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_3CN, CH_2Cl_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_2Cl_2 = 5.32 ppm (^{1}H-NMR); $CDCl_3$ = 77.0 ppm (^{13}C-NMR), CD_2Cl_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 $HCOONH_4$ (189.1 mg, 2.97 mmol) in *i*PrOH/H_2O (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 ^{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).

2.2 Ligand Additive Screening (Figure 1)

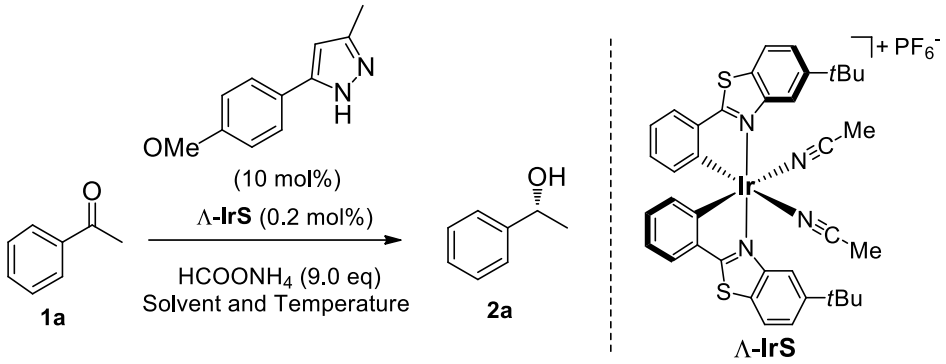
General Procedure. To a biphasic solution of the ligand additive (0.033 mmol) and $HCOONH_4$ (189.1 mg, 2.97 mmol) in *i*PrOH/H_2O (168 μL/168 μL) was added the metal catalyst Λ-**IrS** (0.6-3.1 mg, 0.20-1.0 mol%) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then acetophenone (**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 ^{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).

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 *i*PrOH (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-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 *i*PrOH (entry 1) or THF (entries 2-4)) and H_2O (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 ^{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).

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

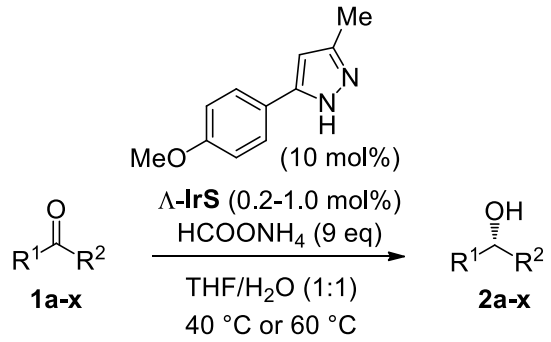


Entry	T (°C)	Solvents	t (h)	Conv. (%)	ee (%)
1	60	*i*PrOH/H_2O (1:1)	3	85	96.0
2	60	THF/H_2O (1:1)	1	77	96.0
3	40	THF/H_2O (1:1)	6	67	97.0
4	20	THF/H_2O (1:1)	24	50	97.4

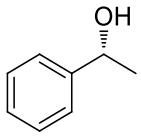
3. Synthesis of Racemic Products as HPLC References

General Procedure. 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 racemic metal catalyst *rac*-**IrS** (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H_2O (168 μL) 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 (*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-1*H*-pyrazole (6.2 mg, 0.033 mmol) and $HCOONH_4$ (189.1 mg, 2.97 mmol) in THF/H_2O (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.



2a

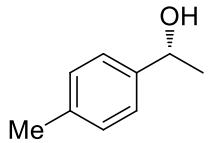
(*R*)-1-phenylethanol (**2a**). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1*H*-pyrazole (6.2 mg, 0.033 mmol) and $HCOONH_4$ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-**IrS** (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H_2O (168 μL) in a brown glass vial. The mixture was stirred 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_r(minor) = 11.6 min, t_r(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, $CDCl_3$): δ 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]



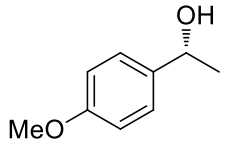
2b

(*R*)-1-(p-tolyl)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 Λ-**IrS** (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H_2O (168 μL) 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_r(minor) = 11.4 min, t_r(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, $CDCl_3$): δ 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]



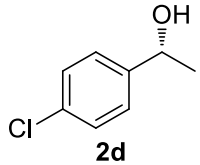
2c

(*R*)-1-(4-methoxyphenyl)ethanol (2c). To a mixtureof 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_2O (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, t_r(minor) = 15.0 min, t_r(major) = 16.0 min).

$[\alpha]^{20}_D$ = +41.1 (c 1.0, $CHCl_3$) (lit.[4]: $[\alpha]^{20}_D$ = +16.5 (c 1.0, $CHCl_3$), (*R*) 96% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): 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]



2d

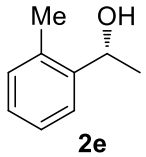
(*R*)-1-(4-chlorophenyl)ethanol (2d). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1*H*-pyrazole (6.2 mg, 0.033 mmol) and $HCOONH_4$ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-**IrS**

(0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H_2O (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, t_r(minor) = 10.4 min, t_r(major) = 11.3 min).

$[\alpha]^{20}_D$ = +39.4 (c 1.0, $CHCl_3$) (lit.[4]: $[\alpha]^{20}_D$ = +44.2 (c 1.0, $CHCl_3$), (*R*) 96% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.33-7.30 (m, 4H), 4.89 (q, J = 6.5 Hz, 1H), 1.78 (br, 1H), 1.48 (d, J = 6.5 Hz, 3H).

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



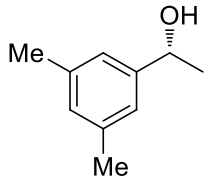
2e

(*R*)-1-(o-tolyl)ethanol (2e). 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_2O (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, t_r(minor) = 14.2 min, t_r(major) = 15.8 min).

$[\alpha]^{20}_D$ = +34.5 (c 1.0, $CHCl_3$) (lit.[5]: $[\alpha]^{20}_D$ = +56.1 (c 1.0, $CHCl_3$), (*R*) 98% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 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]



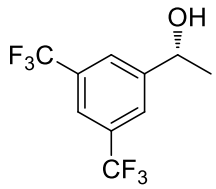
2f

(*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 Λ-**IrS** (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H_2O (168 μL) 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 (c 1.0, $CHCl_3$) (lit.[6]: $[\alpha]^{20}_D$ = +45.4 (c 1.0, $CHCl_3$), (*R*) 95% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 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]



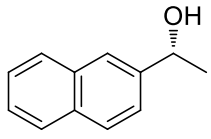
2g

(*R*)-1-(3,5-bis(trifluoromethyl)phenyl)ethanol (2g). 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_2O (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, t_r(minor) = 9.6 min, t_r(major) = 11.3 min).

$[\alpha]^{20}_D$ = +16.3 (c 1.0, $CHCl_3$) (lit.[4]: $[\alpha]^{20}_D$ = +22.6 (c 1.0, $CHCl_3$), (*R*) 94% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): 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]



2h

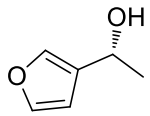
(*R*)-1-(naphthalen-2-yl)ethanol (2h). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1*H*-pyrazole (6.2 mg, 0.033 mmol) and $HCOONH_4$ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-**IrS** (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H_2O (168 μL) in a brown glass vial.

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).

$[\alpha]^{20}_D$ = +38.9 (c 1.0, $CHCl_3$) (lit.[4]: $[\alpha]^{20}_D$ = +40.9 (c 1.0, $CHCl_3$), (*R*) 99% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): 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]



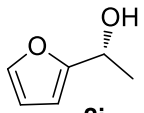
2i

(*R*)-1-(furan-3-yl)ethanol (2i). 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_2O (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.[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, $CDCl_3$): δ 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.[7]



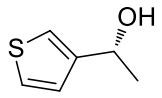
2j

(*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_2O (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.[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, $CDCl_3$): δ 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.[5]



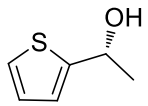
2k

(*R*)-1-(thiophen-3-yl)ethanol (2k). 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_2O (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).

$[\alpha]^{20}_D$ = +25.1 (c 1.0, $CHCl_3$) (lit.[8]: $[\alpha]^{20}_D$ = +47.2 (c 1.0, $CHCl_3$), (*R*) 96% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): 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]



2l

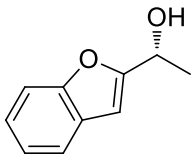
(*R*)-1-(thiophen-2-yl)ethanol (2l). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1*H*-pyrazole (6.2 mg, 0.033 mmol) and $HCOONH_4$ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-**IrS** (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H_2O (168 μL) in a brown glass vial. The mixture 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, $CDCl_3$): δ 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]



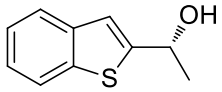
2m

(*R*)-1-(benzofuran-2-yl)ethanol (2m). 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 metal catalyst Λ-**IrS** (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H_2O (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).

$[\alpha]^{20}_D$ = +11.6 (c 1.0, $CHCl_3$) (lit.[4]: $[\alpha]^{20}_D$ = +9.9 (c 1.0, $CHCl_3$), (*R*) 63% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): 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]



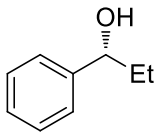
2n

(*R*)-1-(benzo[*b*]thiophen-2-yl)ethanol (2n). 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_2O (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, t_r(minor) = 35.0 min, t_r(major) = 43.0 min).

$[\alpha]^{20}_D$ = +23.0 (c 1.0, $CHCl_3$) (lit.[5]: $[\alpha]^{20}_D$ = +22.9 (c 1.0, $CHCl_3$), (*R*) 93% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): 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]



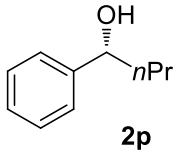
2o

(*R*)-1-phenylpropan-1-ol (2o). To a biphasic solution of 5-(4-methoxyphenyl)-3-methyl-1*H*-pyrazole (4.7 mg, 0.025 mmol) and $HCOONH_4$ (141.8 mg, 2.25 mmol) in THF/H_2O (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, t_r(major) = 18.2 min, t_r(minor) = 21.1 min).

$[\alpha]^{20}_D$ = +45.7 (c 1.0, $CHCl_3$) (lit.[4]: $[\alpha]^{20}_D$ = +45.1 (c 1.0, $CHCl_3$), (*R*) 98% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): 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]



2p

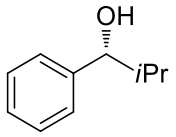
(*R*)-1-phenylbutan-1-ol (2p). To a mixture of 5-(4-methoxyphenyl)-3-methyl-1*H*-pyrazole (6.2 mg, 0.033 mmol) and $HCOONH_4$ (189.1 mg, 2.97 mmol) was added the metal catalyst Λ-**IrS** (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H_2O (168 μL) in a brown glass vial. The mixture was stirred 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).

$[\alpha]^{20}_D$ = +36.4 (c 1.0, $CHCl_3$) (lit.[4]: $[\alpha]^{20}_D$ = +43.0 (c 1.0, $CHCl_3$), (*R*) 97% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): 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]



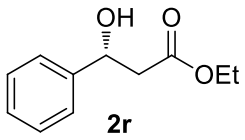
2q

(*R*)-2-methyl-1-phenylpropan-1-ol (2q). To a biphasic solution of 5-(4-methoxyphenyl)-3-methyl-1*H*-pyrazole (3.2 mg, 0.017 mmol) and $HCOONH_4$ (96.5 mg, 1.53 mmol) in THF/H_2O (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 (c 1.0, $CHCl_3$) (lit.[9]: $[\alpha]^{28}_D$ = +21.67 (c 0.42, CH_2Cl_2, (*R*) 71% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.36-7.31 (m, 4H), 7.28-7.27 (m, 1H), 4.37 (d, J = 6.8 Hz, 1H), 1.98-1.93 (m, 1H), 1.60 (br, 1H), 1.01 (d, J = 6.8 Hz, 3H), 0.80 (d, J = 6.8 Hz, 3H).

Other analytic data of **2q** are consistent with the literature.[9]



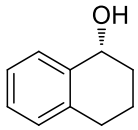
2r

(*R*)-ethyl 3-hydroxy-3-phenylpropanoate (2r). 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_2O (168 μL) 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 °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 **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*-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C, t_r(major) = 17.5 min, t_r(minor) = 19.0 min).

$[\alpha]^{20}_D$ = +41.1 (c 1.0, $CHCl_3$) (lit.[10]: $[\alpha]^{28}_D$ = +48.9 (c 0.84, $CHCl_3$), (*R*) 89% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.33-7.27 (m, 4H), 7.24-7.20 (m, 1H), 5.07 (d, J = 3.5 Hz, 1H), 4.14-4.10 (m, 2H), 3.20 (br, 1H), 2.72-2.62 (m, 2H), 1.20 (t, J = 7.1 Hz, 3H).

Other analytic data of **2r** are consistent with the literature.[10]

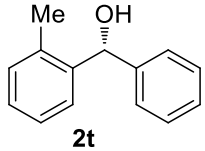


2s

(*R*)-1,2,3,4-tetrahydronaphthalen-1-ol (2s). 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_2O (168 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then 3,4-dihydronaphthalen-1(2*H*)-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, t_r(minor) = 10.5 min, t_r(major) = 13.6 min).

$[\alpha]^{20}_D$ = -26.2 (c 1.0, $CHCl_3$) (lit.[4]: $[\alpha]^{20}_D$= -32.2 (c 1.0, $CHCl_3$), (*R*) 99% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): 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]



2t

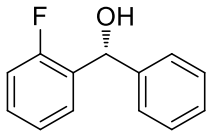
(*R*)-phenyl(o-tolyl)methanol (2t). To a biphasic solution of 5-(4-methoxyphenyl)-3-methyl-1*H*-pyrazole (4.7 mg, 0.025 mmol) and $HCOONH_4$ (141.8 mg, 2.25 mmol) in THF/H_2O (126 μL/126 μL) was added the metal catalyst Λ-**IrS** (1.2 mg, 1.7 μmol) in a brown glass vial. The mixture was stirred for 10 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*-hexane/dichloromethane = 1:1 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*-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C, t_r(minor) = 27.2 min, t_r(major) = 30.8 min).

$[\alpha]^{20}_D$ = +6.8 (c 1.0, $CHCl_3$) (lit.[4]: $[\alpha]^{20}_D$ = +5.4 (c 1.0, $CHCl_3$), (*R*) 86% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.45 (d, J = 7.8 Hz, 1H), 7.26-7.24 (m, 4H), 7.21-7.19 (m, 1H), 7.18-7.17 (m, 1H), 7.14-7.12 (m, 1H), 7.08-7.07 (m, 1H), 5.95 (d, J = 3.6 Hz, 1H), 2.18 (s, 3H), 2.03 (d, J = 3.9 Hz, 1H).

Other analytic data of **2t** are consistent with the literature.[4]



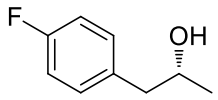
2u

(*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 Λ-**IrS** (0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and H_2O (168 μL) in a brown glass vial. The mixture was stirred for 10 min at room temperature, then (2-fluorophenyl)(phenyl)methanone (**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*-hexane/dichloromethane = 1:1 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*-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C, t_r(major) = 11.5 min, t_r(minor) = 12.9 min).

$[\alpha]^{20}_D$ = +4.5 (c 1.0, $CHCl_3$) (lit.[4]: $[\alpha]^{20}_D$ = +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]



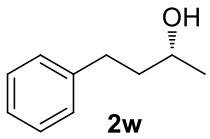
2v

(*R*)-1-(4-fluorophenyl)propan-2-ol (2v). 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_2O (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).

$[\alpha]^{20}_D$ = -2.7 (c 1.0, $CHCl_3$) (lit.[11]: $[\alpha]^{24}_D$ = - 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]



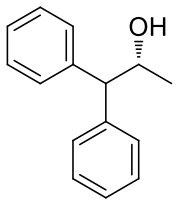
2w

(*R*)-4-phenylbutan-2-ol (2w). 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_2O (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, t_r(major) = 10.3 min, t_r(minor) = 15.1 min).

$[\alpha]^{20}_D$ = -4.4 (c 1.0, $CHCl_3$) (lit.[12]: $[\alpha]^{20}_D$ = +7.9 (c 1.0, $CHCl_3$), (*S*) 33% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): 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]



2x

(*R*)-1,1-diphenylpropan-2-ol (2x). 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_2O (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).

$[\alpha]^{20}_D$ = +4.9 (c 1.0, $CHCl_3$) (lit.[4]: $[\alpha]^{20}_D$ = -4.9 (c 1.0, $CHCl_3$), (*S)* 65% ee). Configuration of the product was assigned as *R* accordingly.

^{1}H-NMR (500 MHz, $CDCl_3$): 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 Λ-IrS in THF at lower concentrations.

Stock solution of 0.53 mM: The chiral iridium complex Λ-**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 Λ-**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-1*H*-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** (0.20 mol%, 0.67 μmol, 168 μL of a 3.97 mM stock solution in THF) and THF/H_2O (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-1*H*-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** (0.050 mol%, 0.168 μmol, 42 μL of a 3.97 mM stock solution in THF) and THF/H_2O (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-1*H*-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/H_2O (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 ^{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).

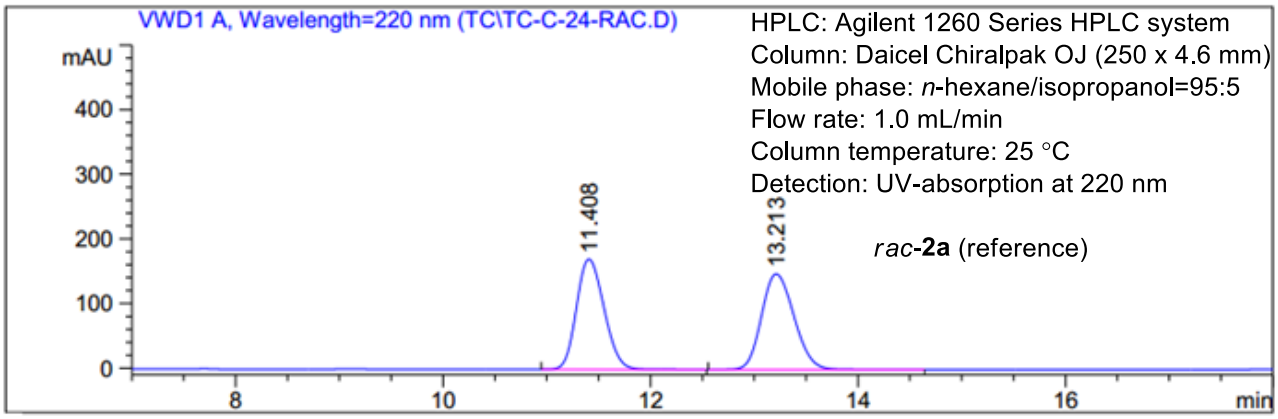
Entry 5: To a mixture of the ligand 5-(4-methoxyphenyl)-3-methyl-1*H*-pyrazole (12.4 mg, 0.066 mmol) and the reducing agent $HCOONH_4$ (376.0 mg, 6.0 mmol) was added the metal catalyst Λ-**IrS** (0.005 mol%, 0.0168 μmol, 32 μL of a 0.53 mM stock solution in THF) and THF/H_2O (304 μL /336 μL) in a brown 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 ^{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).

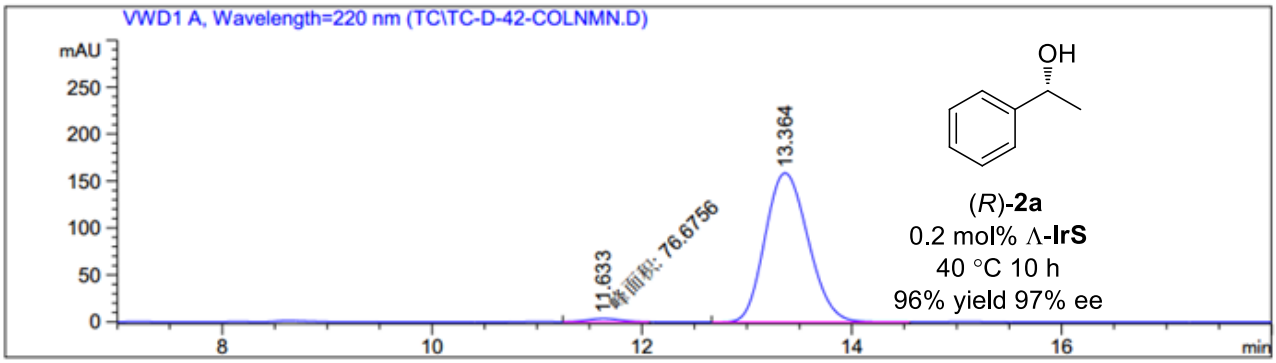
Entry 6: To a mixture of the ligand 5-(4-methoxyphenyl)-3-methyl-1*H*-pyrazole (12.4 mg, 0.066 mmol) and the reducing agent $HCOONH_4$ (376.0 mg, 6.0 mmol) was added the metal catalyst Λ-**IrS** (0.002 mol%, 0.0067 μmol, 25 μL of a 0.27 mM stock solution in THF) and THF/H_2O (311 μL/336 μL) in a brown 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 ^{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).

6. Chiral HPLC Traces

6.1 Determination of enantioselectivities for the ATH reaction catalyzed by Λ-IrS with the pyrazole additive

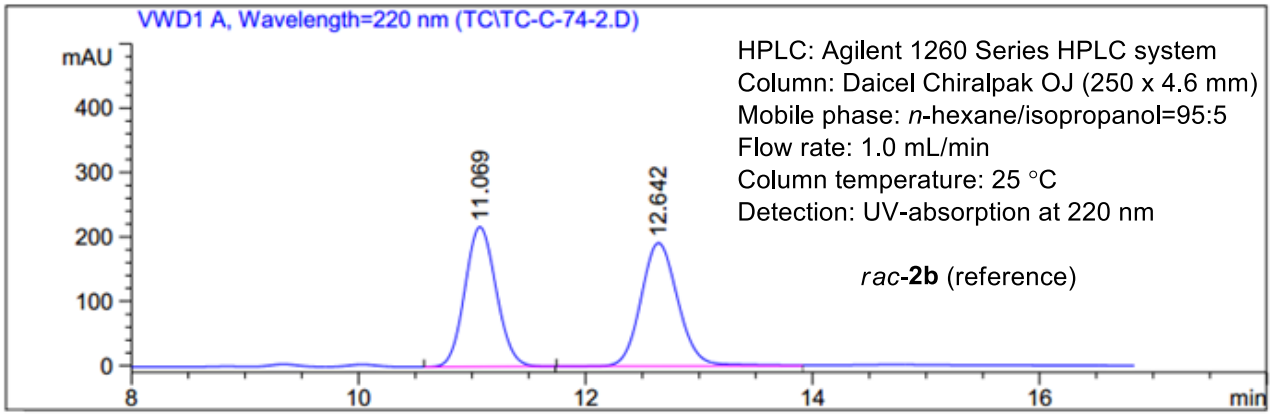
Enantiomeric excess of the ATH products were determined with a Daicel Chiralpak OD-H, OJ, or IC column (250 x 4.6 mm) on an Agilent 1260 Series HPLC System using *n*-hexane/isopropanol as mobile phase, the temperature was 25 °C and UV-absorption was measured at 220 nm.

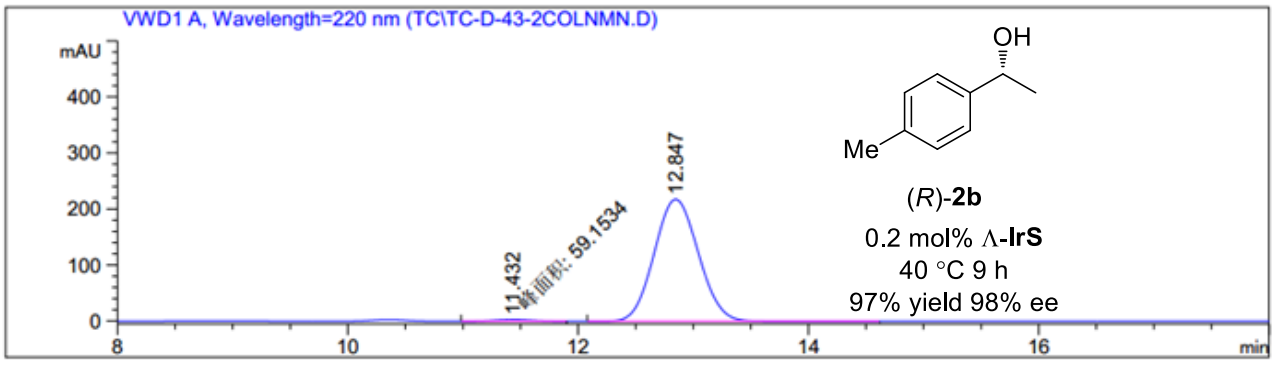




#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.633	MM	0.3662	76.67559	3.48936	1.6636
2	13.364	BV	0.4493	4532.43066	158.64536	98.3364

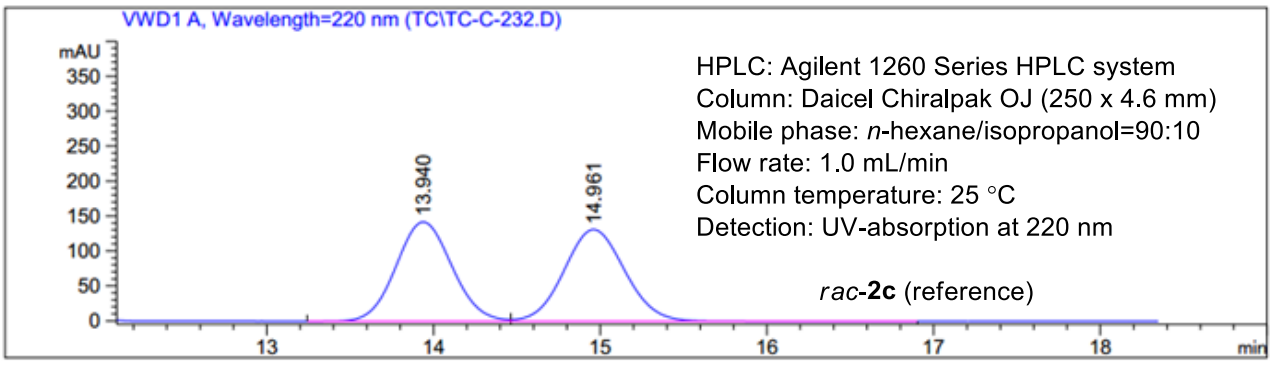
Figure S1. HPLC traces of transfer hydrogenation leading to (*R*)-**2a**.

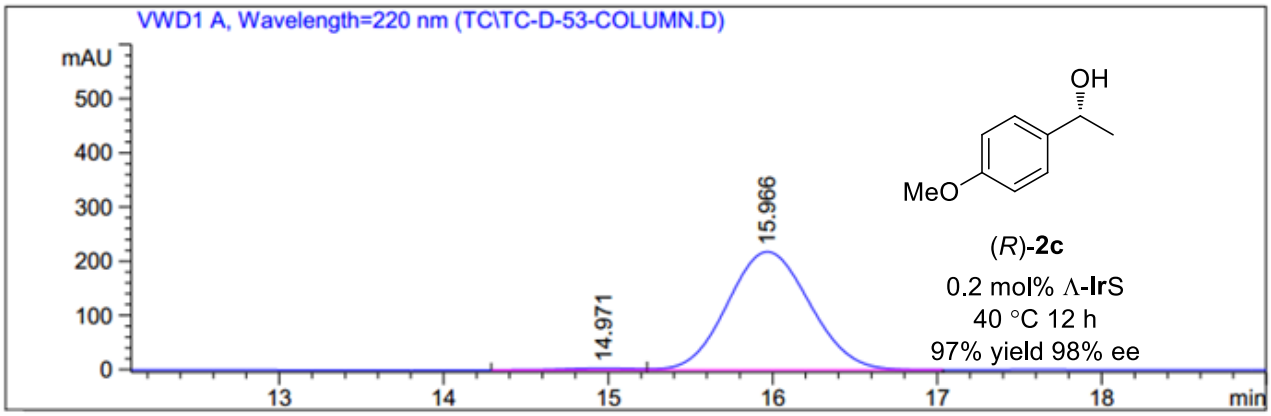




#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.432	MM	0.3726	59.15344	2.64605	1.0098
2	12.847	BB	0.4192	5798.87549	217.39737	98.9902

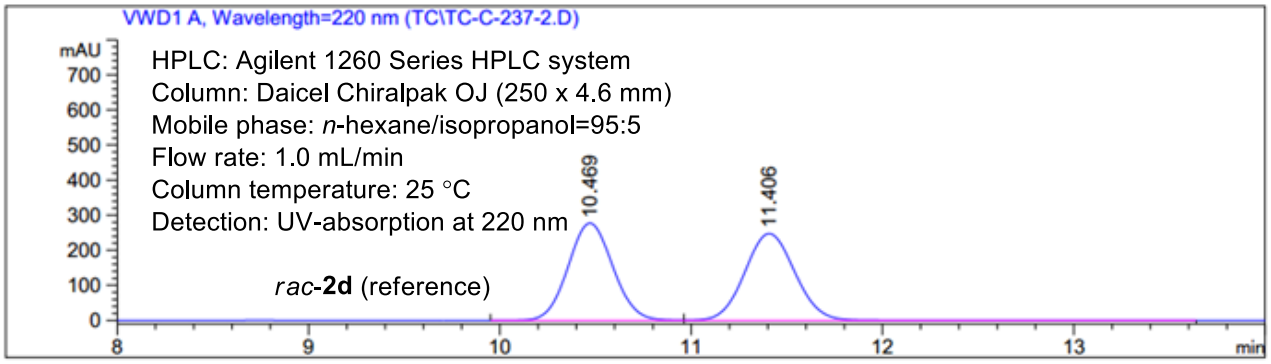
Figure S2. HPLC traces of transfer hydrogenation leading to (*R*)-**2b**.

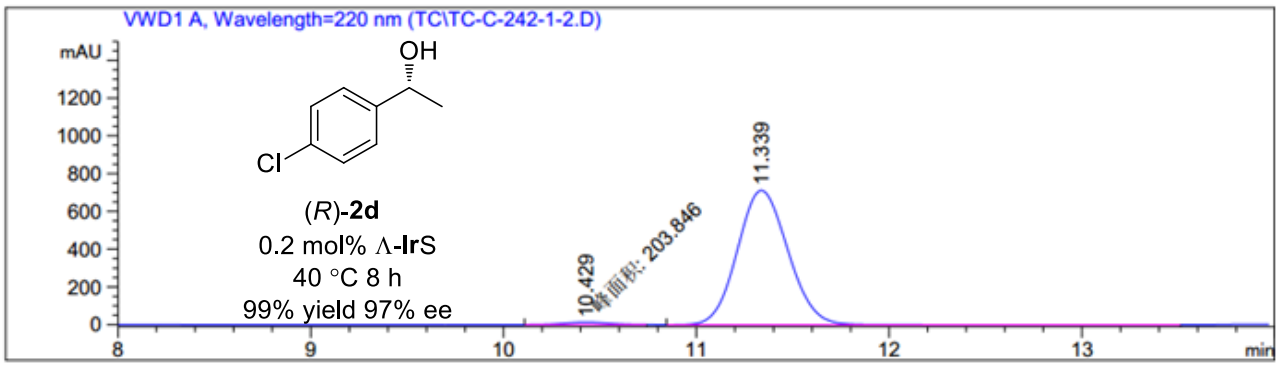




#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.971	BV	0.4466	84.52215	2.98296	1.1008
2	15.966	VB	0.5465	7593.71191	217.92250	98.8992

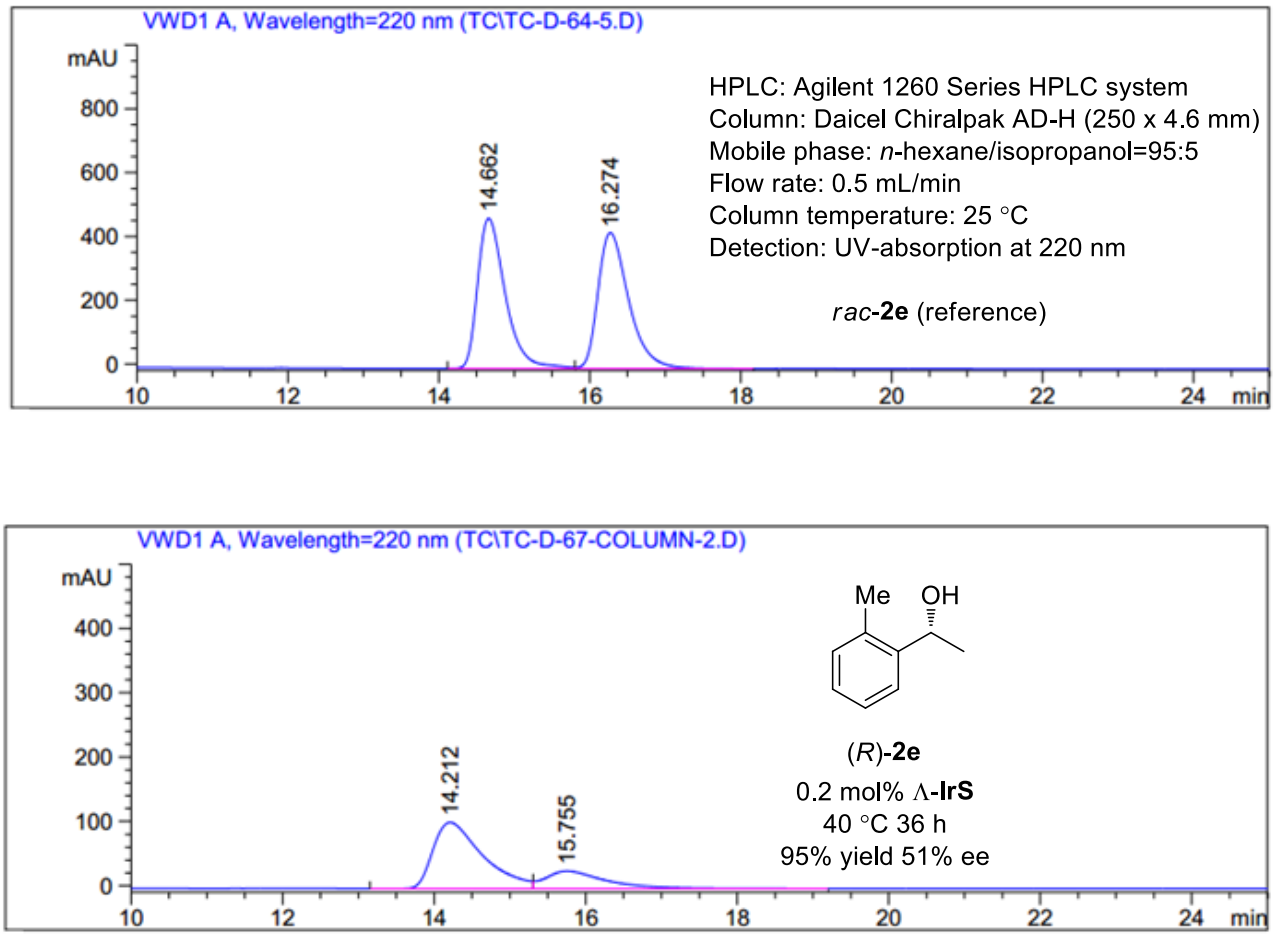
Figure S3. HPLC traces of transfer hydrogenation leading to (*R*)-**2c**.





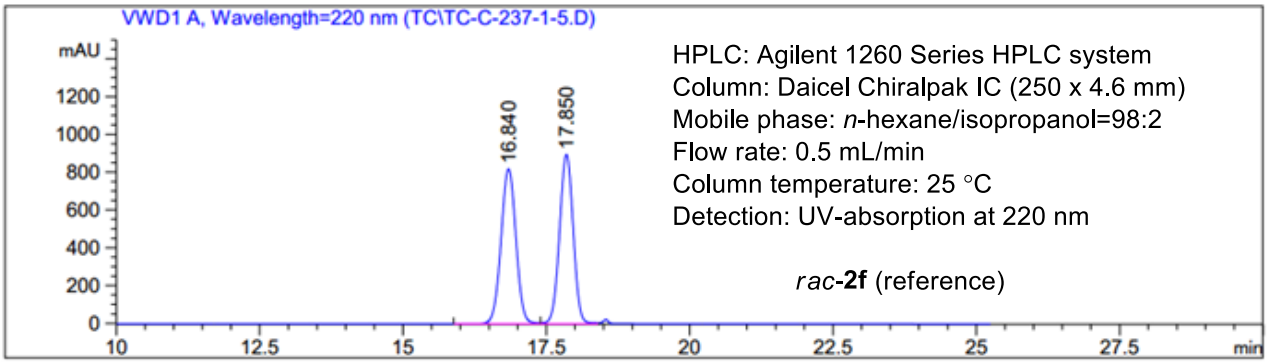
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.429	MM	0.2587	203.84637	13.13248	1.5427
2	11.339	VB	0.2854	1.30097e4	711.17682	98.4573

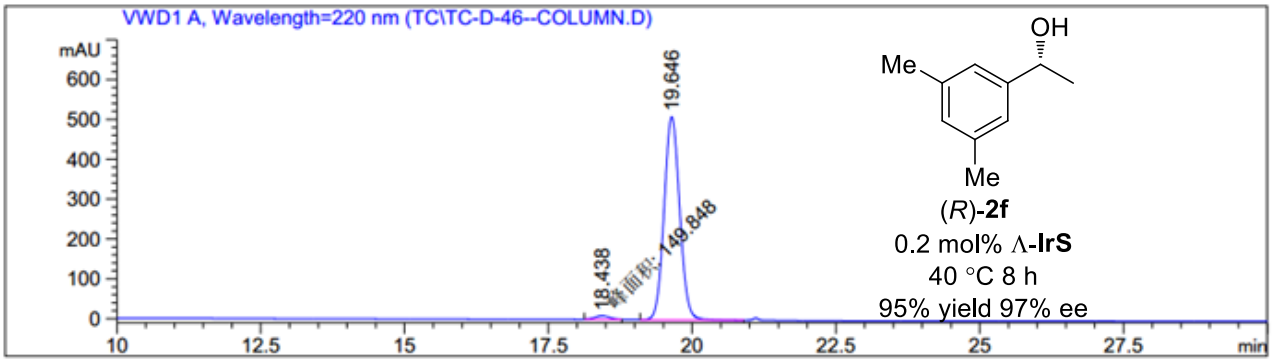
Figure S4. HPLC traces of transfer hydrogenation leading to (*R*)-**2d**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.212	BV	0.6818	4664.16309	102.70131	75.6897
2	15.755	VB	0.7991	1498.05664	27.17680	24.3103

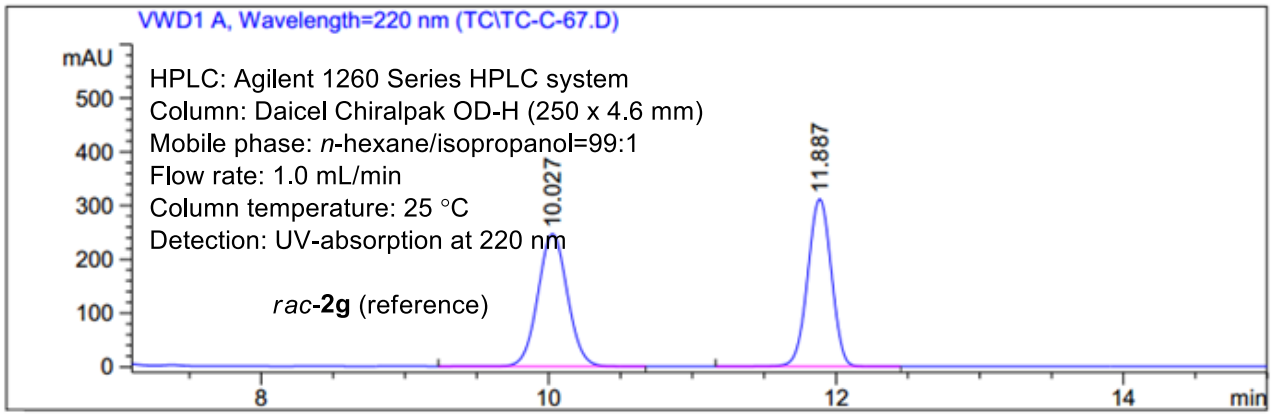
Figure S5. HPLC traces of transfer hydrogenation leading to (*R*)-**2e**.

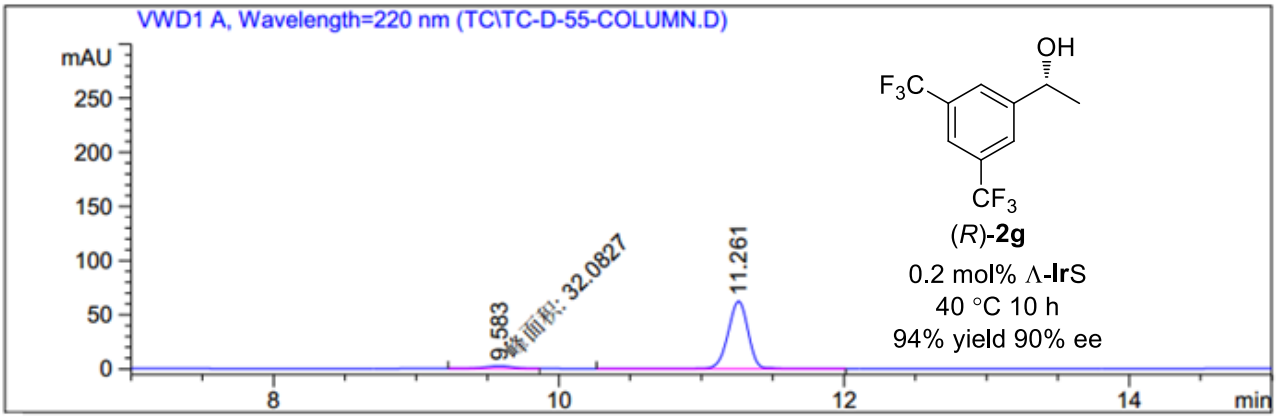




#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.438	MM	0.2851	149.84796	8.75887	1.5310
2	19.646	VB	0.2946	9638.02930	509.72479	98.4690

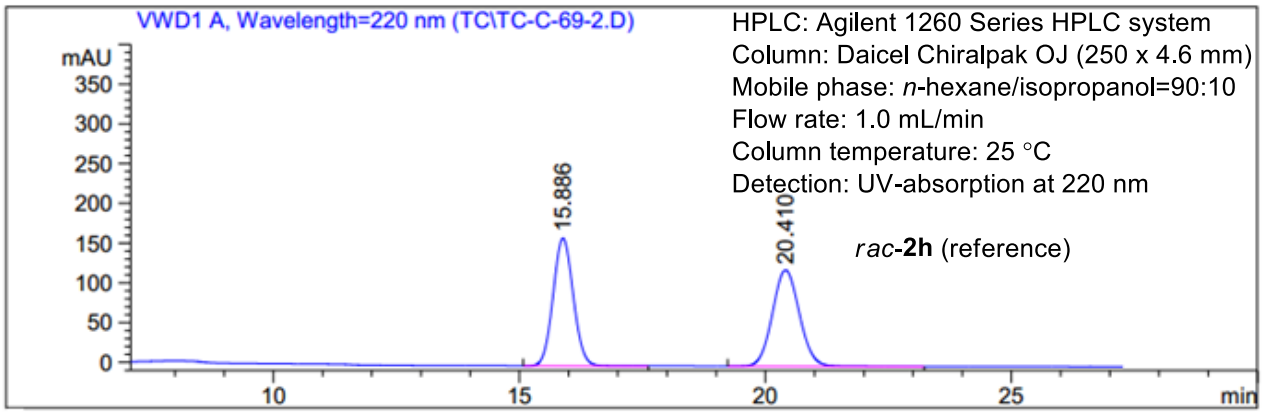
Figure S6. HPLC traces of transfer hydrogenation leading to (*R*)-**2f**.

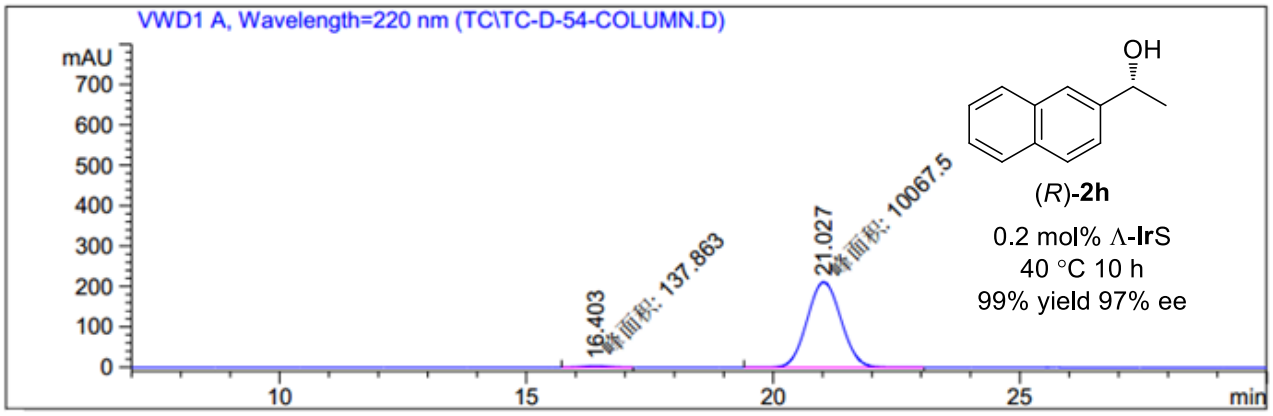




#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.583	MM	0.2279	32.08267	2.34627	5.0391
2	11.261	VB	0.1536	604.59760	62.08014	94.9609

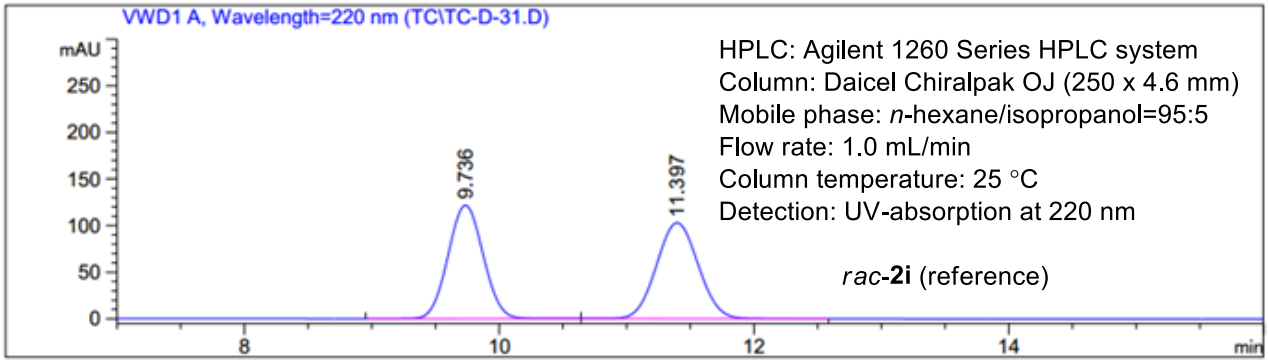
Figure S7. HPLC traces of transfer hydrogenation leading to (*R*)-**2g**.

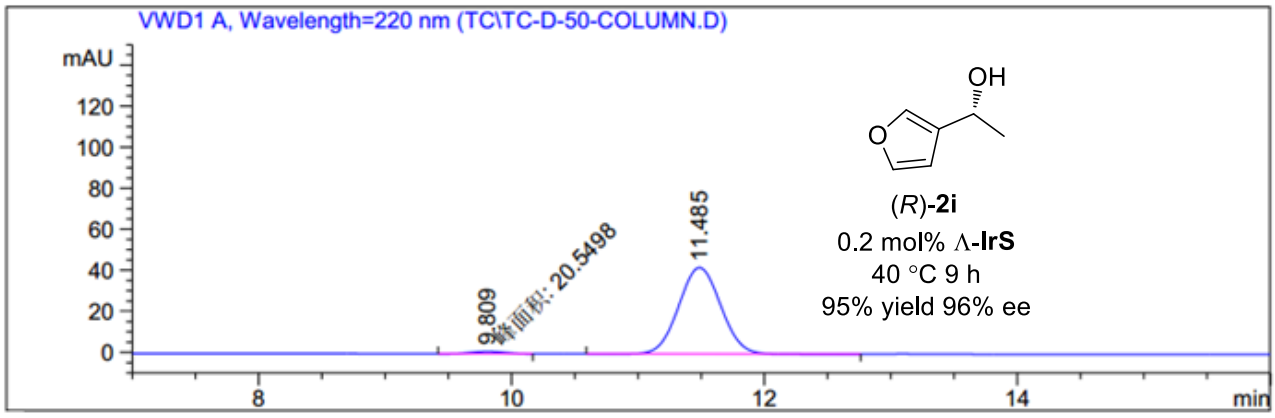




#	[min]		[min]	[mAU*s]	[mAU]	%
1	16.403	MM	0.6052	137.86325	3.79645	1.3509
2	21.027	MM	0.7943	1.00675e4	211.23257	98.6491

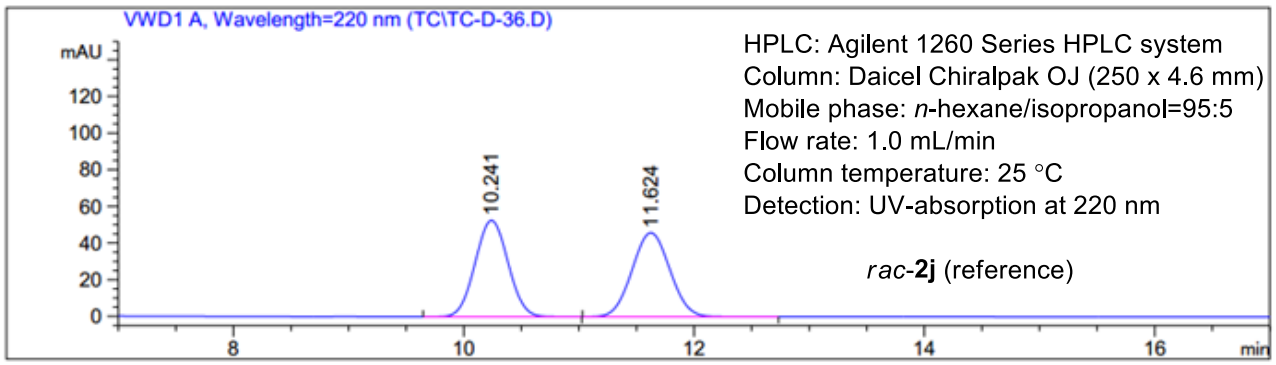
Figure S8. HPLC traces of transfer hydrogenation leading to (*R*)-**2h**.

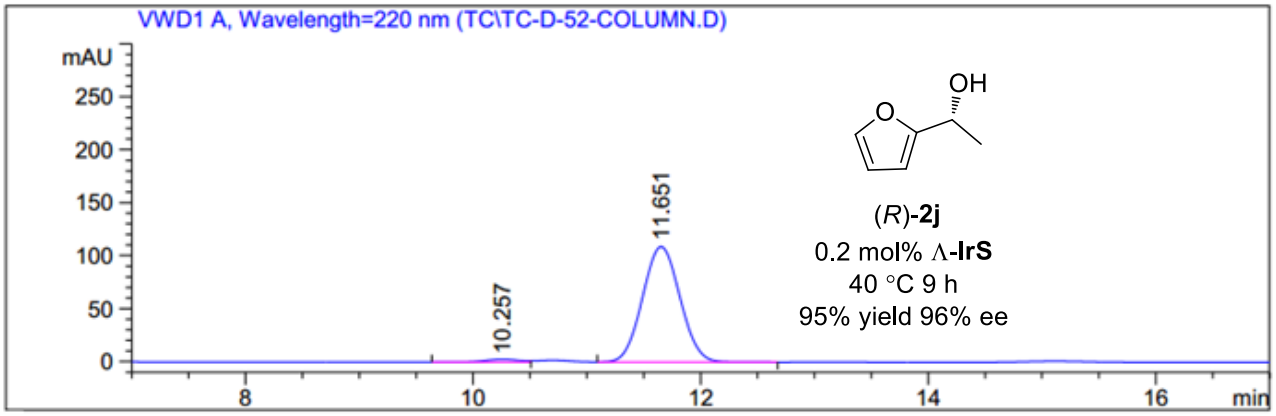




1	9.809	MM	0.3165	20.54984	1.08200	2.0501
2	11.485	VV	0.3639	981.84662	42.12702	97.9499

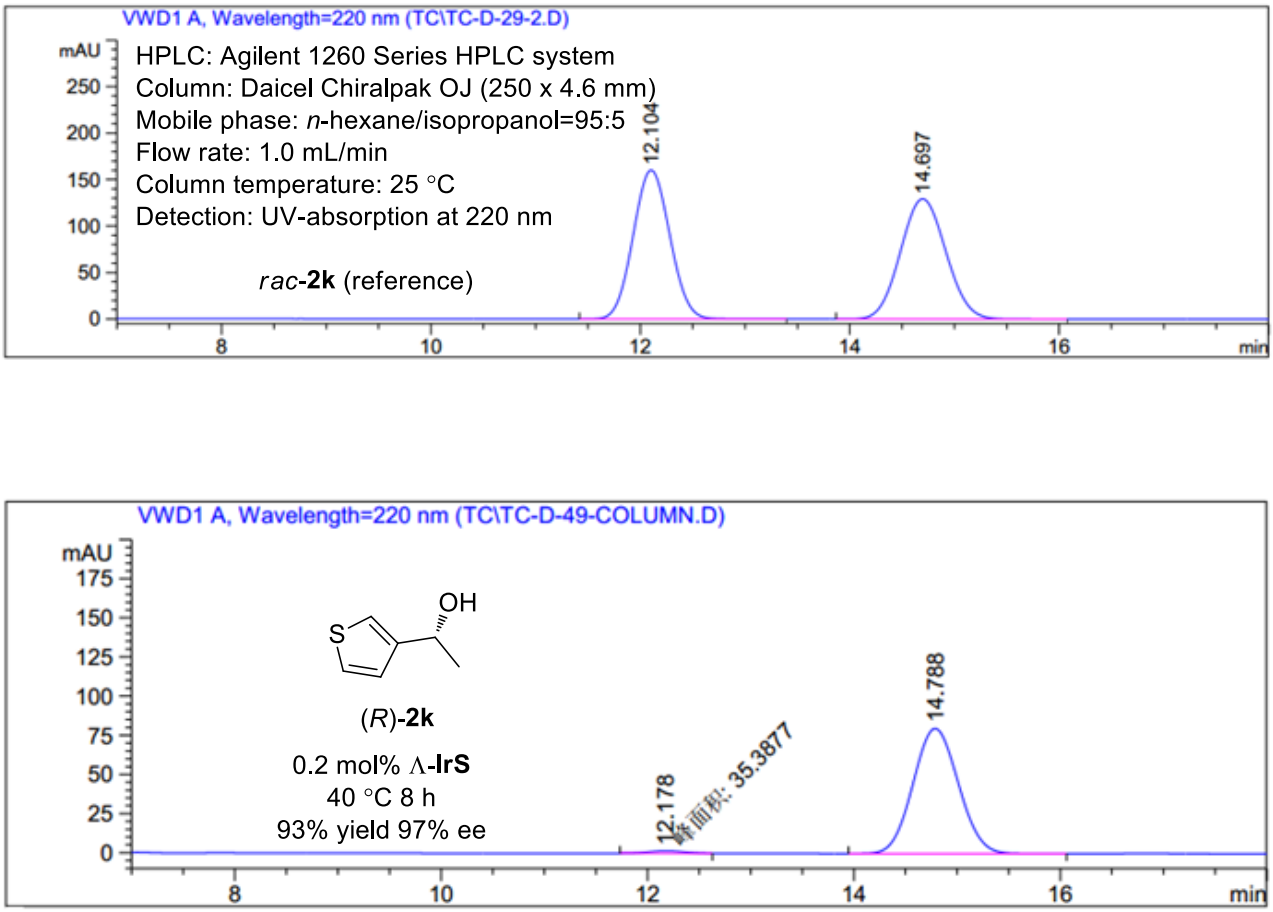
Figure S9. HPLC traces of transfer hydrogenation leading to (*R*)-**2i**.





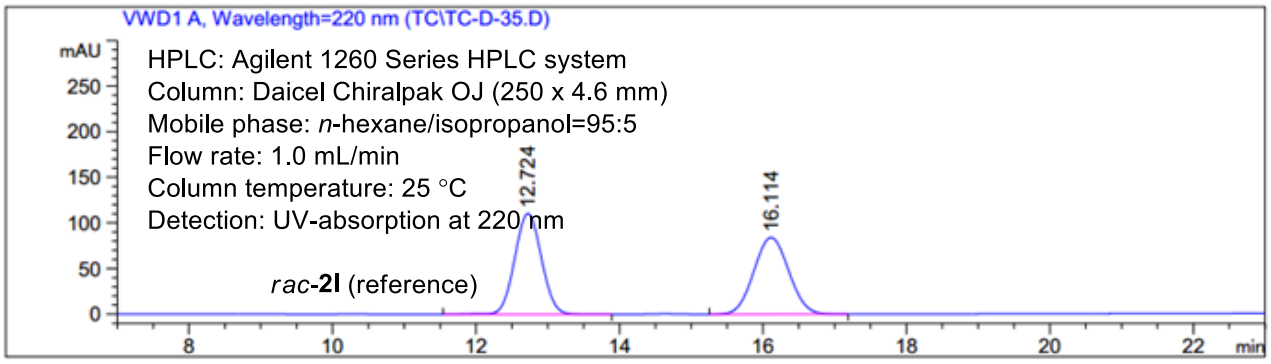
1	10.257	BV	0.3153	53.53700	2.61043	2.0973
2	11.651	VB	0.3596	2499.08472	108.94597	97.9027

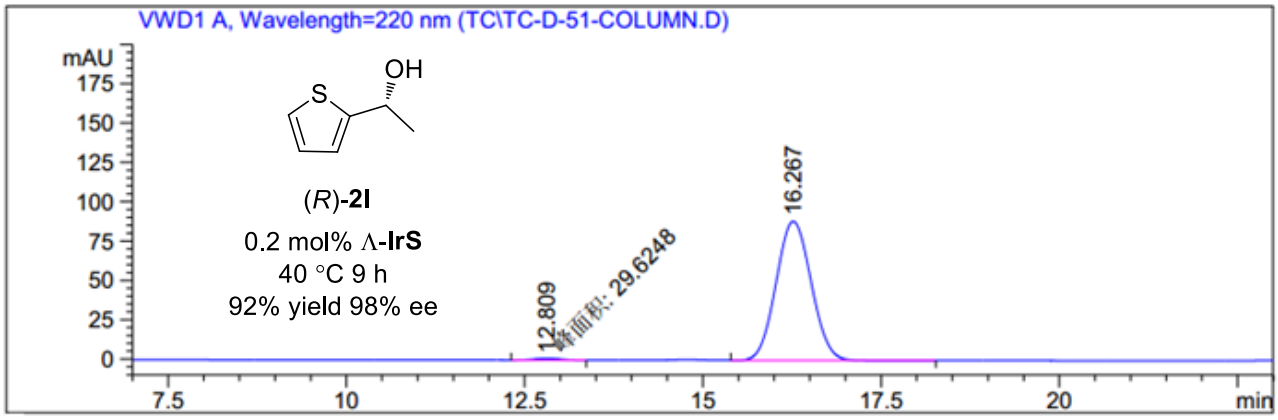
Figure S10. HPLC traces of transfer hydrogenation leading to (*R*)-**2j**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.178	MM	0.3946	35.38769	1.49464	1.4296
2	14.788	BB	0.4805	2439.97192	79.85620	98.5704

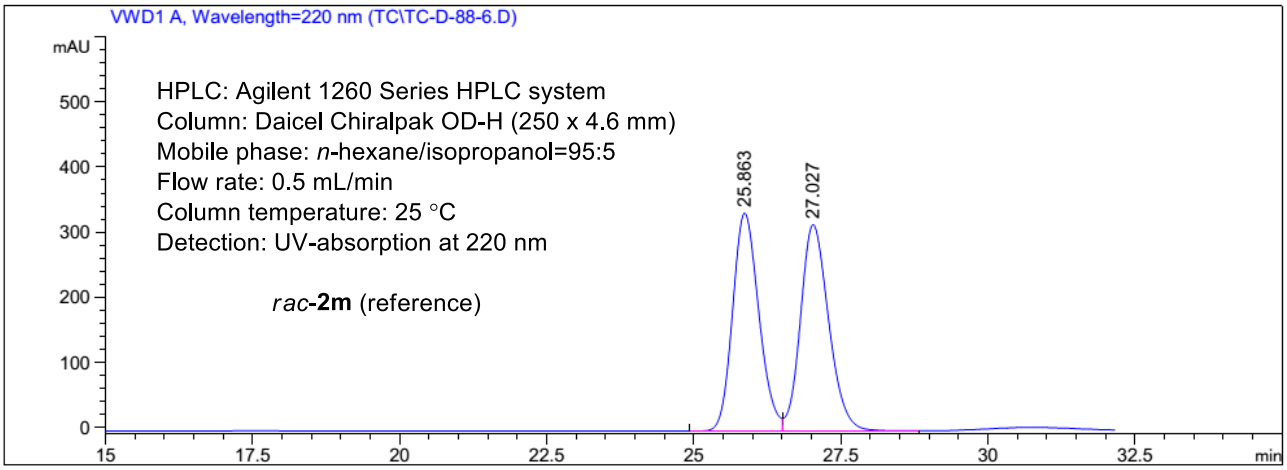
Figure S11. HPLC traces of transfer hydrogenation leading to (*R*)-**2k**.

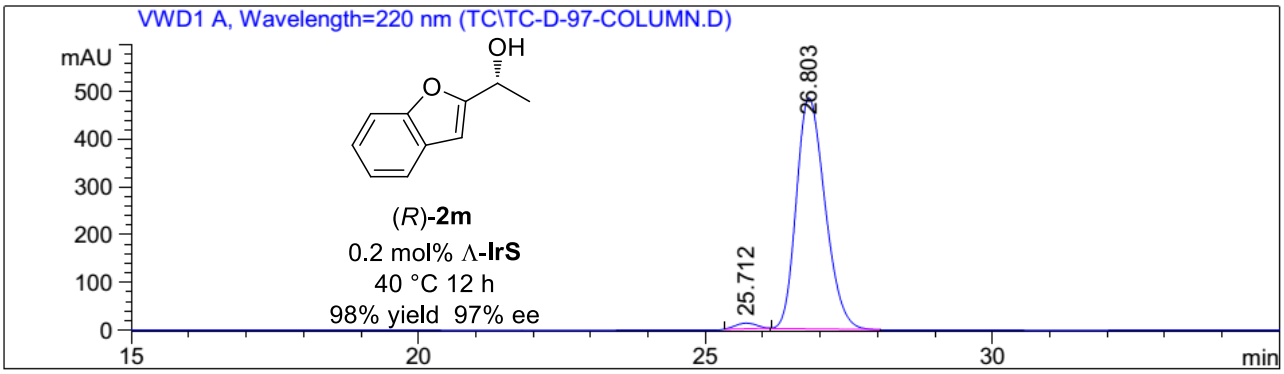




#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.809	MM	0.4267	29.62483	1.15712	0.9674
2	16.267	VB	0.5400	3032.57666	88.44614	99.0326

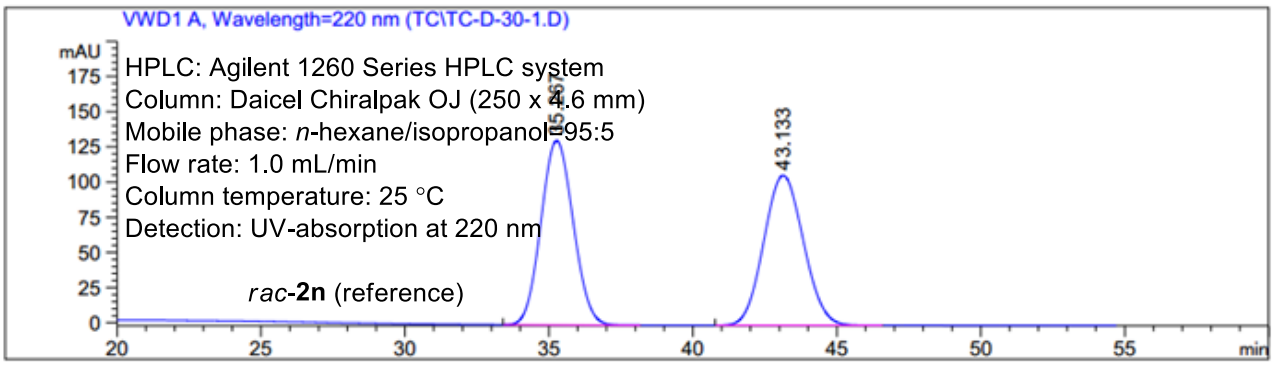
Figure S12. HPLC traces of transfer hydrogenation leading to (*R*)-**2l**.

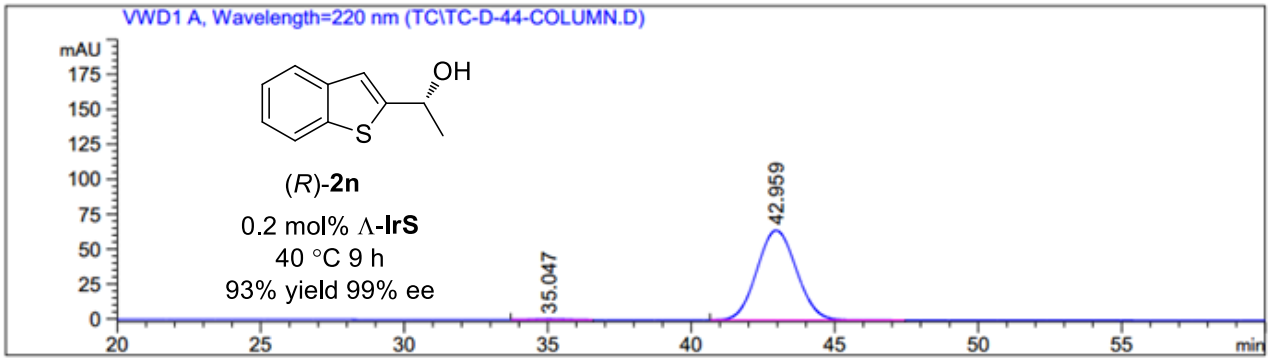




#	[min]		[min]	[mAU*s]	[mAU]	%
1	25.712	MM R	0.4177	290.51434	11.59179	1.6955
2	26.803	MM R	0.5786	1.68435e4	485.18689	98.3045

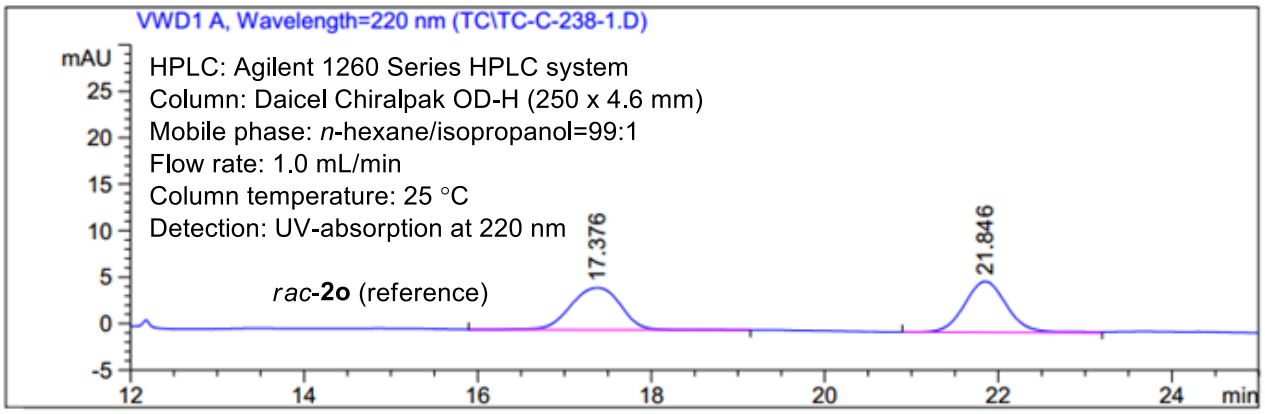
Figure S13. HPLC traces of transfer hydrogenation leading to (*R*)-**2m**.

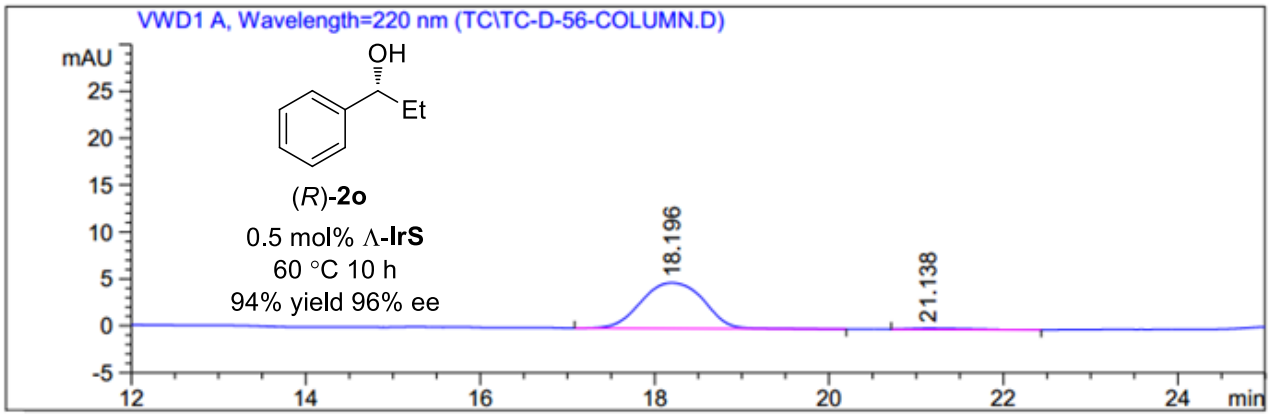




#	[min]		[min]	[mAU*s]	[mAU]	%
1	35.047	BB	0.8842	40.87154	5.47929e-1	0.6635
2	42.959	BB	1.4922	6118.88965	64.07240	99.3365

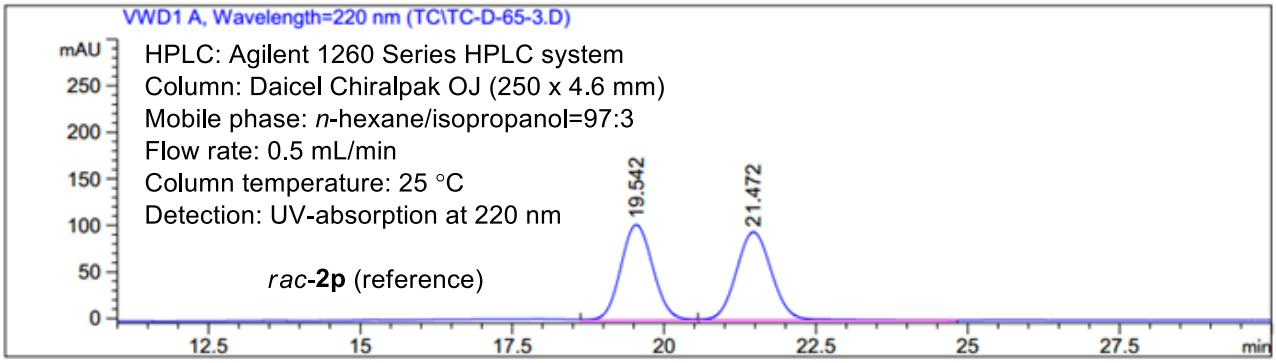
Figure S14. HPLC traces of transfer hydrogenation leading to (*R*)-**2n**.

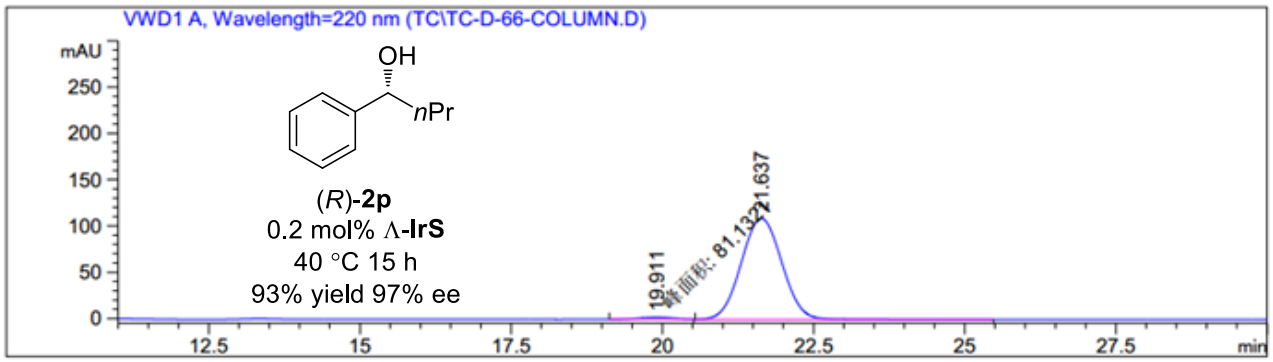




#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.196	BB	0.8300	244.40448	4.86617	97.7939
2	21.138	BB	0.6420	5.51348	1.14446e-1	2.2061

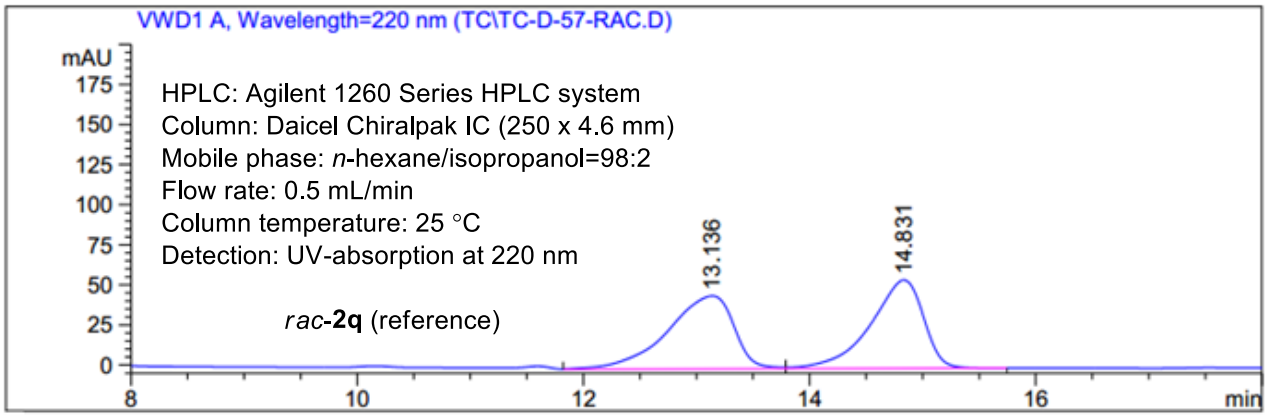
Figure S15. HPLC traces of transfer hydrogenation leading to (*R*)-**2o**.

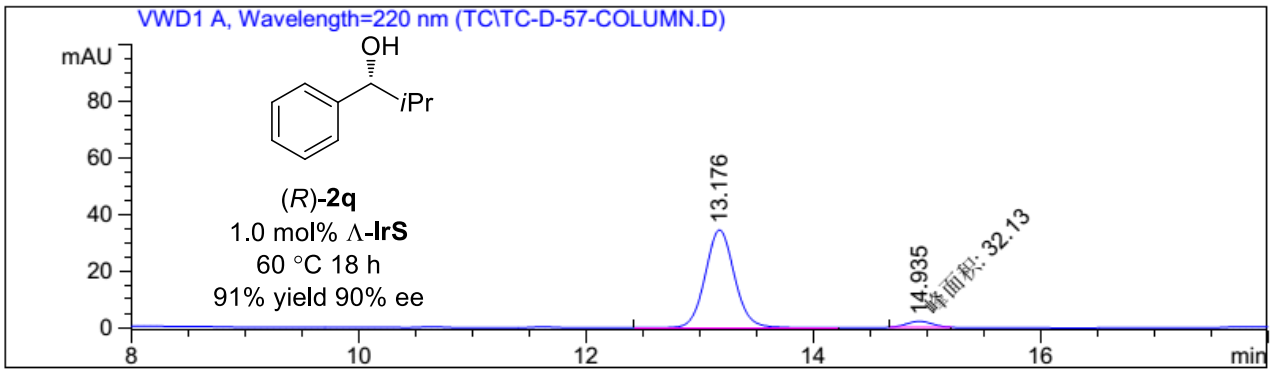




#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.911	MM	0.6420	81.13206	2.10636	1.5642
2	21.637	VB	0.7382	5105.52197	109.06081	98.4358

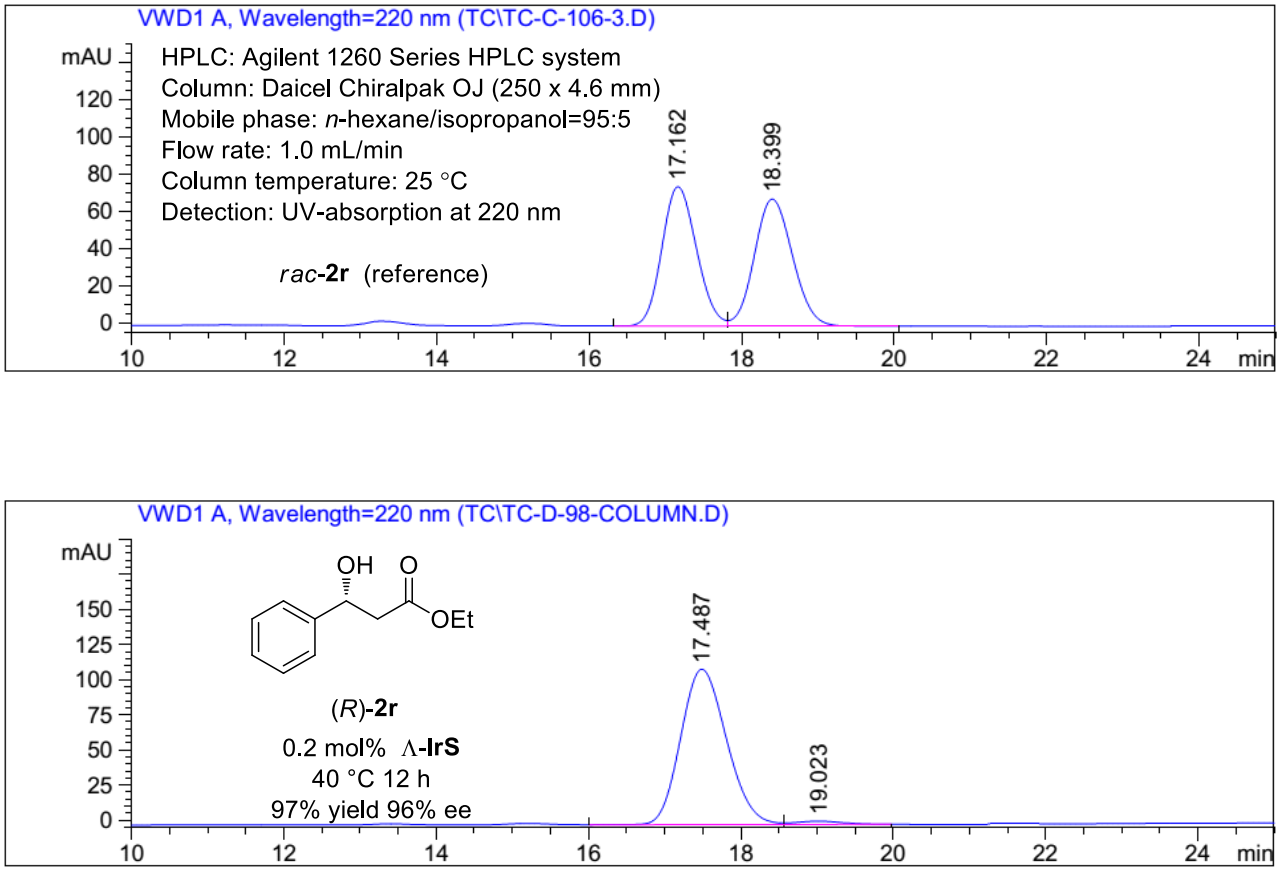
Figure S16. HPLC traces of transfer hydrogenation leading to (*R*)-**2p**.





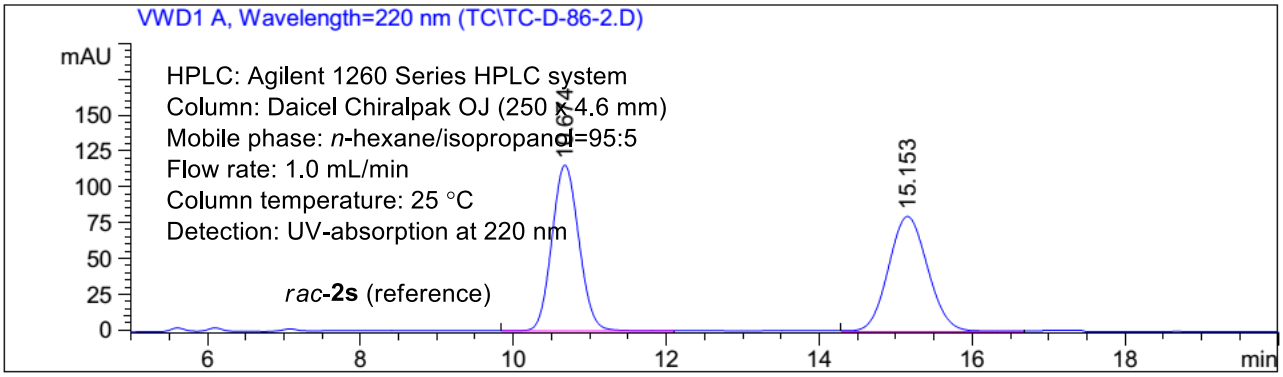
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.176	BB	0.2767	617.85956	34.53353	95.0568
2	14.935	MM	0.2551	32.12996	2.09920	4.9432

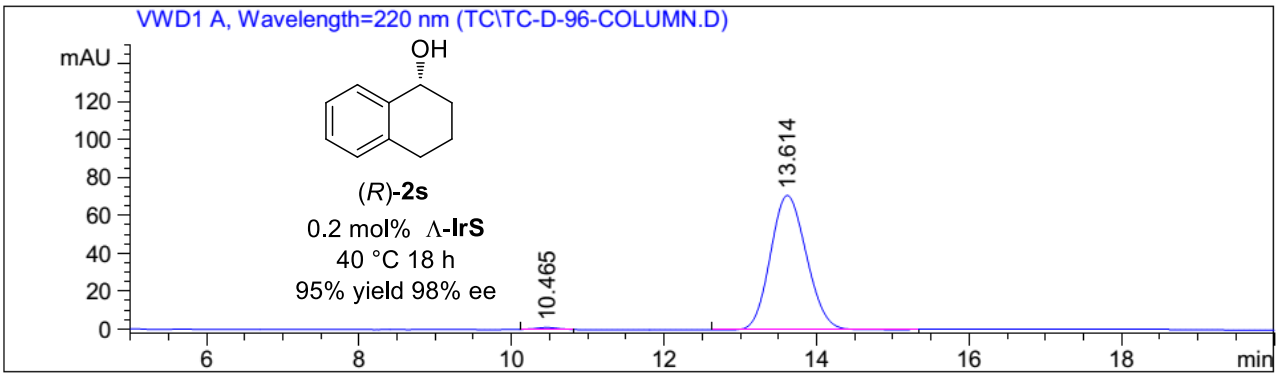
Figure S17. HPLC traces of transfer hydrogenation leading to (*R*)-**2q**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.487	BV	0.6527	4610.70850	110.53075	97.9830
2	19.023	VB	0.6735	94.91219	2.20801	2.0170

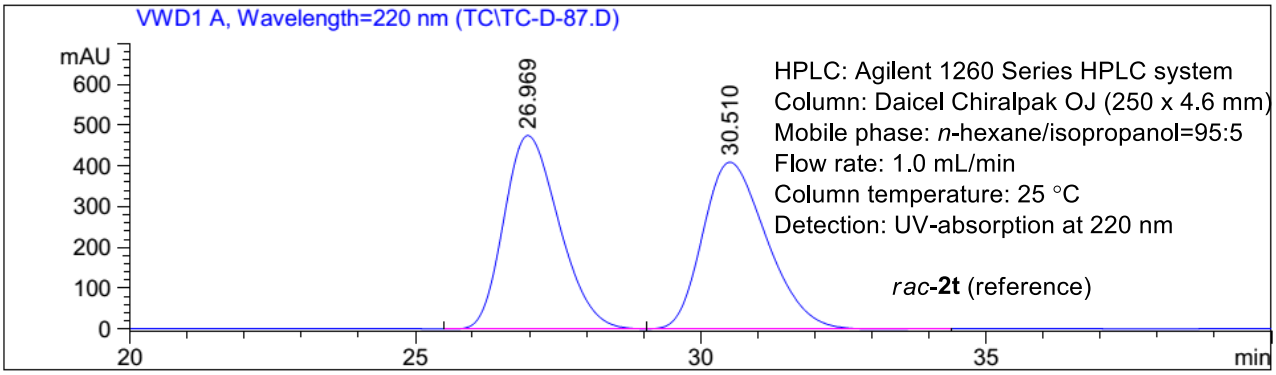
Figure S18. HPLC traces of transfer hydrogenation leading to (*R*)-**2r**.

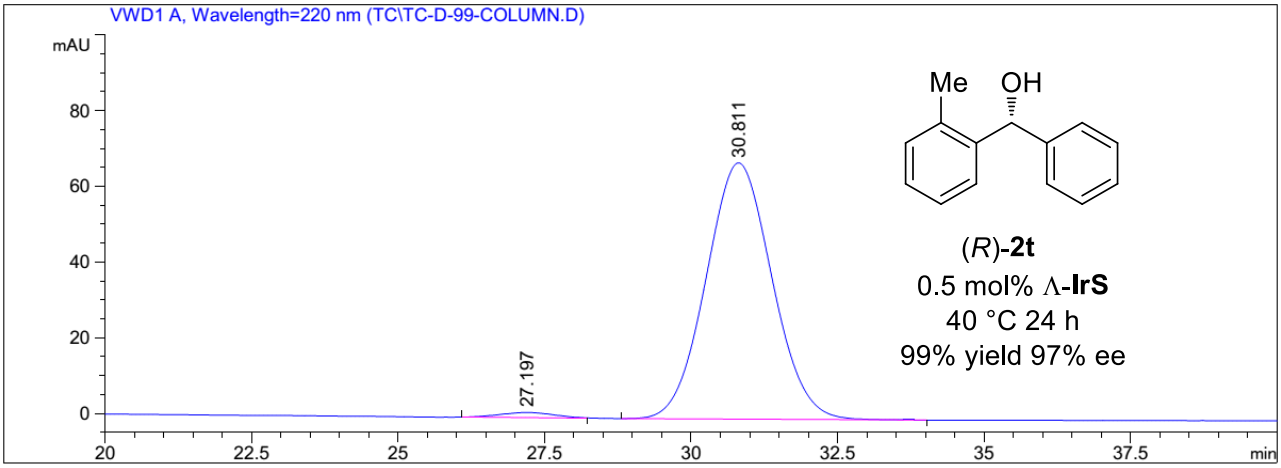




#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.465	MM R	0.3523	21.72536	1.02781	0.9243
2	13.614	MM R	0.5481	2328.70752	70.81310	99.0757

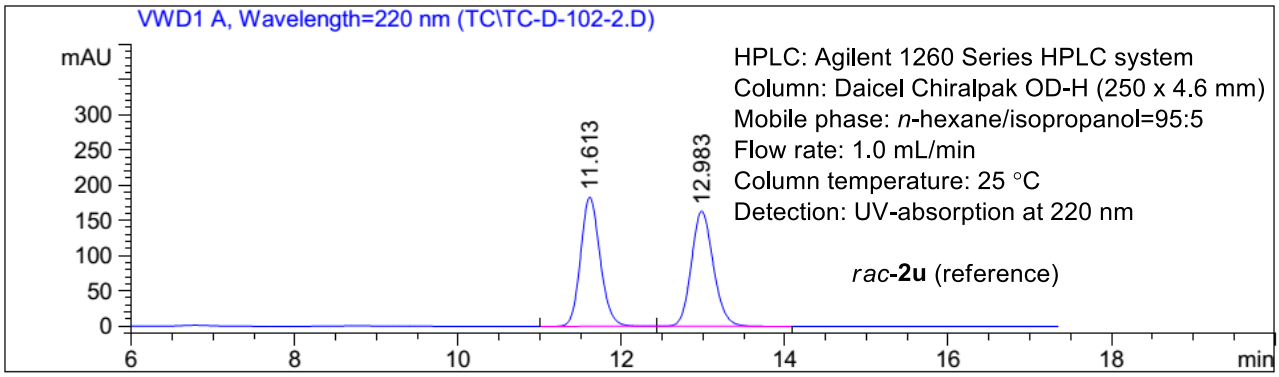
Figure S19. HPLC traces of transfer hydrogenation leading to (*R*)-**2s**.

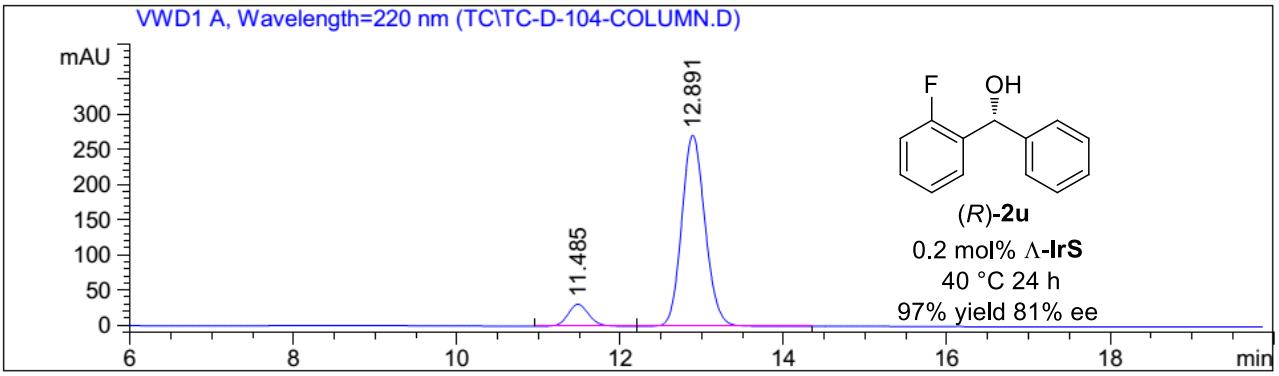




#	[min]		[min]	[mAU*s]	[mAU]	%
1	27.197	MM R	1.0458	82.88673	1.32097	1.5449
2	30.811	BB	1.2163	5282.19873	67.69466	98.4551

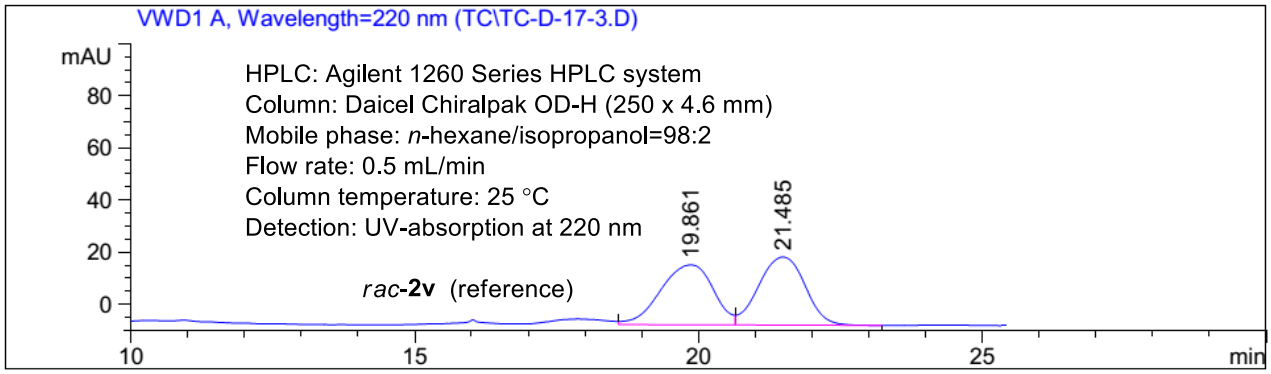
Figure S20. HPLC traces of transfer hydrogenation leading to (*R*)-**2t**.

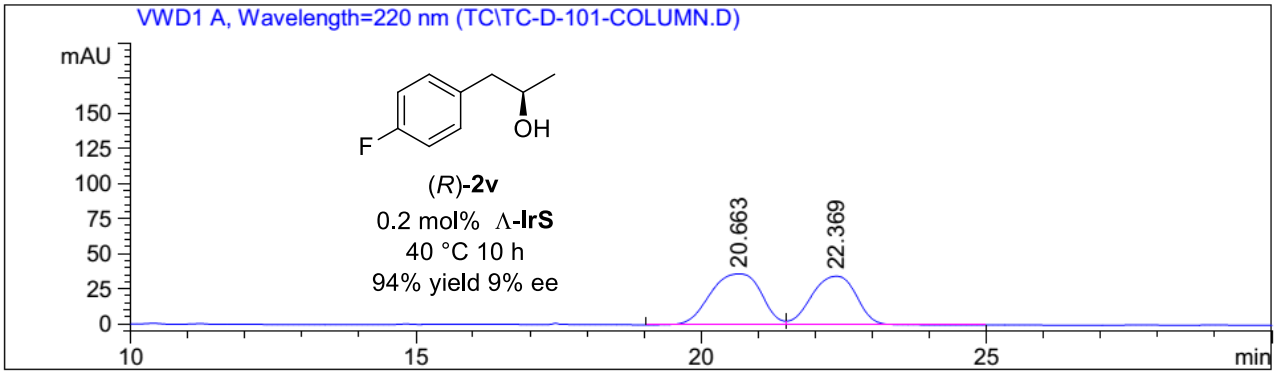




#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.485	BB	0.2750	554.28180	31.24592	9.3280
2	12.891	BV	0.3113	5387.87012	271.72314	90.6720

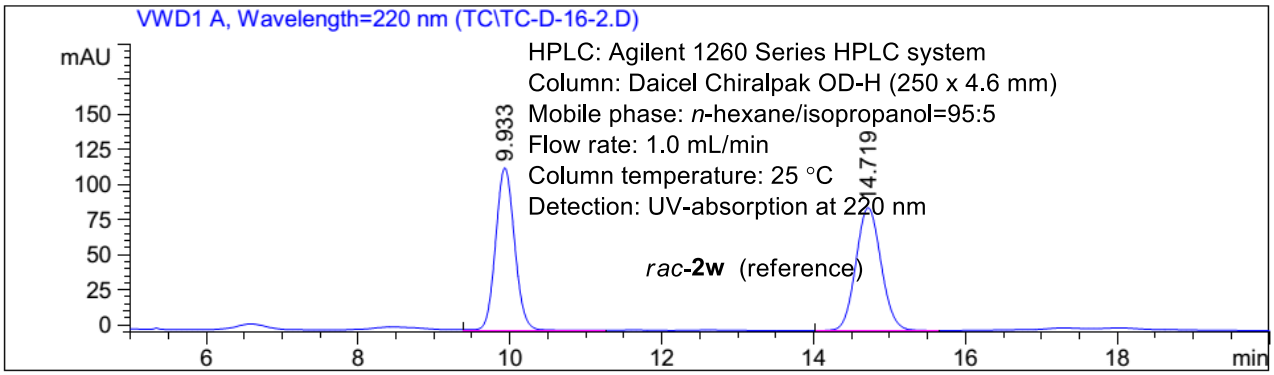
Figure S21. HPLC traces of transfer hydrogenation leading to (*R*)-**2u**.

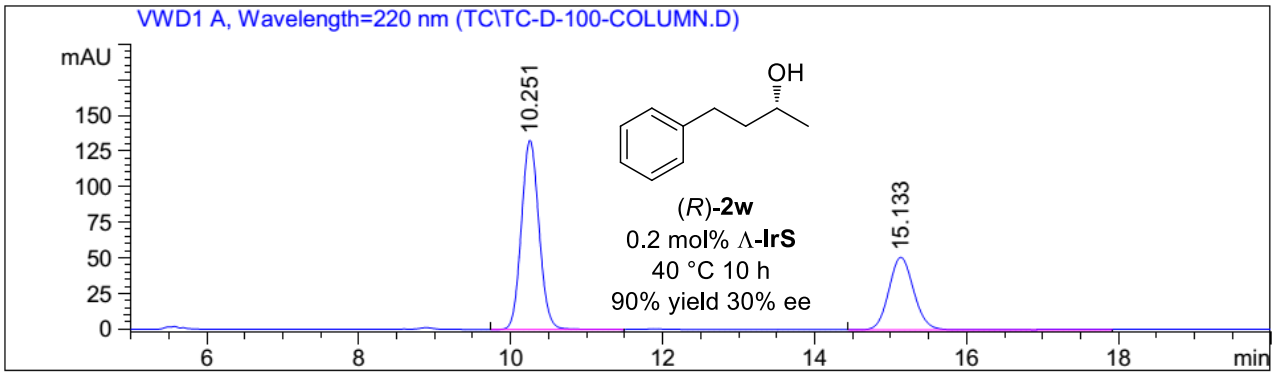




#	[min]		[min]	[mAU*s]	[mAU]	%
1	20.663	BV	1.0212	2266.16870	36.45895	54.3017
2	22.369	VB	0.8952	1907.12305	34.80742	45.6983

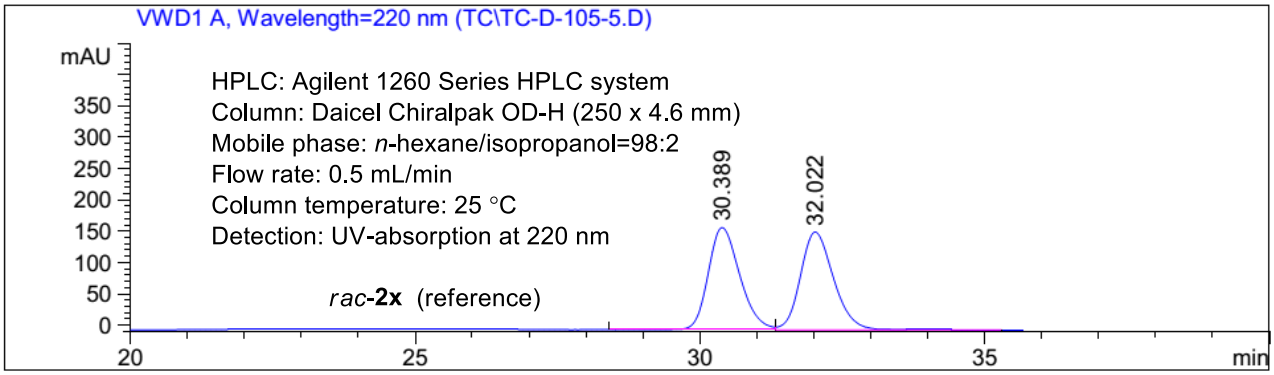
Figure S22. HPLC traces of transfer hydrogenation leading to (*R*)-**2v**.

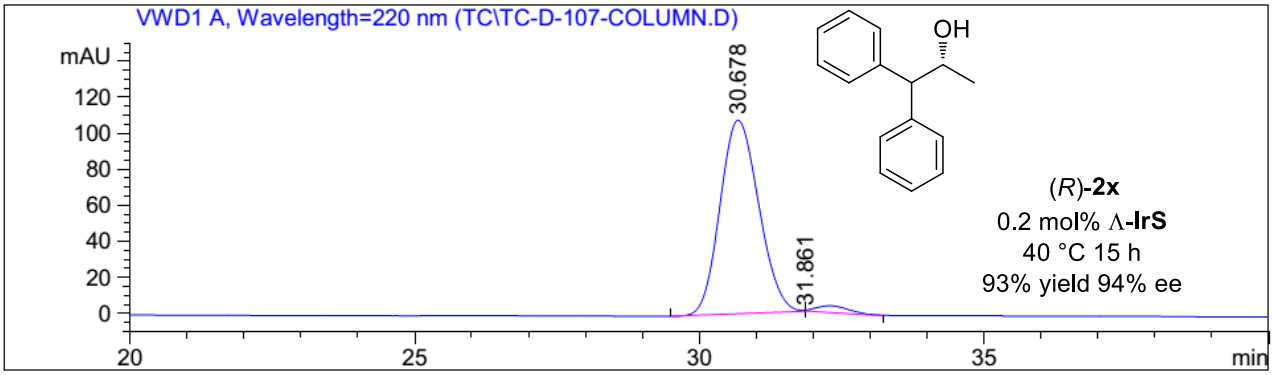




#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.251	BV	0.2536	2157.22681	132.72206	64.8044
2	15.133	BB	0.3561	1171.59924	50.98032	35.1956

Figure S23. HPLC traces of transfer hydrogenation leading to (*R*)-**2w**.



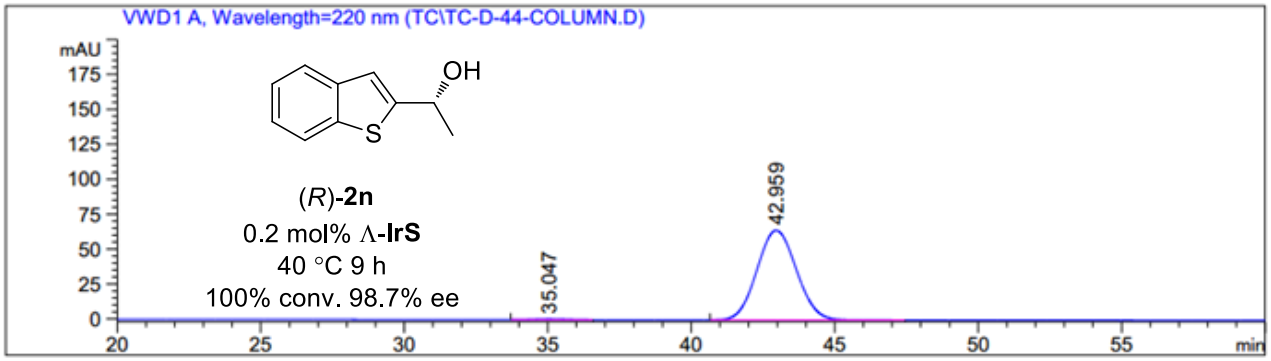


#	[min]		[min]	[mAU*s]	[mAU]	%
1	30.678	MM R	0.7883	5080.43848	107.40982	97.1276
2	31.861	MM R	0.6759	150.24834	4.66038e-1	2.8724

Figure S24. HPLC traces of transfer hydrogenation leading to (*R*)-**2x**.

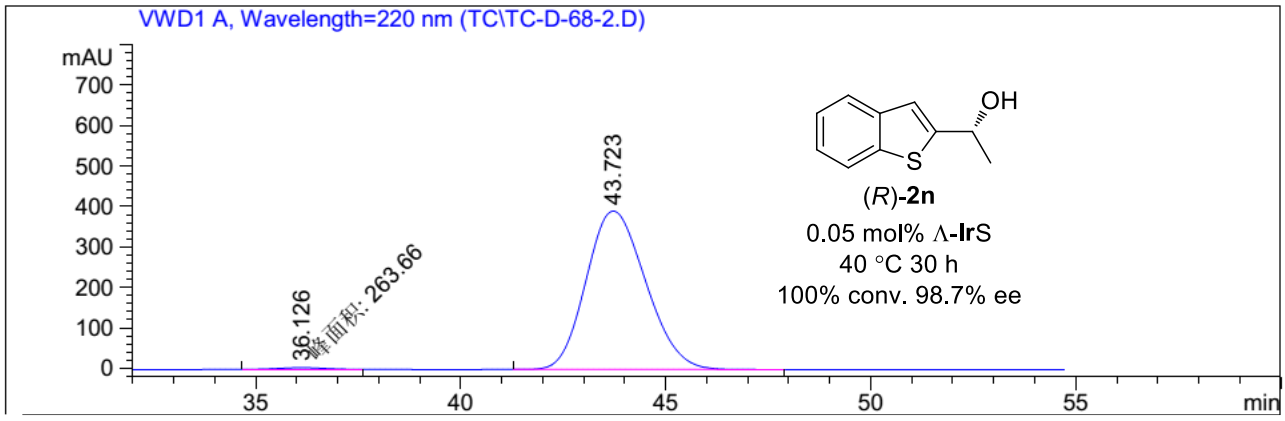
6.2 Determination of enantioselectivities for the ATH reaction of ketone 1n at lower catalyst loadings

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.



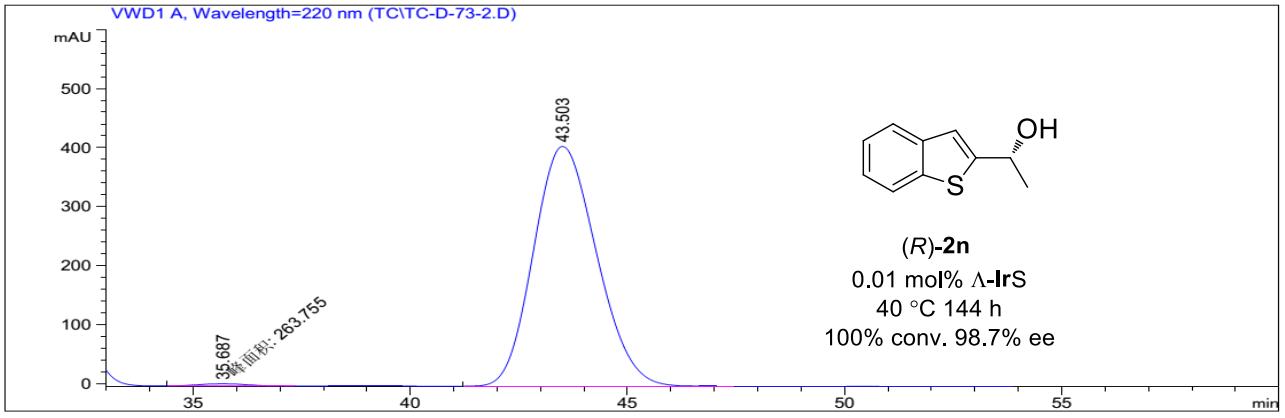
#	[min]		[min]	[mAU*s]	[mAU]	%
1	35.047	BB	0.8842	40.87154	5.47929e-1	0.6635
2	42.959	BB	1.4922	6118.88965	64.07240	99.3365

Figure S25. HPLC trace of the asymmetric transfer hydrogenation leading to (*R*)-**2n** catalyzed by 0.2 mol% Λ-**IrS** at 40°C and the standard conditions (Table1, entry 1).



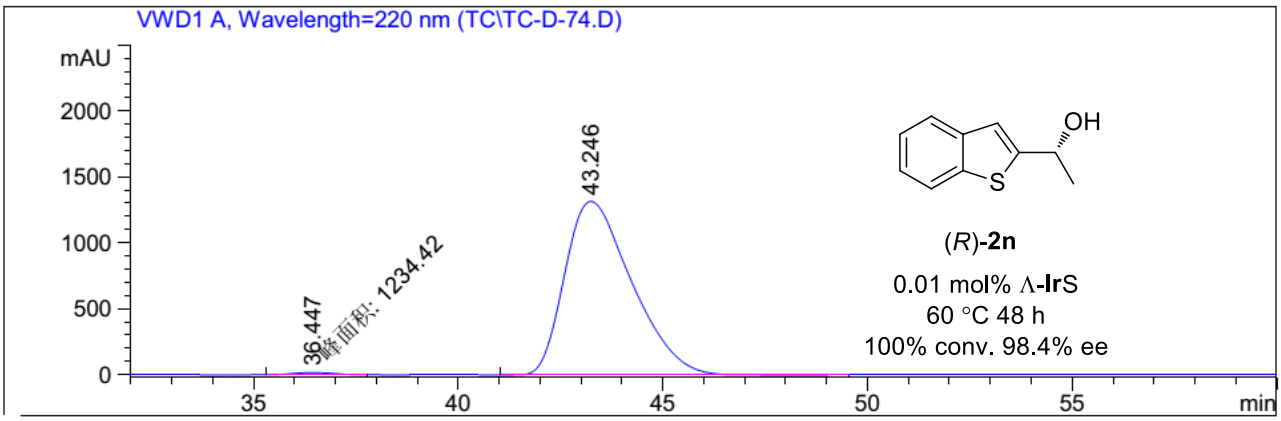
#	[min]		[min]	[mAU*s]	[mAU]	%
1	36.126	MM	1.2510	263.66046	3.51267	0.6637
2	43.723	BB	1.6228	3.94615e4	390.54843	99.3363

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 (Table1, entry 2).



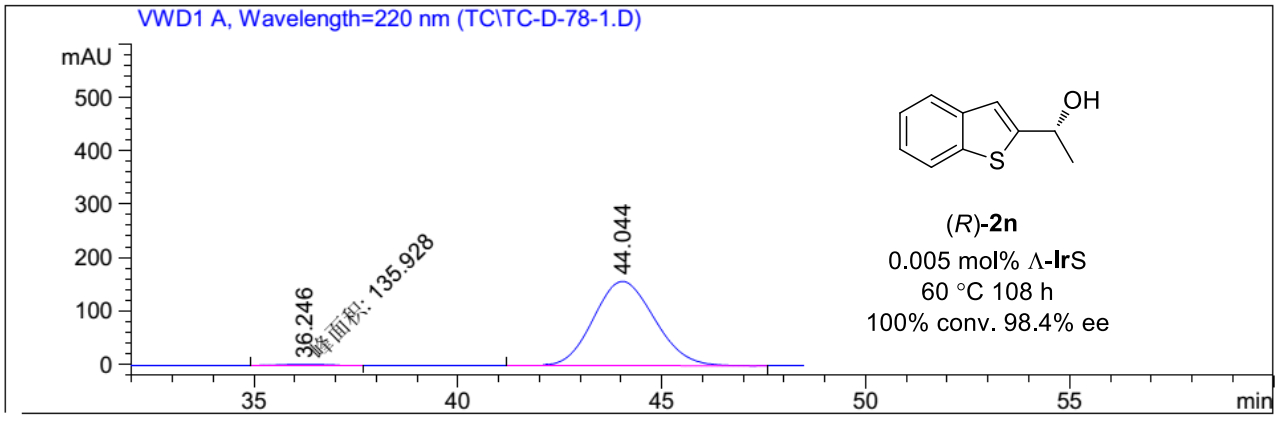
#	[min]		[min]	[mAU*s]	[mAU]	%
1	35.687	MM	1.2368	263.75476	3.55423	0.6397
2	43.503	BB	1.5055	4.09659e4	405.90393	99.3603

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 (Table1, entry 3).



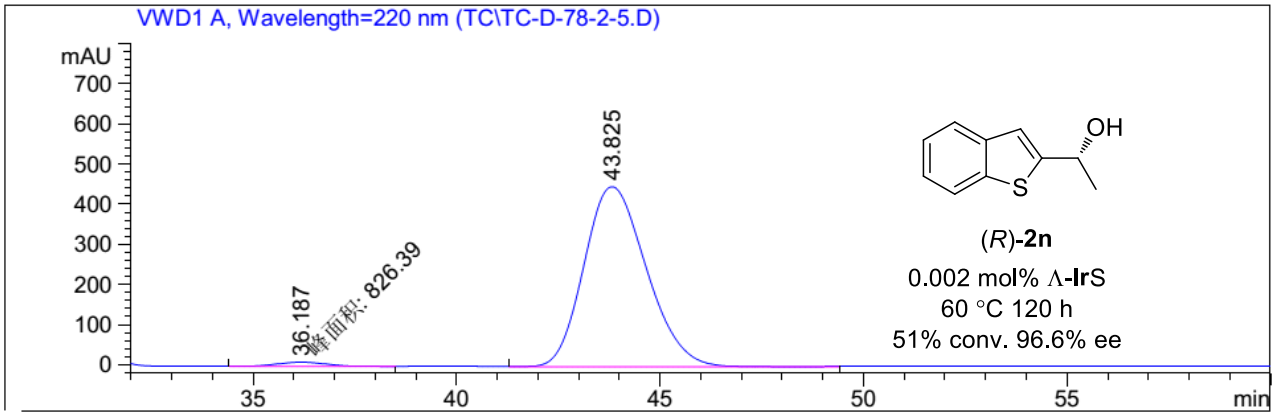
#	[min]		[min]	[mAU*s]	[mAU]	%
1	36.447	MM	1.2472	1234.42114	16.49587	0.8167
2	43.246	BB	1.7322	1.49918e5	1316.87024	99.1833

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 (Table1, entry 4).



#	[min]		[min]	[mAU*s]	[mAU]	%
1	36.246	MM	1.2943	135.92841	1.75029	0.8218
2	44.044	BBA	1.6382	1.64036e4	157.61504	99.1782

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 (Table1, entry 5).

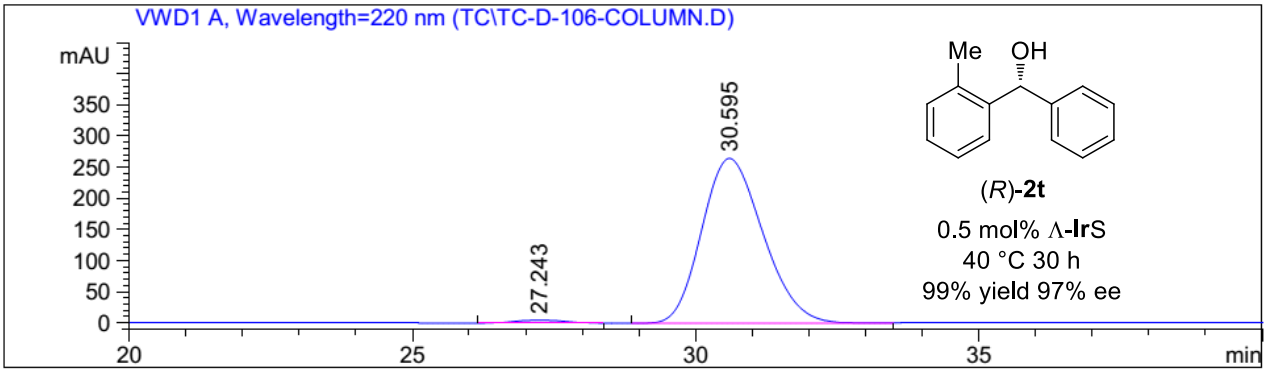


#	[min]		[min]	[mAU*s]	[mAU]	%
1	36.187	MM	1.3765	826.38983	10.00611	1.7023
2	43.825	BB	1.6038	4.77180e4	447.59573	98.2977

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.

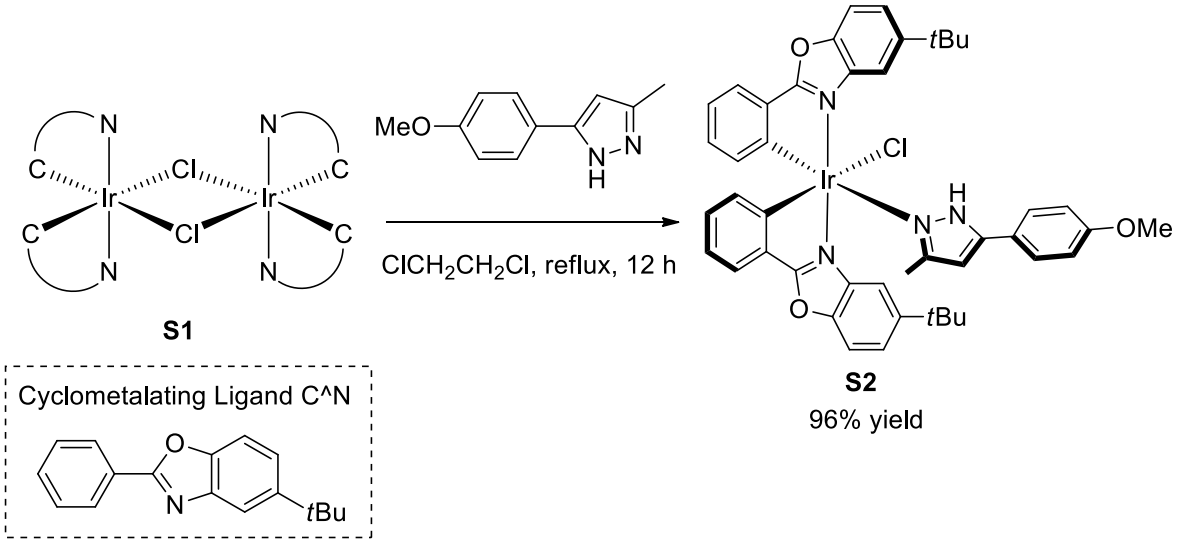


#	[min]		[min]	[mAU*s]	[mAU]	%
1	27.243	MM R	1.0229	315.61676	5.14250	1.5586
2	30.595	BB	1.1574	1.99349e4	265.07941	98.4414

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



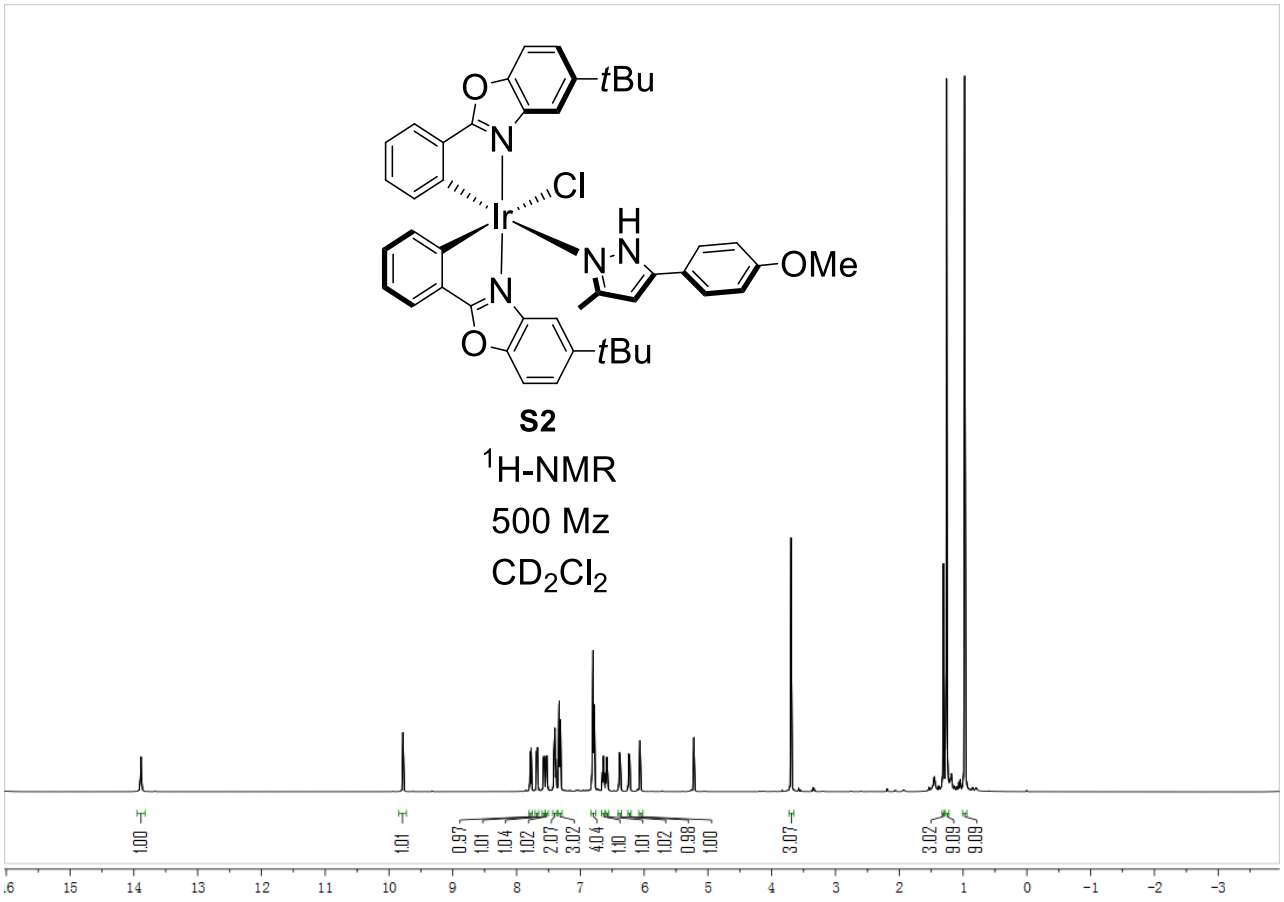
The iridium (III) pyrazole complex **S2** was synthesized following a modified procedure.[13] Accordingly, a mixture of iridium dimer **S1**[3] (200.0 mg, 0.13 mmol) and ligand 5-(4-methoxyphenyl)-3-methyl-1*H*-pyrazole (50.0 mg, 0.26 mmol) in $ClCH_2CH_2Cl$ (10 mL) was heated at reflux (oil bath temperature: 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%)

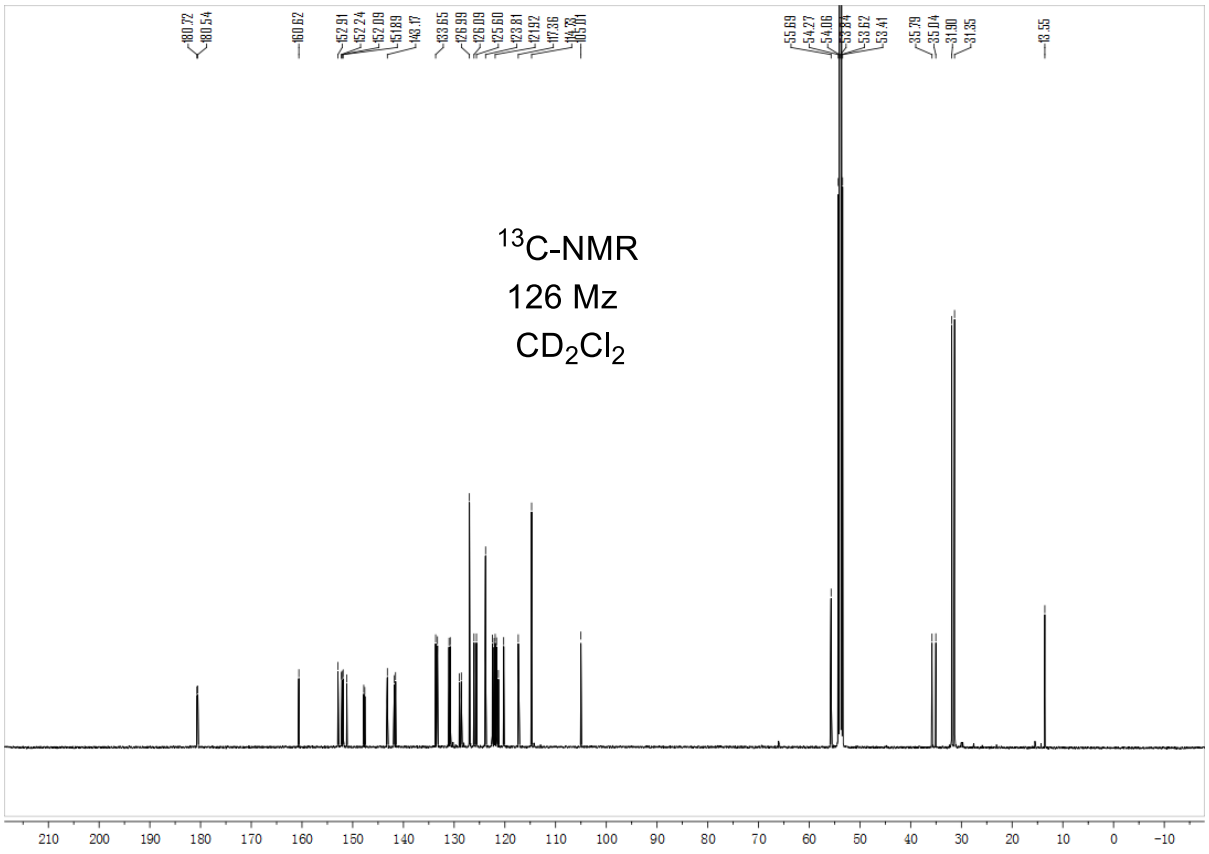
^{1}H-NMR (500 MHz, CD_2Cl_2): δ 13.89 (s, 1H), 9.78 (s, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.6 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.42-7.38 (m, 2H), 7.34-7.31 (m, 3H), 6.81-6.78 (m, 4H), 6.65-6.62 (m, 1H), 6.60-6.57 (m, 1H), 6.38 (d, J = 7.8 Hz, 1H), 6.24 (d, J = 7.5 Hz, 1H), 6.04 (s, 1H), 3.69 (s, 3H), 1.31 (s, 3H), 1.26 (s, 9H), 0.97 (s, 9H).

^{13}C-NMR (126 MHz, CD_2Cl_2): δ 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 $IrC_{45}H_{44}S_2N_4ClONa$ $(M+Na)^+$: 971.2172 , found: 971.2173.




180.72
180.54
160.62
152.91
152.24
152.09
151.89
148.17
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126.99
126.09
125.60
123.81
121.92
117.36
114.78
105.91
55.69
54.27
54.06
53.84
53.62
53.41
35.79
35.04
31.90
31.35
13.55
^{13}C-NMR
126 Mz
CD_2Cl_2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

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.[14] Refinement was done by full-matrix least squares based on F^2 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.

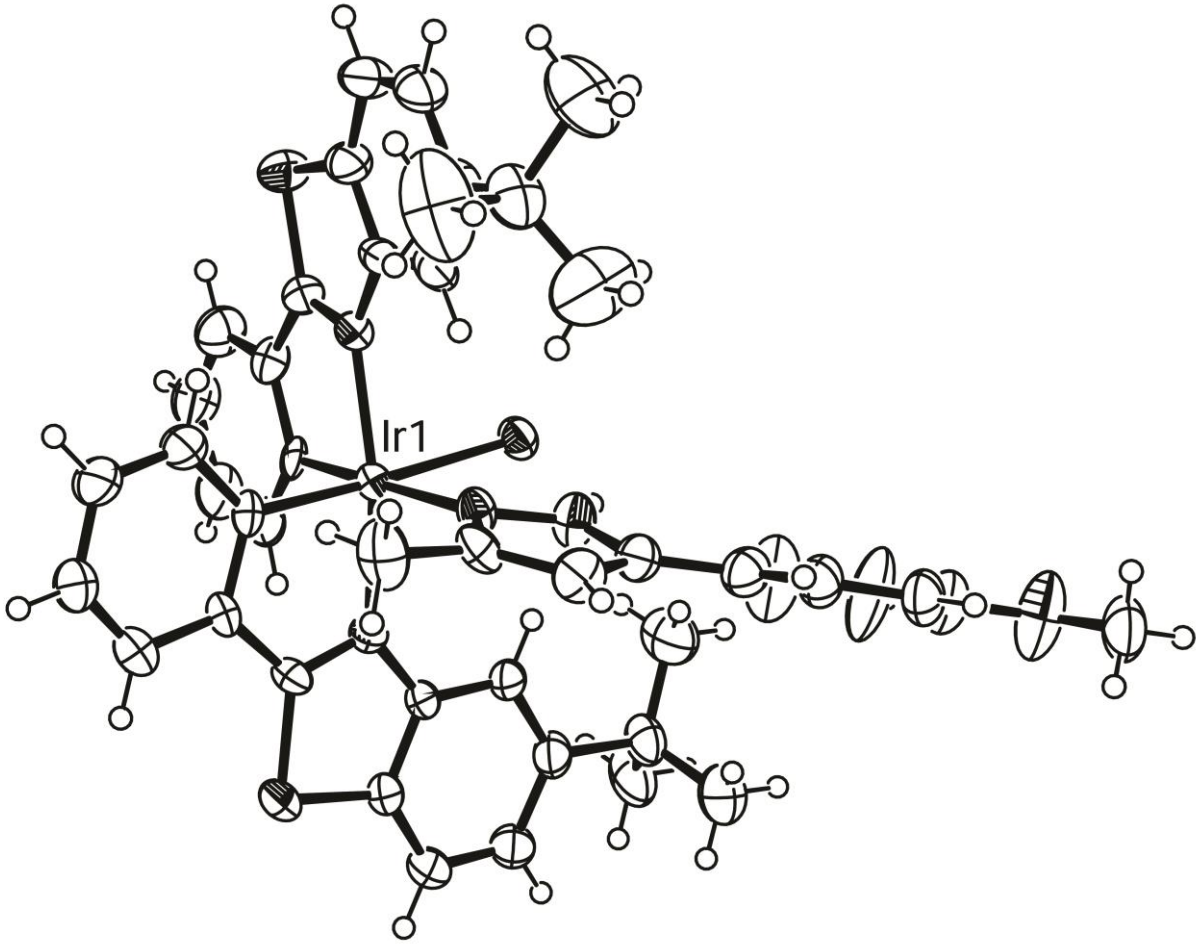

Figure S32. Crystal structure of complex **S2**. ORTEP drawings with 50% thermal ellipsoids. The complex was crystallized as a racemate but only the Λ-enantiomer is shown.

Table S2. Data collection and refinement statistics for the compounds **S2.**

	S2
Empirical formula	$C_{45}H_{44}ClIrN_4OS_2$
Formula weight	948.61
Temperature (K)	173(2) K
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
Cell dimensions	
a, b, c (Å)	18.999, 13.938, 18.330
α, β, γ (°)	90, 100.52, 90
Volume ($Å^3$)	4772.4(17)
Z	4
Density (calculated, mg/m^3)	1.320
Absorption coefficient (mm^{-1})	2.975
F(000)	1904
Crystal size (mm^3)	0.20 x 0.17 x 0.14
Theta range for data collection	2.18 to 26.00°
Index ranges	-23<=h<=23, -17<=k<=17, -22<=l<=22
Reflections collected	28219
Independent reflections	8827 [R(int) = 0.0727]
Completeness	94.0 %
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8827 / 0 / 487
Goodness-of-fit on F^2	0.999
Final R indices [I>2sigma(I)]	R1 = 0.0597, wR2 = 0.1642
R indices (all data)	R1 = 0.0751, wR2 = 0.1909
Largest diff. peak and hole ($e.Å^{-3}$)	1.322 and -2.400

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