Electronic Supplementary Information for the article

Rhodium complexes with planar-chiral cyclopentadienyl ligands: synthesis from tert-butylacetylene and catalytic performance in C-H activation of arylhydroxamates

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General considerations. Unless otherwise stated all reactions were carried out under argon atmosphere in anhydrous solvents, which were purified and dried using standard procedures. The isolation of products was carried out in air. Complex [(cod)RhCl]2 was synthesized according to the literature procedure.1 All other reagents were obtained from commercial sources (Acros, Aldrich, J&K Scientific, Strem, or Vekton) and used as received. High resolution mass spectra were recorded using Bruker microTOF spectrometer with electrospray ionization (ESI). Enantiomeric excess values of the organic products were measured using Shimadzu HPLC equipped with Daicel Chiralpak IA-3 or IB-3 (4.6 × 150 mm) columns and diode array detector with flow rate 1 mL/min. 1H and 13C NMR spectra were measured using Bruker Avance 600MHz or Varian Inova 400MHz spectrometers at 20 °C. The chemical shifts are reported relative to residual signals of the solvent (CHCl3: 7.26 for 1H, 77.16 for 13C; CD3COCHD2: 2.05 for 1H, 29.84 for 13C; CD3S(O)CHD2: 1H: δ 2.50 ppm; 13C: δ 39.52 ppm). The copies of NMR spectra of the new compounds are given at the end of this document.
Synthesis of non-functionalized complexes

An improved synthesis of \([\eta^5\text{-}1,3\text{-}^2\text{Bu}_2\text{-}4\text{-}^2\text{BuCH}_2\text{-}C_5\text{H}_2]\text{RhCl}_2\) (2)

Granular AlCl₃ (162 mg, 0.6 mmol, threefold excess) was placed in the 10 ml Schlenk tube. Then Schlenk tube was evacuated and backfilled argon. AlCl₃ was grinded with a spatula inside the Schlenk tube under argon atmosphere. Then 3 ml of CH₂Cl₂ was added followed by \([\text{cod}]\text{RhCl}_2\) (100 mg, 0.2 mmol).

Resulting mixture was stirred for 10 min. Initial yellow color of the solution changed to green, then became yellow again. Then tert-butylacetylene (198 mg, 2.4 mmol, 300 μL, twofold excess) was added one portion, and the solution immediately became red. The solution was stirred overnight, then 1 ml of concentrated hydrochloric acid was added, and the mixture was stirred vigorously for additional 20 min. The solution opened to air and washed with water twice to remove AlCl₃. The red organic layer was dried with anhydrous Na₂SO₄, evaporated to dryness, and triturated with pentane (3x5 ml) to obtain the orange-red product, which was dried in vacuum. The product has sufficient purity for application in catalysis without additional purification.

Yield: 160 mg, 0.38 mmol, 95%.

¹H NMR (400 MHz, chloroform-d): δ = 5.54 (s, 1H), 5.32 (s, 1H), 2.75 (d, 1H, J = 14.9 Hz), 2.63 (d, 1H, J = 14.9 Hz), 1.43 (s, 9H), 1.34 (s, 9H), 1.00 (s, 9H) ppm.

¹H NMR data is in agreement with those reported previously.

Synthesis of \([\eta^5\text{-}1,3,6\text{-}^2\text{Bu}_3\text{-fulvene}]\text{Rh}(1,5\text{-}C_6\text{H}_12)\text{InBr}_4^-\) (4InBr₄⁻)

Complex \([\text{cod}]\text{RhCl}_2\) (100 mg, 0.2 mmol) and anhydrous InBr₃ (284 mg, 0.8 mmol) were placed in the Schlenk tube. Then CH₂Cl₂ (2 ml) was added and the yellow-green solution was stirred for 5 min. Then tert-butylacetylene (0.6 ml, 4.8 mmol) was added one portion. The yellow-green color of the solution slowly changes to red. After 6 hours, the red reaction mixture was filtered, the precipitate was washed with CH₂Cl₂ (3x3 ml), and the combined solutions were evaporated to dryness. The resulting residue was washed with Et₂O (3x5 ml) and dried in vacuum to give product as red solid. A single crystal suitable for X-ray diffraction was obtained by slow diffusion of Et₂O vapors into the solution of complex in CH₂Cl₂ at 4 °C.

Yield: 250 mg, 0.28 mmol, 70%.

¹H NMR (400 MHz, acetone-d₆): δ = 7.52 (s, 1H), 7.01 (s, 1H) 5.76 (s, 1H), 5.72–5.66 (m, 1H), 5.58–5.48 (m, 1H), 5.48–5.39 (m, 1H), 5.37–5.31 (m, 1H), 2.83 (dd, J = 15.1, 7.7 Hz, 1H), 2.64–2.45 (m, 3H), 2.42–2.32 (m, 1H), 2.31–2.12 (m, 3H), 1.45 (s, 9H), 1.43 (s, 9H), 1.34 (s, 9H).

¹³C NMR (101 MHz, acetone-d₆): δ = 152.5, 139.3 (d, JRh-C = 4.3 Hz), 119.8 (d, JRh-C = 5.3 Hz), 114.4 (d, JRh-C = 3.1 Hz), 104.8 (d, JRh-C = 3.5 Hz), 90.6 (d, JRh-C = 11.3 Hz), 88.4 (d, JRh-C = 11.1 Hz), 87.6 (d, JRh-C = 9.8 Hz), 86.7 (d, JRh-C = 10.3 Hz), 79.7 (d, JRh-C = 4.8 Hz), 39.7, 35.3, 35.1, 34.4, 33.0, 32.7 (CH₃), 30.64 (CH₃), 30.62 (CH₃), 30.0, 29.0 ppm.

Elemental analysis. Calculated for Cᵢ₀H₄₂Br₄InRh×0.5Et₂O: C, 36.20%; H, 5.10%. Found: C, 36.10%; H, 5.05%.
Protonation of the fulvene complex 4 in the presence of acetonitrile

Under argon atmosphere complex $[^{1}\text{Bu}]_{5}\text{-(1,3,6-}^{1}\text{Bu}_{3}\text{-fulvene)}\text{Rh}(1,5\text{-C}_{8}\text{H}_{12})[^{4}\text{BF}_{4}]^{-}$ (108 mg, 0.2 mmol) was dissolved in CH$_{2}$Cl$_{2}$ (1 ml). Then HBF$_{4}$$\times$Et$_{2}$O (27 μL, 0.2 mmol) added and the mixture was stirred for 1 hour. Then MeCN (62 μL, 1.2 mmol, 6 equiv., twofold excess) was added and reaction keep stirred for additional 20 min. Red solution become orange, indicating the formation of the complex $[^{(1}\text{MeCN})_{3}]$[BF$_{4}$)$_{2}$]. The sample was taken out of solution and NMR spectrum was measured (free cyclooctadiene was also detected). Finally, the saturated aqueous solution of NH$_{4}$Cl was added and the mixture was vigorously stirred overnight. The mixture was opened to air and the orange organic phase was separated. Organic solution was dried with anhydrous Na$_{2}$SO$_{4}$, evaporated to dryness. The residue was triturated with pentane (3×5 ml) and dried in vacuum to give the complex 2 as orange-red precipitate.

Yield: 67 mg, 0.16 mmol, 80%.

$^{1}$H NMR data of complex 2 is in agreement with those reported previously.$^{2}$

$^{1}$H NMR spectrum of the presumed intermediate acetonitrile complex $[^{(1}\text{MeCN})_{3}]$[BF$_{4}$)$_{2}$ (acetone-d$_{6}$, 400 MHz): δ = 6.66 (s, 1H), 6.37 (s, 1H), 3.96–3.17 (m, 9H, C$_{6}$H$_{3}$CN), 2.96 (d, 1H, J = 14.7 Hz), 2.36 (d, 1H, J = 14.3 Hz), 1.56 (s, 9H), 1.44 (s, 9H), 1.08 (s, 9H) ppm.

Reaction of the fulvene complex 4 in the presence of chloride anion

Under argon atmosphere complex $[^{1}\text{Bu}]_{5}\text{-}^{1}\text{Bu}_{3}\text{-fulvene)}\text{Rh}(1,5\text{-C}_{8}\text{H}_{12})[^{6}\text{PF}_{6}]^{-}$ (60 mg, 0.1 mmol) was dissolved in CH$_{2}$Cl$_{2}$ (1 ml) and [Et$_{3}$BnN]Cl (23 mg, 0.1 mmol) was added. The red solution became yellow and the reaction mixture was stirred for 6 hours. The solution was open to air and evaporated to dryness. The residue was triturated with pentane (3×5 ml), the combined pentane solutions were passed through a short pad of SiO$_{2}$ and evaporated to give free 1,3,6-$^{1}$Bu$_{3}$-fulvene (established by $^{1}$H NMR,$^{4}$ the yield was not measured). The solid residue was dissolved in benzene and filtered through a short pad of SiO$_{2}$. The resulting yellow solution evaporated to dryness to give [(cod)RhCl]$_{2}$ as yellow powder.

Yield: 20 mg, 0.04 mmol, 80%.
Synthesis of hydroxy-substituted complexes

Synthesis of \( \eta^5\text{-}1\text{-}3\text{-}1\text{Bu}_2\text{-}4\text{-}1\text{Bu}(OH)\text{CH-Cl}_2 \text{Rh}(1,5\text{-}C_8\text{H}_{12}) (5\text{OH}) \)

Under argon atmosphere complex \(^3\) \([ \eta^5\text{-}1\text{-}3\text{-}6\text{-}1\text{Bu}_3\text{-}fulvene] \text{Rh}(1,5\text{-}C_8\text{H}_{12}) \) \(^1\text{PF}_6\) (120 mg, 0.2 mmol; \( \text{BF}_4^- \) or \( \text{InBr}_4^- \) salts can be used as well) and \( \text{K}_2\text{CO}_3 \) (56 mg, 0.4 mmol) were suspended in \( \text{THF} \) (1 ml) and \( \text{H}_2\text{O} \) (36 mg, 2 mmol, 36 \( \mu L \)) was added. The color of the reaction mixture changes from red to brown. The mixture was stirred for 1 hour, then opened to air, and the solvent was evaporated. The residue was dissolved in a small amount of hexane, eluted through a short alumina column with hexane, evaporated and dried in vacuum to give the product \( 5\text{OH} \) as yellow oil.

Yield: 73 mg, 0.154 mmol, 77%.

Since there are two diastereomeric Cp ligands, two sets of signals are observed in the spectrum. Tentative assignment to isomers is marked as A and B.

\(^1\text{H NMR} \) (Chloroform-\( d \), 400 MHz): \( \delta = 4.91 \) (s, 1H, \( \text{Cp}^A \)), 4.80 (s, 1H, \( \text{Cp}^B \)), 4.66 (s, 1H, \( \text{Cp}^S \)), 4.54 (s, 1H, \( \text{Cp}^S \)), 4.45 (s, 1H, \( \text{CpCH}^B \)), 4.44 (s, 1H, \( \text{CpCH}^S \)) 0.40 – 3.90 (m, 6H, \( \text{COD}^\text{Cl} \)), 3.89 – 3.80 (m, 2H, \( \text{COD}^\text{Cl} \)), 2.48 (s, 1H, \( \text{OH}^B \)), 2.35 – 2.11 (m, 8H, \( \text{COD}^\text{Cl} \)), 2.10 – 2.01 (m, 2H, \( \text{COD}^\text{Cl} \)), 1.94 – 1.75 (m, 6H, \( \text{COD}^\text{Cl} \)), 1.37 (s, 1H, \( \text{OH}^B \)), 1.24 (s, 18H, \( ^1\text{Bu}^A^B \)), 1.22 (s, 18H, \( ^1\text{Bu}^A^B \)), 1.17 (s, 9H, \( ^1\text{Bu}^A \)), 1.01 (s, 9H, \( ^1\text{Bu}^A \)).

\( ^{13}\text{C NMR} \) (Chloroform-\( d \), 101 MHZ): \( \delta = 117.76 \) (d, \( J_{\text{Rh-C}} = 5.0 \) Hz), 116.57 (d, \( J_{\text{Rh-C}} = 3.4 \) Hz), 105.68 (d, \( J_{\text{Rh-C}} = 4.4 \) Hz), 83.31 (d, \( J_{\text{Rh-C}} = 3.8 \) Hz), 82.83 (d, \( J_{\text{Rh-C}} = 3.6 \) Hz), 82.49 (d, \( J_{\text{Rh-C}} = 3.8 \) Hz), 79.06 (d, \( J_{\text{Rh-C}} = 4.2 \) Hz), 76.52, 65.88 (d, \( J_{\text{Rh-C}} = 13.8 \) Hz), 65.10 (d, \( J_{\text{Rh-C}} = 13.5 \) Hz), 65.06 (d, \( J_{\text{Rh-C}} = 13.9 \) Hz), 63.80 (d, \( J_{\text{Rh-C}} = 13.6 \) Hz), 36.17, 35.66, 34.03, 32.49, 32.46, 32.37, 32.23, 32.21, 32.19, 31.73, 31.55, 31.25, 29.84 ppm.

HRMS (ESI). Calculated for \( \text{C}_{26}\text{H}_{33}\text{ORh} \) [M]^+ = 474.2363, found 474.2352.

Synthesis of \( \left[ \eta^5\text{-}1\text{-}3\text{-}1\text{Bu}_2\text{-}4\text{-}1\text{Bu}(OH)\text{CH-Cl}_2 \right]_2 \text{RhCl}_2 \) (2OH-Cl).

Under argon atmosphere complex \( 2\text{OH-I} \) (20 mg, 0.032 mmol) was placed in a Schlenk tube (protected from light by aluminum foil) and dissolved in \( \text{CH}_2\text{Cl}_2 \) (2ml). Then \( \text{AgBF}_4 \) (13 mg, 0.066 mmol) was added, the violet solution became bright orange, and the precipitate of \( \text{AgI} \) was formed. The precipitated was filtered off and the solution was transferred to another Schlenk tube which contained \( \text{Et}_3\text{BnNCl} \) (15 mg, 0.064 mmol, 2 equiv.) dissolved in \( \text{CH}_2\text{Cl}_2 \) (1ml). The resulting mixture was stirred for 10 min, then opened to the air and evaporated to dryness.

Orange residue was extracted with benzene and filtered through a short pad of \( \text{SiO}_2 \) to remove \([\text{Et}_3\text{BnN}][\text{BF}_4]\). The filtrate was evaporated to dryness to give the product \( 2\text{OH-Cl} \) as orange powder.

Yield: 11 mg, 0.25 mmol, 79%.

Single crystals of the complex suitable for X-ray diffraction were obtained by slow diffusion of pentane vapors into the solution of complex in \( \text{CDCl}_3 \).

Since there are two diastereomeric Cp ligands, two sets of signals are observed in the spectrum. Tentative assignment to isomers is marked as A and B.
$^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta = 6.33$ (s, 1H, Cp$^A$), 6.12 (s, 1H, Cp$^B$), 5.81 (s, 1H, Cp$^B$), 5.70 (s, 1H), 5.16 (d, 1H, $J = 6.1$ Hz), 4.53 (d, 1H, $J = 3.9$ Hz), 4.48 (d, 1H, $J = 3.7$ Hz), 4.16 (d, 1H, $J = 6.1$ Hz), 4.44 (s, 1H), 1.28 (s, 9H), 1.27 (s, 9H), 1.03 (s, 9H), 0.95 (s, 9H) ppm.

$^{13}$C NMR (DMSO-$d_6$, 101 MHz): $\delta = 132.53$, 129.06, 110.51 (d, $J_{Rh-C} = 6.8$ Hz), 110.25 (d, $J_{Rh-C} = 5.9$ Hz), 107.41 (d, $J_{Rh-C} = 7.4$ Hz), 106.47 (d, $J_{Rh-C} = 7.3$ Hz), 106.32 (d, $J_{Rh-C} = 7.8$ Hz), 101.21 (d, $J_{Rh-C} = 7.5$ Hz), 92.38, 90.13 (d, $J_{Rh-C} = 6.3$ Hz), 87.96 (d, $J_{Rh-C} = 6.0$ Hz), 83.86 (d, $J_{Rh-C} = 7.7$ Hz), 74.32, 70.27, 51.95, 35.76, 35.42, 33.79, 33.73, 31.41, 30.90, 30.72, 30.59, 29.54, 29.48, 27.38, 26.78 ppm.

HRMS (ESI). Calculated for C$_{18}$H$_{31}$ClORh [M$_{monomer}$-Cl]$^+$= 401.1117. Found 401.1118.

**Synthesis of [[$\eta^5$-1,3-$^3$Bu$_2$-4-$^3$Bu(OH)CH-C$_5$H$_2$]RhBr$_2)_2$ (2OH-Br).**

Under argon atmosphere complex 2OH-I (20 mg, 0.032 mmol) was placed in a Schlenk tube (protected from light by aluminum foil) and dissolved in CH$_2$Cl$_2$ (2ml). Then AgBF$_4$ (13 mg, 0.066 mmol) was added, the violet solution became bright orange, and the precipitate of AgI was formed. The precipitated was filtered off and the solution was transferred to another Schlenk tube which contained Et$_4$NBr (21 mg, 0.064 mg, 2 equiv.) in CH$_2$Cl$_2$ (1ml) in another Schlenk tube. Reaction mixture immediately became dark orange. The mixture was stirred for 10 min, then opened to air and evaporated to dryness. The residue was extracted with benzene and filtered through a short pad of SiO$_2$ to remove [Et$_4$N][BF$_4$]. The filtrate was evaporated to dryness to give the product 2OH-Br as orange powder.

Yield: 14 mg, 0.26 mmol, 83%.

Single crystals of the complex suitable for X-ray diffraction were obtained by slow diffusion of pentane vapors into the solution of complex in CDCl$_3$.

Since there are two diastereomeric Cp ligands, two sets of signals are observed in the spectrum. Tentative assignment to isomers is marked as A and B.

$^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta = 6.42$ (s, 1H, Cp$^A$), 6.16 (s, 1H, Cp$^B$), 5.80 (s, 1H, Cp$^B$), 5.70 (s, 1H, Cp$^A$), 4.57 (s, 1H, Cp$^A$), 4.23 (s, 1H, Cp$^B$), 1.46 (s, 18H, Cp$^{A,B}$), 1.30 (s, 9H, Cp$^B$), 1.28 (s, 9H, Cp$^A$), 1.05 (s, 9H, Cp$^B$), 0.96 (s, 9H, Cp$^A$) ppm.

$^{13}$C NMR (DMSO-$d_6$, 101 MHz): $\delta = 111.78$ (d, $J = 6.9$ Hz), 111.35 (d, $J = 5.0$ Hz), 108.21 (d, $J = 10.0$ Hz), 107.64 (d, $J = 8.1$ Hz), 102.90 (d, $J = 7.3$ Hz), 91.79 (d, $J = 7.3$ Hz), 89.26 (d, $J = 6.8$ Hz), 87.72 (d, $J = 6.8$ Hz), 84.22 (d, $J = 8.3$ Hz), 74.18, 70.18, 35.78, 35.66, 33.95, 31.83, 31.16, 30.92, 30.82, 29.89, 29.79, 27.58, 26.91 ppm.


**Synthesis of [[$\eta^5$-1,3-$^3$Bu$_2$-4-$^3$Bu(OH)CH-C$_5$H$_2$]RhI$_2)_2$ (2OH-I).**

In air a solution of I$_2$ (45 mg, 0.18 mmol) in hexane (7 ml) was added dropwise to a stirred yellow solution of the complex 5OH (84 mg, 0.18 mmol) in hexane (5 ml). The dark violet precipitate was formed immediately. After 5 minutes of stirring the solid residue was separated by
centrifugation, washed with pentane (4×5 ml) to remove residual cyclooctadiene and dried in vacuum to give the product 2OH-I as a dark purple powder.
Yield: 103 mg, 0.083 mmol, 94%.

Since there are two diastereomeric Cp ligands, NMR spectra of 2OH-I in non-coordinating solvents (for example, chloroform) are extremely complex due to the formation of homo- and hetero-chiral dimers. The NMR spectra in DMSO are simpler, because DMSO destroys the dimeric structures and form monomeric adducts. Still, two sets of signals are observed in the spectrum (marked as A and B).

1H NMR (DMSO-d$_6$, 400 MHz): δ = 6.52 (s, 1H, Cp$^A$), 6.23 (s, 1H, Cp$^B$), 5.83 (s, 1H, Cp$^A$), 5.69 (s, 1H, Cp$^A$), 5.01 (d, 1H, J=6.9 Hz, Cp$^B$), 4.64 (d, 1H, J=4.2 Hz, Cp$^A$), 4.34 (d, 1H, J=6.5 Hz, Cp$^{A+B}$), 1.47 (s, 18H, Cp$^{A+B}$), 1.32 (s, 9H, Cp$^B$), 1.30 (s, 9H, Cp$^A$), 1.06 (s, 9H, Cp$^B$), 0.98 (s, 9H, Cp$^A$) ppm.

13C NMR (DMSO-d$_6$, 101 MHz): δ = 122.22 (d, J$_{Rh-C}$ = 5.0 Hz), 115.40 (d, J$_{Rh-C}$ = 2.7 Hz), 114.38 (d, J$_{Rh-C}$ = 5.4 Hz), 111.61 (d), 110.20 (d, J$_{Rh-C}$ = 7.2 Hz), 103.96 (d, J$_{Rh-C}$ = 3.8 Hz), 89.22 (d, J$_{Rh-C}$ = 6.3 Hz), 87.96 (d, J$_{Rh-C}$ = 7.3 Hz), 87.34 (d, J$_{Rh-C}$ = 7.6 Hz), 85.34 (d), 74.37, 70.30, 36.17, 35.88, 34.17, 33.96, 32.53, 31.71, 31.22, 30.56, 30.45, 27.93, 27.15 ppm.

HRMS (ESI). Calculated for C$_{36}$H$_{62}$I$_3$O$_2$Rh$_2$ [M-I]$^+$ = 1112.9994. Found 1112.9972.

Synthesis of alkoxy-substituted complexes

Synthesis of (ƞ$^5$-1,3,6-tBu$_3$-4-tBu(CH$_3$O)CH-C$_5$H$_2$)Rh(1,5-C$_8$H$_{12}$) (5OMe).

Under argon atmosphere complex [(ƞ$^5$-1,3,6-tBu$_3$-fulvene)Rh(1,5-C$_8$H$_{12}$)]$^+$PF$_6$$^-$ (101 mg, 0.17 mmol, BF$_4$$^-$ or InBr$_4^-$ salts can be used as well) and tBuOK (19 mg, 0.17 mmol) were dissolved in MeOH (2 ml). The reaction mixture was stirred for 1 hour, then opened to air and the solvent was evaporated. The solid residue was dissolved in a small amount of hexane, eluted through a short alumina column with hexane, evaporated and dried in vacuum to give the complex 5OMe as yellow oil. It should be noted that the product is not stable on silica gel columns.
Yield: 79 mg, 0.16 mmol, 96%.

A single crystal suitable for X-ray diffraction analysis was obtained by slow evaporation of a pentane solution of the complex.

1H NMR (600 MHz, CDCl$_3$) δ 4.68 (d, J = 2.3 Hz, 1H, CH$^Cp$), 4.47 (d, J = 2.2 Hz, 1H, CH$^Cp$), 4.07 (s, 1H, CH$_2$OCH$_3$), 3.98–3.95 (m, 2H, CH$_2$CBH$_{12}$), 3.91–3.88 (m, 2H, CH$_2$CBH$_{12}$), 2.98 (s, 3H, OCH$_3$), 2.31–2.23 (m, 2H, CH$_2$CBH$_{12}$), 2.20–2.13 (m, 2H, CH$_2$CBH$_{12}$), 2.01–1.98 (m, 2H, CH$_2$CBH$_{12}$), 1.81–1.75 (m, 2H, CH$_2$CBH$_{12}$), 1.29 (s, 9H, CH$_3$), 1.20 (s, 9H, CH$_3$), 1.18 (s, 9H, CH$_3$).

13C NMR (151 MHz, CDCl$_3$) δ 119.3 (d, J$_{Rh-C}$ = 3.1 Hz), 118.2 (d, J$_{Rh-C}$ = 4.8 Hz), 105.7 (d, J$_{Rh-C}$ = 4.1 Hz), 83.9 (s), 83.7 (d, J$_{Rh-C}$ = 3.6 Hz), 80.8 (d, J$_{Rh-C}$ = 4.2 Hz), 66.3 (d, J$_{Rh-C}$ = 13.9 Hz), 65.0 (d, J$_{Rh-C}$ = 13.8 Hz), 56.3, 36.1, 33.1, 32.7, 32.3, 32.2, 31.8, 31.2, 27.5.
Synthesis of (η²-1,3-Bu₂-4-Bu(CF₃CH₂O)CH-C₅H₂)Rh(1,5-C₅H₁₂) (5OCH₂CF₃).

Under argon atmosphere [(η²-1,3,6-Bu₃-fulvene)Rh(1,5-C₅H₁₂)]⁺PF₆⁻ (120 mg, 0.2 mmol, BF₄⁻ or InBr₄⁻ salts can be used as well) and anhydrous K₂CO₃ (28 mg, 0.2 mmol) were suspended in THF (1 ml) and TFE (200 mg, 20 mmol, 144 μL) was added. The reaction mixture changes from red to pale yellow. The mixture was stirred for 1 hour, then opened to air and the solvent was evaporated. The solid residue was dissolved in a small amount of hexane, eluted through a short alumina column with hexane, evaporated to give the product as yellow crystals.

It should be noted that complex is not stable at silica gel columns. Unlike most (cyclopentadienyl)Rh(cod) complexes, the compounds containing perfluorinated alcohols 5OCH(CF₃)₂ and 5OCH₂CF₃ form crystals very easily. A single crystal suitable for X-ray diffraction analysis was obtained by slow evaporation of a hexane solution of the complex.

Yield: 89 mg, 0.160 mmol, 80%.

¹H NMR (chloroform-d, 400 MHz): δ = 4.73 (d, 1H, J= 2.4 Hz, Cp), 4.50 (d, 1H, J= 2.5 Hz, Cp), 4.35 (s, 1H, Cp), 4.03 – 3.86 (m, 4H, CH₃cod), 3.54 – 3.37 (m, 1H, OCH₂CF₃), 3.30 – 3.14 (m, 1H, OCH₂CF₃), 3.34 – 2.09 (m, 4H, CH₂-cod), 2.04 – 1.92 (m, 2H, CH₂-cod), 1.85 – 1.71 (m, 2H, CH₂-cod), 1.28 (s, 9H, tBu), 1.20 (s, 9H, tBu), 1.19 (s, 9H, tBu) ppm.

¹³C NMR (chloroform-d, 101 MHz): δ = 83.7 (d, J= 3.7 Hz), 83.3, 81.3 (d, J= 3.1 Hz), 66.7 (d, J= 13.9 Hz), 65.5 (d, J= 13.8 Hz), 65.21 – 64.35 (m, C-F), 36.3, 33.0, 32.6, 32.3, 32.2, 31.2, 29.8 27.3 ppm.

¹⁹F NMR (chloroform-d, 376 MHz): δ = -74.25 (t, J= 8.5 Hz) ppm.


Synthesis of (η²-1,3-Bu₂-4-Bu(CF₃)₂CHO)CH-C₅H₂Rh(1,5-C₅H₁₂) (5OCH(CF₃)₂).

Under argon atmosphere [(η²-1,3,6-Bu₃-fulvene)Rh(1,5-C₅H₁₂)]⁺PF₆⁻ (120 mg, 0.2 mmol, BF₄⁻ or InBr₄⁻ salts can be used as well) and anhydrous K₂CO₃ (28 mg, 0.2 mmol) were suspended in THF (1 ml) and HFIP (336 μL) was added one portion. The color of the reaction mixture changes from red to pale yellow. The reaction mixture was stirred for 1 hour, then opened to air and the solvent was evaporated. The solid residue was dissolved in a small amount of hexane, eluted through a short alumina column with hexane, evaporated to give the product as yellow crystals. A single crystal suitable for X-ray diffraction analysis was obtained by slow evaporation of a hexane solution of the complex.

Yield: 121 mg, 0.194 mmol, 97%.

¹H NMR (chloroform-d, 400 MHz): δ = 4.86 (s, 1H, Cp), 4.79 (s, 1H, Cp), 4.58 (s, 1H, Cp), 4.05 – 3.90 (m, 4H, CH₃-cod), 3.89 – 3.78 (m, 1H, OCH(CF₃)₂), 3.24 – 2.12 (m, 4H, CH₂-cod), 2.02 – 1.92 (m, 2H, CH₂-cod), 1.84 – 1.73 (m, 2H, CH₂-cod), 1.27 (s, 18H, tBu), 1.18 (s, 9H, tBu) ppm.

¹³C NMR (chloroform-d, 101 MHz): δ = 120.54 (d, JRhₐ = 3.1 Hz, C₃C₆), 119.09 (d, JRhₐ = 4.8 Hz, C₃C₆), 100.36 (d, JRhₐ = 4.1 Hz, C₃C₆), 85.24 (C₆C₃H₄Bu), 84.72 (d, JRhₐ = 3.1 Hz, C₆C₃H₁₂), 82.52 (d, JRhₐ = 4.0 Hz, C₆C₃H₁₂), 71.80 (dt, J₉C₃ = 62.8, 31.3 Hz, C₆C₃), 67.22 (d, JRhₐ = 13.9 Hz, C₆C₃H₁₂), 66.01 (d, JRhₐ = 13.9 Hz, C₆C₃H₁₂), 36.65, 32.78 (CH₃), 32.35, 32.06 (CH₃), 31.14 (CH₃), 27.29 ppm.

¹⁹F NMR (chloroform-d, 376 MHz): δ = -71.75 (m), -72.57 (m) ppm.


**Synthesis of halide complexes**

**General procedure for the chloride complexes.** An excess of gaseous Cl₂ was bubbled through a solution of the yellow complex 5OR (0.2 mmol) in hexane (10ml) in the dark. Protection from light is important to avoid side reactions of radical chlorination. The red precipitate was formed immediately. Chlorine was bubbled until the spot of the starting complex disappeared on TLC. Then the solid residue was separated by centrifugation, washed with pentane (4×5ml) and dried in vacuo to give product 2OR-Cl as a red or orange powder.

**Synthesis of [(η⁵-1,3-Bu₂-4⁻¹Bu(CH₃O)CH-C₆H₂)RhCl₄]₂ (2OMe-Cl).**

A single crystal of the complex suitable for X-ray diffraction was obtained by slow diffusion of petroleum ether vapors into the solution of complex in DCE.

¹H NMR (chloroform-d, 400 MHz): δ = 5.54 (s, 1H, Cp), 5.49 (s, 1H, Cp), 4.19 (s, 1H, -CHOCH₃), 3.54 (s, 3H, CHOCH₃), 1.48 (s, 9H, tBu), 1.34 (s, 9H, tBu), 1.08 (s, 9H, tBu) ppm

¹³C NMR (chloroform-d, 101 MHz): δ = 85.67, 81.74 (d, J=4.7 Hz), 60.90, 33.02, 31.51, 30.86, 29.78, 27.97 ppm


**Synthesis of [(η⁵-1,3-Bu₂-4⁻¹Bu(CF₃CH₂O)CH-C₆H₂)RhCl₄]₂ (2OCH₂CF₃-Cl).**

¹H NMR (chloroform-d, 300 MHz): δ = 5.49 (s, 2H, Cp), 5.02 – 4.75 (m, 1H, OCH₂CF₃), 4.39 (s, 1H, Cp), 4.08 – 3.83 (m, 1H, OCH₂CF₃), 1.44 (s, 9H, tBu), 1.32 (s, 9H, tBu), 1.03 (s, 9H, tBu) ppm

¹³C NMR (chloroform-d, 101 MHz): δ = 128.03, 125.26, 122.50, 106.47 (d, J=9.1 Hz, Cp), 85.54 (OCH₂CF₃), 83.50 (d, J=9.6 Hz), 82.91 (d, J=9.6 Hz), 70.32 (q, J=34.0 Hz, CF₃), 38.39, 33.16, 31.78 (CH₃), 30.93, 29.85 (CH₃), 27.89 (CH₃) ppm

¹⁹F NMR (chloroform-d, 282 MHz): δ = −73.17 ppm.


**Synthesis of (η⁵-1,3-Bu₂-4⁻¹Bu(CF₃)₂CHO)CH-C₆H₂)RhCl₂ (2OCH(CF₃)₂-Cl).**

Yield: 100 mg, 0.17 mmol, 85%.

A single crystal of the complex suitable for X-ray diffraction was obtained by slow diffusion of pentane vapors into the solution of complex in DCM.
$^1$H NMR (chloroform-$d$, 400 MHz): $\delta = 5.83$ (s, 1H, Cp), 5.58 (s, 1H, Cp), 4.54 (s, 1H, Cp), 4.08–3.91 (m, 1H, OCH(CF$_3$)$_2$), 1.58 (s, 9H, tBu), 1.41 (s, 9H, tBu), 1.37 (s, 9H, tBu) ppm.

$^{13}$C NMR (chloroform-$d$, 101 MHz): $\delta = 85.26$ (d, $J_{Rb-C} = 3.9$ Hz), 84.88, 79.03 (d, $J_{Rb-C} = 8.6$ Hz), 74.40–72.79 (m), 37.52, 32.59, 31.47, 30.66, 28.92, 27.21 ppm.

$^{19}$F NMR (chloroform-$d$, 376 MHz): $\delta = -72.13$ (bs), -72.63 (bs) ppm.


**General procedure for the bromide complexes.** In air a solution of Br$_2$ (31 $\mu$L, 0.6 mmol, 3 equiv.) in hexane (5 ml) was added dropwise to a stirred solution of the complex 5OR (0.2 mmol) in hexane (5 ml). The dark orange precipitate was formed immediately. After 5 minutes of stirring the solid residue was separated by centrifugation, washed with pentane (4×5ml) and dried in vacuo to give product 2OR-Br as a dark orange powder.

**Synthesis of [[η$^5$-1,3-1Bu$_2$-4-1Bu(CH$_3$O)CH-C$_5$H$_2$]RhBr$_2$]$_2$ (2OMe-Br).**

Yield: 100 mg, 0.093 mmol, 93%.

$^1$H NMR (chloroform-$d$, 400 MHz): $\delta = 5.56$ (s, 1H, Cp), 5.51 (s, 1H, Cp), 4.28 (s, 1H, -CHOCH$_3$), 3.60 (s, 3H, CHOCH$_3$), 1.47 (s, 9H, tBu), 1.32 (s, 9H, tBu), 1.05 (s, 9H, tBu) ppm.

$^{13}$C NMR (chloroform-$d$, 101 MHz): $\delta = 108.52$ (d, $J_{Rb-C} = 4.0$ Hz), 107.28 (d, $J_{Rb-C} = 4.8$ Hz), 105.18 (d, $J_{Rb-C} = 4.6$ Hz), 86.10, 82.23 (d, $J_{Rb-C} = 6.1$ Hz), 81.81 (d, $J_{Rb-C} = 7.4$ Hz), 61.42, 38.70, 33.29, 31.87, 30.91, 30.20, 28.21 ppm.


**Synthesis of [[η$^5$-1,3-1Bu$_2$-4-1Bu(CF$_3$CHO)CH-C$_5$H$_2$]RhBr$_2$]$_2$ (2OCH(CF$_3$)$_2$-Br).**

Yield: 113 mg, 0.166 mmol, 83%.

A single crystal of the complex suitable for X-ray diffraction was obtained by slow diffusion of hexane vapors into the solution of complex in DCE.

$^1$H NMR (chloroform-$d$, 400 MHz): $\delta = 5.88$ (s, 1H), 5.72 (s, 1H), 4.48 (s, 1H), 4.17–3.84 (m, 1H, OCH(CF$_3$)$_2$), 1.61 (s, 9H, tBu), 1.40 (s, 9H, tBu), 1.31 (s, 9H, tBu) ppm.

$^{13}$C NMR (chloroform-$d$, 101 MHz): $\delta = 86.09$ (d, $J_{Rb-C} = 5.1$ Hz), 84.96, 79.02 (d, $J = 7.2$ Hz), 74.40–73.09 (m), 37.35, 32.62, 30.83, 30.46, 28.90, 27.26 ppm.

$^{19}$F NMR (chloroform-$d$, 376 MHz): $\delta = -71.98$ – -72.21 (m), -72.34 – -72.55 (m) ppm.

HRMS (ESI). Calculated for C$_{21}$H$_{31}$BrF$_6$ORh [M$_{monomer}$–Br]$^+$ = 595.0512. Found 595.0500.
Synthesis of \( \left( \eta^5 - 1,3\text{-}t\text{Bu}_2 - 4\text{-}t\text{Bu}((\text{CF}_3)_2\text{CHO})\text{CH}-\text{C}_5\text{H}_2 \right) \text{RhI}_2 \) \( \text{I}_2 \text{OCH(CF}_3)_2 \text{I} \). In air a solution of \( \text{I}_2 \) (25 mg, 0.1 mmol) in hexane (5 ml) was added dropwise to a yellow stirred solution of complex \( \text{5OCH(CF}_3)_2 \) (62 mg, 0.1 mmol) in hexane (2 ml). The dark precipitate was formed immediately. After 5 minutes of stirring the solid was separated by centrifugation, washed with pentane (4×5ml) to remove residual cyclooctadiene and dried in vacuo to give product \( \text{2OCH(CF}_3)_2 \text{I} \) as a dark purple solid. It should be noted that diluted solutions of this complex are green presumably due to the formation of an ionic isomer \( \text{[R}_\text{CpRh(μ-I}_3 \text{)Rh}_\text{R}_\text{Cp}]I} \).

Yield: 38 mg, 0.049 mmol, 98%.

A single crystal of the complex suitable for X-ray diffraction was obtained by slow diffusion of petroleum ether vapors into the solution of complex in DCE.

\(^1\text{H NMR (chloroform-d, 400 MHz):} \delta = 5.89 \text{ (s, 1H, Cp), 5.88 \text{ (s, 1H, Cp), 4.39 \text{ (s, 1H, Cp), 4.20} – 3.96 \text{ (m, 1H, OCH(CF}_3)_2 \text{)}, 1.63 \text{ (s, 9H, tBu), 1.36 \text{ (s, 9H, tBu), 1.17 \text{ (s, 9H, tBu) ppm.}} \)

\(^1\text{H NMR (DMSO-d}_6 \text{, 400 MHz):} \delta = 6.12 \text{ (s, 1H, Cp), 5.65 \text{ (s, 1H, Cp), 5.14 \text{ (s, br, 1H, OCH(CF}_3)_2 \text{)}, 4.83 \text{ (s, 1H), 1.42 \text{ (s, 9H, tBu), 1.30 \text{ (s, 9H, tBu), 1.22 \text{ (s, 9H, tBu) ppm.}} \)

\(^{13}\text{C NMR (DMSO-d}_6 \text{, 101 MHz):} \delta = 110.58, 102.28 \text{ (d, J = 6.8 Hz), 86.37, 86.04 \text{ (d, J = 7.7 Hz), 80.89 \text{ (d, J = 8.0 Hz), 74.41 – 72.75 \text{ (m), 38.31, 33.06, 31.03, 30.41, 29.77, 27.26 ppm.}} \)

\(^{19}\text{F NMR (DMSO-d}_6 \text{, 376 MHz):} \delta = -70.82 \text{ (bs), -71.17 \text{ (bs) ppm.}} \)

HRMS (ESI). Calculated for \( \text{C}_{21}\text{H}_{31}\text{F}_6\text{ORh} \text{[M}_{\text{monomer-}l}^+ = 643.0378 \). Found 643.0656.
Separation of enantiomers of the racemic complexes

Separation of the racemic mixture 2OCH₂CF₃-Cl
In a 5 ml flask a mixture of the racemic chloride complex 2OCH₂CF₃-Cl (35 mg, 0.067 mmol, 1 equiv.) and R-phenylglycinol (32 mg, 0.168 mmol, 2.5 equiv.) was dissolved in acetone (0.4 ml). This orange-yellow mixture was placed on a preparative TLC plate and eluted with hexane/acetone (3:1) mixture. Then, two orange silica gel bands were collected from the plate and placed separately on two Shott glass filters. The products were washed off the silica with a mixture of acetone and a few drops of HCl. The resulting red solutions were evaporated to dryness and extracted with 5 ml of CH₂Cl₂. The red solutions were washed twice with 10% aqueous HCl, dried over anhydrous Na₂SO₄, evaporated to dryness. The resulting oily residues were triturated with pentane to obtain an orange powders of enantiomerically pure complexes 2OCH₂CF₃-Cl-up and 2OCH₂CF₃-Cl-down.

To assess the quality of separation, the enantiomerically pure complex was dissolved in CDCl₃ and 1 equivalent of S-1-phenylethylamine (5.2 µL, 0.04 mmol) was added. The color of the solutions changed from red to orange indicating the formation of diastereomeric adducts. After recording of the spectra, the complex can be regenerated by diluting CDCl₃ from the NMR tube with 5 ml of CH₂Cl₂ and washing the resulting solution twice with 10% aqueous HCl. The organic phase was dried over anhydrous Na₂SO₄ and evaporated to dryness. The resulting oil was triturated with pentane to obtain orange powder of 2OCH₂CF₃-Cl.

Yield of the isomer 2OCH₂CF₃-Cl-up collected from the top band on silica plate: 13 mg, 37% (50% is theoretical maximum), ee > 95%.

Yield of the isomer 2OCH₂CF₃-Cl-down collected from the bottom band on silica plate: 11 mg 31% (50% is theoretical maximum), ee ≈ 80%. The purify can be improved by collecting more narrow bands from TLC plate.

¹H NMR spectra of the individual enantiomers 2OCH₂CF₃-Cl-up and 2OCH₂CF₃-Cl-down completely coincide with the spectrum of the racemic 2OCH₂CF₃-Cl.
Separation of the racemic mixture 2OCH(CF$_3$)$_2$-Cl

In a 5 ml flask, a mixture of the bromide complex 2OCH(CF$_3$)$_2$-Cl (29 mg, 0.05 mmol, 1 equiv.) and R-phenylglycinol (32 mg, 0.2 mmol, 4 equiv.) was dissolved in acetone (0.4 ml). The orange-yellow mixture was spotted on a preparative TLC plate and eluted with hexane/EtOAc (3:1). Then, two orange silica gel bands were collected from the plate and placed separately on two Shott glass filters. The products were washed off the silica with a mixture of acetone and a few drops of HCl. The resulting red solutions was evaporated to dryness, extracted with 5 ml of CH$_2$Cl$_2$. The red solution is washed twice with 10% aqueous HCl. Dried over anhydrous Na$_2$SO$_4$, evaporated to dryness. The resulting oils were triturated with pentane to obtain an orange powders of 2OCH(CF$_3$)$_2$-Cl-up and 2OCH(CF$_3$)$_2$-Cl-down.

To assess the quality of separation, 1 equivalent of S-1-phenylethylamine (5.2 μL, 0.04 mmol) was added to the red solutions of the complexes in CDCl$_3$. The color of the solutions changed to orange indicating the formation of diastereomeric adducts. After recording the spectra, the solutions were diluted with 5 ml CH$_2$Cl$_2$ was washed twice with 10% aqueous HCl. The organic phase was dried over anhydrous Na$_2$SO$_4$ and evaporated to dryness. The resulting oils were triturated with pentane to obtain an orange powders of 2OCH(CF$_3$)$_2$-Cl-up and 2OCH(CF$_3$)$_2$-Cl-down.

Yield of the isomer 2OCH(CF$_3$)$_2$-Cl-up collected from the top band on silica plate: 11 mg, 38% (50% is theoretical maximum), ee > 95%.

Yield of the isomer 2OCH(CF$_3$)$_2$-Cl-down collected from the bottom band on silica plate: 14 mg, 48% (50% is theoretical maximum), ee ≈ 80%. The purify can be improved by collecting more narrow bands from TLC plate.

$^1$H NMR spectra of individual enantiomers 2OCH(CF$_3$)$_2$-Cl-up and 2OCH(CF$_3$)$_2$-Cl-down completely coincides with the spectrum of the racemic complex 2OCH(CF$_3$)$_2$-Cl.
Catalytic Reactions

General procedure: O-pivaloyl hydroxamate 8 (22 mg, 0.10 mmol), rhodium catalyst (2 μmol, 2 mol-% of Rh), and CsOAc (5 mg, 0.025 mmol, 25 mol-%) were placed in a reaction vial and dissolved in MeOH (0.5 mL). Then corresponding alkene (0.20 mmol, 2.0 equiv.) was added to the stirred solution. The resulting mixture was stirred for 16 hours and then the solvent was evaporated in vacuo. The residue was subjected to column chromatography on silica (eluent: CH2Cl2:EtOAc 5:1), which gave target dihydroisoquinolone.

Catalyst 2 OCH2CF3-Cl: Yield 19 mg (0.093 mmol, 93%) colorless solid, ee = 34%
Catalyst 2 OCH(CF3)2-Cl: Yield 19 mg (0.093 mmol, 93%) colorless solid, ee = 54%

1H NMR (chloroform-d, 400 MHz): δ = 8.05 (dd, 1H, J=7.8, 1.4 Hz), 7.45 (td, 1H, J=7.5, 1.4 Hz), 7.34 (td, 1H, J=7.6, 1.2 Hz), 7.20 (d, 1H, J=7.5 Hz), 6.75 (s, 1H), 3.71 (dd, 1H, J=12.5, 4.4 Hz), 3.39 (dt, 1H, J=12.5, 3.9 Hz), 2.82 (tt, 1H, J=7.6, 3.8 Hz), 1.68 (q, 2H, J=7.2 Hz), 1.40 – 1.23 (m, 4H), 0.88 (t, 3H, J=7.0 Hz) ppm.

13C NMR (chloroform-d, 101 MHz): δ = 166.41, 143.40, 132.20, 128.19, 127.11, 44.21, 38.00, 33.16, 29.66, 22.80, 14.11.

The NMR spectra of the product are similar to those previously reported.

HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 90:10, 1.0 ml/min; tr = 5.5 min, tr = 6.2 min.

Catalyst 1,3,4,4a,5,10b-hexahydro-1,4-methanophenanthridin-6(2H)-one (10)
Catalyst 2 OCH2CF3-Cl: Yield 17 mg (0.080 mmol, 80%) colorless solid, ee = 42%
Catalyst 2 OCH(CF3)2-Cl: Yield 18 mg (0.085 mmol, 85%) colorless solid, ee = 76%

1H NMR (chloroform-d, 400 MHz): δ = 8.09 (d, 1H, J=7.8 Hz), 7.45 (t, 1H, J=7.5 Hz), 7.22 (d, 1H, J=7.7 Hz), 6.45 (s, 1H), 3.81 (d, 1H, J=8.9 Hz), 3.12 (d, 1H, J=8.9 Hz),
2.32 (s, 1H), 2.25 (d, 1H, J=3.9 Hz), 1.70 – 1.62 (m, 3H), 1.52 (t, 1H, J=8.8 Hz), 1.25 (d, 1H, J=3.0 Hz), 1.18 (d, 1H, J=10.6 Hz) ppm.

The NMR spectra of the product are similar to those previously reported.³

HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 90:10, 1.0 ml/min; tr = 7.0 min, tr = 16.6 min.
General procedure:
N-(pivaloyloxy)-1H-indole-1-carboxamide 11 (26 mg, 0.10 mmol), rhodium catalyst (2.5 µmol, 2.5 mol-% of Rh), and CsOAc (5 mg, 0.025 mmol, 25 mol-%) were placed in a reaction vial and dissolved in MeOH (0.5 mL). Then corresponding alkene (0.20 mmol, 2.0 equiv.) was added and the mixture was stirred for 16 hours. The resulting solution was diluted with CH₂Cl₂ and transferred to a round-bottom flask. Silica was added to the flask and volatiles were evaporated under a vacuum. The purification was performed by flash column chromatography on silica gel (eluent indicated for each case) to give 3,4-dihydropyrimido[1,6-a]indol-1(2H)-ones.

Cp*RhCl₂/₂ Yield 12 mg (0.05 mmol, 50%)
Catalyst 2: Yield 20 mg (0.083 mmol, 83%), ee = 26%
Catalyst 2OCH₂CF₃-Cl: Yield 21 mg (0.086 mmol, 87%), ee = 2%
Catalyst 2OCH(CF₃)₂-Cl: Yield 19 mg (0.079 mmol, 79%), ee = 2%

¹H NMR (chloroform-d, 400 MHz): δ = 8.33 (d, 1H, J=8.2 Hz), 7.50 (d, 1H, J=7.7 Hz), 7.32 – 7.11 (m, 2 H), 6.35 (s, 1H), 6.30 (s, 1H), 3.72 – 3.40 (m, 1H), 3.26 (t, 1H, J=10.1 Hz), 3.10 (s, 1H), 2.03 – 1.88 (m, 1H), 1.74 – 1.57 (m, 1H), 1.53 – 1.33 (m, 4H), 0.94 (t, 3H, J=6.9 Hz) ppm.

¹³C NMR (chloroform-d, 101 MHz): δ = 152.57, 139.27, 135.46, 129.29, 123.72, 122.76, 120.07, 115.30, 102.74, 44.34, 33.65, 30.96, 29.16, 22.79, 14.07 ppm.


HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 80:20, 1.0 ml/min; tr = 5.2 min, tr = 6.5 min.
**13. Eluent: EtOAc/Hexane 5/1. Beige solid**

Catalyst \([\text{Cp}^*\text{RhCl}_2]\): Yield 18 mg (0.081 mmol, 83%)

Catalyst 2: Yield 18 mg (0.083 mmol, 83%), ee = 32%

Catalyst 2OCH\(_2\)CF\(_3\)-Cl: Yield 17 mg (0.08 mmol, 80%), ee = 22%

Catalyst 2OCH(CF\(_3\))\(_2\)-Cl: Yield 17 mg (0.08 mmol, 80%), ee = 20%

1H NMR (acetone-d6, 400 MHz): \(\delta = 8.29\) (d, 1H, J=8.1 Hz, CH\(_{\text{Ar}}\)), 7.49 (d, 1H, J=7.6 Hz, CH\(_{\text{Ar}}\)), 7.26 – 7.08 (m, 2H, CH\(_{\text{Ar}}\)), 6.90 (s, br, 1H, NH), 6.46 (s, 1H, CH\(_{\text{ind}}\)), 3.94 (dd, 1H, J=10.7, 5.4 Hz), 3.80 (dt, 1H, J=10.7, 7.5 Hz), 3.72 – 3.62 (m, 1H), 3.57 – 3.47 (m, 1H), 3.33 (p, 1H, J=5.8 Hz), 2.99 (s, 1H, OH) ppm

\(^1\)H NMR data is in agreement with those reported previously.\(^6\)

HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 80:20, 1.0 ml/min; tr = 4.7 min, tr = 5.1 min.

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**14. Eluent: Hexane/EtOAc 3/1.**

Catalyst \([\text{Cp}^*\text{RhCl}_2]\): Yield 23 mg (0.091 mmol, 91%)

Catalyst 2: Yield 21 mg (0.083 mmol, 83%), ee = 74%

Catalyst 2OCH\(_2\)CF\(_3\)-Cl: Yield 22 mg (0.087 mmol, 87%), ee = 4%

Catalyst 2OCH(CF\(_3\))\(_2\)-Cl: Yield 23 mg (0.091 mmol, 91%), ee = 46%

1H NMR (chloroform-d, 400 MHz): \(\delta = 8.39\) (d, 1H, J=8.1 Hz), 7.49 (d, 1H, J=7.6 Hz), 7.31 – 7.15 (m, 2H), 6.36 (s, 1H), 6.12 (s, 1H), 3.73 (d, 1H, J=8.6 Hz), 3.27 (d, 1H, J=8.7 Hz), 2.47 (s, 1H), 2.32 (s, 1H), 1.69 – 1.59 (m, 3H), 1.52 – 1.45 (m, 1H), 1.32 – 1.21 (m, 2H) ppm

\(^1\)H NMR data is in agreement with those reported previously.\(^6\)

HPLC: Chiralpak IB-3 column (4.6 × 150 mm), heptane/i-PrOH 98:2, 1.0 ml/min; tr = 18.3 min, tr = 19.9 min.
15a. Eluent: Hexane/EtOAc 3/1

Catalyst [Cp*RhCl₂]: Yield 7 mg (0.027 mmol, 27%)
Catalyst 2: Yield 10 mg (0.039 mmol, 39%), ee = 32%
Catalyst 2OCH₂CF₃-Cl: Yield 5 mg (0.019 mmol, 19%), ee = 10%
Catalyst 2OCH(CF₃)₂-Cl: Yield 2 mg (0.007 mmol, 7%), ee = 30%

¹H NMR (chloroform-d, 400 MHz): δ = 8.36 (d, 1H, J=8.1 Hz, C-H¹), 7.50 (d, 1H, J=7.7 Hz, C-H²),
7.40 (s, 5H, C-H³), 7.33 – 7.15 (m, 2H, C-H⁴), 6.34 (s, 1H), 5.56 (s, 1H), 4.83 (dd, 1H, J=10.6, 4.3 Hz),
3.43 – 3.29 (m, 1H), 3.27 – 3.11 (m, 1H) ppm

¹³C NMR (chloroform-d, 101 MHz): δ = 152.30, 139.99, 135.37, 133.58, 129.46, 129.21, 128.73,
126.36, 123.92, 123.00, 120.16, 115.41, 104.02, 55.31, 31.99 ppm

HRMS (APCI): Exact mass calculated for C₁₅H₁₉N₂O [M+H]+ = 263.1179, found 263.1181.

HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 80:20, 1.0 ml/min; tr = 5.1 min, tr = 6.4 min.
15b. Eluent: Hexane/EtOAc 3/1
Catalyst [Cp*RhCl₂]₂: product was not observed
Catalyst 2: Yield 7 mg (0.026 mmol, 26%), ee = 38%
Catalyst 2OCH₂CF₃-Cl: Yield 15 mg (0.057 mmol, 57%), ee = 10%
Catalyst 2OCH(CF₃)₂-Cl: Yield 19 mg (0.073 mmol, 73%), ee = 56%

¹H NMR (chloroform-d, 400 MHz): δ = 8.38 (d, 1H, J=8.3 Hz), 7.46 (d, 1H, J=7.7 Hz), 7.34 (m, 6H), 7.22 (t, 1H, J=7.6 Hz), 6.38 (s, 1H), 6.09 (s, 1H), 4.42 (t, 1H, J=7.8 Hz), 3.66 (d, 2H, J=8.0 Hz) ppm.
HRMS (APCI): Exact mass calculated for C₁₅H₁₉N₂O [M+H]⁺ = 263.1179, found 263.1181.
¹H NMR data is in agreement with those reported previously.⁷
HPLC: Chiralpak IA-3 column (4.6 × 150 mm), heptane/i-PrOH 80:20, 1.0 ml/min; tr = 6.7 min, tr = 8.2 min.
X-ray diffraction data

X-ray diffraction data for 2OMe-Cl, 2OCH(CF₃)₂-I, and 5OMe were collected at 120 K with a Bruker APEXII DUO CCD diffractometer; data for other compounds were collected at 100 K with a Bruker Quest D8 CMOS diffractometer, both using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans). Structures were solved using Intrinsic Phasing with the ShelXT⁸ structure solution program in Olex2⁹ and then refined with the XL¹⁰ refinement package using Least-Squares minimization against F² in the anisotropic approximation for non-hydrogen atoms. Positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. Crystal data and structure refinement parameters are given in Tables S1 and S2. CCDC 2288541 (2OCH(CF₃)₂-Br), 2288542 (2OCH(CF₃)₂-Cl), 2288540 (5OCH(CF₃)₂), 2288538 (2OCH(CF₃)₂-I), 2288545 (2OCH₂CF₃), 2288539 (2OCH₂Br), 2288536 (2OCH₂Cl), 2288543 (2OMe-Cl), 2288535 (5OMe), and 2288537 (4InBr₄) contain the supplementary crystallographic data for this paper. The Flack parameter s for 2OMe-Cl and 5OMe, which crystallize in the chiral space groups, are 0.46(4) and 0.48(10), respectively.

Table S1. Crystal data and structure refinement parameters.

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<th>Empirical formula</th>
<th>2OCH(CF₃)₂-Br</th>
<th>2OCH(CF₃)₂-Cl</th>
<th>5OCH(CF₃)₂</th>
<th>2OCH(CF₃)₂-I</th>
<th>5OCH₂CF₃</th>
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<td>Monoclinic</td>
<td>Monoclinic</td>
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NMR spectra

$^1$H spectrum of [(η$^5$-1,3,6-$^t$Bu-fulvene)Rh(1,5-C$_8$H$_{12}$)]$^-$InBr$_4$ $^-$ (4InBr$_4$)

13C spectrum of [(η$^5$-1,3,6-$^t$Bu-fulvene)Rh(1,5-C$_8$H$_{12}$)]$^-$InBr$_4$ $^-$ (4InBr$_4$)
$^1$H spectrum of (η$^5$-1,3-$^t$Bu$_2$-4-$^t$Bu(OH)CHC$_5$H$_2$)Rh(1,5-C$_8$H$_{12}$) (5OH).

$^{13}$C spectrum of (η$^5$-1,3-$^t$Bu$_2$-4-$^t$Bu(OH)CHC$_5$H$_2$)Rh(1,5-C$_8$H$_{12}$) (5OH).
$^1$H spectrum of $[(\eta^5-1,3$-$^{t}$Bu$_2$-$^{4}$Bu(HO)CH-$\text{C}_{2}$$\text{H}_{2}$)RhCl$_2$]$2$ (2OH-Cl).

$^{13}$C spectrum of $[(\eta^5-1,3$-$^{t}$Bu$_2$-$^{4}$Bu(HO)CH-$\text{C}_{2}$$\text{H}_{2}$)RhCl$_2$]$2$ (2OH-Cl).
$^1$H spectrum of $[[\eta^5-1,3-\text{Bu}_2-4-\text{Bu}(\text{HO})\text{C}_3\text{H}_2]\text{RhBr}_2]_2$ (2OH-Br). dr 1:1.78

$^{13}$C spectrum of $[[\eta^5-1,3-\text{Bu}_2-4-\text{Bu}(\text{HO})\text{C}_3\text{H}_2]\text{RhBr}_2]_2$ (2OH-Br).
$^{1}H$ spectrum of $[(\eta^{5}-1,3-^{1}Bu_{2}-4-^{1}Bu(HO)CH_{3}H_{2})RhI_{2}]_{2}$ (2OH-I). dr 1: 0.94

$^{13}C$ spectrum of $[(\eta^{5}-1,3-^{1}Bu_{2}-4-^{1}Bu(HO)CH_{3}H_{2})RhI_{2}]_{2}$ (2OH-I).
$^1$H Spectrum of (η²-1,3-Bu₂-4-Bu(CF₃CH₂O)CH-C₅H₂)Rh(1,5-C₈H₁₂) (5OCH₂CF₃).

$^{13}$C Spectrum of (η⁵-1,3-Bu₂-4-Bu(CF₃CH₂O)CH-C₅H₂)Rh(1,5-C₈H₁₂) (5OCH₂CF₃).
$^{19}$F Spectrum of $(\eta^5-1,3$-$^1$Bu$^4$-4$^1$Bu(CF$_3$CH$_2$O)CH-C$_8$H$_2$)Rh(1,5-C$_8$H$_{12}$) (5OCH$_2$CF$_3$).
\(^1\)H Spectrum of \(\eta^5-1,3-i^1\text{Bu}_2-4^1\text{Bu}((\text{CF}_3)_2\text{CHO})\text{CH-C}_5\text{H}_2\text{Rh}(1,5-\text{C}_8\text{H}_{12})\) (5\text{SOCH(CF}_3)_2).
$^{19}$F Spectrum of $(\eta^5-1,3^1\text{Bu}_2-4^1\text{Bu}((\text{CF}_3)_2\text{CHO})\text{CH}-\text{C}_8\text{H}_2)\text{Rh}(1,5-\text{C}_8\text{H}_{12})\ (5\text{OCH}(\text{CF}_3)_2)$. 

\[ \text{OCH(CF}_3)_2 \]
$^1$H spectrum of \([\eta^5-1,3^{-1}\text{Bu}_2-4^{-1}\text{Bu}((\text{CH}_3\text{O})\text{CH-C}_5\text{H}_2)\text{RhCl}_2]_2\) (2OCH$_3$-Cl).

$^{13}$C spectrum of \([\eta^5-1,3^{-1}\text{Bu}_2-4^{-1}\text{Bu}((\text{CF}_3)_2\text{CHO})\text{CH-C}_5\text{H}_2)\text{RhCl}_2]_2\) (2OCH$_3$-Cl).
$^1$H Spectrum of [(η⁵-1,3-ιBu₂-4-ιBu(CF₃CH₂O)CH-C₅H₂)RhCl₂]₂ (2OCH₂CF₃-Cl).

$^{13}$C Spectrum of [(η⁵-1,3-ιBu₂-4-ιBu(CF₃CH₂O)CH-C₅H₂)RhCl₂]₂ (2OCH₂CF₃-Cl).
$^{19}\text{F Spectrum of } [([\eta^5-1,3-\text{Bu}_2-4-\text{Bu}(\text{CF}_3\text{CH}_2\text{O})\text{CH}-\text{C}_5\text{H}_2)\text{RhCl}_2]_2 (2\text{OCH}_2\text{CF}_3-\text{Cl})].$
$^1$H spectrum of (η$^5$-1,3-tBu$_2$-4-tBu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)RhCl$_2$ (2OCH(CF$_3$)$_2$-Cl).

$^{13}$C spectrum of (η$^5$-1,3-tBu$_2$-4-tBu((CF$_3$)$_2$CHO)CH-C$_5$H$_2$)RhCl$_2$ (2OCH(CF$_3$)$_2$-Cl).
$^{19}$F spectrum of ($\eta^5$-1,3-Bu$_2$-4-Bu($\text{CF}_3$)$_2$CHOCH-C$_5$H$_2$)RhCl$_2$ (2OCH($\text{CF}_3$)$_2$-Cl).
$^1$H spectrum of [(η$^5$-1,3-iBu$_2$-4-iBu(CH$_3$O)CH-C$_5$H$_2$)RhBr$_2$]$_2$ (2OMe-Br).

$^{13}$C spectrum of [(η$^5$-1,3-iBu$_2$-4-iBu(CH$_3$O)CH-C$_5$H$_2$)RhBr$_2$]$_2$ (2OMe-Br).
\(^1\)H spectrum of (\(\eta^5\)-1,3-\(\text{Bu}\)_2-4-\(\text{Bu}\)((\text{CF}_3)_2\text{CHO})\(\text{CH}\)-\(\text{C}_5\text{H}_2\))\(\text{RhBr}_2\) (2\(\text{OCH}\)(\(\text{CF}_3\))_2-\(\text{Br}\)).

\(\text{OCH}\)(\(\text{CF}_3\))_2

\[^{13}\text{C}\] spectrum of (\(\eta^5\)-1,3-\(\text{Bu}\)_2-4-\(\text{Bu}\)((\text{CF}_3)_2\text{CHO})\(\text{CH}\)-\(\text{C}_5\text{H}_2\))\(\text{RhBr}_2\) (2\(\text{OCH}\)(\(\text{CF}_3\))_2-\(\text{Br}\)).

\(\text{OCH}\)(\(\text{CF}_3\))_2
$^{19}$F Spectrum of $(\eta^{5}-1,3-\text{Bu}_2-4-\text{Bu}((\text{CF}_3)_2\text{CHO})\text{CH-C}_5\text{H}_2)\text{RhBr}_2$ (2OCH(\text{CF}_3)_2-\text{Br}).
$^1$H spectrum of $[(\eta^5-1,3^2\text{Bu}_2-4^1\text{Bu})(\text{CF}_3\text{CHO})\text{CH-C}_5\text{H}_2]_2\text{RhI}_2)_2$ (2OCH(\text{CF}_3)\_2\_I) in CDCl$_3$. 

$^1$H spectrum of $[(\eta^5-1,3^2\text{Bu}_2-4^1\text{Bu})(\text{CF}_3\text{CHO})\text{CH-C}_5\text{H}_2]_2\text{RhI}_2)_2$ (2OCH(\text{CF}_3)\_2\_I) in DMSO-d$_6$. 

0.88 Hexane
1.17
1.25 Hexane
1.36
1.57 H$_2$O
1.63
$^{13}$C spectrum of \([\eta^5-1,3\text{-}^t\text{Bu}_2-4\text{-}^t\text{Bu}((\text{CF}_3)_2\text{CHO})\text{CHC}_6\text{H}_2]\text{RhI}_2\text{[2]} \text{(2OCH(CF}_3\text{)}_2\text{-I).}

\[\text{OCH(CF}_3\text{)}_2\]

$^{19}$F spectrum of \([\eta^5-1,3\text{-}^t\text{Bu}_2-4\text{-}^t\text{Bu}((\text{CF}_3)_2\text{CHO})\text{CHC}_6\text{H}_2]\text{RhI}_2\text{[2]} \text{(2OCH(CF}_3\text{)}_2\text{-I).}

\[\text{OCH(CF}_3\text{)}_2\]
$^1$H spectrum of 12.

$^{13}$C spectrum of 12.
**1H spectrum of 15a.**

![1H Spectrum](image)

**13C spectrum of 15a**

![13C Spectrum](image)
References


