New Paracyclophane Phosphine for Highly Enantioselective Ruthenium-Catalyzed Hydrogenation of Prochiral Ketones

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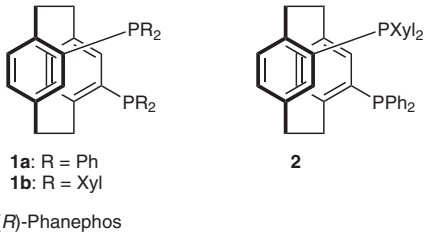
Abstract: The synthesis of a new paracyclophane phosphine is described. This ligand was highly efficient in the ruthenium-catalyzed asymmetric hydrogenation of various aromatic and heteroaromatic ketones.

Key words: paracyclophane, hydrogenation, ruthenium, ketones, P,P-ligands

The design of new chiral ligands for asymmetric catalysis is a highly active field of research.[1] Many chiral diphosphine ligands have been prepared and successfully applied in asymmetric catalysis with excellent enantioselectivities.[2] The [2,2]paracyclophane backbone serves as a powerful tool to develop new and efficient ligands for asymmetric catalysis.[3] The Phanephos (**1**) ligands (Figure 1; Xyl = 3,5-dimethylphenyl), C_2-symmetrical diphosphines with a rigid paracyclophane backbone, belong to the most successful chiral ligands.[4] They have been efficiently used in rhodium-catalyzed hydrogenations of dehydroamino acids[4] and allylic acids,[5] ruthenium-catalyzed hydrogenation of β-keto esters[6] and aromatic ketones,[7] and palladium-catalyzed amination reactions.[8] The chiral C_2-symmetrical phosphinites based on the paracyclophane backbone also proved to be very efficient catalysts for rhodium-catalyzed hydrogenation of *N*-acetyldehydroamino acids and esters.[9] Hems et al. prepared various non-C_2-symmetrical paracyclophane diphosphines by introducing substituents on one of the aromatic rings of Phanephos (**1**). The performance of these ligands was indistinguishable from that of the original Phanephos (**1**) ligands in rhodium-catalyzed hydrogenation of dehydroamino acids and ruthenium-catalyzed hydrogenation of acetophenone.[10] However, apart from this fascinating work, non-C_2-symmetrical paracyclophane diphosphines bearing two different kinds of aryl phosphines have not been synthesized until now. Herein, we wish to report the synthesis of new ligand **2** (Figure 1) and its applications in ruthenium-catalyzed asymmetric hydrogenation of ketones with high activity and excellent enantioselectivities.



1a: R = Ph
1b: R = Xyl

(*R*)-Phanephos

2

Figure 1 Phanephos **1** and new non-C_2-symmetrical paracyclophane phosphine **2**

The monometalation of dibromide **3**[11] by *n*-butyllithium, followed by the addition of chlorodiphenylphosphine led to an air-sensitive diphenylphosphine derivative, which was protected in situ with sulfur to give the air-stable phosphine sulfide **4** in 85% yield (Scheme 1). Butyllithium effected bromine–lithium exchange on **4**, and subsequent quenching with chlorobis(3,5-dimethylphenyl)phosphine followed by in situ protection with sulfur provided bis(phosphine sulfide) **5** in 87% yield (Scheme 1). The deprotection of **5** was accomplished smoothly when Raney nickel[12] in methanol was used, and this gave diphosphine **2** in 92% yield (Scheme 1).

Owing to the inherent atom-economical nature of hydrogenation reactions, hydrogenation of prochiral ketones is a most facile route for generating enantiomerically pure alcohols. A significant breakthrough in ketone hydrogenation was achieved by Noyori and co-workers using diphosphine–ruthenium(II)–diamine complexes.[13] Significantly, this method allowed the development of very efficient catalysts for highly enantioselective hydrogenation of a wide range of prochiral ketones.[14] We found that the ruthenium complex of ligand **2** serves as an excellent catalyst for the asymmetric hydrogenation of various aromatic ketones. Ruthenium catalysts **6a** and **6b** were prepared by reaction of ligand **2** with $[RuCl_2(benzene)]_2$ in *N*,*N*-dimethylformamide–toluene at 115 °C for 4 h, followed by the addition of one equivalent of 1,2-diphenylethylenediamine (DPEN) and reaction at 115 °C for 2 h (Scheme 2).[15]

Next, we examined ketone hydrogenation using ruthenium complexes **6a** and **6b** and acetophenone (**7a**) as the model substrate under standard reaction conditions (*i*-PrOH, 10 bar H_2, *t*-BuOK/Ru 25:1, 1.0–2.0 M solutions) (Table 1). Preliminary results indicated that the efficiency of ruthenium complex **6b** was high compared to that of **6a**

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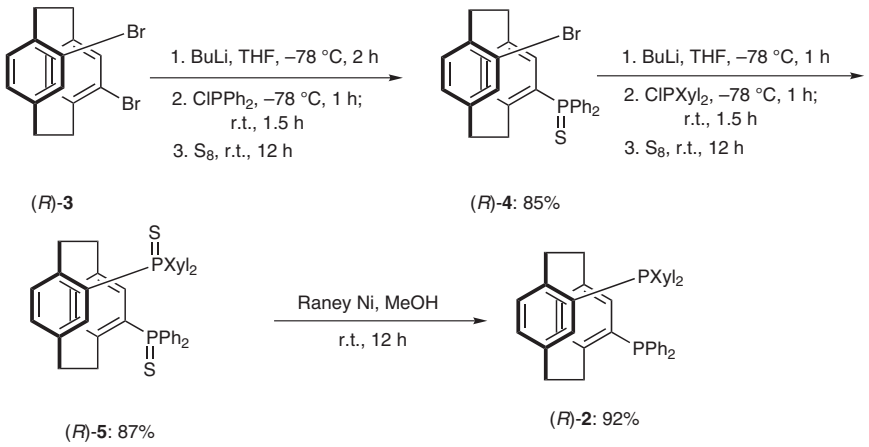
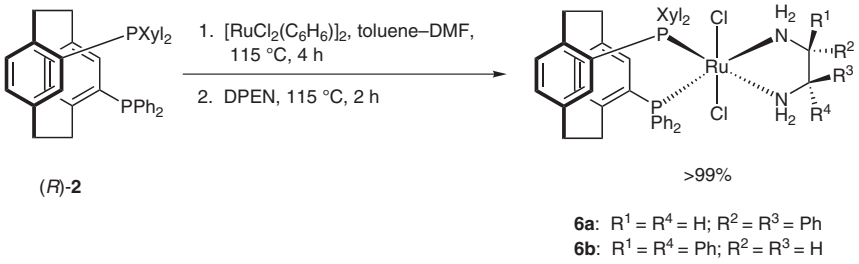


Scheme 1 Synthesis of the new paracyclophane phosphine **2**



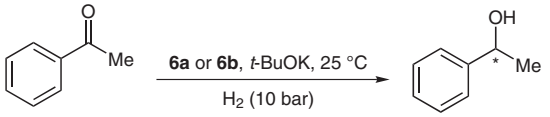
Scheme 2 Preparation of ruthenium complexes **6a** and **6b**

(Table 1, entries 1 and 2). This indicates that the stereochemistry of the diamine plays a major role in achieving high reaction rates and enantioselectivities in ketone hydrogenation.[5] Furthermore, when the substrate/catalyst (S/C) ratio was increased to 10000:1 in the reduction of acetophenone with catalyst **6b**, the desired alcohol **8a** was obtained in quantitative yield, but the enantioselectivity reduced from 97 to 95% ee (Table 1, entries 5 and 6).

In addition, we investigated the scope of the ketone substrates for the asymmetric hydrogenation using **6b** (Table 2). Various types of substituted acetophenone derivatives **7a–l** were reduced in high conversions, thus providing the corresponding chiral alcohols **8a–l** in high enantioselectivities (Table 2).

To explore the substrate scope further, we investigated the asymmetric hydrogenation of ketones **9a–e**, **11a**,**b**, **13**, **15**, and **17** bearing various types of side chains R and Ar at the α-position (Table 3). Elongation of the ketone side chain R from methyl to ethyl, *n*-butyl, *n*-pentyl, or phenethyl did not affect the reactivity or enantioselectivity (Table 3, entries 1–4). Introducing branching at the α-position of the ketone leads to long reaction times and poor selectivities (Table 3, entry 5). We also examined the chemoselective hydrogenation of α,β-unsaturated ketones **11a** and **11b** (Table 3, entries 6 and 7). Ketone **11a** was smoothly reduced to afford the allylic alcohol **12a** in 94% ee, whereas ketone **11b** furnished alcohol **12b** in 37% ee. We also extended this hydrogenation of ketones to heteroaromatic ketones **13**, **15**, and **17**, providing the corresponding alcohols **14**, **16**, and **18** in 96%, 93%, and 92% ee, respectively (Table 3, entries 8–10).

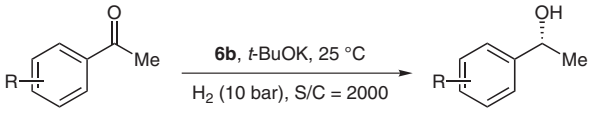
Table 1 Hydrogenation of Acetophenone (**7a**) Catalyzed by Ruthenium Complexes **6a** and **6b**[a]



Entry	Catalyst	S/C[b]	Time (h)	ee[c] (%)
1[d]	**6a**	500	12	25 (*S*)
2	**6b**	500	1	97 (*S*)
3	**6b**	1000	1	97 (*S*)
4	**6b**	2000	1	97 (*S*)
5	**6b**	5000	1.5	97 (*S*)
6[e]	**6b**	10000	2.5	95 (*S*)

[a] Reagents and conditions: 1 M **7a**, cat. **6a** or **6b**, *t*-BuOK (*t*-BuOK/cat. = 25:1), *i*-PrOH, H_2 (10 bar).
[b] S/C = ratio of substrate to catalyst.
[c] The ee was determined by chiral GC or chiral HPLC.
[d] Only 55% conversion was achieved.
[e] *t*-BuOK/cat. = 100:1.

Table 2 Asymmetric Hydrogenation of Substituted Acetophenones **7** Catalyzed by Ruthenium Complex **6b**[a]



7a–l **8a–l**

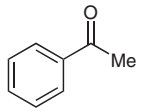
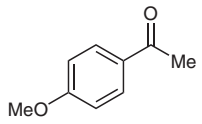
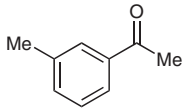
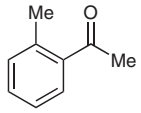
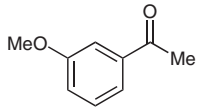
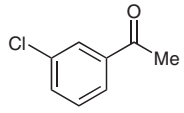
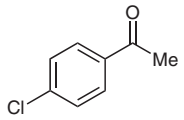
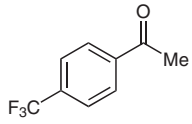
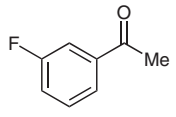
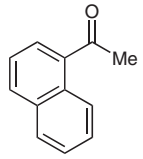
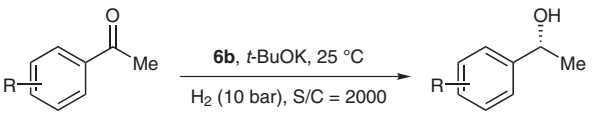
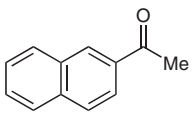
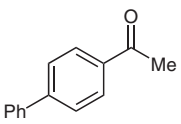
Entry	Substrate	Time (h)	Product[b]	ee[c] (%)
1	 **7a**	1	**8a**	97
2	 **7b**	1.5	**8b**	96
3	 **7c**	1	**8c**	97
4	 **7d**	2	**8d**	94
5	 **7e**	1.5	**8e**	97
6	 **7f**	1.5	**8f**	97
7	 **7g**	1	**8g**	96
8	 **7h**	1	**8h**	94
9	 **7i**	1	**8i**	96
10	 **7j**	2	**8j**	96

Table 2 Asymmetric Hydrogenation of Substituted Acetophenones **7** Catalyzed by Ruthenium Complex **6b**[a] (continued)

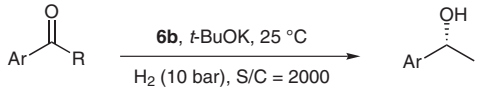


7a–l **8a–l**

Entry	Substrate	Time (h)	Product[b]	ee[c] (%)
11	 **7k**	2	**8k**	97
12	 **7l**	2	**8l**	94

[a] Reagents and conditions: 1 M **7**, **6b** (**7**/**6b** = 2000:1), *t*-BuOK (*t*-BuOK/**6b** = 25:1), *i*-PrOH, H_2 (10 bar).
[b] Full conversion was achieved in each case.
[c] The ee was determined by chiral GC or chiral HPLC.

Table 3 Asymmetric Hydrogenation of Aryl and Hetaryl Ketones Catalyzed by Ruthenium Complex **6b**[a]



9a–e, **11a–b**
13, **15** and **17**

10a–e, **12a–b**
14, **16** and **18**

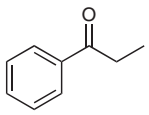
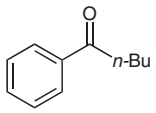
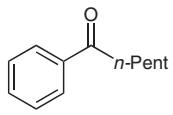
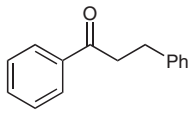
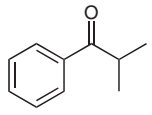
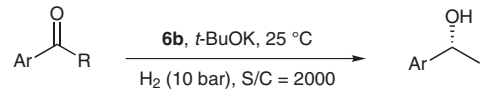
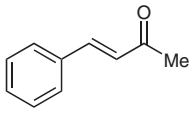
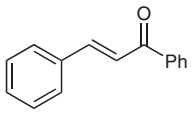
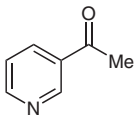
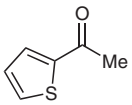
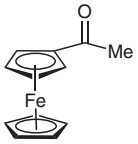
Entry	Substrate	Time (h)	Product[b]	ee[c] (%)
1	 **9a**	1.5	**10a**	97
2	 **9b**	1.5	**10b**	97
3	 **9c**	1.5	**10c**	94
4	 **9d**	2	**10d**	90
5	 **9e**	5	**10e**	38

Table 3 Asymmetric Hydrogenation of Aryl and Hetaryl Ketones Catalyzed by Ruthenium Complex **6b**[a] (continued)



9a–e, **11a–b**
13, **15** and **17**

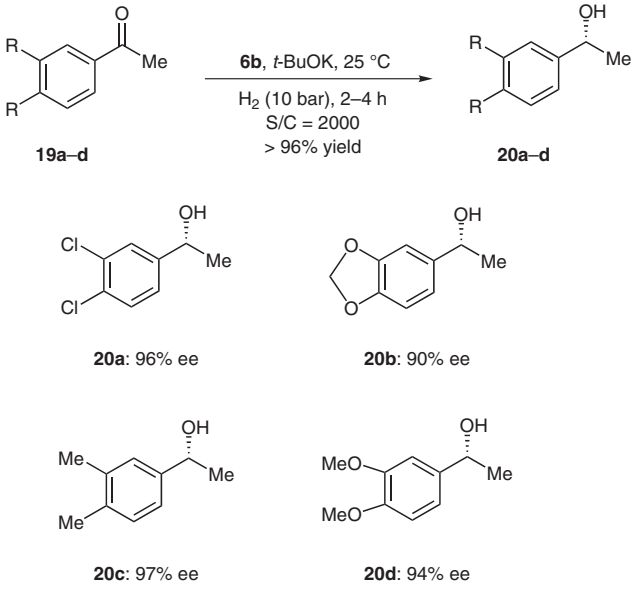
10a–e, **12a–b**
14, **16** and **18**

Entry	Substrate	Time (h)	Product[b]	ee[c] (%)
6	 **11a**	1	**12a**	94
7	 **11b**	2	**12b**	37
8	 **13**	3	**14**	96
9	 **15**	2.5	**16**	93
10	 **17**	4	**18**	92

[a] Reagents and conditions: 1 M ketone, **6b** (ketone/**6b** = 2000:1), *t*-BuOK (*t*-BuOK/**6b** = 25:1), *i*-PrOH, H_2 (10 bar).
[b] Full conversion was achieved in each case.
[c] The ee was determined by chiral GC or chiral HPLC.

To broaden the application of this ruthenium-catalyzed hydrogenation, we attempted the hydrogenation of disubstituted acetophenones **19a–c** using catalyst **6b**, and obtained alcohols **20a–c** in 90–97% ee (Scheme 3). The reduction of ketone **19d** bearing two methoxy groups in *meta* and *para* positions of the aromatic ring was accomplished smoothly, leading to the corresponding alcohol **20d**, a precursor of (–)-salsolidine, in 94% ee (Scheme 3).[16]

In summary, we have described the synthesis of a new non-C_2-symmetrical paracyclophane diphosphine **2**. Its ruthenium(II) complex **6b** prepared from the (*S*,*S*)-diamine is highly effective for the asymmetric hydrogenation of various aromatic ketones, quite comparable to the C_2-symmetrical dixylylphosphine **1b**.[7] The study of new analogues of **2** and their applications is currently underway in our laboratory.



Scheme 3 Asymmetric hydrogenation of disubstituted acetophenones **20** in the presence of catalyst **6b**

All reactions were carried out under an argon atmosphere in dried glassware. Melting points were uncorrected and measured on a Dr. Tottoli (Büchi B-540) apparatus. NMR spectra were recorded on Bruker ARX 200, AC 300, WH 400, and 600 instruments. IR spectra were recorded on a Nicolet 510 or a Perkin-Elmer 281 spectrometer. Mass spectra were recorded on a Varian CH 7A, and high-resolution mass spectra on a Varian MAT 711 spectrometer. Optical rotation values were measured on a Perkin-Elmer 241 polarimeter. All ketone substrates for the catalytic hydrogenation were commercially available and used without further purification.

(*R*)-4-Bromo-12-diphenylphosphinothioyl[2.2]paracyclophane (4)

Dibromide **3** (1.83 g, 5.0 mmol) and THF (15 mL) were added to a 50-mL Schlenk flask under an argon atmosphere. A soln of 1.5 M *n*-BuLi in pentane (3.7 mL, 5.5 mmol) was added slowly to the above soln at –78 °C, and the mixture was stirred for 1 h. $ClPPh_2$ (1.33 g, 6.0 mmol, 1.2 equiv) was added, and the mixture was stirred for 1 h at –78 °C, then warmed to r.t. and stirred for 1.5 h. Sulfur (1.60 g, 50.0 mmol, 10 equiv) was added, and the mixture was stirred overnight at r.t. The mixture was quenched with sat. aq NH_4Cl (20 mL) and the aqueous layer was extracted with CH_2Cl_2 (4 × 30 mL). The combined organic layers were washed with H_2O (50 mL) and brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, *n*-pentane–Et_2O, 10:1).

White solid; yield: 2.14 g (85%); mp 148.1–148.9 °C; $[\alpha]_D^{20}$ –22.9 (*c* 0.4, CH_2Cl_2).

IR (neat): 3440 (br, w), 2912 (w), 1629 (s), 1425 (m), 1325 (m), 1102 (m), 789 (s), 656 (s) cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.83–7.71 (m, 5 H), 7.48–7.35 (m, 6 H), 6.65–6.53 (m, 5 H), 3.60–3.49 (m, 2 H), 3.39–3.35 (m, 1 H), 3.01–2.97 (m, 1 H), 2.90–2.71 (m, 4 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 145.0 (d, *J* = 8.6 Hz), 141.6, 138.6 (d, *J* = 13.0 Hz), 138.5, 136.9 (d, *J* = 3.1 Hz), 136.3, 135.5 (d, *J* = 11.8 Hz), 134.6 (d, *J* = 86.2 Hz), 133.4, 132.9 (d, *J* = 10.6 Hz), 132.8 (d, *J* = 11.8 Hz), 132.2 (d, *J* = 84.6 Hz), 131.9 (d, *J* = 10.2 Hz), 131.3 (d, *J* = 3.1 Hz), 131.2 (d, *J* = 3.0 Hz), 131.1, 128.1 (d,

J = 12.4 Hz), 128.0, (d, J = 12.4 Hz), 127.8 (d, J = 87.2 Hz), 127.2, 35.4, 34.7 (d, J = 4.9 Hz), 33.7 (d, J = 1.1 Hz), 31.92.

^{31}P NMR (81 MHz, $CDCl_3$): δ = 40.44.

MS (EI, 70 eV): m/z (%) = 504 (37), 502 [M^+] (34), 321 (18), 320 (100), 319 (16), 209 (10), 183 (11).

HRMS (EI): m/z calcd for $C_{28}H_{24}{}^{79}BrP^{32}S$: 502.0520; found: 502.0512.

(*R*)-4-Bis(3,5-ditolyl)phosphinothioyl[2.2]paracyclophane (5)

Phosphine sulfide **4** (755 mg, 1.5 mmol) and THF (5 mL) were added to a 25-mL Schlenk flask under an argon atmosphere. A soln of 1.5 M *n*-BuLi in pentane (1.2 mL, 1.7 mmol) was added slowly to the above soln at –78 °C, and the mixture was stirred for 2 h. (3,5-$Me_2C_6H_3)_2PCl$ (500 mg, 1.8 mmol, 1.2 equiv) was added, and the mixture was stirred for 1 h at –78 °C, then warmed to r.t. and stirred for 1.5 h. Sulfur (482 mg, 15.0 mmol, 10 equiv) was added, and the mixture was stirred overnight at r.t. The mixture was quenched with sat. aq NH_4Cl (10 mL), and the aqueous layer was extracted with CH_2Cl_2 (4 × 15 mL). The combined organic layers were washed with H_2O (50 mL) and brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, *n*-pentane–Et_2O, 5:1).

White solid; yield: 910 mg (87%); mp 291 °C; $[\alpha]_D{}^{20}$ –20.9 (*c* 0.4, CH_2Cl_2).

IR (neat): 3441 (br, w), 2785 (w), 1594 (m), 1447 (m), 1389 (m), 1101 (m), 874 (s), 725 (s), 696 (s) cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.96–7.93 (m, 2 H), 7.73–7.69 (m, 2 H), 7.51–7.47 (m, 5 H), 7.33–7.31 (m, 4 H), 7.26–7.23 (m, 2 H), 7.10–7.08 (m, 2 H), 7.02 (br s, 1 H), 6.72–6.69 (m, 2 H), 6.66–6.63 (m, 2 H), 3.42–3.47 (m, 2 H), 3.33–3.26 (m, 2 H), 2.86–2.80 (m, 2 H), 2.71–2.66 (m, 2 H), 2.31 (s, 6 H), 2.23 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.93 (d, J = 9.6 Hz), 144.9 (d, J = 9.6 Hz), 139.6 (d, J = 13.3 Hz), 139.4 (d, J = 13.2 Hz), 137.5 (d, J = 12.9 Hz), 137.3 (d, J = 13.2 Hz), 136.6 (d, J = 3.6 Hz), 136.5 (d, J = 3.7 Hz), 136.1 (d, J = 11.7 Hz), 135.9 (d, J = 12.3 Hz), 135.7 (d, J = 83.3 Hz), 135.0 (d, J = 83.8 Hz), 134.7 (d, J = 11.8 Hz), 134.4 (d, J = 12.0 Hz), 133.2 (d, J = 10.5 Hz), 133.0 (d, J = 3.1 Hz), 132.7 (d, J = 3.5 Hz), 131.6 (d, J = 10.3 Hz), 131.5 (d, J = 84.8 Hz), 131.2 (d, J = 84.8 Hz), 131.1 (d, J = 3.1 Hz), 130.9 (d, J = 10.1 Hz), 130.9 (d, J = 2.8 Hz), 129.3 (d, J = 10.1 Hz), 127.9 (d, J = 12.5 Hz), 127.8 (d, J = 87.7 Hz), 127.8 (d, J = 12.5 Hz), 127.7 (d, J = 88.7 Hz), 35.4 (t, J = 5.2 Hz), 33.8 (d, J = 16.0 Hz), 21.8 (d, J = 0.9 Hz), 21.5 (d, J = 0.9 Hz).

^{31}P NMR (81 MHz, $CDCl_3$): δ = 38.71, 38.39.

MS (EI, 70 eV): m/z (%) = 696 [M^+] (45), 521 (28), 320 (100), 309 (12), 183 (21).

HRMS (EI): m/z calcd for $C_{44}H_{42}P_2{}^{32}S_2$: 696.2203; found: 696.2211.

(*R*)-4-Bis(3,5-ditolyl)phosphino-12-diphenylphosphino[2.2]-paracyclophane (2)

A 100-mL Schlenk flask was charged with a slurry of Raney-Ni in H_2O (1.8 g) under an argon atmosphere. The Raney-Ni was washed with MeOH (4 × 15 mL). A soln of phosphine sulfide **4** (698 mg, 1.0 mmol) in THF (5 mL) was then transferred to this flask, MeOH (30 mL) was added, and the mixture was stirred at r.t. under an argon atmosphere for 12 h (conversion was monitored by ^{31}P NMR). The mixture was filtered under argon, and the Raney Ni residue was washed with THF (4 × 15 mL). Concentration of the combined filtrate under reduced pressure afforded **2**.

White solid; yield: 583 mg (92%); mp 211.0–212.2 °C; $[\alpha]_D{}^{20}$ –22.4 (*c* 0.4, CH_2Cl_2).

IR (neat): 3444 (br, w), 2019 (w), 1655 (s), 1450 (s), 1210 (s), 876 (s), 765 (m), 667 (m), 586 (m) cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.47–7.44 (m, 2 H), 7.41–7.36 (m, 5 H), 7.24–7.20 (m, 5 H), 7.04–7.02 (m, 3 H), 6.65–6.63 (m, 1 H), 6.57–6.48 (m, 6 H), 3.02–2.89 (m, 6 H), 2.63–2.54 (m, 2 H), 2.35 (s, 6 H), 2.18 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.3 (d, J = 14.7 Hz), 143.1 (d, J = 15.1 Hz), 139.5 (d, J = 12.1 Hz), 139.4 (d, J = 13.9 Hz), 139.3 (d, J = 6.1 Hz), 138.9 (d, J = 7.1 Hz), 138.2 (d, J = 12.2 Hz), 138.1 (d, J = 12.6 Hz), 137.5 (d, J = 17.5 Hz), 137.4 (d, J = 16.9 Hz), 137.3 (d, J = 7.9 Hz), 137.2 (d, J = 8.7 Hz), 135.9 (d, J = 0.9 Hz), 135.7 (d, J = 0.9 Hz), 134.2 (d, J = 6.8 Hz), 134.1 (d, J = 6.1 Hz), 133.4 (d, J = 22.8 Hz), 133.3 (d, J = 22.8 Hz), 133.0 (d, J = 20.4 Hz), 132.7 (d, J = 8.7 Hz), 132.3 (d, J = 6.8 Hz), 131.3 (d, J = 1.1 Hz), 130.6 (d, J = 20.9 Hz), 130.3 (d, J = 0.9 Hz), 129.3 (d, J = 0.8 Hz), 128.5 (d, J = 0.8 Hz), 128.3 (d, J = 22.7 Hz), 128.2 (d, J = 22.0 Hz), 35.8 (d, J = 18.7 Hz), 35.7 (d, J = 19.0 Hz), 33.2 (d, J = 2.6 Hz), 33.0 (d, J = 2.5 Hz), 21.4, 21.2.

^{31}P NMR (81 MHz, $CDCl_3$): δ = 0.69, 0.03.

MS (EI, 70 eV): m/z (%) = 632 [M^+] (14), 428 (32), 320 (100), 309 (11).

HRMS (EI): m/z calcd for $C_{44}H_{42}P_2$: 632.2762; found: 632.2777.

Ruthenium–Diamine Complexes 6a and 6b

A 25-mL Schlenk flask under an argon atmosphere was charged with bisphosphine **2** (50 mg, 0.07 mmol, 1.0 equiv) and $[RuCl_2(benzene)]_2$ (16 mg, 0.035 mmol) in anhyd toluene (2.0 mL) and DMF (1.5 mL). The mixture was heated to 115 °C for 4 h, and then 1,2-diphenylethylenediamine (DPEN; 15 mg, 0.07 mmol, 1.0 equiv) was added. After stirring for 2 h at 115 °C, the mixture was allowed to reach r.t. while stirring overnight. The solvent was evaporated under high vacuum and Et_2O (2 mL) and CH_2Cl_2 (2 mL) were added to the crude mixture. After evaporation of the solvent, the desired complexes were obtained as purple compounds in quantitative yields. The residue was used for hydrogenations without any further purification.

Ruthenium–Diamine Complex 6a [{(*R*)-2}$RuCl_2${(*R*,*R*)-DPEN}]

Complex **6a** was prepared with (*R*,*R*)-DPEN.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.46–8.20 (m, 3 H), 8.01–7.45 (m, 3 H), 7.40–7.25 (m, 4 H), 7.20–7.11 (m, 7 H), 7.00–6.85 (m, 7 H), 6.70–6.68 (m, 1 H), 6.60–6.58 (m, 1 H), 6.50–6.39 (m, 6 H), 4.50–4.48 (m, 1 H), 4.11–4.10 (m, 1 H), 2.76–2.69 (m, 2 H), 2.62–2.50 (m, 2 H), 2.29 (s, 6 H), 2.12 (s, 6 H), 1.94–1.87 (m, 2 H), 1.71–1.66 (m, 2 H).

^{31}P NMR (81 MHz, $CDCl_3$): δ = 48.16 (d, J = 28.9 Hz), 44.79 (d, J = 27.0 Hz).

Ruthenium–Diamine Complex 6b [{(*R*)-2}$RuCl_2${(*S*,*S*)-DPEN}]

Complex **6b** was prepared with (*S*,*S*)-DPEN.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.36–8.34 (m, 2 H), 8.30–8.26 (m, 1 H), 8.10–8.05 (m, 1 H), 8.00–7.92 (m, 1 H), 7.40–7.25 (m, 4 H), 7.20–7.10 (m, 8 H), 7.05–6.90 (m, 7 H), 6.76 (s, 1 H), 6.60–6.54 (m, 2 H), 6.47–6.36 (m, 5 H), 4.50–4.48 (m, 1 H), 4.19–4.12 (m, 1 H), 2.86–2.70 (m, 2 H), 2.60–2.55 (m, 2 H), 2.23 (s, 6 H), 2.02 (s, 6 H), 1.95–1.86 (m, 2 H), 1.71–1.66 (m, 2 H).

^{31}P NMR (81 MHz, $CDCl_3$): δ = 47.46 (d, J = 28.1 Hz), 44.19 (d, J = 27.1 Hz).

Hydrogenation of Ketones Catalyzed by Ruthenium Complex 6b; General Procedure

A 10-mL Schlenk flask under an argon atmosphere was charged with catalyst **6b** (2.1 mg, 0.002 mmol) and the appropriate ketone (4 mmol, ketone/catalyst = 2000) in *i*-PrOH (4 mL). A 1.0 M soln

of *t*-BuOK in *i*-PrOH (0.05 mL, 0.05 mmol) was added. The mixture was stirred at r.t. for 15 min, and then transferred under an argon atmosphere to an autoclave equipped with a glass tube and a stirring bar. The autoclave was then purged with H_2 (3 × 5 bar) and finally pressurized to 10 bar. The mixture was stirred for the appropriate time (see Tables 2 and 3) until full conversion was achieved. The H_2 gas was released, the solvent was evaporated, and the residue was filtered through a short pad of silica gel and washed with Et_2O. Conversion was checked by ^1H NMR spectroscopy or GC and enantioselectivity was determined by chiral GC or chiral HPLC.

(*R*)-1-Phenylethanol (8a)
Alcohol **8a** was prepared from **7a** (480 mg, 0.49 mL, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 469 mg (96%); $[\alpha]_D^{20}$ +40.4 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 110 °C, 60 min, constant): 8.5 min (*R*), 8.9 (*S*); 97% ee.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.20–7.29 (m, 5 H), 4.66 (q, *J* = 6.5 Hz, 1 H), 2.80 (br s, 1 H), 1.30 (d, *J* = 6.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.4, 128.8, 127.7, 125.9, 70.6, 25.6.

(*R*)-1-(4-Methoxyphenyl)ethanol (8b)
Alcohol **8b** was prepared from **7b** (600 mg, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 584 mg (96%); $[\alpha]_D^{20}$ +43.6 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 110 °C, 60 min, constant): 26.0 min (*R*), 30.0 (*S*); 96% ee.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.26 (m, 2 H), 6.89–6.86 (m, 2 H), 4.84 (q, *J* = 6.4 Hz, 1 H), 3.79 (s, 3 H), 1.47 (d, *J* = 6.4 Hz, 3 H), 1.83 (br s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.0, 138.0, 126.6, 113.8, 69.9, 55.3, 25.0.

(*R*)-1-(3-Tolyl)ethanol (8c)
Alcohol **8c** was prepared from **7c** (537 mg, 0.54 mL, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 523 mg (96%); $[\alpha]_D^{20}$ +64.2 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 110 °C, 60 min, constant): 9.5 min (*R*), 9.7 (*S*); 97% ee.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.27–7.22 (m, 1 H), 7.19–7.15 (m, 2 H), 7.08 (d, *J* = 7.5 Hz, 1 H), 4.85 (q, *J* = 6.5 Hz, 1 H), 2.36 (s, 3 H), 1.88 (s, 1 H), 1.48 (d, *J* = 6.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.8, 138.1, 128.4, 128.2, 126.1, 122.4, 70.4, 25.1, 21.4.

(*R*)-1-(2-Tolyl)ethanol (8d)
Alcohol **8d** was prepared from **7d** (537 mg, 0.52 mL, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 534 mg (98%); $[\alpha]_D^{20}$ +48.2 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 100 °C, 15 min, 5 °C/min, 160 °C, 30 min): 20.1 min (*R*), 22.1 (*S*); 94% ee.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.49 (m, 1 H), 7.26–7.21 (m, 1 H), 7.19–7.13 (m, 2 H), 5.12 (q, *J* = 6.4 Hz, 1 H), 2.34 (s, 3 H), 1.82 (s, 1 H), 1.46 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.8, 134.2, 130.3, 127.1, 126.3, 124.4, 66.8, 23.9, 18.9.

(*R*)-1-(3-Methoxyphenyl)ethanol (8e)
Alcohol **8e** was prepared from **7e** (601 mg, 0.55 mL, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 584 mg (96%); $[\alpha]_D^{20}$ +54.8 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 100 °C, 60 min, constant): 29.8 min (*R*), 34.7 (*S*); 97% ee.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.2 Hz, 1 H), 6.97–6.95 (m, 2 H), 6.83 (ddd, *J* = 1.0, 2.6, 8.2 Hz, 1 H), 4.88 (q, *J* = 6.5 Hz, 1 H), 3.83 (s, 3 H), 2.00 (br s, 1 H), 1.50 (d, *J* = 6.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.7, 147.6, 129.5, 117.6, 112.8, 110.1, 70.3, 55.2, 25.1.

(*R*)-1-(3-Chlorophenyl)ethanol (8f)
Alcohol **8f** was prepared from **7f** (618 mg, 0.52 mL, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 601 mg (96%); $[\alpha]_D^{20}$ +42.4 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 110 °C, 10 min, 50 °C/min, 160 °C, 30 min): 12.9 min (*R*), 13.2 (*S*); 97% ee.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.36 (m, 1 H), 7.26–7.21 (m, 3 H), 4.89–4.82 (m, 1 H), 1.98 (d, *J* = 3.5 Hz, 1 H), 1.47 (d, *J* = 6.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.8, 134.3, 129.7, 127.5, 125.6, 123.5, 69.8, 25.2.

(*R*)-1-(4-Chlorophenyl)ethanol (8g)
Alcohol **8g** was prepared from **7g** (618 mg, 0.52 mL, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 614 mg (98%); $[\alpha]_D^{20}$ +26.8 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 130 °C, 60 min, constant): 9.2 min (*R*), 10.7 (*S*); 96% ee.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.28 (m, 2 H), 6.90–6.87 (m, 2 H), 4.82 (q, *J* = 6.7 Hz, 1 H), 1.24 (br s, 1 H), 1.30 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.2, 136.5, 124.8, 112.1, 68.2, 24.5.

(*R*)-1-[4-(Trifluoromethyl)phenyl]ethanol (8h)
Alcohol **8h** was prepared from **7h** (753 mg, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 715 mg (94%); $[\alpha]_D^{20}$ +34.9 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 110 °C, 60 min, constant): 9.3 min (*R*), 9.7 (*S*); 94% ee.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.59 (m, 2 H), 7.49–7.46 (m, 2 H), 4.98–4.91 (m, 1 H), 1.98 (d, *J* = 3.3 Hz, 1 H), 1.49 (d, *J* = 6.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.7 (q, *J* = 1.4 Hz), 129.6 (q, *J* = 32.3 Hz), 125.6, 125.4 (q, *J* = 3.9 Hz), 124.1 (q, *J* = 271.6 Hz), 69.8, 25.4.

(*R*)-1-(3-Fluorophenyl)ethanol (8i)
Alcohol **8i** was prepared from **7i** (552 mg, 0.49 mL, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 532 mg (95%); $[\alpha]_D^{20}$ +42.4 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 110 °C, 10 min, 50 °C/min, 160 °C, 20 min): 8.5 min (*R*), 10.1 (*S*); 96% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23–7.19 (m, 1 H), 7.05–7.00 (m, 2 H), 6.90–6.85 (m, 1 H), 4.81 (q, *J* = 6.5 Hz, 1 H), 1.96 (br s, 1 H), 1.40 (d, *J* = 6.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.0 (d, *J* = 246.1 Hz), 148.5 (d, *J* = 6.4 Hz), 129.9 (d, *J* = 7.7 Hz), 120.9 (d, *J* = 2.6 Hz), 114.2 (d, *J* = 21.2 Hz), 112.3 (d, *J* = 21.2 Hz), 69.7 (d, *J* = 2.1 Hz), 25.2.

(*R*)-1-(1-Naphthyl)ethanol (8j)

Alcohol **8j** was prepared from **7j** (681 mg, 0.61 mL, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 661 mg (96%); $[\alpha]_D^{20}$ +68.8 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 115 °C, 15 min, 15 °C/min, 160 °C, 60 min): 26.8 min (*S*), 27.4 (*R*); 96% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.13–8.12 (m, 1 H), 7.89–7.86 (m, 1 H), 7.77 (d, *J* = 8.2 Hz, 1 H), 7.67 (d, *J* = 7.2 Hz, 1 H), 7.55–7.45 (m, 3 H), 5.70–5.62 (m, 1 H), 2.02 (d, *J* = 2.8 Hz, 1 H), 1.67 (d, *J* = 6.57 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.3, 133.8, 130.2, 128.9, 127.9, 126.0, 125.6, 125.5, 123.1, 122.0, 67.1, 24.3.

(*R*)-1-(2-Naphthyl)ethanol (8k)

Alcohol **8k** was prepared from **7k** (681 mg, 0.52 mL, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 675 mg (98%); $[\alpha]_D^{20}$ +60.4 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 115 °C, 15 min, 15 °C/min, 160 °C, 60 min): 25.5 min (*R*), 26.3 (*S*); 97% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84–7.80 (m, 4 H), 7.51–7.44 (m, 3 H), 5.05 (q, *J* = 6.5 Hz, 1 H), 1.98 (br s, 1 H), 1.58 (d, *J* = 6.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.2, 133.3, 132.9, 128.3, 127.9, 127.6, 126.1, 125.8, 123.8, 123.7, 70.5, 25.1.

(*R*)-1-Biphenyl-4-ylethanol (8l)

Alcohol **8l** was prepared from **7l** (785 mg, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 769 mg (97%); $[\alpha]_D^{20}$ +51.0 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 100 °C, 7 min, 5 °C/min, 160 °C, 60 min): 40.6 min (*R*), 42.7 (*S*); 94% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.57 (m, 4 H), 7.46–7.41 (m, 4 H), 7.37–7.32 (m, 1 H), 4.95 (q, *J* = 6.5 Hz, 1 H), 1.87 (br s, 1 H), 1.54 (d, *J* = 6.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.8, 140.8, 140.4, 128.7, 127.2, 127.1, 125.8, 70.1, 25.1.

(*R*)-1-Phenylpropan-1-ol (10a)

Alcohol **10a** was prepared from **9a** (537 mg, 0.54 mL, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 523 mg (96%); $[\alpha]_D^{20}$ +32.4 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 110 °C, 60 min, constant): 11.9 min (*R*), 13.2 (*S*); 97% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.26 (m, 5 H), 4.60 (t, *J* = 6.5 Hz, 1 H), 1.94 (br s, 1 H), 1.84–1.76 (m, 2 H), 0.93 (t, *J* = 6.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.6, 128.4, 127.4, 125.9, 76.0, 31.9, 10.1.

(*R*)-1-Phenylpentan-1-ol (10b)

Alcohol **10b** was prepared from **9b** (649 mg, 0.66 mL, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 624 mg (95%); $[\alpha]_D^{20}$ +28.9 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 100 °C, 15 min, 5 °C/min, 160 °C, 45 min): 24.3 min (*S*), 24.4 (*R*); 97% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.29 (m, 4 H), 7.25–7.21 (m, 1 H), 4.61 (t, *J* = 7.2 Hz, 1 H), 1.84 (br s, 1 H), 1.78–1.62 (m, 2 H), 1.38–1.16 (m, 4 H), 0.85 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.9, 128.4, 127.4, 125.9, 74.7, 38.8, 28.0, 22.6, 14.0.

(*R*)-1-Phenylhexan-1-ol (10c)

Alcohol **10c** was prepared from **9c** (713 mg, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 714 mg (96%); $[\alpha]_D^{20}$ +36.0 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 100 °C, 15 min, 5 °C/min, 160 °C, 45 min): 26.6 min (*S*), 26.7 (*R*); 94% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.24 (m, 5 H), 4.63–4.62 (m, 1 H), 1.86 (d, *J* = 3.1 Hz, 1 H), 1.79–1.60 (m, 2 H), 1.45–1.27 (m, 6 H), 0.89–0.84 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.0, 128.4, 127.4, 125.9, 74.5, 39.1, 31.7, 25.5, 22.5, 14.0.

(*R*)-1,3-Diphenylpropan-1-ol (10d)

Alcohol **10d** was prepared from **9d** (841 mg, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 815 mg (96%); $[\alpha]_D^{20}$ +41.2 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral HPLC (Chiracel OD-H column, flow rate 0.5 mL/min, heptane–*i*-PrOH, 90:10, λ = 215 nm, 25 °C): t_R = 22.7 min (minor), t_R = 25.5 min (major); 90% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.19 (m, 10 H), 4.72–4.66 (m, 1 H), 2.76–2.67 (m, 2 H), 2.20–1.98 (m, 2 H), 1.90 (d, *J* = 3.6 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.5, 141.7, 128.5, 128.4, 128.3, 127.6, 125.9, 125.8, 73.9, 40.4, 32.0.

(*R*)-2-Methyl-1-phenylpropan-1-ol (10e)

Alcohol **10e** was prepared from **9e** (593 mg, 0.60 mL, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 541 mg (90%); $[\alpha]_D^{20}$ +12.8 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 110 °C, 30 min, 5 °C/min, 160 °C, 45 min): 17.9 min (*R*), 18.6 (*S*); 38% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.23 (m, 5 H), 4.34 (d, *J* = 7.1 Hz, 1 H), 1.98–1.89 (m, 2 H), 0.99 (d, *J* = 7.0 Hz, 3 H), 0.79 (d, *J* = 7.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.6, 128.1, 127.3, 126.5, 80.0, 35.2, 19.0, 18.2.

(*R*,*E*)-4-Phenylbut-3-en-2-ol (12a)

Alcohol **12a** was prepared from **11a** (585 mg, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 563 mg (90%); $[\alpha]_D^{20}$ +36.8 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 115 °C, 20 min, 5 °C/min, 160 °C, 30 min): 18.8 min (*R*), 19.7 (*S*); 94% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.30 (m, 4 H), 7.28–7.22 (m, 1 H), 6.58 (dd, *J* = 0.9, 15.9 Hz, 1 H), 6.27 (dd, *J* = 6.4, 15.8 Hz, 1 H), 4.55–4.46 (m, 1 H), 1.71 (br s, 1 H), 1.39 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.7, 133.5, 129.4, 128.5, 127.6, 126.4, 68.9, 23.4.

(*R*,*E*)-1,3-Diphenylprop-2-en-1-ol (12b)
Alcohol **12b** was prepared from **11b** (833 mg, 0.52 mL, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 816 mg (98%); $[\alpha]_D^{20}$ +2.0 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral HPLC (Chiracel OD-H column, flow rate 0.5 mL/min, heptane–*i*-PrOH, 90:10, λ = 215 nm, 25 °C): t_R = 14.8 min (minor), t_R = 19.1 min (major); 37% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.21 (m, 10 H), 6.69 (d, *J* = 0.9, 15.8 Hz, 1 H), 6.38 (d, *J* = 6.4, 15.8 Hz, 1 H), 5.38 (d, *J* = 6.4 Hz, 1 H), 2.12 (br s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.7, 136.5, 131.5, 130.5, 128.6, 128.5, 127.8, 127.7, 126.6, 126.3, 75.1.

(*R*)-1-(3-Pyridyl)ethanol (14)
Alcohol **14** was prepared from **13** (484 mg, 0.44 mL, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 483 mg (98%); $[\alpha]_D^{20}$ +21.8 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 40 °C, 15 min, 3 °C/min, 160 °C, 60 min): 45.8 min (*R*), 46.8 (*S*); 96% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50–8.42 (m, 2 H), 7.71 (tt, *J* = 7.9, 1.7 Hz, 1 H), 7.27–7.23 (m, 1 H), 4.91 (q, *J* = 6.6 Hz, 1 H), 2.98 (br s, 1 H), 1.49 (d, *J* = 6.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.4, 147.2, 141.3, 133.3, 123.5, 67.8, 25.2.

(*R*)-1-(2-Thienyl)ethanol (16)
Alcohol **16** was prepared from **15** (505 mg, 0.43 mL, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 502 mg (98%); $[\alpha]_D^{20}$ +16.4 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 100 °C, 15 min, 5 °C/min, 160 °C, 60 min): 12.4 min (*R*), 14.5 (*S*); 92% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22 (dd, *J* = 1.6, 4.6 Hz, 1 H), 6.98–6.94 (m, 2 H), 5.16–5.08 (m, 1 H), 2.06 (br s, 1 H), 1.59 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.8, 126.6, 124.4, 123.1, 66.2, 25.2.

(*R*)-1-Ferrocenylethanol (18)
Alcohol **18** was prepared from **17** (912 mg, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 865 mg (94%); $[\alpha]_D^{20}$ –30.2 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral HPLC (Chiracel OJ column, flow rate 0.6 mL/min, heptane–*i*-PrOH, 95:5, λ = 215 nm, 25 °C): t_R = 34.8 min (major), t_R = 37.2 min (minor); 94% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.58–4.50 (m, 1 H), 4.22–4.20 (m, 2 H), 4.18 (s, 5 H), 4.15 (t, *J* = 1.9 Hz, 2 H), 1.85 (d, *J* = 4.7 Hz, 1 H), 1.43 (d, *J* = 6.3 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 94.5, 68.3, 67.9, 67.8, 66.1, 66.1, 65.6, 23.7.

1-(3,4-Dichlorophenyl)ethanol (20a)
Alcohol **20a** was prepared from **19a** (756 mg, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 745 mg (98%); $[\alpha]_D^{20}$ +35.8 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 160 °C, 60 min, constant): 6.6 min (*R*), 7.1 (*S*); 97% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 2.1 Hz, 1 H), 7.39 (d, *J* = 8.3 Hz, 1 H), 7.18 (ddd, *J* = 0.6, 2.1, 8.3 Hz, 1 H), 4.84 (q, *J* = 6.5 Hz, 1 H), 1.91 (br s, 1 H), 1.45 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.0, 132.5, 131.2, 130.4, 127.5, 124.7, 69.2, 25.3.

MS (EI, 70 eV): *m*/*z* (%) = 190 [M^+] (35), 175 (100), 147 (47), 111 (70).

HRMS (EI): *m*/*z* calcd for $C_8H_8Cl_2O$: 189.9952; found: 189.9953.

1-(1,3-Benzodioxol-5-yl)ethanol (20b)
Alcohol **20b** was prepared from **19b** (657 mg, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 625 mg (94%); $[\alpha]_D^{20}$ +42.6 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 100 °C, 7 min, 5 °C/min, 160 °C, 60 min): 19.7 min (*R*), 20.1 (*S*); 90% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.87 (d, *J* = 1.8 Hz, 1 H), 6.80 (ddd, *J* = 0.5, 1.8, 8.0 Hz, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 5.92 (s, 2 H), 6.80 (q, *J* = 6.4 Hz, 1 H), 1.90 (br s, 1 H), 1.44 (d, *J* = 6.40 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.7, 146.8, 139.9, 118.6, 108.0, 106.0, 100.9, 70.2, 25.1.

MS (EI, 70 eV): *m*/*z* (%) = 166 [M^+] (71), 151 (97), 148 (12), 123 (27), 93 (100).

HRMS (EI): *m*/*z* calcd for $C_9H_{10}O_3$: 166.0630; found: 166.0623.

1-(3,4-Dimethylphenyl)ethanol (20c)
Alcohol **20c** was prepared from **19c** (593 mg, 0.59 mL, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 583 mg (97%); $[\alpha]_D^{20}$ +50.0 (*c* 1.0, $CHCl_3$).

The ee was determined by chiral GC (DEX-CB column, 100 °C, 7 min, 5 °C/min, 160 °C, 60 min): 15.4 min (*R*), 15.7 (*S*); 96% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15 (br s, 1 H), 7.12–7.09 (m, 2 H), 4.84 (q, *J* = 6.7 Hz, 1 H), 2.27 (s, 3 H), 2.26 (s, 3 H), 1.85 (br s, 1 H), 1.48 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.3, 136.6, 135.7, 129.7, 126.7, 122.7, 70.2, 25.0, 19.8, 19.4.

MS (EI, 70 eV): *m*/*z* (%) = 150 [M^+] (43), 135 (82), 107 (100), 91 (49).

HRMS (EI): *m*/*z* calcd for $C_{10}H_{14}O$: 150.1045; found: 150.1035.

1-(3,4-Dimethoxyphenyl)ethanol (20d)
Alcohol **20d** was prepared from **19d** (721 mg, 4.0 mmol) by the general procedure described above for the hydrogenation of ketones catalyzed by ruthenium complex **6b** (2.1 mg, 0.002 mmol).

Colorless oil; yield: 714 mg (98%); $[\alpha]_D^{20}$ +49.6 (*c* 1.0, $CDCl_3$).

The ee was determined by chiral GC (DEX-CB column, 120 °C, 120 min, constant): 46.5 min (*R*), 50.5 (*S*); 94% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.92 (d, *J* = 2.0 Hz, 1 H), 6.87–6.86 (m, 1 H), 6.83 (s, 1 H), 4.86–4.79 (m, 1 H), 3.88 (s, 3 H), 3.85 (s, 3 H), 1.86 (d, *J* = 2.2 Hz, 1 H), 1.47 (d, *J* = 6.7 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.0, 148.3, 138.5, 117.5, 111.0, 108.6, 70.2, 55.9, 55.8, 25.0.

MS (EI, 70 eV): *m*/*z* (%) = 182 [M^+] (59), 167 (100), 139 (81), 124 (13).

HRMS (EI): *m*/*z* calcd for $C_{10}H_{14}O_3$: 182.0943; found: 182.0923.

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