
O49	0.082(11)	0.36(3)	0.36(3)	0.30(3)	0.067(15)	0.099(15)
O71	0.062(4)	0.043(3)	0.046(3)	0.017(3)	0.016(3)	0.027(3)
Ir1	0.0521(2)	0.02623(17)	0.0469(2)	0.01364(15)	0.02258(17)	0.02145(15)
C102	0.028(3)	0.054(4)	0.038(4)	0.026(3)	0.008(3)	0.011(3)
C103	0.029(4)	0.056(5)	0.052(5)	0.026(4)	0.007(3)	0.014(3)
C104	0.027(4)	0.062(4)	0.046(5)	0.024(4)	0.009(3)	0.014(3)
C105	0.024(4)	0.060(4)	0.058(5)	0.022(4)	0.008(4)	0.009(3)
C106	0.027(4)	0.053(5)	0.064(6)	0.024(4)	0.013(4)	0.008(3)
C107	0.025(3)	0.050(4)	0.047(5)	0.023(3)	0.007(3)	0.006(3)
C109	0.020(3)	0.040(4)	0.043(4)	0.019(3)	0.002(3)	0.000(3)
C110	0.024(3)	0.046(4)	0.040(4)	0.024(3)	0.003(3)	0.008(3)
C111	0.026(3)	0.045(4)	0.034(4)	0.024(3)	0.005(3)	0.012(3)
C112	0.023(4)	0.045(4)	0.045(5)	0.021(3)	0.004(3)	0.010(3)
C113	0.025(4)	0.045(4)	0.041(4)	0.017(3)	0.002(3)	0.012(3)
C114	0.027(4)	0.045(4)	0.045(5)	0.019(3)	0.000(3)	0.009(3)
C115	0.030(4)	0.045(4)	0.034(4)	0.020(3)	-0.002(3)	0.003(3)
C116	0.042(5)	0.066(6)	0.073(7)	0.028(5)	0.022(5)	0.024(5)
C119	0.030(4)	0.041(4)	0.058(4)	0.009(3)	-0.006(3)	0.006(3)
C120	0.034(5)	0.045(4)	0.072(5)	0.022(3)	0.003(4)	0.007(4)
C121	0.048(6)	0.042(4)	0.085(6)	0.015(4)	-0.001(5)	0.011(4)
C122	0.058(6)	0.053(5)	0.080(6)	0.005(4)	-0.011(5)	0.012(4)
C123	0.080(8)	0.056(5)	0.067(6)	-0.006(4)	-0.009(5)	0.018(5)
C124	0.058(6)	0.061(5)	0.055(4)	0.003(4)	-0.010(4)	0.019(5)
C125	0.107(9)	0.082(7)	0.055(6)	0.009(5)	-0.011(5)	0.030(6)
C126	0.133(11)	0.147(14)	0.085(10)	0.043(10)	-0.005(8)	0.014(9)
C127	0.164(14)	0.147(14)	0.074(8)	0.023(8)	-0.041(9)	0.014(11)
C128	0.085(7)	0.051(5)	0.110(9)	-0.005(5)	-0.003(6)	0.021(5)
C129	0.093(8)	0.059(8)	0.133(13)	-0.005(8)	0.006(7)	0.031(6)
C130	0.108(9)	0.049(7)	0.133(12)	-0.007(7)	-0.019(8)	0.012(6)
C131	0.054(5)	0.059(6)	0.077(5)	0.035(4)	0.021(4)	0.029(4)
C132	0.056(6)	0.136(12)	0.131(11)	0.083(10)	0.035(6)	0.030(6)
C133	0.059(6)	0.056(6)	0.074(6)	0.037(5)	0.024(4)	0.027(5)
C135	0.019(3)	0.027(4)	0.023(3)	0.007(3)	0.003(2)	0.007(3)
C136	0.021(3)	0.029(4)	0.021(3)	0.011(3)	0.007(2)	0.006(3)
C137	0.019(3)	0.023(3)	0.020(3)	0.001(3)	0.004(2)	0.005(2)
C138	0.018(3)	0.028(4)	0.027(3)	0.007(3)	0.004(3)	0.009(3)
C139	0.022(3)	0.029(4)	0.026(3)	0.009(3)	0.008(2)	0.004(3)
C140	0.025(3)	0.030(4)	0.020(3)	0.009(3)	0.006(2)	0.009(3)
C142	0.026(3)	0.032(4)	0.027(3)	0.013(3)	0.007(2)	0.010(3)
C143	0.027(4)	0.035(4)	0.028(3)	0.013(3)	0.002(3)	0.009(3)
C145	0.032(3)	0.040(4)	0.028(3)	0.012(3)	0.003(3)	0.012(3)

C146	0.030(4)	0.037(4)	0.031(4)	0.010(3)	0.001(3)	0.012(3)
C147	0.032(4)	0.046(5)	0.043(4)	0.012(4)	-0.005(3)	0.011(3)
C148	0.047(4)	0.056(5)	0.035(4)	0.014(4)	-0.008(3)	0.017(4)
C149	0.054(4)	0.048(5)	0.029(4)	0.010(3)	-0.005(3)	0.016(4)
C150	0.043(4)	0.036(4)	0.026(3)	0.011(3)	0.001(3)	0.009(3)
C151	0.079(7)	0.070(5)	0.033(4)	0.020(4)	0.002(4)	0.028(5)
C152	0.119(9)	0.127(8)	0.037(4)	0.034(5)	0.015(5)	0.073(7)
C153	0.070(13)	0.088(11)	0.037(7)	0.023(7)	-0.007(7)	0.014(10)
C154	0.033(9)	0.066(10)	0.048(7)	0.022(6)	-0.014(6)	-0.015(7)
C155	0.079(14)	0.086(13)	0.052(7)	0.038(7)	0.002(7)	0.022(12)
C156	0.123(9)	0.085(6)	0.050(5)	0.034(4)	0.014(5)	0.052(7)
C157	0.112(8)	0.128(8)	0.029(5)	0.023(5)	0.009(5)	0.076(7)
C158	0.125(11)	0.162(10)	0.088(10)	-0.012(8)	-0.014(8)	0.101(8)
C159	0.129(9)	0.213(16)	0.094(11)	0.082(11)	0.029(7)	0.095(9)
C163	0.155(10)	0.066(7)	0.060(6)	0.033(5)	0.035(6)	0.056(7)
C164	0.204(14)	0.123(13)	0.115(12)	0.058(10)	0.051(10)	0.104(12)
C165	0.205(14)	0.090(10)	0.107(10)	0.016(8)	0.016(9)	0.048(9)
C166	0.083(14)	0.098(11)	0.033(8)	0.024(8)	0.007(9)	0.048(10)
C167	0.093(15)	0.092(11)	0.039(9)	0.024(8)	0.004(9)	0.045(11)
C168	0.126(19)	0.086(12)	0.055(10)	0.036(10)	0.027(13)	0.056(13)
C173	0.030(5)	0.072(5)	0.060(4)	0.035(4)	0.011(4)	0.009(4)
C174	0.043(6)	0.077(6)	0.076(6)	0.043(5)	0.018(4)	0.019(5)
C176	0.058(7)	0.095(7)	0.070(6)	0.047(5)	0.011(5)	0.018(6)
C177	0.031(5)	0.072(5)	0.052(4)	0.030(4)	0.006(4)	0.002(4)
C179	0.018(4)	0.064(4)	0.041(4)	0.014(3)	0.002(3)	-0.004(3)
C180	0.022(4)	0.063(5)	0.052(4)	0.015(4)	0.006(3)	0.002(3)
C182	0.052(6)	0.061(5)	0.065(6)	0.022(4)	0.012(5)	0.021(5)
C183	0.049(6)	0.064(6)	0.076(6)	0.016(5)	0.008(5)	0.022(5)
C184	0.056(7)	0.086(7)	0.072(6)	0.017(5)	0.018(5)	0.027(6)
C185	0.034(5)	0.084(6)	0.067(6)	0.011(5)	0.012(4)	0.016(5)
N101	0.013(3)	0.048(3)	0.050(4)	0.021(3)	0.003(3)	0.005(2)
N134	0.014(3)	0.039(4)	0.028(3)	0.017(3)	0.002(2)	0.004(2)
N172	0.018(3)	0.063(4)	0.046(4)	0.024(3)	0.003(3)	0.000(3)
N175	0.048(5)	0.090(6)	0.074(5)	0.045(5)	0.008(4)	0.012(5)
N181	0.021(3)	0.052(4)	0.047(4)	0.013(3)	0.001(3)	0.003(3)
O108	0.021(3)	0.051(3)	0.054(4)	0.020(3)	0.006(2)	0.005(2)
O141	0.027(2)	0.033(3)	0.022(2)	0.012(2)	0.0035(19)	0.005(2)
O144	0.030(3)	0.036(3)	0.033(3)	0.008(2)	-0.002(2)	0.011(2)
O178	0.050(4)	0.077(4)	0.043(3)	0.022(3)	0.007(3)	0.008(3)
Ir2	0.01836(16)	0.0439(2)	0.03618(18)	0.01902(15)	0.00422(12)	0.00798(13)
I1	0.063(3)	0.122(4)	0.091(3)	0.068(3)	0.035(2)	0.019(2)
I2	0.094(3)	0.090(4)	0.055(2)	0.029(2)	0.0188(19)	0.001(2)
I3	0.144(5)	0.121(5)	0.096(4)	0.040(3)	0.056(3)	-0.010(3)
I4	0.036(2)	0.053(3)	0.052(3)	0.0075(19)	0.0153(18)	0.0004(17)
I5	0.0361(8)	0.0452(14)	0.0448(10)	0.0129(8)	0.0138(6)	0.0075(7)
I6	0.058(3)	0.049(3)	0.068(4)	0.022(3)	0.006(3)	-0.006(2)
I7	0.054(5)	0.079(8)	0.069(9)	0.007(7)	0.043(6)	-0.017(5)
I8	0.121(4)	0.082(4)	0.095(3)	0.031(3)	0.021(3)	-0.039(3)
I9	0.098(2)	0.0767(18)	0.115(3)	0.0612(19)	-0.0467(17)	-0.0441(15)
I10	0.128(3)	0.056(2)	0.131(4)	0.047(2)	0.015(3)	0.0022(19)
I11	0.171(6)	0.075(3)	0.124(5)	0.067(4)	-0.054(5)	-0.044(4)
I12	0.168(5)	0.114(4)	0.094(3)	0.035(2)	0.021(3)	0.006(3)
I13	0.100(10)	0.084(9)	0.116(11)	0.033(7)	0.029(7)	0.027(7)
I14	0.37(2)	0.330(18)	0.243(14)	0.096(12)	0.039(13)	-0.040(15)
I15	0.29(2)	0.131(13)	0.165(16)	0.017(11)	-0.011(14)	0.049(13)
I17	0.132(5)	0.176(7)	0.068(5)	-0.008(4)	0.025(4)	0.073(5)
I18	0.0576(6)	0.0483(7)	0.0798(12)	0.0237(6)	0.0285(6)	0.0290(5)
O400	0.089(9)	0.088(8)	0.203(15)	0.111(10)	0.066(9)	0.036(7)
C300	0.14(2)	0.14(2)	0.15(2)	0.08(2)	0.10(2)	0.06(2)
Cl1	0.055(3)	0.129(5)	0.069(3)	0.032(3)	0.019(2)	0.032(3)

Cl2	0.264(12)	0.153(7)	0.220(10)	0.118(7)	0.178(10)	0.127(8)
C400	0.24(5)	0.059(19)	0.26(5)	-0.05(3)	0.20(5)	-0.05(2)
Cl3	0.076(5)	0.077(4)	0.154(7)	0.041(5)	0.043(5)	0.040(4)
Cl4	0.124(8)	0.145(9)	0.139(8)	-0.004(7)	0.069(7)	-0.045(7)
C500	0.06(2)	0.08(3)	0.08(3)	0.02(2)	-0.006(19)	-0.001(19)
Cl5	0.075(8)	0.065(7)	0.196(15)	-0.028(8)	-0.015(8)	0.012(6)
Cl6	0.085(8)	0.147(11)	0.084(7)	0.041(8)	0.030(6)	0.019(7)

Table S5. Hydrogen coordinates and isotropic displacement parameters (Å^2) for cat112_0m_sq.

	x	y	z	U(eq)	Occupancy
H3	0.6718	0.4233	0.1027	0.051	1
H5	0.9344	0.5309	0.1902	0.078	1
H6	0.8762	0.5981	0.2562	0.084	1
H12	0.2997	0.4780	0.2103	0.068	1
H13	0.2944	0.5652	0.2854	0.084	1
H15	0.5746	0.6394	0.3185	0.074	1
H16M	0.8794	0.4550	0.0781	0.063	1
H16N	0.8992	0.4095	0.1181	0.063	1
H20	0.4205	0.7018	0.4863	0.121	1
H22	0.4277	0.8320	0.3952	0.088	1
H24	0.4254	0.5503	0.3810	0.157	1
H25A	0.5716	0.6186	0.4463	0.234	1
H25B	0.5306	0.5472	0.4556	0.234	1
H25C	0.5177	0.6181	0.4936	0.234	1
H26A	0.3272	0.5130	0.4275	0.310	1
H26B	0.2975	0.5842	0.4295	0.310	1
H26C	0.3696	0.5789	0.4810	0.310	1
H27	0.4218	0.8143	0.5289	0.124	1
H28A	0.3028	0.8598	0.4567	0.183	1
H28B	0.3074	0.8731	0.5206	0.183	1
H28C	0.2720	0.7964	0.4786	0.183	1
H29A	0.4731	0.9147	0.4831	0.242	1
H29B	0.5431	0.8816	0.5167	0.242	1
H29C	0.4773	0.9240	0.5464	0.242	1
H30	0.4184	0.7008	0.2704	0.090	1
H31A	0.5470	0.8323	0.3301	0.193	1
H31B	0.5264	0.7987	0.2649	0.193	1
H31C	0.5761	0.7618	0.3050	0.193	1
H32A	0.3596	0.7855	0.2448	0.163	1
H32B	0.3735	0.8298	0.3075	0.163	1
H32C	0.2980	0.7578	0.2816	0.163	1
H35	0.2304	0.4478	0.0597	0.086	1
H37	-0.0210	0.3226	0.0342	0.087	1
H38	0.0441	0.2598	0.0893	0.069	1
H44	0.6203	0.4031	0.2257	0.046	1
H45	0.6268	0.3126	0.2615	0.043	1
H47	0.3502	0.2348	0.2011	0.037	1
H48A	0.0018	0.3914	-0.0241	0.173	0.74(2)
H48B	0.0223	0.4584	0.0279	0.173	0.74(2)
H48C	0.0766	0.4757	0.0250	0.173	0.26(2)
H48D	0.0755	0.4155	-0.0279	0.173	0.26(2)
H52	0.5301	0.1505	0.3616	0.049	1
H54	0.5416	0.0496	0.2093	0.036	1
H56	0.4428	0.2869	0.3250	0.066	1
H57A	0.5504	0.3599	0.4021	0.144	1
H57B	0.6001	0.3360	0.3535	0.144	1
H57C	0.6098	0.3026	0.4023	0.144	1
H58A	0.3763	0.2058	0.3654	0.105	1
H58B	0.4048	0.2839	0.4048	0.105	1
H58C	0.4696	0.2320	0.4139	0.105	1
H59	0.5775	-0.0025	0.2753	0.058	1
H60A	0.6706	0.0135	0.3610	0.091	1
H60B	0.6441	0.0854	0.3854	0.091	1
H60C	0.7046	0.0777	0.3406	0.091	1
H61A	0.4297	-0.0205	0.2913	0.090	1

H61B	0.4708	0.0266	0.3539	0.090	1
H61C	0.4994	-0.0451	0.3325	0.090	1
H62	0.4931	0.1813	0.1499	0.042	1
H63A	0.4216	0.0360	0.1249	0.070	1
H63B	0.4059	0.0781	0.0820	0.070	1
H63C	0.3599	0.0923	0.1333	0.070	1
H64A	0.5961	0.0767	0.1386	0.059	1
H64B	0.6435	0.1576	0.1612	0.059	1
H64C	0.5828	0.1234	0.0991	0.059	1
H67A	0.6151	0.2969	0.0943	0.046	1
H67B	0.5147	0.2428	0.0709	0.046	1
H69A	0.5762	0.2774	-0.0585	0.061	1
H69B	0.4808	0.2276	-0.0586	0.061	1
H75	0.3858	0.5784	0.1435	0.072	1
H76	0.3162	0.6223	0.0776	0.080	1
H77	0.3027	0.5671	-0.0144	0.074	1
H78	0.3663	0.4697	-0.0385	0.067	1
H68	0.6404(19)	0.261(5)	0.017(5)	0.066	1
H17	0.8039	0.3369	0.0516	0.078	1
H49	0.1524	0.4434	-0.0165	0.327	0.74(2)
H50	-0.0604	0.3892	0.0055	0.153	0.26(2)
H103	-0.1043	0.0537	-0.1862	0.052	1
H105	-0.3595	-0.0809	-0.2371	0.056	1
H106	-0.2968	-0.1728	-0.2739	0.056	1
H112	0.2768	-0.0705	-0.2406	0.043	1
H113	0.2805	-0.1839	-0.2812	0.044	1
H115	0.0017	-0.2440	-0.3038	0.044	1
H11A	-0.2731	0.0883	-0.1998	0.067	0.25
H11B	-0.3480	0.0349	-0.1857	0.067	0.25
H11C	-0.3485	0.0357	-0.1868	0.067	0.75
H11D	-0.2514	0.0705	-0.1414	0.067	0.75
H121	0.1761	-0.4285	-0.2684	0.074	1
H123	0.1705	-0.4209	-0.4204	0.092	1
H125	0.1067	-0.2548	-0.3966	0.105	1
H12A	0.2471	-0.2966	-0.4467	0.191	1
H12B	0.2698	-0.2365	-0.3894	0.191	1
H12C	0.2100	-0.2280	-0.4439	0.191	1
H12D	0.0907	-0.3780	-0.4821	0.215	1
H12E	0.0536	-0.3125	-0.4904	0.215	1
H12F	0.0072	-0.3567	-0.4564	0.215	1
H128	0.1997	-0.5224	-0.3299	0.110	1
H12G	0.3036	-0.4853	-0.3998	0.155	1
H12H	0.3084	-0.5492	-0.3767	0.155	1
H12I	0.3408	-0.4720	-0.3354	0.155	1
H13A	0.1266	-0.5490	-0.4424	0.167	1
H13B	0.0633	-0.5514	-0.3997	0.167	1
H13C	0.1301	-0.6038	-0.4094	0.167	1
H131	0.1427	-0.2576	-0.2152	0.070	1
H13D	0.0028	-0.3345	-0.2346	0.144	1
H13E	0.0549	-0.3283	-0.1735	0.144	1
H13F	0.0521	-0.3940	-0.2236	0.144	1
H13G	0.2217	-0.2808	-0.1393	0.085	1
H13H	0.2871	-0.2824	-0.1812	0.085	1
H13I	0.2316	-0.3531	-0.1768	0.085	1
H136	0.3293	0.0402	-0.0941	0.027	1
H138	0.5937	0.1206	-0.0969	0.029	1
H139	0.5406	0.1417	-0.1800	0.031	1
H14A	0.4586	0.0777	-0.0103	0.036	1
H14B	0.5037	0.0182	-0.0404	0.036	1
H147	-0.0340	-0.0032	-0.3172	0.051	1

H148	-0.0250	0.0420	-0.3887	0.058	1
H150	0.2497	0.1247	-0.3269	0.043	1
H153	0.1231	0.0546	-0.5393	0.081	0.5
H155	-0.0019	0.2062	-0.4727	0.085	0.5
H157	0.1931	0.0160	-0.4187	0.102	1
H15A	0.0788	-0.0540	-0.4923	0.199	1
H15B	0.1751	-0.0743	-0.4994	0.199	1
H15C	0.1311	-0.0292	-0.5341	0.199	1
H15D	0.3297	0.0822	-0.4301	0.197	1
H15E	0.2939	0.0481	-0.4953	0.197	1
H15F	0.3207	0.0015	-0.4574	0.197	1
H160	0.0336	0.2016	-0.5507	0.095	0.5
H16A	0.1247	0.1307	-0.6113	0.116	0.5
H16B	0.1581	0.2047	-0.5653	0.116	0.5
H16C	0.0802	0.1931	-0.6202	0.116	0.5
H16D	-0.0797	0.0812	-0.5948	0.072	0.5
H16E	-0.0788	0.1412	-0.6228	0.072	0.5
H16F	-0.0909	0.1553	-0.5614	0.072	0.5
H163	0.0040	0.1741	-0.3521	0.103	1
H16G	-0.0657	0.2610	-0.3518	0.200	1
H16H	-0.0837	0.2182	-0.4153	0.200	1
H16I	-0.0053	0.2887	-0.3891	0.200	1
H16J	0.1716	0.2429	-0.3209	0.208	1
H16K	0.0996	0.2689	-0.2866	0.208	1
H16L	0.1273	0.3052	-0.3301	0.208	1
H166	0.2077	0.1167	-0.5188	0.082	0.5
H168	0.0814	0.2548	-0.4482	0.098	0.5
H169	0.1739	0.1877	-0.5575	0.123	0.5
H17A	0.0554	0.1662	-0.5893	0.185	0.5
H17B	0.0787	0.2424	-0.5941	0.185	0.5
H17C	0.0288	0.2281	-0.5479	0.185	0.5
H17X	0.2886	0.2625	-0.4916	0.248	0.5
H17Y	0.2488	0.3149	-0.5199	0.248	0.5
H17Z	0.2740	0.2482	-0.5564	0.248	0.5
H17D	0.2466	-0.1132	-0.1198	0.072	1
H17E	0.1398	-0.1533	-0.1297	0.072	1
H17F	0.1155	-0.0908	-0.0043	0.084	1
H17G	0.2190	-0.0419	0.0231	0.084	1
H182	0.0603	0.1500	-0.2103	0.070	1
H183	-0.0103	0.2279	-0.1607	0.077	1
H184	-0.0190	0.2276	-0.0716	0.086	1
H185	0.0375	0.1438	-0.0391	0.077	1
H175	0.265(3)	-0.107(7)	-0.032(5)	0.103	1
H117	-0.1819	0.1081	-0.1195	0.098	0.25
H118	-0.2302	0.1422	-0.1822	0.105	0.75
H144	0.5902	0.1497	0.0059	0.052	1
H30A	0.7086	0.0594	-0.3258	0.147	0.667
H30B	0.8129	0.0637	-0.2969	0.147	0.667
H40A	0.8363	0.3457	-0.1700	0.235	0.5
H40B	0.9436	0.3748	-0.1433	0.235	0.5
H50A	0.2822	0.1875	-0.4392	0.093	0.333
H50B	0.3874	0.2324	-0.4216	0.093	0.333

Table S6. Torsion angles [°] for cat112_0m_sq.

C7-C2-C3-C4	-1.6(14)
N1-C2-C3-C4	-176.4(9)
C2-C3-C4-C5	1.7(14)
C2-C3-C4-C16	178.6(9)
C3-C4-C5-C6	-0.9(17)
C16-C4-C5-C6	-177.8(11)
C4-C5-C6-C7	-0.1(19)
C5-C6-C7-C2	0.3(19)
C5-C6-C7-O8	176.6(11)
C3-C2-C7-C6	0.6(17)
N1-C2-C7-C6	176.5(11)
C3-C2-C7-O8	-176.4(9)
N1-C2-C7-O8	-0.5(11)
N1-C9-C10-C15	-174.9(10)
O8-C9-C10-C15	8.6(17)
N1-C9-C10-C11	2.6(13)
O8-C9-C10-C11	-173.9(10)
C15-C10-C11-C12	-0.8(15)
C9-C10-C11-C12	-178.4(9)
C15-C10-C11-Ir1	176.8(8)
C9-C10-C11-Ir1	-0.8(11)
C10-C11-C12-C13	2.6(15)
Ir1-C11-C12-C13	-174.6(8)
C11-C12-C13-C14	-3.1(17)
C12-C13-C14-C15	1.7(17)
C12-C13-C14-C18	177.8(11)
C13-C14-C15-C10	0.1(16)
C18-C14-C15-C10	-176.2(10)
C11-C10-C15-C14	-0.5(16)
C9-C10-C15-C14	176.7(10)
C3-C4-C16-O17	-7.6(13)
C5-C4-C16-O17	169.3(9)
C15-C14-C18-C19	-104.1(16)
C13-C14-C18-C19	79.7(18)
C15-C14-C18-C23	79.5(16)
C13-C14-C18-C23	-96.7(14)
C23-C18-C19-C20	-3(2)
C14-C18-C19-C20	-178.9(15)
C23-C18-C19-C24	-178.8(16)
C14-C18-C19-C24	5(3)
C18-C19-C20-C21	1(3)
C24-C19-C20-C21	177.3(18)
C19-C20-C21-C22	1(3)
C19-C20-C21-C27	175.0(16)
C20-C21-C22-C23	-1(2)
C27-C21-C22-C23	-175.1(13)
C21-C22-C23-C18	-0.4(19)
C21-C22-C23-C30	177.4(13)
C19-C18-C23-C22	2(2)
C14-C18-C23-C22	178.7(12)
C19-C18-C23-C30	-175.5(14)
C14-C18-C23-C30	0.9(19)
C20-C19-C24-C25	-66(2)
C18-C19-C24-C25	111(2)
C20-C19-C24-C26	53(3)
C18-C19-C24-C26	-131(2)
C20-C21-C27-C29	129(2)
C22-C21-C27-C29	-57(2)
C20-C21-C27-C28	-100(2)
C22-C21-C27-C28	74(2)
C22-C23-C30-C32	-46.6(18)
C18-C23-C30-C32	131.2(13)
C22-C23-C30-C31	76.5(15)
C18-C23-C30-C31	-105.8(14)
C39-C34-C35-C36	-0.5(18)
N33-C34-C35-C36	179.6(12)
C34-C35-C36-C37	1(2)
C34-C35-C36-C48	-179.5(15)
C35-C36-C37-C38	-1(2)
C48-C36-C37-C38	179.5(15)
C36-C37-C38-C39	0.6(18)
C35-C34-C39-C38	0.1(16)
N33-C34-C39-C38	-180.0(9)
C35-C34-C39-O40	179.7(10)
N33-C34-C39-O40	-0.3(10)
C37-C38-C39-C34	-0.1(16)
C37-C38-C39-O40	-179.7(10)
N33-C41-C42-C47	-174.8(8)
O40-C41-C42-C47	6.6(13)
N33-C41-C42-C43	2.1(11)
O40-C41-C42-C43	-176.5(7)
C47-C42-C43-C44	-1.8(11)
C41-C42-C43-C44	-178.8(7)
C47-C42-C43-Ir1	175.4(6)
C41-C42-C43-Ir1	-1.5(8)
C42-C43-C44-C45	2.3(11)
Ir1-C43-C44-C45	-174.4(6)
C43-C44-C45-C46	-0.9(13)
C44-C45-C46-C47	-1.2(12)
C44-C45-C46-C50	173.5(8)
C45-C46-C47-C42	1.8(11)
C50-C46-C47-C42	-172.8(7)
C43-C42-C47-C46	-0.2(12)
C41-C42-C47-C46	176.3(7)
C37-C36-C48-O50	11(4)
C35-C36-C48-O50	-169(3)
C37-C36-C48-O49	-158(3)
C35-C36-C48-O49	23(4)
C47-C46-C50-C51	-100.5(10)
C45-C46-C50-C51	85.0(10)
C47-C46-C50-C55	82.2(10)
C45-C46-C50-C55	-92.3(9)
C55-C50-C51-C52	3.6(13)
C46-C50-C51-C52	-173.7(8)
C55-C50-C51-C56	-173.4(9)
C46-C50-C51-C56	9.4(13)
C50-C51-C52-C53	-0.7(14)
C56-C51-C52-C53	176.2(9)
C51-C52-C53-C54	-2.2(13)
C51-C52-C53-C59	179.1(9)
C52-C53-C54-C55	2.3(12)
C59-C53-C54-C55	-178.9(8)
C53-C54-C55-C50	0.4(12)
C53-C54-C55-C62	-178.1(8)
C51-C50-C55-C54	-3.5(12)
C46-C50-C55-C54	173.9(7)

C51-C50-C55-C62	175.0(8)
C46-C50-C55-C62	-7.7(11)
C50-C51-C56-C57	-92.8(12)
C52-C51-C56-C57	90.3(13)
C50-C51-C56-C58	141.0(10)
C52-C51-C56-C58	-35.8(14)
C52-C53-C59-C61	66.6(12)
C54-C53-C59-C61	-112.1(10)
C52-C53-C59-C60	-59.6(12)
C54-C53-C59-C60	121.8(9)
C54-C55-C62-C64	-57.5(10)
C50-C55-C62-C64	124.0(8)
C54-C55-C62-C63	67.1(10)
C50-C55-C62-C63	-111.4(9)
C70-C66-C67-N68	9.0(10)
N65-C66-C67-N68	-174.8(10)
N65-C66-C70-O71	-0.9(11)
C67-C66-C70-O71	176.6(7)
N65-C66-C70-C69	-174.5(8)
C67-C66-C70-C69	3.0(12)
N68-C69-C70-C66	-13.4(11)
N68-C69-C70-O71	175.4(11)
N65-C72-C73-N74	4.3(13)
O71-C72-C73-N74	-172.3(9)
N65-C72-C73-C78	-173.7(9)
O71-C72-C73-C78	9.7(15)
N74-C75-C76-C77	0.1(18)
C75-C76-C77-C78	-1.4(18)
N74-C73-C78-C77	0.4(16)
C72-C73-C78-C77	178.2(10)
C76-C77-C78-C73	1.2(16)
O8-C9-N1-C2	1.6(11)
C10-C9-N1-C2	-175.3(9)
O8-C9-N1-Ir1	173.9(6)
C10-C9-N1-Ir1	-3.0(12)
C7-C2-N1-C9	-0.7(11)
C3-C2-N1-C9	174.6(10)
C7-C2-N1-Ir1	-169.3(8)
C3-C2-N1-Ir1	6.0(18)
O40-C41-N33-C34	-1.5(10)
C42-C41-N33-C34	179.7(7)
O40-C41-N33-Ir1	177.2(5)
C42-C41-N33-Ir1	-1.6(9)
C35-C34-N33-C41	-179.0(12)
C39-C34-N33-C41	1.1(10)
C35-C34-N33-Ir1	2.9(19)
C39-C34-N33-Ir1	-177.1(7)
O71-C72-N65-C66	1.2(10)
C73-C72-N65-C66	-175.8(8)
O71-C72-N65-Ir1	-179.3(6)
C73-C72-N65-Ir1	3.8(11)
C70-C66-N65-C72	-0.1(10)
C67-C66-N65-C72	-176.5(11)
C70-C66-N65-Ir1	-179.4(7)
C67-C66-N65-Ir1	4.2(18)
C66-C67-N68-C69	-17.5(9)
C70-C69-N68-C67	19.0(10)
C76-C75-N74-C73	1.3(16)
C76-C75-N74-Ir1	-166.8(9)
C78-C73-N74-C75	-1.6(16)
C72-C73-N74-C75	-179.6(9)
C78-C73-N74-Ir1	167.9(8)
C72-C73-N74-Ir1	-10.1(11)
N1-C9-O8-C7	-1.9(12)
C10-C9-O8-C7	174.8(10)
C6-C7-O8-C9	-175.3(12)
C2-C7-O8-C9	1.4(12)
N33-C41-O40-C39	1.3(9)
C42-C41-O40-C39	-180.0(8)
C34-C39-O40-C41	-0.5(10)
C38-C39-O40-C41	179.1(10)
N65-C72-O71-C70	-1.7(10)
C73-C72-O71-C70	175.1(9)
C66-C70-O71-C72	1.6(10)
C69-C70-O71-C72	172.9(12)
C107-C102-C103-C104	0.5(13)
N101-C102-C103-C104	-178.5(9)
C102-C103-C104-C105	-0.5(13)
C102-C103-C104-C116	177.8(8)
C103-C104-C105-C106	1.2(15)
C116-C104-C105-C106	-177.1(9)
C104-C105-C106-C107	-1.7(15)
C103-C102-C107-O108	-179.8(8)
N101-C102-C107-O108	-0.5(10)
C103-C102-C107-C106	-1.3(14)
N101-C102-C107-C106	178.0(8)
C105-C106-C107-O108	-179.9(9)
C105-C106-C107-C102	1.8(14)
N101-C109-C110-C115	176.9(8)
O108-C109-C110-C115	-4.9(14)
N101-C109-C110-C111	-0.8(11)
O108-C109-C110-C111	177.5(8)
C115-C110-C111-C112	0.8(12)
C109-C110-C111-C112	178.4(7)
C115-C110-C111-Ir2	-175.4(7)
C109-C110-C111-Ir2	2.3(9)
C110-C111-C112-C113	-1.0(12)
Ir2-C111-C112-C113	174.5(6)
C111-C112-C113-C114	-0.2(13)
C112-C113-C114-C115	1.6(13)
C112-C113-C114-C119	-173.2(8)
C113-C114-C115-C110	-1.8(13)
C119-C114-C115-C110	172.8(8)
C111-C110-C115-C114	0.7(13)
C109-C110-C115-C114	-176.6(8)
C105-C104-C116-O118	-121.7(10)
C103-C104-C116-O118	60.0(12)
C105-C104-C116-O117	121.6(17)
C103-C104-C116-O117	-56.7(18)
C115-C114-C119-C124	100.1(12)
C113-C114-C119-C124	-85.3(12)
C115-C114-C119-C120	-82.3(11)
C113-C114-C119-C120	92.3(11)
C124-C119-C120-C121	2.8(14)
C114-C119-C120-C121	-174.8(9)
C124-C119-C120-C131	-175.3(10)
C114-C119-C120-C131	7.1(13)
C119-C120-C121-C122	0.8(16)
C131-C120-C121-C122	178.9(10)
C120-C121-C122-C123	-3.7(18)

C120-C121-C122-C128	177.1(11)
C121-C122-C123-C124	3.1(19)
C128-C122-C123-C124	-177.6(12)
C120-C119-C124-C123	-3.2(16)
C114-C119-C124-C123	174.3(10)
C120-C119-C124-C125	174.9(11)
C114-C119-C124-C125	-7.6(16)
C122-C123-C124-C119	0.3(18)
C122-C123-C124-C125	-177.8(13)
C119-C124-C125-C126	101.5(16)
C123-C124-C125-C126	-80.5(17)
C119-C124-C125-C127	-131.6(15)
C123-C124-C125-C127	46(2)
C121-C122-C128-C129	-107.8(17)
C123-C122-C128-C129	73.0(17)
C121-C122-C128-C130	117.5(16)
C123-C122-C128-C130	-61.7(19)
C121-C120-C131-C133	56.2(13)
C119-C120-C131-C133	-125.7(10)
C121-C120-C131-C132	-68.3(12)
C119-C120-C131-C132	109.8(11)
C140-C135-C136-C137	-1.9(10)
N134-C135-C136-C137	178.6(7)
C135-C136-C137-C138	0.4(10)
C135-C136-C137-C143	179.7(7)
C136-C137-C138-C139	0.8(11)
C143-C137-C138-C139	-178.6(7)
C137-C138-C139-C140	-0.3(11)
C138-C139-C140-O141	-179.8(7)
C138-C139-C140-C135	-1.4(11)
C136-C135-C140-C139	2.6(11)
N134-C135-C140-C139	-177.9(7)
C136-C135-C140-O141	-178.7(6)
N134-C135-C140-O141	0.9(8)
C136-C137-C143-O144	-159.6(7)
C138-C137-C143-O144	19.8(10)
N134-C142-C145-C150	175.2(8)
O141-C142-C145-C150	-7.8(13)
N134-C142-C145-C146	-3.8(11)
O141-C142-C145-C146	173.1(7)
C150-C145-C146-C147	0.8(12)
C142-C145-C146-C147	179.8(7)
C150-C145-C146-Ir2	-176.3(7)
C142-C145-C146-Ir2	2.7(9)
C145-C146-C147-C148	-0.8(12)
Ir2-C146-C147-C148	175.8(7)
C146-C147-C148-C149	0.8(15)
C147-C148-C149-C150	-0.6(15)
C147-C148-C149-C151	-179.0(9)
C148-C149-C150-C145	0.5(13)
C151-C149-C150-C145	178.9(9)
C146-C145-C150-C149	-0.6(13)
C142-C145-C150-C149	-179.6(8)
C148-C149-C151-C152	-104.7(14)
C150-C149-C151-C152	77.0(15)
C148-C149-C151-C156	73.0(15)
C150-C149-C151-C156	-105.3(14)
C156-C151-C152-C153	-25(3)
C149-C151-C152-C153	153.0(18)
C156-C151-C152-C157	177.4(15)
C149-C151-C152-C157	-5(2)
C156-C151-C152-C166	19(2)
C149-C151-C152-C166	-163.1(14)
C151-C152-C153-C154	19(3)
C157-C152-C153-C154	179.3(18)
C166-C152-C153-C154	-72(3)
C152-C153-C154-C155	-13(3)
C152-C153-C154-C160	175.4(18)
C153-C154-C155-C156	13(4)
C160-C154-C155-C156	-176(2)
C154-C155-C156-C151	-16(3)
C154-C155-C156-C163	-176(2)
C154-C155-C156-C168	87(4)
C152-C151-C156-C155	22(2)
C149-C151-C156-C155	-155.7(16)
C152-C151-C156-C163	-178.5(15)
C149-C151-C156-C163	4(2)
C152-C151-C156-C168	-20(2)
C149-C151-C156-C168	162.8(17)
C151-C152-C157-C158	116.6(18)
C153-C152-C157-C158	-43(2)
C166-C152-C157-C158	-86(2)
C151-C152-C157-C159	-120.9(17)
C153-C152-C157-C159	80(2)
C166-C152-C157-C159	36.5(19)
C155-C154-C160-C161	125(3)
C153-C154-C160-C161	-63(3)
C155-C154-C160-C162	-65(3)
C153-C154-C160-C162	107(3)
C155-C156-C163-C164	1(3)
C151-C156-C163-C164	-157.4(16)
C168-C156-C163-C164	44(3)
C155-C156-C163-C165	-120(2)
C151-C156-C163-C165	81.8(17)
C168-C156-C163-C165	-77(2)
C151-C152-C166-C167	-15(3)
C153-C152-C166-C167	95(3)
C157-C152-C166-C167	-174(2)
C152-C166-C167-C168	10(4)
C152-C166-C167-C169	-178(2)
C166-C167-C168-C156	-10(5)
C169-C167-C168-C156	178(2)
C155-C156-C168-C167	-81(4)
C151-C156-C168-C167	14(4)
C163-C156-C168-C167	174(3)
C168-C167-C169-C170	-78(4)
C166-C167-C169-C170	110(3)
C168-C167-C169-C171	101(4)
C166-C167-C169-C171	-71(5)
C177-C173-C174-N175	-8.7(11)
N172-C173-C174-N175	179.3(12)
N172-C173-C177-O178	1.5(11)
C174-C173-C177-O178	-173.3(8)
N172-C173-C177-C176	174.6(8)
C174-C173-C177-C176	-0.2(12)
N175-C176-C177-C173	8.9(12)
N175-C176-C177-O178	179.3(11)
N172-C179-C180-N181	-6.6(12)
O178-C179-C180-N181	174.7(8)
N172-C179-C180-C185	174.4(9)

O178-C179-C180-C185	-4.3(15)
N181-C182-C183-C184	4.7(17)
C182-C183-C184-C185	-1.6(18)
N181-C180-C185-C184	2.1(16)
C179-C180-C185-C184	-178.9(10)
C183-C184-C185-C180	-1.7(17)
O108-C109-N101-C102	1.4(10)
C110-C109-N101-C102	179.8(7)
O108-C109-N101-Ir2	-179.5(5)
C110-C109-N101-Ir2	-1.1(10)
C103-C102-N101-C109	178.7(10)
C107-C102-N101-C109	-0.5(9)
C103-C102-N101-Ir2	0.0(16)
C107-C102-N101-Ir2	-179.2(7)
O141-C142-N134-C135	0.0(9)
C145-C142-N134-C135	177.3(7)
O141-C142-N134-Ir2	-174.2(5)
C145-C142-N134-Ir2	3.0(9)
C136-C135-N134-C142	178.9(8)
C140-C135-N134-C142	-0.6(8)
C136-C135-N134-Ir2	-9.4(14)
C140-C135-N134-Ir2	171.1(6)
O178-C179-N172-C173	-1.7(10)
C180-C179-N172-C173	179.4(8)
O178-C179-N172-Ir2	178.9(5)
C180-C179-N172-Ir2	0.0(10)
C177-C173-N172-C179	0.1(10)
C174-C173-N172-C179	172.3(12)
C177-C173-N172-Ir2	179.2(7)
C174-C173-N172-Ir2	-9(2)
C177-C176-N175-C174	-14.1(12)
C173-C174-N175-C176	14.3(12)
C185-C180-N181-C182	0.8(13)
C179-C180-N181-C182	-178.2(8)
C185-C180-N181-Ir2	-171.3(7)
C179-C180-N181-Ir2	9.6(9)
C183-C182-N181-C180	-4.3(15)
C183-C182-N181-Ir2	167.0(8)
N101-C109-O108-C107	-1.7(9)
C110-C109-O108-C107	180.0(8)
C102-C107-O108-C109	1.3(9)
C106-C107-O108-C109	-177.2(9)
N134-C142-O141-C140	0.5(8)
C145-C142-O141-C140	-176.5(7)
C139-C140-O141-C142	177.8(8)
C135-C140-O141-C142	-0.9(8)
C173-C177-O178-C179	-2.4(10)
C176-C177-O178-C179	-173.1(12)
N172-C179-O178-C177	2.6(9)
C180-C179-O178-C177	-178.6(8

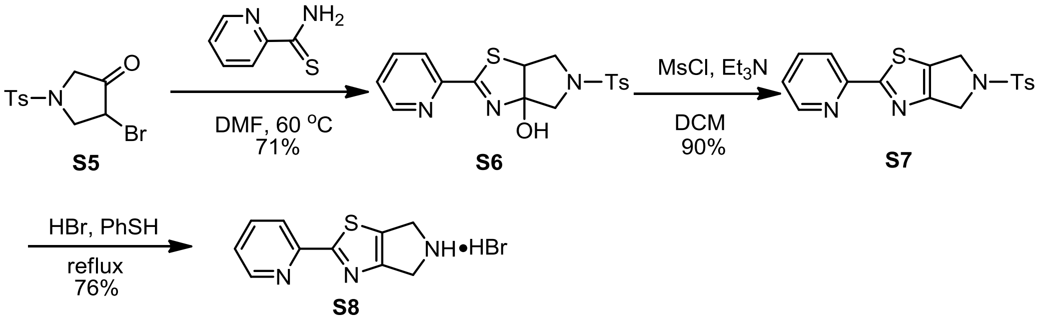
Table S7. Hydrogen bonds for cat112_0m_sq [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N68-H68...O17	0.781(10)	2.64(6)	3.327(10)	148(11)
N68-H68...I17	0.781(10)	3.29(9)	3.859(12)	132(10)
O17-H17...I17	0.84	2.96	3.467(11)	121.0
O17-H17...O400	0.84	1.96	2.778(14)	164.4
N175-H175...O144#1	0.783(10)	2.18(5)	2.939(11)	162(15)
O117-H117...I17#2	0.84	3.33	3.59(3)	101.3
O117-H117...I18#2	0.84	3.12	3.38(3)	101.1
O118-H118...I18#2	0.84	2.66	3.382(11)	145.1
O144-H144...N68	0.84	1.96	2.780(9)	165.2

Symmetry transformations used to generate equivalent atoms:

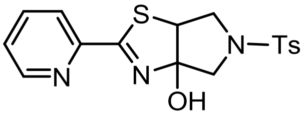
#1 -x+1,-y,-z #2 x-1,y,z

8. Investigation of an Analogous Thiazole Iridium Catalyst



Scheme S8. Synthesis of the thiazole ligand **S8**.

Compound S6



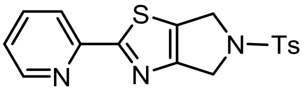
The compound **S5**[S11] (0.500 g, 1.57 mmol) and pyridine-2-carbothioamide (0.22 g, 1.57 mmol) were dissolved in DMF (5.0 mL). The mixture was stirred at 60 °C for 6 h, then cooled to room temperature. The solvent was concentrated under a reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: hexane/EtOAc = 2:1) to give compound **S6** (0.421g, 71%) as a white solid.

^{1}H NMR (300 MHz, DMSO) δ 8.70–8.64 (m, 1H), 8.03 (dt, J = 7.9, 1.3 Hz, 1H), 8.00-7.93 (m, 1H), 7.66 (d, J = 8.1 Hz, 2H), 7.63–7.57 (m, 1H), 7.41 (d, J = 7.8 Hz, 2H), 7.02 (s, 1H), 3.93 (dd, J = 7.4, 3.9 Hz, 1H), 3.55 (dd, J = 10.8, 7.5 Hz, 1H), 3.49 (d, J = 10.3 Hz, 1H), 3.22 (dd, J = 10.8, 3.9 Hz, 1H), 3.14 (d, J = 10.1 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (75 MHz, DMSO) δ 169.2, 149.4, 143.9, 137.3, 130.9, 129.8, 127.8, 126.6, 121.7, 117.0, 116.9, 59.5, 56.3, 53.9, 21.0.

IR (film) ν_{max}: 3673, 3406, 3098, 3057, 2924, 2874, 1660 1516, 1498,1465,1337, 1298, 1156, 1071, 1031, 1002, 798, 711, 623, 591, 540, 504 cm^{-1}.

2-(Pyridin-2-yl)-5-tosyl-5,6-dihydro-4*H*-pyrrolo[3,4-*d*]thiazole (S7)



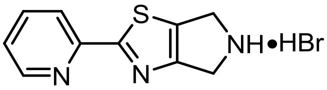
To a solution of **S6** (0.420 g, 1.12 mmol) in CH_2Cl_2 (4.0 mL) at 0 °C was added MsCl (0.17 mL, 2.24 mmol), and then Et_3N (1.30 mL, 9.30 mmol) was gradually added at the same temperature. After being stirred at room temperature for 2 h, water (1.0 mL) was added, and the mixture was extracted with CH_2Cl_2 (4 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 1:1) to afford compound **S7** (0.360 g, 90%) as a white solid.

^{1}H NMR (300 MHz, DMSO-d$_6$) δ 8.59 (d, J = 4.5 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.97–7.88 (m, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.50–7.45 (m, 1H), 7.43 (d, J = 8.1 Hz, 2H), 4.70–4.62 (m, 2H), 4.59–4.51 (m, 2H), 2.36 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d$_6$) δ 173.8, 155.4, 150.1, 150.0, 144.0, 137.8, 133.2, 130.4, 130.1, 127.4, 125.4, 118.9, 50.2, 49.5, 20.9.

IR (film) ν_{max}: 3055, 2945, 2863, 1584, 1533, 1336, 1153, 1095, 1035, 855, 713, 672, 599, 538 cm^{-1}.

2-(Pyridin-2-yl)-5,6-dihydro-4*H*-pyrrolo[3,4-*d*]thiazole hydrobromide (S8)



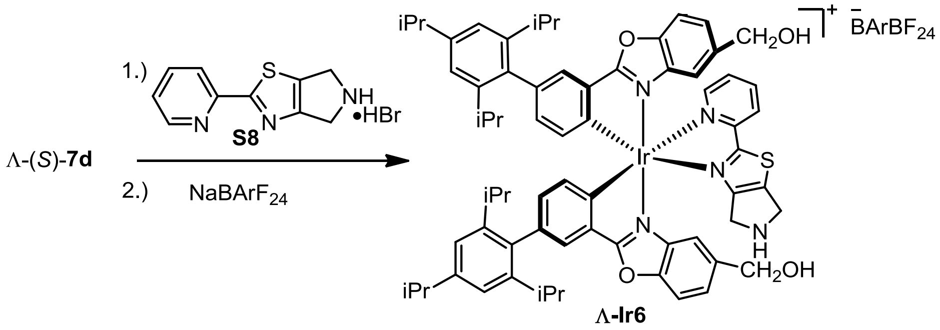
To a solution of **S7** (0.300 g, 0.84 mmol) in HBr (48%, 3mL) was added thiophenol (0.26 mL, 2.52 mmol). After being stirred at 100 °C for 1 h, the mixture was cooled to room temperature and concentrated under a reduced pressure. To the residue, 1 mL of water and 2 mL of ether were added and the mixture was stirred for 0.5 h. The organic layer was separated, and the water layer was concentrated under a reduced pressure. MeCN (10 mL) was added, and the formed solid was filtered, and washed with MeCN (5 mL × 2) to give **S8** (0.180 g, 76%) as a yellow solid.

^{1}H NMR (300 MHz, DMSO-d$_6$) δ 10.00 (br s, 1H), 8.64 (d, J = 4.8 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.93 (td, J= 7.6, 1.7 Hz, 1H), 7.57–7.48 (m, 1H), 7.35 (br s, 1H), 4.69–4.57 (m, 2H), 4.53–4.42 (m, 2H).

^{13}C NMR (75 MHz, DMSO-d$_6$) δ 175.3, 155.3, 150.0, 149.8, 138.0, 130.4, 125.7, 119.1, 47.3, 45.9.

IR (film) ν_{max}: 3374, 3069, 2934, 2706, 1606, 1516, 1449, 1363, 1296, 1155, 979, 885, 780, 604, 542 cm^{-1}.

HRMS (ESI, *m*/*z*) calcd for $C_{10}H_{10}N_3S_1$ $[M+H]^+$: 204.0590, found: 204.0592.



Scheme S9. Synthesis of the analogous thiazole iridium catalyst **Λ-Ir6**.

Preparation of an analogous thiazole iridium catalyst Λ-Ir6. A suspension of the iridium auxiliary complex Λ-(*S*)-**7d** (127.3 mg, 0.10 mmol), ligand **S8** (56.6 mg, 0.20 mmol), and NH_4PF_6 (815.0 mg, 0.50 mmol) in acetonitrile (10 mL) was stirred at 60 °C for 12 h under argon in the dark. Then, the reaction mixture was concentrated to dryness and subjected to a flash silica gel chromatography (eluent: MeOH/CH_2Cl_2 = 1:30) to give the pure yellow solid as a hexafluorophosphate salt (103.0 mg, 0.074 mmol, yield: 74%). The product was directly suspended in CH_2Cl_2. Sodium tetrakis[(3,5-di-trifluoromethyl)phenyl]borate ($NaBArF_{24}$) (62.3 mg, 0.070 mmol) was added in one portion and the mixture was stirred at room temperature for 10 min. After removal of the CH_2Cl_2 in vacuo, the residue was taken up in Et_2O (about 2.0 mL) twice and centrifuged. The combined organic layers were dried and concentrated in vacuo to give the pure product Λ-**Ir6** (140.6 mg, yield: 90%) as an organge solid.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.37 (d, *J* = 5.4 Hz, 1H), 8.17 (m, 2H), 7.76 (m, 10H), 7.62 (dd, *J* = 8.5, 4.0 Hz, 2H), 7.58 (dd, *J* = 5.6, 2.1 Hz, 1H), 7.54 (s, 4H), 7.33 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.27 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.15–7.04 (m, 4H), 6.92 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.86 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.20 (d, *J* = 0.8 Hz, 1H), 5.88 (d, *J* = 0.8 Hz, 1H), 4.73 (d, *J* = 14.0 Hz, 1H), 4.65 (d, *J* = 14.0 Hz, 1H), 4.59 (d, *J* = 13.7 Hz, 1H), 4.54 (d, *J* = 13.7 Hz, 1H), 4.45 (dt, *J* = 15.5, 2.8 Hz, 1H), 4.29 (dt, *J* = 15.6, 2.6 Hz, 1H), 3.75 (dt, *J* = 14.9, 2.8 Hz, 1H), 3.12 (dt, *J* = 14.7, 2.9 Hz, 1H), 2.93 (hept, *J* = 6.5 Hz, 1H),, 2.84–2.68 (m, 2H), 2.62–2.46 (m, 2H), 2.25 (br s, 3H), 1.31–1.26 (m, 12H), 1.20–1.12 (m, 9H), 1.08 (d, *J* = 6.9 Hz, 3H), 1.07 (d,

J = 6.9 Hz, 3H), 1.03 (d, J = 6.9 Hz, 3H), 0.99 (d, J = 6.9 Hz, 3H), 0.95 (d, J = 6.9 Hz, 3H).

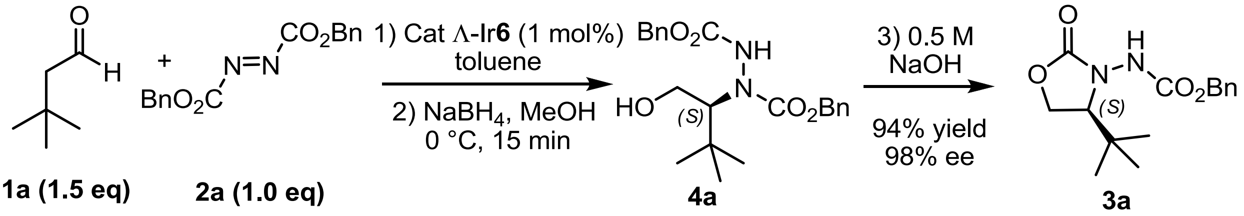
^{13}C NMR (75 MHz, CD_2Cl_2) δ 178.2, 178.1, 173.0, 164.6, 163.1, 162.5, 161.8, 161.2, 153.6, 153.0, 149.8, 149.7, 149.1, 149.0, 147.3, 147.2, 146.9, 146.8, 145.3, 142.7, 141.6, 141.3, 140.8, 140.2, 138.1, 138.0, 136.4, 136.4, 135.7, 135.26, 135.24, 135.1, 133.6, 133.1, 130.4, 129.7, 129.58, 129.54, 129.50, 129.4, 129.3, 129.16, 129.12, 129.08, 129.04, 128.29, 128.26, 128.0, 126.8, 124.7, 124.3, 123.5, 123.2, 121.1, 121.0, 120.8, 118.0, 117.96, 117.91, 117.86, 117.80, 112.5, 112.3, 111.6, 64.2, 64.0, 54.2, 53.8, 53.4, 48.7, 47.7, 34.8, 31.0, 30.9, 30.8, 30.7, 24.4, 24.3, 24.2.

IR (film) ν_{max}: 3361, 3042, 2960, 2871, 1604, 1516, 1449, 1354, 1274, 1122, 1039, 885, 780, 673, 600 cm^{-1}.

HRMS (ESI, *m/z*) calcd for $C_{68}H_{73}IrN_5O_4S_1$ $[M-BArF_{24}]^+$: 1248.5020, found: 1248.5012.

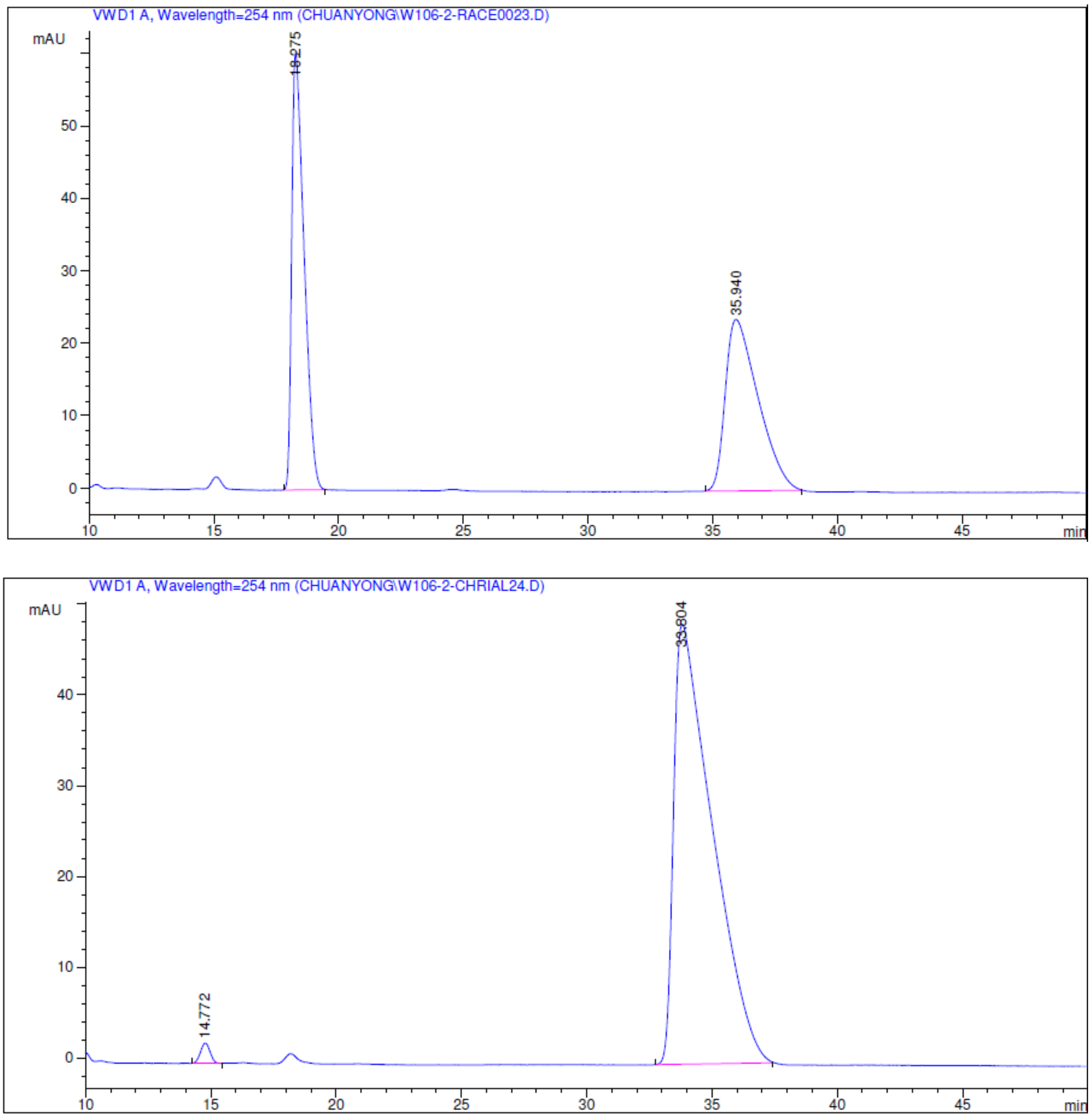
CD (MeOH): λ, nm (Δε, M^{-1}cm^{-1}) 416 (–11), 362 (+42), 339 (+46), 272 (–23), 241 (–26).

Iridium-Catalyzed Model Reaction with Catalyst Λ-Ir6.



Scheme S10. The aymmetric α-amination of aldehydes **1a** with **Λ-Ir6**.

Azodicarboxylate **2a** (60.0 mg, 0.20 mmol) and Λ-**Ir6** (1 mol%) were mixed in a brown glass vial in anhydrous toluene (200.0 μL, 1.0 M), followed by the addition of 3,3-dimethylbutyraldehyde **1a** (37.6 μL, 0.30 mmol) at 0 °C. While being stirred at room temperature under argon atmosphere for 12 h, the addition product precipitated. MeOH (200.0 μL) was added followed by a careful addition of $NaBH_4$ (10.0 mg, 0.26 mmol) at 0 °C. After 15 min, NaOH (0.5 M, 0.52 mL) was added and after an additional 2 h, the mixtures were diluted with water. The aqueous phase was extracted with EtOAc (4 × 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc:hexane = 1:4→1:1) to provide **3a** (54.8 mg, yield: 94%) as a white solid. Enantiomeric excess established by HPLC analysis using a Daicel Chiralpak IC column, ee = 98% (HPLC: IC, 254 nm, 40 °C, hexane/ isopropanol = 70/ 30, flow rate 0.5 mL/ min, t_r(minor)= 14.8 min, t_r(major) = 33.8 min); $[\alpha]_D^{20}$ –10.3 (*c* 1.0, $CHCl_3$).



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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s    [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1  14.772 BB    0.3544   58.99294    2.23634   1.1222
   2  33.804 BB    1.4041 5198.03662   48.46875  98.8778
```

Figure S36. HPLC traces of *rac*-**3a** and (*S*)-**3a** (Λ-**Ir6** catalyzed reaction). Area integration = 98.8:1.1 (98% ee, Daicel Chiralpak IC, hexane/isopropanol = 70:30, flow rate = 0.5 mL/min).

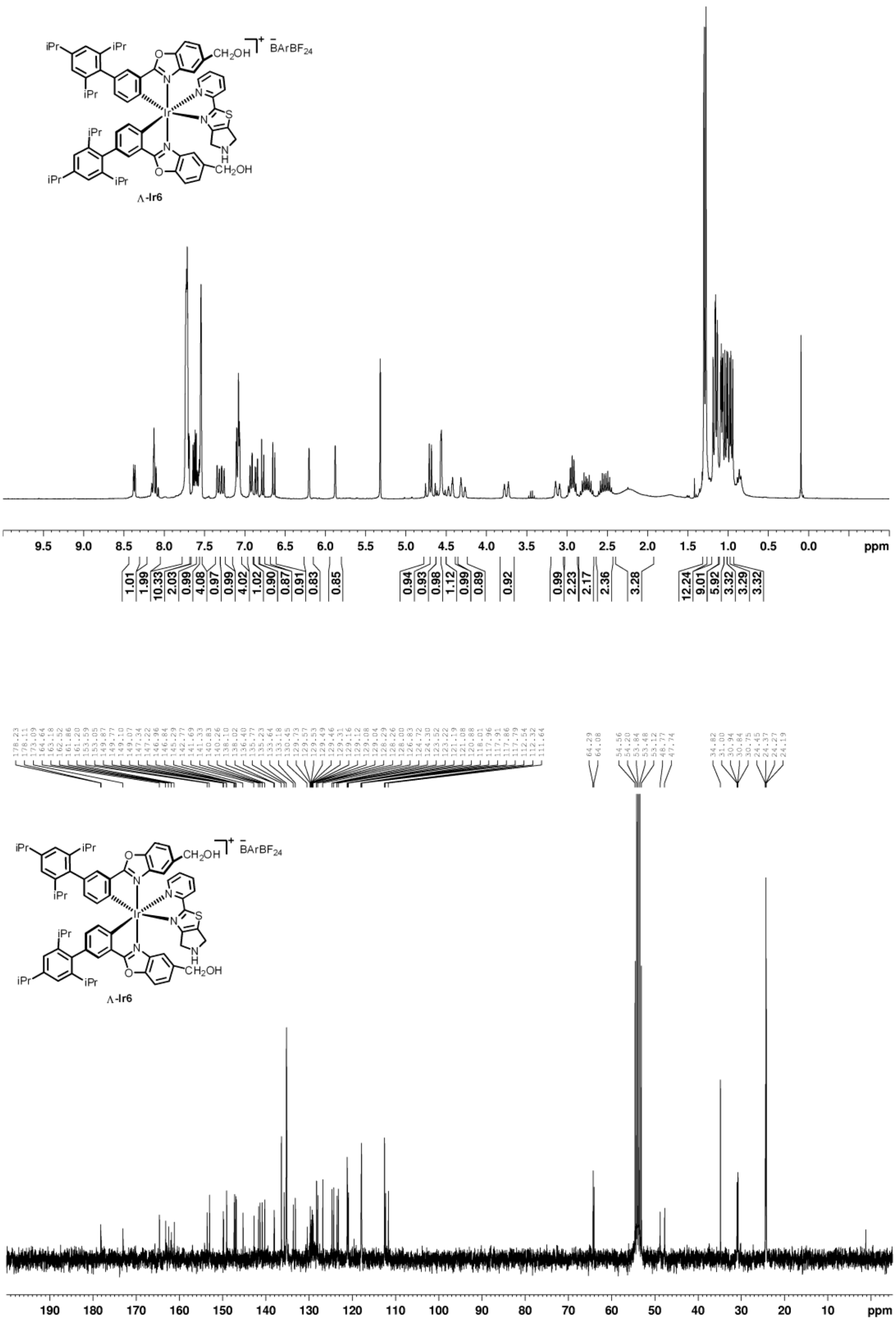

Figure S37. ^{1}H-NMR and ^{13}C-NMR spectrum of Λ-**Ir6**.

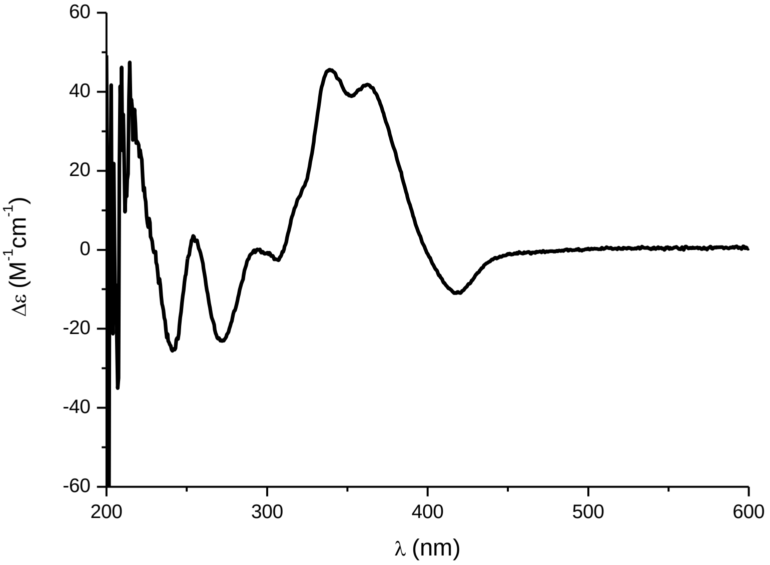

Figure S38. CD spectrum of catalyst Λ-**Ir6** recorded in CH_3OH (0.2 mM).

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