Electronic Supplementary Information

Chiral-at-Metal Iridium Complex for Efficient Enantioselective Transfer Hydrogenation of Ketones

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1. General Information

Synthesis of the ligands and catalysts were typically carried out under an atmosphere of argon with magnetic stirring unless stated otherwise. Catalysis reactions were performed under air in a brown glass vial. Solvents were distilled under argon from calcium hydride (CH$_3$CN, CH$_2$Cl$_2$) or sodium/benzophenone (THF, toluene). Pyrazole additives,$^1$ Λ-RhO,$^2$ Λ-IrO,$^3$ and Λ-IrS$^3$ were prepared according to published procedures. All other reagents were purchased from Acros, Aldrich, Alfa and J&K, and used without further purification. Flash column chromatography was performed with silica gel (300-400 mesh, Yantai Jiangyou Silica Gel Development Co., Ltd). $^1$H-NMR and $^{13}$C-NMR spectra were recorded on a Bruker AM (500 MHz) spectrometer at ambient temperature. NMR standards were used as follows: CDCl$_3$ = 7.26 ppm ($^1$H-NMR) CD$_2$Cl$_2$ = 5.32 ppm ($^1$H-NMR); CDCl$_3$ = 77.0 ppm ($^{13}$C-NMR), CD$_2$Cl$_2$ = 53.8 ppm ($^{13}$C-NMR). Chiral HPLC chromatograms were obtained from an Agilent 1260 Series HPLC system. High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0T FT-MS instrument using ESI technique. Optical rotations were measured on a Anton Paar MCP 500 polarimeter at concentrations of 1.0 g/100 mL. The ee values of products were determined by chiral HPLC, while the absolute configurations of the produced chiral secondary alcohols were assigned by comparison of optical rotations with published examples.$^4$-$^{12}$
2. Optimization of the ATH Reaction with Acetophenone 1a

2.1 Metal Catalyst Screening (Figure 1)

**General Procedure.** To a biphasic solution of HCOONH₄ (189.1 mg, 2.97 mmol) in iPrOH/H₂O (168 µL/168 µL) was added the metal catalyst Λ-RhO (2.7 mg, 0.0033 mmol), Λ-IrO (3.0 mg, 0.0033 mmol), or Λ-IrS (3.1 mg, 0.0033 mmol) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then acetophenone (1a, 40.0 mg, 0.33 mmol) was added. The reaction solution was stirred at 60 °C for 22-24 h. Conversion was determined by ¹H-NMR and enantiomeric excess established by HPLC analysis using a Daicel Chiralpak OJ column (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C).

2.2 Ligand Additive Screening (Figure 1)

**General Procedure.** To a biphasic solution of the ligand additive (0.033 mmol) and HCOONH₄ (189.1 mg, 2.97 mmol) in iPrOH/H₂O (168 µL/168 µL) was added the metal catalyst Λ-IrS (0.6-3.1 mg, 0.20-1.0 mol%) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then acetophenone (1a, 40.0 mg, 0.33 mmol) was added. The reaction solution was stirred at 60 °C for the indicated time. Conversion was determined by ¹H-NMR and enantiomeric excess established by HPLC analysis using a Daicel Chiralpak OJ column (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C).

2.3 Optimization of the Reaction Temperature and Solvents (Table S1)

*Preparation of stock solutions of the catalyst Λ-IrS.* A stock solution in THF (3.97 mM): The chiral iridium complex Λ-IrS (1.92 mg, 2.02 µmol) was dissolved in freshly distilled THF (508 µL). A stock solution in iPrOH (3.97 mM): The chiral iridium complex Λ-IrS (1.92 mg, 2.02 µmol) was dissolved in freshly distilled isopropanol (508 µL). The stock solutions were prepared freshly and used for the low-loading catalysis reactions.
**General Procedure.** To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol and HCOONH₄ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-IrS (0.67 μmol, 168 μL of a 3.97 mM stock solution in iPrOH (entry 1) or THF (entries 2-4)) and H₂O (168 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then acetophenone (1a, 40.0 mg, 0.33 mmol) was added. The reaction solution was stirred at 20 °C, 40 °C or 60 °C for the indicated time. Conversion was determined by ¹H-NMR and enantiomeric excess established by HPLC analysis using a Daicel Chiralpak OJ column (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C).

**Table S1.** Optimization of the reaction temperatures and solvents for the ATH reaction.

<table>
<thead>
<tr>
<th>Entry</th>
<th>T (°C)</th>
<th>Solvents</th>
<th>t (h)</th>
<th>Conv. (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>iPrOH/H₂O (1:1)</td>
<td>3</td>
<td>85</td>
<td>96.0</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>THF/H₂O (1:1)</td>
<td>1</td>
<td>77</td>
<td>96.0</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>THF/H₂O (1:1)</td>
<td>6</td>
<td>67</td>
<td>97.0</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>THF/H₂O (1:1)</td>
<td>24</td>
<td>50</td>
<td>97.4</td>
</tr>
</tbody>
</table>
3. Synthesis of Racemic Products as HPLC References

**General Procedure.** To a mixture of 5-(4-methoxyphenyl)-3-methyl-1\textit{H}-pyrazole (6.2 mg, 0.033 mmol) and HCOONH\textsubscript{4} (189.1 mg, 2.97 mmol) was added the racemic metal catalyst \textit{rac-IrS} (0.67 \textmu mol, 168 \textmu L of a 3.97 mM stock solution in THF) and H\textsubscript{2}O (168 \textmu L) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1a-x (0.33 mmol) was added. The reaction solution was stirred at 40 °C until complete disappearance of the starting material (detected by TLC), cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (\textit{n}-hexane/dichloromethane = 1:1 to 1:2) to afford the racemic product as HPLC reference for determination of enantiomeric excess in the ATH reaction of ketones.
4. Substrate Scope

**General Procedure (Figure 2).** To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH₄ (189.1 mg, 2.97 mmol) in THF/H₂O (168 μL/168 μL) was added the metal catalyst Λ-IrS (0.6-3.1 mg, 0.20-1.0 mol%) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1a-x (0.33 mmol) was added. The reaction solution was stirred at 40 °C or 60 °C for the indicated time until complete disappearance of the starting material, cooled down to room temperature, then dried by high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford products 2a-x. Enantiomeric excess was determined by chiral HPLC analysis.

(R)-1-phenylethanol (2a). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH₄ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-IrS (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H₂O (168 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then acetophenone (1a, 40.0 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 10 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product 2a as a light yellow liquid (39.1 mg, 0.32 mmol, yield: 96%). Enantiomeric excess was established by HPLC analysis using a Daicel
Chiralpak OJ column, ee = 97% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C, t\(_f\) (minor) = 11.6 min, t\(_f\) (major) = 13.4 min).

\([\alpha]^{20}_D = +36.0\) (c 1.0, CHCl\(_3\)) (lit.\(^4\): \([\alpha]^{20}_D = +59.5\) (c 1.0, CHCl\(_3\)), (R) 98% ee). Configuration of the product was assigned as R accordingly.

\(^{1}\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.38-7.33 (m, 4H), 7.30-7.26 (m, 1H), 4.90 (q, J = 6.5 Hz, 1H), 1.88 (br, 1H), 1.50 (d, J = 6.5 Hz, 3H).

Other analytic data of 2a are consistent with the literature.\(^4\)

\((R)-1-(p\text{-tolyl})\text{ethanol (2b)}\). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1\(H\)-pyrazole (6.2 mg, 0.033 mmol) and HCOONH\(_4\) (189.1 mg, 2.97 mmol) was added the metal catalyst \(\Lambda\text{-IrS}\) (0.67 \(\mu\)mol, 168 \(\mu\)L of a 3.97 mM stock solution in THF) and H\(_2\)O (168 \(\mu\)L) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1-(p-tolyl)ethanone (1b, 44.7 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 9 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product 2b as a light yellow liquid (44.2 mg, 0.32 mmol, yield: 97%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OJ column, ee = 98% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C, t\(_f\) (minor) = 11.4 min, t\(_f\) (major) = 12.8 min).

\([\alpha]^{20}_D = +41.8\) (c 1.0, CHCl\(_3\)) (lit.\(^4\): \([\alpha]^{20}_D = +55.4\) (c 1.0, CHCl\(_3\)), (R) 99% ee). Configuration of the product was assigned as R accordingly.

\(^{1}\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.26 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 4.86 (q, J = 6.5 Hz, 1H), 2.34 (s, 3H), 1.83 (br, 1H), 1.48 (d, J = 6.5 Hz, 3H).

Other analytic data of 2b are consistent with the literature.\(^4\)

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(R)-1-(4-methoxyphenyl)ethanol (2c). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH₄ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-IrS (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H₂O (168 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1-(4-methoxyphenyl)ethanone (1c, 50.0 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 12 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product 2c as a light yellow liquid (47.2 mg, 0.31 mmol, yield: 97%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OJ column, ee = 98% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 90:10, flow rate: 1.0 mL/min, 25 °C, tᵣ(minor) = 15.0 min, tᵣ(major) = 16.0 min).

[α]²⁰D = +41.1 (c 1.0, CHCl₃) (lit.⁴: [α]²⁰D = +16.5 (c 1.0, CHCl₃), (R) 96% ee). Configuration of the product was assigned as R accordingly.

¹H-NMR (500 MHz, CDCl₃): δ 7.31 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 4.87 (q, J = 6.4 Hz, 1H), 3.81 (s, 3H), 1.70 (br, 1H), 1.48 (d, J = 6.4 Hz, 3H).

Other analytic data of 2c are consistent with the literature.⁴

(R)-1-(4-chlorophenyl)ethanol (2d). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH₄ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-IrS
(0.67 µmol, 168 µL of a 3.97 mM stock solution in THF) and H₂O (168 µL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1-(4-chlorophenyl)ethanone (1d, 51.6 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 8 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product 2d as a light yellow liquid (51.9 mg, 0.33 mmol, yield: 99%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OJ column, ee = 97% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C, tᵣ(minor) = 10.4 min, tᵣ(major) = 11.3 min).

\[ [\alpha]^{20}_{D} = +39.4 \text{ (c 1.0, CHCl}_3) \text{ (lit. } [\alpha]^{20}_{D} = +44.2 \text{ (c 1.0, CHCl}_3), (R) 96\% \text{ ee)} \]. Configuration of the product was assigned as \( R \) accordingly.

\(^1\)H-NMR (500 MHz, CDCl₃): \( \delta \) 7.33-7.30 (m, 4H), 4.89 (q, \( J = 6.5 \text{ Hz} \), 1H), 1.78 (br, 1H), 1.48 (d, \( J = 6.5 \text{ Hz} \), 3H).

Other analytic data of 2d are consistent with the literature.⁴

(R)-1-(o-tolyl)ethanol (2e). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH₄ (189.1 mg, 2.97 mmol) was added the metal catalyst \( \Lambda-\text{IrS} \) (0.67 µmol, 168 µL of a 3.97 mM stock solution in THF) and H₂O (168 µL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1-(o-tolyl)ethanone (1e, 44.6 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 36 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product 2e as a light yellow liquid (42.4 mg, 0.31 mmol, yield: 95%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak AD-H column, ee = 51% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 0.5 mL/min, 25 °C, tᵣ(minor) = 14.2 min, tᵣ(major) = 15.8 min).
\([\alpha]^{20}_D = +34.5 \text{ (c 1.0, CHCl}_3)\) (lit.\(^5\)) \([\alpha]^{20}_D = +56.1 \text{ (c 1.0, CHCl}_3), (R) 98\% \text{ ee}\). Configuration of the product was assigned as \(R\) accordingly.

\(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.51 (d, \(J = 8.7\) Hz, 1H), 7.24-7.22 (m, 1H), 7.19-7.13 (m, 2H), 5.14 (q, \(J = 6.2\) Hz, 1H), 2.35 (s, 3H), 1.70 (br, 1H), 1.48 (d, \(J = 6.5\) Hz, 3H).

Other analytic data of \(2e\) are consistent with the literature.\(^5\)

\((R)-1\)-(3,5-dimethylphenyl)ethanol (2f). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1\(H\)-pyrazole (6.2 mg, 0.033 mmol) and HCOONH\(_4\) (189.1 mg, 2.97 mmol) was added the metal catalyst \(\Lambda\)-IrS (0.67 \(\mu\)mol, 168 \(\mu\)L of a 3.97 mM stock solution in THF) and H\(_2\)O (168 \(\mu\)L) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1-(3,5-dimethylphenyl)ethanone (1f, 50.0 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 8 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (\(n\)-hexane/dichloromethane = 1:1 to 1:2) to afford product 2f as a light yellow solid (47.3 mg, 0.32 mmol, yield: 95%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak IC column, ee = 97\%. (250 x 4.6 mm, 220 nm, \(n\)-hexane/isopropanol = 98:2, flow rate: 0.5 mL/min, 25 °C, \(t_r\)(minor) = 18.4 min, \(t_r\)(major) = 19.6 min).

\([\alpha]^{20}_D = +38.9 \text{ (c 1.0, CHCl}_3)\) (lit.\(^6\)) \([\alpha]^{20}_D = +45.4 \text{ (c 1.0, CHCl}_3), (R) 95\% \text{ ee}\). Configuration of the product was assigned as \(R\) accordingly.

\(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 6.99 (s, 2H), 6.92 (s, 1H), 4.83 (q, \(J = 6.6\) Hz, 1H), 2.32 (s, 6H), 1.74 (br, 1H), 1.49 (d, \(J = 6.5\) Hz, 3H).

Other analytic data of 2f are consistent with the literature.\(^6\)
(R)-1-(3,5-bis(trifluoromethyl)phenyl)ethanol (2g). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH₄ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-IrS (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H₂O (168 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1-(3,5-bis(trifluoromethyl)phenyl)ethanone (1g, 85.3 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 10 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (*n*-hexane/dichloromethane = 1:1 to 1:2) to afford product 2g as a light yellow solid (80.9 mg, 0.31 mmol, yield: 94%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 90% (250 x 4.6 mm, 220 nm, *n*-hexane/isopropanol = 99:1, flow rate: 1.0 mL/min, 25 °C, tᵣ(minor) = 9.6 min, tᵣ(major) = 11.3 min).

[α]⁺²⁰ₒ = +16.3 (c 1.0, CHCl₃) (lit.⁴: [α]⁺²⁰ₒ = +22.6 (c 1.0, CHCl₃), (R) 94% ee). Configuration of the product was assigned as R accordingly.

¹H-NMR (500 MHz, CDCl₃): δ 7.85 (s, 2H), 7.79 (s, 1H), 5.07-5.03 (m, 1H), 1.97 (d, J = 3.8 Hz, 1H), 1.56 (d, J = 6.3 Hz, 3H).

Other analytic data of 2g are consistent with the literature.⁴

(R)-1-(naphthalen-2-yl)ethanol (2h). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH₄ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-IrS (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H₂O (168 μL) in a brown glass vial.
The mixture was stirred for 10 min at room temperature, then 1-(naphthalen-2-yl)ethanone (1h, 56.6 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 10 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product 2h as a light yellow solid (56.8 mg, 0.33 mmol, yield: 99%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OJ column, ee = 97% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 90:10, flow rate: 1.0 mL/min, 25 °C, t_r(minor) = 16.4 min, t_r(major) = 21.0 min).

[α]_D^20 = +38.9 (c 1.0, CHCl₃) (lit. [^4^]: [α]_D^20 = +40.9 (c 1.0, CHCl₃), (R) 99% ee). Configuration of the product was assigned as R accordingly.

^1^H-NMR (500 MHz, CDCl₃): δ 7.85-7.82 (m, 4H), 7.52-7.45 (m, 3H), 5.08 (q, J = 6.5 Hz, 1H), 1.92 (br, 1H), 1.48 (d, J = 6.5 Hz, 3H).

Other analytic data of 2h are consistent with the literature[^4^].

(R)-1-(furan-3-yl)ethanol (2i). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH₄ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-IrS (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H₂O (168 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1-(furan-3-yl)ethanone (1i, 36.1 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 8 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product 2i as a light yellow liquid (34.8 mg, 0.31 mmol, yield: 95%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OJ column, ee = 96% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C, t_r(minor) = 9.8 min, t_r(major) = 11.4 min).
$[\alpha]^{20}_D = +4.9$ (c 1.0, CHCl$_3$) (lit.\textsuperscript{7}: $[\alpha]^{20}_D = +9.6$ (c 1.0, CHCl$_3$), ($R$) 83\% ee). Configuration of the product was assigned as $R$ accordingly.

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.39 (s, 2H), 6.43 (s, 1H), 4.89-4.87 (m, 1H), 1.62 (br, 1H), 1.50 (d, $J = 6.5$ Hz, 3H).

Other analytic data of 2i are consistent with the literature.\textsuperscript{7}

![Diagram](image)

**$(R)$-1-(furan-2-yl)ethanol (2j).** To a mixture of 5-(4-methoxyphenyl)-3-methyl-1$_H$-pyrazole (6.2 mg, 0.033 mmol) and HCOONH$_4$ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-IrS (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H$_2$O (168 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1-(furan-2-yl)ethanone (1j, 36.6 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 9 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel ($n$-hexane/dichloromethane = 1:1 to 1:2) to afford product 2j as a light yellow liquid (35.5 mg, 0.32 mmol, yield: 95\%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OJ column, ee = 96\% (250 x 4.6 mm, 220 nm, $n$-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C, $t_r$(minor) = 10.3 min, $t_r$(major) = 11.7 min).

$[\alpha]^{20}_D = +15.7$ (c 1.0, CHCl$_3$) (lit.\textsuperscript{5}: $[\alpha]^{20}_D = +14.5$ (c 1.0, CHCl$_3$), ($R$) 94\% ee). Configuration of the product was assigned as $R$ accordingly.

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.38 (s, 1H), 6.34-6.33 (m, 1H), 6.23 (d, $J = 3.2$ Hz, 1H), 4.92-4.87 (m, 1H), 1.88 (d, $J = 4.9$ Hz, 1H), 1.55 (d, $J = 6.5$ Hz, 3H).

Other analytic data of 2j are consistent with the literature.\textsuperscript{5}
(R)-1-(thiophen-3-yl)ethanol (2k). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH₄ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-IrS (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H₂O (168 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1-(thiophen-3-yl)ethanone (1k, 42.0 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 8 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product 2k as a light yellow liquid (39.7 mg, 0.31 mmol, yield: 93%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OJ column, ee = 97% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C, t_r(minor) = 12.2 min, t_r(major) = 14.8 min).

[α]²⁰_D = +25.1 (c 1.0, CHCl₃) (lit.¹⁸: [α]²⁰_D = +47.2 (c 1.0, CHCl₃), (R) 96% ee). Configuration of the product was assigned as R accordingly.

¹H-NMR (500 MHz, CDCl₃): δ 7.31-7.30 (m, 1H), 7.21-7.20 (m, 1H), 7.11-7.10 (m, 1H), 4.99 (q, J = 6.4 Hz, 1H), 1.76 (br, 1H), 1.53 (d, J = 6.4 Hz, 3H).

Other analytic data of 2k are consistent with the literature.⁸

(R)-1-(thiophen-2-yl)ethanol (2l). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH₄ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-IrS (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H₂O (168 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1-(thiophen-2-yl)ethanone 1l (42.0...
mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 9 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product $2l$ as a light yellow liquid (39.4 mg, 0.31 mmol, yield: 92%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OJ column, ee = 98% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C, $t_r$(minor) = 12.8 min, $t_r$(major) = 16.3 min).

$[\alpha]^{20}_D = +21.6$ (c 1.0, CHCl$_3$) (lit.$^5$: $[\alpha]^{20}_D = +19.9$ (c 1.0, CHCl$_3$), (R) 96% ee). Configuration of the product was assigned as R accordingly.

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.25-7.24 (m, 1H), 6.99-6.96 (m, 2H), 5.17-5.12 (m, 1H), 1.93 (d, J = 4.0 Hz, 1H), 1.61 (d, J = 6.4 Hz, 3H).

Other analytic data of $2l$ are consistent with the literature.$^5$

(R)-1-(benzofuran-2-yl)ethanol ($2m$). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH$_4$ (189.1 mg, 2.97 mmol) was added metal catalyst $\Lambda$-IrS (0.67 µmol, 168 µL of a 3.97 mM stock solution in THF) and H$_2$O (168 µL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1-(benzofuran-2-yl)ethanone ($1m$, 53.3 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 12 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product $2m$ as a light yellow liquid (52.4 mg, 0.33 mmol, yield: 98%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 97% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 0.5 mL/min, 25 °C, $t_r$(minor) = 25.6 min, $t_r$(major) = 26.8 min).

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[α]^{20}_D = +11.6 (c 1.0, CHCl₃) (lit.⁴: [α]^{20}_D = +9.9 (c 1.0, CHCl₃), (R) 63% ee). Configuration of the product was assigned as R accordingly.

¹H-NMR (500 MHz, CDCl₃): δ 7.48-7.46 (m, 1H), 7.40-7.38 (m, 1H), 7.22-7.20 (m, 1H), 7.16-7.13 (m, 1H), 6.54 (s, 1H), 4.97-4.93 (m, 1H), 2.05 (br, 1H), 1.57 (d, J = 6.6 Hz, 3H).

Other analytic data of 2m are consistent with the literature.⁴

(R)-1-(benzo[b]thiophen-2-yl)ethanol (2n). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH₄ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-IrS (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H₂O (168 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1-(benzo[b]thiophen-2-yl)ethanone (1n, 58.6 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 9 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product 2n as a light yellow solid (55.0 mg, 0.31 mmol, yield: 93%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OJ column, ee = 99% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C, tᵣ(minor) = 35.0 min, tᵣ(major) = 43.0 min).

[α]^{20}_D = +23.0 (c 1.0, CHCl₃) (lit.⁵: [α]^{20}_D = +22.9 (c 1.0, CHCl₃), (R) 93% ee). Configuration of the product was assigned as R accordingly.

¹H-NMR (500 MHz, CDCl₃): δ 7.81 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.35-7.28 (m, 2H), 7.2 (s, 1H), 5.23-5.19 (m, 1H), 2.05 (d, J = 4.6 Hz, 1H), 1.66 (d, J = 6.4 Hz, 3H).

Other analytic data of 2n are consistent with the literature.⁵
(R)-1-phenylpropan-1-ol (2o). To a biphasic solution of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (4.7 mg, 0.025 mmol) and HCOONH₄ (141.8 mg, 2.25 mmol) in THF/H₂O (126 μL/126 μL) was added the metal catalyst Λ-IrS (1.2 mg, 1.7 μmol, 0.50 mol%) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then propiophenone (1o, 33.5 mg, 0.25 mmol) was added. The reaction solution was stirred at 60 °C for 10 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product 2o as a yellow solid (32.0 mg, 0.24 mmol, yield: 94%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 96% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 99:1, flow rate: 1 mL/min, 25 °C, tᵣ(major) = 18.2 min, tᵣ(minor) = 21.1 min).

[α]ᵣ²⁰D = +45.7 (c 1.0, CHCl₃) (lit.⁴: [α]ᵣ²⁰D = +45.1 (c 1.0, CHCl₃), (R) 98% ee). Configuration of the product was assigned as R accordingly.

¹H-NMR (500 MHz, CDCl₃): δ 7.37-7.34 (m, 4H), 7.29-7.25 (m, 1H), 4.60 (t, J = 6.6 Hz, 1H), 1.87-1.71 (m, 3H), 0.92 (t, J = 7.4 Hz, 3H).

Other analytic data of 2o are consistent with the literature.⁴

(R)-1-phenylbutan-1-ol (2p). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH₄ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-IrS (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H₂O (168 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1-phenylbutan-1-one (1p, 49.3 mg, 0.33
mmol) was added. The reaction solution was stirred at 40 °C for 15 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product 2p as a light yellow solid (46.6 mg, 0.31 mmol, yield: 93%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OJ column, ee = 97% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 97:3, flow rate: 0.5 mL/min, 25 °C, t_r(minor) = 19.9 min, t_r(major) = 21.6 min).

[α]^{20}_D = +36.4 (c 1.0, CHCl₃) (lit.^[4] [α]^{20}_D = +43.0 (c 1.0, CHCl₃), (R) 97% ee). Configuration of the product was assigned as R accordingly.

^1H-NMR (500 MHz, CDCl₃): δ 7.35-7.34 (m, 4H), 7.30-7.27 (m, 1H), 4.70-4.67 (m, 1H), 1.84-1.76 (m, 2H), 1.72-1.65 (m, 1H), 1.41-1.48 (m, 1H), 1.37-1.29 (m, 1H), 0.93 (t, J = 7.3 Hz, 3H).

Other analytic data of 2p are consistent with the literature.^[4]

(R)-2-methyl-1-phenylpropan-1-ol (2q). To a biphasic solution of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (3.2 mg, 0.017 mmol) and HCOONH₄ (96.5 mg, 1.53 mmol) in THF/H₂O (84 μL/84 μL) was added the metal catalyst Λ-IrS (1.6 mg, 3.4 μmol) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 2-methyl-1-phenylpropan-1-one (1q, 24.5 mg, 0.17 mmol) was added. The reaction solution was stirred at 60 °C for 10 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product 2q as a yellow solid (22.6 mg, 0.15 mmol, yield: 91%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak IC column, ee = 90% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 98:2, flow rate: 0.5 mL/min, 25 °C, t_r(major) = 13.2 min, t_r(minor) = 14.9 min).
\[ \alpha \]^{20}_D = +6.2 \text{ (c 1.0, CHCl}_3\text{)} \] (lit.\textsuperscript{9}: \[ \alpha \]^{28}_D = +21.67 \text{ (c 0.42, CH}_2\text{Cl}_2\text{)} \text{(R) 71\% ee}). Configuration of the product was assigned as \( R \) accordingly.

\[ ^1\text{H-NMR (500 MHz, CDCl}_3\text{): } \delta \text{ 7.36-7.31 (m, 4H), 7.28-7.27 (m, 1H), 4.37 (d, } J = 6.8 \text{ Hz, 1H), 1.98-1.93 (m, 1H), 1.60 (br, 1H), 1.01 (d, } J = 6.8 \text{ Hz, 3H), 0.80 (d, } J = 6.8 \text{ Hz, 3H).} \]

Other analytic data of \( 2q \) are consistent with the literature.\textsuperscript{9}

\[
\text{(R)-ethyl 3-hydroxy-3-phenylpropanoate (2r). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH}_4\text{ (189.1 mg, 2.97 mmol) was added the metal catalyst } \Lambda\text{-IrS (0.67 } \mu\text{mol, 168 } \mu\text{L of a 3.97 } \text{mM stock solution in THF) and } \text{H}_2\text{O (168 } \mu\text{L) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then ethyl 3-oxo-3-phenylpropanoate (1r, 64.0 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 } ^\circ\text{C for 12 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (} n\text{-hexane/dichloromethane = 1:1 to 1:2) to afford product 2r as a yellow liquid (62.3 mg, 0.32 mmol, yield: 97\%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OJ column, ee = 96\% (250 x 4.6 mm, 220 nm, } n\text{-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 } ^\circ\text{C, } t_(\text{major}) = 17.5 \text{ min, } t_(\text{minor}) = 19.0 \text{ min).}}
\]

\[ [\alpha]^{20}_D = +41.1 \text{ (c 1.0, CHCl}_3\text{)} \] (lit.\textsuperscript{10}: \[ [\alpha]^{28}_D = +48.9 \text{ (c 0.84, CHCl}_3\text{), (R) 89\% ee}). Configuration of the product was assigned as \( R \) accordingly.

\[ ^1\text{H-NMR (500 MHz, CDCl}_3\text{): } \delta \text{ 7.33-7.27 (m, 4H), 7.24-7.20 (m, 1H), 5.07 (d, } J = 3.5 \text{ Hz, 1H), 4.14-4.10 (m, 2H), 3.20 (br, 1H), 2.72-2.62 (m, 2H), 1.20 (t, } J = 7.1 \text{ Hz, 3H).} \]

Other analytic data of \( 2r \) are consistent with the literature.\textsuperscript{10}
(R)-1,2,3,4-tetrahydronaphthalen-1-ol (2s). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH₄ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-IrS (0.67 µmol, 168 µL of a 3.97 mM stock solution in THF) and H₂O (168 µL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 3,4-dihydronaphthalen-1(2H)-one (1s, 48.6 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 18 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product 2s as a yellow liquid (46.6 mg, 0.32 mmol, yield: 95%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OJ column, ee = 98% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C, tₜ(minor) = 10.5 min, tₜ(major) = 13.6 min).

[α]²⁰\text{D} = -26.2 (c 1.0, CHCl₃) (lit.⁴: [α]²⁰\text{D}= -32.2 (c 1.0, CHCl₃), (R) 99% ee). Configuration of the product was assigned as R accordingly.

¹H-NMR (500 MHz, CDCl₃): δ 7.38-7.36 (m, 1H), 7.16-7.12 (m, 2H), 7.05-7.03 (m, 1H), 4.73-4.71 (m, 1H), 2.79-2.74 (m, 1H), 2.69-2.63 (m, 1H), 1.95-1.82 (m, 3H), 1.74-1.69 (m, 1H), 1.60 (br, 1H).

Other analytic data of 2s are consistent with the literature.⁴

(R)-phenyl(o-tolyl)methanol (2t). To a biphasic solution of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (4.7 mg, 0.025 mmol) and HCOONH₄ (141.8 mg, 2.25 mmol) in THF/H₂O (126 µL/126 µL) was added the metal catalyst Λ-IrS (1.2 mg, 1.7 µmol) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then phenyl(o-tolyl)methanone (1t, 32.6 mg, 0.25 mmol) was added. The reaction solution was stirred at 40 °C for 24 h, cooled down to room
temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel \((n\text{-hexane/dichloromethane} = 1:1 \text{ to } 1:2)\) to afford product \(2t\) as a yellow solid (31.4 mg, 0.16 mmol, yield: 99%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OJ column, ee = 97% (250 x 4.6 mm, 220 nm, \(n\text{-hexane/isopropanol} = 95:5\), flow rate: 1.0 mL/min, 25 °C, \(t(\text{minor}) = 27.2 \text{ min}, t(\text{major}) = 30.8 \text{ min}\).

\([\alpha]^{20}_D = +6.8 \text{ (c 1.0, CHCl}_3\text{)}\) (lit.\(^4\); \([\alpha]^{20}_D = +5.4 \text{ (c 1.0, CHCl}_3\text{)}, (R) 86\% \text{ ee}\). Configuration of the product was assigned as \(R\) accordingly.

\(^1\text{H-NMR}\) (500 MHz, CDCl\(_3\)): \(\delta 7.45\) \((\text{d, } J = 7.8 \text{ Hz, } 1\text{H}), 7.26-7.24\) \((\text{m, } 4\text{H}), 7.21-7.19\) \((\text{m, } 1\text{H}), 7.18-7.17\) \((\text{m, } 1\text{H}), 7.14-7.12\) \((\text{m, } 1\text{H}), 7.08-7.07\) \((\text{m, } 1\text{H}), 5.95\) \((\text{d, } J = 3.6 \text{ Hz, } 1\text{H}), 2.18\) \((\text{s, } 3\text{H}), 2.03\) \((\text{d, } J = 3.9 \text{ Hz, } 1\text{H})\).

Other analytic data of \(2t\) are consistent with the literature.\(^4\)

\(\text{(R)-(2-fluorophenyl)(phenyl)methanol (2u)}\). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1\(H\)-pyrazole (6.2 mg, 0.033 mmol) and HCOONH\(_4\) (189.1 mg, 2.97 mmol) was added the metal catalyst \(\Lambda\text{-IrS}\) (0.67 \(\mu\)mol, 168 \(\mu\)L of a 3.97 mM stock solution in THF) and H\(_2\)O (168 \(\mu\)L) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then (2-fluorophenyl)(phenyl)methane (1u, 66.7 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 24 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel \((n\text{-hexane/dichloromethane} = 1:1 \text{ to } 1:2)\) to afford product \(2u\) as a yellow solid (65.3 mg, 0.32 mmol, yield: 97%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 81% (250 x 4.6 mm, 220 nm, \(n\text{-hexane/isopropanol} = 95:5\), flow rate: 1.0 mL/min, 25 °C, \(t(\text{major}) = 11.5 \text{ min, } t(\text{minor}) = 12.9 \text{ min}\).
[α]$_D^{20}$ = +4.5 (c 1.0, CHCl$_3$) (lit.$^4$: [α]$_D^{20}$ = +5.52 (c 1.0, CHCl$_3$), (R) 90% ee). Configuration of the product was assigned as R accordingly.

$^1$H-NMR (500 MHz, CDCl$_3$): δ 7.46-7.43 (m, 1H), 7.35-7.33 (m, 2H), 7.29-7.26 (m, 2H), 7.22-7.20 (m, 1H), 7.19-7.16 (m, 1H), 7.10-7.07 (m, 1H), 6.97-6.93 (m, 1H), 6.09 (d, J = 3.9 Hz, 1H), 2.21 (d, J = 4.1 Hz, 1H).

Other analytic data of 2u are consistent with the literature.$^4$

(R)-1-(4-fluorophenyl)propan-2-ol (2v). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH$_4$ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-IrS (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H$_2$O (168 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1-(4-fluorophenyl)propan-2-one (1v, 50.6 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 10 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product 2v as a yellow liquid (47.8 mg, 0.31 mmol, yield: 94%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 9% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 98:2, flow rate: 0.5 mL/min, 25 °C, t$_r$(major) = 20.7 min, t$_r$(minor) = 22.4 min).

[α]$_D^{20}$ = -2.7 (c 1.0, CHCl$_3$) (lit.$^{11}$: [α]$_D^{21}$ = - 29.2 (c 2.25, CHCl$_3$), (R) 37% ee). Configuration of the product was assigned as R accordingly.

$^1$H-NMR (500 MHz, CDCl$_3$): δ 7.12-7.08 (m, 2H), 6.96-6.92 (m, 2H), 3.95-3.91 (m, 1H), 2.71-2.67 (m, 1H), 2.62-2.58 (m, 1H), 1.39 (br, 1H), 1.17 (d, J = 6.2 Hz, 3H).

Other analytic data of 2v are consistent with the literature.$^{11}$
(R)-4-phenylbutan-2-ol (2w). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH₄ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-IrS (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H₂O (168 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 4-phenylbutan-2-one (1w, 49.3 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 10 h, cooled down to room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product 2w as a yellow liquid (44.7 mg, 0.30 mmol, yield: 90%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 30% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C, tᵣ(major) = 10.3 min, tᵣ(minor) = 15.1 min).

[α]²⁰ᵣ = -4.4 (c 1.0, CHCl₃) (lit.¹²: [α]²⁰ᵣ = +7.9 (c 1.0, CHCl₃), (S) 33% ee). Configuration of the product was assigned as R accordingly.

¹H-NMR (500 MHz, CDCl₃): δ 7.23-7.22 (m, 2H), 7.14-7.10 (m, 3H), 3.80-3.73 (m, 1H), 3.72-2.66 (m, 1H), 2.64-2.58 (m, 1H), 1.76-1.66 (m, 2H), 1.26 (br, 1H), 1.16 (d, J = 6.2 Hz, 3H).

Other analytic data of 2w are consistent with the literature.¹²

(R)-1,1-diphenylpropan-2-ol (2x). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (6.2 mg, 0.033 mmol) and HCOONH₄ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-IrS (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H₂O (168 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 1,1-diphenylpropan-2-one (1x, 70.0 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C for 15 h, cooled down to
room temperature, then dried under high vacuum. The residue was purified by flash chromatography on silica gel (n-hexane/dichloromethane = 1:1 to 1:2) to afford product 2x as a yellow solid (65.3 mg, 0.31 mmol, yield: 93%). Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 94% (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 98:2, flow rate: 0.5 mL/min, 25 °C, t_r(major) = 30.7 min, t_r(minor) = 31.9 min).

[α]_{20}^{D} = +4.9 (c 1.0, CHCl₃) (lit.⁴: [α]_{20}^{D} = -4.9 (c 1.0, CHCl₃), (S) 65% ee). Configuration of the product was assigned as R accordingly.

¹H-NMR (500 MHz, CDCl₃): δ 7.32-7.31 (m, 2H), 7.25-7.23 (m, 2H), 7.21-7.19 (m, 4H), 7.17-7.15 (m, 1H), 7.12-7.09 (m, 1H), 4.49-4.46 (m, 1H), 3.73 (d, J = 8.8 Hz, 1H), 1.60 (br, 1H), 1.12 (d, J = 6.2 Hz, 3H).

Other analytic data of 2x are consistent with the literature.⁴
5. ATH Reaction of Ketone 1n at Different Catalyst Loadings

**Preparation of stock solutions of the catalyst \( \Lambda\text{-IrS} \) in THF at lower concentrations.**

Stock solution of 0.53 mM: The chiral iridium complex \( \Lambda\text{-IrS} \) (1.34 mg, 1.41 μmol) was dissolved in freshly distilled THF (2.66 mL). The stock solution was prepared freshly and used for the low-loading catalysis reactions.

Stock solution of 0.27 mM: The chiral iridium complex \( \Lambda\text{-IrS} \) (1.34 mg, 1.41 μmol) was dissolved in freshly distilled THF (5.22 mL). The stock solution was prepared freshly and used for the low-loading catalysis reactions.

**Procedures for Table 1**

**Entry 1:** To a mixture of the ligand 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (12.4 mg, 0.066 mmol) and the reducing agent HCOONH\(_4\) (376.0 mg, 6.0 mmol) was added the metal catalyst \( \Lambda\text{-IrS} \) (0.20 mol%, 0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and THF/H\(_2\)O (168 μL/336 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 2-acetyl benzothiophene (1n, 70.0 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C or 60 °C for the indicated time. Conversion was determined by \(^1\)H-NMR and enantiomeric excess established by HPLC analysis using a Daicel Chiralpak OJ column (250 x 4.6 mm, 220 nm, \( n\)-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C).

**Entry 2:** To a mixture of the ligand 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (12.4 mg, 0.066 mmol) and the reducing agent HCOONH\(_4\) (376.0 mg, 6.0 mmol) was added the metal catalyst \( \Lambda\text{-IrS} \) (0.050 mol%, 0.168 μmol, 42 μL of a 3.97 mM stock solution in THF) and THF/H\(_2\)O (294 μL/336 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 2-acetyl benzothiophene (1n, 70.0 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C or 60 °C for the indicated time. Conversion was determined by \(^1\)H-NMR and enantiomeric excess established by HPLC analysis using a Daicel Chiralpak OJ column (250 x 4.6 mm, 220 nm, \( n\)-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C).

**Entry 3-4:** To a mixture of the ligand 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (12.4 mg, 0.066 mmol) and the reducing agent HCOONH\(_4\) (376.0 mg, 6.0 mmol) was added the metal catalyst
Λ-IrS (0.010 mol%, 0.034 μmol, 64 μL of a 0.53 mM stock solution in THF) and THF/H₂O (272 μL /336 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 2-acetyl benzothiophene (1n, 70.0 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C or 60 °C for the indicated time. Conversion was determined by ¹H-NMR and enantiomeric excess established by HPLC analysis using a Daicel Chiralpak OJ column (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C).

**Entry 5:** To a mixture of the ligand 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (12.4 mg, 0.066 mmol) and the reducing agent HCOONH₄ (376.0 mg, 6.0 mmol) was added the metal catalyst Λ-IrS (0.005 mol%, 0.0168 μmol, 32 μL of a 0.53 mM stock solution in THF) and THF/H₂O (304 μL /336 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 2-acetyl benzothiophene (1n, 70.0 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C or 60 °C for the indicated time. Conversion was determined by ¹H-NMR and enantiomeric excess established by HPLC analysis using a Daicel Chiralpak OJ column (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C).

**Entry 6:** To a mixture of the ligand 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (12.4 mg, 0.066 mmol) and the reducing agent HCOONH₄ (376.0 mg, 6.0 mmol) was added the metal catalyst Λ-IrS (0.002 mol%, 0.0067 μmol, 25 μL of a 0.27 mM stock solution in THF) and THF/H₂O (311 μL/336 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 2-acetyl benzothiophene (1n, 70.0 mg, 0.33 mmol) was added. The reaction solution was stirred at 40 °C or 60 °C for the indicated time. Conversion was determined by ¹H-NMR and enantiomeric excess established by HPLC analysis using a Daicel Chiralpak OJ column (250 x 4.6 mm, 220 nm, n-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C).
6. Chiral HPLC Traces

6.1 Determination of enantioselectivities for the ATH reaction catalyzed by \( \Lambda \)-IrS with the pyrazole additive

Enantiomeric excess of the ATH products were determined with a Daicel Chiralpak OD-H, OJ, or IC column (250 x 4.6 mm) on an Agilent 1260 Series HPLC System using \( n \)-hexane/isopropanol as mobile phase, the temperature was 25 °C and UV-absorption was measured at 220 nm.

![HPLC trace of transfer hydrogenation leading to (R)-2a](image)

<table>
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<th>[min]</th>
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<th>[mAU]</th>
<th>%</th>
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**Figure S1.** HPLC traces of transfer hydrogenation leading to (R)-2a.
Figure S2. HPLC traces of transfer hydrogenation leading to (R)-2b.
**Figure S3.** HPLC traces of transfer hydrogenation leading to (R)-2c.

- **HPLC:** Agilent 1260 Series HPLC system
- **Column:** Daicel Chiralpak OJ (250 x 4.6 mm)
- **Mobile phase:** n-hexane/isopropanol=90:10
- **Flow rate:** 1.0 mL/min
- **Column temperature:** 25 °C
- **Detection:** UV-absorption at 220 nm

** rac-2c (reference)**

** (R)-2c

- **0.2 mol% L-IrS**
- **40 °C 12 h**
- **97% yield 98% ee**

<table>
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Figure S4. HPLC traces of transfer hydrogenation leading to (R)-2d.
**Figure S5.** HPLC traces of transfer hydrogenation leading to (R)-2e.
Figure S6. HPLC traces of transfer hydrogenation leading to (R)-2f.
Figure S7. HPLC traces of transfer hydrogenation leading to \((R)-2g\).
Figure S8. HPLC traces of transfer hydrogenation leading to (R)-2h.
Figure S9. HPLC traces of transfer hydrogenation leading to (R)-2i.

HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OJ (250 x 4.6 mm)
Mobile phase: n-hexane/isopropanol=95:5
Flow rate: 1.0 mL/min
Column temperature: 25 °C
Detection: UV-absorption at 220 nm

\( \text{rac-2i (reference)} \)

\((R)-2i\)
0.2 mol% \( \Lambda \)-IrS
40 °C 9 h
95% yield 96% ee
Figure S10. HPLC traces of transfer hydrogenation leading to (R)-2j.

---

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HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OJ (250 x 4.6 mm)
Mobile phase: n-hexane/isopropanol=95:5
Flow rate: 1.0 mL/min
Column temperature: 25 °C
Detection: UV-absorption at 220 nm

rac-2j (reference)

(R)-2j
0.2 mol% Λ-IrS
40 °C 9 h
95% yield 96% ee
Figure S11. HPLC traces of transfer hydrogenation leading to (R)-2k.
Figure S12. HPLC traces of transfer hydrogenation leading to (R)-2I.
Figure S13. HPLC traces of transfer hydrogenation leading to (R)-2m.
**Figure S14.** HPLC traces of transfer hydrogenation leading to (R)-2n.

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Figure S15. HPLC traces of transfer hydrogenation leading to (R)-2o.
Figure S16. HPLC traces of transfer hydrogenation leading to (R)-2p.

**HPLC traces of transfer hydrogenation leading to (R)-2p.**

**Legend:**
- **HPLC:** Agilent 1260 Series HPLC system
- **Column:** Daicel Chiralpak OJ (250 x 4.6 mm)
- **Mobile phase:** n-hexane/isopropanol=97:3
- **Flow rate:** 0.5 mL/min
- **Column temperature:** 25 °C
- **Detection:** UV-absorption at 220 nm

**Compound:** rac-2p (reference)

**Reaction Conditions:**
- 0.2 mol% Λ-IrS
- 40 °C 15 h
- 93% yield 97% ee

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**Notes:**
- **Wavelength:** 220 nm
- **Column Type:** TC-TC-D-66-COLUMN.D
- **Instrument:** VWD1 A
Figure S17. HPLC traces of transfer hydrogenation leading to (R)-2q.
Figure S18. HPLC traces of transfer hydrogenation leading to (R)-2r.
Figure S19. HPLC traces of transfer hydrogenation leading to (R)-2s.

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Figure S20. HPLC traces of transfer hydrogenation leading to (R)-2t.

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Figure S21. HPLC traces of transfer hydrogenation leading to (R)-2u.
Figure S22. HPLC traces of transfer hydrogenation leading to (R)-2v.
Figure S23. HPLC traces of transfer hydrogenation leading to (R)-2w.
Figure S24. HPLC traces of transfer hydrogenation leading to (R)-2x.

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</table>
6.2 Determination of enantioselectivities for the ATH reaction of ketone 1n at lower catalyst loadings

Enantiomeric excess were determined with a Daicel Chiralpak OJ column (250 x 4.6 mm) on an Agilent 1260 Series HPLC System using n-hexane/isopropanol = 95:5 as mobile phase, the flow rate was 1.0 mL/min, the temperature was 25 °C and UV-absorption was measured at 220 nm.

Figure S2. HPLC trace of the asymmetric transfer hydrogenation leading to (R)-2n catalyzed by 0.2 mol% \( \Lambda \)-IrS at 40°C and the standard conditions (Table1, entry 1).
Figure S26. HPLC trace of the asymmetric transfer hydrogenation leading to (R)-2n catalyzed by 0.05 mol% Λ-IrS at 40°C and the standard conditions (Table 1, entry 2).

Figure S27. HPLC trace of the asymmetric transfer hydrogenation leading to (R)-2n catalyzed by 0.01 mol% Λ-IrS at 40°C and the standard conditions (Table 1, entry 3).
Figure S28. HPLC trace of the asymmetric transfer hydrogenation leading to (R)-2n catalyzed by 0.01 mol% Λ-IrS at 60°C and the standard conditions (Table 1, entry 4).

Figure S29. HPLC trace of the asymmetric transfer hydrogenation leading to (R)-2n catalyzed by 0.005 mol% Λ-IrS at 60°C and the standard conditions (Table 1, entry 5).
Figure S30. HPLC trace of the asymmetric transfer hydrogenation leading to (R)-2n catalyzed by 0.002 mol% Λ-IrS at 60°C and the standard conditions (Table1, entry 6).
6.3 Determination of enantioselectivity for the ATH reaction of ketone 1t on gram-scale

Enantiomeric excess was determined with a Daicel Chiralpak OJ column (250 x 4.6 mm) on an Agilent 1260 Series HPLC System using n-hexane/isopropanol = 95:5 as mobile phase, the flow rate was 1.0 mL/min, the temperature was 25 °C and UV-absorption was measured at 220 nm.

![HPLC trace of the asymmetric transfer hydrogenation in gram-scale leading to (R)-2t.](image)

<table>
<thead>
<tr>
<th></th>
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<th>[min]</th>
<th>[mAU*s]</th>
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**Figure S31.** HPLC trace of the asymmetric transfer hydrogenation in gram-scale leading to (R)-2t.
7. Single Crystal Diffraction

7.1 Synthesis of an iridium(III) pyrazole complex for crystallization

The iridium (III) pyrazole complex S2 was synthesized following a modified procedure.\textsuperscript{13} Accordingly, a mixture of iridium dimer S1\textsuperscript{3} (200.0 mg, 0.13 mmol) and ligand 5-(4-methoxyphenyl)-3-methyl-1H-pyrazole (50.0 mg, 0.26 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (10 mL) was heated at reflux (oil bath temperature: 100 °C) for 12 h under argon atmosphere. The reaction solution was cooled down to room temperature, then concentrated into to 2 mL, to which diethyl ether (2 mL) was added to afford a yellow precipitate. The solid was collected after centrifuge, washed with diethyl ether (2 mL x 3) and dried under vacuum. The analytically pure product was obtained by recrystallization from dichloromethane/n-hexane. Yield: 120 mg (96%)

\textsuperscript{1}H-NMR (500 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta\) 13.89 (s, 1H), 9.78 (s, 1H), 7.78 (d, \(J = 8.4\) Hz, 1H), 7.68 (d, \(J = 8.6\) Hz, 1H), 7.57 (d, \(J = 7.5\) Hz, 1H), 7.53 (d, \(J = 7.6\) Hz, 1H), 7.42-7.38 (m, 2H), 7.34-7.31 (m, 3H), 6.81-6.78 (m, 4H), 6.65-6.62 (m, 1H), 6.60-6.57 (m, 1H), 6.38 (d, \(J = 7.8\) Hz, 1H), 6.24 (d, \(J = 7.5\) Hz, 1H), 6.04 (s, 1H), 3.69 (s, 3H), 1.31 (s, 9H), 1.26 (s, 9H), 0.97 (s, 9H).

\textsuperscript{13}C-NMR (126 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta\) 180.7, 180.5, 160.6, 152.9, 152.2, 152.1, 151.9, 151.2, 147.8, 147.6, 143.2, 141.8, 141.6, 133.7, 133.3, 131.0, 130.8, 129.0, 128.6, 127.0, 126.9, 126.1, 125.6, 123.8, 123.7, 122.5, 122.1, 121.9, 121.7, 121.3, 120.3, 117.4, 114.7, 105.0, 55.7, 35.8, 35.0, 31.9, 31.4, 13.6.
IR (film): ν (cm⁻¹) 3643, 2957, 2920, 2849, 2349, 2304, 2029, 1959, 1692, 1659, 1614, 1581, 1552, 1536, 1510, 1469, 1439, 1413, 1295, 1084, 996, 833, 758, 738, 672, 522.

HRMS (ESI, m/z) calcd for IrC₄₅H₄₄S₂N₄ClONa (M+Na)⁺: 971.2172, found: 971.2173.
$^{13}$C-NMR
126 Mz
$\text{CD}_2\text{Cl}_2$
7.2 Crystallography with the iridium(III) pyrazole complex S2

Crystals of compound S2 were obtained by slow diffusion from the solution in dichloromethane layered with n-hexane. Diffraction data were collected on a Bruker Apex CCD area detector employing graphite-monochromated Mo-Kα radiation (= 0.71073 Å). The crystal was kept at 200 K during data collection. The structure was solved by SHELXL-97.\textsuperscript{14} Refinement was done by full-matrix least squares based on F² data of one twin domain using SHELXL-97. The structure is shown in Figure S32. Data collection and refinement statistics are given in Table S2. Crystallographic data (excluding structure factors) for S2 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1450140.

**Figure S32.** Crystal structure of complex S2. ORTEP drawings with 50% thermal ellipsoids. The complex was crystallized as a racemate but only the Λ-enantiomer is shown.
Table S2. Data collection and refinement statistics for the compounds S2.

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<td>Largest diff. peak and hole (e.Å⁻³)</td>
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8. References


