Chiral Cyclopentadienyl Cobalt(III) Complexes Enable Highly Enantioselective 3d-Metal-Catalyzed C-H Functionalizations

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General Methods

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring, unless otherwise indicated. Dichloromethane and diethyl ether were purified by an Innovative Technology Solvent Delivery System degassed *via* freeze-pump-thaw technique and stored over 4 Å molecular sieves in a nitrogen-filled glove box. TFE and HFIP were degassed *via* freeze-pump-thaw technique and stored over 3 Å molecular sieves in a nitrogen-filled glove box. Chemicals were used as obtained from the suppliers unless otherwise indicated. Flash chromatography was performed with Silicycle silica gel 60 (0.040-0.063 µm grade). Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F254). Compounds were either visualized under UV-light at 254 nm or by dipping the plates in an aqueous potassium permanganate solution followed by heating. Proton nuclear magnetic resonance (^1H NMR) data was acquired on a Bruker *AVANCE400* (400 MHz), Bruker *DRX-400* (400 MHz), Bruker *AVANCEIII-400* (400 MHz) or Bruker *DRX-600* (600 MHz) spectrometer at 298 K unless otherwise noted. Chemical shifts (δ) are reported in parts per million (ppm) relative to incompletely deuterated CDCl_3 (s, 7.26 ppm) or C_6D_6 (s, 7.16 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet, br, broad. Proton-decoupled Carbon-13 nuclear magnetic resonance ($^{13}\text{C}\{^1\text{H}\}$ NMR) data were acquired on a Bruker *AVANCE400* (101 MHz), Bruker *DRX-400* (101 MHz), Bruker *AVANCEIII-400* (101 MHz) or Bruker *DRX600* (151 MHz) spectrometer at 298 K. Chemical shifts are reported in ppm relative to CDCl_3 (77.16 ppm) or C_6D_6 (128.06 ppm). Proton-decoupled ^{19}F nuclear magnetic resonance ($^{19}\text{F}\{^1\text{H}\}$ NMR) data were acquired at 376 MHz on a Bruker *AVANCEIII-400* spectrometer at 298 K. Infrared (IR) data were recorded on an Alpha-P Bruker FT-IR Spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). HRMS ESI measurements were performed by an Agilent LC-MS TOF and Xevo G2-S QTOF mass spectrometers. APPI-FT-MS analyses were performed on a LTQ Orbitrap FTMS instrument. High resolution mass values are given in m/z . Optical rotations were measured on a Polartronic M polarimeter using a 10.0 cm cell with a Na 589 nm filter. X-ray analysis was performed by Dr. R. Scopelliti and Dr. F. Tirani at the EPF Lausanne.

Synthesis of Reagents

Ligand Synthesis

Figure 1: Ligands **L1-L7** utilized for Co-complexation.

Ligands **L1**¹, **L2**², **L3**², **L4**³, **L5**⁴, **L6**⁵, **L7**⁵ were synthesized following the corresponding procedure.

Cobalt Complex Synthesis

Scheme 1: Cobalt complexation.

The synthesis for complex **Co7** was optimized by changing stoichiometry and reaction atmosphere (see table 1). The optimized conditions were then applied for the synthesis of **Co1**, **Co2** and **Co3**. The syntheses of other cobalt complexes have not been repeated under the optimized conditions and are described as they were executed.

Cobalt complex **Cp*Co(CO)I₂**

Cp*Co(CO)I₂ was prepared following a procedure reported by Matsunaga *et al.*⁶

Figure 2: X-Ray Structure of **Cp*Co(CO)I₂** (CCDC: 1898853).

Cobalt complex **Co1**

In an N₂-filled glovebox, a flame dried Schlenk tube was charged with Co₂(CO)₈ (61.3 mg, 170 μmol, 1.10 equiv.). A solution of **L1** (40.0 mg, 155 μmol, 1.00 equiv.) in dry DCM (2.58 mL) was added. CO gas was bubbled through the resulting solution for 5 min at 20 °C. The black reaction mixture was stirred at 37 °C for 6 h under CO atmosphere. All volatiles were evaporated by Schlenk technique. A solution of iodine (47.2 mg, 186 μmol, 1.20 equiv.) in distilled Et₂O (2.58 mL) was added to the black residue. The reaction vessel was connected to a Schlenk line to release carbon monoxide and the dark violet mixture was stirred at room temperature for 1 h. All volatiles were evaporated and the residue was purified by column chromatography on silica gel (gradient: DCM/pentane = 0% → 50%). The dark violet fractions were collected and concentrated under reduced pressure to obtain 39.0 mg (65.0 μmol, 42% yield) of the desired product as a black solid.

¹H NMR (600 MHz) δ = 7.48 – 7.45 (m, 4H), 7.42 – 7.38 (m, 1H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 2H), 6.17 (t, *J* = 2.3 Hz, 1H), 5.73 (d, *J* = 2.3 Hz, 1H), 4.89 (d, *J* = 2.3 Hz, 1H), 4.78 (d, *J* = 8.1 Hz, 1H), 4.43 (dd, *J* = 10.8, 7.2 Hz, 1H), 3.34 (ddd, *J* = 12.8, 10.8, 8.1 Hz, 1H), 2.72 (dd, *J* = 12.8, 7.8 Hz, 1H) ppm; **¹³C{¹H} NMR** (150 MHz) δ = 195.0, 141.4, 138.2, 129.3 (2C), 128.3, 127.7, 127.23, 127.19, 121.0, 118.6, 97.4, 81.7, 73.5, 44.2, 42.0, 41.2 ppm; **IR (ATR)**: $\tilde{\nu}$ = 3085, 2924, 2835, 2062, 1600, 1493, 1447, 1367, 1079, 1030, 842, 752, 698 cm⁻¹; **HRMS (APPI)**: calcd. for [C₂₀H₁₇CoI]⁺, [M-CO-I]⁺: 442.9701; found: 442.9700; **[α]_D²⁰**: - 105.6 (*c* = 0.30, CHCl₃).

Cobalt complex **Co2**

In an N₂-filled glovebox, a flame dried Schlenk tube was charged with Co₂(CO)₈ (48.9 mg, 136.0 μmol, 1.10 equiv.). A solution of **L2** (50.0 mg, 124 μmol, 1.00 equiv.) in dry DCM (2.00 mL) was added. CO gas was bubbled through the resulting solution for 5 min at 20 °C. The black reaction mixture was stirred at 37 °C for 6 h under CO atmosphere. The volatiles were evaporated by Schlenk technique. A solution of iodine (37.6 mg, 148 μmol, 1.20 equiv.) in dry degassed Et₂O (2.00 mL) was added to the black residue. The reaction vessel was connected to a Schlenk line to release carbon monoxide and the dark violet mixture was stirred at room temperature for 1 h. All volatiles were evaporated and the residue was purified by column chromatography on silica gel (gradient: DCM/pentane = 0% → 50%). The dark violet fractions were collected and concentrated under reduced pressure to obtain 84.0 mg (113 μmol, 91% yield) of the desired product as a black solid.

¹H NMR (600 MHz, CDCl₃) δ = 7.88 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.38 (m, 3H), 7.24 (s, 1H), 7.15 – 7.07 (m, 3H), 7.02 (d, *J* = 8.4 Hz, 1H), 5.85 – 5.81 (m, 1H), 5.77 – 5.73 (m, 1H), 5.48 – 5.42 (m, 1H), 4.12 (s, 3H), 4.06 (d, *J* = 16.2 Hz, 1H), 3.97 (s, 3H), 3.90 (d, *J* = 14.1 Hz, 1H), 3.60 (d, *J* = 14.1 Hz, 1H), 2.77 (d, *J* = 16.2 Hz, 1H) ppm; **¹³C{¹H} NMR** (150 MHz, CDCl₃) δ = 196.8, 155.7, 154.8, 138.1, 136.9, 134.2, 133.9, 127.22, 127.19, 127.11, 127.07, 127.0, 126.9, 126.8 (3×C), 124.5, 124.3, 123.7, 106.28, 106.26, 104.4, 103.4, 94.8, 90.7, 85.4, 55.8, 55.4, 26.7, 24.7 ppm; **IR (ATR)**: $\tilde{\nu}$ = 3062, 2935, 2061, 1697, 1503, 1451, 1238, 1114, 1019, 907, 730 cm⁻¹; **HRMS (APPI)**: calcd. for [C₂₉H₂₃CoIO₂]⁺, [M-CO-I]⁺: 589.0069; found: 589.0068; **[α]_D²⁰**: - 91.2 (*c* = 0.30, CHCl₃).

Figure 3: X-Ray Structure of **Co2** (CCDC: 1898842).

Cobalt complex **Co3**

A flame-dried MW tube was charged with **L3** (20.0 mg, 43.0 μmol , 1.00 equiv.), $\text{Co}_2(\text{CO})_8$ (17.1 mg, 48.0 μmol , 1.10 equiv.) and distilled DCM (720 μL) in an N_2 -filled glove box. The black solution was stirred at 40 $^\circ\text{C}$ for 6 h in a sealed tube under nitrogen atmosphere. All volatiles were evaporated under a stream of nitrogen at room temperature. The black residue was dissolved with distilled Et_2O (720 μL) and a solution of I_2 (13.2 mg, 52.0 μmol , 1.20 equiv.) in distilled Et_2O (1.00 mL) was added to the Co-complex solution. The reaction vessel was connected to a Schlenk line to release carbon monoxide and the dark violet mixture was stirred at room temperature for 1 h. Pentane (2.00 mL) was added to the crude mixture and the solution was purified by flash column chromatography on silica gel (gradient: DCM/pentane = 0% $\rightarrow$ 50%). The dark violet fractions were collected and concentrated under reduced pressure to obtain 26.0 mg (32.0 μmol , 75% yield) of the desired product as a black solid. **^1H NMR** (400 MHz, CDCl_3) δ = 7.85 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.49 – 7.35 (m, 3H), 7.20 (s, 1H), 7.10 (dtd, J = 8.0, 6.7, 1.3 Hz, 2H), 7.01 (d, J = 8.5 Hz, 2H), 5.86 (t, J = 2.2 Hz, 1H), 5.79 (t, J = 2.6 Hz, 1H), 5.51 (t, J = 2.2 Hz, 1H), 4.92 (hept, J = 6.1 Hz, 1H), 4.77 (hept, J = 6.1 Hz, 1H), 4.12 (d, J = 16.2 Hz, 1H), 3.88 (d, J = 13.7 Hz, 1H), 3.42 (d, J = 13.7 Hz, 1H), 2.74 (d, J = 16.2 Hz, 1H), 1.73 (d, J = 6.1 Hz, 3H), 1.56 (d, J = 6.1 Hz, 3H), 1.50 (d, J = 6.1 Hz, 3H), 1.39 (d, J = 6.1 Hz, 3H) ppm; **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, CDCl_3) δ = 196.5, 154.2, 152.6, 138.5, 137.0, 134.3, 134.0, 127.3, 127.1, 127.0, 126.9 (four peaks), 126.8, 126.7, 124.4, 124.3, 124.1, 107.8, 107.5, 104.4, 101.0, 96.7, 93.4, 83.9, 71.2, 70.1, 26.3, 24.8, 22.5, 22.4, 22.3, 22.0 ppm; **IR (ATR)**: 3061, 2974, 2931, 2870, 2061, 1617, 1593, 1436, 1384, 1373, 1292, 1085, 908, 835, 730, 468 cm^{-1} ; **HRMS (ESI)**: calcd. for $[\text{C}_{33}\text{H}_{31}\text{CoIO}_2]^+$, $[\text{M}-\text{CO}-\text{I}]^+$: 645.0701; found: 645.0702; **mp**: a sample was heated over 410 $^\circ\text{C}$, no change was observed; **$[\alpha]_D^{20}$** : - 29.5 (c = 1.00, CHCl_3).

Cobalt complex **Co4**

In an N_2 -filled glovebox, a flame-dried Schlenk tube was charged with $\text{Co}_2(\text{CO})_8$ (63.2 mg, 185 μmol , 0.55 equiv.). A solution of **L4** (150 mg, 336 μmol , 1.00 equiv.) in dry DCM (6.90 mL) was added. The Schlenk tube was connected to a Schlenk line for CO evolution and stirred at 37 $^\circ\text{C}$ for 6 h. The volatiles were evaporated by Schlenk technique. A solution of

iodine (46.9 mg, 185 μmol , 0.550 equiv.) in dry degassed Et_2O (4.60 mL) was added to the black residue. The reaction vessel was connected to a Schlenk line to release carbon monoxide and the dark violet mixture was stirred at room temperature for 1 h. All volatiles were evaporated and the residue was purified by column chromatography on silica gel (gradient: DCM/pentane = 0% $\rightarrow$ 50%). The dark violet fractions were collected and concentrated under reduced pressure to obtain 116 mg (147 μmol , 44% yield) of the desired product as a black solid. The analytical data match literature values.³ $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.86 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.36 (s, 1H), 7.24 (s, 1H), 7.16 – 7.05 (m, 3H), 6.98 (d, J = 8.4 Hz, 1H), 4.12 (s, 3H), 4.09 (d, J = 16.2 Hz, 1H), 3.98 (s, 3H), 3.82 (d, J = 14.2 Hz, 1H), 3.68 (d, J = 14.2 Hz, 1H), 2.64 – 2.57 (m, 4H), 2.34 (s, 3H), 2.24 (s, 3H) ppm.

Figure 4: X-Ray Structure of **Co4** (CCDC: 1898843).

Cobalt complex **Co5**

In an N_2 -filled glovebox, a flame dried Schlenk tube was charged with $\text{Co}_2(\text{CO})_8$ (22.0 mg, 61.0 μmol , 0.55 equiv.). A solution of **L5** (53.0 mg, 111 μmol , 1.00 equiv.) in dry DCM (2.30 mL) was added. The Schlenk tube was connected to a Schlenk line for CO evolution and stirred at 37 $^\circ\text{C}$ for 6 h. The resulting solution was evaporated by Schlenk technique. A solution of iodine (15.5 mg, 61.0 μmol , 0.55 equiv.) in dry degassed Et_2O (1.50 mL) was added to the solid black residue. The reaction vessel was connected to a Schlenk line to release carbon monoxide and the dark violet mixture was stirred at room temperature for 1 h. All volatiles were evaporated and the product was purified by column chromatography on silica gel (gradient: DCM/pentane = 0% $\rightarrow$ 50%). The dark violet fractions* were collected and concentrated under

*Some fractions also contained desilylated complex.

reduced pressure to obtain 20.0 mg (24.0 μmol , 22% yield) of the desired product as a black solid. **^1H NMR** (600 MHz, CDCl_3) δ = 7.88 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.45 (ddd, J = 7.9, 6.9, 1.0 Hz, 1H), 7.43 – 7.40 (m, 2H), 7.23 (s, 1H), 7.14 – 7.07 (m, 3H), 7.01 (d, J = 8.3 Hz, 1H), 5.64 (d, J = 1.7 Hz, 1H), 5.61 (d, J = 1.7 Hz, 1H), 4.14 (d, J = 15.9 Hz, 1H), 4.11 (s, 3H), 3.96 (s, 3H) 3.85 (d, J = 13.8 Hz, 1H), 3.28 (d, J = 13.8 Hz, 1H), 2.73 (d, J = 15.9 Hz, 1H), 0.53 (s, 9H) ppm; **$^{13}\text{C}\{^1\text{H}\}$ NMR** (150 MHz, CDCl_3) δ = 197.6, 155.8, 154.7, 138.1, 136.9, 134.4, 133.9, 127.4, 127.23, 127.21, 127.1, 127.0, 126.9 (3 $\times$ C), 126.5, 124.64, 124.57, 124.3, 106.33, 106.27, 105.7, 102.3, 102.0, 101.1, 89.7, 55.7, 55.5, 25.4, 24.5, 0.4 ppm; **IR (ATR)**: $\tilde{\nu}$ = 3060, 2954, 2059, 1619, 1596, 1449, 1422, 1236, 1113, 1020, 909, 836 cm^{-1} ; **HRMS (ESI)**: calcd. for $[\text{C}_{32}\text{H}_{31}\text{CoIO}_2\text{Si}]^+$, $[\text{M}-\text{CO}-\text{I}]^+$: 661.0475; found: 661.0493; **$[\alpha]_D^{20}$** : - 109.9 (c = 0.30, CHCl_3).

Cobalt complex Co6

In an N_2 -filled glovebox, a flame-dried Schlenk tube was charged with $\text{Co}_2(\text{CO})_8$ (90.0 mg, 264 μmol , 0.55 equiv.). A solution of **L6** (214 mg, 479 μmol , 1.00 equiv.) in dry DCM (10.0 mL) was added. The Schlenk tube was connected to a Schlenk line for CO evolution and stirred at 37 $^\circ\text{C}$ for 6 h. The resulting solution was evaporated by Schlenk technique. A solution of iodine (66.9 mg, 264 μmol , 0.55 equiv.) in dry degassed Et_2O (6.00 mL) was added to the solid black residue. The reaction vessel was connected to a Schlenk line to release carbon monoxide and the dark violet mixture was stirred at room temperature for 1 h. All volatiles were evaporated and product was purified by silica gel column chromatography (gradient: DCM/pentane = 0% $\rightarrow$ 50%). The dark violet fractions were collected and concentrated under reduced pressure to obtain 155 mg (197 μmol , 41% yield) of the desired product as a black solid. **^1H NMR** (600 MHz, CDCl_3) δ = 7.88 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.23 (s, 1H), 7.15 – 7.07 (m, 3H), 7.00 (d, J = 8.5 Hz, 1H), 5.57 (s, 1H), 5.50 (s, 1H), 4.11 (s, 3H), 4.03 (d, J = 16.3 Hz, 1H), 3.96 (s, 3H), 3.78 (d, J = 13.9 Hz, 1H), 3.59 (hept, J = 7.0 Hz, 1H), 3.41 (d, J = 13.9 Hz, 1H), 2.75 (d, J = 16.3 Hz, 1H), 1.41 (d, J = 7.0 Hz, 3H), 1.39 (d, J = 7.0 Hz, 3H) ppm; **$^{13}\text{C}\{^1\text{H}\}$ NMR** (150 MHz, CDCl_3) δ = 198.3, 155.8, 154.7, 138.1, 137.0, 134.3, 133.9, 127.3, 127.23, 127.18, 127.1, 127.0, 126.9 (2 $\times$ C), 126.8, 126.7, 124.6, 124.5, 124.3, 110.4, 106.33, 106.27, 100.1, 98.3, 95.7, 93.9, 55.7, 55.5, 27.6, 25.7, 24.4, 24.0, 22.5 ppm; **IR (ATR)**: $\tilde{\nu}$ = 3062, 3003, 2961, 2054, 1596, 1449, 1423, 1329, 1296, 1239, 1166, 1113, 1019, 906 cm^{-1} ; **HRMS (APPI)**: calcd. for $[\text{C}_{32}\text{H}_{29}\text{CoIO}_2]^+$, $[\text{M}-\text{CO}-\text{I}]^+$: 631.0538; found: 631.0528; **$[\alpha]_D^{20}$** : - 155.3 (c = 0.20, CHCl_3).

Figure 5: X-Ray Structure of **Co6** (CCDC: 1898844).

Cobalt complex **Co7**

In a N₂ filled glovebox, a flame dried Schlenk tube was charged with Co₂(CO)₈ (129 mg, 358 μmol, 1.10 equiv.). A solution of **L6** (150 mg, 326 μmol, 1.00 equiv.) in dry DCM (5.00 mL) was added. CO gas was bubbled through the resulting solution for 5 min at 20 °C. The black reaction mixture was stirred at 37 °C for 6 h under CO atmosphere. All volatiles were evaporated by Schlenk technique. A solution of iodine (99.0 mg, 391 μmol, 1.20 equiv.) in dry degassed Et₂O (5.00 mL) was added solution to the black residue. The reaction vessel was connected to a Schlenk line to release carbon monoxide and the dark violet mixture was stirred at room temperature for 1 h. All volatiles were evaporated and the residue was purified by column chromatography on silica gel (gradient: DCM/pentane = 0% → 50%). The dark violet fractions were collected and concentrated under reduced pressure to obtain 210 mg (262 μmol, 80% yield) of the desired product as a black solid. ¹H NMR (500 MHz, CDCl₃) δ = 7.88 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.39 (s, 1H), 7.24 (s, 1H), 7.16 – 7.07 (m, 3H), 7.01 (d, *J* = 8.4 Hz, 1H), 5.56 (s, 1H), 5.45 (s, 1H), 4.18 (d, *J* = 16.3 Hz, 1H), 4.10 (s, 3H), 3.96 (s, 3H), 3.72 (d, *J* = 13.8 Hz, 1H), 3.49 (d, *J* = 13.8 Hz, 1H), 2.81 (d, *J* = 16.3 Hz, 1H), 1.54 (s, 9H) ppm; ¹³C{¹H} NMR (151 MHz, CDCl₃) δ = 197.9, 156.1, 154.7, 138.1, 137.0, 134.4, 133.9, 127.4, 127.20, 127.17, 127.1, 127.02, 127.0, 126.9, 126.81, 126.78, 124.7, 124.6, 124.2, 114.0, 106.3 (2×C), 100.2, 98.0, 94.5, 91.8, 55.7, 55.4, 32.5, 32.0, 25.7, 24.3 ppm; IR (ATR): $\tilde{\nu}$ = 3063, 2958, 2925, 2054, 1618, 1596, 1449, 1228, 1113, 1019, 906, 832, 729 cm⁻¹; HRMS (ESI): calcd. for, [C₃₃H₃₁CoIO₂]⁺, [M-CO-I]⁺: 645.0706, found 645.0725; [α]_D²⁰: - 104.4 (*c* = 0.30, CHCl₃).

Figure 6: X-Ray Structure of **Co7** (CCDC: 1898852).

Table 1: Optimisation table for complexation of **L7**:

Entry	Co ₂ (CO) ₈ [equiv.]	Atmosphere	I ₂ [equiv.]	Yield [%]
1	0.55	N ₂	0.55	40
2	0.55	CO	0.55	55
3	1.1	CO	1.2	80

N-Chloroamides

Figure 7: *N*-Chloroamides **1a-1g**.

N-Chloroamides **1a-1g** were synthesized following the procedure of Zhu *et al.*⁷

Styrenes, Acrylates and Other Vinyl Compounds

All styrenes, acrylates and other vinyl compounds were obtained from commercial suppliers. Liquid compounds with stabilizers were purified prior to their use by column chromatography on aluminium oxide (basic, Brockman 1, 50-200 μm , 60 Å). Solid compounds were used as supplied.

Asymmetric Co(III) Catalyzed Reaction

General Procedure for Optimization Table

Scheme 2: Reaction procedure for optimizing the conditions.

Cobalt catalyst (5.00 μmol, 10.0 mol%) was loaded into a flame dried vessel under air. Inside an N_2 -filled glovebox, the respective base (60.0 μmol, 1.20 equiv.), silver triflate (2.57 mg, 10.0 μmol, 20.0 mol%) and the respective solvent (250 μL) were added. The tube was sealed with a septum and the suspension was stirred at 20 °C for 5 min. Styrene (8.62 μL, 75.0 μmol, 1.50 equiv.) and a solution of *N*-chlorobenzamide (7.78 mg, 50.0 μmol, 1.00 equiv.) in the respective solvent (250 μL) were added and the resulting brown mixture was stirred for 18 h at 40 °C in the absence of light. The reaction was then quenched by addition of AcOH (100 μL) and EtOAc (500 μL), stirred for 15 min at 20 °C, and subsequently filtered through a pad of silica gel *in vacuo*. The resulting crude mixture was analyzed by quantitative NMR with CH_2Br_2 as the internal standard. For *er* determination, the crude mixture was purified by column chromatography on silica gel (eluent pentane/EtOAc 15% → 25%) and analyzed by HPLC using a chiral stationary phase (Chiralpak ID, 4.6 x 250 mm; 20% *i*-PrOH/hexane, 1.0 mL/min, 254 nm).

General Procedure A (5.00 mol% Catalyst Loading)

Scheme 3: Conditions for general procedure A.

Cobalt catalyst **Co7** (8.00 mg, 10.0 μmol , 5.00 mol%) was loaded into a flame-dried reaction vessel. In N_2 -filled glovebox, caesium pivalate (56.2 mg, 240 μmol , 1.20 equiv.) and silver triflate (5.14 mg, 20.0 μmol , 10.0 mol%) were added. The reaction vessel was sealed with a septum and dry, degassed HFIP (1.00 mL) was added. The resulting mixture was stirred at 20 $^\circ\text{C}$ for 5 min. Then, the respective vinyl (300 μmol , 1.50 equiv.) and a solution of the respective *N*-chloroamide (200 μmol , 1.00 equiv.) in HFIP (1.00 mL) were added. The reaction mixture was stirred at 40 $^\circ\text{C}$ for 18 h in the absence of light. It was then quenched by addition of AcOH (0.200 mL) and EtOAc (1.00 mL). The crude reaction mixture was filtered through a pad of silica gel, all volatiles were evaporated and the residue was purified by column chromatography on silica gel (pentane/EtOAc 15% $\rightarrow$ 25%).

General Procedure B (5.00 mol% Catalyst Loading, Solid Reactant)

Scheme 4: Conditions for general procedure B.

Cobalt catalyst **Co7** (8.00 mg, 10.0 μmol , 5.00 mol%) was loaded into a flame-dried reaction vessel. In an N_2 -filled glovebox, caesium pivalate (56.2 mg, 240 μmol , 1.20 equiv.) and silver triflate (5.14 mg, 20.0 μmol , 10.0 mol%) were added. The reaction vessel was sealed with a septum and dry, degassed HFIP (1.00 mL) was added. The resulting mixture was stirred at 20 $^\circ\text{C}$ for 5 min. Then, HFIP (1.00 mL), the respective vinyl (300 μmol , 1.50 equiv.) and the respective solid *N*-chloroamide (200 μmol , 1.00 equiv.) were added. The reaction mixture was stirred at 40 $^\circ\text{C}$ for 18 h in the absence of light. It was then quenched by addition of AcOH (0.200 mL) and EtOAc (1.00 mL). The crude reaction mixture was filtered through a pad of silica gel, all volatiles were evaporated and the residue was purified by column chromatography on silica gel (gradient: EtOAc/pentane = 15% $\rightarrow$ 25%).

General Procedure C (10.0 mol% Catalyst Loading)

Scheme 5: Conditions for general procedure C.

Cobalt catalyst **Co7** (16.0 mg, 20.0 μmol , 10.0 mol%) was loaded in a flame-dried reaction vessel. In an N_2 -filled glovebox, caesium pivalate (56.2 mg, 240 μmol , 1.20 equiv.) and silver triflate (10.3 mg, 40.0 μmol , 20.0 mol%) were added. The reaction vessel was sealed with a septum and dry, degassed HFIP (1.00 mL) was added. The resulting mixture was stirred at 20 $^\circ\text{C}$ for 5 min. Then, the respective vinyl (300 μmol , 1.50 equiv.) and a solution of the respective *N*-chloroamide (200 μmol , 1.00 equiv.) in HFIP (1.00 mL) were added. The reaction mixture was stirred at 40 $^\circ\text{C}$ for 18 h in the absence of light. It was then quenched by addition of AcOH (0.200 mL) and EtOAc (1.00 mL). The crude reaction mixture was filtered through a pad of silica gel, all volatiles were evaporated and the residue was purified by column chromatography on silica gel (pentane/EtOAc = 15% $\rightarrow$ 25%).

Racemic reaction

The racemic samples for enantioenriched dihydroisoquinolinones were obtained by the procedure of Zhu *et al.* utilizing $\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$.⁸

(-)-(S)-3-phenyl-3,4-dihydroisoquinolin-1(2H)-one (3aa)

General Procedure A. Yield: 87% (39.0 mg, 175 μmol), white solid. The spectra match with the literature values⁹. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ = 8.11 (dd, J = 7.7, 1.4 Hz, 1H), 7.46 (td, J = 7.5, 1.5 Hz, 1H), 7.43 – 7.33 (m, 6H), 7.20 (d, J = 7.5 Hz, 1H), 6.09 (s, 1H), 4.89 (dd, J = 11.0, 4.8 Hz, 1H), 3.21 (dd, J = 15.7, 11.0 Hz, 1H), 3.13 (dd, J = 15.7, 4.8 Hz, 1H) ppm; **R_f** : 0.43 (hexane/EtOAc = 1/1); **$[\alpha]_D^{20}$** -161.0 (c = 1.00, CHCl_3); **Chiral HPLC**: Chiralpak ID, 4.6 x 250 mm; 20% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (minor) = 18.6 min, tr (major) = 20.1 min, 99.6/0.4 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.635	MM	0.4894	36.94972	1.25841	0.4058
2	20.108	BB	0.4946	9069.29102	276.54721	99.5942

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.256	BB	0.4647	1482.02771	49.02868	49.7024
2	20.140	BB	0.4631	1499.77356	49.83626	50.2976

(-)-(S)-6-Methoxy-3-phenyl-3,4-dihydroisoquinolin-1(2H)-one (3ba)

General Procedure B. 10 mol% **Co7** and 20 mol% AgOTf loadings were used. Yield: 61% (31.2 mg, 123 μ mol), brown solid. The spectra match with the literature values⁹. **¹H NMR** (400 MHz, CDCl₃) δ = 8.06 (d, J = 8.6, 1H), 7.41 – 7.29 (m, 5H), 6.87 (dd, J = 8.6, 2.2 Hz, 1H), 6.66 (d, J = 1.8 Hz, 1H), 6.15 (s, 1H), 4.83 (dd, J = 10.5, 5.2 Hz, 1H), 3.83 (s, 3H), 3.16 (dd, J = 15.7, 10.5 Hz, 1H), 3.08 (dd, J = 15.7, 5.2 Hz, 1H) ppm; ***R*_f**: 0.40 (CHCl₃/MeOH 40:1); [α]_D²⁰: -152 (c = 1.00,

CHCl₃); **Chiral HPLC**: Chiralpak IA, 4.6 x 250 mm; 30% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (minor) = 12.9 min, tr (major) = 16.4 min, 98.9/1.1 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.916	MM	0.6295	100.18176	2.65222	1.0579
2	16.395	MM	0.5370	9369.50195	290.80994	98.9421

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.862	MM	0.4336	3162.65186	121.57381	50.2993
2	16.451	MM	0.5374	3125.01563	96.91401	49.7007

(–)-(S)-6-Methyl-3-phenyl-3,4-dihydroisoquinolin-1(2H)-one (3ca)

General Procedure A. Yield: 63% (30.0 mg, 126 μmol), white solid. The spectra match with the literature values⁹. **¹H NMR** (400 MHz, CDCl₃) δ = 8.00 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.30 (m, 5H), 7.18 (d, *J* = 7.9 Hz, 1H), 6.99 (s, 1H), 6.01 (s, 1H), 4.84 (dd, *J* = 10.8, 4.8 Hz, 1H), 3.16 (dd, *J* = 15.6, 10.8 Hz, 1H), 3.08 (dd, *J* = 15.6, 4.8 Hz, 1H), 2.38 (s, 3H) ppm; ***R*_f**: 0.30 (hexane/EtOAc = 2/1); **[α]_D²⁰**: -163.2 (*c* = 1.00, CHCl₃); **Chiral HPLC**: Chiralpak ID, 4.6 x 250 mm; 20% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (minor) = 24.1 min, tr (major) = 28.4 min, 98.7/1.3 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.195	MM	1.0914	20.62240	3.14936e-1	1.2663
2	28.368	BB	0.7522	1607.93311	32.00111	98.7337

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.642	BB	0.7183	743.46063	13.84928	49.5041
2	28.550	BB	0.6928	758.35571	15.23226	50.4959

(-)-(S)-7-Methyl-3-phenyl-3,4-dihydroisoquinolin-1(2H)-one (3da)

General Procedure A. Yield: 73% (34.6 mg, 146 μ mol), white solid. The spectra match with the literature values⁹. **¹H NMR** (400 MHz, CDCl₃) δ = 7.94 (m, 1H), 7.41 – 7.30 (m, 5H), 7.27 (dd, J = 7.7, 1.1 Hz, 1H), 7.07 (d, J = 7.7 Hz, 1H), 6.06 (s, 1H), 4.83 (dd, J = 10.5, 5.3 Hz, 1H), 3.15 (dd, J = 15.7, 10.5 Hz, 1H), 3.10 (dd, J = 15.7, 5.3 Hz, 1H), 2.39 (s, 3H) ppm; ***R*_f**: 0.30 (hexane/EtOAc = 2/1); **$[\alpha]_D^{20}$** : -175.3 (c = 1.00, CHCl₃); Chiral HPLC: Chiralpak IA, 4.6 x 250 mm; 10% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (major) = 11.9 min, tr (minor) = 13.7 min, 99.6/0.4 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.971	BB	0.3114	3959.29175	185.24413	99.5768
2	13.794	MM	0.3470	16.82598	8.08053e-1	0.4232

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.002	BB	0.3217	563.57397	25.71541	50.4299
2	13.712	BB	0.3597	553.96527	22.61925	49.5701

X-Ray structure of **3da** (CCDC No: 1898858).

(-)-(S)-6-Bromo-3-phenyl-3,4-dihydroisoquinolin-1(2H)-one (3ea)

General Procedure B. Yield: 89% (54.0 mg, 179 μ mol), white solid. The spectra match with the literature values⁹. ¹H NMR (400 MHz, CDCl₃) δ = 7.93 (d, J = 8.2 Hz, 1H), 7.51 (dd, J = 8.2, 1.4 Hz, 1H), 7.44 – 7.33 (m, 6H), 6.11 (s, 1H), 4.92 (dd, J = 10.7, 4.8 Hz, 1H), 3.19 (dd, J = 15.9, 10.7 Hz, 1H), 3.11 (dd, J = 15.9, 4.8 Hz, 1H) ppm; R_f : 0.30 (hexane/EtOAc = 2/1); $[\alpha]_D^{20}$: -113.5 (c = 1.00, CHCl₃); Chiral HPLC: Chiralpak ID, 4.6 x 250 mm; 30% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (minor) = 14.9 min, tr (major) = 17.7 min, 98.7/1.3 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.964	MM	0.7389	60.73653	1.36993	1.2821
2	17.777	MM	0.6252	4676.41406	124.67016	98.7179

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.828	BB	0.4944	2143.42725	64.05936	50.3932
2	17.869	BB	0.5477	2109.97778	57.82320	49.6068

(-)-(S)-6-Chloro-3-phenyl-3,4-dihydroisoquinolin-1(2H)-one (3fa)

General Procedure B. The spectra match with the literature values⁹. Yield: 82% (42.1 mg, 163 μ mol), white solid. **¹H NMR** (400 MHz, CDCl₃) δ = 8.02 (d, J = 8.3 Hz, 1H), 7.42 – 7.28 (m, 6H), 7.16 (s, 1H), 6.47 (br.s, 1H), 4.84 (dd, J = 9.6, 5.7 Hz, 1H), 3.16 (dd, J = 16.9, 9.6 Hz, 1H), 3.11 (dd, J = 16.9, 5.7 Hz, 1H) ppm; ***R*_f**: 0.30 (hexane/EtOAc = 2/1); **$[\alpha]_D^{20}$** : -126.8 (c = 1.00, CHCl₃); **Chiral HPLC**: Chiralpak ID, 4.6 x 250 mm; 20% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (minor) = 16.9 min, tr (major) = 20.1 min, 99.4/0.6 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.886	BB	0.3807	72.54469	2.30811	0.6087
2	20.056	BB	0.5769	1.18458e4	298.57205	99.3913

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.652	BB	0.4760	4564.64844	143.13995	50.0703
2	20.255	BB	0.5674	4551.83447	118.69341	49.9297

(-)-(S)-6-Fluoro-3-phenyl-3,4-dihydroisoquinolin-1(2H)-one (3ga)

General Procedure B. Yield: 87% (41.9 mg, 174 μ mol), white solid. The spectra match with the literature values⁹. **¹H NMR** (400 MHz, CDCl₃) δ = 8.14 (dd, J = 8.6, 5.8 Hz, 1H), 7.43 – 7.33 (m, 5H), 7.06 (dt, J = 8.6, 2.3 Hz, 1H), 6.90 (dd, J = 8.7, 2.1 Hz, 1H), 5.94 (s, 1H), 4.87 (dd, J = 11.0, 4.8 Hz, 1H), 3.21 (dd, J = 15.9, 11.0 Hz, 1H), 3.12 (dd, J = 15.9, 4.8 Hz, 1H) ppm; **¹⁹F NMR** (376 MHz, CDCl₃) δ = -106.5 (td, J = 8.7, 5.8 Hz) ppm; **R_f** : 0.30 (hexane/EtOAc = 2/1); **$[\alpha]_D^{20}$** : -152.3 (c = 1.00, CHCl₃); Chiral HPLC: Chiralpak ID, 4.6 x 250 mm; 20% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (minor) = 14.9 min, tr (major) = 16.6 min, 99.3/0.7 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.912	MM	0.5072	11.65764	3.83080e-1	0.6734
2	16.599	BB	0.4077	1719.42188	64.35673	99.3266

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.773	BB	0.3893	477.97998	18.63434	49.6491
2	16.644	BB	0.4086	484.73721	18.09230	50.3509

(-)-(S)-3-(4-methoxyphenyl)-3,4-dihydroisoquinolin-1(2H)-one (3ab)

General Procedure A. Yield: 87% (44.0 mg, 174 μ mol), white solid. The spectra match with the literature values⁹. **¹H NMR** (400 MHz, CDCl₃) δ = 8.11 (dd, J = 7.6, 1.4 Hz, 1H), 7.46 (td, J = 7.5, 1.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 8.7 Hz, 2H), 7.19 (d, J = 7.4 Hz, 1H), 6.91 (d, J = 8.6 Hz, 2H), 6.02 (s, 1H), 4.81 (dd, J = 11.4, 4.5 Hz, 1H), 3.82 (s, 3H), 3.19 (dd, J = 15.7, 11.4 Hz, 1H), 3.07 (dd, J = 15.7, 4.5 Hz, 1H) ppm; ***R*_f**: 0.27 (hexane/EtOAc = 1/1); **$[\alpha]_D^{20}$** : -108.2 (c = 1.00, CHCl₃); **Chiral HPLC**: Chiralpak IB, 4.6 x 250 mm; 20% *i*-PrOH/hexane, 1.0 mL/min, 266 nm; tr (major) = 11.9 min, tr (minor) = 13.4 min, 99.5/0.5 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.916	MM	0.4281	2.40783e4	937.46393	99.5464
2	13.468	MM	0.2165	109.72580	6.04914	0.4536

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.857	MM	0.3534	4183.92822	197.29222	50.8945
2	13.379	MM	0.3854	4036.86328	174.55865	49.1055

(-)-(S)-3-(4-(*tert*-butyl)phenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ac)

General Procedure A. Yield: 81% (45.0 mg, 161 μ mol), white solid. The spectra match with the literature values⁹. **¹H NMR** (400 MHz, CDCl₃) δ = 8.13 (dd, J = 7.7, 1.4 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.44 – 7.31 (m, 5H), 7.19 (d, J = 7.6 Hz, 1H), 5.98 (s, 1H), 4.84 (dd, J = 11.4, 4.6 Hz, 1H), 3.21 (dd, J = 15.7, 11.4 Hz, 1H), 3.13 – 2.99 (m, 1H), 1.33 (s, 9H)

ppm; ***R*_f**: 0.23 (hexane/EtOAc = 1/1); **$[\alpha]_D^{20}$** : -111.7 (c = 1.00, CHCl₃); **Chiral HPLC**: Chiralpak IA, 4.6 x 250 mm; 20% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (minor) = 7.1 min, tr (major) = 8.5 min, 98.1/1.9 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.101	BB	0.2599	107.34383	5.74767	1.9387
2	8.538	VB	0.2507	5429.61279	322.10098	98.0613

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.743	BB	0.2012	3929.55762	291.63528	50.0759
2	8.384	BB	0.2405	3917.64014	242.42659	49.9241

(-)-(S)-3-(p-tolyl)-3,4-dihydroisoquinolin-1(2H)-one (3ad)

General Procedure A. Yield: 88% (42.0 mg, 177 μ mol), white solid. The spectra match with the literature values⁹. **¹H NMR** (400 MHz, CDCl₃) δ = 8.12 (dd, J = 7.8, 1.4 Hz, 1H), 7.46 (td, J = 7.5, 1.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.22 – 7.16 (m, 3H), 6.08 (s, 1H), 4.82 (dd, J = 11.2, 4.7 Hz, 1H), 3.19 (dd, J = 15.7, 11.2 Hz, 1H), 3.09 (dd, J = 15.7, 4.7 Hz, 1H), 2.36 (s, 3H) ppm; **R_f**: 0.42 (hexane/EtOAc = 1/1); **[α]_D²⁰**: -154.5 (c = 1.00, CHCl₃); **Chiral HPLC**:

Chiralpak ID, 4.6 x 250 mm; 20% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; (minor) = 17.3 min, tr (major) = 24.8 min, tr 99.5/0.5 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.316	BB	0.3738	50.18780	1.73348	0.4890
2	24.846	BB	0.5871	1.02127e4	239.68126	99.5110

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.144	BB	0.3700	3993.09424	161.77075	49.4146
2	25.106	BB	0.6087	4087.70972	102.17645	50.5854

(-)-(S)-3-(*m*-tolyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ae)

General Procedure A. Yield: 88% (42.0 mg, 177 μ mol), pale yellow solid.

The spectra match with the literature values⁹. **¹H NMR** (400 MHz, CDCl₃)

δ = 8.12 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.46 (td, *J* = 7.4, 1.5 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.23 – 7.12 (m, 4H), 6.11 (s, 1H), 4.82 (dd, *J* = 11.3, 4.7 Hz, 1H), 3.20 (dd, *J* = 15.7, 11.2 Hz, 1H), 3.10 (dd, *J* = 15.8, 4.7 Hz, 1H),

2.37 (s, 3H) ppm; **R_f**: 0.53 (hexane/EtOAc = 1/1); **[α]_D²⁰**: -154.8 (c = 1.00, CHCl₃); **Chiral HPLC**: Chiralpak IC, 4.6 x 250 mm; 20% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (major) = 15.6 min, tr (minor) = 17.8 min, 99.6/0.4 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.699	BB	0.3492	1.11487e4	486.68979	99.6092
2	17.800	BB	0.3144	43.74466	1.68782	0.3908

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.567	BB	0.3479	7756.94287	345.48438	50.2020
2	17.287	BB	0.3893	7694.51953	308.21170	49.7980

(-)-(S)-3-(4-fluorophenyl)-3,4-dihydroisoquinolin-1(2H)-one (3af)

General Procedure A. Yield: 85% (41.0 mg, 170 μ mol), white solid. The spectra match with the literature values⁹. **¹H NMR** (400 MHz, CDCl₃) δ = 8.11 (dd, J = 7.8, 1.4 Hz, 1H), 7.47 (td, J = 7.5, 1.4 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.18 (d, J = 7.5 Hz, 1H), 7.11 – 7.01 (m, 2H), 6.13 (s, 1H), 4.86 (dd, J = 10.3, 5.3 Hz, 1H), 3.24 – 3.07 (m, 2H) ppm; **¹⁹F{¹H} NMR** (376 MHz, CDCl₃) δ = -113.4 ppm; ***R*_f**: 0.37 (hexane/EtOAc = 1/1); **$[\alpha]_D^{20}$** : -164.8 (c = 1.00, CHCl₃); **Chiral HPLC**: Chiralpak IA, 4.6 x 250 mm; 20% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (minor) = 9.3 min, tr (major) = 10.8 min, 99.5/0.5 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.305	BB	0.2506	31.36759	1.75449	0.4932
2	10.882	BB	0.2941	6328.47021	315.36829	99.5068

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.343	BB	0.2600	1555.59143	87.23252	50.5125
2	11.014	BB	0.2980	1524.02478	74.70451	49.4875

(-)-methyl (S)-1-oxo-1,2,3,4-tetrahydroisoquinoline-3-carboxylate (**3ag**)

General Procedure C. Yield: 68% (28.0 mg, 136 μ mol), white solid. The spectra match with the literature values.⁸ **¹H NMR** (400 MHz, CDCl₃) δ = 8.08 (dd, J = 7.7, 1.4 Hz, 1H), 7.47 (td, J = 7.5, 1.5 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.24 (d, J = 7.5 Hz, 1H), 6.48 (s, 1H), 4.41 (ddd, J = 10.1, 5.2, 2.0 Hz, 1H), 3.80 (s, 3H), 3.33 (dd, J = 15.7, 5.1 Hz, 1H), 3.21 (dd, J = 15.7, 10.0 Hz, 1H) ppm; ***R*_f**: 0.17 (hexane/EtOAc = 1/1); **[α]_D²⁰**: -62.6 (c = 1.00, CHCl₃); **Chiral HPLC**: Chiralpak IA, 4.6 x 250 mm; 20% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (major) = 10.7 min, tr (minor) = 11.9 min, 90.8/9.2 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.729	BB	0.3204	336.58124	15.31702	90.8362
2	11.922	BB	0.3041	33.95538	1.48872	9.1638

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.670	MM	0.3478	2732.14868	130.94331	49.6601
2	11.755	MM	0.3824	2769.54419	120.70953	50.3399

(-)-tert-butyl (S)-1-oxo-1,2,3,4-tetrahydroisoquinoline-3-carboxylate (3ah)

General Procedure A. Yield: 75% (37.0 mg, 150 μ mol), white solid.

^1H NMR (400 MHz, CDCl_3) δ = 8.07 (dd, J = 7.7, 1.4 Hz, 1H), 7.46 (td, J = 7.5, 1.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 7.5 Hz, 1H), 6.35 (s, 1H), 4.27 (ddd, J = 10.7, 4.9, 1.7 Hz, 1H), 3.26 (dd, J = 15.7, 5.0 Hz, 1H),

3.14 (dd, J = 15.6, 10.7 Hz, 1H), 1.47 (s, 9H) ppm; **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, CDCl_3) δ = 169.4,

165.3, 136.6, 132.6, 128.7, 128.3, 127.6, 127.5, 83.3, 53.8, 31.7, 28.1 ppm; **IR (ATR)**: 3225, 2976,

2930, 1731, 1669, 1605, 1464, 1392, 1368, 1323, 1310, 1244, 1148, 1007, 842, 742, 568 cm^{-1} ;

HRMS (ESI): calcd. for $[\text{C}_{14}\text{H}_{18}\text{NO}_3]^+$, $[\text{M}+\text{H}]^+$: 248.1281; found: 248.1284; **R_f** : 0.36

(hexane/EtOAc = 1/1); **$[\alpha]_D^{20}$** : -75.5 (c = 1.00, CHCl_3); **Chiral HPLC**: Chiralpak ID, 4.6 x 250 mm;

20% *i*-PrOH/hexane, 1.0 mL/min, 274 nm; tr (major) = 18.7 min, tr (minor) = 23.3 min, 98.9/1.1 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.752	BB	0.4555	2292.48926	76.97083	98.8727
2	23.352	MM	0.5352	26.13833	8.13951e-1	1.1273

(-)-(S)-3-(morpholine-4-carbonyl)-3,4-dihydroisoquinolin-1(2H)-one (**3ai**)

With catalyst **Co7**: General Procedure C. Yield: 44% (23.0 mg, 88.0 μ mol), white solid. **¹H NMR** (400 MHz, CDCl₃) δ = 8.05 (dd, J = 7.7, 1.4 Hz, 1H), 7.46 (td, J = 7.5, 1.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 7.5 Hz, 1H), 6.75 (s, 1H), 4.67 (dd, J = 11.4, 4.1 Hz, 1H), 3.79 – 3.66 (m, 5H), 3.63 – 3.47 (m, 3H), 3.19 (dd, J = 15.5, 11.4 Hz, 1H), 3.03 (dd, J = 15.5, 4.1 Hz, 1H) ppm; **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 168.2, 165.3, 136.2, 132.6, 129.0, 128.3, 127.9, 127.3, 66.9, 66.6, 51.8, 46.1, 42.9, 32.2 ppm; **IR (ATR)**: 3276, 2962, 2921, 2854, 1665, 1606, 1463, 1434, 1270, 1244, 1113, 1038, 748, 568 cm⁻¹; **HRMS (ESI)**: calcd. for [C₁₄H₁₇N₂O₃]⁺, [M+H]⁺: 261.1234; found: 261.1231; **R_f**: 0.04 (hexane/EtOAc = 1/1); **[α]_D²⁰**: -154.3 (c = 0.50, CHCl₃); **Chiral HPLC**: Chiralpak IA, 4.6 x 250 mm; 30% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (major) = 21.4 min, tr (minor) = 27.6 min, 99.5/0.5 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.496	MM	1.7169	5120.15186	49.70392	99.5275
2	27.655	MM	0.7420	24.30559	5.45931e-1	0.4725

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.748	MM	1.7566	6081.45654	57.70035	49.7869
2	27.297	MM	1.9100	6133.51221	53.52092	50.2131

With catalyst **Co6**: General Procedure C. The amount of alkene was increased to 85.0 mg, 0.60 mmol, 3.0 equiv. Yield: 74% (38.5 mg, 148 μ mol), white solid. ; $[\alpha]_D^{20}$: -151.0 (c = 1.00, CHCl_3).

Chiral HPLC: Chiralpak IF, 4.6 x 250 mm; 50% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (major) = 36.9 min, tr (minor) = 52.6 min, 93.2/6.8 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.933	MM	3.1758	3342.76538	17.54282	93.1865
2	52.576	MM	3.6862	244.41191	1.10507	6.8135

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.812	MM	3.1323	3678.53906	19.57321	50.0604
2	50.631	MM	3.8431	3669.66064	15.91445	49.9396

(+)-(R)-2-(1-oxo-1,2,3,4-tetrahydroisoquinolin-3-yl)isoindoline-1,3-dione (3aj)

General procedure A. *N*-Vinyl phthalimide was added to the reaction mixture as a solid. Yield: 68% (40.0 mg, 137 μ mol), white solid. **¹H NMR** (400 MHz, CDCl₃) δ = 8.06 (d, *J* = 7.7, 0.9 Hz, 1H), 7.79-7.73 (m, 2H), 7.71-7.65 (m, 2H), 7.50 (td, *J* = 7.5, 1.3 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 6.91 (s, 1H), 6.03-5.97 (m, 1H), 3.60 (dd, *J* = 16.6, 4.5 Hz, 1H), 3.51 (dd, *J* = 16.6, 6.5 Hz, 1H) ppm; **¹³C{¹H} NMR** δ = (101 MHz, CDCl₃) 167.4, 165.6, 136.5, 134.5, 132.7, 131.6, 127.9, 127.8, 127.4, 127.3, 123.7, 58.2, 31.4 ppm; **IR (ATR)** 3317, 3061, 2959, 1776, 1713, 1672, 1468, 1387, 1364, 1323, 1284, 1111, 742, 718 cm⁻¹; **HRMS (ESI/QTOF)** calcd. for [C₁₇H₁₂N₂NaO₃]⁺, [M+Na]⁺: 315.0740; found: 315.0745; **R_f**: 0.45

(hexane/EtOAc = 1/2); $[\alpha]_D^{20}$: -151.7 ($c = 1.00$, CHCl_3); **Chiral HPLC**: Chiralpak IB, 4.6 x 250 mm; 40% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (major) = 12.0 min, tr (minor) = 14.5 min, 98.8/1.2 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.007	MM	0.6004	1686.64880	46.81775	98.8405
2	14.549	MM	1.1710	19.78591	2.81601e-1	1.1595

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.091	MM	0.6075	1217.20422	33.39114	50.3636
2	14.664	MM	1.1298	1199.62830	17.69657	49.6364

(-)-(R)-3-butyl-3,4-dihydroisoquinolin-1(2H)-one (3ak)

General Procedure A. Yield: 86% (35.0 mg, 172 μmol), off-white solid. The spectra match with the literature values¹⁰. **^1H NMR** (400 MHz, CDCl_3) δ = 8.05 (d, $J = 7.6$, 1H), 7.44 (t, $J = 7.6$, 1H), 7.33 (d, $J = 7.6$, 1H), 7.20 (d, $J = 7.5$, 1H), 6.09 (s, 1H), 3.73 – 3.63 (m, 1H), 2.97 (dd, $J = 15.6$, 4.3, 1H), 2.81 (dd, $J = 15.6$, 10.4, 1H), 1.60 (t, $J = 7.2$, 7.2, 2H), 1.37 (s, 4H), 0.92 (t, $J = 6.7$, 3H) ppm; **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, CDCl_3) δ = 166.4, 138.3, 132.4, 128.7, 128.1, 127.6, 127.2, 51.5, 35.2, 34.5, 27.7, 22.6, 14.1 ppm;

R_f: 0.33 (hexane/EtOAc = 2/1); [α]_D²⁰: -33.5 (*c* = 1.00, CHCl₃); Chiral HPLC: Chiralpak IB, 4.6 x 250 mm; 10% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; *tr* (minor) = 7.7 min, *tr* (major) = 8.2 min, 95.5/4.5 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.705	MM	0.1904	239.76312	20.98948	4.4989
2	8.222	MM	0.2430	5089.66064	349.04739	95.5011

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.708	BV	0.2131	3242.24048	234.81270	49.8747
2	8.357	VB	0.2193	3258.53223	219.34908	50.1253

(-)-(R)-3-hexyl-3,4-dihydroisoquinolin-1(2H)-one (3aI)

General Procedure A. Yield: 74% (34.3 mg, 148 μ mol), off-white solid.

The spectra match with the literature values.⁸ ¹H NMR (400 MHz, CDCl₃) δ = 8.04 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.42 (dt, *J* = 7.5, 1.3 Hz, 1H),

7.32 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.53 (s, 1H), 3.72 – 3.63 (m, 1H), 2.96 (dd, *J* = 15.6, 4.4 Hz, 1H), 2.79 (dd, *J* = 15.6, 10.3 Hz, 1H), 1.68 – 1.52 (m, 2H), 1.47 – 1.22 (m, 8H), 0.87 (t, *J* = 6.7 Hz, 3H) ppm; **R_f**: 0.40 (hexane/EtOAc = 1/1); [α]_D²⁰: -49.0 (*c* = 1.00, CHCl₃); Chiral HPLC:

Chiralpak IB, 4.6 x 250 mm; 10% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (minor) = 7.2 min, tr (major) = 7.9 min, 94.7/5.3 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.217	BV	0.1865	184.71696	14.71328	5.2937
2	7.882	VB	0.2069	3304.63574	236.62422	94.7063

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.165	MM	0.2045	1123.16492	91.55611	50.7639
2	7.931	MM	0.2220	1089.36230	81.76936	49.2361

(–)-(S)-3-(2-(benzyloxy)ethyl)-3,4-dihydroisoquinolin-1(2H)-one (3am)

General Procedure C. Yield: 78% (44.0 mg, 156 μ mol), off-white solid.

^1H NMR (400 MHz, CDCl_3) δ = 8.06 (d, J = 7.6, 1H), 7.43 (t, J = 7.4, 1H), 7.40 – 7.28 (m, 6H), 7.17 (d, J = 7.4, 1H), 6.68 (s, 1H), 4.55 (s, 2H), 3.95 – 3.86 (m, 1H), 3.71 – 3.56 (m, 2H), 2.98 – 2.81 (m, 2H), 2.03 – 1.89 (m, 1H), 1.87 – 1.76 (m, 1H) ppm; **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, CDCl_3) δ = 166.5 (see HMBC), 138.1, 137.9, 132.3, 128.7, 128.1, 128.0, 127.9, 127.5, 127.2, 73.5, 68.0, 50.9, 35.2, 34.9 ppm; **IR (ATR)**: 3201, 3064, 2918, 2861, 1664,

1605, 1578, 1465, 1398, 1341, 1092, 744, 698 cm^{-1} ; R_f : 0.12 (hexane/EtOAc = 2/1); $[\alpha]_D^{20}$: -35.0 (c = 1.00, CHCl_3); **HRMS (ESI)**: calcd. for $[\text{C}_{18}\text{H}_{20}\text{NO}_2]^+$, $[\text{M}+\text{H}]^+$: 282.1489; found: 282.1490; **Chiral HPLC**: Chiralpak IA, 4.6 x 250 mm; 20% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (major) = 8.5 min, tr (minor) = 9.5 min, 92.8/7.2 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.548	BB	0.2500	2248.19629	132.48329	92.8169
2	9.460	BB	0.2691	173.98825	10.09525	7.1831

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.571	MM	0.2918	194.30489	11.09902	50.7945
2	9.453	MM	0.3252	188.22621	9.64654	49.2055

(-)-(S)-3-(2-hydroxyethyl)-3,4-dihydroisoquinolin-1(2H)-one (3an)

General Procedure C. Increased amount of CsOPiv (84.0 mg, 360 μmol , 1.80 equiv.) used. Yield: 49% (18.6 mg, 97.0 μmol), white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 8.02 (dd, J = 7.5, 0.9 Hz, 1H), 7.59 (s, 1H), 7.43 (td, J

= 7.5 Hz, 1.3 Hz, 1H), 7.33 (t, $J = 7.5$, 1H), 7.18 (d, $J = 7.5$ Hz, 1H), 4.04 – 3.89 (m, 2H), 3.89 – 3.81 (m, 1H), 3.74 (s, 1H), 2.93 (dd, $J = 15.6$, 5.1 Hz, 1H), 2.87 (dd, $J = 15.6$, 10.4 Hz, 1H), 1.98 – 1.87 (m, 1H), 1.83 – 1.74 (m, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) $\delta = 166.7$, 138.3, 132.4, 128.5, 128.0, 127.5, 127.2, 60.9, 51.4, 37.0, 34.9 ppm; IR (ATR): 3305, 2925, 2882, 1652, 1604, 1465, 1400, 1341, 1064, 1034, 745 cm^{-1} ; R_f : 0.60 (DCM/MeOH = 10/1); $[\alpha]_D^{20}$: -106.5 ($c = 1.00$, CHCl_3); HRMS (ESI/QTOF): calcd. for $[\text{C}_{11}\text{H}_{14}\text{NO}_2]^+$, $[\text{M}+\text{H}]^+$: 192.1019; found: 192.1012; Chiral HPLC: Chiralpak IC, 4.6 x 250 mm; 20% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (minor) = 36.6 min, tr (major) = 42.0 min, 98.1/1.9 er.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.623	MM	0.9457	76.20451	1.34305	1.9325
2	42.002	MM	1.1396	3867.07324	56.55775	98.0675

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.565	BB	0.7724	1341.36731	23.06903	49.9933
2	42.142	BB	0.8005	1341.72583	19.85131	50.0067

X-Ray structure of racemic **3an** (CCDC No: 1898854).

(-)-(R)-4-(2-hydroxyethyl)-3,4-dihydroisoquinolin-1(2H)-one (**3an'**)

General procedure C. Increased amount of CsOPiv (84.0 mg, 360 μ mol, 1.80 equiv.) used. Yield: 21% (8.0 mg, 42.0 μ mol), white solid. The spectra match with the literature values.¹¹ Absolute configuration determined by comparison with the reported $[\alpha]_D^{20}$ value.¹² **¹H NMR** (400 MHz, CDCl₃) δ = 8.06 (d, J = 7.6 Hz, 1H), 7.46 (td, J = 7.6 Hz, 1.3 Hz, 1H), 7.36 (td, J = 7.6, 1.0 Hz, 1H), 7.26 (d, J = 7.6 Hz, 1H), 6.56 – 6.43 (m, 1H), 3.80 – 3.69 (m, 2H), 3.68 – 3.61 (m, 1H), 3.47 – 3.40 (m, 1H), 3.17 – 3.09 (m, 1H), 2.00 – 1.86 (m, 3H) ppm; **R_f**: 0.50 (DCM/MeOH = 10/1); **$[\alpha]_D^{20}$** : -93.3 (c = 0.50, CHCl₃);

Chiral HPLC: Chiralpak IG, 4.6 x 250 mm; 20% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (major) = 13.2 min, tr (minor) = 14.8 min, 78.2/21.8 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.179	BB	0.4374	2131.45972	74.59124	78.2432
2	14.851	BB	0.4572	592.68628	18.82913	21.7568

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.187	BB	0.4351	1686.38513	60.14092	50.0028
2	14.811	BB	0.4750	1686.19775	54.49282	49.9972

(+)-(S)-3-Acetoxymethyl-3,4-dihydroisoquinolin-1(2H)-one (3ao)

General Procedure A. Yield: 77% (33.7 mg, 154 μ mol), white solid. The spectra match with the literature values.¹³ **¹H NMR** (400 MHz, CDCl₃) δ = 8.06 (dd, J = 7.7, 1.0 Hz, 1H), 7.45 (td, J = 7.5 Hz, J = 1.3 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 7.5 Hz, 1H), 6.62 (s, 1H), 4.25 (dd, J = 11.0, 4.3 Hz, 1H), 4.08 (dd, J = 11.0, 7.9 Hz, 1H), 4.04 – 3.96 (m, 1H), 3.04 (dd, J = 15.7, 4.8 Hz, 1H), 2.90 (dd, J = 15.7, 9.0 Hz, 1H), 2.07 (s, 3H) ppm; ***R*_f**: 0.40 (DCM/EtOAc = 2/1); **$[\alpha]_D^{20}$** : +3.63 (c = 1.00, CHCl₃); **Chiral HPLC**: Chiralpak IA, 4.6 x 250 mm; 30% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (major) = 6.9 min, tr (minor) = 8.3 min, 95.8/4.2 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.944	MM	0.2495	4389.61279	293.19315	95.8227
2	8.307	MM	0.3832	191.36317	8.32394	4.1773

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.058	BB	0.2264	1943.45068	125.66042	49.4715
2	8.359	BB	0.2676	1984.97217	109.44734	50.5285

X-Ray structure of **3ao** (CCDC No: 1898856).

(-)-(S,E)-3-(5-phenylpent-1-en-1-yl)-3,4-dihydroisoquinolin-1(2H)-one (**3ap**)

General procedure A. Yield: 76% (44.0 mg, 152 μ mol), white solid.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 8.07 (dd, J = 7.7, 0.8 Hz, 1H), 7.44 (td, J = 7.5 Hz, 1.3 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.22 – 7.12 (m, 4H), 6.08 (s, 1H), 5.74 (dt, J = 15.2, 6.7 Hz, 1H), 5.51 (ddt, J = 15.2, 7.3, 1.1 Hz, 1H), 4.25 – 4.17 (m, 1H), 3.00 (dd, J = 15.6, 4.8 Hz, 1H), 2.91 (dd, J = 15.6, 9.8 Hz, 1H), 2.58 (t, J = 7.6 Hz, 2H), 2.08 (q, J = 7.1 Hz, 2H), 1.70 (quintet, J = 7.6 Hz, 2H) ppm; **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, CDCl_3) δ = 166.2, 142.2, 137.8, 133.9, 132.4, 129.7, 128.6, 128.5, 128.4, 128.0, 127.5, 127.2, 125.9, 53.8, 35.3, 35.2, 31.7, 30.7 ppm; **IR (ATR)**: 3199, 3025, 2928, 1661, 1604, 1463, 1391, 1316, 1155, 967, 745, 699 cm^{-1} ; **R_f** = 0.60 (hexane/EtOAc = 1:2); **$[\alpha]_D^{20}$** : -34.9 (c = 1.00, CHCl_3); **HRMS (ESI/QTOF)**: calcd. for $[\text{C}_{20}\text{H}_{22}\text{NO}]^+$, $[\text{M}+\text{H}]^+$: 292.1696; found 292.1701; **Chiral HPLC**: Chiralpak IC, 4.6 x 250 mm; 30% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (major) = 18.7 min, tr (minor) = 26.7 min, 98.6/1.4 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.732	BB	0.4764	2905.75708	94.59905	98.5981
2	26.701	MM	0.7442	41.31579	9.25253e-1	1.4019

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.825	BB	0.4828	1218.48401	39.61681	50.3897
2	26.696	BB	0.6509	1199.63867	26.86788	49.6103

(-)-(S)-3-(6-methylhepta-1,5-dien-2-yl)-3,4-dihydroisoquinolin-1(2H)-one (3aq)

Cobalt catalyst **Co7** (16.0 mg, 20.0 μ mol, 10.0 mol%) was loaded into a flame-dried reaction vessel. In N_2 -filled glovebox, caesium pivalate (56.2 mg, 240 μ mol, 1.20 equiv.), caesium carbonate (32.6 mg, 0.10 mmol, 0.50 equiv.) and silver triflate (10.3 mg, 40.0 μ mol, 20.0 mol%) were added. The reaction vessel was sealed with a septum and dry, degassed HFIP (1.33 mL) was added. The resulting mixture was stirred at 20 °C for 5 min. Then, dry and degassed 1,2-dichloroethane (660 μ L), myrcene (600 μ mol, 3.00 equiv.) and solid *N*-chloroamide (200 μ mol, 1.00 equiv.) were added. The reaction mixture was stirred at 40 °C for 18 h in the absence of light. The crude reaction mixture was filtered through a pad of silica gel, all volatiles were evaporated and the residue was purified by column chromatography on silica gel (gradient: EtOAc/pentane = 0% $\rightarrow$ 50%). Yield: 73% (37.3 mg, 146 μ mol), yellow oil. **1H NMR** (400 MHz, $CDCl_3$) δ = 8.07 (dd, J = 7.7, 1.0 Hz, 1H), 7.45 (td, J = 7.5 Hz, 1.4 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.20 (d, J = 7.5 Hz, 1H), 5.81 (s, 1H), 5.15 (s, 1H), 5.13-5.07 (m, 1H), 5.01 (s, 1H), 4.23 (dd, J = 9.7, 5.4 Hz, 1H), 3.05 (dd, J = 15.7, 5.4 Hz, 1H), 2.99 (dd, J = 15.7, 9.7 Hz, 1H), 2.22-2.06 (m, 4H), 1.70 (s, 3H), 1.61 (s, 3H) ppm; **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) δ = 166.6, 148.4, 137.8, 132.7, 132.5, 128.6, 128.1, 127.5, 127.3, 123.4, 112.0, 56.3, 34.3, 32.9, 26.7, 25.8, 17.9 ppm; **IR (ATR)**: 3201, 3080, 2920, 1664, 1604, 1578, 1462, 1389, 1289, 1155, 901, 742, 529 cm^{-1} ; **R_f** : 0.5 (hexane/EtOAc = 1/2); **$[\alpha]_D^{20}$** : -108.2 (c = 1.00, $CHCl_3$); **HRMS (ESI/QTOF)**: calcd. for $[C_{17}H_{22}NO]^+$, $[M+H]^+$: 256.1696; found: 256.1705; **Chiral HPLC**: Chiralpak IC, 4.6 x 250 mm; 30% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (major) = 9.3 min, tr (minor) = 10.3 min, 99.5/0.5 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.317	MM	0.2359	3794.96924	268.09064	99.5379
2	10.205	MM	0.2841	17.61980	1.03354	0.4621

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.248	BB	0.2123	510.27451	37.12674	49.4128
2	10.039	BB	0.2330	522.40228	34.43539	50.5872

(-)-(4a*R*,10b*R*)-1,4a,5,10b-tetrahydrophenanthridin-6(2*H*)-one (3ar)

General Procedure A. Yield: 74% (29.0 mg, 147 μ mol), white solid. The spectra match with the literature values⁹. **¹H NMR** (400 MHz, CDCl₃) δ = 8.08 (dd, J = 7.8, 1.4 Hz, 1H), 7.49 (td, J = 7.5, 1.4 Hz, 1H), 7.36 (td, J = 7.5, 1.3 Hz, 1H), 7.29 – 7.21 (m, 1H), 6.08 – 5.98 (m, 1H), 5.82 – 5.74 (m, 2H), 4.31 – 4.21 (m, 1H), 3.00 – 2.87 (m, 1H), 2.27 – 2.18 (m, 2H), 2.07 – 1.90 (m, 1H), 1.75 – 1.65 (m, 1H) ppm; ***R***: 0.30 (hexane/EtOAc = 1/1); **$[\alpha]_D^{20}$** : -38.8 (c = 1.00, CHCl₃); **Chiral HPLC**: Chiralpak IA, 4.6 x 250 mm; 20% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (major) = 7.4 min, tr (minor) = 9.7 min, 86.5/13.5 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.421	BB	0.2106	4170.90088	288.69327	86.5464
2	9.754	BB	0.2728	648.36328	34.88499	13.4536

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.455	BB	0.2098	590.48840	41.04910	49.6356
2	9.736	BB	0.2694	599.15784	32.45769	50.3644

(+)-(6a*R*,12a*R*,*Z*)-6a,7,8,11,12,12a-hexahydrocycloocta[*c*]isoquinolin-5(6*H*)-one (3as)

General Procedure A. Yield: 53% (24.0 mg, 106 μ mol), white solid. The spectra match with the literature values.⁸ **¹H NMR** (400 MHz, CDCl₃) δ = 8.05 (d, J = 7.7 Hz, 1H), 7.45 (td, J = 7.5, 1.6 Hz, 1H), 7.34 (td, J = 7.5, 1.3 Hz, 1H), 7.22 – 7.15 (m, 1H), 5.88 (s, 1H), 5.74 – 5.56 (m, 2H), 4.00 – 3.91 (m, 1H), 3.25 (dd, J = 12.2, 4.0 Hz, 1H), 2.90 – 2.73 (m, 1H), 2.68 – 2.55 (m, 1H), 2.53 – 2.40 (m, 1H), 2.26 – 2.03 (m, 3H), 1.86 (ddd, J = 14.0, 6.7, 3.2 Hz, 1H), 1.58 (ddt, J = 9.4, 7.2, 4.7 Hz, 1H) ppm; ***R*_f**: 0.26 (hexane/EtOAc = 1/1); **$[\alpha]_D^{20}$** : +46.9 (c = 1.00, CHCl₃); **Chiral HPLC**: Chiralpak IC, 4.6 x 250 mm;

30% *i*-PrOH/hexane, 1.0 mL/min, 286 nm; tr (minor) = 13.4 min, tr (major) = 20.3 min, 87.5/12.5
er.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.419	BB	0.3210	192.03568	9.22048	12.4835
2	20.361	BB	0.4869	1346.27881	40.17783	87.5165

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.469	BB	0.2875	36.79034	1.72010	50.0817
2	20.626	MM	0.5649	36.67028	1.08187	49.9183

(-)-(6a*S*,7*R*,12*R*,12a*R*)-6a,7,12,12a-tetrahydro-7,12-epoxybenzo[*b*]phenanthridin-5(6*H*)-one (3at)

General Procedure A. Yield: 91% (48.0 mg, 182 μ mol), white solid. The spectra match with the literature values.¹⁴ **¹H NMR** (400 MHz, CDCl₃) δ = 8.20 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.58 (td, *J* = 7.6, 7.5, 1.4 Hz, 1H), 7.45 – 7.37 (m, 4H), 7.34 – 7.20 (m, 2H), 7.08 (s, 1H), 5.34 (s, 1H), 5.27 (s, 1H), 4.02 (d, *J* = 8.5 Hz, 1H), 3.40 (d, *J* = 8.4 Hz, 1H) ppm; **IR (ATR)**: 3674, 3662, 2987, 2971, 2901, 1669, 1473, 1406, 1382, 1257, 1066, 1056, 857, 755, 656 cm⁻¹; ; **HRMS (ESI)**: calcd.

for [C₁₇H₁₄NO₂]⁺, [M+H]⁺: 264.1019; found: 264.1019; **R_f**: 0.28 (hexane/EtOAc = 1/1); **[α]_D²⁰**: -33.5 (*c* = 1.00, CHCl₃); **Chiral HPLC**: Chiralpak IB, 4.6 x 250 mm; 20% *i*-PrOH/hexane, 1.0 mL/min, 210 nm; tr (minor) = 20.1 min, tr (major) = 35.0 min, 97.8/2.2 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.201	MM	1.2877	199.02097	2.57583	2.1767
2	35.079	BB	1.3661	8944.35742	85.10497	97.8233

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.480	BB	0.9073	1045.02771	13.80223	49.7517
2	36.017	BB	1.0297	1055.46033	12.17130	50.2483

X-Ray structure of **3at** (CCDC No: 1898857).

(+)-phenyl (6a*S*,12a*R*)-5-oxo-5,6,6a,7,12,12a-hexahydro-7,12-epiminobenzo[*b*]phenanthridine-13-carboxylate (**3au**)

General procedure A. The alkene was added as a solid. Yield: 85% (65.0 mg, 170 μ mol), white foam. **¹H NMR** (600 MHz, CD₃CN, 70 °C) δ = 8.08 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.62 (td, *J* = 7.3, 0.8 Hz, 1H), 7.58 (d, *J* = 6.9 Hz, 1H), 7.49 (d, *J* = 7.0 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.36-7.30 (m, 2H), 7.27 (t, *J* = 7.7 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.77 (s, 2H), 6.60 (s, 1H), 5.36 (s, 2H), 4.00 (dd, *J* = 8.5, 1.8 Hz, 1H), 3.48 (d, *J* = 8.5 Hz, 1H) ppm; **¹³C{¹H} NMR** (150 MHz, CD₃CN, 70 °C) δ = 163.6, 154.0, 152.2, 146.2, 143.0, 139.0, 133.8, 130.33, 130.31, 129.0, 128.7, 128.5, 128.4, 127.9, 126.6, 122.7, 122.4, 121.5, 71.7, 71.2, 57.7, 43.5 ppm; **IR (ATR)**: 3272, 3063, 1721, 1670, 1602, 1474, 1400, 1337, 1201, 1164, 1047, 751; ***R*_f** = 0.6 (toluene/*i*-PrOH = 10:1); **[α]_D²⁰**: +7.33 (*c* = 0.50, CHCl₃); **HRMS (ESI/QTOF)**: calcd. for [C₂₄H₁₈N₂NaO₃]⁺, [M+Na]⁺: 405.1210; found 405.1212; **Chiral HPLC**: Chiralpak IA, 4.6 x 250 mm; 40% *i*-PrOH/hexane, 1.0 mL/min, 254 nm; tr (minor) = 14.0 min, tr (major) = 20.4 min, 96.4/3.6 *er*.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.011	MM	1.0078	50.46725	8.34571e-1	3.6050
2	20.400	MM	0.9403	1349.43787	23.91899	96.3950

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.765	BB	0.6135	1140.61194	25.51890	50.4907
2	20.427	BB	0.6568	1118.44287	20.29887	49.5093

Steric Maps

Buried volumes and steric maps were generated with SambVca 2.0.¹⁵

Co2

Co4

V Free	V Buried	V Total	V Exact
86.1	93.4	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
48.0	52.0	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	18.1	26.8	44.9	40.3	59.7
NW	22.4	22.5	44.9	49.9	50.1
NE	22.9	22.0	44.8	51.0	49.0
SE	22.7	22.1	44.9	50.6	49.4

Co6

V Free	V Buried	V Total	V Exact
89.3	90.3	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
49.7	50.3	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	18.2	26.7	44.9	40.5	59.5
NW	23.2	21.7	44.9	51.6	48.4
NE	24.7	20.2	44.8	55.0	45.0
SE	23.2	21.7	44.9	51.7	48.3

Co7

V Free	V Buried	V Total	V Exact
89.4	90.1	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
49.8	50.2	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	20.1	24.8	44.9	44.8	55.2
NW	24.6	20.3	44.9	54.8	45.2
NE	23.2	21.7	44.8	51.7	48.3
SE	21.5	23.3	44.9	48.0	52.0

References

- (1) Wang, S.-G.; Park, S. H.; Cramer, N. A Readily Accessible Class of Chiral Cp Ligands and their Application in Ru^{II}-Catalyzed Enantioselective Syntheses of Dihydrobenzoindoles *Angew. Chem., Int. Ed.* **2018**, *57*, 5459.
- (2) Ye, B.; Cramer, N. A Tunable Class of Chiral Cp Ligands for Enantioselective Rhodium(III)-Catalyzed C–H Alkylations of Benzamides *J. Am. Chem. Soc.* **2013**, *135*, 636.
- (3) Smits, G.; Audic, B.; Wodrich, M. D.; Corminboeuf, C.; Cramer, N. A β -Carbon elimination strategy for convenient in situ access to cyclopentadienyl metal complexes *Chem. Sci.* **2017**, *8*, 7174.
- (4) Audic, B.; Wodrich, M. D.; Cramer, N. Mild complexation protocol for chiral Cp^xRh and Ir complexes suitable for in situ catalysis *Chem. Sci.* **2019**, *10*, 781.
- (5) Sun, Y.; Cramer, N. Tailored trisubstituted chiral Cp^xRh^{III} catalysts for kinetic resolutions of phosphinic amides *Chem. Sci.* **2018**, *9*, 2981.
- (6) Sun, B.; Yoshino, T.; Matsunaga, S.; Kanai, M. Air-Stable Carbonyl(pentamethylcyclopentadienyl)cobalt Diiodide Complex as a Precursor for Cationic (Pentamethylcyclopentadienyl)cobalt(III) Catalysis: Application for Directed C-2 Selective C–H Amidation of Indoles *Adv. Synth. Catal.* **2014**, *356*, 1491.
- (7) Yu, X.; Chen, K.; Guo, S.; Shi, P.; Song, C.; Zhu, J. Direct Access to Cobaltacycles via C–H Activation: *N*-Chloroamide-Enabled Room-Temperature Synthesis of Heterocycles *Org. Lett.* **2017**, *19*, 5348.
- (8) Yu, X.; Chen, K.; Wang, Q.; Zhang, W.; Zhu, J. Co(III)-Catalyzed *N*-chloroamide-directed C–H activation for 3,4-dihydroisoquinolone synthesis *Org. Chem. Front.* **2018**, *5*, 994.
- (9) Ye, B.; Cramer, N. Chiral Cyclopentadienyl Ligands as Stereocontrolling Element in Asymmetric C–H Functionalization *Science* **2012**, *338*, 504.
- (10) Grunewald, G. L.; Romero, F. A.; Chieu, A. D.; Fincham, K. J.; Bhat, S. R.; Criscione, K. R. Exploring the active site of phenylethanolamine *N*-methyltransferase: 3-alkyl-7-substituted-1,2,3,4-tetrahydroisoquinoline inhibitors *Biorg. Med. Chem.* **2005**, *13*, 1261.
- (11) Trifonova, E. A.; Ankudinov, N. M.; Kozlov, M. V.; Sharipov, M. Y.; Nelyubina, Y. V.; Perekalin, D. S. Rhodium(III) Complex with a Bulky Cyclopentadienyl Ligand as a Catalyst for Regioselective Synthesis of Dihydroisoquinolones through C–H Activation of Arylhydroxamic Acids *Chem. – Eur. J.* **2018**, *24*, 16570.
- (12) Smith, A. B.; Cantin, L.-D.; Pasternak, A.; Guise-Zawacki, L.; Yao, W.; Charnley, A. K.; Barbosa, J.; Sprengeler, P. A.; Hirschmann, R.; Munshi, S.; Olsen, D. B.; Schleif, W. A.; Kuo, L. C. Design, Synthesis, and Biological Evaluation of Monopyrrolinone-Based HIV-1 Protease Inhibitors *J. Med. Chem.* **2003**, *46*, 1831.
- (13) Heinrich, M. R.; Blank, O.; Wölfel, S. Reductive Carbodiazenylation of Nonactivated Olefins via Aryl Diazonium Salts *Org. Lett.* **2006**, *8*, 3323.
- (14) Trifonova, E. A.; Ankudinov, N. M.; Mikhaylov, A. A.; Chusov, D. A.; Nelyubina, Y. V.; Perekalin, D. S. A Planar-Chiral Rhodium(III) Catalyst with a Sterically Demanding Cyclopentadienyl Ligand and Its Application in the Enantioselective Synthesis of Dihydroisoquinolones *Angew. Chem., Int. Ed.* **2018**, *57*, 7714.
- (15) Poater, A.; Ragone, F.; Giudice, S.; Costabile, C.; Dorta, R.; Nolan, S. P.; Cavallo, L. Thermodynamics of *N*-Heterocyclic Carbene Dimerization: The Balance of Sterics and Electronics *Organometallics* **2008**, *27*, 2679.

Spectra

3ak

3ak

3am

138.1
137.9
132.3
128.7
128.1
128.0
127.9
127.5
127.2

77.2 CDCl₃
73.5
68.0
50.9
35.2
34.9