Supporting Information

Asymmetric Lewis Acid Catalysis Directed by Octahedral Rhodium Centrochirality

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1. General Information

All reactions were carried out under an atmosphere of nitrogen or argon with magnetic stirring. Catalysis reactions were performed using standard Schlenk glassware techniques (Michael reactions) or in brown glass vials (enolate chemistry). Solvents were distilled under nitrogen from calcium hydride (CH₃CN, CH₂Cl₂), sodium/benzophenone (THF), or magnesium turnings/iodine (MeOH). ¹H NMR and proton decoupled ¹³C NMR spectra were recorded on Bruker Avance 300 (300 MHz), Bruker AM (400 MHz) or Bruker AM (500 MHz) spectrometers at ambient temperature. NMR standards were used as follows: ¹H NMR spectroscopy: $\delta = 7.26$ ppm (CDCl₃), $\delta = 5.32$ ppm (CD₂Cl₂). ¹³C{¹H} NMR spectroscopy: $\delta = 77.1$ ppm (CDCl₃), $\delta = 53.8$ ppm (CD₂Cl₂). IR spectra were recorded on a Bruker Alpha FT-IR spectrophotometer or on a Nicolet Avatar 330 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 3 scans). High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0 TFT-MS instrument using ESI technique. Chiral HPLC chromatography was performed with an Agilent 1200 HPLC system. Optical rotations were measured with a Perkin-Elmer 241 or 341 polarimeter at concentrations of 1.0 g/100 mL. Substrates 4 and 4', 1 tert-butyl β -ketoesters, 2 and complexes Λ - and Δ -Ir³ were synthesized according to reported procedures. All other reagents were commercially available and used without further purification.

2. Synthesis of Rhodium Catalysts Λ -Rh and Δ -Rh

5-tert-Butyl-2-phenylbenzo[d]oxazole (1)

The compound was synthesized following a published procedure with slight modifications.⁴ A solution of 2-amino-4-*tert*-butylphenol (0.825 g, 5.0 mmol) and benzaldehyde (0.50 mL, 5.0 mmol) in *m*-xylene (16.0 mL) was stirred at 120 °C for 30 min. 4-Methoxy-TEMPO (46.5 mg, 5 mol%) was added to the mixture and the reaction was stirred at this temperature for further 8 h under an oxygen atmosphere. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/*n*-hexane = 1:20) to obtain the product **1** (1.152 g, 4.6 mmol, yield: 92%) as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 8.29-8.22 (m, 2H), 7.81 (d, *J* = 1.8 Hz, 1H), 7.56-7.48 (m, 4H), 7.42 (dd, *J* = 8.6, 1.9 Hz, 1H), 1.40 (s, 9H).

All spectroscopic data are in agreement with the literature.⁵

Precursor Rhodium Complex rac-2



Compound *rac*-**2** was synthesized according to a route reported by Mesmaeker for rhodium(III) μ -chloro-bridged dimers with related cyclometalated ligands.⁶ Accordingly, 5-*tert*-butyl-2-phenylbenzo[*d*]oxazole **1** (1.030 g, 4.1 mmol) was added to RhCl₃•3H₂O (418.5 mg, 2.0 mmol) in a mixture of 2-ethoxyethanol and water (3:1, 92.0 mL). The reaction mixture was heated at 120 °C for 24 h under an atmosphere of nitrogen. The resulting precipitate was collected by centrifugation, washed with methanol and dried to obtain the product *rac*-**2** (792.4 mg, 0.62 mmol, yield: 62%) as a pale yellow solid.

¹H NMR (300 MHz, CD_2Cl_2) δ 8.38 (t, J = 1.2 Hz, 4H), 7.58 (dd, J = 7.6, 1.3 Hz, 4H), 7.31-7.20 (m, 8H), 6.97 (td, J = 7.4, 0.9 Hz, 4H), 6.77 (td, J = 7.6, 1.5 Hz, 4H), 6.12 (d, J = 7.9 Hz, 4H), 1.22 (s, 36H).

¹³C NMR (75 MHz, CD₂Cl₂) δ 170.4 (4C), 164.8 (4C), 164.4 (4C), 149.0 (4C), 148.0 (4C), 139.6 (4C), 133.6 (4C), 131.4 (4C), 125.5 (4C), 124.1 (4C), 123.1 (4C), 115.8 (4C), 110.5 (4C), 35.4 (4C), 31.8 (12C).

IR (film): v (cm⁻¹) 3055, 2957, 2870, 1589, 1526, 1441, 1373, 1271, 1196, 1120, 1075, 1027, 929, 892, 808, 727, 702, 647, 448.

HRMS (ESI, m/z) calcd for C₆₈H₆₄Rh₂N₄O₄Cl [M–Cl]⁺: 1241.2721, found: 1241.2709.

Rhodium Auxiliary Complexes Λ -(*S*)-3 and Δ -(*R*)-3



The rhodium auxiliary complexes Λ -(*S*)-**3** and Δ -(*R*)-**3** were synthesized according to a reported method⁷ with some modifications. To a solution of NaOMe (16.2 mg, 0.30 mmol) in methanol (16.0 mL), L-proline (34.5 mg, 0.30 mmol) or D-proline (34.5 mg, 0.30 mmol) was added in one portion. The mixture was stirred for 10 min, to which a suspension of rhodium dimer (201.3 mg, 0.15 mmol) was added. The mixture was stirred and heated at 50 °C for 12 h. After the mixture cooled to room temperature, CH₂Cl₂ (16.0 mL) was added. The reaction mixture was stirred for a further 12 h to give a clear, yellow solution. The solvent was removed in vacuo and the mixture of two diastereoisomers was washed with dichloromethane / diethyl ether (1:6, v/v) until the filtrate was almost colorless. The residual insoluble solid was dried and collected as Λ -(*S*)-**3** (77.4 mg, 36%) or Δ -(*R*)-**3** (86.1 mg, 40%). The absolute configurations of the obtained Λ -(*S*)/ Δ -(*R*) configured rhodium(III) complexes were assigned by an X-ray crystal structure of Δ -(*R*)-**3**. CD spectroscopy confirmed that the complexes are enantiomers.

¹H NMR (300 MHz, CD_2Cl_2) δ 8.17 (d, J = 1.8 Hz, 1H), 7.84-7.79 (m, 2H), 7.73 (dd, J = 15.2, 8.8 Hz, 2H), 7.63 (td, J = 9.0, 1.8 Hz, 2H), 7.36 (d, J = 1.6 Hz, 1H), 7.12-7.02 (m, 2H), 6.95 (td, J = 7.5, 1.5 Hz, 2H), 6.76 (d, J = 7.7 Hz, 1H), 6.49 (d, J = 7.7 Hz, 1H), 4.34-4.17 (m, 2H), 2.80-2.67 (m, 1H), 2.30-2.13 (m, 2H), 2.07-1.94 (m, 1H), 1.68-1.53 (m, 2H), 1.45 (d, J = 7.6 Hz, 18H).

¹³C NMR (75 MHz, CD₂Cl₂) δ 180.5, 172.7, 172.6, 171.5, 171.4, 167.4, 167.0, 166.1, 165.7, 151.4, 150.6, 149.09, 149.06, 138.9, 138.3, 135.4, 134.4, 131.7, 131.3, 131.2, 131.0, 126.3, 126.0, 124.3, 124.2, 123.5, 123.1, 115.7, 112.2, 111.5, 111.1, 64.3, 49.7, 35.8, 35.6, 32.0, 31.9, 30.4, 27.3. IR (film): v (cm⁻¹) 3146, 3056, 2958, 1591, 1524, 1445, 1373, 1270, 1191, 1122, 1077, 1033, 928, 814, 773, 648, 550, 449.

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\Lambda-(S)-3:
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HRMS (ESI, *m/z*) calcd for C₃₉H₄₁RhN₃O₄ [M+H]⁺: 718.2147, found: 718.2133.

CD (MeOH): λ, nm (Δε, M⁻¹cm⁻¹) 394 (-28), 353 (+41), 295 (-34), 253 (+23), 233 (-6), 216 (+53), 203 (-80).

 Δ -(*R*)-**3**:

HRMS (ESI, *m*/*z*) calcd for C₃₉H₄₀RhN₃O₄Na [M+Na]⁺: 740.1966, found: 740.1930.

CD (MeOH): λ, nm (Δε, M⁻¹cm⁻¹) 394 (+15), 353 (-18), 295 (+22), 253 (-9), 233 (+6), 216 (-24), 203 (+45).

Synthesis of Non-Racemic Rhodium Catalysts



A suspension of the rhodium auxiliary complex Λ -(*S*)-**3** (71.7 mg, 0.10 mmol) or Δ -(*R*)-**3** (71.7 mg, 0.10 mmol) and NH₄PF₆ (163.0 mg, 1.00 mmol) in acetonitrile (20.0 mL) was heated at 50 °C for 12 h under nitrogen in the dark. The reaction mixture was concentrated to dryness and subjected to flash silica gel chromatography (100% CH₂Cl₂ to CH₂Cl₂/CH₃CN = 15:1) to give the enantiopure catalyst Λ -**Rh** (72.2 mg, 0.087 mmol, 87%) or Δ -**Rh** (74.7 mg, 0.090 mmol, 90%) as a pale yellow solid. The absolute configurations of the obtained Λ - and Δ -configured rhodium(III) complexes

were verified by CD spectroscopy and confirmed by an X-ray crystal structure of Δ -**Rh**. The enantiomeric purity was verified by HPLC analysis with a chiral stationary phase.

¹H NMR (300 MHz, CD₂Cl₂) δ 7.88 (d, *J* = 1.6 Hz, 2H), 7.80-7.74 (m, 6H), 7.09 (td, *J* = 7.5, 0.9 Hz, 2H), 6.94 (td, *J* = 7.6, 1.5 Hz, 2H), 6.40 (d, *J* = 7.8 Hz, 2H), 2.31 (s, 6H), 1.46 (s, 18H).

¹³C NMR (75 MHz, CD₂Cl₂) *δ* 171.5, 160.2, 159.8, 151.2, 148.9, 138.2, 133.5, 132.4, 130.6, 126.3, 125.3, 124.6, 122.0, 113.4, 112.0, 35.7, 31.9, 3.7.

IR (film): v (cm⁻¹) 2957, 1593, 1528, 1446, 1381, 1274, 1193, 1126, 1081, 1033, 931, 835, 730, 649, 555, 449.

Λ -**Rh**:

HRMS (ESI, *m*/*z*) calcd for C₃₈H₃₈RhN₄O₂ [M–PF₆]⁺: 685.2044, found: 685.2036.

CD (MeOH): λ , nm ($\Delta\epsilon$, M⁻¹cm⁻¹) 390 (-48), 350 (+104), 295 (-92), 242 (+56), 228 (+5), 218 (+24), 204 (-46).

∆-**Rh**:

HRMS (ESI, *m/z*) calcd for C₃₈H₃₈RhN₄O₂ [M–PF₆]⁺: 685.2044, found: 685.2026.

CD (MeOH): λ , nm ($\Delta\epsilon$, M⁻¹cm⁻¹) 390 (+51), 350 (-104), 295 (+94), 242 (-58), 228 (-20), 218 (-34), 204 (+57).

3. Catalysis Reactions

3.1. Asymmetric Michael Reactions

General Procedure (Reactions of Table 1). To a solution of catalyst Δ -Ir or Δ -Rh (1 mol%) in distilled, anhydrous THF (entries 1 and 4: 0.20 mL, 1.0 M; entries 2, 3, 5 and 6: 0.40 mL, 0.5 M) was added the 2-acyl imidazole 4 or 4' (0.20 mmol) in a Schlenk tube. After being stirred at room temperature for 20 min, the corresponding nucleophile was added at room temperature or 5 °C. The reaction was stirred at the indicated temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/*n*-hexane = 1:2 to 2:1) to afford the products **5a-f**. The dr values were determined by ¹H NMR analysis of the crude products, and the ee values were determined by chiral HPLC chromatography using a Chiralpak IC or AD-H column.

(R)-3-(1H-Indol-3-yl)-1-(1-methyl-1H-imidazol-2-yl)butan-1-one (5a)



Starting from **4** (30.2 mg, 0.20 mmol) and 1*H*-indole (58.6 mg, 0.50 mmol) according to the general procedure to give **5a** as a white solid (catalyzed by Δ -**Ir**: 51.9 mg, yield: 97%, ee: 96%; catalyzed by Δ -**Rh**: 50.2 mg, yield: 94%, ee: 95%). Enantiomeric excess established by HPLC analysis using a Chiralpak IC column (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 85:15, flow rate 0.5 mL/min, 40 °C, t_r (major) = 22.4 min, t_r (minor) = 25.9 min); $[\alpha]_D^{20} = +13.8^\circ$ (*c* 0.5, CH₂Cl₂) for 95% ee of **5a** (Lit.³ $[\alpha]_D^{20} = -14.5^\circ$ (*c* 2.7, CH₂Cl₂) for 96% ee of product with *S*-configuration).

¹H NMR (300 MHz, CDCl₃) δ 8.41 (br s, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.34-7.28 (m, 1H), 7.22-7.05 (m, 3H), 7.01-6.95 (m, 2H), 3.93 (s, 3H), 3.91-3.78 (m, 1H), 3.66-3.34 (m, 2H), 1.40 (d, J = 6.9 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) *δ* 192.4, 143.4, 136.5, 128.9, 127.0, 126.7, 121.9, 121.5, 120.3, 119.3, 119.1, 111.2, 46.8, 36.2, 27.2, 21.8.

All spectroscopic data were in agreement with the literature.¹

(*R*)-2-(4-(1-Methyl-1*H*-imidazol-2-yl)-4-oxobutan-2-yl)malononitrile (5b)



Starting from **4** (30.2 mg, 0.20 mmol) and malononitrile (15.8 mg, 0.24 mmol) according to the general procedure to give **5b** as a colorless oil (catalyzed by Δ -**Ir**: 41.5 mg, yield: 96%, ee: 89%; catalyzed by Δ -**Rh**: 41.5 mg, yield: 96%, ee: 92%). Enantiomeric excess established by HPLC analysis using a Chiralpak AD-H column (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 25 °C, t_r (major) = 22.8 min, t_r (minor) = 24.1 min); $[\alpha]_D^{20} = -33.2^\circ$ (*c* 0.4, CH₂Cl₂) for 92% ee of **5b**.

¹H NMR (300 MHz, CDCl₃) δ 7.15 (s, 1H), 7.08 (s, 1H), 4.37 (d, J = 4.9 Hz, 1H), 3.99 (s, 3H), 3.47 (dd, J = 18.0, 5.3 Hz, 1H), 3.28 (dd, J = 18.0, 8.2 Hz, 1H), 2.89-2.71 (m, 1H), 1.36 (d, J = 6.9 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 189.6, 142.4, 129.8, 127.9, 112.5, 111.5, 41.6, 36.2, 31.9, 28.2, 17.3. All spectroscopic data were in agreement with the literature.⁸

(*R*)-2-(3-(1-Isopropyl-1*H*-imidazol-2-yl)-3-oxo-1-phenylpropyl)malononitrile (5c)



Starting from **4'** (45.8 mg, 0.20 mmol) and malononitrile (15.8 mg, 0.24 mmol) according to the general procedure to give **5c** as a colorless oil (catalyzed by Δ -**Ir**: 24.7 mg, yield: 40%, ee: 88%; catalyzed by Δ -**Rh**: 55.8 mg, yield: 91%, ee: 95%). Enantiomeric excess established by HPLC analysis using a Chiralpak AD-H column (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 0.8 mL/min, 25 °C, t_r (minor) = 13.0 min, t_r (major) = 23.6 min); $[\alpha]_D^{20} = -0.4^\circ$ (*c* 0.8, CH₂Cl₂) for 95% ee of **5c**.

¹H NMR (300 MHz, CDCl₃) δ 7.46-7.35 (m, 5H), 7.30 (d, J = 0.9 Hz, 1H), 7.19 (d, J = 0.8 Hz, 1H), 5.42 (dt, J = 13.4, 6.7 Hz, 1H), 4.53-4.45 (m, 1H), 4.03-3.88 (m, 2H), 3.87-3.72 (m, 1H), 1.41 (dd, J = 8.6, 6.7 Hz, 6H).

¹³C NMR (75 MHz, CDCl₃) δ 188.7, 141.5, 136.5, 130.2, 129.2, 129.0, 128.2, 122.1, 112.0, 111.7, 49.5, 41.7, 41.2, 29.3, 23.55, 23.52.

IR (film): *v* (cm⁻¹) 3034, 2983, 2909, 2254, 1670, 1497, 1465, 1454, 1395, 1371, 1254, 1199, 1162, 1087, 971, 914, 772, 731, 700, 671, 646, 591, 548, 488, 407. HRMS (ESI, *m/z*) calcd for C₁₈H₁₈N₄ONa [M+Na]⁺: 329.1373, found: 329.1369.

(*R*)-2,2-Dimethyl-5-(4-(1-methyl-1*H*-imidazol-2-yl)-4-oxobutan-2-yl)-1,3-dioxane-4,6-dione (5d)



Starting from **4** (30.2 mg, 0.20 mmol) and 2,2-dimethyl-1,3-dioxane-4,6-dione (86.5 mg, 0.6 mmol) according to the general procedure to give **5d** as a white solid (catalyzed by Δ -**Ir**: 58.3 mg, yield: 99%, ee: 68%; catalyzed by Δ -**Rh**: 58.3 mg, yield: 99%, ee: 85%). Enantiomeric excess established by HPLC analysis using a Chiralpak AD-H column (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 0.8 mL/min, 40 °C, t_r (major) = 24.9 min, t_r (minor) = 26.6 min); $[\alpha]_D^{20} = -3.3^\circ$ (*c* 0.8, CH₂Cl₂) for 95% ee of **5d** (catalyzed by Δ -**Rh** (2 mol%) at room temperature).

¹H NMR (300 MHz, CDCl₃) δ 7.13 (d, J = 0.9 Hz, 1H), 7.03 (s, 1H), 4.22-4.16 (m, 1H), 3.98 (s, 3H), 3.56 (dd, J = 7.2, 5.0 Hz, 2H), 3.24-3.10 (m, 1H), 1.77 (d, J = 5.8 Hz, 6H), 1.21 (d, J = 7.0 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 192.3, 165.2, 164.7, 142.9, 129.2, 127.2, 104.7, 49.3, 41.9, 36.2, 28.9, 28.4, 26.9, 17.3.

IR (film): *v* (cm⁻¹) 3136, 2928, 2883, 1780, 1739, 1667, 1459, 1408, 1298, 1200, 1151, 1086, 1053, 991, 958, 914, 871, 787, 698, 670, 634, 596, 544, 496, 426.

HRMS (ESI, m/z) calcd for C₁₄H₁₉N₂O₅ [M+H]⁺: 295.1288, found: 295.1282.

(*R*)-*tert*-Butyl 1-((*R*)-4-(1-methyl-1*H*-imidazol-2-yl)-4-oxobutan-2-yl)-2-oxocyclopentanecarboxylate (5e)



Starting from **4** (30.2 mg, 0.20 mmol) and *tert*-butyl 2-oxocyclopentanecarboxylate (73.7 mg, 0.40 mmol) according to the general procedure to give **5e** (major product) as a colorless oil (catalyzed by

 Δ -**Ir**: 27.4 mg, yield: 41%, ee: 97%, dr: 3:1; catalyzed by Δ -**Rh**: 55.5 mg, yield: 83%, ee: 99%, dr: 4:1). The dr was determined by ¹H NMR and the enantiomeric excess established by HPLC analysis using a Chiralpak AD-H column (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 0.5 mL/min, 40 °C, t_r (minor) = 26.4 min, t_r (major) = 29.5 min); $[\alpha]_D^{20} = +13.1^\circ$ (*c* 1.4, CH₂Cl₂) for 99% ee of **5e**.

¹H NMR (300 MHz, CDCl₃) δ 7.08 (d, J = 0.8 Hz, 1H), 6.99 (s, 1H), 3.96 (s, 3H), 3.22 (dd, J = 16.6, 10.3 Hz, 1H), 3.08-2.97 (m, 1H), 2.74 (dd, J = 16.6, 2.6 Hz, 1H), 2.50-2.30 (m, 2H), 2.21-2.06 (m, 1H), 2.01-1.85 (m, 3H), 1.42 (s, 9H), 0.94 (d, J = 6.7 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) *δ* 214.5, 191.2, 169.2, 143.2, 128.9, 127.0, 82.0, 65.8, 41.7, 38.6, 36.2, 32.4, 29.4, 27.9, 19.4, 16.4.

IR (film): v (cm⁻¹) 3112, 2970, 2868, 1743, 1715, 1673, 1462, 1405, 1368, 1283, 1246, 1151, 1125, 1005, 979, 914, 834, 775, 695, 589, 549, 434.

HRMS (ESI, *m*/*z*) calcd for C₁₈H₂₇N₂O₄ [M+H]⁺: 335.1965, found: 335.1964.

(*R*)-*tert*-Butyl 2-((*R*)-4-(1-methyl-1*H*-imidazol-2-yl)-4-oxobutan-2-yl)-1-oxo-2,3-di-hydro-1*H*-indene-2-carboxylate (5f)



Starting from **4** (30.2 mg, 0.20 mmol) and *tert*-butyl 1-oo-2,3-dihydro-1*H*-indene-2-carboxylate (92.9 mg, 0.40 mmol) according to the general procedure to give **5f** (major product) as a colorless oil (catalyzed by Δ -**Ir**: 68.1 mg, yield: 89%, ee: 97%, dr: 10:1; catalyzed by Δ -**Rh**: 70.4 mg, yield: 92%, ee: 96%, dr: 14:1). Enantiomeric excess established by HPLC analysis using a Chiralpak AD-H column (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 97:3, flow rate 0.5 mL/min, 25 °C, t_r (major) = 84.2 min, t_r (minor) = 168.0 min); $[\alpha]_D^{20} = -96.9^\circ$ (*c* 0.7, CH₂Cl₂) for 97% ee of **5f**. The dr value was determined by ¹H NMR as shown below. The relative configuration was assigned by X-ray crystallography.



Figure S1. ¹H NMR of the crude product (*R*,*R*)-**5f** and its diastereomer from an iridium-catalyzed reaction. Calculated dr = 10:1 according to relative areas of integration.

¹H NMR (300 MHz, CDCl₃) δ 7.74 (d, *J* = 7.6 Hz, 1H), 7.65-7.56 (m, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.40-7.32 (m, 1H), 7.13 (d, *J* = 0.9 Hz, 1H), 7.03 (s, 1H), 4.01 (s, 3H), 3.69 (d, *J* = 17.5 Hz, 1H), 3.51-3.39 (m, 1H), 3.32-3.18 (m, 2H), 3.09 (dd, *J* = 16.3, 2.8 Hz, 1H), 1.36 (s, 9H), 0.76 (d, *J* = 6.7 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 202.4, 191.2, 169.3, 154.1, 143.3, 136.0, 135.2, 128.9, 127.6, 127.0, 126.3, 124.6, 82.1, 65.9, 42.4, 36.3, 33.1, 33.0, 27.8, 15.2.

IR (film): *v* (cm⁻¹) 2969, 2930, 1705, 1673, 1604, 1464, 1406, 1369, 1332, 1252, 1213, 1146, 1092, 986, 913, 844, 769, 743, 694, 651, 590, 517, 466.

HRMS (ESI, m/z) calcd for C₂₂H₂₇N₂O₄ [M+H]⁺: 383.1965, found: 383.1962.

3.2. Asymmetric α -Aminations

General Procedure (Reactions of Table 2). To a solution of the 2-acyl imidazole **6a-g** (0.20 mmol), synthesized from their respective Weinreb amides,⁹ in anhydrous *i*PrOH (0.10 mL, 2.0 M) was added metal catalyst Λ -**Ir** (3.7 mg, 0.0040 mmol, 2 mol%) or Λ -**Rh** (0.1-1 mol%) in a brown glass vial. After being stirred at room temperature for 30 min, dibenzyl azodicarboxylate (125.5 mg, 0.40 mmol, 2.0 eq, purity of \geq 95%) was added. The reaction was stirred at 20 °C, resulting in a precipitate of the products (*R*)-**7a-f**. After the reaction was completed (monitored by TLC), the precipitate was isolated by centrifugation and washed with Et₂O/*n*-hexane (v/v = 1:4) until the filtrate was almost colorless to give the white solid products (*R*)-**7a-f**. In the case of product (*R*)-**7g** formation, after the 2-acyl imidazole **6g** was consumed completely (monitoring by TLC), the mixture was diluted with CH₂Cl₂ and directly subjected to flash silica gel column chromatography with EtOAc/*n*-hexane = 1:2 to afford the product (*R*)-**7g** as a colorless oil. Enantiomeric excess values were determined by chiral HPLC chromatography.

Procedure for Determination of Initial Rates. To a solution of the 2-acyl imidazole **6a** (0.20 mmol) in anhydrous *i*PrOH (0.10 mL, 2.0 M) was added metal catalyst *rac*-**Ir** (1.84 mg, 0.0020 mmol, 1 mol%) or *rac*-**Rh** (1.66 mg, 0.0020 mmol, 1 mol%) in a brown glass vial. After being stirred at room temperature for 30 min, dibenzyl azodicarboxylate (125.5 mg, 0.40 mmol, 2.0 eq, purity \geq 95%) was added. The reaction was stirred at 20 °C and conversions were determined by ¹H NMR analysis of the crude mixture using mesitylene as an internal standard.

rac-**Ir** (1 mol%): 35 min => 15% conversion, 90 min => 34% conversion. *rac*-**Rh** (1 mol%): 2 min => 18% conversion, 5 min => 39% conversion. Result: ratio of initial rates rhodium catalysis / iridium catalysis = 21.

(*R*)-Dibenzyl 1-(2-(1-methyl-*1H*-imidazol-2-yl)-2-oxo-1-phenylethyl)hydrazine-1,2-dicarboxylate (7a)



Starting from **6a** (40.0 mg, 0.20 mmol) and dibenzyl azodicarboxylate (125.5 mg, 0.40 mmol, 2.0 eq) according to the general procedure to give (*R*)-**7a** as a white solid. Catalyzed by Λ -**Ir** (3.7 mg, 0.0040 mmol, 2 mol%): 85.7 mg, yield: 86%, *ee*: 92% (crude)/>99.5% (isolated); catalyzed by Λ -**Rh** (0.33 mg, 0.40 µmol, 0.2 mol%): 87.6 mg, yield: 88%, *ee*: 96% (crude)/>99.5% (isolated); catalyzed by Λ -**Rh** (0.17 mg, 0.20 µmol, 0.1 mol%): 82.7 mg, yield: 83%, *ee*: 94% (crude)/>99.5% (isolated). Enantiomeric excess established by HPLC analysis using a Chiralpak AD-H column (λ = 254 nm, eluents: *n*-hexane/isopropanol = 60:40, flow rate: 1.0 mL/min, 25 °C, t_r (major) = 15.3 min, t_r (minor) = 20.4 min); $[\alpha]_D^{20} = -174^\circ$ (c = 0.4, CHCl₃) for (*R*)-**7a** (>99.5% *ee*).

¹H NMR (500 MHz, CDCl₃) *δ* 7.47-7.35 (m, 2H), 7.33-7.13 (m, 12H), 7.12-6.90 (m, 5H), 5.34-4.42 (m, 4H), 4.03-3.73 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) *δ* 189.0, 156.3, 155.1, 141.1, 136.0, 135.9, 132.7, 130.3, 129.8, 128.4, 128.3, 128.0, 127.84, 127.77, 127.5, 127.2, 68.1, 67.8, 66.9, 35.8.

IR (film): *v* (cm⁻¹) 3321, 3069, 3032, 2956, 1716, 1681, 1497, 1454, 1402, 1338, 1290, 1218, 1157, 1120, 1080, 1052, 1028, 914, 848, 778, 737, 697, 649.

HRMS (ESI, *m*/*z*) calcd for C₂₈H₂₆N₄NaO₅ [M+Na]⁺: 521.1795, found: 521.1803.

(*R*)-Dibenzyl 1-(2-(1-methyl-*1H*-imidazol-2-yl)-2-oxo-1-o-tolylethyl)hydrazine-1,2-dicarboxylate (7b)



Starting from **6b** (42.8 mg, 0.20 mmol) and dibenzyl azodicarboxylate (125.5 mg, 0.40 mmol, 2.0 eq) according to the general procedure to give (*R*)-**7b** as a white solid. Catalyzed by Λ -**Ir** (3.7 mg, 0.0040 mmol, 2 mol%): 83.0 mg, yield: 81%, *ee*: 91% (crude)/>99.5% (isolated); catalyzed by Λ -**Rh** (0.33 mg, 0.40 µmol, 0.2 mol%): 86.0 mg, yield: 84%, *ee*: 94% (crude)/>99.5% (isolated). Enantiomeric excess established by HPLC analysis using a Chiralpak AD-H column (λ = 254 nm, eluents: *n*-hexane/isopropanol = 60:40, flow rate: 1.0 mL/min, 25 °C, t_r (major) = 16.1 min, t_r (minor) = 17.9 min); $[\alpha]_D^{20} = -126.8^\circ$ (c = 0.6, CHCl₃) for (*R*)-**7b** (>99.5% *ee*).

¹H NMR (500 MHz, CDCl₃) *δ* 7.48-6.91 (m, 17H), 6.88 (s, 1H), 5.33-4.30 (m, 4H), 3.93-3.78 (m, 3H), 2.73-1.66 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 190.2, 156.3, 155.1, 141.0, 139.5, 138.7, 135.8, 135.2, 131.4, 130.7, 130.6, 130.0, 129.1, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.2, 125.3, 125.0, 68.0, 66.7, 64.0, 35.7, 19.4.

IR (film): *v* (cm⁻¹) 3341, 3064, 3031, 2956, 1753, 1716, 1677, 1497, 1455, 1402, 1359, 1292, 1216, 1158, 1119, 1059, 1028, 970, 917, 777, 738, 697, 579.

HRMS (ESI, *m*/*z*) calcd for C₂₉H₂₈N₄NaO₅ [M+Na]⁺: 535.1952, found: 535.1950.

(R)-Dibenzyl 1-(1-(4-methoxyphenyl)-2-(1-methyl-1H-imidazol-2-yl)-2-oxoethyl)hydrazine-1,2-





Starting from **6c** (46.0 mg, 0.20 mmol) and dibenzyl azodicarboxylate (125.5 mg, 0.40 mmol, 2.0 eq) according to the general procedure to give (*R*)-**7c** as a white solid. Catalyzed by Λ -**Ir** (3.7 mg, 0.0040 mmol, 2 mol%): 91.8 mg, yield: 87%, *ee*: 95% (crude)/99% (isolated); catalyzed by Λ -**Rh** (0.33 mg, 0.40 µmol, 0.2 mol%): 89.8 mg, yield: 85%, *ee*: 97% (crude)/99% (isolated). Enantiomeric excess established by HPLC analysis using a Chiralpak AD-H column (λ = 254 nm, eluents: *n*-hexane/isopropanol = 60:40, flow rate: 1.0 mL/min, 25 °C, t_r (major) = 20.6 min, t_r (minor) = 28.7 min); [α]_D²⁰ = -155° (c = 1.0, CHCl₃) for (*R*)-**7c** (99% *ee*).

¹H NMR (500 MHz, CDCl₃) *δ* 7.46 (br, 1H), 7.37-7.12 (m, 10H), 7.13-6.84 (m, 5H), 6.84-6.66 (m, 2H), 5.31-4.55 (m, 4H), 4.01-3.55 (m, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 189.0, 159.6, 156.2, 155.5, 141.0, 135.7, 131.7, 129.8, 128.3, 128.1, 127.9, 127.8, 127.7, 127.5, 127.2, 124.4, 113.8, 68.0, 67.0, 66.8, 55.0, 35.9.

IR (film): *v* (cm⁻¹) 3322, 3032, 2957, 1716, 1679, 1609, 1513, 1454, 1402, 1289, 1249, 1178, 1116, 1081, 1029, 916, 753, 697.

HRMS (ESI, m/z) calcd for C₂₉H₂₈N₄NaO₆[M+Na]⁺: 551.1901, found: 551.1902.

$(\it R) - Dibenzyl 1 - (1 - (4 - chlorophenyl) - 2 - (1 - methyl - 1H - imidazol - 2 - yl) - 2 - oxoethyl) hydrazine - 1, 2 - imidazol - 2 - yl) - 2 - oxoethyl - 1, 2 - imidazol - 2 - yl) - 2 - oxoethyl - 2 - imidazol - 2 - yl) - 2 - oxoethyl - 2 - imidazol - 2 - imidazol$





Starting from **6d** (46.8 mg, 0.20 mmol) and dibenzyl azodicarboxylate (125.5 mg, 0.40 mmol, 2.0 eq) according to the general procedure to give (*R*)-**7d** as a white solid (catalyzed by Λ -**Ir** (3.7 mg, 0.0040 mmol, 2 mol%): 87.2 mg, yield: 82%, *ee*: 79% (crude)/84% (isolated); catalyzed by Λ -**Rh** (0.83 mg, 0.0010 mmol, 0.5 mol%): 88.3 mg, yield: 83%, *ee*: 95% (crude)/97% (isolated)). Enantiomeric excess established by HPLC analysis using a Chiralpak AD-H column (λ = 254 nm, eluents: *n*-hexane/isopropanol = 60:40, flow rate: 1.0 mL/min, 25 °C, t_r (major) = 16.9 min, t_r (minor) = 21.2 min); $[\alpha]_D^{20} = -152.6^\circ$ (c = 1.0, CHCl₃) for (*R*)-**7d** (97% *ee*).

¹H NMR (500 MHz, CDCl₃) *δ* 7.44 (br, 1H), 7.37-6.85 (m, 17H), 5.31-4.60 (m, 4H), 4.02-3.62 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 188.5, 156.2, 155.2, 140.9, 135.7, 134.5, 131.6, 131.4, 130.0, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.4, 68.3, 67.1, 65.8, 35.9.

IR (film): *v* (cm⁻¹) 3313, 3032, 2955, 2924, 1719, 1680, 1492, 1455, 1401, 1356, 1288, 1218, 1157, 1050, 1014, 915, 815, 740, 696.

HRMS (ESI, *m/z*) calcd for C₂₈H₂₅ClN₄NaO₅ [M+Na]⁺: 555.1406, found: 555.1408.

(*R*)-Dibenzyl 1-(2-(1-methyl-*1H*-imidazol-2-yl)-1-(naphthalen-2-yl)-2-oxoethyl)hydrazine-1,2dicarboxylate (7e)



Starting from **6e** (50.0 mg, 0.20 mmol) and dibenzyl azodicarboxylate (125.5 mg, 0.40 mmol, 2.0 eq) according to the general procedure to give (*R*)-**7e** as a white solid. Catalyzed by Λ -**Ir** (3.7 mg,

0.0040 mmol, 2 mol%): 91.0 mg, yield: 83%, *ee*: 90% (crude)/>99.5% (isolated); catalyzed by Λ -**Rh** (0.33 mg, 0.40 µmol, 0.2 mol%): 94.2 mg, yield: 86%, *ee*: 96% (crude)/99% (isolated). Enantiomeric excess established by HPLC analysis using a Chiralpak AD-H column (λ = 254 nm, eluents: *n*-hexane/isopropanol = 60:40, flow rate: 1.0 mL/min, 25 °C, t_r (major) = 21.8 min, t_r (minor) = 31.3 min); [α]_D²⁰ = -167.8° (c = 0.55, CHCl₃) for (*R*)-7e (>99.5% *ee*).

¹H NMR (500 MHz, CDCl₃) *δ* 7.86-7.34 (m, 8H), 7.34-7.10 (m, 7H), 7.09-6.93 (m, 3H), 6.90-6.69 (m, 3H), 5.35-4.28 (m, 4H), 3.88 (br s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 188.8, 156.3, 155.3, 141.0, 135.6, 133.0, 132.9, 130.0, 129.8, 129.7, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.3, 126.3, 125.9, 68.2, 66.9, 66.8, 35.8.

IR (film): *v* (cm⁻¹) 3317, 3031, 2957, 1716, 1678, 1497, 1454, 1402, 1355, 1288, 1217, 1157, 1051, 1015, 976, 916, 817, 754, 696, 556, 478.

HRMS (ESI, *m*/*z*) calcd for C₃₂H₂₈N₄NaO₅ [M+Na]⁺: 571.1952, found: 571.1958.

(*R*)-Dibenzyl 1-(2-(1-methyl-*1H*-imidazol-2-yl)-1-(thiophen-3-yl)-2-oxoethyl)hydrazine-1,2dicarboxylate (7f)



Starting from **6f** (41.2 mg, 0.20 mmol) and dibenzyl azodicarboxylate (125.5 mg, 0.40 mmol, 2.0 eq) according to the general procedure to give (*R*)-**7f** as a white solid. Catalyzed by Λ -**Ir** (3.7 mg, 0.0040 mmol, 2 mol%): 71.6 mg, yield: 71%, *ee*: 80% (crude)/94% (isolated); catalyzed by Λ -**Rh** (0.33 mg, 0.40 µmol, 0.2 mol%): 64.5 mg, yield: 64%, *ee*: 90% (crude)/97% (isolated). Enantiomeric excess established by HPLC analysis using a Chiralpak AD-H column (λ = 254 nm, eluents: *n*-hexane/isopropanol = 60:40, flow rate: 1.0 mL/min, 25 °C, t_r (major) = 18.0 min, t_r (minor) = 22.9 min); $[\alpha]_D^{20} = -92.95^\circ$ (c = 2.1, CHCl₃) for (*R*)-**7f** (94% *ee*).

¹H NMR (500 MHz, CDCl₃) *δ* 7.58 (br, 1H), 7.45-6.87 (m, 16H), 5.34-4.57 (m, 4H), 4.06-3.65 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 188.5, 155.6, 155.2, 140.9, 135.9, 135.7, 132.3, 129.9, 128.9, 128.4, 128.3, 128.1, 127.9, 127.7, 127.6, 127.4, 126.9, 126.6, 125.4, 68.1, 67.1, 63.5, 35.9.

IR (film): *v* (cm⁻¹) 3320, 3109, 3032, 2955, 2922, 1899, 1720, 1679, 1497, 1454, 1402, 1356, 1288, 1218, 1157, 1081, 1051, 978, 914, 841, 778, 739, 697, 558. HRMS (ESI, *m/z*) calcd for C₂₆H₂₄N₄NaO₅S [M+Na]⁺: 527.1360, found: 527.1361.

(*R*)-Dibenzyl 1-(1-(1-methyl-*1H*-imidazol-2-yl)-1-oxopropan-2-yl)hydrazine-1,2-dicarboxylate (7g)



Starting from **6g** (27.6 mg, 0.20 mmol) and dibenzyl azodicarboxylate (125.5 mg, 0.40 mmol, 2.0 eq) according to the general procedure to give (*R*)-**7g** as a colorless oil. Catalyzed by Λ -**Ir** (3.7 mg, 0.0040 mmol, 2 mol%): 74.1 mg, yield: 85%, *ee*: 91%; catalyzed by Λ -**Rh** (1.66 mg, 0.0020 mmol, 1 mol%): 82.8 mg, yield: 95%, *ee*: 92%). Enantiomeric excess established by HPLC analysis using a Chiralpak AD-H column (λ = 254 nm, eluents: *n*-hexane/isopropanol = 60:40, flow rate: 1.0 mL/min, 25 °C, t_r (minor) = 15.2 min, t_r (major) = 19.5 min); $[\alpha]_D^{20} = -6.2^\circ$ (c = 1.1, CHCl₃) for (*R*)-**7g** (91% *ee*).

¹H NMR (500 MHz, CDCl₃) δ 7.82 (br, 1H), 7.40-6.99 (m, 11H), 6.94 (s, 1H), 5.68-5.59 (m, 1H), 5.29-4.88 (m, 4H), 3.82-3.62 (m, 3H), 1.65-1.45 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) *δ* 191.1, 156.3, 155.9, 140.0, 135.6, 129.1, 128.1, 128.0, 127.9, 127.7, 127.0, 67.5, 67.0, 60.5, 35.5, 14.6.

IR (film): *v* (cm⁻¹) 3310, 3032, 2955, 1717, 1681, 1498, 1455, 1403, 1358, 1294, 1219, 1156, 1048, 1027, 969, 911, 778, 740, 697, 629.

HRMS (ESI, *m*/*z*) calcd for C₂₃H₂₄N₄NaO₅ [M+Na]⁺: 459.1639, found: 459.1633.

4. Assignment of Absolute Configurations

The absolute configurations of the asymmetric Michael reactions were assigned by comparison of the optical rotations of product **5a** with literature values.³ The absolute configurations of the α -amination products were assigned by converting product **7g** to the corresponding reported alcohol **S3** and comparing the optical rotation of this material with the literature value.¹⁰



Conversion of 2-acylimidazole 7g to ester S2.¹¹ To a solution of **7g** (265.2 mg, 0.607 mmol) in CH₃CN (6.0 mL, 0.1 M, freshly distilled over CaH₂) was added 4 Å MS (300 mg, 50 mg/0.1 mmol of **7g**) under argon atmosphere. The suspension was stirred vigorously under a positive pressure of argon for 2 h at room temperature, then MeOTf (206 μ L, 1.82 mmol, 3.0 eq) was added and stirred at room temperature for 26 h. After that, methanol (1.5 mL) and DBU (136 μ L, 0.91 mmol, 1.5 eq) were added successively at room temperature. After stirring at room temperature for 1 h, the solvent was evaporated and the residue was directly purified by flash silica chromatography with EtOAc/*n*-hexane = 1:10 to 1:8 to afford the **S2** (182.8 mg, 0.473 mmol, 78%) as a colorless oil. HRMS (ESI, *m/z*) calcd for C₂₀H₂₂N₂NaO₆ [M+Na]⁺: 409.1370, found: 409.1370.

Reduction of ester S2 to alcohol S3. A solution of diisobutylaluminum hydride (0.875 mmol, 1.0 M in *n*-hexane) was added to a cold (0 °C) solution of **S2** (135 mg, 0.35 mmol) in THF (1.4 mL, 0.25 M) under argon atmosphere. The resulting mixture was stirred continuously for an additional 3 h. The mixture was quenched with an aqueous solution of saturated sodium tartrate and stirred

vigorously for 30 min at room temperature. The reaction mixture was extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/*n*-hexane) to afford the pure product **S3** (107.7 mg, 0.30 mmol, 86%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.43-7.21 (m, 10H), 6.65 (s, 1H), 5.42-4.86 (m, 4H), 4.65-3.90 (m, 2H), 3.57-3.30 (m, 2H), 1.00 (d, *J* = 6.6 Hz, 3H).

 $[\alpha]_D^{20} = -21.3^\circ$ (c = 0.6, CHCl₃). (Lit.^{10a} $[\alpha]_D^{20} = -22.5^\circ$ (c = 0.4, CHCl₃) for product with *R* configuration). All other spectroscopic data were in agreement with the literature.^{10,12}

5. HPLC on Chiral Stationary Phase

5.1. Enantiomeric Purities of the Rhodium Catalysts

The analysis was performed with a Daicel Chiralpak IB (250×4.6 mm) HPLC column on an Agilent 1200 Series HPLC System. The column temperature was 25 °C and UV-absorption was measured at 254 nm. Solvent A = 0.1% TFA, solvent B = MeCN.



Figure S2. HPLC trace for the racemic reference complexes Δ/Λ -**Rh**. (Daicel Chiralpak IB, with a linear gradient of 30% to 41% B in 60 min, flow rate = 0. 6 mL/min).



Figure S3. HPLC trace for the complex Δ -**Rh**. Integration of peak areas > 100:1 e.r.



Figure S4. HPLC trace for the complex Λ -Rh. Integration of peak areas > 100:1 e.r.

5.2. Enantioselectivities of the Asymmetric Michael Reactions

Enantiomeric purities of the compounds **5a-f** were determined with a Daicel Chiralpak IC or AD-H ($250 \times 4.6 \text{ mm}$) HPLC column on an Agilent 1200 Series HPLC System using *n*-hexane/isopropanol as mobile phase, column temperature = 40 °C or 25 °C, UV-absorption was measured at 254 nm.



Figure S5. HPLC traces of *rac*-**5a** (reference HPLC trace on the top) and (*R*)-**5a**. Area integration = 98.0:2.0 (second trace, 96% ee, catalyzed by Δ -**Ir**) and 97.4:2.6 (third trace, 95% ee, catalyzed by Δ -**Rh**).



Figure S6. HPLC traces of *rac*-**5b** (reference HPLC trace on the top) and (*R*)-**5b**. Area integration = 94.5:5.5 (second trace, 89% ee, catalyzed by Δ -**Ir**) and 95.8:4.2 (third trace, 92% ee, catalyzed by Δ -**Rh**).



Figure S7. HPLC traces of *rac*-**5c** (reference HPLC trace on the top) and (*R*)-**5c**. Area integration = 93.9:6.1 (second trace, 88% ee, catalyzed by Δ -**Ir**) and 97.4:2.6 (third trace, 95% ee, catalyzed by Δ -**Rh**).



Figure S8. HPLC traces of *rac*-**5d** (reference HPLC trace on the top) and (*R*)-**5d**. Area integration = 84.1:15.9 (second trace, 68% ee, catalyzed by Δ -**Ir** (1 mol%) at room temperature), 92.4:7.6 (third trace, 85% ee, catalyzed by Δ -**Rh** (1 mol%) at room temperature), 97.0:3.0 (fourth trace, 94% ee, catalyzed by Δ -**Rh** (1 mol%) at 5 °C), 97.7:2.3 (fifth trace, 95% ee, catalyzed by Δ -**Rh** (2 mol%) at room temperature).



Figure S9. HPLC traces of *rac*-**5e** (reference HPLC trace on the top) and (*R*,*R*)-**5e**. Area integration = 98.4:1.6 (second trace, 97% ee, catalyzed by Δ -**Ir**) and 99.4:0.6 (third trace, 99% ee, catalyzed by Δ -**Rh**).



Figure S10. HPLC traces of *rac*-**5f** (reference HPLC trace on the top) and (*R*,*R*)-**5f**. Area integration = 98.6:1.4 (second trace, 97% ee, catalyzed by Δ -**Ir**) and 97.9:2.1 (third trace, 96% ee, catalyzed by Δ -**Rh**).

5.3. Enantioselectivities of the Asymmetric α-Aminations

Enantiomeric purities of the compounds (*R*)-**7a-g** were determined with a Daicel Chiralpak AD-H HPLC column (250 x 4.6 mm) on an Agilent 1260 Series HPLC System using *n*-hexane/isopropanol as the mobile phase. The column temperature was 25 $^{\circ}$ C and the UV-absorption was measured at 254 nm.



Figure S11. HPLC traces of *rac*-**7a** (reference HPLC trace on the top) and (*R*)-**7a**. Area integration = 96.2:3.8 (second trace, 92% *ee* of crude (*R*)-**7a**, catalyzed by Λ -**Ir**) and 99.8:0.2 (third trace, >99.5% *ee* of isolated (*R*)-**7a**, catalyzed by Λ -**Ir**).



Figure S12. HPLC traces of (*R*)-**7a**. Area integration = 98.1:1.9 (first trace, 96% *ee* of crude (*R*)-**7a**, catalyzed by Λ -**Rh** (0.2 mol%)) and 99.8:0.2 (second trace, >99.5% *ee* of isolated (*R*)-**7a**, catalyzed by Λ -**Rh** (0.2 mol%)).



Figure S13. HPLC traces of (*R*)-**7a**. Area integration = 97.2:2.8 (first trace, 94% *ee* of crude (*R*)-**7a**, catalyzed by Λ -**Rh** (0.1 mol%)) and 99.8:0.2 (second trace, >99.5% *ee* of isolated (*R*)-**7a**, catalyzed by Λ -**Rh** (0.1 mol%)).



Figure S14. HPLC traces of *rac*-7**b** (reference HPLC trace on the top) and (*R*)-7**b**. Area integration = 95.6:4.4 (second trace, 91% *ee* of crude (*R*)-7**b**, catalyzed by Λ -I**r**) and 99.9:0.1 (third trace, >99.5% *ee* of isolated (*R*)-7**b**, catalyzed by Λ -I**r**).



Figure S15. HPLC traces of (*R*)-**7b**. Area integration = 96.9:3.1 (first trace, 94% *ee* of crude (*R*)-**7b**, catalyzed by Λ -**Rh**) and 99.8:0.2 (second trace, >99.5% *ee* of isolated (*R*)-**7b**, catalyzed by Λ -**Rh**).



Figure S16. HPLC traces of *rac*-7c (reference HPLC trace on the top) and (*R*)-7c. Area integration = 97.5:2.5 (second trace, 95% *ee* of crude (*R*)-7c, catalyzed by Λ -Ir) and 98.9:1.1 (third trace, 99% *ee* of isolated (*R*)-7c, catalyzed by Λ -Ir).



Figure S17. HPLC traces of (*R*)-7c. Area integration = 98.5:1.5 (first trace, 97% *ee* of crude (*R*)-7c, catalyzed by Λ -Rh) and 99.3:0.7 (second trace, 99% *ee* of isolated (*R*)-7c, catalyzed by Λ -Rh).



Figure S18. HPLC traces of *rac*-7d (reference HPLC trace on the top) and (*R*)-7d. Area integration = 89.5:10.5 (second trace, 79% *ee* of crude (*R*)-7d, catalyzed by Λ -Ir) and 91.9:8.1 (third trace, 84% *ee* of isolated (*R*)-7d, catalyzed by Λ -Ir).



Figure S19. HPLC traces of (*R*)-7d. Area integration = 97.6:2.4 (first trace, 95% *ee* of crude (*R*)-7d, catalyzed by Λ -Rh) and 98.4:1.6 (second trace, 97% *ee* of isolated (*R*)-7d, catalyzed by Λ -Rh).



Figure S20. HPLC traces of *rac*-7e (reference HPLC trace on the top) and (*R*)-7e. Area integration = 94.8:5.2 (second trace, 90% *ee* of crude (*R*)-7e, catalyzed by Λ -Ir) and 99.8:0.2 (third trace, >99.5% *ee* of isolated (*R*)-7e, catalyzed by Λ -Ir).



Figure S21. HPLC traces of (*R*)-**7e**. Area integration = 97.8:2.2 (first trace, 96% *ee* of crude (*R*)-**7e**, catalyzed by **A**-**Rh**) and 99.3:0.7 (second trace, 99% *ee* of isolated (*R*)-**7e**, catalyzed by **A**-**Rh**).



Figure S22. HPLC traces of *rac*-**7f** (reference HPLC trace on the top) and (*R*)-**7f**. Area integration = 90:10 (second trace, 80% *ee* of crude (*R*)-**7f**, catalyzed by Λ -**Ir**) and 97.2:2.8 (third trace, 94% *ee* of isolated (*R*)-**7f**, catalyzed by Λ -**Ir**).



Figure S23. HPLC traces of (*R*)-**7f**. Area integration = 95:5 (first trace, 90% *ee* of crude (*R*)-**7f**, catalyzed by **A-Rh**) and 98.5:1.5 (second trace, 97% *ee* of isolated (*R*)-**7f**, catalyzed by **A-Rh**).



Figure S24. HPLC traces of *rac*-**7g** (reference HPLC trace on the top) and (*R*)-**7g**. Area integration = 95.7:4.3 (second trace, 91% *ee* of isolatd (*R*)-**7g**, catalyzed by **A-Ir**) and 95.9:4.1 (third trace, 92% *ee* of isolated (*R*)-**7g**, catalyzed by **A-Rh**).

6. Investigation of the Proposed Catalyst-Coordinated Substrate

To a solution of Δ -**Rh** (10.0 mg, 0.012 mmol) in CD₂Cl₂ (0.70 mL) at room temperature was added substrate **4** (9.5 mg, 0.063 mmol). The mixture was stirred at room temperature for 20 min and then analyzed by ¹H NMR spectroscopy. The ¹H NMR analysis is consistent with a fast bidentate coordination of **4** to Δ -**Rh** under release of the coordinated acetonitrile ligands.



Figure S25. ¹H NMR spectra of acylimidazole substrate 4, catalyst Δ -**Rh**, and a mixture of 4 and Δ -**Rh**.



Figure S26. Excerpts of the ¹H NMR spectra from Figure S25.

7. Investigation of the Configurational Stability of the Rhodium Catalyst

7.1. Catalyst Stability Investigated by ¹H NMR

The rhodium complex Δ -**Rh** (5.0 mg) was dissolved in CD₂Cl₂ and kept in the NMR tube at room temperature under reduced light. ¹H NMR spectra were recorded after 2, 4, 6 and 8 days.



Figure S27. ¹H NMR of Δ -**Rh** recorded in CD₂Cl₂ over 8 days.

7.2. Catalyst Stability Investigated by HPLC on Chiral Stationary Phase

Enantiopure pure rhodium complex Λ -**Rh** (2.0 mg) was dissolved in CH₂Cl₂ (1.0 mL, HPLC grade) and kept in a brown glass vial at room temperature. The HPLC spectra were collected after 2-8 days. HPLC conditions: Daicel Chiralpak IB (250 × 4.6 mm) HPLC column, the column temperature was 25 °C and UV-absorption was measured at 254 nm. Solvent A = 0.1% TFA, solvent B = MeCN with a linear gradient of 30% to 41% B in 60 min at a flow rate = 0.6 mL/min.



Figure S28. HPLC trace of the freshly prepared Λ -Rh in CH₂Cl₂ (>99% ee).



Figure S29. HPLC trace after 2 days in CH₂Cl₂ (>99% ee).



Figure S30. HPLC trace after 4 days in CH₂Cl₂ (>99% ee).



Figure S31. HPLC trace after 6 days in CH₂Cl₂ (>99% ee).



Figure S32. HPLC trace after 8 days in CH₂Cl₂ (>99% ee).

8. NMR Spectra of New Rhodium Complexes



Figure S33. ¹H NMR and ¹³C NMR spectrum of *rac-2*.



Figure S34. ¹H NMR and ¹³C NMR spectrum of Δ -(*R*)-**3**.



Figure S35. ¹H NMR and ¹³C NMR spectrum of Δ -**Rh**.

9. Single Crystal X-Ray Diffraction

Crystals of Δ -(*R*)-**3** and Δ -**Rh** were obtained by slow diffusion from a solution of the compounds in CH₂Cl₂ layered with Et₂O at room temperature for several weeks. Crystals of the *R*-enantiomer of **5d** and racemic **5f** were obtained by slow diffusion from a solution of the compounds in CH₂Cl₂ layered with hexane at 5 °C for several days. Single crystals suitable for X-ray diffraction of the substrate coordinated rhodium catalyst (here denoted as **Rh1**) were obtained by reacting **4'** (0.060 mmol) with Δ/Λ -**Rh** (0.060 mmol) overnight at room temperature in CH₂Cl₂ (2.0 mL). After the slow addition of *n*-hexane (5.0 mL), crystals were collected after several days (70% yield). Single crystals of the iridium enolate complex were obtained as follows: To a solution of the racemic iridium catalyst (46.0 mg, 0.050 mmol) in CH₂Cl₂ (1.0 mL) was added the substrate **6a** (15.0 mg, 0.075 mmol). After 2 hours, the reaction was concentrated and purified by chromatography over silica gel using CH₂Cl₂/EtOAc (50:1), affording a pale yellow solid (42.8 mg, 0.048 mmol). Single crystals suitable for X-ray diffraction were obtained by slow diffusion from a solution of the compound in CH₂Cl₂ layered with *n*-hexane at room temperature for several days.

Crystal data and details of the structure determination are presented in Table S1. X-ray data were collected with a Bruker 3 circuit D8 Quest diffractometer with MoKa radiation (microfocus tube with multilayer optics) and Photon 100 CMOS detector. Scaling and absorption correction was performed by using the SADABS¹³ software package of Bruker. Structures were solved using direct methods in SHELXS-97¹⁴ and refined using the full matrix least squares procedure in SHELXL-2013¹⁵. The hydrogen atoms were placed in calculated positions and refined as riding on their respective C atom, and Uiso(H) was set at 1.2 Ueq(Csp^2) and 1.5 Ueq(Csp^3). Disorder of PF_6 ions, solvent molecules or methylene groups was refined using restraints for both the geometry and the anisotropic displacement factors. In the packing of **Rh1** there are holes present that contain diffuse electron density that may belong to heavily disordered solvent molecules. This was taken into account using the "squeeze" procedure in the PLATON¹⁶ program system. The determination of the absolute configuration of the light atom structure **5d** by means of refining the "Flack parameter²¹⁷ was not possible. The absolute configurations of compounds Δ -(*R*)-3, Δ -**Rh**, and the absolute structure of **Rh1** have been determined.¹⁷ CCDC 1027144-1027147 and 1014508 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and details of the structure determination.

Metal Complexes:

	Δ -(R)- 3	Δ- Rh	Rh1	Ir-enolate complex
Empiric formula	$2(C_{39}H_{40}N_{3}O_{4}Rh)$ $\cdot 3(CH_{2}Cl_{2})$	$\begin{array}{c} C_{38}H_{38}N_4O_2Rh\cdot F_6P\\ \cdot CH_2Cl_2 \end{array}$	$\begin{array}{c} C_{49}H_{48}N_4O_3Rh\cdot F_6P\\ \cdot 2(CH_2Cl_2) \end{array}$	$\begin{array}{c} C_{46}H_{43}IrN_4O_3\\ \cdot CH_2Cl_2 \end{array}$
Formula weight	1690.07	915.53	1158.64	976.97
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Orthorhombic, Pna2 ₁	Monoclinic, C2/c
a, b, c (Å)	13.919 (6), 19.144 (9), 28.616 (11)	13.1445 (5), 13.6427 (6), 22.5166 (8)	17.7761 (6), 22.9437 (8), 13.1111 (4)	38.9286(14), 13.3583(5), 17.0015(7)
α, β, γ (°)	90, 90, 90	90, 90, 90	90, 90, 90	90, 111.4793(12), 90
$V(\text{\AA}^3)$	7625 (6)	4037.8 (3)	5347.4 (3)	8227.1(5)
Ζ	4	4	4	8
μ (mm ⁻¹)	0.70	0.66	0.62	3.423
Crystal size (mm)	0.44 imes 0.07 imes 0.06	$0.51 \times 0.24 \times 0.17$	$0.26 \times 0.06 \times 0.03$	0.13 x 0.07 x 0.02
T_{\min}, T_{\max}	0.76, 0.96	0.75, 0.90	0.88, 0.98	0.77, 0.94
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	64188, 14187, 12148	39009, 9272, 8540	56957, 9643, 8691	86572, 7482, 6105
R _{int}	0.064	0.042	0.050	0.087
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.606	0.650	0.602	0.601
$R[F^2 > 2\sigma(F^2)],$ wR(F ²), S	0.036, 0.068, 1.02	0.029, 0.058, 1.03	0.035, 0.089, 1.03	0.030, 0.064, 1.04
No. of reflections	14187	9272	9643	7482
No. of parameters	996	590	705	568
No. of restraints	114	168	106	68
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	0.57, -0.43	0.51, -0.40	1.12, -0.51	0.85, -0.91
Absolute structure parameter	-0.020 (10)	-0.033 (8)	-0.015 (8)	-
CCDC no.	1027144	1027145	1028075	1014508

Organic Reaction Products:

	5d	5f
Empiric formula	$C_{14}H_{18}N_2O_5$	$C_{22}H_{26}N_2O_4$
Formula weight	294.30	382.45
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/c$
a, b, c (Å)	5.4571 (2), 15.3289 (6), 17.4084 (9)	10.1905 (5), 11.5731 (6), 17.4203 (8)
α, β, γ (°)	90, 90, 90	90, 97.5045 (16), 90
$V(\text{\AA}^3)$	1456.24 (11)	2036.88 (17)
Ζ	4	4
μ (mm ⁻¹)	0.10	0.09
Crystal size (mm)	$0.45 \times 0.08 \times 0.05$	$0.40 \times 0.30 \times 0.08$
T_{\min}, T_{\max}	0.95, 0.99	0.93, 0.99
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	11088, 2707, 2478	47435, 4679, 3939
R _{int}	0.037	0.037
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.605	0.650
$R[F^2 > 2\sigma(F^2)],$ $wR(F^2), S$	0.029, 0.067, 1.05	0.038, 0.114, 1.12
No. of reflections	2707	4679
No. of parameters	194	258
No. of restraints	0	0
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	0.15, -0.20	0.35, -0.35
Absolute structure parameter	0.3 (4)	_
CCDC no.	1027146	1027147



Figure S36. Crystal structure of Δ -(*R*)-**3**. ORTEP drawing with 50% probability thermal ellipsoids.



Figure S37. Crystal structure of Δ -**Rh**. ORTEP drawing with 50% probability thermal ellipsoids. The hexafluorophosphate counteranion is omitted for clarity.



Figure S38. Crystal structure of racemic **Rh1**. ORTEP drawing with 50% probability thermal ellipsoids. The hexafluorophosphate counteranion is omitted for clarity.



Figure S39. Crystal structure of a racemic iridium enolate complex. ORTEP drawing with 50% probability thermal ellipsoids. The hexafluorophosphate counteranion is omitted for clarity.



Figure S40. Crystal structure of 5d. ORTEP drawing with 50% probability thermal ellipsoids.



Figure S41. Crystal structure of racemic **5f** to verify the relative configuration. ORTEP drawing with 50% probability thermal ellipsoids.

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