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Asymmetric Hydroboration of Styrenes Catalyzed by Cationic Chiral Phosphine-Rhodium(I) Complexes

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Abstract: Reaction of styrene with catecholborane in the presence of 1 mol % of a cationic phosphine-rhodium catalyst prepared in situ from $[Rh(COD)_2]BF_4$ and 1,4-bis(diphenylphosphino)butane proceeded regioselectively to give, after oxidation, 1-phenylethanol in a quantitative yield. The regioselectivity forming benzylic alcohols was also observed in the reaction of substituted styrenes. Use of (*R*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) as a chiral ligand for the rhodium-catalyzed hydroboration of substituted styrenes ($ArCH{=}CH_2$) gave optically active (*R*)-1-arylethanols (ArCH(OH)Me) in high yields. The enantiomeric purities of the alcohols are 96% ee, 94% ee, 91% ee, 85% ee, 89% ee, and 82% ee for Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 3-ClC_6H_4, 4-$MeOC_6H_4$, and 2-$MeOC_6H_4$, respectively.

Introduction

Hydroboration of alkenes and alkynes is among the most valuable synthetic techniques in organic chemistry, the organoboranes formed being readily converted into various kinds of organic compounds.[1] Advances in Brown's group have greatly expanded the scope of the hydroboration, including more selective boron reagents which realize the high regioselectivity forming carbon-boron bond at the less hindered end of the multiple bond,[1] as well as the asymmetric synthesis of alcohols, for example, with isopinocampheylboranes.[2] Recently, increasing attention has been paid to the potential application of the rhodium-catalyzed hydroboration with catecholborane, which was first reported by Männig and Nöth,[3] to organic synthesis. Evans[4] and Burgess[5] have reported control of regio- and/or diastereoselectivity in catalyzed or uncatalyzed hydroboration of allylic compounds. First examples of catalytic asymmetric hydroboration have been reported by Burgess[6] and Suzuki[7] in 1988, where 1,1- and 1,2-disubstituted olefins were subjected to the reaction catalyzed by rhodium complexes prepared by mixing $[RhCl(diene)]_2$ with chiral phosphine ligands. We have found[8] that the use of a certain cationic phosphine-rhodium catalyst for hydroboration of styrene derivatives makes the regioselectivity opposite to the uncatalyzed hydroboration[9] to produce benzylic boranes exclusively and that high enantioselectivity is attained in the catalytic hydroboration of styrenes giving rise to optically active 1-arylethanols. The catalytic asymmetric hydroboration complements the uncatalyzed asymmetric hydroboration with the chiral alkylboranes that has been successfully used for internal alkenes.[2] Very recently, Brown has

reported catalytic asymmetric hydroboration of styrenes with chiral oxazaborolidines instead of catecholborane.[10,11] Here we describe in detail the catalytic asymmetric hydroborations of styrenes.

Results and discussion

Styrene (**1a**) was allowed to react with catecholborane in THF. It was found that 1 mol % of rhodium complexes catalyze the hydroboration at room temperature to give 1-phenylethylborane **2a** and/or its regioisomer 2-phenylethylborane **3a**, the oxidation of which gave 1-phenylethanol (**4a**) and/or 2-phenylethanol (**5a**), respectively (Scheme 1), while the hydroboration did not take place at all in the absence of catalysts under the reaction conditions. The catalytic activity of the rhodium complexes and the regioselectivity forming **2a** or **3a** were dependent strongly on phosphine ligands and an electronic charge on the rhodium. The reaction conditions and results are summarized in Table 1.

Scheme 1

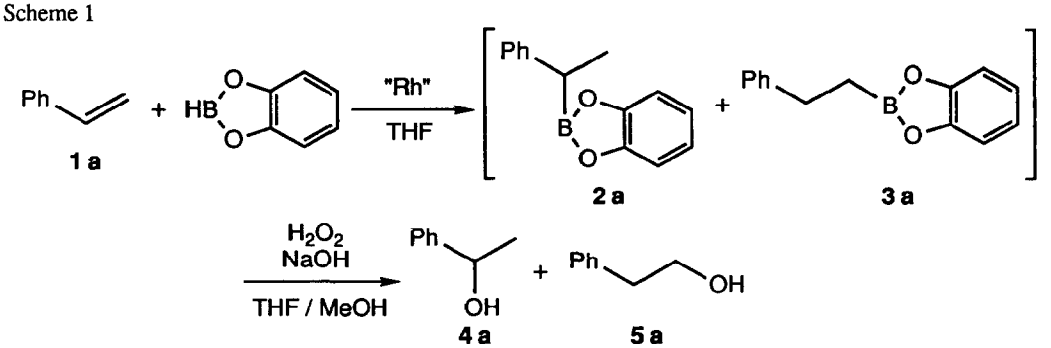


Table 1. Hydroboration of Styrene (**1a**) with Catecholborane Catalyzed by Rhodium Complexes.[a]

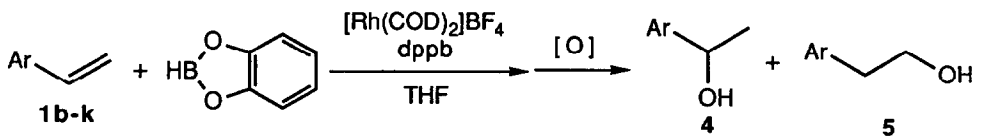
entry	Rh complex	added ligand	yield[b] (%)	**4a** / **5a**[c]
1	$[Rh(COD)_2]BF_4$	dppb	99	>99 / 1
2	$[Rh(COD)(dppb)]BF_4$	–	86	>99 / 1
3	$[Rh(COD)_2]BF_4$	dppe	84	89 / 11
4	$[Rh(COD)_2]BF_4$	PPh_3	93	>99 / 1
5	$RhCl(PPh_3)_3$	–	79	10 / 90
6	1/2 $[RhCl(COD)]_2$	dppe	50	34 / 66
7	1/2 $[RhCl(COD)]_2$	dppb	83	45 / 55
8	1/2 $[RhCl(COD)]_2$	dppf	83	10 / 90
9	1/2 $[RhCl(COD)]_2$	–	37	27 / 73
10	$[Rh(COD)_2]BF_4$	–	61	57 / 43

[a] All reactions were carried out in THF at room temperature or at 25 °C for 30 min in the presence of 1 mol % of a rhodium complex. Styrene/catecholborane/Rh/P = 1.0/1.1/0.010/0.022. [b] Isolated yield of alcohols **4a** and **5a** by preparative TLC on silica gel. [c] Determined on the basis of the isolated yields of **4a** and **5a**.

Exclusive formation of secondary alkyl borane **2a** was observed in the hydroboration with catecholborane catalyzed by rhodium complexes that have tertiary phosphine ligands and a positive charge on rhodium. Thus, the hydroboration in the presence of 1 mol % of a cationic rhodium complex generated in situ by mixing $[Rh(COD)_2]BF_4$ with 1,4-bis(diphenylphosphino)butane (dppb) was completed in 30 min at room temperature to give 1-phenylethanol (**4a**) with perfect regioselectivity (>99/1) in a quantitative yield (entry 1 in Table 1). Preformed phosphine-rhodium complex, $[Rh(COD)(dppb)]BF_4$, showed a similar catalytic activity and regioselectivity (entry 2). Cationic triphenylphosphine complex can be also used as the regioselective catalyst (entry 4). The regioselectivity observed here is in striking contrast to that reported in uncatalyzed hydroboration of styrene with dialkylboranes where 2-phenylethylboranes are formed preferentially.[1] On the other hand, formation of primary alkyl borane **3a** was observed with neutral rhodium catalysts. Chlorotris(triphenylphosphine)rhodium ($RhCl(PPh_3)_3$) gave 2-phenylethanol (**5a**) in 90% selectivity (entry 5). Other neutral rhodium complexes generated in situ from $[Rh(COD)Cl]_2$ and bisphosphine ligands, 1,2-bis(diphenylphosphino)ethane (dppe), 1,1'-bis(diphenylphosphino)ferrocene (dppf), and dppb all gave **5a** as a main product (entries 6-8). Recently, Burgess and coworkers have reported the same selectivity forming **5a** in the hydroboration catalyzed by $RhCl(PPh_3)_3$.[5d] Rhodium complexes lacking phosphine ligands gave low yields of both isomers **4a** and **5a** with low selectivity (entries 9 and 10).

Substituted styrenes on the phenyl ring **1b-1h** and vinylarenes **1i-1k** were examined for the regiochemistry in the hydroboration with catecholborane in the presence of the cationic phosphine-rhodium complex generated from $[Rh(COD)_2]BF_4$ and dppb (Scheme 2). Results summarized in Table 2 show that mono-substituted styrenes **1b-1g** with chloro, methyl, and methoxy groups at either 2, 3, or 4 position all underwent the catalytic hydroboration to yield 1-arylethanols **4b-4g** with the perfect regioselectivity (>99/1) regardless of the electron-releasing or electron-withdrawing nature of the substituents (entries 1-6). Sterically hindered vinylarenes **1h** and **1i** required a longer reaction time to complete the catalytic hydroboration at 25 °C and the regioselectivity forming **4** was significantly lower (entries 7 and 8). The high regioselectivity forming secondary alkyl alcohol **4j** was also observed in the reaction of vinylferrocene (**1j**) (entry 9).

Scheme 2



1b: Ar = 4-ClC_6H_4 **1g**: Ar = 2-$MeOC_6H_4$
1c: Ar = 4-MeC_6H_4 **1h**: Ar = 2,4,6-$Me_3C_6H_2$
1d: Ar = 4-$MeOC_6H_4$ **1i**: Ar = 2-naphthyl
1e: Ar = 3-ClC_6H_4 **1j**: Ar = ferrocenyl
1f: Ar = 2-ClC_6H_4 **1k**: Ar = 2-pyridyl

Hydroboration of β-substituted styrenes **6** with the cationic rhodium-dppb catalyst also proceeded with high regioselectivity forming benzylic borane (Scheme 3). Thus, (*E*)-1-phenylpropene (**6a**) and indene (**6d**) gave benzylic alcohols **7a** (>98/2) and **7d** (>99/1), respectively, in high yields after oxidation (entries 1 and 3 in Table 3). It is rather surprising that the preferential formation of benzylic alcohols was observed in the reaction of α-substituted styrenes **9a** and **9b**, which gave tertiary alcohols **10** and primary alcohols **11** in a ratio of about 2 to 1 (entries 4 and 6). Catalytic hydroboration of 1-octene (**12**) with catecholborane took place at 25 °C

Table 2. Hydroboration of Styrenes **1** with Catecholborane Catalyzed by Cationic Rhodium Complex Generated from $[Rh(COD)_2]BF_4$ and dppb.[a]

entry	olefin (Ar in $ArCH{=}CH_2$)	time (h)	yield[b] (%)	**4** / **5**[c]
1	**1b** (4-ClC_6H_4)	1	91	>99 / 1
2	**1c** (4-MeC_6H_4)	0.5	88	>99 / 1
3	**1d** (4-$MeOC_6H_4$)	0.5	99	>99 / 1
4	**1e** (3-ClC_6H_4)	0.5	98	>99 / 1
5	**1f** (2-ClC_6H_4)	1	99	>99 / 1
6	**1g** (2-$MeOC_6H_4$)	0.5	82	>99 / 1
7	**1h** (2,4,6-$Me_3C_6H_2$)	16	76	63 / 37
8	**1i** (2-naphthyl)	16	82	65 / 35
9	**1j** (ferrocenyl)	16	80	97 / 3
10	**1k** (2-pyridyl)	16	0	–

[a] All reactions were carried out at 25 °C in THF in the presence of 1 mol % of cationic rhodium complex generated from $[Rh(COD)_2]BF_4$ and dppb. Olefin/catecholborane/$[Rh(COD)_2]BF_4$/dppb = 1.0/1.1/0.01.0/0.011. [b] Isolated yield of alcohols **4** and **5** by preparative TLC on silica gel. [c] Determined on the basis of the isolated yields of **4** and **5**.

to give alcohols **13** and **14** in a quantitative yield. The main product was primary alcohol **14** even if the cationic rhodium-dppb complex was used as catalyst (Scheme 4, entry 7 in Table 3). The selectivity of 92% to form primary alcohol **14** over secondary alcohol **13** is almost the same selectivity reported in uncatalyzed hydroboration of 1-alkene with catecholborane at an elevated temperature.[9] High *exo* selectivity was observed in the hydroboration of norbornene (**15**) (entry 8), this selectivity being generally observed in uncatalyzed hydroboration.[9]

Scheme 3

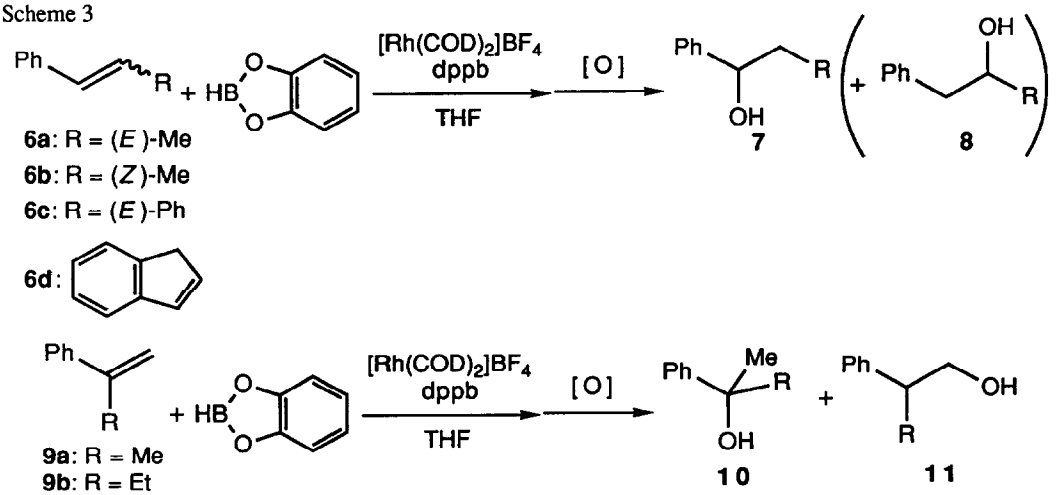
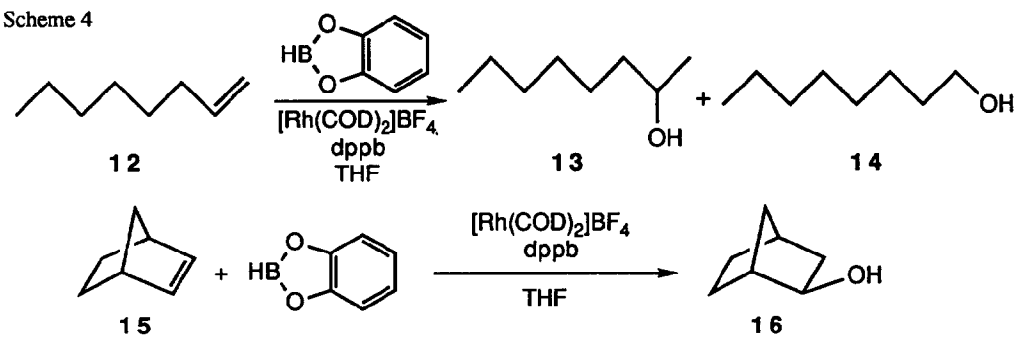


Table 3. Hydroboration of Substituted Styrenes Catalyzed by Cationic Rhodium Complex Generated from $[Rh(COD)_2]BF_4$ and dppb.[a]

entry	olefin	time (h)	yield[b] (%)	product (ratio)[c]	
1	**6a**: (*E*)-1-phenylpropene	15	89	**7a/8a**	(>98 / 2)
2	**6c**: (*E*)-stilbene	17	79	**7c**	–
3	**6d**: indene	1	80	**7d/8d**	(>99 / 1)
4	**9a**: 2-phenylpropene	15	96	**10a/11a**	(70 / 30)
5[d]	**9a**: 2-phenylpropene	0.5	37	**10a/11a**	(20 / 80)
6	**9b**: 2-phenyl-1-butene	4.5	70	**10b/11b**	(66 / 34)
7	**12**: 1-octene	0.5	99	**13/14**	(8 / 92)
8	**15**: norbornene	1	54	**16**	(>99 / 1)[e]

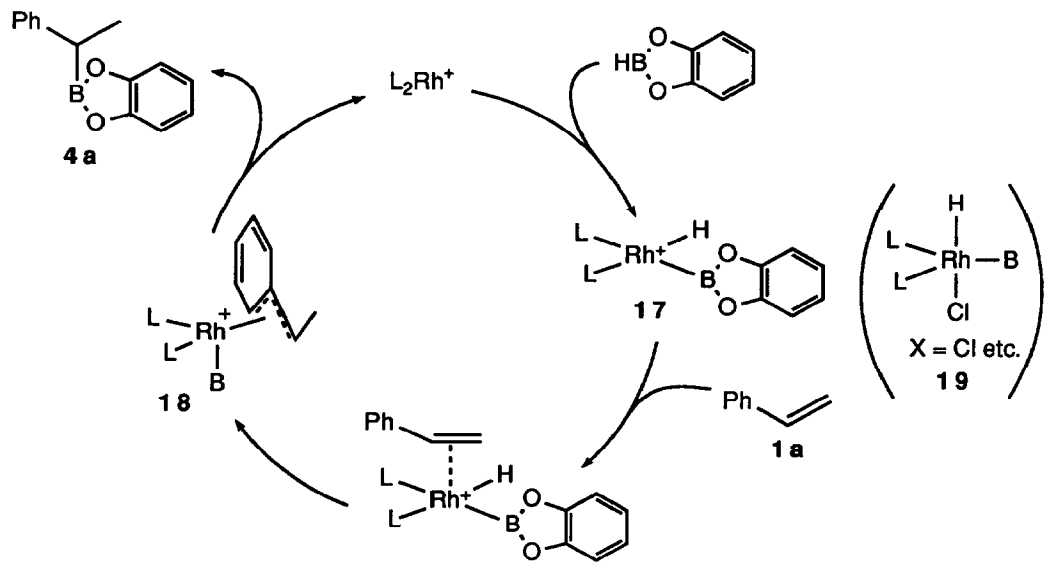
[a] All reactions were carried out at 25 °C in THF in the presence of cationic rhodium complex generated from $[Rh(COD)_2]BF_4$ and dppb. Olefin/catecholborane/$[Rh(COD)_2]BF_4$/dppb = 1.0/1.1/0.010/0.011. [b] Isolated yield of alcohols by preparative TLC on silica gel. [c] Determined on the basis of the isolated yields of alcohols. [d] PPh_3 was used as ligand (Rh/P = 1/2.2). [e] Ratio of *exo*-**16** to *endo*-**16**.

Scheme 4



To summarize the regiochemistry in the rhodium-catalyzed hydroboration of terminal olefins, high selectivity forming secondary alkyl boranes is observed only with the olefins where aromatic groups are attached to the double bond. The use of cationic phosphine-rhodium complexes is also essential for the regioselectivity. Rhodium-catalyzed hydroboration has been proposed to proceed through an alkyl(boryl)rhodium(III) intermediate which has been formed by oxidative addition of catecholborane to rhodium(I) followed by insertion of alkene into the resulting H-Rh bond.[3,4b,5d,12] The high regioselectivity observed here in the hydroboration of styrenes may be illustrated by Scheme 5, which involves η^3-benzylrhodium complex **18** as a key intermediate.[13] A cationic rhodium complex should have one additional vacant coordination site compared with the corresponding neutral complex, which is exemplified by cationic hydride species **17** and neutral one **19**. It is probable that the cationic rhodium allows formation of the η^3-benzyl complex which requires one more coordination site than η^1-alkyl complex. Reductive elimination from the η^3-benzyl(boryl)rhodium **18** will produce the secondary alkyl borane **4** regioselectively.

Scheme 5



The high regioselectivity attained above prompted us to study asymmetric synthesis of optically active 1-arylethanols by catalytic hydroboration with cationic rhodium complexes coordinated with chiral phosphine ligands. Several chiral phosphine ligands were examined for enantioselectivity in the hydroboration of styrene (**1a**) (Scheme 6). The enantiomeric purity of 1-phenylethanol (**4a**), obtained by oxidation of the hydroboration product **2a** with alkaline hydroperoxide, was determined by HPLC analysis of its 3,5-dinitrophenyl carbamate **20a** with a chiral stationary phase column. It was found that (*R*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl ((*R*)-BINAP)[14] is the most effective chiral ligand giving a high yield of (*R*)-**4a** with 57% ee in the reaction at 25 °C (entry 1 in Table 4). Other chiral ligands, (2*S*,3*S*)-bis(diphenylphosphino)butane ((*S*,*S*)-chiraphos),[15] [(*R*)-*N*,*N*-dimethyl-1-[(*S*)-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine ((*R*)-(*S*)-BPPFA),[16] and (+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ((+)-DIOP),[17] were all less enantioselective for the present reaction (entries 2-4). The very high regioselectivity forming secondary alcohol **4a** was observed

Scheme 6

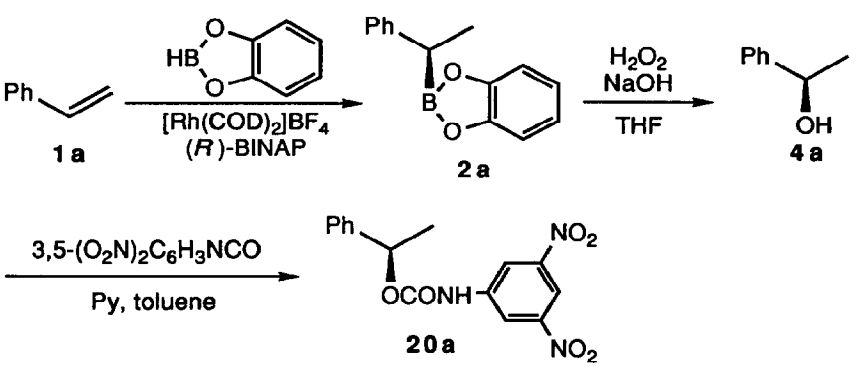


Table 4. Asymmetric Hydroboration of Styrene (**1a**) with Catecholborane Catalyzed by Rhodium-(*R*)-BINAP Complex.[a]

entry	ligand	solvent	temp (°C)	time (h)	yield[b] (%)	**4a**/**5a**[c]	% ee[d] (config)[e]
1	(*R*)-BINAP	THF	25	0.5	92	>99 / 1	57.0 (*R*)[f]
2	(*R*)-(*S*)-BPPFA	THF	25	0.5	77	95 / 5	22.1 (*R*)
3	(*S*,*S*)-chiraphos	THF	25	0.5	98	>99 / 1	15.5 (*S*)
4	(+)-DIOP	THF	25	0.5	87	>99 / 1	4.0 (*R*)
5[g]	(+)-DIOP	THF	25	0.5	64	18 / 82	3.1 (*R*)
6	(*R*)-BINAP	THF	−30	0.5	90	>99 / 1	75.7 (*R*)
7	(*R*)-BINAP	THF	−50	1	71	>99 / 1	81.0 (*R*)
8	(*R*)-BINAP	THF	−78	1	0	–	–
9	(*R*)-BINAP	DME	−30	0.5	57	>99 / 1	78.3 (*R*)
10	(*R*)-BINAP	DME	−50	1	54	>99 / 1	88.5 (*R*)
11	(*R*)-BINAP	DME	−78	6	64	>99 / 1	96.1 (*R*)
12[h]	(*R*)-BINAP	DME	−78	2	91	>99 / 1	96.2 (*R*)[i]
13	(*R*)-BINAP[j]	DME	−78	2	92	>99 / 1	93.5 (*R*)[k]
14[h]	(*S*)-BINAP	DME	−78	2	87	>99 / 1	92.3 (*S*)[l]
15	(*R*)-BINAP	benzene	25	0.5	90	>99 / 1	60.1 (*R*)
16	(*R*)-BINAP	toluene	*m*	*m*	74	85 / 15	73.2 (*R*)
17	(*R*)-BINAP	CH_2Cl_2	−78	5	0	–	–

[a] All reactions were carried out in the presence of 1 mol % of a cationic rhodium complex generated from $[Rh(COD)_2]BF_4$ and a chiral ligand, unless otherwise noted. Styrene/catecholborane/$[Rh(COD)_2]BF_4$-/ligand = 1.0/1.1/0.010/0.011. [b] Isolated yield of alcohols **4a** and **5a** by preparative TLC on silica gel. [c] Determined on the basis of the isolated yields of **4a** and **5a**. [d] Determined by HPLC analysis of 3,5-dinitrophenyl carbamate derivative **20a** (Sumichiral OA-4100). [e] The absolute configuration was determined by comparison of the optical rotation with that reported for optically pure (*S*)-(−)-**4a**, $[\alpha]_D^{22}$ −52.5 (*c* 1.3, CH_2Cl_2) (ref 18). [f] $[\alpha]_D^{23}$ +29.5 (*c* 1.3, CH_2Cl_2). [g] $[RhCl(COD)]_2$ was used. [h] Reaction with 2 mol % of the catalyst. [i] $[\alpha]_D^{23}$ +48.6 (*c* 1.0, CH_2Cl_2). [j] Isolated BINAP/Rh complex, [Rh(COD)((*R*)-BINAP)]BF_4 was used. [k] $[\alpha]_D^{23}$ +48.3 (*c* 1.0, CH_2Cl_2). [l] $[\alpha]_D^{23}$ −46.1 (*c* 1.0, CH_2Cl_2). [m] The reaction was carried out at −78 °C for 1 h and then at −30 °C for 18 h.

with all the chiral ligands when the cationic rhodium complex $[Rh(COD)_2]BF_4$ was used. Neutral catalyst generated from DIOP and $[RhCl(COD)]_2$ gave primary alcohol **5a** as a main isomer (entry 5), which is as expected from the selectivity shown above.

High catalytic activity of the cationic rhodium/BINAP complex made it possible to carry out the asymmetric hydroboration at lower temperature. The enantioselectivity was dependent strongly on the reaction temperature. The reaction in THF at 25 °C, −30 °C, and −50 °C gave **4a** of 57.0%, 75.7%, and 81.0% ee, respectively (entries 1, 6, and 7). An attempt to carry out the reaction at −78 °C was unsuccessful because catecholborane was frozen and was not soluble in THF at the low temperature (entry 8). It was found that 1,2-dimethoxyethane (DME) is the solvent of choice for the hydroboration at the low temperature. Reaction at −78 °C for 2 h in the presence of 2 mol % of the rhodium catalyst gave 91% yield of **4a** with 96.2% ee (entry 12).

Table 5. Asymmetric Hydroboration of Styrene Derivatives with Catecholborane Catalyzed by Rhodium-(*R*)-BINAP Complex.[a]

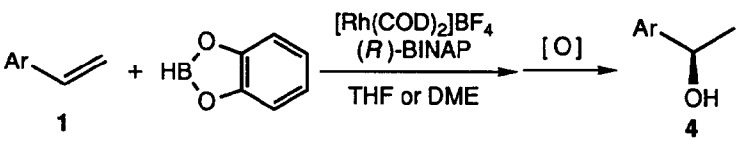
entry	olefin	solvent	temp (°C)	time (h)	yield[b] (%)	product (ratio)[c]		% ee[d] (config)[e]
1	**1b**: 4-Cl	THF	−50	1	82	**4b/5b**	(>99 / 1)	81.5 (*R*)
2[f]	**1b**: 4-Cl	DME	−78	6	98	**4b/5b**	(>99 / 1)	90.5 (*R*)[g]
3[f]	**1c**: 4-Me	DME	−78	2	77	**4c/5c**	(>99 / 1)	93.8 (*R*)[h]
4	**1d**: 4-MeO	THF	−30	0.5	74	**4d/5d**	(>99 / 1)	85.1 (*R*)
5	**1d**: 4-MeO	THF	−50	2	49	**4d/5d**	(>99 / 1)	86.1 (*R*)
6[f]	**1d**: 4-MeO	THF/DME[i]	−78	6	54	**4d/5d**	(>99 / 1)	88.5 (*R*)[j]
7[f]	**1e**: 3-Cl	DME	−78	2	99	**4e/5e**	(>99 / 1)	84.6 (*R*)[k,l]
8	**1f**: 2-Cl	THF	−50	1	30	**4f/5f**	(>99 / 1)	72.1 (*R*)[k,m]
9	**1g**: 2-MeO	THF	−30	0.5	84	**4g/5g**	(>99 / 1)	81.5 (*R*)[n]
10	**1h**: 2,4,6-Me3	THF	−30	16	15	**4h/5h**	(1 / >99)	–
11	**1i**: 2-naphthyl	THF	−30	24	36	**4i/5i**	(44 / 56)	13.2 (*S*)[o]
12	**1j**: ferrocenyl	THF	−30	24	81	**4j/5j**	(>99 / 1)	58[p] (*R*)[p]
13	**6a**: (*E*)-β-Me	THF	25	34	65	**7a/8a**	(>99 / 1)	42.3 (*S*)[q]
14	**6b**: (*Z*)-β-Me	THF	25	48	58	**7a/8a**	(>99 / 1)	18.1 (*S*)[r]
15	**6c**: (*E*)-β-Ph	THF	25	50	48	**7c**	–	16.4 (*S*)[s]
16	**6d**: indene	THF	25	3	65	**7d/8d**	(93 / 7)	13.1 (*S*)[t]
17	**9a**: α-Me	THF	25	3.5	27	**10a/11a**	(39 / 61)	19.2[u] (*S*)[u]
18	**9b**: α-Et	THF	25	41	50	**10b/11b**	(1 / >99)	46.5[v] (*S*)[v]
19	**15**: norbornene	THF	25	1	61	**16**	(1 / >99)[w]	14.8[x] (2*S*)[x]

[a] All reactions were carried out in the presence of 1 mol % of cationic rhodium complex generated from $[Rh(COD)_2]BF_4$ and (*R*)-BINAP, unless otherwise noted. Olefin/catecholborane/$[Rh(COD)_2]BF_4$/BINAP = 1.0/1.1/0.010/0.011. [b] Isolated yield by preparative TLC on silica gel. [c] The ratios were calculated from isolated yields of the products. [d] Determined by HPLC analysis of 3,5-dinitrophenyl carbamate derivatives. [e] The absolute configurations were determined by comparison of the optical rotations with those reported for optically pure alcohols. (*R*)-(+)-**4b**: $[\alpha]_D^{21}$ +49.9 (*c* 2, Et_2O) (ref 19). (*R*)-(+)-**4c**: α_D^{20} +56.0 (neat, 1 dm) (ref 20). (*R*)-(+)-**4d**: α_D +45.2 (neat, 1 dm) (ref 21). (*S*)-(−)-**4g**: $[\alpha]_D$ −59 (*c* 1.18, toluene) (ref 22). (*S*)-(−)-**4i**: $[\alpha]_D$ −41.5 (*c* 4.92, EtOH) (ref 23). (*S*)-(+)-**4j**: $[\alpha]_D^{25}$ +29.3 (*c* 1.7, benzene) (ref 24). (*S*)-(−)-**7a**: $[\alpha]_D$ −45.45 (*c* 5.15, $CHCl_3$) (ref 23, 25). (*R*)-(−)-**7c** (65% ee) $[\alpha]_D^{23}$ −36.7 (*c* 1, EtOH) (ref 26). (*S*)-(−)-**7d**: $[\alpha]_D^{22}$ −32.98 (*c* 3, $CHCl_3$) (ref 23). (*S*)-(−)-**11a** was $[\alpha]_D^{17}$ −17.5 (*c* 0.476, benzene) (ref 27). (*R*)-(−)-**11b**: $[\alpha]_D^{22}$ −21.0 (*c* 1.01, EtOH) (ref 28). (1*S*, 2*S*, 4*R*)-(−)-*exo*-**16**: $[\alpha]_D^{25}$ −3.14 (*c* 3.1, $CHCl_3$) (ref 29). [f] Reaction with 2 mol % of the catalyst. [g] $[\alpha]_D^{21}$ +46.1 (*c* 1.0, Et_2O). [h] $[\alpha]_D^{25}$ +51.6 (*c* 1.0, $CHCl_3$). [i] THF/DME = 1/3. [j] $[\alpha]_D^{20}$ +47.2 (*c* 1.0, $CHCl_3$). [k] Assigned by similarity in elution order in the HPLC analysis. [l] $[\alpha]_D^{20}$ +36.7 (*c* 1.0, $CHCl_3$). [m] $[\alpha]_D^{20}$ +22.4 (*c* 1.1, $CHCl_3$). [n] $[\alpha]_D^{20}$ +48.9 (*c* 1.1, toluene). [o] $[\alpha]_D^{20}$ −7.5 (*c* 0.1, EtOH). [p] The value was calculated from the optical rotation of **4j**, $[\alpha]_D^{25}$ −17.0 (*c* 1.1, benzene). [q] $[\alpha]_D^{20}$ −20.6 (*c* 1.0, $CHCl_3$). [r] $[\alpha]_D^{20}$ −9.6 (*c* 1.0, $CHCl_3$). [s] $[\alpha]_D^{23}$ +10.6 (*c* 1.0, EtOH). [t] $[\alpha]_D^{22.5}$ −3.81 (*c* 1.2, $CHCl_3$). [u] Enantiomeric excess of 2-phenyl-1-propanol (**11a**), $[\alpha]_D^{17}$ −4.0° (*c* 0.9, benzene). [v] Enantiomeric excess of 2-phenyl-1-butanol (**11b**), $[\alpha]_D^{22}$ +8.0 (*c* 1.1, EtOH). [w] The ratio between *exo*-**16** and *endo*-**16**. [x] Enantiomeric excess of *exo*-**16**, $[\alpha]_D^{25}$ −1.0 (*c* 1.1, $CHCl_3$).

Preformed phosphine-rhodium complex, [Rh(COD)((*R*)-BINAP)]BF_4, exhibited almost the same selectivity as the in situ catalyst prepared by mixing [$Rh(COD)_2$]BF_4 with (*R*)-BINAP (entry 13). The hydroboration product, (*R*)-1-phenylethylborane **2a**, could be isolated as a chemically pure sample ($[\alpha]_D^{20}$ –55.6 (c 1.7, benzene), 93.5% ee), before oxidation, by distillation of the reaction mixture without loss of the enantiomeric purity. The enantioselectivity in DME is generally a little higher than in THF, though the reaction is slower in DME (entries 6-11).

Mono-substituted styrenes on the phenyl ring **1b-g** were transformed efficiently into the corresponding (*R*)-1-arylethanols **4b-g** by the catalytic asymmetric hydroboration with the cationic rhodium/(*R*)-BINAP catalyst (Scheme 7). The regioselectivity forming secondary alkyl boranes was perfect (>99/1) for all the mono-substituted styrenes (entries 1-9 in Table 5). The enantiomeric purity of the alcohols **4b**, **4c**, and **4d** obtained for the reaction of para-substituted styrenes at –78 °C ranged between 89% and 94% ee, indicating that the functional groups at the para-position do not have a great influence on the enantioselectivity. High selectivity was also observed in the reaction of meta-substituted styrene **1e** (entry 7), though substituents at ortho-position lowered the selectivity (entries 8 and 9). Styrenes **6a-d**, which are substituted at β position, did not undergo the catalytic hydroboration at such a low temperature as –30 °C, and the temperature of 25 °C was required to make the reaction proceed in a reasonable rate. The enantiomeric purities of the alcohols **7a-d** were not so high as those of **4**, probably due to the relatively high reaction temperature (entries 13-16). It is noteworthy that alcohols **7a-d** have (*S*) configuration, which is opposite to that of alcohols **4** obtained by the reaction of substituted styrenes on the phenyl. Primary alcohols **11** were formed in preference to tertiary alcohols **10** in the reaction of α-substituted styrenes **9** (entries 17 and 18). The regioselectivity toward benzylic boranes with the cationic rhodium/BINAP catalyst is lower than that with the dppb complex (see Table 3). Optically active primary alcohol **11b** was obtained by the catalytic hydroboration though the enantioselectivity was not sufficiently high.

Scheme 7



Experimental Section

General. Optical rotations were measured with a Perkin-Elmer 241 or JASCO DIP-370 polarimeter. ^1H NMR spectra were measured with a Varian VXR-200 (200 MHz) or JEOL JNM-EX-90 (90 MHz) spectrometer. HPLC analysis were performed on a Shimadzu LC-6A or LC-9A liquid Chromatograph system.

Materials. Catecholborane which was commercially available from Aldrich Chemical Co. was distilled under reduced pressure (bp 76-77 °C/100 mmHg[9]) before use. PPh_3, dppb, (+)-DIOP,[17] (*S*,*S*)-chiraphos,[15] (*R*)-BINAP,[14] $RhCl(PPh_3)_3$ from Aldrich Chemical Company, Inc., and (*R*)-(*S*)-BPPFA[16] from Kanto Chemical Co. Inc. were commercially available. Rhodium complexes [$Rh(COD)_2$]BF_4,[15] [$Rh(COD)_2$]ClO_4,[15] [$RhCl(COD)]_2$,[15] [Rh(COD)(dppb)]BF_4,[15] and [Rh(COD)((*R*)-BINAP)]BF_4[30] were prepared in a similar manner to the reported procedures. THF, dimethoxyethane (DME), benzene, and toluene were distilled from sodium benzophenone ketyl or lithium aluminum hydride under nitrogen.

Preparation of 2-Methoxystyrene (1g). To a solution of 1.53 g (11.2 mmol) of 2-methoxybenzaldehyde in 15 ml of dry ether was added dropwise at room temperature 16 ml (13.6 mmol) of 0.85 M ether

solution of trimethylsilylmethylmagnesium chloride under a nitrogen atmosphere and stirring was continued for 30 min. The mixture was quenched by addition of 10 ml of 30% aqueous H_2SO_4 with vigorous stirring. After continuous stirring over 20 min, the ether layer was separated and was washed with aqueous NaOH and aqueous NH_4Cl. A small amount of 4-*tert*-butylcatechol was added to inhibit the polymerization. The layer was dried over $MgSO_4$ and concentrated. The residue was purified by bulb-to-bulb distillation (bath temp. 60 °C/2.0 mmHg) to give 1.34 g (9.96 mmol, 89%) of 2-methoxystyrene (**1g**). ^1H NMR ($CDCl_3$/TMS) δ 3.85 (s, 3 H), 5.26 (dd, J = 11.1 and 1.7 Hz, 1 H), 5.73 (dd, J = 17.7 and 1.5 Hz, 1 H), 6.80-7.15 (m, 3 H), 7.24 (td, J = 7.8 and 1.9 Hz, 1 H), 7.47 (dd, J = 7.7 and 1.7 Hz, 1 H).

Catalytic Hydroboration with Catecholborane. General procedure. All the reactions were carried out under argon or nitrogen atmosphere. A mixture of rhodium complex (Rh = 0.01 mmol) and phosphine ligand (Rh/P = 1/2.2) in dry THF (1 ml) was stirred at 25 °C for 10-30 min, and olefin (1.0 mmol) was added. Catecholborane (132 mg, 1.1 mmol) was added at 25 °C and the mixture was allowed to stir at the same temperature for a given period (see Tables 1-3). The mixture was cooled with an ice bath and quenched with methanol (2 ml). After addition of 3 M aqueous NaOH (2.4 ml) and 30% aqueous H_2O_2 (0.24 ml, 2.2 mmol), the mixture was allowed to warm to room temperature over 3 h under vigorous stirring, and was extracted with ether. The organic layer was washed with 2 portions of 1 M aqueous NaOH and aqueous NH_4Cl and was dried over $MgSO_4$. Preparative TLC of the residue on silica gel (hexane/ether = 1/1) gave pure products. Experimental results are summarized in Tables 1-3. ^1H NMR ($CDCl_3$/TMS) spectra for the products are shown below. **1-Phenylethanol (4a)**: δ 1.49 (d, J = 6.4 Hz, 3 H), 1.91 (bs, 1 H), 4.89 (q, J = 6.4 Hz, 1 H), 7.2-7.4 (m, 5 H). **2-Phenylethanol (5a)**: δ 1.63 (bs, 1 H), 2.86 (t, J = 6.6 Hz, 2 H), 3.84 (t, J = 6.6 Hz, 2 H), 7.15-7.4 (m, 5 H). **1-(4-Chlorophenyl)ethanol (4b)**: δ 1.46 (d, J = 6.6 Hz, 3 H), 1.96 (bs, 1 H), 4.86 (q, J = 6.6 Hz, 1 H), 7.25-7.35 (m, 4 H). **1-(4-Methylphenyl)ethanol (4c)**: δ 1.47 (d, J = 6.5 Hz, 3 H), 1.86 (bs, 1 H), 2.34 (s, 3 H), 4.85 (q, J = 6.5 Hz, 1 H), 7.2-7.3, 7.3-7.4 (m, 4 H). **1-(4-Methoxyphenyl)ethanol (4d)**: δ 1.47 (d, J = 6.4 Hz, 3 H), 1.87 (bs, 1 H), 3.80 (s, 3 H), 4.84 (q, J = 6.4 Hz, 1 H), 6.8-6.95, 7.25-7.35 (m, 4 H). **1-(3-Chlorophenyl)ethanol (4e)**: δ 1.48 (d, J = 6.5 Hz, 3 H), 1.94 (bs, 1 H), 4.87 (q, J = 6.5 Hz, 1 H), 7.15-7.3, 7.35-7.45 (m, 4 H). **1-(2-Chlorophenylethanol (4f)**: δ 1.48 (d, J = 6.6 Hz, 3 H), 2.08 (bs, 1 H), 5.28 (q, J = 6.6 Hz, 1 H), 7.1-7.4, 7.5-7.65 (m, 4 H). **1-(2-Methoxyphenyl)ethanol (4g)**: δ 1.51 (d, J = 6.7 Hz, 3 H), 2.46 (bs, 1 H), 3.87 (s, 3 H), 5.10 (q, J = 6.7 Hz, 1 H), 6.8-7.0 7.2-7.4 (m, 4 H). **1-(2,4,6-Trimethylphenyl)ethanol (4h)**: δ 1.51 (d, J = 6.8 Hz, 3 H), 1.73 (bs, 1 H), 2.24 (s, 3 H), 2.41 (s, 6 H), 5.35 (q, J = 6.8 Hz, 1 H), 6.81 (s, 2 H) **2-(2,4,6-Trimethylphenyl)ethanol (5h)**: δ 1.69 (bs, 1 H), 2.24 (s, 3 H), 2.31 (s, 6 H), 2.91 (t, J = 7.5 Hz, 2 H), 3.72 (t, J = 7.5 Hz, 2 H), 6.84 (s, 2 H). **1-(2-Naphthyl)ethanol (4i)**: δ 1.57 (d, J = 6.4 Hz, 3 H), 1.90 (bs, 1 H), 5.06 (q, J = 6.4 Hz, 1 H), 7.4-7.55, 7.75-7.85 (m, 7 H). **2-(2-Naphthyl)ethanol (5i)**: δ 1.48 (bs, 1 H), 3.03 (t, J = 6.5 Hz, 2 H), 3.94 (t, J = 6.5 Hz, 2 H), 7.3-7.55, 7.65-7.85 (m, 7 H). **1-Ferrocenylethanol (4j)**: δ 1.44 (d, J = 6.4 Hz, 3 H), 1.86 (bs, 1 H), 4.05-4.25 (m, 4 H), 4.20 (s, 5 H), 4.45-4.55 (m, 1 H). **2-Ferrocenylethanol (5j)**: δ 1.55 (bs, 1 H), 2.56 (t, J = 6.4 Hz, 2 H), 3.72 (t, J = 6.4 Hz, 2 H), 4.1-4.3 (m, 9 H). **1-Phenyl-1-propanol (7a)**: δ 0.92 (t, J = 7.4 Hz, 3 H), 1.67 (bs, 1 H), 1.65-1.95 (m, 2 H), 4.60 (t, J = 6.6 Hz, 1 H), 7.2-7.4 (m, 5 H). **1-Phenyl-2-propanol (8a)**: δ 1.25 (d, J = 6.2 Hz, 3 H), 1.58 (bs, 1 H), 2.6-2.9 (m, 2 H), 3.95-4.15 (m, 1 H), 7.15-7.45 (m, 5 H). **1,2-Diphenylethanol (7c)**: δ 1.88 (bs, 1 H), 2.9-3.15 (m, 2 H), 4.90 (dd, J = 8.0 and 5.4 Hz,1 H), 7.1-7.4 (m, 10 H). **1-Indanol (7d)**: δ 1.8-2.0 (m, 1 H), 2.17 (bs, 1 H), 2.35-2.55 (m, 1 H), 2.65-2.95 (m, 1H),

2.95-3.15 (m, 1 H), 5.19 (t, J = 6.1 Hz, 1 H), 7.1-7.3, 7.3-7.45 (m, 4 H). **2-Indanol (8d)**: δ 2.23 (bs, 1 H), 2.9-3.3 (m, 4 H), 4.63 (m, 1 H), 7.1-7.3 (m, 4 H). **1-Phenyl-2-propanol (10a)**: δ 1.58 (s, 6 H), 1.71 (bs, 1 H), 7.15-7.4, 7.45-7.55 (m, 5 H). **2-Phenyl-1-propanol (11a)**: δ 1.28 (d, J = 7.0 Hz, 3 H), 1.48 (bs, 1 H), 2.96 (sextet, J = 6.9 Hz, 1 H), 3.71 (d, J = 6.8 Hz, 2 H), 7.15-7.4 (m, 5 H). **1-Phenyl-2-butanol (10b)**: δ 0.80 (t, J = 7.4 Hz, 3 H), 1.55 (s, 6 H), 1.69 (s, 1H), 1.75-1.95 (m, 2 H), 7.2-7.5 (m, 5 H). **2-Phenyl-1-butanol (11b)**: δ 0.83 (t, J = 7.4 Hz, 3 H), 1.43 (bs, 1 H), 1.40-1.85 (m, 2 H), 2.68 (qd, J = 8.8 and 5.8 Hz, 1 H), 3.65-3.85 (m, 2 H), 7.1-7.4 (m, 5 H). **2-Octanol (13)**: δ 0.8-1.0 (m, 3 H), 1.19 (d, J = 6.4 Hz, 3 H), 1.2-1.5, 1.5-1.7 (m, 11 H), 3.78 (sextet, J = 6.4 Hz, 1 H). **1-Octanol (14)**: δ 0.8-1.0 (m, 3 H), 1.1-1.5 (m, 11 H), 1.5-1.7 (m, 2 H), 3.64 (t, J = 6.5 Hz, 2 H). ***exo*-Norborneol (16)**: δ 0.9-1.2, 1.2-1.75 (m, 9 H), 2.1-2.18 (m, 1 H), 2.2-2.3 (m, 1 H), 3.76 (bd, J = 8.0 Hz, 1 H).

Catalytic Asymmetric Hydroboration of Styrenes with Catecholborane. General Procedure. The hydroboration was carried out in essentially the same manner as above. The alcohols obtained were converted into 3,5-dinitrophenyl carbamates **20** by the following procedure, which were analyzed by HPLC. A mixture of alcohol (2 mg), 3,5-dinitrophenyl isocyanate (5 mg), and pyridine (5 μl) in toluene (0.5 ml) was stirred at 60-70 °C for 30 min. The mixture was evaporated, diluted with chloroform, and filtered. The filtrate was analyzed by HPLC with a chiral stationary phase column (Sumichiral OA-4100 (hexane/dichloromethane/ethanol = 100/20/1) for **4**, **7**, and **16**, and Sumichiral OA-1100 (hexane/dichloromethane/ethanol = 100/20/1) for **11**). Reaction conditions and results including absolute configurations, specific rotations, and enantiomeric purities of the products are summarized in Tables 4 and 5. ^{1}H NMR data are shown above.

Isolation of (*R*)-1-Phenylethyl-1,3,2-benzodioxaborole ((*R*)-2a). A mixture of 92.4 mg (0.10 mmol) of [Rh(COD)((*R*)-BINAP)]BF_4 and 525 mg (5.0 mmol) of styrene (**1a**) in dry DME (2 ml) was cooled to –78 °C under nitrogen, and then catecholborane (664 mg, 5.5 mmol) was added. The mixture was stirred at the same temperature for 2 h, and concentrated under reduced pressure. Bulb-to-bulb distillation (bath temp. 110-130 °C/0.15 mmHg) gave 1.12 g (4.99 mmol, 99%) of (*R*)-1-phenylethyl-1,3,2-benzodioxaborole ((*R*)-**2a**). The regioisomer **3a** was not detected by ^{1}H NMR analysis. ^{1}H NMR ($CDCl_3$/TMS) δ 1.59 (d, J = 7.5, 3 H), 2.98 (q, J = 7.5 Hz, 1 H), 6.95-7.45 (m, 9 H). Anal. Calcd. for $C_{14}H_{13}BO_2$: C, 75.05; H, 5.85. Found: C, 75.02; H, 5.73. $[\alpha]_D^{20}$ –55.6 (c 1.7, benzene), (*R*)-93.5% ee.

Oxidation of (*R*)-2a into (*R*)-1-Phenylethanol (4a). To a solution of 228 mg (1.0 mmol) of **2a** obtained above in 1 ml of THF was added at 0 °C 2.4 ml of 3 M aqueous NaOH and 0.24 ml of 30% aqueous H_2O_2,. The mixture was stirred at room temperature for 3 h and extracted with ether. The organic layer was washed with 2 portions of 1 M aqueous NaOH and aqueous NH_4Cl, dried over $MgSO_4$, and concentrated. The residue was purified by preparative TLC on silica gel (hexane/ether = 1/1) to give 115 mg (0.939 mmol, 92%) of (*R*)-**4a**. $[\alpha]_D^{23}$ +48.3 (c 1.0, dichloromethane) ((*S*)-**4a**: $[\alpha]_D^{22}$ –52.5 (c 2.3, dichloromethane) (ref 18)). The enantiomeric purity of **2a** was determined to be 93.5% by HPLC analysis of its 3,5-dinitrophenyl carbamate **20a** (see above).

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