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A new chiral catalytic source with an N–P=O structural framework containing a proximal hydroxyl group for the borane-mediated asymmetric reduction of prochiral ketones

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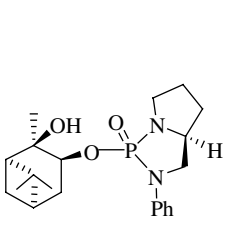
Abstract—(5*S*)-2-[(1*R*,2*R*,3*S*,5*R*)-2-Hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yloxy]-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane has been successfully employed as a novel chiral catalytic source (4 mol %) for borane-mediated asymmetric reduction of prochiral ketones thus providing the resulting secondary alcohols with up to 96% enantiomeric excess.

1. Introduction

Boron based chiral reducing agents/catalysts occupy a special place in chiral chemistry, particularly in asymmetric reductions, because of their extensive use in efficiently and conveniently transforming prochiral ketones into the corresponding secondary alcohols with high enantioselectivities.[1–11] The recent elegant work of Wills and coworkers[12–17] on the applications of molecules containing the N–P=O structural framework as novel chiral catalysts for borane-mediated asymmetric reduction of prochiral ketones has generated a new interest[18–21] in the chemistry of asymmetric reductions. In continuation of our work in the development of novel chiral catalytic sources containing N–P=O structural framework for borane-mediated asymmetric reductions,[20,21] we herein report the application of (5*S*)-2-[(1*R*,2*R*,3*S*,5*R*)-2-hydroxy-2,6,6-trimethylbicyclo[3.1.1]-heptan-3-yloxy]-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane **1** as a catalytic source for the borane-mediated asymmetric reduction of prochiral ketones to provide the resulting secondary alcohols in 59–96% enantiomeric excess.

Recently, we have reported the applications of (1*R*,2*R*)-1,2-bis[{(5*S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo-[3.3.0]octan-2-yl}methylamino]cyclohexane **2**, 1,4-bis-[(5*S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]-octan-2-yl]piperazine **3** and (2*S*,5*S*)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo[3.3.0]octane **4** as useful chiral catalysts/sources for borane-mediated asymmetric reduction of prochiral α-halo ketones.[20,21] The work of Wills et al.,[12,22] Buono et al.,[18,23] on the role of a proximal hydroxyl group in the catalysts in the asymmetric reduction of prochiral ketones, has led us to design a catalyst containing such a proximal hydroxyl group. We planned to prepare the catalyst **1** and study its catalytic applications in the reduction of prochiral ketones.



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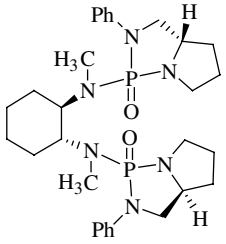

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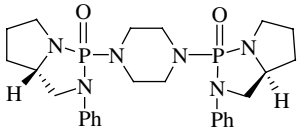

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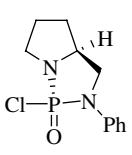

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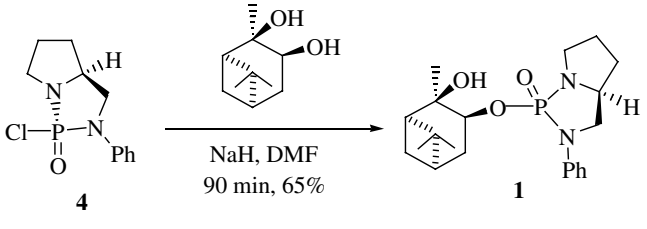
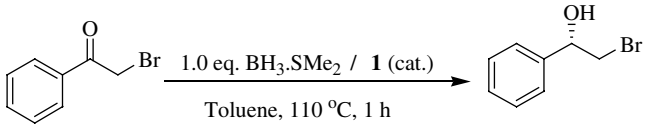
2. Results and discussion

The desired catalyst **1** was prepared via treatment of **4** with (−)-pinane-2,3-diol in the presence of NaH (Eq. 1). We first examined the borane-mediated asymmetric reduction of phenacyl bromide under the influence of **1** with different catalytic amounts (Eq. 2, Table 1). The best results were seen when phenacyl bromide **5a** was treated with borane-dimethyl sulfide under the influence of **1** (4 mol%) in refluxing toluene for 1 h, providing the desired alcohol (*S*)-2-bromo-1-phenylethanol **6a** in 88% yield with 91% enantiomeric excess.



4 **1** (1)



5a **6a** (2)

Table 1. Asymmetric reduction of phenacyl bromide **5a**[a]

Entry	Catalyst **1** (mol%)	Yield (%)[b] **6a**	Enantiomeric purity (%)[c] **6a**	Configuration[d]
1	2	81	71	*S*
2	3	80	87	*S*
3	**4**	**88**	**91**	***S***
4	5	80	89	*S*
5	7	84	87	*S*
6	10	86	83	*S*

[a] All reactions were carried out on a 0.5 mM scale of phenacyl bromide with 0.5 mM of $BH_3{\cdot}SMe_2$ in the presence of **1** in toluene for 1 h at 110 °C.

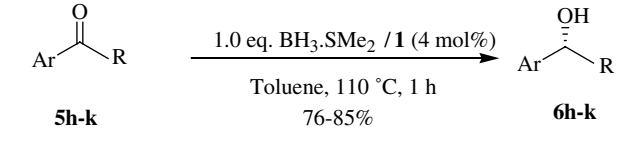
[b] Isolated yields of alcohols after purification by column chromatography (silica gel, 5% ethyl acetate in hexanes).

[c] Determined by HPLC analysis using the chiral column, Chiralcel-OD.

[d] The absolute configuration was assigned by comparison of the sign of the specific rotation with that of the reported molecule.[24]

We then employed a representative class of prochiral α-halo ketones **5b–g** for a borane-mediated asymmetric reduction under the catalytic influence of the molecule **1** (4 mol%) to provide the resulting secondary alcohols **6b–g** with high enantiomeric excesses (86–96%) (Eq. 3, Table 2). Enantiomeric excesses of the chiral alcohols **6a–d** were determined by HPLC analysis using the chiral column (Chiralcel-OD) with reference to the corresponding racemic alcohols while the enantiomeric purities of alcohols **6e–g** were determined by ^{1}H NMR analysis of their acetates in the presence of a chiral shift reagent, [Eu(hfc)$_3$], with reference to their corresponding racemic acetates.

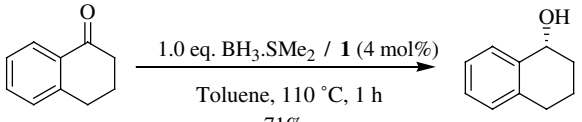
With a view to examine the catalytic efficiency of **1**, we also performed the reduction of acetophenone **5h** under the influence of **1** (4 mol%) with $BH_3{\cdot}SMe_2$. The resulting (*R*)-1-phenylethanol **6h** was obtained in 63% enantiomeric purity. To understand the applicability of this catalyst **1**, we subjected the representative prochiral ketones **5i–l** to a borane-mediated reduction under the influence of catalyst **1** (4 mol%). The resulting secondary alcohols **6i–l** were obtained in 59–67% enantiomeric excesses (Eqs. 4 and 5, Table 3). The enantiomeric excesses of the chiral alcohols **6h–l** were determined by HPLC analysis using the chiral column [Chiralcel-OD (**6h**, **i**, **k**, **l**) or Chiralcel-OD-H (**6j**)] with reference to the corresponding racemic alcohols. From these studies it is quite clear that α-halo ketones provide much better enantioselectivities than simple aryl alkyl ketones.



5h-k **6h-k**

R = Me, Et, Pr
Ar = phenyl, naphth-1-yl

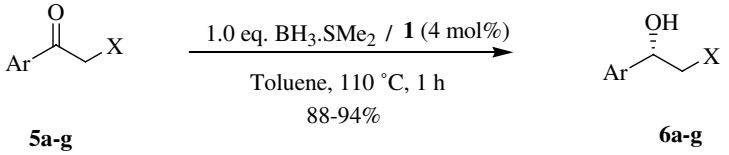
59-67% ee (4)



5l **6l**

70% ee (5)

It is worth comparing these results (for reduction of α-halo ketones) with those of our earlier catalysts.



5a-g **6a-g**

X = Br, Cl
Ar = phenyl,4-methylphenyl, 4-bromophenyl, 4-chlorophenyl, 4-nitrophenyl

86-96% ee (3)

Table 2. Asymmetric reduction of prochiral α-halo ketones[a]

Substrate	Ar	X	Product	Yield (%)[b]	$[\alpha]_D^{25}$	Conf.[c]	Ee (%)[d]
5a	Phenyl	Br	**6a**	88	+41.5 (*c* 1.2, $CHCl_3$)	*S*	91
5b	Phenyl	Cl	**6b**	91	+42.1 (*c* 1.0, C_6H_{12})	*S*	86
5c	4-Methylphenyl	Br	**6c**	94	+39.9 (*c* 1.1, $CHCl_3$)	*S*	91
5d	4-Methylphenyl	Cl	**6d**	92	+44.0 (*c* 1.0, $CHCl_3$)	*S*	88
5e	4-Bromophenyl	Br	**6e**	89	+33.8 (*c* 2.4, $CHCl_3$)	*S*	96[e]
5f	4-Chlorophenyl	Br	**6f**	92	+39.0 (*c* 1.0, $CHCl_3$)	*S*	89[e]
5g	4-Nitrophenyl	Br	**6g**	90	+33.2 (*c* 1.0, $CHCl_3$)	*S*	92[e]

[a] All reactions were carried out on a 1 mM scale of α-halo ketone with 1 mM of $BH_3{\cdot}SMe_2$ in the presence of **1** (4 mol %) in toluene for 1 h at 110 °C.
[b] Isolated yields of alcohols after purification by column chromatography (silica gel, 5% ethyl acetate in hexanes).
[c] The absolute configuration was assigned by comparison of the signs of specific rotations with those reported.[20,21,24,25]
[d] Determined by HPLC analysis using the chiral column, Chiralcel-OD.
[e] Enantiomeric excesses were determined by ^{1}H NMR (200 MHz) analysis of the acetates in the presence of the chiral shift reagent, [Eu(hfc)$_3$], with reference to the corresponding racemic acetates.

Table 3. Enantioselective reduction of prochiral ketones[a]

Entry	Ketone	Product	Yield (%)[b]	$[\alpha]_D^{25}$	Conf.[c]	Ee (%)[d]
1	Acetophenone **5h**	**6h**	80	+29.0 (*c* 1.0, MeOH)	*R*	63
2	Propiophenone **5i**	**6i**	85	+30.7 (*c* 1.9, $CHCl_3$)	*R*	67
3	Butyrophenone **5j**	**6j**	83	+28.0 (*c* 0.7, benzene)	*R*	59[e]
4	1-Acenaphthone **5k**	**6k**	76	+50.3 (*c* 1.08, ether)	*R*	63
5	α-Tetralone **5l**	**6l**	71	−16.4 (*c* 0.75, MeOH)	*R*	70

[a] All reactions were carried out on a 1 mM scale of prochiral ketone with 1 mM of $BH_3{\cdot}SMe_2$ in the presence of **1** (4 mol %) in toluene for 1 h at 110 °C.
[b] Isolated yields of alcohols after purification by column chromatography (silica gel, 5% ethyl acetate in hexanes).
[c] The absolute configuration was assigned by the comparison of the signs of the specific rotations with those reported.[26–28]
[d] Enantiomeric excesses were determined by the HPLC analysis using the chiral column, Chiralcel-OD.
[e] Enantiomeric excess was determined by the HPLC analysis using the chiral column, Chiralcel-OD-H.

Though catalyst **3** offers slightly better enantioselectivities (90–95% ee), the reaction requires more catalyst (30 mol %).[20] The present catalyst **1** provides (86–96% ee with 4 mol % **1**) slightly better enantioselectivities than the chiral source **4** (81–91% ee with 5 mol % **4**).[21] From these comparisons it appears that proximal hydroxyl group has some advantage on borane-mediated asymmetric reductions of prochiral α-halo ketones.[29]

In an attempt to understand the mechanistic pathway of the reduction process, we attempted to recover the catalyst by carrying out the reduction of acetophenone (2 mM) with $BH_3{\cdot}SMe_2$ (2 mM) in the presence of catalyst **1** (0.08 mM). However, we found that the catalyst was not recoverable intact in the reaction as shown by the ^{31}P NMR spectrum of the reaction mixture, which showed broad signals at δ 80–115 whereas the ^{31}P NMR spectrum of the original catalyst showed a single peak at δ 19.88. To understand the nature of the catalyst we also treated **1** (0.1 mM) with $BH_3{\cdot}SMe_2$ (0.2 mM) in toluene (0.5 mL) for 10 min at reflux and recorded the ^{31}P NMR spectrum of the reaction mixture, which showed broad signals at δ 85–125. Since the enantioselectivities were also reasonably high in the case of acetophenone **5h** and the other ketones **5i**–**l**, it suggests that the diazaborolidine was not generated during the reaction process.[21,30] From these studies, it is clear that the catalyst was not intact, as it probably decomposed during the course of reaction. Though the nature of the catalyst and the reaction pathway are not clearly understood, we have developed a novel chiral catalytic source for borane-mediated asymmetric reductions of prochiral ketones, in particular α-halo ketones, to provide the resulting secondary alcohols in up to 96% enantiomeric excesses. Studies are currently underway to understand the mechanism of the reduction process.

3. Experimental

All melting points were recorded on a Superfit (India) capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Jasco-FT-IR model 5300 or Perkin–Elmer model 1310 spectrometer. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded in deuterochloroform ($CDCl_3$) on a Bruker-AC-200 spectrometer using tetramethylsilane (TMS, $\delta = 0$) as the internal standard. ^{31}P NMR (81 MHz) spectra were recorded on a Bruker-AC-200 spectrometer using 85% H_3PO_4 ($\delta = 0$ ppm) as the external standard. Elemental analyses were recorded on a Perkin–Elmer 240C-CHN analyzer. Mass spectra were recorded on an HP 5989 A (LC) (CI method) mass spectrometer. HPLC analyses of alcohols were carried out on a Shimadzu LC-10AD instrument using a chiral column (Chiralcel-OD or Chiralcel-OD-H). Optical rotations were measured on a Jasco DIP 370 digital polarimeter. We have previously prepared **6a**–**f** molecules and reported the spectral data.[20] The present spectral data (IR, ^{1}H NMR, ^{13}C NMR) of **6a**–**f** is in agreement with the earlier data.

3.1. (5*S*)-2-[(1*R*,2*R*,3*S*,5*R*)-2-Hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yloxy]-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane 1

To a stirred suspension of oil free NaH (2.0 mM, 48 mg) in DMF, was added slowly (1*R*,2*R*,3*S*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]heptane-2,3-diol (1.0 mM, 170 mg) at room temperature. After 5 min, the reaction mixture was cooled to 0 °C and (2*S*,5*S*)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane **4** (1.10 mM, 282.7 mg) added slowly. Then the reaction mixture was stirred for 90 min at room temperature and quenched with water and diluted with ether (10 mL). The organic layer was separated and the aqueous layer extracted with ether (3×20 mL). The combined organic layer was dried over anhydrous sodium sulfate and the solvent removed under reduced pressure. The crude product thus obtained, was purified by column chromatography (silica gel, 25% ethyl acetate in hexanes) followed by crystallization (40% ethyl acetate in hexanes) to afford the desired (5*S*)-2-[(1*R*,2*R*,3*S*,5*R*)-2-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yloxy]-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane as white needles (254 mg, 65%); mp 138–140 °C; $[\alpha]_D^{25}$ −22.3 (*c* 1.05, $CHCl_3$); IR (KBr): 3335, 1602, 1523, 1325, 1242 cm^{-1}; ^1H NMR: δ 0.89 (s, 3H), 1.31 (s, 3H), 1.41–2.57 (m, 13H), 2.95–3.12 (m, 1H), 3.16–3.48 (m, 3H), 4.02–4.21 (m, 1H), 4.53–4.78 (m, 2H), 6.58–6.72 (m, 3H), 7.08–7.23 (m, 2H); ^{13}C NMR: δ 24.17, 24.77 (d, $J = 9.1$ Hz), 26.01, 27.03, 28.72, 30.06 (d, $J = 8.9$ Hz), 34.89 (d, $J = 5.8$ Hz), 38.95, 39.64, 47.11 (d, $J = 3.5$ Hz), 48.88, 51.69 (d, $J = 8.2$ Hz), 58.81 (d, $J = 6.6$ Hz), 76.73, 86.22, 112.45, 116.67, 129.04, 148.35; ^{31}P NMR: δ 19.88; MS (LC-CI) (*m*/*z*): 390 $(M)^+$, 391 $(M+H)^+$; Anal. Calcd for $C_{21}H_{31}N_2O_3P$: C, 64.59; H, 8.00; N, 7.17. Found: C, 64.48; H, 8.05; N, 7.12%.

3.2. Representative procedure. Asymmetric reduction of phenacyl bromide: synthesis of (*S*)-2-bromo-1-phenylethanol 6a

To a stirred solution of (5*S*)-2-[(1*R*,2*R*,3*S*,5*R*)-2-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yloxy]-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **1** (0.04 mM, 15.6 mg) in toluene (5 mL) was added borane-dimethyl sulfide (1.0 mM, 76 mg) at room temperature and the reaction mixture heated to 110 °C. Once the temperature was stabilized at 110 °C, phenacyl bromide (1.0 mM, 199 mg) in toluene (2 mL) was added dropwise over a period of 10 min after which stirring continued for a further 1 h (monitored by TLC). The reaction mixture was then allowed to cool to room temperature and quenched with methanol. The solvent was removed under reduced pressure and the residue obtained, purified by column chromatography (silica gel, 5% ethyl acetate in hexanes) to provide the desired (*S*)-2-bromo-1-phenylethanol **6a** in 88% yield (177 mg) as a colorless oil; $[\alpha]_D^{25}$ +41.5 (*c* 1.2, $CHCl_3$) {lit.[24] $[\alpha]_D^{25}$ −39.0 (*c* 8.00, $CHCl_3$), (*R*)-configuration, 93% ee}; 91% ee, the enantiomeric excess was determined by HPLC using a chiral column [Chiralcel-OD, 90:10 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm, retention times: 8.12 min (*S*) and 9.60 min (*R*)].

3.3. (*S*)-2-Chloro-1-phenylethanol 6b

Colorless oil; yield 91%; $[\alpha]_D^{25}$ +42.1 (*c* 1.0, cyclohexane) {lit.[24] $[\alpha]_D^{25}$ −48.1 (*c* 1.73, cyclohexane), (*R*)-configuration, 100% ee}; 86% ee, the enantiomeric purity was determined by HPLC using a chiral column [Chiralcel-OD, 90:10 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm, retention times: 7.89 min (*S*) and 9.09 min (*R*)].

3.4. (*S*)-2-Bromo-1-(4-methylphenyl)ethanol 6c

Viscous liquid; yield 94%; $[\alpha]_D^{25}$ +39.9 (*c* 1.1, $CHCl_3$) {lit.[20] $[\alpha]_D^{25}$ +41.8 (*c* 1.0, $CHCl_3$), (*S*)-configuration, 95% ee}; 91% ee, the enantiomeric excess was determined by HPLC using a chiral column [Chiralcel-OD, 97.5:2.5 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm, retention times: 16.15 min (*S*) and 19.36 min (*R*)].

3.5. (*S*)-2-Chloro-1-(4-methylphenyl)ethanol 6d

Colorless oil; yield 92%; $[\alpha]_D^{25}$ +44.0 (*c* 1.0, $CHCl_3$) {lit.[20] $[\alpha]_D^{25}$ +47.2 (*c* 1.1, $CHCl_3$), (*S*)-configuration, 92% ee}; 88% ee, the enantiomeric excess was determined by HPLC using a chiral column [Chiralcel-OD, 97.5:2.5 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm, retention times: 14.64 min (*S*) and 16.80 min (*R*)].

3.6. (*S*)-2-Bromo-1-(4-bromophenyl)ethanol 6e

White solid; yield 89%; mp 71–72 °C; $[\alpha]_D^{25}$ +33.8 (*c* 2.4, $CHCl_3$) {lit.[25] $[\alpha]_D^{25}$ −31.0 (*c* 2.9, $CHCl_3$), (*R*)-configuration, 94% ee}; 96% ee, the enantiomeric excess was determined by ^1H NMR spectral analysis of the corresponding acetate in the presence of chiral shift reagent, $Eu(hfc)_3$, with reference to the racemic acetate.[20]

3.7. (*S*)-2-Bromo-1-(4-chlorophenyl)ethanol 6f

Colorless oil; yield 92%; $[\alpha]_D^{25}$ +39.0 (*c* 1.0, $CHCl_3$) {lit.[20] $[\alpha]_D^{25}$ +38.6 (*c* 1.15, $CHCl_3$), (*S*)-configuration, 91% ee}; 89% ee, the enantiomeric excess was determined by ^1H NMR spectral analysis of the corresponding acetate in the presence of chiral shift reagent, $Eu(hfc)_3$, with reference to the racemic acetate.[20]

3.8. (*S*)-2-Bromo-1-(4-nitrophenyl)ethanol 6g

Light yellow solid; yield 90%; mp 78–80 °C; $[\alpha]_D^{25}$ +33.2 (*c* 1.0, $CHCl_3$) {lit.[21] $[\alpha]_D^{25}$ +32.0 (*c* 1.0, $CHCl_3$), (*S*)-configuration, 91% ee}; 92% ee, the enantiomeric excess was determined by ^1H NMR spectral analysis of the corresponding acetate in the presence of chiral shift reagent, $Eu(hfc)_3$, with reference to the racemic acetate; IR (KBr): 3543 cm^{-1}; ^1H NMR: δ 2.77 (d, 1H, $J = 3.6$ Hz), 3.45–3.73 (m, 2H), 4.98–5.10 (m, 1H), 7.58 (d, 2H, $J = 8.6$ Hz), 8.23 (d, 2H, $J = 8.6$ Hz); ^{13}C NMR: δ 39.13, 72.68, 123.80, 127.01, 147.54, 147.83.

3.9. (*S*)-1-Acetoxy-2-bromo-1-(4-nitrophenyl)ethane

Light yellow solid; yield 75%; mp 102–105 °C; $[\alpha]_D^{25}$ +46.6 (*c* 0.9, $CHCl_3$); IR (KBr): 1751 cm^{-1}; ^1H NMR: δ 2.18 (s, 3H), 3.58–3.74 (m, 2H), 5.99–6.08 (m, 1H), 7.55 (d, 2H, $J = 8.6$ Hz) 8.25 (d, 2H, $J = 8.6$ Hz); ^{13}C NMR: 20.87, 33.38, 73.70, 124.00, 127.73, 144.61, 148.26, 169.56.

3.10. (*R*)-1-Phenylethanol 6h

Colorless oil; yield 80%; $[\alpha]_D^{25}$ +29.0 (*c* 1.0, MeOH) {lit.[26] $[\alpha]_D^{25}$ +44.12 (*c* 3.0, MeOH), (*R*)-configuration, 97% ee}; 63% ee, the enantiomeric excess was determined by HPLC using a chiral column [Chiralcel-OD, 95:5 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm, retention times: 8.76 min (*R*) and 10.72 min (*S*)]; IR (neat): 3362 cm^{-1}; ^1H NMR: δ 1.46 (d, 3H, $J = 6.8$ Hz), 2.10 (br s, 1H), 4.84 (q, 1H, $J = 6.8$ Hz), 7.18–7.41 (m, 5H); ^{13}C NMR: δ 25.11, 70.43, 125.45, 127.49, 128.54, 145.94.

3.11. (*R*)-1-Phenylpropan-1-ol 6i

Colorless oil; yield 85%; $[\alpha]_D^{25}$ +30.7 (*c* 1.9, $CHCl_3$) {lit.[26] $[\alpha]_D^{25}$ +43.03 (*c* 5.1, $CHCl_3$), (*R*)-configuration, 96% ee}; 67% ee, the enantiomeric purity was determined by HPLC using a chiral column [Chiralcel-OD, 95:5 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm, retention times: 8.32 min (*R*) and 10.05 min (*S*)]; IR (neat): 3373 cm^{-1}; ^1H NMR: δ 0.93 (t, 3H, $J = 7.0$ Hz), 1.68–1.93 (m, 3H), 4.61 (t, 1H, $J = 6.8$ Hz), 7.22–7.44 (m, 5H); ^{13}C NMR: δ 10.12, 31.85, 75.93, 126.02, 127.41, 128.35, 144.66.

3.12. (*R*)-1-Phenylbutan-1-ol 6j

Colorless oil; yield 83%; $[\alpha]_D^{25}$ +28.0 (*c* 0.7, benzene) {lit.[27] $[\alpha]_D^{25}$ −45.2 (*c* 4.81, benzene), (*S*)-configuration, 100% ee}; 59% ee, the enantiomeric excess was determined by HPLC using a chiral column [Chiralcel-OD-H, 95:5 hexanes/*i*-PrOH, 0.7 mL/min, 254 nm, retention times: 12.30 min (*R*) and 13.10 min (*S*)]; IR (neat): 3300 cm^{-1}; ^1H NMR: δ 0.93 (t, 3H, $J = 7.0$ Hz), 1.21–1.91 (m, 5H), 4.68 (t, 1H, $J = 6.6$ Hz), 7.19–7.40 (m, 5H); ^{13}C NMR: δ 13.93, 19.00, 41.23, 74.33, 125.93, 127.38, 128.36, 145.02.

3.13. (*R*)-1-(Naphth-1-yl)ethanol 6k

Colorless oil; yield 76%; $[\alpha]_D^{25}$ +50.3 (*c* 1.08, ether) {lit.[28] $[\alpha]_D^{25}$ +82.1 (*c* 1.0, ether), (*R*)-configuration, >99% ee}; 63% ee, the enantiomeric excess was determined by HPLC using a chiral column [Chiralcel-OD, 95:5 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm, retention times: 24.44 min (*S*) and 37.72 min (*R*)]; IR (neat): 3368 cm^{-1}; ^1H NMR: δ 1.64 (d, 3H, $J = 6.0$ Hz), 2.65 (br s, 1H), 5.59 (q, 1H, $J = 6.0$ Hz), 7.36–8.20 (m, 7H); ^{13}C NMR: 24.41, 67.04, 122.11, 123.28, 125.57, 126.04, 127.89, 128.94, 130.36, 133.89, 144.51.

3.14. (*R*)-1,2,3,4-Tetrahydronaphth-1-ol 6l

Colorless oil; yield 71%; $[\alpha]_D^{25}$ −16.4 (*c* 0.75, MeOH) {lit.[26] $[\alpha]_D^{25}$ −23.14 (*c* 1.3, MeOH), (*R*)-configuration, 94% ee}; 70% ee, the enantiomeric excess was determined by HPLC using a chiral column [Chiralcel-OD, 97.5:2.5 hexanes/*i*-PrOH, 0.4 mL/min, 254 nm, retention times 35.50 min (*S*) and 39.52 min (*R*)]; IR (neat): 3356 cm^{-1}; ^1H NMR: δ 1.45–2.14 (m, 5H), 2.61–2.92 (m, 2H), 4.70–4.92 (m, 1H), 7.04–7.33 (m, 3H), 7.38–7.56 (m, 1H); ^{13}C NMR: δ 18.84, 29.19, 32.21, 67.96, 126.02, 127.38, 128.60, 128.84, 137.00, 138.86.

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29. With a view to have a quick understanding of the influence of proximal hydroxyl group on the enantioselectivities, we have briefly compared our results with that of catalysts **A** (Wills),[22] **B**, and **C** (Buono).[18,23] The Wills catalyst **A** shows better enantioselectivities than our catalyst **1**. The Buono catalyst **B** offers better enantioselectivities in some cases than our catalyst **1** while our catalyst **1** shows better enantioselectivities than **B** in certain cases. However, the catalyst **C** and our catalyst **1** provide similar enantioselectivities. The Corey chemzyme **D**[31] offers better enantioselectivities than all these catalysts.
30. The reduction of acetophenone with $BH_3{\cdot}SMe_2$ in the presence of (*S*)-2-anilinomethylpyrrolidine (10 mol %) provided (*R*)-1-phenylethanol in 14% enantiomeric purity. Asami, M.; Sato, S.; Watanabe, H. *Chem. Lett.* **2000**, 990–991.
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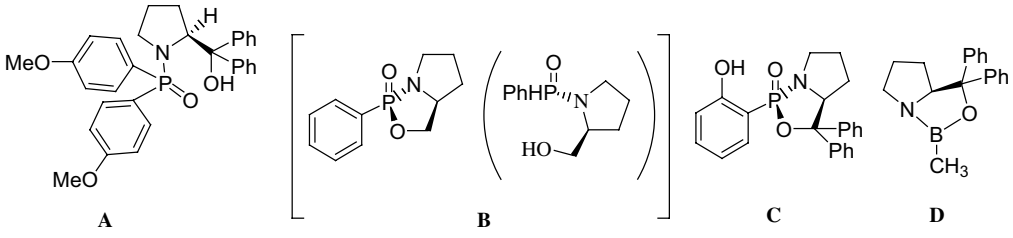

A **B** **C** **D**