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Air-Stable Racemization Catalysts for the Dynamic Kinetic Resolution of Secondary Alcohols

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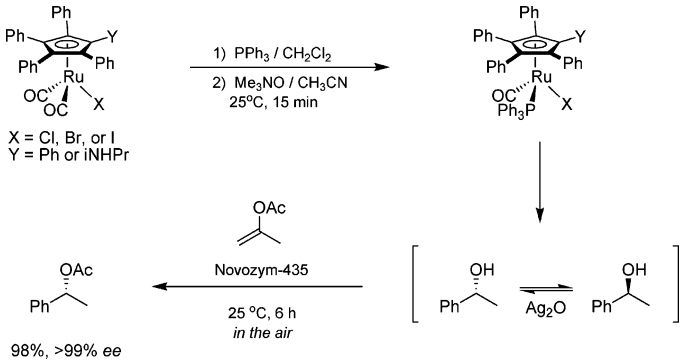

The substitution of a carbonyl ligand with PPh_3 in cyclopentadienylruthenium dicarbonyl complexes produces a new class of recyclable alcohol racemization catalysts. The catalysts are active at room temperature under aerobic conditions in the presence of silver oxide. Furthermore, the catalysts are compatible with the use of a lipase and isopropenyl acetate for the dynamic kinetic resolution (DKR) of secondary alcohols under ambient conditions.

Introduction

Enantiomerically pure secondary alcohols are important chiral building blocks in asymmetric synthesis.[1] Many asymmetric transformations have been developed for preparing enantiomerically pure compounds by using chiral transition-metal complexes[2] or enzymes.[3] However, the resolution of racemic mixtures is still the most common process to prepare enantiomerically pure compounds on industrial scales. Enzymatic kinetic resolution (KR) of secondary alcohols is one of the most potent industrial processes. However, the KR has the intrinsic limitation that the yield cannot exceed 50% for the desired product. Dynamic kinetic resolution (DKR), in which KR is coupled with the catalytic racemization of alcohol substrates, is a solution to overcome the limitation.[4] A number of Rh, Ir, and Ru complexes have been tested for the racemization of secondary alcohols.[5] However, only a few of them have been successfully incorporated in chemoenzymatic DKR.[6] Recently, our group has reported that aminocyclopentadienyl ruthenium complex **1** can be combined with lipase or subtilisin to convert racemic secondary alcohols into the optically pure (*R*)- and (*S*)-acetates at room temperature, respectively (Scheme 1).[7]

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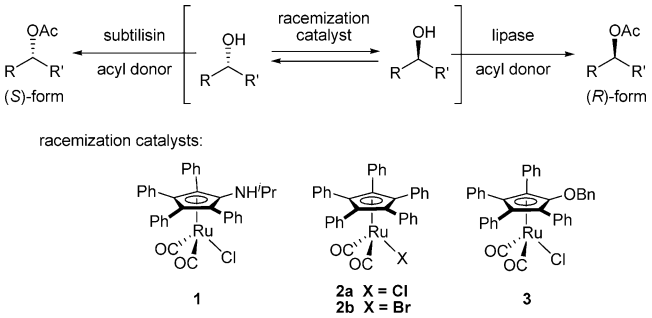
SCHEME 1. Chemoenzymatic DKR of Secondary Alcohols

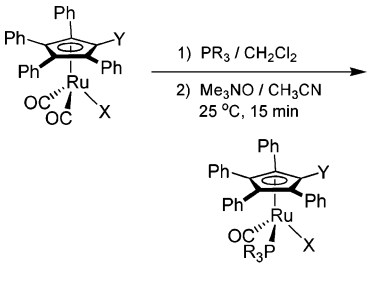


Bäckvall and co-workers have also reported a highly efficient ruthenium complex **2** for the DKR of secondary alcohols at room temperature.[8] However, the DKR with **1** or **2** requires anaerobic conditions due to the formation of air-sensitive intermediates and, therefore, are not suitable for use under ambient conditions. More recently, our group has developed air-stable alcohol racemization catalysts including **3**.[9] The catalyst **3**, however, requires 1 equiv of potassium phosphate and long reaction time (20−72 h) for alcohol DKR. We herein report new air-stable alcohol racemization catalysts that are reusable and highly active at room temperature. Furthermore, the catalysts are compatible with enzymes for the DKR of various secondary alcohols at room temperature in the air.

Results and Discussion

Synthesis of Alcohol Racemization Catalysts. The previous alcohol racemization catalysts **1**−**3** have two carbonyl ligands in common. However, we expected that substituting a carbonyl group with a phosphine would lead to development of more efficient alcohol racemization catalysts by varying the steric and electronic properties of the phosphine ligand. Thus, phosphine-substituted derivatives (**4**−**6**) were prepared on the basis of the known synthetic method for (η^5-Ph_5C_5)Ru(CO)(PPh_3)Br (**5b**).[10] The known method requires high reaction temperature (150 °C) and long reaction time (15 h) to give **5a**−**c** only in 50−68% yields. Meanwhile, the use of trimethylamine *N*-oxide improved the reaction remarkably. The substitution reactions took place more rapidly (15 min) even under milder conditions (25 °C) to give better yields (65−96%) (Scheme 2).

SCHEME 2. Synthesis of Phosphine- or Phosphite-Substituted Ruthenium Complexes



4 X=Cl, Y=NHiPr, R=Ph (94 %)
5a X=Cl, Y=Ph, R=Ph (95 %)
5b X=Br, Y=Ph, R=Ph (95 %)
5c X=I, Y=Ph, R=Ph (96 %)
6a X=Br, Y=Ph, R=Me (65 %)
6b X=Br, Y=Ph, R=OPh (97 %)
6c X=Br, Y=Ph, R=OMe (94 %)

TABLE 1. Catalytic Racemization of (*S*)-1-Phenylethanol with Catalyst 4 in the Air[a]

entry	additive (mol %)	ee[b] (%)
1	Ag_2O (10)	9.8
2	Ag_2O (5)	23.5
3	Ag_2O (10)	14.7[c]
4	Ag_2O (10)	27.4[d]
5	Ag_2O (20)	9.6
6	Ag_2O (50)	9.5
7	Ag_3PO_4 (10)	65.0
8	AgOTf (10)	98.4
9	$AgNO_3$ (10)	99.0
10	AgOAc (10)	98.5
11	KO^{t}Bu (5)	0.0[e]
12	K_3PO_4 (10)	79.4
13	K_2CO_3 (10)	99

[a] (*S*)-1-Phenylethanol (>99% ee, 0.25 mmol) dissolved in toluene (0.5 mL) was added to a flask containing **4** (4 mol %) and additive, and the resulting mixture was stirred at 25 °C for 1 h in the air. [b] The % ee values were measured by GC equipped with a chiral column. [c] 2 mol % of **4** was used. [d] 1 mol % of **4** was used. [e] After 30 min, 9.5% of acetophenone was produced.

Catalytic Racemization of Secondary Alcohols. The ruthenium complexes **4**−**6** were tested on the catalytic racemization of (*S*)-1-phenylethanol (Table 1). Contrary to our hope, all of the newly synthesized ruthenium complexes did not show any activity in alcohol racemization without base. However, we expected the generation of active species from these ruthenium complexes with a proper base, and then eventually found Ag_2O, which has been used as a base in coupling reactions[11−13] and in the preparation of silver alkoxide complexes.[14] The optical purity of 1-phenylethanol was 9.8% ee after 1 h of reaction with 4 mol % of **4** and 10 mol % of Ag_2O in toluene, and the racemization was completed in 1.5 h at room temperature in

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(13) Pd-catalyzed coupling reaction: (a) Lightfoot, A. P.; Twiddle, S. J. R.; Whiting, A. *Synlett* **2005**, 529. (b) Chen, H.; Deng, M.-Z. *J. Org. Chem.* **2000**, *65*, 4444. (c) Chen, H.; Deng, M.-Z. *Org. Lett.* **2000**, *2*, 1649. (d) Uenishi, J.; Beau, J.-M.; Armstrong, R. W.; Kishi, Y. *J. Am. Chem. Soc.* **1987**, *109*, 4756.

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TABLE 2. Catalytic Racemization of (*S*)-1-Phenylethanol with Other Ru Complexes[a]

entry	catalyst	solvent	*t* (h)	ee[b] (%)
1	none	toluene	10.0	>99
2	**1**	toluene	5.0	5.1
3	**2a**	toluene	5.0	40.6
4	**3**	toluene	5.0	52.4
5	**4**	toluene	1.5	0.0 (40.0)[c]
6	**5a**	toluene	2.0	0.0 (48.0)[c]
7	**5b**	toluene	1.0	0.0 (32.0)[c]
8	**5c**	toluene	1.0	0.0 (29.1)[c]
9	**6a**	toluene	10.0	97.6
10	**6b**	toluene	10.0	89.0
11	**6c**	toluene	10.0	98.2
12	**5b**	benzene	1.0	0.0
13	**5b**	THF	1.0	0.0
14	**5b**[d]	THF	1.0	0.0
15	**5b**	CH_2Cl_2	1.0	20.8
16	**5b**	acetone	1.0	74.8
17	**5b**	EtOAc	1.0	82.1
18	**5b**	CH_2=CHOAc	1.0	97.6

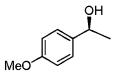
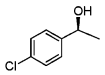
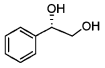
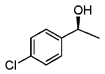
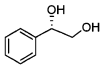
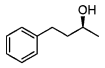
[a] (*S*)-1-Phenylethanol (>99% ee, 0.25 mmol) dissolved in toluene (0.5 mL) was added to a flask containing catalyst (4 mol %) and Ag_2O (10 mol %), and the resulting mixture was stirred at 25 °C in the air. [b] The % ee values were measured after 1 h by GC equipped with a chiral column. [c] The % ee values in parentheses were measured after 30 min. [d] **5b** and Ag_2O recovered from the ninth reuse were employed.

the air (entry 1). Decreasing the amount of **4** decreased the racemization rate (entries 3 and 4), but increasing the amount of Ag_2O more than 10 mol % did not increase the rate (entries 5 and 6). Silver phosphate was helpful for the racemization, although its efficiency was much lower than that of Ag_2O (entry 7). Other silver salts such as AgOTf, AgOAc, and $AgNO_3$, however, were ineffective for the racemization with **4** under the same conditions (entries 8−10). The racemization with **4** and potassium *tert*-butoxide was completed in 30 min, but **4** was decomposed during the racemization and 9.5% of acetophenone as side product was produced (entry 11). Other bases such as K_3PO_4 and K_2CO_3 did not help **4** in racemizing the alcohol (entries 12 and 13).

Ag_2O was tested for the racemization with other ruthenium complexes, **1**−**6** (Table 2). Ag_2O alone did not racemize the alcohol (entry 1) and was not so effective on the racemization with **1**−**3** (entries 2−4). The racemization with **5b** or **5c** was faster than that with **4** (entries 7 and 8), whereas the racemization with ruthenium chloride complex **5a**, trimethyl phosphine complex **6a**, triphenyl phosphite complex **6b**, or trimethyl phosphite complex **6c** was slower than that with **4** (entries 6 and 9−11). According to the ee values obtained after 30 min (entries 5−8), there might be no induction period for the racemization with **4** or **5**. Among solvents tested, benzene and tetrahydrofuran (THF) were as effective as toluene, while dichloromethane was less effective (entries 12−15). Acetone and ethyl acetate (EtOAc) hindered the racemization significantly (entries 16 and 17). In particular, vinyl acetate, which is a popular acyl donor for enzymatic acylation, inhibited the racemization almost completely (entry 18). Meanwhile, it is noticeable that **5b** and Ag_2O can be recovered and reused at least 10 times without activity loss (entry 14).[15]

The catalyst system, **5b** and Ag_2O, was employed for the racemization of various secondary alcohols in the air (Table 3). The racemizations of 1-(4-methoxyphenyl)ethanol, 1-(4-chlorophenyl)ethanol, and indanol were slower than that of 1-phenylethanol (entries 1−4). In particular, the racemization of 1-(4-chlorophenyl)ethanol was 8 times slower (entry 3). However, increasing reaction temperature can increase the rate (entries 6−8). 1-Phenyl-1,2-ethanediol was also racemized successfully. It is remarkable that aliphatic alcohols such as 3-phenyl-2-propanol, 4-phenyl-2-butanol, and 2-octanol can be racemized with rates comparable to those for benzylic alcohols under the same conditions (entries 9−11).

TABLE 3. Catalytic Racemization of Secondary Alcohols Using 5b and Ag_2O[a]

Entry	Substrate	Temp (°C)	*t* (h)	Yield[b] (%)	ee[c] (%)
1		25	1	99.2	0.0
2		25	3	94.0	0.0
3		25	8	94.0	9.0
4		25	8	98.5	3.0
5		25	9	97.5	7.2
6		50	2	97.0	0.0
7		50	2	97.0	0.0
8		50	2	97.3	0.0
9		25	2.5	98.6	0.0
10		25	5	96.2	0.0
11		25	5	97.5	2.5[d]

[a] The mixture of alcohol (0.25 mmol), **5b** (4 mol %), and Ag_2O (10 mol %) in toluene (0.5 M) was stirred in the air. [b] Determined by GC. [c] Measured by HPLC equipped with a chiral column. [d] Determined by GC after conversion to 2-octyl acetate.

Dynamic Kinetic Resolution of Secondary Alcohols. The activities of **2b**, **4**, and **5a**−**c** were compared in the DKR of 1-phenylethanol in the air (Table 4) with *Candida antarctica* lipase B (CALB) as the lipase and isopropenyl acetate as the acyl donor. The DKR with **2b** requires potassium *tert*-butoxide to activate **2b** and also requires sodium carbonate to maintain its activity during the DKR.[8c] The product yield is only 60% in the DKR with **2b** (entry 1) and in that with **5b** and 10 mol % of Ag_2O under aerobic conditions after 15 h (entry 2). Addition of base such as Na_2CO_3 did not improve the yield (entry 3). Interestingly, however, increasing the amount of Ag_2O to 1 equiv completed the DKR in 6 h to give (*R*)-1-phenylethyl acetate in 98% (entry 4). After the DKR, the catalysts could be recovered, but additional Ag_2O was required for the next use. The DKR with **5c** was as successful as that with **5b** (entry 5), while those with **5a** and **4** were not completed in 6 h (entries 6 and 7).

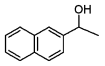
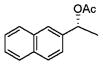
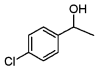
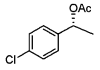
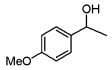
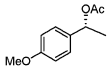
(15) The yields of racemic 1-phenylethanol in the reuse: 2nd, 99 %; 3rd, 99 %; 4th, 98 %; 5th, 98 %; 6th, 98 %; 7th, 99 %; 8th, 98 %; 9th, 98 %.

TABLE 4. DKR of 1-Phenylethanol in the Air[a]

entry	catalyst	additive (mol %)	*t* (h)	yield[b,c] (%)	ee[d] (%)
1	**2b**	KO^{t}Bu (5) Na_2CO_3 (100)	15	60	>99
2	**5b**	Ag_2O (10)	15	60	>99
3	**5b**	Ag_2O (10) Na_2CO_3 (100)	15	60	>99
4	**5b**	Ag_2O (100)	6	98 (95)	>99
5	**5c**	Ag_2O (100)	6	96 (92)	>99
6	**5a**	Ag_2O (100)	6	85	>99
7	**4**	Ag_2O (100)	6	89	>99

[a] A mixture of alcohol (1.0 mmol), ruthenium catalyst (4 mol %), Ag_2O, Novozym-435 (8 mg), and isopropenyl acetate (2.0 mmol) in toluene (3.2 mL) was stirred at 25 °C in the air. [b] Determined by GC. [c] Numbers in parentheses show isolated yields. [d] Determined by GC equipped with a chiral column.

TABLE 5. DKR of Secondary Alcohols[a]

Entry	Substrate	Product	*t* (h)	Yield[b,c] (%)	ee[b] (%)
1			8	95 (93)	>99[d]
2			10	94 (92)	>99[d]
3			8	97 (94)	>99
4			8	75 (73)	>99
5			20	93	99
6			20	96	99

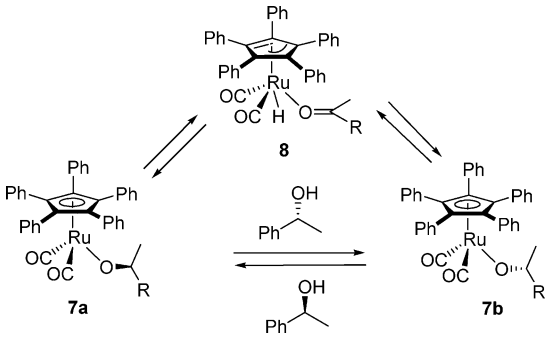
[a] A mixture of alcohol (1.0 mmol), **5b** (4 mol %), Ag_2O (1.0 mmol), Novozym-435 (8 mg), and isopropenyl acetate (2.0 mmol) in toluene (3.2 mL) was stirred at 25 °C in the air. [b] Determined by GC equipped with a chiral column. [c] Numbers in parentheses show isolated yields. [d] Determined by HPLC equipped with a chiral column.

Dynamic Kinetic Resolution of Various Secondary Alcohols. On the basis of the results obtained from the DKR of 1-phenylethanol, **5b** was selected as the racemization catalyst and applied to the DKRs of various secondary alcohols (Table 5). The catalyst system was effective for aliphatic alcohols as well as for benzylic alcohols. 1-(Naphthalen-1-yl)ethanol and 1-(naphthalen-2-yl)ethanol were converted into the corresponding (*R*)-acetates (>99% ee), respectively, in excellent yields (entries 1 and 2). The DKR of 1-(*p*-chlorophenyl)ethanol was also successful, whereas 1-(4-methoxyphenyl)ethanol gave the corresponding (*R*)-acetate only in 75% yield due to the side reaction producing 1-(4-methoxyphenyl)ethanone (entries 3 and 4). 3-Phenyl-2-propanol and 2-octanol were also transformed successfully into the corresponding (*R*)-acetates (99% ee) in 93% and 96% yield, respectively, although a longer reaction time (20 h) was needed (entries 5 and 6).

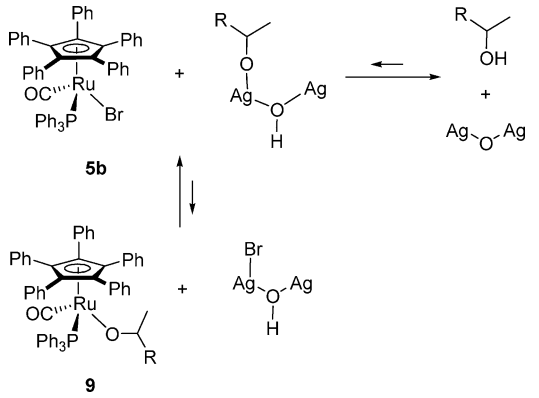
Studies for the Role of Silver Oxide. To get a clue for the role of silver oxide, a mixture of 1-phenylethanol, **5b**, and Ag_2O in methylene chloride-d_2 was subjected to NMR experiments (^{1}H, ^{13}C, and ^{31}P). However, no intermediate was detected, and only the resonance peaks for 1-phenylethanol and **5b** were observed during the racemization of 1-phenylethanol.[16] In addition, interestingly, the silver oxide recovered from the racemization was the same as the original silver oxide and did not show any sign for the formation of silver bromide in the XRD analysis.[16] With these observations, it is hard to propose a persuasive mechanism for the racemization with our catalyst system. However, it has been shown that a ruthenium alkoxide (**7a** or **7b**) is formed during the racemization with **2b** by the aid of a strong base such as potassium *tert*-butoxide (Scheme 3).[8b] The alkoxides **7a** and **7b** are in equilibrium through the formation of ruthenium hydride complex **8** and through alcohol exchange. Thus, the analogous alkoxide complex **9** would be formed from **5b** and silver oxide. In this reaction silver oxide acts as the base for the deprotonation of an alcohol (Scheme 4). The equilibrium far shifted to **5b** and silver oxide can explain the failure to detect **9** and alkoxide intermediates.

(16) See the Supporting Information.

SCHEME 3. Reported Mechanism for Ru-Catalyzed Racemization of Secondary Alcohol



SCHEME 4. Proposed Mechanism for Racemization of Secondary Alcohol with 5b and Ag_2O



Conclusion

In summary, we have synthesized a new class of air-stable and recyclable alcohol racemization catalysts and demonstrated that they are applicable to the DKR of aliphatic alcohols as well as benzylic ones at room temperature. The catalysts are readily synthesized from the corresponding ruthenium dicarbonyl complexes through simple ligand-substitution reactions. The efficiency of the catalysts in the DKR is comparable to that of the parent ruthenium dicarbonyl complexes. In contrast to the dicarbonyl complexes, however, our catalysts do not require the strong base such as potassium *tert*-butoxide to be activated for alcohol racemization and DKR and are stable during the DKR under aerobic conditions.

Experimental Section

Synthesis of [2,3,4,5-Ph$_4$(η^5-C$_4$CNH^{i}Pr)]Ru(CO)(Cl)(PPh$_3$) (4). In a 100 mL flask equipped with a grease-free high-vacuum

stopcock were dissolved [2,3,4,5-Ph_4(η^5-C_4CNH^iPr)]$Ru(CO)_2Cl$ (200 mg, 0.323 mmol) and triphenylphosphine (93.2 mg, 0.355 mmol) in dry CH_2Cl_2 (5 mL). After the flask was filled with argon and closed, trimethylamine *N*-oxide (48.5 mg, 0.646 mmol) dissolved in acetonitrile (2 mL) was slowly added to the first solution and stirred for 15 min at room temperature. The resulting solution was concentrated and chromatographed on silica gel column to give a red solid **4** (260 mg, 94% yield). Mp: >180 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70−7.68 (m, 2H), 7.45−7.39 (m, 6H), 7.32−7.02 (m, 20H), 6.97−6.90 (m, 3H), 6.60 (t, J = 7.6 Hz, 2H), 6.48 (d, J = 7.7 Hz, 2H), 3.40 (d, J = 8.0 Hz, 1H), 3.17 (m, 1H), 0.94 (d, J = 6.1 Hz, 3H), 0.63 (d, J = 6.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.8 (d, J_{cp} = 23.2 Hz, CO), 137.7 (C1 of Cp), 135.0−126.9 (42 resonance, aromatic), 99.9, 96.3 (C 3, 4 of Cp), 82.9, 80.7 (C 2, 5 of Cp), 45.6, 25.8, 24.5. ^{31}P NMR (121 MHz, $CDCl_3$): δ 42.39 (s) external std. H_3PO_4 in D_2O. IR (KBr, cm^{-1}): γ(CO) 1933 (s). MS (FAB, *m*/*z*): 854.0 [M^+ + 1]. Anal. Calcd for $C_{51}H_{43}ClNOPRu$: C, 71.78; H, 5.08; N, 1.64. Found: C, 71.79; H, 5.09; N, 1.87.

(η^5-Ph_5Cp)Ru(CO)(Cl)(PPh_3) (5a). From (η^5-Ph_5C_5)$Ru(CO)_2$-Cl (300 mg, 0.470 mmol), triphenylphosphine (136 mg, 0.517 mmol), and trimethylamine *N*-oxide (70.6 mg, 0.940 mmol) was obtained red solid **5a** (390 mg, 95% yield). Mp: >190 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47−7.41 (m, 6H), 7.31−7.28 (m, 3H), 7.14−7.06 (m, 11H), 6.88 (t, J = 7.8 Hz, 10H), 6.78 (d, J = 7.8 Hz, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.5 (d, J_{cp} = 26.1 Hz, CO), 134.8−127.4 (48 resonances, aromatic), 103.4 (C of Cp). ^{31}P NMR (121 MHz, $CDCl_3$): δ 40.61 (s) external std. H_3PO_4 in D_2O. IR (KBr, cm^{-1}): γ(CO) 1943 (s). MS (FAB, *m*/*z*): 872.4 [M^+] Anal. Calcd for $C_{54}H_{40}ClOPRu$: C, 74.34; H, 4.62. Found: C, 74.38; H, 4.65.

(η^5-Ph_5Cp)Ru(CO)(Br)(PPh_3) (5b). From (η^5-Ph_5C_5)$Ru(CO)_2$-Br (300 mg, 0.440 mmol), triphenylphosphine (127 mg, 0.484 mmol), and trimethylamine *N*-oxide (66.1 mg, 0.880 mmol) was obtained red solid **5b** (383 mg, 95% yield). Mp: >200 °C dec .^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47−7.41 (m, 6H), 7.32−7.27 (m, 3H), 7.15−7.05 (m, 11H), 6.88 (t, J = 7.5 Hz, 10H), 6.79 (d, J = 7.2 Hz, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.6 (d, J_{cp} = 25.5 Hz, CO), 135.1−127.3 (48 resonances, aromatic), 103.5 (C of Cp). ^{31}P NMR (121 MHz, $CDCl_3$): δ 41.20 (s) external std. H_3PO_4 in D_2O. IR (KBr, cm^{-1}): γ(CO) 1942 (s). Anal. Calcd for $C_{54}H_{40}$-BrOPRu: C, 70.74; H, 4.40. Found: C, 70.73; H, 4.40.

(η^5-Ph_5Cp)Ru(CO)(I)(PPh_3) (5c). From (η^5-Ph_5C_5)$Ru(CO)_2$I (300 mg, 0.411 mmol), triphenylphosphine (162 mg, 0.616 mmol), and trimethylamine *N*-oxide (61.7 mg, 0.822 mmol) was obtained brown solid **5c** (380 mg, 96% yield). Mp: 210 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46−7.40 (m, 6H), 7.30−7.28 (m, 2H), 7.14−7.06 (m, 12H), 6.90−6.81 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.1 (d, J_{cp} = 23.9 Hz, CO), 136.0−127.3 (48 resonances, aromatic), 103.8 (C of Cp). ^{31}P NMR (121 MHz, $CDCl_3$): δ 42.66 (s) external std. H_3PO_4 in D_2O. IR (KBr, cm^{-1}): γ(CO) 1940 (s). MS (FAB, *m*/*z*): 964.0 [M^+]. Anal. Calcd for $C_{54}H_{40}IOPRu$: C, 67.29; H, 4.18. Found: C, 67.10; H, 4.36.

(η^5-Ph_5Cp)Ru(CO)(Br)(PMe_3) (6a). From (η^5-Ph_5C_5)$Ru(CO)_2$-Br (200 mg, 0.292 mmol), trimethylphosphine (36 μL, 0.350 mmol), and trimethylamine *N*-oxide (43.8 mg, 0.584 mmol) was obtained orange-brown solid **6a** (139 mg, 65% yield). Mp: 220−223 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16−7.02 (m, 25H), 1.60 (d, J_{PH} = 9.7 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.3 (d, J_{cp} = 24.0 Hz, CO), 132.7, 132.0, 127.5, 102.8, (C of Cp), 18.4 (d, J_{CP} = 35.0 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 6.98 (s) external std H_3PO_4 in D_2O. IR (KBr, cm^{-1}): γ(CO) 1942 (s). MS (FAB, *m*/*z*): 731.9 [M^+ + 1]. Anal. Calcd for $C_{39}H_{34}BrOPRu$: C, 64.11; H, 4.69. Found: C, 64.37; H, 4.71.

(η^5-Ph_5Cp)Ru(CO)(Br)[$P(OPh)_3$] (6b). From (η^5-Ph_5C_5)$Ru(CO)_2$-Br (200 mg, 0.292 mmol), triphenyl phosphite (115 μL, 0.438 mmol), and trimethylamine *N*-oxide (43.8 mg, 0.584 mmol) was obtained yellow solid **6b** (273 mg, 97% yield). Mp: 180−181 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19−6.92 (m, 40H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.1 (d, J_{cp} = 32.8 Hz, CO), 152.2, 132.9, 132.6, 131.2, 129.5, 127.7, 127.5, 124.9, 121.4, 121.3, 104.4 (d, J_{cp} = 3.2 Hz, C of Cp). ^{31}P NMR (121 MHz, $CDCl_3$): δ 121.5 (s) external std H_3PO_4 in D_2O. IR (KBr, cm^{-1}): γ(CO) 1978 (s). Anal. Calcd for $C_{54}H_{40}BrO_4PRu$: C, 67.22; H, 4.18. Found: C, 67.25; H, 4.33.

(η^5-Ph_5Cp)Ru(CO)(Br)[$P(OMe)_3$] (6c). From (η^5-Ph_5C_5)$Ru(CO)_2$-Br (200 mg, 0.292 mmol), trimethyl phosphite (52.0 μL, 0.438 mmol), and trimethylamine *N*-oxide (43.8 mg, 0.584 mmol) was obtained orange solid **6c** (214 mg, 94% yield). Mp: 205−206 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.14−7.00 (m, 25H), 3.70 (d, J_{PH} = 11 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.9 (d, J_{cp} = 33.8 Hz, CO), 138.0, 133.2, 132.9, 131.7, 130.1, 128.4, 127.5, 127.3, 127.1, 126.2, 104.0 (d, J_{cp} = 3.1 Hz, C of Cp), 54.3 (d, J_{CP} = 7.7 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 136.9 (s) external std. H_3PO_4 in D_2O. IR (KBr, cm^{-1}): γ(CO) 1954 (s). Anal. Calcd for $C_{39}H_{34}BrO_4PRu$: C, 60.16; H, 4.40. Found: C, 60.33; H, 4.57.

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Supporting Information Available: Experimental procedures, characterization data, and NMR and XRD studies for racemization of (*S*)-1-phenylethanol. This material is available free of charge via the Internet at http://pubs.acs.org.

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