

# Toward effective chiral catalysts containing the N–P=O structural framework for the borane-mediated asymmetric reduction of prochiral ketones

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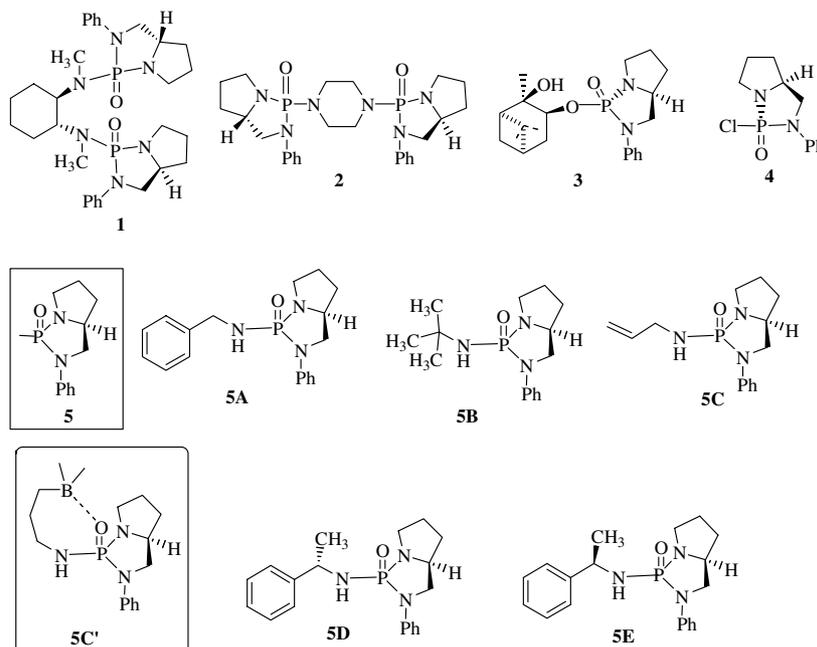
**Abstract**—Representative chiral catalysts containing the N–P=O structural framework having (5*S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane moiety with amino groups of varying steric requirements on phosphorus, have been synthesized and their applications in the borane-mediated asymmetric reduction of prochiral ketones described.

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## 1. Introduction

Since the ingenious introduction of chiral catalysts containing the N–P=O structural framework by Wills,<sup>1–8</sup> there has been an increasing interest in the

development of novel different classes of chiral catalysts containing the N–P=O structural framework for the borane-mediated asymmetric reduction of prochiral ketones<sup>9</sup> with the aim of providing simple and convenient methodologies for the synthesis of secondary



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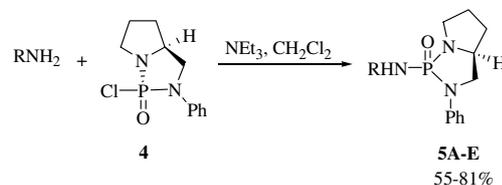
alcohols in high enantiomeric purities.<sup>10–16</sup> In continuation of our interest<sup>13,14,16</sup> in the borane-mediated asymmetric reduction of prochiral ketones, we herein report the synthesis and applications of representative chiral catalysts containing the N–P=O structural framework thus providing a simple methodology for the synthesis of secondary alcohols in up to 94% enantiomeric purities.

## 2. Results and discussion

We recently reported the synthesis and applications of four chiral catalysts, (1*R*,2*R*)-1,2-bis[*(5S)*-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octan-2-yl]methylamino]cyclohexane **1**, 1,4-bis[*(5S)*-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octan-2-yl]piperazine **2**, (*5S*)-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 **3**, and (2*S*,5*S*)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo[3.3.0]octane **4** for the borane-mediated asymmetric reduction of prochiral ketones thus providing a simple methodology for the synthesis of secondary alcohols in high enantiomeric purities.<sup>13,14,16</sup>

With a view to further understanding the role of bicyclic framework [(*5S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane moiety] **5** and the influence of amino groups of varying steric requirements on the phosphorus of this bicyclic framework **5** and also with a view for developing better catalysts for borane-mediated asymmetric reduction of prochiral ketones, we planned to synthesize and study the applications of three representative molecules (*5S*)-1,3-diaza-2-(benzylamino)-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **5A**, (*5S*)-1,3-diaza-2-(*t*-butylamino)-2-phospha-2-oxo-3-phenyl-

bicyclo[3.3.0]octane **5B** and (*5S*)-1,3-diaza-2-(allylamino)-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **5C**. The desired chiral catalysts, **5A–C**, were prepared via the reaction of **4** with appropriate amine (benzylamine, *t*-butylamine, and allylamine, respectively) (Eq. 1).

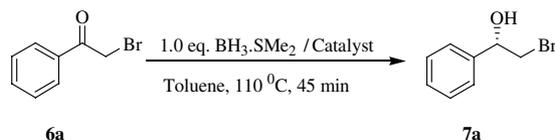


RNH<sub>2</sub> = benzylamine (18 h, rt), *t*-butylamine (12 h, reflux), allylamine (12 h, rt), (*S*)-1-phenylethylamine (2 d, rt), (*R*)-1-phenylethylamine (2 d, rt)

(1)

We first examined the borane-mediated asymmetric reduction of phenacyl bromide **6a** under the influence of the chiral molecule **5A** with different catalytic amounts. The best results were obtained when phenacyl bromide **6a** (1 mM) was treated with borane-dimethyl sulfide (1 mM) under the influence of **5A** (5 mol%) in refluxing toluene for 45 min, thus providing the desired alcohol (*S*)-2-bromo-1-phenylethanol **7a** with 89% enantiomeric purity in 82% yield (Eq. 2, Table 1). Similarly, we have also examined the potential of chiral molecule **5B** as a catalyst for the borane-mediated asymmetric reduction of phenacyl bromide **6a**. Thus, we have performed the reduction of phenacyl bromide **6a** in the presence of chiral phosphoramidate **5B** (5 mol% and also 10 mol%) in refluxing toluene for 45 min to provide the desired alcohol (*S*)-2-bromo-1-phenylethanol **7a** in 85% (with 5 mol%) and 84% (with 10 mol%) enantiomeric excess (Eq. 2, Table 1).

**Table 1.** Asymmetric reduction of phenacyl bromide **6a**<sup>a</sup>: a comparison of catalytic efficiency of **5A–E** and 1:1 mixture of **5D** and **5E**



(2)

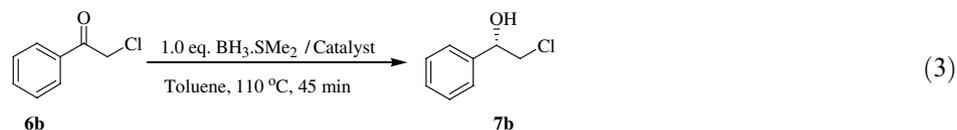
Catalyst	Mol%	Yield (%) <sup>b</sup> <b>7a</b>	Enantiomeric purity (%) <sup>c</sup> <b>7a</b>	Configuration <sup>d</sup>
<b>5A</b>	5	82	89	<i>S</i>
	10	87	86	<i>S</i>
	20	85	81	<i>S</i>
<b>5B</b>	5	86	85	<i>S</i>
	10	83	84	<i>S</i>
<b>5C</b>	5	84	81	<i>S</i>
	10	82	83	<i>S</i>
<b>5D</b>	<b>5</b>	<b>86</b>	<b>89</b>	<b><i>S</i></b>
	10	85	88	<i>S</i>
<b>5E</b>	5	81	88	<i>S</i>
	10	82	89	<i>S</i>
<b>5D</b> and <b>5E</b> (1:1)	5	80	85	<i>S</i>
	10	82	86	<i>S</i>

<sup>a</sup> All reactions were carried out on 1 mM scale of phenacyl bromide **6a** with 1 mM of BH<sub>3</sub>·SMe<sub>2</sub> in the presence of catalyst in toluene for 45 min at 110 °C.

<sup>b</sup> Yields of alcohol after purification by column chromatography (silica gel, 5% ethyl acetate in hexanes).

<sup>c</sup> Determined by HPLC analysis using the chiral column, Chiralcel-OD.

<sup>d</sup> Absolute configuration was assigned by comparison of the sign of the specific rotation with that reported.<sup>18</sup>

**Table 2.** Asymmetric reduction of phenacyl chloride **6b**<sup>a</sup>: a comparison of catalytic potential of **5A–E** and 1:1 mixture of **5D** and **5E**

Catalyst	Mol%	Yield (%) <sup>b</sup> <b>7b</b>	Enantiomeric purity (%) <sup>c</sup> <b>7b</b>	Configuration <sup>d</sup>
<b>5A</b>	5	82	84	<i>S</i>
<b>5B</b>	5	81	65	<i>S</i>
<b>5C</b>	5	83	61	<i>S</i>
<b>5D</b>	<b>5</b>	<b>85</b>	<b>87</b>	<b><i>S</i></b>
<b>5E</b>	5	83	84	<i>S</i>
<b>5D and 5E</b> (1:1)	5	80	82	<i>S</i>

<sup>a</sup> All reactions were carried out on 1 mM scale of phenacyl chloride **6b** with 1 mM of  $\text{BH}_3\cdot\text{SMe}_2$  in the presence of catalyst in toluene for 45 min at 110 °C.

<sup>b</sup> Yields of alcohol after purification by column chromatography (silica gel, 5% ethyl acetate in hexanes).

<sup>c</sup> Determined by HPLC analysis using the chiral column, Chiralcel-OD.

<sup>d</sup> Absolute configuration was assigned by comparison of the sign of the specific rotation with that reported.<sup>18</sup>

We have next employed (*S*)-1,3-diaza-2-(allylamino)-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **5C** containing the allylamino group on phosphorus in the (*S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane moiety **5** with a view to examine the influence of borane moiety **5C'**, which might have been formed due to the hydroboration of the olefinic group in (*S*)-1,3-diaza-2-(allylamino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane **5C**. Thus, we have carried out the reduction of phenacyl bromide **6a** in the presence of chiral phosphoramidate **5C** (5 mol% and 10 mol%) in refluxing toluene for 45 min to provide the desired alcohol (*S*)-2-bromo-1-phenylethanol **7a** in 81% (with 5 mol%) and 83% (with 10 mol%) enantiomeric excesses (Eq. 2, Table 1).

Next, we directed our studies to investigate the role of chiral amino group on phosphorus in the bicyclic moiety **5**. In this direction, we have first selected (*S*)-1-phenylethylamine as a chiral amine for our study. The required (*S*)-1,3-diaza-2-[(*S*)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **5D** was prepared via the treatment of (*2S,5S*)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo[3.3.0]octane **4** with (*S*)-1-phenylethylamine in the presence of triethylamine (Eq. 1).<sup>17</sup> Then we have first carried out the reduction of phenacyl bromide **6a** in the presence of chiral phosphoramidate **5D** (5 mol% as well as 10 mol%) in refluxing toluene for 45 min under the influence of  $\text{BH}_3\cdot\text{SMe}_2$ . In both cases the resulting secondary alcohol (*S*)-2-bromo-1-phenylethanol **7a** was obtained in similar enantioselectivities [89% (with 5 mol%) and 88% (with 10 mol%) enantiomeric excesses] (Eq. 2, Table 1).

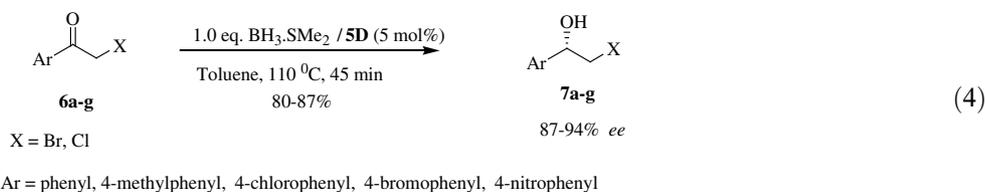
In order to examine the effect of (*R*)-1-phenylethylamino group on phosphorus in the bicyclic moiety **5**, we next prepared (*S*)-1,3-diaza-2-[(*R*)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **5E** via the treatment of (*2S,5S*)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo[3.3.0]octane **4** with (*R*)-1-phenylethylamine in the presence of triethylamine (Eq. 1).<sup>17</sup> We then carried out the reduction of phenacyl bromide

**6a** using 5 mol% and 10 mol% chiral phosphoramidate **5E** in refluxing toluene for 45 min under the influence of  $\text{BH}_3\cdot\text{SMe}_2$ . In both cases the resulting secondary alcohol (*S*)-2-bromo-1-phenylethanol **7a** was obtained in similar enantioselectivities (88% and 89% enantiomeric excess, respectively) (Eq. 2, Table 1).

With a view to examining the effect of combination of both the catalysts (*S*)-1,3-diaza-2-[(*S*)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **5D** and (*S*)-1,3-diaza-2-[(*R*)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **5E**, we carried out the reduction of phenacyl bromide **6a** in the presence of 1:1 mixture of chiral phosphoramidates **5D** and **5E** (2.5:2.5 mol% and 5:5 mol%) in refluxing toluene for 45 min under the influence of  $\text{BH}_3\cdot\text{SMe}_2$ . In both cases the resulting secondary alcohol (*S*)-2-bromo-1-phenylethanol **7a** was obtained in similar enantioselectivities that is, 85% (with 2.5 mol% **5D**+2.5 mol% **5E**) and 86% (with 5 mol% **5D**+5 mol% **5E**) enantiomeric excesses (Eq. 2, Table 1).

We also examined the applications of all these catalysts [**5A–E**, and **5D:5E** (1:1)] for the reduction of phenacyl chloride **6b** under the influence of  $\text{BH}_3\cdot\text{SMe}_2$  with a view to understand the selectivity when 'Cl' is present in the substrate instead of 'Br'. The desired secondary alcohol, (*S*)-2-chloro-1-phenylethanol **7b** was obtained in 61–87% enantiomeric excess (Eq. 3, Table 2).

From Tables 1 and 2 it is quite clear that chiral phosphoramidate (*S*)-1,3-diaza-2-[(*S*)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **5D** provided better enantioselectivities in the borane-mediated asymmetric reduction of phenacyl bromide **6a** and phenacyl chloride **6b** than the other phosphoramidates **5A–C** and **5E** and 1:1 mixture of **5D** and **5E**. We have, therefore, employed the catalyst **5D** for the reduction of a representative class of prochiral  $\alpha$ -halo ketones **6c–g** to provide the chiral secondary alcohols **7c–g** in high enantiomeric excesses (89–94%) (Eq. 4, Table 3). Enantiomeric excesses of the chiral alcohols **7c** and **7d**

**Table 3.** Asymmetric reduction of prochiral  $\alpha$ -halo ketones using the catalyst **5D**<sup>a</sup>

Substrate Ar	X	Product	Yield (%) <sup>b</sup>	$[\alpha]_D^{25}$	Conf. <sup>c</sup>	Ee (%) <sup>d</sup>
Phenyl <b>6a</b>	Br	<b>7a</b>	86	+39.4 (c 1.0, CHCl <sub>3</sub> )	S	89
Phenyl <b>6b</b>	Cl	<b>7b</b>	85	+42.8 (c 1.5, C <sub>6</sub> H <sub>12</sub> )	S	87
4-Methylphenyl <b>6c</b>	Br	<b>7c</b>	84	+38.9 (c 1.08, CHCl <sub>3</sub> )	S	91
4-Methylphenyl <b>6d</b>	Cl	<b>7d</b>	82	+44.9 (c 1.0, CHCl <sub>3</sub> )	S	89
4-Chlorophenyl <b>6e</b>	Br	<b>7e</b>	87	+39.9 (c 1.0, CHCl <sub>3</sub> )	S	90 <sup>e</sup>
4-Bromophenyl <b>6f</b>	Br	<b>7f</b>	80	+32.2 (c 0.9, CHCl <sub>3</sub> )	S	94 <sup>e</sup>
4-Nitrophenyl <b>6g</b>	Br	<b>7g</b>	82	+32.1 (c 1.0, CHCl <sub>3</sub> )	S	91 <sup>e</sup>

<sup>a</sup> All reactions were carried out on 1 mM scale of  $\alpha$ -halo ketone with 1 mM of BH<sub>3</sub>·SMe<sub>2</sub> in the presence of catalyst **5D** (5 mol %) in toluene for 45 min at 110 °C.

<sup>b</sup> Yields of alcohols after purification by column chromatography (silica gel, 5% ethyl acetate in hexanes).

<sup>c</sup> Absolute configuration was assigned by comparison of the sign of the specific rotation with that reported.<sup>13,16,18,19</sup>

<sup>d</sup> Determined by HPLC analyses using the chiral column, Chiralcel-OD.

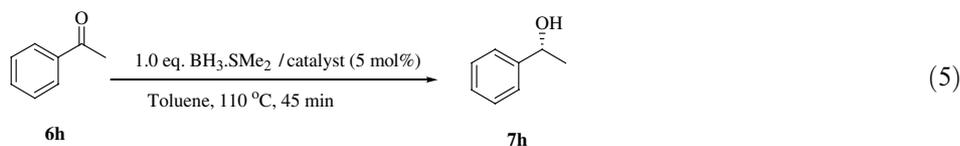
<sup>e</sup> Enantiomeric excesses were determined by <sup>1</sup>H NMR (200 MHz) spectral analyses of the acetates in the presence of the chiral shift reagent, Eu(hfc)<sub>3</sub>, with reference to the corresponding racemic acetates.

were determined by HPLC analyses using the chiral column, Chiralcel-OD with reference to the corresponding racemic alcohols. Enantiomeric excesses of alcohols **7e–g** were determined by <sup>1</sup>H NMR spectral analyses of their acetates in the presence of chiral shift reagent, Eu(hfc)<sub>3</sub>, with reference to their corresponding racemic acetates.

With a view to have a better understanding of the chiral directing potential of the catalysts **5A–E** and 1:1 mixture of **5D** and **5E**, we also performed the reduction of acetophenone **6h** under the influence of these catalysts (**5A–E** and 1:1 mixture of **5D** and **5E**) (5 mol %) in the presence of BH<sub>3</sub>·SMe<sub>2</sub>. The resulting alcohol **7h** was obtained in 52–72% enantiomeric excess (Eq. 5, Table 4). In this case also the chiral phosphoramidate (*S*)-1,

3-diaza-2-[(*S*)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **5D** provided better enantioselectivity (72% ee) than the other catalysts.

We next employed the chiral phosphoramidate **5D** for the reduction of representative class of aryl alkyl ketones **6i–n** with a view to understand the generality of the catalyst **5D**. The resulting secondary alcohols **7i–n** were obtained in 43–76% enantiomeric excess (Eqs. 6 and 7, Table 5). The enantiomeric excesses of alcohols **7i**, **7j**, and **7n** were determined by HPLC analyses using chiral column, Chiralcel-OD with reference to corresponding racemic alcohols. The enantiomeric excesses of alcohols **7k–m** were determined by HPLC analyses of their acetates using chiral column, Chiralcel-OJ-H with reference to corresponding racemic acetates.

**Table 4.** Borane-mediated asymmetric reduction of acetophenone **6h**<sup>a</sup>: a comparison of catalytic potential of molecules **5A–E** and 1:1 mixture of **5D** and **5E**

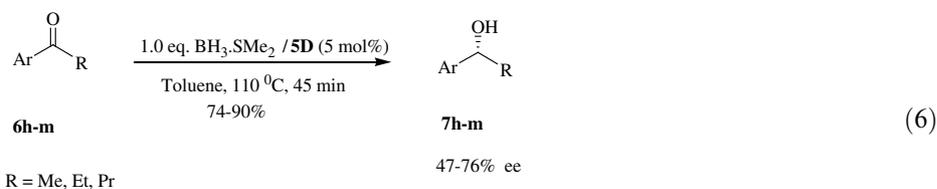
Catalyst	Yield (%) <sup>b</sup> <b>7h</b>	Enantiomeric excess (%) <sup>c</sup> <b>7h</b>	Configuration <sup>d</sup>
<b>5A</b>	74	62	R
<b>5B</b>	84	60	R
<b>5C</b>	82	52	R
<b>5D</b>	<b>87</b>	<b>72</b>	<b>R</b>
<b>5E</b>	85	70	R
<b>5D</b> and <b>5E</b> (1:1)	72	64	R

<sup>a</sup> All reactions were carried out on 1 mM scale of acetophenone **6h** with 1 mM of BH<sub>3</sub>·SMe<sub>2</sub> in the presence of catalyst (5 mol %) in toluene for 45 min at 110 °C.

<sup>b</sup> Yields of alcohol after purification by column chromatography (silica gel, 5% ethyl acetate in hexanes).

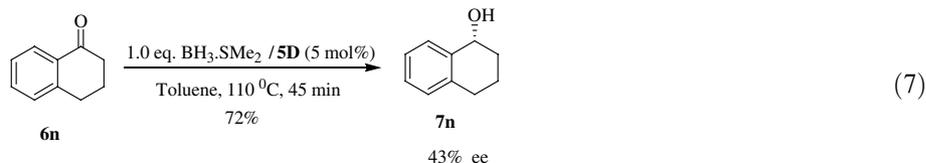
<sup>c</sup> Determined by HPLC analysis using the chiral column, Chiralcel-OD.

<sup>d</sup> Absolute configuration was assigned by comparison of the sign of the specific rotation with that reported.<sup>20</sup>

**Table 5.** Enantioselective reduction of aryl alkyl ketones using the catalyst **5D**<sup>a</sup>

R = Me, Et, Pr

Ar = phenyl, 4-methylphenyl, 4-chlorophenyl, 4-bromophenyl



Ketone	Product	Yield (%) <sup>b</sup>	$[\alpha]_{\text{D}}^{25}$	Ee (%) <sup>c</sup>	Conf. <sup>d</sup>
Acetophenone <b>6h</b>	<b>7h</b>	87	+32.6 (c 1.60, MeOH)	72	R
Propiophenone <b>6i</b>	<b>7i</b>	81	+27.8 (c 0.79, CHCl <sub>3</sub> )	61	R
Butyrophenone <b>6j</b>	<b>7j</b>	80	+21.95 (c 1.5, benzene)	47	R
4-Methylacetophenone <b>6k</b>	<b>7k</b>	77	+22.9 (c 0.6, MeOH)	51 <sup>d</sup>	R
4-Chloroacetophenone <b>6l</b>	<b>7l</b>	74	+38.4 (c 1.25, Et <sub>2</sub> O)	76 <sup>e</sup>	R
4-Bromoacetophenone <b>6m</b>	<b>7m</b>	90	+30.0 (c 1.0, CHCl <sub>3</sub> )	74 <sup>e</sup>	R
$\alpha$ -Tetralone <b>6n</b>	<b>7n</b>	72	-10.6 (c 0.9, MeOH)	43	R

<sup>a</sup> All reactions were carried out on 1 mM scale of prochiral ketone with 1 mM of BH<sub>3</sub>·SMe<sub>2</sub> in the presence of **5D** (5 mol%) in toluene for 45 min at 110 °C.

<sup>b</sup> Yields of alcohols after purification by column chromatography (silica gel, 5% ethyl acetate in hexanes).

<sup>c</sup> Enantiomeric excesses were determined by HPLC analyses using the chiral column, Chiralcel-OD.

<sup>d</sup> Absolute configuration was assigned by comparison of the sign of the specific rotation with that reported.<sup>20–22</sup>

<sup>e</sup> Enantiomeric excesses were determined by HPLC analyses of the corresponding acetates using the chiral column, Chiralcel-OJ-H.

### 3. Conclusion

From these results it is quite evident that in the case of phenacyl bromide **6a** all the catalysts [**5A–E**, **5D**, and **5E** (1:1)] offer similar enantioselectivities (81–89% ee). In the case of phenacyl chloride **6b** the catalysts **5A**, **5D**, **5E**, and **5D** and **5E** (1:1) provide similar selectivities (82–87% ee), while the catalysts **5B** and **5C** provide slightly inferior selectivities (65%, 61% ee, respectively). But in the case of acetophenone **6h** the catalysts **5D** and **5E** offer similar selectivities (72%, 70% ee, respectively), while the catalysts **5A–C**, and **5D** and **5E** (1:1) provide slightly inferior selectivities (52–64% ee). In conclusion, bicyclic [(*5S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane] moiety mostly controls the stereochemical course of the reaction, while the groups on phosphorus have little or no significant role in directing the stereochemical course of the reaction. Studies are under way to design and synthesize appropriate chiral catalysts with the N–P=O structural framework with a view to achieve higher enantioselectivities in the borane-mediated reduction of prochiral ketones.

### 4. Experimental

All melting points were recorded on a Superfit (India) capillary melting point apparatus and were uncorrected. IR spectra were recorded on Jasco-FT-IR model 5300 or Perkin Elmer model 1310 spectrometer. <sup>1</sup>H NMR (200 MHz) and <sup>13</sup>C NMR (50 MHz) spectra were

recorded in deuteriochloroform (CDCl<sub>3</sub>) on a Bruker-AC-200 spectrometer using tetramethylsilane (TMS,  $\delta = 0$ ) as internal standard. <sup>31</sup>P NMR (81 MHz) spectra were recorded on Bruker-AC-200 spectrometer using 85% H<sub>3</sub>PO<sub>4</sub> ( $\delta = 0$  ppm) as external standard. Elemental analyses were recorded on Perkin–Elmer 240C-CHN analyzer. Mass spectra were recorded on VG7070H and AutoSpec mass spectrometer. HPLC analyses were carried out on Shimadzu LC-10AD instrument using chiral column (Chiralcel-OD or Chiralcel-OJ-H). Optical rotations were measured on Jasco DIP 370 digital polarimeter.

We have previously prepared **7a–j** and **7n** molecules and reported the spectral data.<sup>13,16</sup> The present spectral data (IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR) of **7a–j**, **7n** are in agreement with the earlier data. (*R*)-1-Acetoxy-1-(4-methylphenyl)ethane, (*R*)-1-acetoxy-1-(4-chlorophenyl)ethane, and (*R*)-1-acetoxy-1-(4-bromophenyl)ethane were prepared from the corresponding alcohols **7k–m** according to the reported procedure.<sup>13,18</sup>

#### 4.1. Preparation of catalysts

##### 4.1.1. Representative procedure

**4.1.1.1. (*5S*)-1,3-Diaza-2-(benzylamino)-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **5A**.** To a stirred solution of (*2S,5S*)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo[3.3.0]octane **4** (0.5 mM, 128 mg) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) were successively added triethylamine

(1 mM, 101 mg) and benzylamine (0.5 mM, 53.5 mg) at room temperature. After 18 h (monitored by TLC) the reaction mixture was diluted with water (5 mL). Organic layer was separated and aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 15$  mL). The combined organic layer was washed successively with water and brine and was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the residue, thus obtained was purified by column chromatography (silica gel, 25% ethyl acetate in hexanes) to provide the desired (5*S*)-1,3-diaza-2-(benzylamino)-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **5A** as a crystalline solid (98 mg) in 60% yield; mp: 117–120 °C;  $[\alpha]_{\text{D}}^{25} = -42.3$  (*c* 1.05,  $\text{CHCl}_3$ ); IR (KBr):  $\nu$  3190, 1599, 1207  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  1.57–2.17 (m, 4H), 2.83–3.25 (m, 2H), 3.30–3.51 (m, 1H), 3.65–4.16 (m, 5H), 6.92–7.06 (m, 1H), 7.09–7.46 (m, 9H);  $^{13}\text{C}$  NMR:  $\delta$  26.27, 32.23, 44.85, 45.06, 48.95 (d,  $J = 16.6$  Hz), 57.86 (d,  $J = 8.5$  Hz), 116.41 (d,  $J = 4.2$  Hz), 121.00, 126.94, 127.24, 128.26, 129.04, 139.81 (d,  $J = 6.2$  Hz), 141.88 (d,  $J = 5.8$  Hz);  $^{31}\text{P}$  NMR:  $\delta$  21.16; mass ( $m/z$ ): 327 ( $\text{M}^+$ ); analysis calcd for  $\text{C}_{18}\text{H}_{22}\text{N}_3\text{OP}$ : C, 66.04; H, 6.77; N, 12.84; Found: C, 66.29; H, 6.75; N, 12.75%.

**4.1.1.2. (5*S*)-1,3-Diaza-2-(*t*-butylamino)-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **5B**.** Time: 12 h (reflux); yield: 55%; Mp: 129–132 °C;  $[\alpha]_{\text{D}}^{25} = -36.8$  (*c* 1.05,  $\text{CHCl}_3$ ); IR (KBr):  $\nu$  3171, 1601, 1224  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  1.13 (s, 9H), 1.57–2.19 (m, 4H), 2.66 (d, 1H,  $J = 8.8$  Hz), 2.83–3.07 (m, 1H), 3.30–3.46 (m, 1H), 3.61–3.89 (m, 3H), 6.88–6.98 (m, 1H), 7.12–7.38 (m, 4H);  $^{13}\text{C}$  NMR:  $\delta$  26.15, 31.00 (d,  $J = 4.9$  Hz), 32.70, 44.44, 47.96 (d,  $J = 17.0$  Hz), 50.75, 57.13 (d,  $J = 7.3$  Hz), 116.29 (d,  $J = 4.0$  Hz), 120.61, 128.86, 142.05 (d,  $J = 5.5$  Hz);  $^{31}\text{P}$  NMR:  $\delta$  17.17; MS ( $m/z$ ): 293 ( $\text{M}^+$ ); analysis calcd for  $\text{C}_{15}\text{H}_{24}\text{N}_3\text{OP}$ : C, 61.42; H, 8.25; N, 14.32; Found: C, 61.26; H, 8.30; N, 14.35%.

**4.1.1.3. (5*S*)-1,3-Diaza-2-(allylamino)-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **5C**.** Time: 12 h (rt); yield: 58%; Mp: 70–72 °C;  $[\alpha]_{\text{D}}^{25} = -33.2$  (*c* 1.1,  $\text{CHCl}_3$ ); IR (KBr):  $\nu$  3190, 1599, 1201  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  1.59–2.18 (m, 4H), 2.72–3.09 (m, 2H), 3.22–3.51 (m, 3H), 3.63–3.94 (m, 3H), 4.92–5.19 (m, 2H), 5.60–5.82 (m, 1H), 6.90–7.01 (m, 1H), 7.14–7.37 (m, 4H);  $^{13}\text{C}$  NMR:  $\delta$  26.17, 32.14, 43.53, 44.85, 48.95 (d,  $J = 16.8$  Hz), 57.73 (d,  $J = 8.4$  Hz), 114.82, 116.28 (d,  $J = 4.1$  Hz), 120.81, 128.91, 136.48 (d,  $J = 5.9$  Hz), 141.88 (d,  $J = 5.9$  Hz);  $^{31}\text{P}$  NMR:  $\delta$  21.38; mass ( $m/z$ ): 277 ( $\text{M}^+$ ); analysis calcd for  $\text{C}_{14}\text{H}_{20}\text{N}_3\text{OP}$ : C, 60.64; H, 7.27; N, 15.15; Found: C, 60.84; H, 7.30; N, 15.18%.

**4.1.1.4. (5*S*)-1,3-Diaza-2-[(*S*)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **5D**.** Time: 2 days (rt); yield: 80%; Mp: 148–150 °C;  $[\alpha]_{\text{D}}^{25} = -104.2$  (*c* 1.125,  $\text{CHCl}_3$ ); IR (KBr):  $\nu$  3211, 1601, 1205  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  1.22 (d, 3H,  $J = 6.6$  Hz), 1.46–2.06 (m, 4H), 2.48–2.69 (m, 1H), 3.24–3.83 (m, 5H), 3.97–4.18 (m, 1H), 6.91–7.02 (m, 1H), 7.15–7.39 (m, 9H);  $^{13}\text{C}$  NMR:  $\delta$  25.06 (d,  $J = 7.9$  Hz), 26.50, 32.25, 43.98, 49.33 (d,  $J = 16.0$  Hz), 51.19, 57.37 (d,  $J = 9.5$  Hz), 116.29 (d,  $J = 4.0$  Hz), 120.83, 125.86, 126.64, 128.13, 129.07,

142.22 (d,  $J = 5.6$  Hz), 146.00;  $^{31}\text{P}$  NMR:  $\delta$  17.88; mass (FAB) ( $m/z$ ): 342 ( $\text{M}^+ + 1$ ); analysis calcd for  $\text{C}_{19}\text{H}_{24}\text{N}_3\text{OP}$ : C, 66.85; H, 7.09; N, 12.31; Found: C, 66.70; H, 7.12; N, 12.25%.

**4.1.1.5. (5*S*)-1,3-Diaza-2-[(*R*)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **5E**.** Time: 2 days (rt); viscous liquid; yield: 81%;  $[\alpha]_{\text{D}}^{25} = -22.9$  (*c* 1,  $\text{CHCl}_3$ ); IR (neat):  $\nu$  3211, 1601, 1201  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  1.40 (d, 3H,  $J = 6.6$  Hz), 1.51–2.18 (m, 4H), 2.83–3.42 (m, 4H), 3.56–3.88 (m, 2H), 4.16–4.38 (m, 1H), 6.80–7.45 (m, 10H);  $^{13}\text{C}$  NMR:  $\delta$  25.04 (d,  $J = 8.1$  Hz), 26.06, 32.33, 44.76, 47.76 (d,  $J = 16.9$  Hz), 51.70, 57.72 (d,  $J = 8.2$  Hz), 116.28 (d,  $J = 3.7$  Hz), 120.50, 125.78, 126.51, 127.91, 128.57, 141.66 (d,  $J = 6.0$  Hz), 144.53;  $^{31}\text{P}$  NMR:  $\delta$  20.14; mass ( $m/z$ ): 341 ( $\text{M}^+$ ); analysis calcd for  $\text{C}_{19}\text{H}_{24}\text{N}_3\text{OP}$ : C, 66.85; H, 7.09; N, 12.31; Found: C, 66.66; H, 7.15; N, 12.35%.

## 4.2. Application of catalyst **5D**

### 4.2.1. Representative procedure using the catalyst **5D**

**4.2.1.1. Asymmetric reduction of phenacyl bromide **6a**: synthesis of (*S*)-2-bromo-1-phenylethanol **7a**.** To a stirred solution of (5*S*)-1,3-diaza-2-[(*S*)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo[3.3.0]octane **5D** (0.05 mM, 17.1 mg) in toluene (5 mL) was added borane–dimethyl sulfide (1.0 mM, 76 mg) at room temperature and the reaction mixture was heated to 110 °C. Once the temperature has stabilized at 110 °C, phenacyl bromide **6a** (1.0 mM, 199 mg) in toluene (2 mL) was added dropwise over 10 min and stirring continued for further 45 min (monitored by TLC). Then the reaction mixture was allowed to cool to room temperature and quenched with methanol. The solvent was removed under reduced pressure and the residue obtained was purified by column chromatography (silica gel, 5% ethyl acetate in hexanes) to provide the desired (*S*)-2-bromo-1-phenylethanol **7a** in 86% (173 mg) yield as a colorless oil;  $[\alpha]_{\text{D}}^{25} = +39.4$  (*c* 1.0,  $\text{CHCl}_3$ ) [lit.<sup>17</sup>  $[\alpha]_{\text{D}}^{25} = -39.0$  (*c* 8.00,  $\text{CHCl}_3$ ), (*R*)-configuration, 93% ee] 89% 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: 8.04 min (*S*) and 9.65 min (*R*)].

**4.2.1.2. (*S*)-2-Chloro-1-phenylethanol **7b**.** Colorless oil; yield 85%;  $[\alpha]_{\text{D}}^{25} = +42.8$  (*c* 1.5, cyclohexane) [lit.<sup>18</sup>  $[\alpha]_{\text{D}}^{25} = -48.1$  (*c* 1.73, cyclohexane), (*R*)-configuration, 100% ee] 87% 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: 8.08 min (*S*) and 9.58 min (*R*)].

**4.2.1.3. (*S*)-2-Bromo-1-(4-methylphenyl)ethanol **7c**.** Colorless oil; yield: 84%;  $[\alpha]_{\text{D}}^{25} = +38.9$  (*c* 1.08,  $\text{CHCl}_3$ ) [lit.<sup>13</sup>  $[\alpha]_{\text{D}}^{25} = +41.8$  (*c* 1.0,  $\text{CHCl}_3$ ), (*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 mL/min, 254 nm, retention times: 15.76 min (*S*) and 18.86 min (*R*)].

**4.2.1.4. (S)-2-Chloro-1-(4-methylphenyl)ethanol 7d.**

Colorless oil; yield: 82%;  $[\alpha]_{\text{D}}^{25} = +44.9$  (*c* 1.0,  $\text{CHCl}_3$ ) [lit.<sup>13</sup>  $[\alpha]_{\text{D}}^{25} = +47.2$  (*c* 1.1,  $\text{CHCl}_3$ ), (*S*)-configuration, 92% ee] 89% ee, the enantiomeric excess was determined by HPLC using a chiral column [Chiralcel-OD, 97.5:2.5 hexanes-*i*-PrOH, 1 mL/min, 254 nm, retention times: 14.06 min (*S*) and 16.20 min (*R*)].

**4.2.1.5. (S)-2-Bromo-1-(4-chlorophenyl)ethanol 7e.**

Colorless oil; yield: 87%;  $[\alpha]_{\text{D}}^{25} = +39.9$  (*c* 1.0,  $\text{CHCl}_3$ ) [lit.<sup>13</sup>  $[\alpha]_{\text{D}}^{25} = +38.6$  (*c* 1.15,  $\text{CHCl}_3$ ), (*S*)-configuration, 91% ee] 90% ee, the enantiomeric purity was determined by <sup>1</sup>H NMR spectral analysis of the corresponding acetate in the presence of chiral shift reagent, Eu(hfc)<sub>3</sub>, with reference to the racemic acetate.

**4.2.1.6. (S)-2-Bromo-1-(4-bromophenyl)ethanol 7f.**

Colorless solid; yield: 80%; mp: 70–72 °C;  $[\alpha]_{\text{D}}^{25} = +32.2$  (*c* 0.9,  $\text{CHCl}_3$ ) [lit.<sup>19</sup>  $[\alpha]_{\text{D}}^{25} = -31.0$  (*c* 2.9,  $\text{CHCl}_3$ ), (*R*)-configuration, 94% ee] 94% ee, the enantiomeric excess was determined by <sup>1</sup>H NMR spectral analysis of the corresponding acetate in the presence of chiral shift reagent, Eu(hfc)<sub>3</sub>, with reference to the racemic acetate.

**4.2.1.7. (S)-2-Bromo-1-(4-nitrophenyl)ethanol 7g.**

Light yellow solid; yield: 82%; mp: 80–81 °C;  $[\alpha]_{\text{D}}^{25} = +32.1$  (*c* 1.0,  $\text{CHCl}_3$ ) [lit.<sup>14</sup>  $[\alpha]_{\text{D}}^{25} = +32.0$  (*c* 1.0,  $\text{CHCl}_3$ ), (*S*)-configuration, 91% ee] 91% ee, the enantiomeric excess was determined by <sup>1</sup>H NMR spectral analysis of the corresponding acetate in the presence of chiral shift reagent, Eu(hfc)<sub>3</sub>, with reference to the racemic acetate.

**4.2.1.8. (R)-1-Phenylethanol 7h.**

Colorless oil; yield: 87%;  $[\alpha]_{\text{D}}^{25} = +32.6$  (*c* 1.60, MeOH) [Lit.<sup>20</sup>  $[\alpha]_{\text{D}}^{25} = +44.1$  (*c* 3.0, MeOH), (*R*)-configuration, 97% ee] 72% 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: 9.08 min (*R*) and 10.90 min (*S*)].

**4.2.1.9. (R)-1-Phenylpropan-1-ol 7i.**

Colorless oil; yield: 81%;  $[\alpha]_{\text{D}}^{25} = +27.8$  (*c* 0.79,  $\text{CHCl}_3$ ) [lit.<sup>20</sup>  $[\alpha]_{\text{D}}^{25} = +43.0$  (*c* 5.1,  $\text{CHCl}_3$ ), (*R*)-configuration, 96% ee] 61% 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: 8.11 min (*R*) and 9.86 min (*S*)].

**4.2.1.10. (R)-1-Phenylbutan-1-ol 7j.**

Colorless oil; yield: 80%;  $[\alpha]_{\text{D}}^{25} = +21.95$  (*c* 1.5, benzene) [lit.<sup>21</sup>  $[\alpha]_{\text{D}}^{25} = -45.2$  (*c* 4.81, benzene), (*S*)-configuration, 100% ee] 47% ee, the enantiomeric excess was determined by HPLC using a chiral column [Chiralcel-OD, 95:5 hexanes-*i*-PrOH, 0.7 mL/min, 254 nm, retention times: 11.27 min (*R*) and 12.78 min (*S*)].

**4.2.1.11. (R)-1-(4-Methylphenyl)ethanol 7k.**

Colorless oil; yield: 77%;  $[\alpha]_{\text{D}}^{25} = +22.9$  (*c* 0.6, MeOH) [lit.<sup>22</sup>  $[\alpha]_{\text{D}}^{25} = -43.5$  (*c* 0.994, MeOH), (*S*)-configuration, >99% ee] 51% ee, the enantiomeric excess was determined by

HPLC analysis of its corresponding acetate with respect to corresponding racemic acetate using a chiral column [Chiralcel-OJ-H, 95:5 hexanes-*i*-PrOH, 1.0 mL/min, 254 nm, retention times: 7.66 min (*R*) and 10.82 min (*S*)]; IR (neat):  $\nu$  3352  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR:  $\delta$  1.48 (d, 3H, *J* = 6.6 Hz), 2.25 (bs, 1H), 2.37 (s, 3H), 4.84 (q, 1H, *J* = 6.6 Hz), 7.17 (d, 2H, *J* = 8.0 Hz), 7.27 (d, 2H, *J* = 8.0 Hz); <sup>13</sup>C NMR:  $\delta$  21.10, 25.08, 70.17, 125.40, 129.15, 137.06, 142.97.

**4.2.1.12. (R)-1-Acetoxy-1-(4-methylphenyl)ethane.**

Colorless oil; yield: 83%; IR (neat):  $\nu$  1739  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR:  $\delta$  1.53 (d, 3H, *J* = 6.8 Hz), 2.06 (s, 3H), 2.35 (s, 3H), 5.87 (q, 1H, *J* = 6.8 Hz), 7.16 (d, 2H, *J* = 8.2 Hz), 7.26 (d, 2H, *J* = 8.2 Hz); <sup>13</sup>C NMR:  $\delta$  21.10, 21.32, 22.07, 72.22, 126.14, 129.16, 137.60, 138.77, 170.27.

**4.2.1.13. (R)-1-(4-Chlorophenyl)ethanol 7l.**

Colorless oil; yield: 74%;  $[\alpha]_{\text{D}}^{25} = +38.4$  (*c* 1.25,  $\text{Et}_2\text{O}$ ) [lit.<sup>22</sup>  $[\alpha]_{\text{D}}^{25} = -49.0$  (*c* 1.84,  $\text{Et}_2\text{O}$ ), (*S*)-configuration, >99% ee] 76% ee, the enantiomeric excess was determined by HPLC analysis of its corresponding acetate with respect to corresponding racemic acetate using a chiral column [Chiralcel-OJ-H, 95:5 hexanes-*i*-PrOH, 1.0 mL/min, 254 nm, retention times: 6.83 min (*R*) and 8.06 min (*S*)]; IR (neat):  $\nu$  3352  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR:  $\delta$  1.41 (d, 3H, *J* = 6.4 Hz), 2.81 (bs, 1H), 4.77 (q, 1H, *J* = 6.4 Hz), 7.13–7.33 (m, 4H); <sup>13</sup>C NMR:  $\delta$  25.13, 69.54, 126.78, 128.49, 132.92, 144.25.

**4.2.1.14. (R)-1-Acetoxy-1-(4-chlorophenyl)ethane.**

Colorless oil; yield: 89%; IR (neat):  $\nu$  1738  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR:  $\delta$  1.52 (d, 3H, *J* = 6.8 Hz), 2.07 (s, 3H), 5.85 (q, 1H, *J* = 6.8 Hz), 7.25–7.38 (m, 4H); <sup>13</sup>C NMR:  $\delta$  21.31, 22.18, 71.64, 127.59, 128.74, 133.71, 140.32, 170.21.

**4.2.1.15. (R)-1-(4-Bromophenyl)ethanol 7m.**

Colorless oil; yield: 90%;  $[\alpha]_{\text{D}}^{25} = +30.0$  (*c* 1.0,  $\text{CHCl}_3$ ) [lit.<sup>22</sup>  $[\alpha]_{\text{D}}^{25} = -37.9$  (*c* 1.13,  $\text{CHCl}_3$ ), (*S*)-configuration, >99% ee] 74% ee, the enantiomeric excess was determined by HPLC analysis of its acetate with respect to corresponding racemic acetate using a chiral column [Chiralcel-OJ-H, 95:5 hexanes-*i*-PrOH, 1.0 mL/min, 254 nm, retention times: 7.13 min (*R*) and 8.38 min (*S*)]; IR (neat):  $\nu$  3358  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR:  $\delta$  1.47 (d, 3H, *J* = 6.8 Hz), 1.79 (d, 1H, *J* = 4.0 Hz), 4.80–4.95 (m, 1H), 7.25 (d, 2H, *J* = 8.8 Hz), 7.47 (d, 2H, *J* = 8.8 Hz); <sup>13</sup>C NMR:  $\delta$  25.09, 69.51, 121.00, 127.13, 131.43, 144.75.

**4.2.1.16. (R)-1-Acetoxy-1-(4-bromophenyl)ethane.**

Colorless oil; yield: 80%; IR (neat):  $\nu$  1736  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR:  $\delta$  1.50 (d, 3H, *J* = 6.6 Hz), 2.06 (s, 3H), 5.80 (q, 1H, *J* = 6.6 Hz), 7.21 (d, 2H, *J* = 8.3 Hz), 7.46 (d, 2H, *J* = 8.3 Hz); <sup>13</sup>C NMR:  $\delta$  21.15, 22.03, 71.54, 121.71, 127.83, 131.62, 140.82, 169.95.

**4.2.1.17. (R)-1,2,3,4-Tetrahydronaphth-1-ol 7n.**

Colorless oil; yield: 72%;  $[\alpha]_{\text{D}}^{25} = -10.6$  (*c* 0.9, MeOH) [lit.<sup>20</sup>  $[\alpha]_{\text{D}}^{25} = -23.1$  (*c* 1.3, MeOH), (*R*)-configuration, 94% ee] 43% 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 36.25 min (*S*) and 41.08 min (*R*)].

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### References and notes

- Burns, B.; Studley, J. R.; Wills, M. *Tetrahedron Lett.* **1993**, *34*, 7105–7106.
- Burns, B.; King, N. P.; Studley, J. R.; Tye, H.; Wills, M. *Tetrahedron: Asymmetry* **1994**, *5*, 801–804.
- Gamble, M. P.; Studley, J. R.; Wills, M. *Tetrahedron Lett.* **1996**, *37*, 2853–2856.
- Gamble, M. P.; Studley, J. R.; Wills, M. *Tetrahedron: Asymmetry* **1996**, *7*, 3071–3074.
- Burns, B.; Gamble, M. P.; Simm, A. R. C.; Studley, J. R.; Alcock, N. W.; Wills, M. *Tetrahedron: Asymmetry* **1997**, *8*, 73–78.
- Burns, B.; King, N. P.; Tye, H.; Studley, J. R.; Gamble, M. P.; Wills, M. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1027–1038.
- Gamble, M. P.; Smith, A. R. C.; Wills, M. *J. Org. Chem.* **1998**, *63*, 6068–6071.
- Buono, G.; Chiodi, O.; Wills, M. *Synlett* **1999**, 377–388.
- For borane-mediated asymmetric reductions of prochiral ketones see reviews: (a) Brown, H. C.; Jadhav, P. K.; Singaram, B. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer: Heidelberg, 1986; Vol. 4, pp 307–356; (b) Brown, H. C.; Ramachandran, P. V. *Acc. Chem. Res.* **1992**, *25*, 16–24; (c) Corey, E. J.; Helal, C. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1986–2012; (d) Singh, V. K. *Synthesis* **1992**, 605–617; (e) Deloux, L.; Srebnik, M. *Chem. Rev.* **1993**, *93*, 763–784.
- Chiodi, O.; Fotiadu, F.; Sylvestre, M.; Buono, G. *Tetrahedron Lett.* **1996**, *37*, 39–42.
- Peper, V.; Martens, J. *Tetrahedron Lett.* **1996**, *37*, 8351–8354.
- Brunel, J. M.; Legrand, O.; Buono, G. *Eur. J. Org. Chem.* **2000**, 3313–3321.
- Basavaiah, D.; Jayapal Reddy, G.; Chandrashekar, V. *Tetrahedron: Asymmetry* **2001**, *12*, 685–689.
- Basavaiah, D.; Jayapal Reddy, G.; Chandrashekar, V. *Tetrahedron: Asymmetry* **2002**, *13*, 1125–1128.
- Li, K.; Zhou, Z.; Wang, L.; Chen, Q.; Zhao, G.; Zhou, Q.; Tang, C. *Tetrahedron: Asymmetry* **2003**, *14*, 95–100.
- Basavaiah, D.; Jayapal Reddy, G.; Chandrashekar, V. *Tetrahedron: Asymmetry* **2004**, *15*, 47–52.
- (a) Yamashita, K.; Oshikawa, T. *Chem. Abstr.* **1998**, *128*, 282940s; (b) Oshikawa, T.; Yamashita, M.; Kumagai, S.; Seo, K.; Kobayashi, J. *J. Chem. Soc., Chem. Commun.* **1995**, 435–436.
- Imuta, M.; Kawai, K. I.; Ziffer, H. *J. Org. Chem.* **1980**, *45*, 3352–3355.
- Hiratake, J.; Inagaki, M.; Nishioka, T.; Oda, J. *J. Org. Chem.* **1988**, *53*, 6130–6133.
- Prasad, K. R. K.; Joshi, N. N. *Tetrahedron: Asymmetry* **1996**, *7*, 3147–3152.
- Noyori, R.; Tomino, I.; Tanimoto, Y.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6709–6716.
- Nakamura, K.; Matsuda, T. *J. Org. Chem.* **1998**, *63*, 8957–8964.