EXPERIMENTAL

**Melting Points:** All melting points were recorded on a Superfit (India) capillary melting point apparatus and are uncorrected.

**Boiling Points:** Boiling points refer to the temperature measured using short path distillation units and are uncorrected.

**Elemental Analysis:** Elemental analyses were performed on a Perkin–Elmer 240C-CHN analyzer.

**Infrared Spectra:** Infrared spectra were recorded on a JASCO FT/IR-5300 spectrophotometer. All the spectra were calibrated against polystyrene absorption at 1601 cm\(^{-1}\). Solid samples were recorded as KBr wafers and liquid samples as thin film between NaCl plates or solution spectra in CH\(_2\)Cl\(_2\).

**Nuclear Magnetic Resonance Spectra:** Proton magnetic resonance spectra and carbon-13 magnetic resonance spectra were recorded on a BRUKER-AC-200 spectrometer. \(^1\)H NMR (200 MHz) spectra for all the samples were measured in chloroform-d, unless otherwise mentioned, with TMS (\(\delta = 0\) ppm) as internal standard.

C NMR (50 MHz) spectra for all the samples were measured in chloroform-d, unless otherwise mentioned, with its middle peak of the triplet (\(\delta = 77.10\) ppm) as internal standard. \(^31\)P NMR (81 MHz) spectra for all the samples were measured in chloroform-d, unless otherwise mentioned, using 85% H\(_3\)PO\(_4\) (\(\delta = 0\) ppm) as external standard.
Spectral assignments are as follows: (1) chemical shifts on the 6 scale, (2) standard abbreviation for multiplicity, that is, s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, dd = doublet of doublet, td = triplet of doublet, dt = doublet of triplet, b = broad, d of ABq = doublet of AB quartet, (3) number of hydrogens integrated for the signal, (4) coupling constant J in Hertz.

Mass Spectral Analysis: Mass spectra were recorded either on VG7070H mass spectrometer using EI technique or on Auto spec mass spectrometer using LSIMS technique (EI & FAB) and HP 5989 A (LC) (CI-method) mass spectrometer.

Optical Rotations: Optical rotations were measured on Jasco DIP-370 digital polarimeter at the wavelength of the sodium D-line (589 nm) at ambient temperature.

Chromatography: Analytical Thin Layer Chromatography (TLC) was performed on glass plates (7 x 2 cm) coated with Acme's silica gel GF 254 (254 μm) containing 13% calcium Sulfate as a binder. The spots were visualized by short exposure to iodine vapor or UV light. Column chromatography was carried out using Acme's silica gel (100-200 mesh). High pressure liquid chromatography (HPLC) analysis was carried out on Shimadzu LC-10AD Chromatopac equipped with SPD-10A UV-VIS detector using HPLC grade solvents. Enantiomeric purities were determined using chiral column. Chiralcel-OD (24 cm), Chiralcel-OD-H (24 cm) and Chiralcel-OJ-H (24 cm) supplied by Daicel, Japan.
X-ray Crystallography:

The X-ray diffraction measurements were carried out at 293 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromated, Mo-Kα (\(\lambda = 0.71073\) Å) radiation with CAD4 software. The single crystal was fixed to a capillary head by an appropriate fixing material. Primary unit cell constants were determined with a set of 25 narrow frame scans. Intensity data were collected by the ω scan mode. Stability of the crystal during the measurements was monitored measuring the intensity of the standard reflections after every one and half hour intervals. No appreciable variation of the crystal was detected. The data were reduced using XTAL program. No absorption correction was applied. The structure was resolved by direct methods and refined by full-matrix least-squares using the SHELXS-86 and SHELXL-93 program packages respectively.

General: All the solvents were dried and distilled using suitable drying agents before use. Moisture sensitive reactions were carried out using standard syringe-septum techniques under nitrogen atmosphere. All reactions were monitored using Thin Layer Chromatography (TLC).
Resolution of cis / trans-1,2-diaminocyclohexane [(+)-160]:

Resolution was carried out following the literature procedure.\textsuperscript{160}

To a stirred solution of L-(+)-tartaric acid (37.5 g, 250 mM) in distilled water (100 mL) was added a mixture of cis / trans-1,2-diaminocyclohexane [(+)-160] (60.1 mL, 490 mM) at a rate such that the reaction temperature just reached 70 °C. To the resulting solution was added glacial acetic acid (25 mL, 436 mM) at a rate such that the reaction temperature just reached 90 °C. A white precipitate formed immediately upon addition of the acid, and the slurry was vigorously stirred for 2 h. Then the reaction mixture was cooled to 5 °C and stirred for 2 h. The precipitate was collected by vacuum filtration and thus obtained, wet cake was washed with cold water (3 x 50 mL) followed by methanol (5 x 50 mL). The solid, thus obtained, was air dried to yield \((R,R)-1,2\)-diammonium cyclohexane mono-(+) tartrate salt (31 g) as a white solid.

To this \((R,R)-1,2\)-diammoniumcyclohexane mono-(+) tartrate salt, saturated KOH solution (100 mL) was added and stirred for 5 min at room temperature and extracted with dichloromethane (5 x 100 mL). The combined organic layer was dried over anhydrous Na\(_2\)SO\(_4\). The solvent was evaporated and the oil, thus obtained, was distilled to furnish the enantiomerically pure \((R,R)-1,2\)-diaminocyclohexane \([(R,R)-160]\) as a low melting solid (9.16 g) in 68% yield (from tartaric acid salt).

\[\text{Bp: } 70-75 \, ^\circ\text{C} / 10 \, \text{mm}\]

\([\alpha]_D^{25} : -23.13 \, (c \, 1.5, \, \text{1N HCl}) [\text{Lit.}^{172} [\alpha]_D^{25} : -25.0 \, (c \, 5, \, \text{1N HCl})].\]

\text{IR (neat): } v 3323 \, \text{cm}^{-1}\]
$^1$H NMR: 8 0.79-1.45 (m, 8H), 1.46-1.89 (m, 4H), 2.01-2.37 (m, 2H).

$^{13}$C NMR: δ 25.33, 35.45, 57.62.

**(R,R)-1,2-Diaminocyclohexane-N,N'-diethyl dicarbamate [(R,R)-161]:**

This compound was prepared according to the known procedure.$^{161}$

To a stirred solution of NaOH (9.4 g, 235 mM) in water (45 mL), was added (R, R)-1,2-diaminocyclohexane (5.70 g, 50 mM) and the resulting mixture was stirred vigorously at 0 °C for 10 min. A solution of ethyl chloroformate (10.2 mL, 107 mM) in benzene (45 mL) was added over a period of 30 min at 0 °C. The mixture was then stirred vigorously at room temperature for 2 h. The resulting white precipitate was filtered and dried under vacuum (phosphorus pentoxide) for 3 h and recrystallized from absolute ethanol to provide 10.06 g (78%) of the desired dicarbamate (R,R)-161 as a white solid.

Mp: 167-169 °C (Lit.$^{161}$ 166.5-168.5 °C)

[α]D$^{25}$: +43.25 (c 1.60, CHCl$_3$) [Lit.$^{161}$ [α]D$^{25}$: + 45.50 (c 1.0, CHCl$_3$)].

IR (KBr): ν 3412, 1680 cm$^{-1}$

$^1$H NMR: δ 1.22 (t, 6H, J=6.8 Hz), 1.59-1.89 (m, 4H), 1.95-2.20 (m, 4H), 3.32-3.48 (m, 2H), 4.09 (q, 4H, J=6.8 Hz), 4.95 (b, 2H).

$^{13}$C NMR: 5 14.49, 24.75, 32.73, 55.09, 60.58, 156.95.

**(R,R)-N,N'-Dimethyl-1,2-diaminocyclohexane [(R,R)-162]:**

This molecule was prepared according to the literature procedure.$^{161}$
To a stirred suspension of LAH (5.5 g, 144.9 mM) in THF (200 mL) was added (R,R)-1,2-diaminocyclohexane-N,N'-diethyl dicarbamate [(R,R)-161] (4.9 g, 18.97 mM) portion wise at 0 °C. After stirring for 1 h at room temperature, the reaction mixture was heated under reflux for 14 h. The resulting gray suspension was cooled to 0 °C. Water (6 mL), 15% NaOH (6 mL) and water (20 mL) were successively added, and stirring continued for 1 h at room temperature. The resulting white precipitate (lithium salts) was filtered off and rinsed with warm THF (2 x 50 mL). The filtrates were combined and the solvent was evaporated under reduced pressure. The residue was acidified (10% HCl) (pH=2) and extracted with dichloromethane (3 x 50 mL). The aqueous layer was treated with NaOH (10%) until basic pH, and then extracted with dichloromethane (3 x 50 mL). The combined organic layer was dried over anhydrous Na₂SO₄ and solvent was evaporated to give a yellowish residue which solidified (low melting solid) to furnish 2.43 g (90% yield) of the desired amine (R,R)-162.

[α]D²⁵: -143.46 (c 1.50, CHCl₃) [Lit.¹⁶¹ [α]D²⁵: -144.2 (c 1.15, CHCl₃)].

IR (neat): ν 3300, 2930, 1448, 1145 cm⁻¹

¹H NMR: 8 0.8-1.45 (m, 4H), 1.60-3.33 (m, 8H), 2.46 (s, 6H).

¹³C NMR: δ 24.66, 30.46, 33.12, 62.83.

(S)-5-Oxopyrrolidine-2-carboxanilide (164):

This molecule was prepared according to the known procedure.¹⁵⁸

A mixture of L-glutamic acid (163) (10 g, 68 mM) and aniline (75 mL) was stirred for
1 h at 195-200 °C. After 1 h, the reaction mixture becomes clear solution and stirring was continued for further 30 min. Aniline was distilled off under reduced pressure. The hot oily residue was dissolved in acetone (60 mL) and cooled. The solid was separated by filtration and crystallized from methanol, to provide (S)-5-oxopyrrolidine-2-carboxanilide (164) as a crystalline solid.

Mp: 185 °C (Lit. 158 189-191 °C)
Yield: 3.72 g (27%)
$[\alpha]_D^{25}$: +18.52 (c 0.98, MeOH) [Lit. 158 $[\alpha]_D^{25}$: +18.6 (c 1, MeOH)].

IR (KBr): ν 3327, 1666 cm$^{-1}$

$^1$H NMR (20% DMSO-d$_6$ in CDCl$_3$): δ 2.09-2.51 (m, 4H), 4.12-4.32 (m, 2H), 4.60 (b, 1H), 6.91-7.10 (m, 1H), 7.11-7.32 (m, 2H), 7.33-7.68 (m, 2H), 9.15 (bs, 1H).

$^{13}$C NMR (20% DMSO-d$_6$ in CDCl$_3$): δ 25.42, 29.47, 57.47, 120.17, 124.27, 128.76, 137.98, 170.72, 178.90.

(S)-2-Anilinomethylpyrrolidine (3):

This compound was prepared according to the literature procedure.

To a stirred suspension of lithium aluminum hydride (2.99 g, 78.78 mM) in THF (90 mL), (S)-5-oxopyrrolidine-2-carboxanilide (164) (6.02 g, 29.5 mM) was added portion wise at 0 °C. After the addition was complete, the reaction mixture was refluxed for 4 h with stirring. The reaction mixture was cooled to 5 °C and water (4 mL) was added
carefully by dropwise, followed by addition of 2.5 N sodium hydroxide solution. Then the reaction mixture was diluted with dichloromethane and stirred for 5 min. The organic layer was decanted and the residue was extracted with dichloromethane (3 X 100 mL). The combined organic layer was dried over Na₂SO₄. The Solvent was evaporated and the residue was distilled under reduced pressure to afford the (S)-2-anilinomethylpyrrolidine (3) as a viscous liquid (4.19 g) in 81% yield.

**Bp:** 118-121 °C / 0.4 mm (Lit. 117-120 °C / 0.4 mm)

**[α]D²⁵:** +18.06 (c 1.5, EtOH) [Lit. 158 [α]D²⁵: +18.5 (c 1.087, EtOH)].

**IR (neat):** v 3331 cm⁻¹

**¹H NMR:** 5 1.32-1.59 (m, 1H), 1.61-2.02 (m, 3H), 2.82-3.03 (m, 3H), 3.10-3.22 (m, 1H), 3.28-3.43 (m, 1H), 4.10 (b, 2H), 6.60-6.79 (m, 3H), 7.11-7.23 (m, 2H).

**¹²C NMR:** 5 25.81, 29.60, 46.56, 48.71, 57.76, 113.01, 117.24, 129.20, 148.40.

(2S,5S)-1,3-Diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane[(2S,5S)-165]:

This molecule was prepared according to the literature procedure.¹⁵⁹

To a stirred solution of (S)-2-anilinomethylpyrrolidine (3) (4.4 g, 25 mM) and triethyl amine (6.96 mL, 50 mM) in THF (160 mL) was added POCl₃ (2.33 mL, 25 mM) in THF (20 mL) dropwise over 30 min at 0 °C. Then the reaction mixture was stirred for
2 h at room temperature. The salts formed, were filtered off and the THF solution was evaporated under reduced pressure. The residue, thus obtained, was purified by column chromatography (silica gel, 35% ethyl acetate in hexanes). The solid, thus obtained, was crystallized from 1:1 mixture of ethyl acetate, hexanes to provide the desired (2S,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane [(2S,5S)-165] as white needles (3.7 g) in 58% yield.

Mp: 138-140 °C [Lit.\textsuperscript{159} 135 °C]

[\alpha]_D^{25} : +127.2 (c 2.1, CHCl\textsubscript{3})

IR(KBr): v 1601, 1269 1172 cm\textsuperscript{-1}

\textsuperscript{1}H NMR: 5 1.51-1.79 (m, 1H), 1.92-2.25 (m, 3H), 3.08-4.28 (m, 5H), 7.01-7.42 (m, 5H).

\textsuperscript{13}C NMR: 5 27.03 (d, J=4.15 Hz), 30.98, 44.73, 50.75 (d, J=18.6 Hz), 58.58 (d, J=9.45 Hz), 117.85 (d, J=3.95 Hz), 123.22, 129.16, 140.01 (d, J=4.95 Hz).

\textsuperscript{31}P NMR: 5 18.47 (CDCl\textsubscript{3}); 20.88 (DMSO-d\textsubscript{6}).

MS (m/z): 257 (M\textsuperscript{+})

Analysis calcd. for C\textsubscript{11}H\textsubscript{14}ClN\textsubscript{2}OP: C, 51.47; H, 5.50; N, 10.91.

Found: C, 51.70; H, 5.47; N, 10.85.
(1R,2R)-1,2-Bis[{(55)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl}methylamino]cyclohexane (158):

To a stirred solution of (2S,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane [(2S,5S)-165] (1.0 g, 3.92 mM) in CH₂Cl₂ (20 mL) were added triethylamine (0.793 g, 7.84 mM) and (1R,2R)-1,2-di(methylamino)cyclohexane [(R,R)-162] (0.278 g, 1.96 mM) at room temperature. After 20 h (monitored by TLC) the reaction mixture was diluted with water (10 mL). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3 x 25 mL). The combined organic layer was washed successively with water and brine and was dried over anhydrous Na₂SO₄. The solvent was removed in vacuo and the residue, thus obtained, was purified by column chromatography (silica gel, 35% ethyl acetate in hexanes) to afford the desired (1R,2R)-1,2-bis[{(55)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl}methylamino]cyclohexane (158) as a crystalline solid (0.863 g) in 76% yield.

Mp: 260-262 °C

[α]₀^{25} : +35.00 (c 1.40, CHCl₃)

IR (KBr): v 2934, 1601, 1502, 1305, 1215 cm⁻¹

¹H NMR: 6 1.12-2.19 (m, 16H), 2.30 (s, 3H), 2.35 (s, 3H), 2.75-3.03 (m, 2H), 3.30-3.51 (m, 2H), 3.54-4.04 (m, 8H), 6.92-7.39 (m, 10H).

¹³C NMR: 5 25.52, 26.06, 30.62, 32.47, 45.43, 48.88 (d, J=16.3 Hz), 55.66, 58.07 (d, J=8.0 Hz), 117.47 (d, J=3.4 Hz), 121.27, 128.68.
141.64 (d, J=5.7 Hz).

$^{31}$P NMR: 5 23.37.

MS (FAB) (m/z): 583 (M+H)$^+$

Analysis calcd. for C$_{30}$H$_{44}$N$_6$O$_2$P$_2$: C, 61.84; H, 7.61; N, 14.42

Found: C, 61.75; H, 7.64; N, 14.52.

Asymmetric reduction of phenacyl chloride (166a) using 30 mol% (1R,2R)-1,2-bis[{(5S)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl}methylamino]cyclohexane (158):

(1R,2R)-1,2-bis[{(5S)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl}-methyllamino]cyclohexane (158) (87.39 mg, 0.15 mM) was first dried by azeotropic drying with anhydrous toluene (2 x 3 mL) under nitrogen. The phosphoramidate 158 was then diluted with toluene (5 mL) and to this stirred solution, borane-dimethyl sulphide (38 mg, 0.5 mM) was added and the reaction mixture was heated to 110 °C. Once the temperature has stabilized at 110 °C, phenacyl chloride (166a) (77 mg, 0.5 mM) in toluene (1 mL) was added dropwise. After completion of the addition, the reaction mixture was stirred for a further 90 min (monitored by TLC) at 110 °C. Then the reaction mixture was allowed to cool to room temperature and quenched with saturated NH$_4$Cl solution. The organic layer was separated and the aqueous layer was extracted with ether (3 x 10 mL). The combined organic layer was dried over anhydrous Na$_2$SO$_4$, and the solvent was removed under reduced pressure. The residue was purified by
column chromatography (silica gel, 5% ethyl acetate in hexanes) to obtain the desired (S)-2-chloro-1-phenylethanol [(S)-167a] in 94% yield (73.6 mg), as a colorless oil.

\[ \alpha \]_D^{25}: +39.7 (c 2.25, cyclohexane) [Lit.\textsuperscript{162} \[ \alpha \]_D^{25}: -48.10 (c 1.73, cyclohexane), \textit{R}-configuration, 100% ee].

Enantiomeric purity: 82% (determined by HPLC using chiral column, Chiralcel-OD).

IR (neat): v 3408 cm\(^{-1}\)

\( ^1 \text{H} \) NMR: 5 2.63 (d, 1H, J = 3.0 Hz), 3.59-3.82 (m, 2H), 4.88-4.96 (m, 1H).

7.28-7.49 (m, 5H).

\( ^{13} \text{C} \) NMR: 8 50.77, 74.11, 126.11, 128.45, 128.67, 140.10.

Determination of enantiomeric purity:

HPLC analysis (solvent system, hexanes: IPA / 95:05; flow rate: 0.5 mL / min) of the racemic alcohol (+)-167a showed two peaks at 20.91 min (S) and 23.65 min (R) in 1:1 ratio on chiral column, Chiralcel-OD. Similar HPLC analysis of the chiral alcohol (S)-167a showed two peaks at 20.55 min (S) and 23.50 min (R) in the ratio of 91:9 indicating that its enantiomeric purity is 82%.

(+)-2-Chloro-1-phenylethanol [(+)-167a]:

To a stirred solution of phenacyl chloride (166a) (154.6 mg, 1 mM) in toluene (5 mL) was added BH\textsubscript{3}.SMe\textsubscript{2} (76 mg, 1 mM) and refluxed for 2 h. 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, thus obtained, was purified by column chromatography (silica gel, 5% ethyl acetate in hexanes) to provide the desired (+)-2-chloro-1-phenylethanol [(+)-167a] as a colorless oil.

Yield: 91% (142 mg).

This molecule has identical IR, $^1$H & $^{13}$C NMR spectral data as that of the chiral molecule (S)-167a.

(S)-2-Bromo-1-phenylethanol [(S)-167b]:

This molecule was obtained as a colorless liquid via the asymmetric reduction of phenacyl bromide (166b) with BH$_3$.SMe$_2$ in the presence of 30 mol% (1R,2R)-1,2-bis[{(5S)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl}methylamino]-cyclohexane (158), following the similar procedure described for the molecule (S)-167a.

Yield: 88%

$[\alpha]_D^{25}$: +39.4 (c 2.0, CHC1$_3$) [Lit.$^{162}$ $[\alpha]_D^{25}$: -39.0 (c 8.00, CHCl$_3$), R-configuration, 93% ee]

Enantiomeric purity: 89% (determined by HPLC using chiral column, Chiralcel-OD).

IR(neat): $\nu$ 3387 cm$^{-1}$

$^1$H NMR: 5 2.62 (d, 1H, $J = 3.8$ Hz), 3.50-3.71 (m, 2H), 4.87-5.03 (m, 1H), 7.32-7.51 (m, 5H).

$^{13}$C NMR: 8 40.08, 73.84, 126.03, 128.47, 128.70, 140.43.
Determination of enantiomeric purity:

Racemic alcohol (±)-167b showed two peaks in equal intensity on HPLC analysis (chiral column, Chiralcel-OD, solvent system, hexanes: IPA / 90:10; flow rate: 0.5 mL/min; retention times: 17.11 min and 20.82 min) arising from S and R enantiomers. The chiral alcohol (S)-167b showed two peaks in 94.5:5.5 ratio [retention times: 17.09 min (S) and 20.80 min (R) respectively] on similar HPLC analysis, indicating that its enantiomeric purity is 89%.

(±)-2-Bromo-1-phenylethanol [(±)-167b]:

This compound was obtained via the reaction of phenacyl bromide (166b) with BH$_3$.SMe$_2$ in toluene following the similar procedure described for the molecule (+)-167a, as colorless liquid.

Yield: 87%

The spectral data (IR, $^1$H & $^{13}$C NMR) of this molecule are in full agreement with that of the chiral molecule (S)-167b.

1,4-Bis[(5S)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl]piperazine (159):

This product was prepared via the reaction of (2S,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane [(2S,5S)-165] (1 g, 3.92 mM) with piperazine (0.169 g, 1.96 mM) at room temperature for 20 h following the similar procedure
mentioned for molecule 158, as a crystalline solid (0.91 g), in 88% yield (after purification by column chromatography, silica gel, 1% methanol in ethyl acetate).

Mp: 260 °C (dec.)

$[\alpha]_{D}^{25}$: -59.40 (c 1.40, CHCl$_3$)

IR (KBr): ν 2957, 1602, 1500, 1300, 1224 cm$^{-1}$

$^1$H NMR: 5 1.51-2.12 (m, 8H), 2.73-3.85 (m, 18H), 6.83-7.29 (m, 10H).

$^{13}$C NMR: 8 26.06, 32.07, 44.37, 44.97, 48.86 (d, J = 16.6 Hz), 57.88 (d, J = 8.0 Hz), 116.23 (d, J = 3.7 Hz), 121.04, 128.93, 141.57 (d, J = 5.4 Hz).

$^{31}$P NMR: δ 20.51

MS (ES) (m/z): 527 (M+H)$^+$

Analysis calcd. for C$_{26}$H$_{36}$N$_6$O$_2$P$_2$: C, 59.30; H, 6.89; N, 15.96.

Found: C, 59.42; H, 6.91; N, 15.85.

(S)-2-Chloro-1-phenylethanol [(S)-167a]:

This compound was obtained as a colorless liquid by the asymmetric reduction of phenacyl chloride (166a) with BH$_3$SMe$_2$ in the presence of 30 mol % 1,4-bis[(S)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl]piperazine (159), following the similar procedure described for the molecule (S)-167a using the catalyst 158.

Yield: 91%
Enantiomeric purity: 90 % [determined by HPLC using chiral column, Chiralcel-OD with reference to racemic alcohol (+)-167a].

**Determination of enantiomeric purity:**

HPLC analysis (solvent system, hexanes: IPA / 95:05; flow rate: 0.5 mL / min) of the alcohol (S)-167a (for similar HPLC analysis of racemic alcohol see page no. 132) on chiral column, Chiralcel-OD showed two peaks at 20.90 min (S) and 23.63 min (R) in the ratio of 95:5 indicating that its enantiomeric purity is 90%.

This molecule has identical IR, $^1$H & $^{13}$C NMR data as that of the chiral molecule (S)-167a, prepared from the asymmetric reduction of phenacyl chloride (166a) using the catalyst 158 (page no. 132).

**((S)-2-Bromo-1-phenylethanol)** [(S)-167b]:

This molecule was obtained *via* the asymmetric reduction of phenacyl bromide (166b) with BH$_3$.SMe$_2$ in the presence of 30 mol % 1,4-bis[(5S)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl]piperazine (159), following the similar procedure described for the molecule (S)-167a using the catalyst 158, as a colorless liquid.

Yield: 92%

$[\alpha]_D^{25}$: +42.45 (c 2.0, CHCl$_3$) [Lit.$^{162}$ $[\alpha]_D^{25}$: -39.0 (c 8.00, CHCl$_3$), R-configuration, 93% ee].
Enantiomeric purity: 94 % (determined by HPLC using chiral column, Chiralcel-OD).

**Determination of enantiomeric purity:**

Racemic alcohol $(\pm)$-167b showed two peaks in equal intensity on HPLC analysis (Chiralcel-OD, solvent system, hexanes: IPA / 95:05; flow rate: 0.5 mL / min) retention times 20.45 min (S) and 23.96 min (R) arising from S and R enantiomers. The chiral alcohol (S)-167b showed two peaks at (retention times) 20.48 min (S) and 23.91 min (R) in the ratio of 97:3 on similar HPLC analysis, indicating that the reaction is 94 % enantioselective.

The spectral data (1R, $^1$H & $^{13}$C NMR) of this molecule are in the full agreement with that of the chiral molecule (S)-167b, prepared from the asymmetric reduction of phenacyl bromide (166b) using the catalyst 158 (page no. 133).

**Tetrabutylammonium tribromide (TBA Br$_3$):**

This compound was prepared following the literature procedure. 

To a stirred solution of tetrabutylammonium bromide (9.67 g, 30 mM) and potassium bromide (1.19 g, 10 mM) in water (60 mL) was added dropwise hydrobromic acid (48%, 7 mL) at room temperature. After 10 minutes, the orange precipitate formed, was filtered and recrystallized from ether-dichloromethane (1:1) to provide TBA Br$_3$ as orange crystals.

Yield: 95% (13.73 g).

Mp: 74 °C (Lit.$^{163}$ 74-75 °C).
4-Methylphenacyl bromide (166c):

This molecule was prepared according to the known procedure.

To a stirred solution of 4-methylacetophenone (168) (4 mM, 0.54 g) in dichloromethane (50 mL)-methanol (20 mL) was added TBA Br₃ (4.4 mM, 2.12 g) at room temperature. After stirring for 5 h at 35 °C (until a decoloration of the orange solution), the solvent was removed and the residue, thus obtained, was extracted with ether (4 × 30 mL). The combined organic layer was dried over anhydrous Na₂SO₄ and the solvent was evaporated. The crude product thus obtained was recrystallized from ethanol-water (1:2) to provide the 4-methylphenacyl bromide (166c) as a colorless solid.

Yield: 80% (0.68 g)

Mp: 49-51 °C (Lit. 163 45-48 °C).

IR (KBr): v 1689 cm⁻¹

¹H NMR: 5.243 (s, 3H), 4.433 (s, 2H), 7.29 (d, 2H, J=8.0 Hz) 7.88(d, 2H, J=8.0 Hz).

¹³C NMR: 5 21.7, 30.95, 129.03, 129.54, 131.54, 144.96, 190.88.

4-Chlorophenacyl bromide (166d):

This product was obtained as colorless needles via the treatment of p-chloroacetophenone (169) with TBA Br₃ following the similar procedure described for the molecule 166c.

Time: 6 h.
Yield: 84%

Mp: 94-96 °C (Lit.163 97-97.5 °C)

IR (KBr): ν 1695 cm⁻¹

¹H NMR: δ 4.40 (s, 2H), 7.47 (d, 2H, J=8.8 Hz), 7.93 (d, 2H, J=8.8 Hz).

¹³C NMR: δ 30.51, 129.18, 130.32, 132.23, 140.44, 190.0.

4-Bromophenacyl bromide (166e):

This product was prepared according to the literature procedure.¹⁶⁴

To a stirred solution of 4-bromoacetophenone (170) (0.995 g, 5 mM) in glacial acetic
acid (2 mL), was added bromine (0.25 mL, 5 mM) at 15 °C. After stirring at room
temperature for 30 min, the reaction mixture was cooled to 0 °C. Thus obtained, crude
solid was filtered, washed with ethanol till it become colorless and recrystallized from
ethanol to furnish the pure 4-bromophenacyl bromide (166e) as colorless needles.

Yield: 68% (0.95 g)

Mp: 109-111 °C (Lit.¹⁶⁴ 109 °C)

IR (KBr): ν 1699 cm⁻¹

¹H NMR: δ 4.40 (s, 2H), 7.63 (d, 2H, J=8.6 Hz), 7.85 (d, 2H, J=8.6 Hz).

¹³C NMR: δ 30.51, 129.22, 130.36, 132.16, 132.61, 190.33.
4-Methylphenacyl chloride (166f):

To a stirred suspension of AlCl₃ (1.48 g, 1.11 mM) in toluene (3 mL) at 10 °C was added, chloroacetyl chloride (0.564 g, 5 mM) dropwise over a period of 15 min. The reaction mixture was heated at 50 °C for 2 h. Then the reaction mixture was cooled to 0 °C and quenched with ice cooled water (8 mL) and extracted with ether (3 x 20 mL). The combined organic layer was dried over anhydrous Na₂SO₄ and the solvent was evaporated. The crude product, thus obtained, was recrystallized from ether-hexane mixture (1:5) to provide the 4-methylphenacyl chloride (166f) as a white solid.

Yield: 30% (0.252 g)
Mp: 50-52 °C
IR (KBr): ν 1699 cm⁻¹
¹H NMR: 5.242 (s, 3H), 4.68 (s, 2H), 7.29 (d, 2H, J=8.2 Hz) 7.85(d, 2H, J=8.2 Hz).
¹³C NMR: 6.21,45.95, 128.33, 129.33, 131.51, 144.80, 190.40.

4-Ethylphenacyl chloride (166g):

This compound was prepared by treatment of ethylbenzene with chloroacetyl chloride following the similar procedure described for the molecule 166f, as a colorless solid.

Time: 2 h
(S)-2-Bromo-1-(4-methylphenyl)ethanol [(S)-167c]:

This molecule was prepared via the asymmetric reduction of 4-methylphenacyl bromide (166c) with BH₃·SMe₂ in the presence of 30 mol% 1,4-bis[(5S)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl]piperazine (159), as a viscous liquid, following the similar procedure described for the molecule (S)-167a using the catalyst 158.
Determination of enantiomeric purity:

HPLC analysis (chiral column, chiralcel-OD, solvent system, hexanes : IPA / 95:05; flow rate: 0.5 mL / min) of the racemic compound (+)-167c showed two peaks at 26.01 min (S) and 28.53 min (R) in 1:1 ratio. Similar HPLC analysis of the chiral alcohol (S)-167c showed two peaks at 26.05 min (S) and 28.58 min (R) in the ratio of 97.5:2.5 indicating that the reaction is 95% enantioselective.

(+)-2-Bromo-1-(4-methylphenyl)ethanol [(±)-167c] :

This compound was prepared by treatment of 4-methylphenacyl bromide (166c) with BH3.SMe2 following the similar procedure described for the molecule (+)-167a, as a colorless liquid.

Yield: 89%

The spectral data (IR, 1H & 13C NMR) of this molecule are in full agreement with that of the chiral molecule (S)-167c.

(S)-2-Bromo-1-(4-chlorophenyl)ethanol [(S)-167d] :

This product was obtained as a colorless liquid via the asymmetric reduction of 4-chlorophenacyl bromide (166d) with BH3.SMe2 in the presence of 30 mol% 1,4-bis[(5S)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl]piperazine (159), following the similar procedure described for the molecule (S)-167a using the catalyst 158.

Yield: 90%
$\alpha_d^{25}$: +38.60 (c 1.15, CHCl$_3$).

Enantiomeric purity: 91% [determined by $^1$H NMR spectral analysis of the corresponding acetate (S)-171 in the presence of chiral shift reagent, Eu(hfc)3].

IR (neat): $\nu$ 3242 cm$^{-1}$

$^1$H NMR: $\delta$ 2.64 (bs, 1H), 3.43-3.68 (m, 2H), 4.91 (1H, dd, $J = 8.6, 3.6$ Hz), 7.22-7.41 (m, 4H).

$^{13}$C NMR: $\delta$ 39.64, 73.05, 127.39, 128.81, 134.15, 138.86.

**Determination of enantiomeric purity:**

The $^1$H NMR spectrum of racemic acetate (+)-171 (5 mg) was recorded in the presence of Eu(hfc)3 (20 mg). The original singlet at $\delta$ 2.13 due to acetoxy methyl (OCOMe) protons splits into two distinct singlets of equal integration arising due to S and R enantiomers. Acetate (S)-171 of chiral alcohol of (S)-167d was subjected to similar $^1$H NMR analysis in which the original singlet of acetoxy methyl (OCOMe) protons showed two singlets in the ratio of 95.5:4.5 indicating the enantiomeric purity of alcohol (S)-167d is 91%.

(S)-1-Acetoxy-2-bromo-1-(4-chlorophenyl)ethane [(S)-171]:

This molecule was prepared according to the literature procedure described for the synthesis of (R)-1-acetoxy-2-bromo-1-phenylethane.$^{162}$

A solution of (S)-2-bromo-1-(4-chlorophenyl)ethanol [(S)-167d] (80 mg, 0.34 mM) and
pyridine (4 mL) in acetic anhydride (20 mL) was stirred at room temperature for 10 h. The reaction mixture was diluted with water (80 mL) and the reaction mixture was extracted with ether (3 x 20 mL). The combined organic layer was washed successively with aqueous 5 % HCl and 10 % sodium bicarbonate solution and the organic layer was dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residue, thus obtained was purified by column chromatography (5% ethyl acetate in hexanes) to provide the desired (S)-1-acetoxy-2-bromo-1-(4-chlorophenyl)ethane [(S)-171] as a colorless oil.

Yield: 80% (75.4 mg)

\[\chi_d^{25}: +54.1 \text{ (c 1.35, CHCl}_3\text{)}\]

IR (neat): \(\nu 1745 \text{ cm}^{-1}\)

\(^1\text{H NMR:} 5 2.13 \text{ (s, 3H), 3.53-3.69 (m, 2H), 5.90-5.99 (m, 1H), 7.23-7.40 (m, 4H).}\)

\(^{13}\text{C NMR} 6 20.89, 33.88, 74.10, 128.06, 128.93, 134.73, 136.22, 169.69.\)

\(+\)-2-Bromo-1-(4-chlorophenyl)ethanol [(\(+\)-167d)]:

This compound was obtained as a colorless oil via the reaction between 4-chlorophenacyl bromide (166d) and BH₃SMe₂ following the similar procedure described for the molecule (\(+\)-167a).

Yield: 87%
This molecule has identical IR, $^1$H & $^{13}$C NMR data as that of the chiral molecule (S)-167d.

(±)-1-Acetoxy-2-bromo-1-(4-chlorophenyl)ethane [(±)-171]:
This product was prepared as a colorless liquid via the treatment of (±)-2-bromo-1-(4-chlorophenyl)ethanol [(±)-167d] with acetic anhydride in presence of pyridine, following the procedure described for the compound (S)-171.
Yield: 80%
The spectral data (IR, $^1$H & $^{13}$C NMR) of this molecule is in full agreement with that of the chiral molecule (S)-171.

(S)-2-Bromo-1-(4-bromophenyl)ethanol [(S)-167e]:
This molecule was obtained via the asymmetric reduction of 4-bromophenacyl bromide (166e) with BH$_3$.SMe$_2$, in the presence of 30 mol% 1,4-bis[(S)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl]piperazine (159), as a white solid, following the similar procedure described for the molecule (S)-167a using the catalyst 158.
Yield: 76%
Mp: 70-72 °C
$[\alpha]_D^{25}$: +32.75 (c 1.3, CHCl$_3$) [Lit.$^{165}$ $[\alpha]_D^{25}$: -31.0 (c 2.9, CHCl$_3$), $R$-configuration, 94% ee].
Enantiomeric purity: 93% [determined by $^1$H NMR spectral analysis of the corresponding acetate (S)-172 in the presence of chiral shift
reagent, Eu(hfc)₃].

IR(KBr): ν 3242 cm⁻¹

¹H NMR: 8 2.65 (d, 1H, J = 3.0 Hz), 3.42-3.69 (m, 2H), 4.86-4.96 (m, 1H),
7.27 (d, 2H, J = 8.4 Hz), 7.51 (d, 2H, J = 8.4 Hz).

¹³C NMR: δ 39.65, 73.10, 122.34, 127.71, 131.79, 139.35.

Determination of enantiomeric purity:
The ¹H NMR spectrum of racemic acetate (±)-172 (5 mg) was recorded in the presence of Eu(hfc)₃ (15 mg). It was observed that the original singlet at δ 2.13 due to acetoxy methyl (OCOMe) protons splits into two distinct singlets of equal integration indicating that the two singlets arise from S and R enantiomers. The acetate (S)-172 of chiral alcohol (S)-167e was subjected to ¹H NMR analysis under identical conditions. The original singlet of acetoxy methyl protons (OCOMe) showed two distinct singlets in the ratio of 96.5:3.5, indicating that the enantiomeric purity of alcohol (S)-167e is 93%.

(S)-1-Acetoxy-2-bromo-1-(4-bromophenyl)ethane[(S)-172]:
This compound was prepared by treating (S)-2-bromo-1-(4-bromophenyl)ethanol [(S)-166e] with acetic anhydride in presence of pyridine following the similar procedure described for the molecule (S)-171, as a colorless liquid.

Yield: 70%
[α]D$^{25}$: +42.2 (c 2.50, CHCl₃)

IR (neat): ν 1743 cm$^{-1}$

$^1$H NMR: 8 2.13 (s, 3H), 3.50-3.69 (m, 2H), 5.86-5.98 (m, 1H), 7.23 (d, 2H, J = 8.4 Hz), 7.51 (d, 2H, J = 8.4 Hz).

$^{13}$C NMR: δ 20.95, 33.83, 74.18, 122.93, 128.38, 131.93, 136.74, 169.68.

(±)-2-Bromo-1-(4-bromophenyl)ethanol

This compound was prepared by treatment of 4-bromophenacyl bromide (166e) with BH$_3$.SMe$_2$ following the similar procedure described for the molecule (±)-167a, as a white solid.

Yield: 77%

Mp: 70-72 °C

The spectral data (IR, $^1$H & $^{13}$C NMR) of this molecule are in full agreement with that of the chiral molecule (S)-167e.

(±)-1-Acetoxy-2-bromo-1-(4-bromophenyl)ethane [(±)-172]:

This compound was prepared as a colorless liquid via the treatment of (±)-2-bromo-1-(4-bromophenyl)ethanol [(±)-167e] with acetic anhydride in presence of pyridine, according to the procedure described for the compound (S)-171.

Yield: 85%
This molecule has identical IR, $^1$H & $^{13}$C NMR data as that of the chiral molecule (S)-172.

**(S)-2-Chloro-1-(4-methylphenyl)ethanol [(S)-167f]:**

This molecule was prepared by the asymmetric reduction of 4-methylphenacyl chloride (166f) with BH$_3$.SMe$_2$ in the presence of 30 mol% 1,4-bis[(5S)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl]piperazine (159), as a colorless liquid, following the similar procedure described for the molecule (S)-167a using the catalyst 158.

Yield: 96%

$[\alpha]_D^{25}$: +47.2 (c 1.10, CHCl$_3$)

Enantiomeric purity: 92% (determined by HPLC using chiral column, Chiralcel-OD).

IR(neat): $\nu$ 3414 cm$^{-1}$

$^1$H NMR: 5 2.36 (s, 3H), 2.62 (b, 1H), 3.58-3.80 (m, 2H), 4.87 (1H, dd, J = 8.2, 3.8 Hz), 7.19 (d, 2H, J = 7.8 Hz), 7.28 (d, 2H, J = 7.8 Hz).

$^{13}$C NMR: 5 21.14, 50.74, 73.94, 126.02, 129.32, 137.11, 138.20.

**Determination of enantiomeric purity:**

The enantiomeric purity was determined by HPLC analysis using chiral column, Chiralcel-OD. The racemic alcohol (+)-167f showed two peaks at 21.41 min (S) and 23.50 min (R) in 1:1 ratio (solvent system, hexanes: IPA / 95:05; flow rate: 0.5 mL / min). Similar HPLC analysis of the chiral alcohol (S)-167f showed two peaks at 21.49
min (S) and 23.54 min (R) in the ratio of 96:4 indicating that its enantiomeric purity is 92%.

(±)-2-Chloro-1-(4-methylphenyl)ethanol [(±)-167fJ:
This compound was prepared by the treatment of 4-methylphenacyl chloride (166f) with BH₃.SMe₂ following the similar procedure described for the molecule (±)-167a, as a colorless liquid.
Yield: 92%
The spectral data (IR, ¹H & ¹³C NMR) of this molecule are in full agreement with that of the chiral molecule (S)-167f.

(S)-2-Chloro-1-(4-ethylphenyl)ethanol [(S)-167g]:
This product was obtained via the asymmetric reduction of 4-ethylphenacyl chloride (166g) with BH₃.SMe₂ in the presence of 30 mol% 1,4-bis[(5S)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl]piperazine (159), as a colorless liquid, following the similar procedure described for the molecule (S)-167a using the catalyst 158.
Yield: 84%
[α]D²⁵: +41.0 (c 1.0, CHCl₃).
Enantiomeric purity: 92% (determined by HPLC using chiral column Chiralcel-OD)
IR (neat): v 3408 cm⁻¹
¹H NMR: 8 1.23 (t, 3H, J = 7.8 Hz), 2.58-2.70 (m, 3H), 3.59-3.80 (m, 2H),
4.84-4.93 (m, 1H), 7.20 (d, 2H, J = 8.2 Hz), 7.30 (d, 2H, J = 8.2 Hz).

$^{13}$C NMR: 6 15.48, 28.58, 50.76, 74.00, 126.11, 128.14, 137.35, 144.58.

**Determination of enantiomeric purity:**

HPLC analysis of the racemic alcohol (±)-167g showed two peaks at 19.08 min and 20.92 min due to $S$ & $R$ enantiomers in 1:1 ratio (Chiralcel-OD, solvent system, hexanes: IPA / 95:05; flow rate: 0.5 mL / min). The chiral alcohol ($S$)-167g showed two peaks at 19.00 min ($S$) and 20.88 min ($R$) in 96:4 ratio on similar HPLC analysis, indicating that its enantiomeric purity is 92%.

$(\pm)$-2-Chloro-1-(4-ethylphenyl)ethanol [(±)-167g]:

This product was prepared as a colorless oil by the treatment of 4-ethylphenacyl chloride (166g) with BH$_3$.SMe$_2$ following the similar procedure described for the molecule (±)-167a.

Yield: 88%

This molecule has identical IR, $^1$H & $^{13}$C NMR data as that of the chiral molecule ($S$)-167g.

Asymmetric reduction of prochiral ketones using 5 mol% (2S,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane [(2S,5S)-165]:

Spectral data (IR, $^1$H & $^{13}$C NMR) of the chiral alcohols (5)-167a, (S)-167b, (S)-167c.
(S)-167d, (S)-167e and (S)-167f prepared using (25,55)-165 as a catalyst, are in full agreement with that of the chiral alcohols (S)-167a, (S)-167b, (S)-167c, (S)-167d, (S)-167e and (S)-167f prepared via the asymmetric reduction of corresponding prochiral ketones (166a-f) using the catalysts 158 or 159. Therefore, we have not presented this data again in this section.\textsuperscript{w}

Similarly, spectral data (IR, $^1$H & $^{13}$C NMR) of the acetates (S)-171 & (S)-172 of chiral alcohols (S)-167d & (S)-167e [obtained via the asymmetric reduction of corresponding prochiral ketones (166d & 166e) using the catalyst (2S,5S)-165] are in full agreement with that of the acetates (S)-171 & (S)-172 of chiral alcohols (S)-167d & (S)-167e | obtained via the asymmetric reduction of corresponding prochiral ketones (166d & 166e) using the catalyst 159]. Therefore, these spectral data are also not presented again in this section.\textsuperscript{w}

General procedure: Borane-mediated asymmetric reduction of phenacyl bromide (166b) using 5 mol% (2S,5S)-165: (S)-2-Bromo-1-phenylethanol [(S)-167b]:

Borane-dimethyl sulphide (1.0 mM, 76 mg) was added to a stirred solution of (2S,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane [(2S,5S)-165] (0.05 mM, 12.8 mg) in toluene (5 mL) and the reaction mixture was heated to 110 °C. A solution of phenacyl bromide (166b) (1.0 mM, 199 mg) in toluene (2 mL) was added

\textsuperscript{w}Though it looks repetitive, with a view to have better understanding and perspective the details of the determination of enantiomeric purities of the chiral alcohols [HPLC analysis and $^1$H NMR spectral analysis using chiral shift reagent, Eu(hfc)$_3$] have been Presented in each case.
dropwise over 10 min and the reaction mixture was stirred for a further 45 min (monitored by TLC) at 110 °C. Then the reaction mixture was allowed to cool to room temperature and quenched with saturated NH₄Cl solution. The organic layer was separated and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic layer was dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure. The residue, thus obtained, was purified by column chromatography (silica gel, 5% ethyl acetate in hexanes) to provide the pure (S)-2-bromo-l-phenylethanol [(S)-167b] as a colorless oil.

Yield: 89% (179 mg)

\[ [\alpha]_D^{25} = +39.0 \text{ (c 1.0, CHCl}_3) \] [Lit.\textsuperscript{162} [\alpha]_D^{25} = -39.0 \text{ (c 8.00, CHCl}_3), R-configuration, 93% ee]

Enantiomeric purity: 87% [determined by HPLC using chiral column, Chiralcel-OD].

**Determination of enantiomeric purity:**

HPLC analysis (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min) of the racemic alcohol (+)-167b showed two peaks at 8.62 min (S) and 10.63 min (R) in 1:1 ratio on chiral column, Chiralcel-OD. The chiral alcohol (S)-167b showed two peaks at 8.63 min (S) and 10.63 min (R) in the ratio of 93.5:6.5 on similar HPLC analysis, indicating that its enantiomeric purity is 87%.
(S)-2-Chloro-1-phenylethanol [(S)-167a]:

This compound was obtained as a colorless liquid by the asymmetric reduction of phenacyl chloride (166a) with BH$_3$.SMe$_2$ in the presence of 5 mol% (2S,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane [(2S,5S)-165], following the similar procedure described for the molecule (S)-167b.

Yield: 93%

[\[\alpha\]$_D^{25}$]: +40.0 (c 1.0, cyclohexane) [Lit.$^{162}$ [\[\alpha\]$_D^{25}$]: -48.10 (c 1.73, cyclohexane), $\alpha$-configuration, 100% ee].

Enantiomeric purity: 81% (determined by HPLC using chiral column, Chiralcel-OD).

**Determination of enantiomeric purity:**

HPLC analysis using chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min) of the racemic alcohol (+)-167a showed two peaks at 7.94 min (S) and 9.22 min (R) in 1:1 ratio. Similar HPLC analysis of the alcohol (S)-167a showed two peaks at 8.18 min (S) and 9.65 min (R) in the ratio of 90.5:9.5 indicating that the reduction is 81% enantioselective.

(S)-2-Bromo-1-(4-methylphenyl)ethanol [(S)-167c]:

This molecule was prepared via the asymmetric reduction of 4-methylphenacyl bromide (166c) with BH$_3$.SMe$_2$ in the presence of 5 mol% (2S,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane [(2S,5S)-165], as a viscous liquid, following the similar procedure described for the molecule (S)-167b.
Yield: 87%

$[\alpha]_D^{25}$: +37.5 (c 1.0, CHCl₃).

Enantiomeric purity: 83% [determined by HPLC using chiral column Chiralcel-OD with reference to racemic alcohol (+)-167c].

**Determination of enantiomeric purity:**

HPLC analysis (solvent system, hexanes: IPA / 95:05; flow rate: 0.5 mL / min) of the chiral alcohol (S)-167c (for similar HPLC analysis of racemic alcohol see page no. 142) showed two peaks at 26.05 min (S) and 28.56 min (R) on chiral column Chiralcel-OD in the ratio of 91.5:8.5 indicating that its enantiomeric purity is 83%.

**(S)-2-Bromo-1-(4-chlorophenyl)ethanol [(S)-167d]:**

This compound was obtained via the asymmetric reduction of 4-chlorophenacyl bromide (166d) with BH₃.SMe₂ in the presence of 5 mol% (2S,5S)-3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane [(2S,5S)-165], as a colorless liquid, following the similar procedure described for the molecule (S)-167b.

Yield: 80 %

$[\alpha]_D^{25}$: +37.9 (c 1.2, CHCl₃).

Enantiomeric purity: 88% [determined by $^1$H NMR spectral analysis of the corresponding acetate (S)-171 in the presence of chiral shift reagent, Eu(hfc)₃, with reference to racemic acetate (+)-171].
(S)-1-Acetoxy-2-bromo-1-(4-chlorophenyl)ethane [(S)-167d]

This molecule was prepared as a colorless liquid via the treatment of (S)-2-bromo-1-(4-chlorophenyl)ethanol [(S)-167d] with acetic anhydride in presence of pyridine following the similar procedure as described for the molecule (S)-171 (page no. 143).

Yield: 80 %

\[\alpha\]_D^25: +56.10 (c 1.05, CHCl₃).

**Determination of enantiomeric purity:**

The \(^1\)H NMR spectrum of chiral acetate (S)-171 (5 mg) (for similar \(^1\)H NMR spectral analysis of racemic acetate, see page no. 143) was recorded in the presence of Eu(hfc)₃ (20 mg). The original singlet at 6 2.13 due to acetoxy methyl (OCOMe) protons splits into two distinct singlets in the ratio of 94:6 indicating that the enantiomeric purity of alcohol (S)-167d is 88%.

(S)-2-Bromo-1-(4-bromophenyl)ethanol [(S)-167e]:

This molecule was obtained as a white solid via the asymmetric reduction of 4-bromophenacyl bromide (166e) with BH₃.SMe₂ in the presence of 5 mol% (2S,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane [(2S,5S)-165], following the similar procedure described for the molecule (S)-167b.

Yield: 88%

Mp: 70-72 °C
[\alpha]_D^{25}: +30.7 (c 2.4, CHCl_3) [Lit.\textsuperscript{165} [\alpha]_D^{25}: -31.0 (c 2.9, CHCl_3), R-configuration, 94% ee].

Enantiomeric purity: 86% [determined by \textsuperscript{1}H NMR spectral analysis of the corresponding acetate (S)-172 in the presence of chiral shift reagent, Eu(hfc)_3].

**(S)-1-Acetoxy-2-bromo-1-(4-bromophenyl)ethane [(S)-172]:**

This molecule was prepared as a colorless liquid \textit{via} the treatment of (S)-2-bromo-1-(4-bromophenyl)ethanol (S)-167e with acetic anhydride in presence of pyridine following the similar procedure described for the molecule (S)-171 (page no. 143).

Yield: 70 %

[\alpha]_D^{25}: +42.55 (c 0.94, CHCl_3).

**Determination of enantiomeric purity:**

The \textsuperscript{1}H NMR spectrum of racemic acetate (+)-172 (5 mg) was recorded in the presence of Eu(hfc)_3 (20 mg). It was observed that the original singlet at \(\delta\) 2.13 due to acetoxy methyl (OCOMe) protons splits into two distinct singlets of equal integration indicating that the two singlets arise from S and R enantiomers. The acetate (S)-172 of chiral alcohol (S)-167e was subjected to \textsuperscript{1}H NMR analysis under identical conditions. The original singlet at \(\delta\) 2.13 due to acetoxy methyl (OCOMe) protons splits into two distinct singlets in the ratio of 93:7 indicating that the enantiomeric purity of alcohol (S)-167e is 86%. 
(S)-2-Chloro-1-(4-methylphenyl)ethanol[(S)-167f]:

This molecule was prepared by the asymmetric reduction of 4-methylphenacyl chloride (166f) with BH₃.SMe₂ in the presence of 5 mol% (2S,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane [(2S,5S)-165], as a colorless liquid, following the similar procedure described for the molecule (S)-167b.

Yield: 91%

\[\alpha\]D²⁵: +42.0 (c 1.0, CHCl₃).

Enantiomeric purity: 82% (determined by HPLC using chiral column, Chiralcel-OD).

Determination of enantiomeric purity:

HPLC analysis of the racemic alcohol (±)-167f on chiral column, Chiralcel-OD (solvent system, hexanes: IPA/97.5:2.5; flow rate: 0.8 mL/min) showed two peaks at 16.32 min (5) and 18.36 min (R) in 1:1 ratio. Similar HPLC analysis of the chiral alcohol (5)-167f showed two peaks at 16.29 min (5) and 18.36 min (R) in the ratio of 91:9 indicating that its enantiomeric purity is 32%.

4-Nitrophenacyl bromide (166h):

This compound was obtained as a light yellow solid via the treatment of 4-nitroacetophenone (174) with TBA Br₃ following the similar procedure described for the molecule 166c.

Time: 6 h

Yield: 72%
Mp: 94-96 °C (Lit. 96-96.5 °C)

IR (KBr): ν 1703 cm⁻¹

¹H NMR: 8 4.45 (s, 2H), 8.15 (d, 2H, J=8.8 Hz), 8.34 (d, 2H, J=8.8 Hz)

¹³C NMR: 8 30.11, 124.13, 130.15, 138.54, 150.86, 189.96.

(S)- 2-Bromo-1-(4-nitrophenyl)ethanol [(S)-167h]:

This compound was obtained via the asymmetric reduction of 4-nitrophenacyl bromide (166h) with BH₃.SMe₂ in the presence of 5 mol% (2S,5S)-3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane [(2S,5S)-165], as a white solid, following the similar procedure described for the molecule (S)-167b.

Yield: 78%

Mp: 78-80 °C

[α]D²⁵: +32.0 (c 1.0, CHCl₃).

Enantiomeric purity: 91% [determined by ¹H NMR spectral analysis of the corresponding acetate (S)-173 in the presence of chiral shift reagent, Eu(hfc)₃].

IR (KBr): ν 3543 cm⁻¹

¹H NMR: 5 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).

¹³C NMR: 5 39.13, 72.68, 123.80, 127.01, 147.54, 147.83.
Determination of enantiomeric purity:

The $^1$H NMR spectrum of racemic acetate (±)-173 (5 mg) was recorded in the presence of Eu(hfc)$_3$ (20 mg). The original singlet at $\delta$ 2.18 due to acetoxy methyl (OCOMe) protons splits into two distinct singlets of equal integration arising due to S and R enantiomers. Acetate (S)-173 of chiral alcohol (S)-167h was subjected to similar $^1$H NMR analysis. The original singlet of acetoxy methyl (OCOMe) protons showed two singlets in the ratio of 95.5:4.5 indicating that the enantiomeric purity of the alcohol (S)-167h is 91%.

(S)-1-Acetoxy-2-bromo-1-(4-nitrophenyl)ethane [(S)-173]:

This compound was prepared by the reaction of (S)-2-bromo-1-(4-nitrophenyl)ethanol [(S)-167h] with acetic anhydride in presence of pyridine following the similar procedure described for the molecule (S)-171 (page no. 143), as a colorless liquid.

Yield: 75%

$[\alpha]_D^{25}$: +47.33 (c 0.9, CHCl$_3$)

IR (KBr): v 1751 cm$^{-1}$

$^1$H NMR: $\delta$ 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: $\delta$ 20.87, 33.38, 73.70, 124.00, 127.73, 144.61, 148.26, 169.56.
(±)-2-Bromo-1-(4-nitrophenyl)ethanol [(±)-167h]:

This compound was prepared by the treatment of 4-nitrophenacyl bromide (166h) with BH₃.SMe₂ following the similar procedure described for the molecule (±)-167a, as a colorless liquid.

Yield: 89%

The spectral data (IR, ¹H & ¹³C NMR) of this molecule are in full agreement with that of the chiral molecule (S)-167h.

(±)-1-Acetoxy-2-bromo-1-(4-nitrophenyl)ethane [(±)-173]:

This molecule was obtained, as a colorless liquid via the reaction of (±)-2-bromo-1-(4-nitrophenyl)ethanol [(±)-167h] with acetic anhydride in presence of pyridine following the similar procedure described for the molecule (S)-171 (page no. 143).

Yield: 70%

The spectral data (IR, ¹H & ¹³C NMR) of this molecule are in full agreement with that of the chiral molecule (S)-173.

(R)-1-Phenylethanol [(R)-176a]:

This product was obtained as a colorless liquid by the asymmetric reduction of acetophenone (175a) with BH₃.SMe₂ in the presence of 5 mol% (2S,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane [(2S,5S)-165], following the similar procedure described for the molecule (S)-167b.

Yield: 85%
[α]$_D^{25}$: +27.5 (c 0.4, MeOH) [Lit.$^{167}$ [α]$_D^{25}$: +37.7 (c 3.81, MeOH), R-configuration, 84% ee]

Enantiomeric purity: 62% (determined by HPLC using chiral column, Chiralcel-OD).

IR(neat): ν 3362 cm$^{-1}$

$^1$H NMR: δ 1.46 (d, 3H, J=6.8 Hz), 2.10 (bs, 1H), 4.84 (q, 1H, J=6.8 Hz), 7.18-7.41 (m, 5H).

$^{13}$C NMR: 82 25.11, 70.43, 125.45, 127.49, 128.54, 145.94.

Determination of enantiomeric purity:

HPLC analysis of the racemic alcohol (+)-176a showed two peaks at 13.83 min (R) and 15.91 min (S) in 1:1 ratio on chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 95:05; flow rate: 0.5 mL / min). The chiral alcohol (R)-176a showed two peaks at 13.89 min (R) and 15.99 min (S) in the ratio of 81:19 on similar HPLC analysis, indicating that its enantiomeric purity is 62%.

(±)-l-Phenylethanol [(±)-176a]:

This compound was obtained as a colorless oil via the reaction between acetophenone (175a) and BH$_3$·SMe$_2$ following the similar procedure described for the molecule (+)-167a.

Yield: 84%

This molecule has identical IR, $^1$H & $^{13}$C NMR spectral data as that of the chiral molecule (R)-176a.
Chiral catalyst 165A (recovered catalyst):

To a stirred solution of (2S,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo-(3.3.0)octane [(2S,5S)-165] (0.2 mM, 51.4 mg) in toluene (5 mL) was added borane-dimethyl sulphide (4.0 mM, 304 mg) and the reaction mixture was heated to 110 °C. Once the temperature has stabilized at 110 °C, phenacyl bromide (166b) (4.0 mM, 796 mg) in toluene (3 mL) was added dropwise over 10 min. After the completion of the addition, the mixture was stirred for further 45 min (monitored by TLC) at 110 °C. The reaction mixture was cooled to room temperature and quenched with methanol (to destroy the excess borane). Solvent was evaporated and the residue was diluted with ether. The solid, thus obtained was filtered, washed with ether and dried under reduced pressure to provide the chiral catalyst 165A (40 mg) as a light yellow solid.

IR (KBr): \( \nu \) 3219, 1194 cm\(^{-1}\)

Mp: 126-129 °C (dec.)

\(^1\)H NMR (DMSO-\(d_6\)): 5 1.48-2.23 [m, (4 x n) H], 2.69-4.21 [m, (5 x n) H], 6.50-6.73 [m, (3 x n) H], 7.00-7.42 [m, (2 x n) H] \((n\) can be 1 or any integer more than 1) the proton count has been written as \((x \text{ ri})\) as the exact structure is not known].

\(^{13}\)C NMR (DMSO-\(d_6\)): 5 23.17, 27.82, 44.21, 44.78, 58.64, 112.73, 116.91, 129.26, 148.18.

\(^{31}\)P NMR (DMSO-\(d_6\)): 8 0.01, 2.48.

\(^{11}\)B NMR (DMSO-\(d_6\)): 6 2.85 (weak broad signal).
The solvent (filtrate) from the above reaction was evaporated and the residue (alcohol) thus obtained, was purified by column chromatography (silica gel, 5% ethyl acetate in hexanes) to obtain the desired (S)-2-bromo-1-phenylethanol [(S)-167b], as a colorless oil.

Yield: 87% (0.70 g)

\[ \alpha \]_D\text{25} = +38.89 (c 0.54, CHCl₃) \text{[Lit.}^{162} \alpha \]_D\text{25} = -39.0 (c 8.00, CHCl₃), R-configuration, 93% ee].

Enantiomeric purity: 85% (determined by HPLC using chiral column, Chiralcel-OD).

**Determination of enantiomeric purity:**

HPLC analysis (solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL / min) of the racemic alcohol (+)-167b showed two peaks at 13.95 min (S) and 15.62 min (R) in 1:1 ratio on chiral column, Chiralcel-OD. Similar HPLC analysis of the chiral alcohol (S)-167b showed two peaks at 13.49 min (S) and 15.34 min (R) in the ratio of 92.5:7.5 indicating that the reduction is 85% enantioselective.

**Asymmetric reduction of phenacyl bromide (166b) using the catalyst 165A:**

(S)-2-Bromo-1-phenylethanol [(S)-167b]:

This molecule was prepared via the asymmetric reduction of phenacyl bromide (166b) (1mM) with BH₃.SMe₂ (1mM) in the presence of catalyst 165A (12.8 mg), as a colorless liquid, following the similar procedure described for the molecule (S)-167b using the chiral source (2S,5S)-165.

Yield: 85%
[(\(\alpha\))]\(_D^{25}\): +37.12 (c 0.62, CHCl\(_3\)) [Lit.\(^{162}\) [(\(\alpha\))]\(_D^{25}\): -39.0 (c 8.00, CHCl\(_3\)), \(R\)-configuration, 93\% ee].

Enantiomeric purity: 85\% [determined by HPLC using chiral column, Chiralcel-OD with reference to racemic alcohol (+)-167b].

**Determination of enantiomeric purity:**

HPLC analysis (chiral column, Chiralcel-OD, solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL / min) of the chiral alcohol (S)-167b (for similar HPLC analysis of racemic alcohol see page no. 163) showed two peaks at 13.49 min (S) and 15.34 min (R) in the ratio of 92.50:7.50 indicating that its enantiomeric purity is 85\%.

**(S)-2-Chloro-l-phenylethanol [(S)-167a]:**

This compound was obtained as a colorless liquid by the asymmetric reduction of phenacyl chloride (166a) (1mM) with BH\(_3\).SMe\(_2\) (1mM) in the presence of 12.8 mg of catalyst 165A following the similar procedure described for the molecule (S)-167b using the chiral source (2S,5S)-165.

Yield: 86\%

[(\(\alpha\))]\(_D^{25}\): +39.78 (c 1.0, cyclohexane) [Lit.\(^{162}\) [(\(\alpha\))]\(_D^{25}\): -48.10 (c 1.73, cyclohexane), \(R\)-configuration, 100\% ee].

Enantiomeric purity: 78\% (determined by HPLC using chiral column, Chiralcel-OD).
Determination of enantiomeric purity:

Racemic alcohol (±)-167a showed two peaks in equal intensity on HPLC analysis (chiral column, Chiralcel-OD, solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL/min; retention times: 12.94 and 14.63 min) arising from $S$ and $R$ enantiomers. The chiral alcohol (S)-167a showed two peaks in 89:11 ratio [retention times: 12.86 min ($S$) and 14.61 min ($R$) respectively] on similar HPLC analysis, indicating that its enantiomeric purity is 78%.

Preparation of chiral catalyst 165B:

To a stirred solution of (2S,5$S$)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo-(3.3.0)octane [(2S,5S)-165] (0.2 mM, 51.4 mg) in toluene, was added BH$_3$.SMe$_2$ (22.8 mg, 0.3 mM) and refluxed for 10 minutes. The reaction mixture was cooled to room temperature and the excess borane was destroyed by the addition of methanol. The resulting solid was filtered, washed with ether and dried under reduced pressure to provide a light yellow solid 165B (41 mg).

Mp: 126-129$^0$C (dec.)

IR (KBr): $\nu$ 3219, 1194 cm$^{-1}$

$^1$H NMR (DMSO-d$_6$): 8 1.52-2.22[m, (4 $x$ ri) H], 3.01-3.94[m, (5 $x$ n )H], 6.52-6.73[m, (3 $x$ ri) H], 7.07-7.23[m, (2 $x$ n )H] [( $n$ can be 1 or any integer more than 1) the proton count has been written as (x ri) as the exact structure is not known].
$^{13}$C NMR (DMSO-d$_6$): 23.02, 27.66, 43.99, 44.52, 58.41, 112.56, 116.71, 129.10, 148.03.

$^{31}$P NMR (DMSO-d$_6$): 0.01, 2.37.

$^{11}$B NMR (DMSO-d$_6$): 2.80 (weak broad signal).

Asymmetric reduction of phenacyl bromide (166b) using catalyst 165B:

(S)-2-Bromo-1-phenylethanol [(S)-167b]:

This molecule was prepared as a colorless liquid via the asymmetric reduction of phenacyl bromide (166b) (1mM) with BH$_3$SMe$_2$ (1mM) in the presence of 12.8 mg of catalyst 165B, following the similar procedure described for the molecule (S)-167b using the chiral source (2S,5S)-165.

Yield: 85%

$[\alpha]_D^{25}$: +36.06 (c 0.66, CHCl$_3$) [Lit.$^{162}$ $[\alpha]_D^{25}$: -39.0 (c 8.00, CHCl$_3$), R-configuration, 93% ee].

Enantiomeric purity: 82% [determined by HPLC using chiral column, Chiralcel-OD with reference to racemic alcohol (\(+\))-167b].

Determination of enantiomeric purity:

The alcohol \((S\)-161b\) (for similar HPLC analysis of racemic alcohol see page no. 163) showed two peaks at (retention times) 13.52 min \((S)\) and 15.30 min \((R)\) in the ratio of 91:9 on HPLC analysis using chiral column (Chiralcel-OD, solvent system, hexanes:
IPA / 95:05; flow rate: 1.0 mL / min) indicating that the reaction is 82% enantio-selective.

**((S)-2-Chloro-1-phenylethanol [(S)-167a]:**

This compound was obtained as a colorless liquid by the asymmetric reduction of phenacyl chloride (166a) (1mM) with BH$_3$.SMe$_2$ (1mM) in the presence of 12.8 mg of catalyst 165B following the similar procedure described for the molecule (S)-167b.

Yield: 83%

[α]$_D^{25}$: +38.40 (c 0.5, cyclohexane) [Lit.$^{162}$ [α]$_D^{25}$: -48.10 (c 1.73, cyclohexane), $R$-configuration, 100% ee].

Enantiomeric purity: 81% [determined by HPLC using chiral column. Chiralcel-OD with reference to racemic alcohol (+)-167a].

**Determination of enantiomeric purity:**

HPLC analysis using chiral column, Chiralcel-OD of the chiral (S)-167a (for similar HPLC analysis of racemic alcohol see page no. 165) showed two peaks at 12.93 min ($S$) and 14.65 min ($R$) in the ratio of 90.5:9.5 (solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL / min) indicating that its enantiomeric purity is 81%.

**$N'$-(Naphth-1-yl)-5-oxo-(2S)-pyrrolidine-2-carboxamide (181):**

To a stirred solution of (L)-pyroglutamic acid (179) (3.09 g, 24 mM) in THF (100 mL), DCC (4.95 g, 240 mM) and 1-naphthylamine (180) (3.44 g, 24 mM) were added at 0°C.
After stirring for 15 h at 0 °C, precipitate formed (DCU) was removed through filtration. Solvent was evaporated under reduced pressure. The residue, thus obtained was purified by column chromatography (silica gel, 2.5% methanol in ethyl acetate) followed by crystallization (ethyl acetate) to provide the desired N’-(naphth-1-yl)-5-oxo-(2S)-pyrrolidine-2-carboxamide (181) as a white solid.

Yield: 49% (2.98 g)
Mp: 189-191 °C
[α]D²⁵: -7.53 (c 1.09, methanol)
IR (KBr): ν 3250, 1722, 1669 cm⁻¹
¹H NMR: 6 2.09-2.88 (m, 4H), 4.23-4.37 (m, 1H), 7.19-7.91 (m, 7H), 9.18 (bs, 1H).
¹³C NMR: 5 24.74, 28.77, 56.17, 121.07, 121.48, 124.58, 125.03, 127.21, 127.38, 131.86, 133.13, 170.90, 177.43.

(2S)-2-(1-Naphthylaminomethyl)pyrroidine (182):
This compound was obtained as a viscous liquid via the treatment of N’-(naphth-1-yl)-5-oxo-(2S)-pyrrolidine-2-carboxamide (181) with lithium aluminum hydride in THF, following the similar procedure described for the molecule 3.
Time: 6 h
Yield: 62%
Bp: 160-163 °C / 0.3 mm (Lit.²⁷ 159-161 °C / 0.3 mm)
[\[\alpha\]_D^\circ]^\text{25} +29.46 (c 1.02, ethanol) [Lit.\textsuperscript{27} [\[\alpha\]_D^\circ]^\text{25} +29.50 (c 1.03, ethanol)]

IR (neat): \text{v 3344 cm}^{-1}

\text{^1H NMR:} \begin{align*}
5 & 1.41-2.10 (m, 5H), 2.91-3.69 (m, 5H), 4.96 (bs, 1H), 6.60 (d, 1H, J=7.2 Hz), 7.18-7.51 (m, 4H), 7.71-7.98 (m, 2H).
\end{align*}

\text{^13C NMR:} \begin{align*}
5 & 25.97, 29.82, 46.65, 48.71, 57.54, 104.44, 117.19, 120.24, 123.76, 124.58, 125.68, 126.64, 128.56, 134.42, 143.97.
\end{align*}

\text{(2S,5S)-1,3-Diaza-2-phospha-2-oxo-2-chloro-3-(naphth-1-yl)bicyclo(3.3.0)octane}}

\text{[\textit{(2S,5S)-177}]:}

This product was obtained as a white solid via the treatment of (2S)-2-(\textit{n}-naphthylaminomethyl)pyrrolidine (182) with POCI_3 in the presence of triethylamine following the similar procedure described for the molecule (2S,5S)-165.

\text{Time:} 4h

\text{Yield:} 31%

\text{Mp:} 97-99 °C

\text{No}^\text{25}: +5.0 (c 1.0, CHCl_3)

\text{IR (KBr):} \text{v 1275 cm}^{-1}

\text{^1H NMR:} \begin{align*}
5 & 1.52-1.85 (m, 1H), 1.93-2.29 (m, 3H), 3.09-3.33 (m, 1H), 3.43-3.88 (m, 3H), 4.21-4.46 (m, 1H), 7.37-7.68 (m, 4H), 7.73-7.93 (m, 2H), 8.20-8.34 (m, 1H).
\end{align*}

\text{^13C NMR:} \begin{align*}
5 & 27.47 (d, J=4.7 Hz), 30.83, 45.07, 56.05 (d, J=20.5 Hz), 60.42
\end{align*}
(d, J=8.7 Hz), 123.44, 124.38, 125.53, 126.53, 126.77, 128.16, 128.30, 131.35 (J=3.2 Hz), 134.85, 134.97.

$^{31}$P NMR: 6 19.28

Analysis calcd. for $\text{C}_{15}\text{H}_{16}\text{N}_{2}\text{OPCl}$: C, 58.74; H, 5.26; N, 9.13.

Found: C, 58.60; H, 5.20; N, 9.08.

Asymmetric reduction of phenacyl bromide (166b) using (25,55)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-(naphth-1-yl)bicyclo(3.3.0)octane [(2S,5S)-177] as a catalyst:

(S)-2-Bromo-1-phenylethanol [(S)-167b]:

This molecule was prepared via the asymmetric reduction of phenacyl bromide (166b) with BH$_3$.SMe$_2$ in the presence of 20 mol% (25,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-(naphth-1-yl)bicyclo(3.3.0)octane [(2S,5S)-177], as a colorless liquid, following the similar procedure described for the molecule (S)-167b using chiral source (2S,5S)-165.

Yield: 89 %

$[\alpha]_D^{25}$: +25.1 (c 1.39, CHCl$_3$) [Lit.$^{162} [\alpha]_D^{25}$: -39.0 (c 8.00, CHCl$_3$), $R$-configuration, 93% ee].

Enantiomeric purity: 55% [determined by HPLC using chiral column, Chiralcel-OD with reference to racemic alcohol (+)-167b].
Determination of enantiomeric purity:

HPLC analysis of the chiral alcohol (S)-167b (for similar HPLC analysis of racemic alcohol see page no. 152) using chiral column (Chiralcel-OD, solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL/min) showed two peaks at 8.51 min (S) and 10.50 min (R). The peaks are in the ratio of 77.5:22.5 indicating that its enantiomeric purity is 55%.

(R)-1-Phenylethanol [(R)-176a]:

This compound was obtained as a colorless liquid by the borane-mediated asymmetric reduction of acetophenone (175a) in the presence of 20 mol% (2S,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-(naphth-1-yl)bicyclo(3.3.0)octane [(2S,5S)-177], following the similar procedure described for the molecule (S)-167b using chiral source (2S,5S)-165.

Yield: 84%

[α]_D^{25}: +19.9 (c 5.0, MeOH) [Lit.167 [α]_D^{25}: +37.7 (c 3.81, MeOH), R-configuration, 84% ee].

Enantiomeric purity: 44% [determined by HPLC using chiral column, Chiralcel-OD]

Determination of enantiomeric purity:

HPLC analysis of the racemic alcohol (+)-176a showed two peaks at 8.60 min (R) and 10.28 min (S) in 1:1 ratio on chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL/min). Similar HPLC analysis of the chiral alcohol (R)-
176a showed two peaks at 8.43 (R) min and 9.95 (S) min in the ratio of 72:28 indicating that its enantiomeric purity is 44%.

**(S)-N-(tert-Butoxycarbonyl)indoline-2-carboxylic** acid (184):

This compound was prepared according to the known procedure. To a stirred solution of (S)-indoline-2-carboxylic acid (183) (1.3 g, 8 mM) in dioxane (8 mL) and 0.5 M NaOH (16 mL) was added slowly di-tert-butyldicarbonate (2.09 g, 9.6 mM) in dioxane (8 mL) at 0 °C. The reaction mixture was stirred for 16 h at room temperature. Then the reaction mixture was diluted with hexanes (10 mL) and organic layer was removed. Aqueous layer was acidified with saturated citric acid and extracted with ethyl acetate (3 x 25 mL). The combined organic layer was washed with brine, and dried over anhydrous sodium Sulfate. The solvent was removed under reduced pressure and the crude product, thus obtained was purified by recrystallization (1:1 mixture of ethyl acetate and hexanes) to provide the desired (S)-N-(tert-butoxycarbonyl)indoline-2-carboxylic acid (184) as a white solid.

Yield: 85% (1.79 g)

Mp: 125-126 °C (Lit.\textsuperscript{168} 124.1-124.8 °C)

[\(\alpha\)]\textsubscript{D}\textsuperscript{25}: -75.30 (c 1.0, CHCl\textsubscript{3}) [Lit.\textsuperscript{168} [\(\alpha\)]\textsubscript{D}\textsuperscript{25}: -77.3 (c 1.0, CHCl\textsubscript{3})]

IR (KBr): \nu 3300-2500, 1707, 1602 cm\textsuperscript{-1}

\textsuperscript{1}H NMR: 5 1.52 (s, 9H), 3.12-3.34 (m, 1H), 3.42-3.67 (m, 1H), 4.91 (m, 1H), 6.91-7.06 (m, 1H), 7.07-7.31 (m, 3H), 10.15 (b, 1H).
N-Phenyl-(S)-N\textsuperscript{a}-(\textit{tert}-butoxycarbonyl)indoline-2-carboxamide (185):

This molecule was prepared according to the literature procedure.\textsuperscript{168}

To a stirred solution of (S)-N-(\textit{tert}-butoxycarbonyl)indoline-2-carboxylic acid (184) (1.316 g, 5 mM) in THF (10 mL), was added a THF solution (7.5 mL) of N-methylmorpholine (0.55 mL, 5 mM) at -15 °C. After stirring for 15 min, isobutyl chloroformate (0.71 mL, 5.5 mM) in THF (7.5 mL) was added slowly to the reaction mixture at -15 °C and the stirring was continued for 15 min. Then a THF solution (7.5 mL) of aniline (0.46 mL, 5 mM) was added at -15 °C and the reaction mixture was stirred at room temperature for 14 h. To this reaction mixture, water (25 mL) and ethyl acetate (50 mL) were added and stirred for 5 min. The organic layer was separated and washed successively with 1 M HCl, saturated sodium hydrogen carbonate solution, and brine. The organic layer was dried over anhydrous sodium Sulfate and the solvent was removed under reduced pressure. The crude product, thus obtained was purified by column chromatography (silica gel, 30% ethyl acetate in hexanes) to provide the N-phenyl-(S)-N\textsuperscript{a}-(\textit{tert}-butoxycarbonyl)indoline-2-carboxamide (185) as white solid.

Yield: 69% (1.167 g)

Mp: 178-180 °C (Lit.\textsuperscript{168} 178.3-178.8 °C)
$[\alpha]_D^{25}$: -71.6 (c 2.5, CHCl$_3$) [Lit.$^{168}$ $[\alpha]_D^{25}$: -67.6 (c 1.0, CHCl$_3$)

IR (KBr): ν 3314, 1701, 1672, 1601 cm$^{-1}$

$^1$H NMR: 6 1.57 (s, 9H), 3.40-3.71 (m, 2H), 4.94-5.09 (m, 1H), 6.98-7.55 (m, 9H), 7.70 (bs, 1H).

$^{13}$C NMR: 6 28.34, 31.54, 62.55, 82.77, 115.59, 119.94, 123.51, 124.41, 124.94, 127.66, 129.00, 129.74, 137.70, 141.37, 153.28, 169.38.

**N-Phenyl-(S)-indoline-2-carboxamide (186):**

This product was prepared according to the known procedure.

To a stirred solution of N-phenyl-(S)-N$^{\alpha}$-(tert-butoxycarbonyl)indoline-2-carboxamide (185) (1.0 g, 2.95 mM) in dichloromethane (60 mL) was added trifluoroacetic acid (4.55 mL) at room temperature and stirring continued for 3 h. Then additional 12 mL of trifluoroacetic acid was added and the reaction mixture was stirred for further 1 h. The solvent and excess trifluoroacetic acid were removed under reduced pressure. Then the residue was diluted with dichloromethane (40 mL) and washed successively with saturated NaHCO$_3$ solution, water and brine. The organic layer was dried over anhydrous sodium Sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, 35% ethyl acetate in hexanes) to furnish N-phenyl-(S)-indoline-2-carboxamide (186) as white solid.
Yield: 95% (0.67 g)

Mp: 126-128 °C (Lit. 125.3-126.8 °C)

$\alpha_D^{25}$: -238 (c 0.95, CHCl₃) [Lit. 168 $\alpha_D^{25}$: -236.6 (c 1.0, CHCl₃)

IR (KBr): ν 3423, 3341, 1645 cm⁻¹

$^1$H NMR: δ 3.19 (dd, 1H, J=8.6, 16.4 Hz), 3.64 (dd, 1H, J=11.2, 16.4 Hz), 4.32 (bs, 1H), 4.41-4.59 (m, 1H), 6.70-7.42 (m, 7H), 7.57 (d, 2H, J=7.8 Hz), 8.98 (bs, 1H).

$^{13}$C NMR: δ 35.76, 61.79, 111.51, 119.72, 121.23, 124.47, 124.98, 127.81, 128.30, 129.09, 137.51, 149.17, 172.04.

(S)-2-(Anilinomethyl)indoline (187):  
This compound was prepared following the literature procedure. 168  
To a stirred suspension of lithium aluminum hydride (0.26 g, 6.83 mM) in THF (13 mL), N-phenyl-(S)-indoline-2-carboxamide (186) (0.54 g, 2.27 mM) in THF (13 mL) was added at 0 °C. After the addition was complete, the reaction mixture was stirred for 50 h at room temperature. Then saturated aqueous sodium Sulfate solution was added to the reaction mixture at 0 °C and the resulting precipitate was removed by filtration. The organic layer (filtrate) was dried over anhydrous sodium Sulfate and the solvent was removed under reduced pressure. The crude product, thus obtained, was purified by column chromatography (silica gel, 40% ethyl acetate in hexanes) to furnish (S)-2-(anilinomethyl)indoline (187) as white solid.
Yield: 83% (0.422 g)

Mp: 62-63 °C (Lit. 61.2-61.6 °C)

$[\alpha]_D^{25}: +85.2$ (c 0.75, CHCl$_3$) [Lit. 61.2-61.6 °C]

IR (KBr): v 3373, 1602 cm$^{-1}$

$^1$H NMR: 8 2.85 (dd, 1H, J=7.4, 15.6 Hz), 3.15 (dd, 1H, J=9.0, 15.6 Hz), 3.22 (d, 1H, J=5.8 Hz), 3.98 (bs, 2H), 4.05-4.20 (m, 1H), 6.57-6.82 (m, 5H), 6.92-7.26 (m, 4H).

$^{13}$C NMR: 8 33.62, 48.59, 58.50, 109.69, 113.02, 117.72, 118.99, 124.91, 127.48, 128.44, 129.35, 148.25, 150.58.

$(2R,5S)$-1,3-Diaza-2-phospha-2-oxo-2-chloro-3-phenyltricyclo(4.6.0.0$^{2,5}$)dodeca-7(12),8,10-triene [(2R,5S)-178]:

This product was obtained as a white solid via the treatment of (S)-2-(anilinomethyl)indoline (187) with POCl$_3$ in the presence of triethylamine, following the similar procedure described for the molecule (2S,5S)-165.

Time: 6 h

Yield: 32%

$[\alpha]_D^{25}: +55.62$ (c 0.80, CHCl$_3$).

Mp: 198 °C

IR(KBr): v 1601, 1278 cm$^{-1}$

$^1$H NMR: 8 3.09 (dd, 1H, J=9.2, 15.8 Hz), 3.27-3.48 (m, 1H), 3.61-3.78 (m,
1H), 4.05 (ddd, 1H, J=7.0, 9.0, 28.6 Hz), 4.80-4.98 (m, 1H), 7.01-7.48 (m,9H).

\[^{13}\text{C}\text{ NMR:}\]
6 35.67, 52.43 (d, J=16.7 Hz), 59.43 (d, J=10.0 Hz), 114.52, 118.82 (d, J=3.8 Hz), 123.81, 124.25, 125.50, 128.18, 129.58, 132.35 (d, J=9.3 Hz), 139.72, 141.45.

\[^{31}\text{P}\text{ NMR:}\]
5 10.07.

Analysis calcd. for C\textsubscript{15}H\textsubscript{16}N\textsubscript{2}OPCl:  C, 59.13; H, 4.63; N, 9.19.
Found:  C, 59.25; H, 4.60; N, 9.22.

Asymmetric reduction of phenacyl bromide (166b) in the presence of (2R,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenyltricyclo(4.6.0.0\textsuperscript{2}5)trideca-7(12),8,10-triene [(2R,5S)-178] as a catalyst:

(S)-2-Bromo-1-phenylethanol [(S)-167b]:

This molecule was prepared via the asymmetric reduction of phenacyl bromide (166b) with BH\textsubscript{3}.SMe\textsubscript{2} in the presence of 10 mol% (2R,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenyltricyclo(4.6.0.0\textsuperscript{1.5})dodeca-7(12),8,10-triene [(2R,5S)-178], as a colorless liquid, following the similar procedure described for the molecule (S)-167b using the chiral source (2S,5S)-165.

Yield: 87%

[\mathbf{[\alpha]}\textsubscript{D}\textsuperscript{25}]: +28.8 (c 1.25, CHC\textsubscript{3}) [Lit.\textsuperscript{162} [\mathbf{[\alpha]}\textsubscript{D}\textsuperscript{25}]: -39.0 (c 8.00, CHCl\textsubscript{3}), \textit{R}-configuration, 93% ee].
Enantiomeric purity: 65% [determined by HPLC using chiral column Chiralcel-OD with reference to racemic alcohol (+)-167b].

**Determination of enantiomeric purity:**

HPLC analysis using chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 95:5; flow rate: 1.0 mL / min) of the chiral alcohol (S)-167b (for similar HPLC analysis of racemic alcohol see page no. 163) showed two peaks at 13.89 min (S) and 15.53 min (R) in the ratio of 82.5:17.5 indicating that its enantiomeric purity is 65%.

**(R)-1-Phenylethanol [(R)-176a]:**

This compound was obtained as a colorless liquid by the asymmetric reduction of acetophenone (175a) with BH$_3$.SMe$_2$ in the presence of 10 mol% (2R,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenyltricyclo(4.6.0.0$^3$5)dodeca-7(12),8,10-triene [(2R,5S)-178], following the similar procedure described for the molecule (S)-167b using the chiral source (2S,5S)-165.

**Yield:** 85%

$[\alpha]_D^{25}$: +15.6 (c 2.25, MeOH) [Lit.$^{167}$ $[\alpha]_D^{25}$: +37.7 (c 3.81, MeOH), R-configuration, 84% ee].

Enantiomeric purity: 35% [determined by HPLC using chiral column, Chiralcel-OD with reference to racemic alcohol (±)-176a].
Determination of enantiomeric purity:

HPLC analysis on chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL/min) of the chiral alcohol \( (R)-176a \) (for similar HPLC analysis of racemic alcohol see page no. 171) showed two peaks at 8.59 min \( (R) \) and 10.34 min \( (S) \) in the ratio of 72.5:37.5 indicating that its enantiomeric purity is 35 %.

\((55)-2-[(1R,2R,3S,5R)-2-Hydroxy-2,6,6-trimethylbicyclo(3.1.1)heptan-3-yloxy]-1,3-
diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane(188)\):

To a stirred suspension of oil free NaH (2.0 mM, 48 mg) in DMF, was added slowly \((1R,2R,3S,5R)-2,6,6\)-trimethylbicyclo[3.1.1]heptane-2,3-diol \( (189) \) (1.0 mM, 170 mg) at room temperature. After 5 min the reaction mixture was cooled to 0 °C and \((25,55)-1,3\)-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane \( \text{[(2S,5S)-165]} \) (1.10 mM, 282.7 mg) was 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 was extracted with ether (3 X 20 mL). The combined organic layer was dried over anhydrous sodium Sulfate and the solvent was 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 \((55)-2-[(1R,2R,3S,5R)-2-hydroxy-2,6,6\)-trimethylbicyclo(3.1.1)heptan-3-yloxy]-1,3-diaza-2-
Phospha-2-oxo-3-phenylbicyclo(3.3.0)octane \( (188) \) as white needles.
Yield: 65% (254 mg)

Mp: 138-140°C

[α]D 25: -22.28 (c 1.05, CHCl₃).

IR (KBr): ν 3335, 1602, 1523, 1325, 1242 cm⁻¹

¹H NMR: 5 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).

¹³C NMR: 5 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.

MS (LC-Cl) (m/z): 390 (M)+, 391 (M+H)+

³¹P NMR: 5 19.88.

Analysis calcd. for C₂₁H₃₁N₂O₃P: C, 64.59; H, 8.00; N, 7.17.

Found: C, 64.48; H, 8.05; N, 7.12.

Asymmetric reduction of prochiral ketones using 4 mol% (SS)-2-[(1R,2R,3S,5R)-2-hydroxy-2,6,6-trimethylbicyclo(3.1.1)heptan-3-yl oxy]-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane(188):

Spectral data (IR, ¹H & ¹³C NMR) of the chiral alcohols (S)-167a, (S)-167b, (S)-167c, (S)-167d, (S)-167e, (S)-167f, (S)-167h and (R)-1 76a (prepared in this section using the
catalyst 188) are in full agreement with that of the chiral alcohols (S)-167a, (S)-167b, (S)-167c, (S)-167d, (S)-167e, (S)-167f, (S)-167h, and (R)-176a prepared via the asymmetric reduction of corresponding prochiral ketones 166a-f, 166h, 175a using the catalysts 159 or (2S,5S)-165. Therefore, we have not presented their spectral data again in this section.  

Similarly, spectral data (IR, $^1$H & $^{13}$C NMR) of the acetates (5)-171, (5)-172 and (S)-173 of alcohols (5)-167d, (S)-167e and (S)-167h are in complete agreement with that of the acetates (S)-171, (S)-172 and (S)-173 of alcohols (S)-167d, (S)-167e and (S)-167h [obtained via the asymmetric reduction of corresponding prochiral ketones 166d, 166c and 166h using the catalyst 159 or (2S,5S)-165]. Therefore, we have not presented their spectral data in this section.  

General procedure for asymmetric reduction of prochiral ketones using 4 mol% (5S)-2-[(1R,2R,3S,5R)-2-hydroxy-2,6,6-trimethylbicyclo(3.1.1)heptan-3-yl-oxy]-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (188):

(5)-2-Bromo-1-phenylethanol [(S)-167b]:

To a stirred solution of (5S)-2-[(1R,2R,3S,5R)-2-hydroxy-2,6,6-trimethylbicyclo(3.1.1)heptan-3-yl-oxy]-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (188) (0.04

1 Though it looks repetitive, with a view to have better understanding and perspective the details of the determination of enantiomeric purities of the chiral alcohols [HPLC analysis and $^1$H NMR spectral analysis using chiral shift reagent, Eu(hfc)$_3$] have been Presented in each case.
mM, 15.6 mg) in toluene (5 mL) was added borane-dimethyl sulphide (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 (166b) (1.0 mM, 199 mg) in toluene (2 mL) was added dropwise over 10 min and stirring was continued for further 1 h (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, thus obtained was purified by column chromatography (silica gel, 5% ethyl acetate in hexanes) to provide the desired (S)-2-bromo-1-phenylethanol [(S)-167b] in 88% yield (177 mg) as a colorless oil.

\[ \alpha \]$_{D}^{25}$: +41.5 (c 1.2, CHCl$_3$) [Lit.$^{162}$ \[ \alpha \]$_{D}^{25}$: -39.0 (c 8.00, CHCl$_3$), R-configuration, 93% ee].

Enantiomeric purity: 91% [determined by HPLC using chiral column, Chiralcel-OD with reference to racemic alcohol (+)-167b].

**Determination of enantiomeric purity:**

HPLC analysis using chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min) of the chiral alcohol (S)-167b (for similar HPLC analysis of racemic alcohol see page no.152) showed two peaks at 8.12 min (S) and 9.60 min (R) in the ratio of 95.5:4.5 indicating that its enantiomeric purity is 91%.
(S)-2-Chloro-1-phenylethanol [(S)-167a]:

This molecule was prepared as a colorless liquid by the asymmetric reduction of phenacetyl chloride (166a) with BH$_3$.SMe$_2$ in the presence of 4 mol% chiral source 188, following the similar procedure described for the molecule (S)-167b.

Yield: 91%

$[\alpha]_D^{25}$: +42.1 (c 1.0, cyclohexane) [Lit.$^{162}$ $[\alpha]_D^{25}$: -48.10 (c 1.73, cyclohexane), $R$-configuration, 100% ee].

Enantiomeric purity: 86% [determined by HPLC using chiral column, Chiralcel-OD with reference to racemic alcohol (+)-167a].

**Determination** of enantiomeric purity:

The alcohol (S)-167a (for similar HPLC analysis of racemic alcohol see page no. 153) showed two peaks at (retention times) 7.89 min (S) and 9.09 min (R) in the ratio of 93.0:7.0 on HPLC analysis using chiral column (Chiralcel-OD, solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min) indicating that the reaction is 86% enantioselective.

(S)-2-Bromo-1-(4-methylphenyl)ethanol [(S)-167c]:

This compound was prepared via the asymmetric reduction of 4-methylphenacetyl bromide (166c) with BH$_3$.SMe$_2$ in the presence of 4 mol% chiral source 188, as a viscous liquid, following the similar procedure described for the molecule (S)-167b.

Yield: 94%
Enantiomeric purity: 91% (determined by HPLC using chiral column, Chiralcel-OD).

**Determination of enantiomeric purity:**

HPLC analysis (chiral column, Chiralcel-OD, solvent system, hexanes: IPA / 97.5:2.5; flow rate: 1.0 mL / min) of the racemic alcohol (+)-167c showed two peaks at 15.76 min (S) and 18.86 min (R) in 1:1 ratio. Similar HPLC analysis of the chiral alcohol (S)-167c showed two peaks at 16.15 min (S) and 19.36 min (R) in the ratio of 95.5:4.5 indicating that its enantiomeric purity is 91%.

**(S)-2-Bromo-1-(4-chlorophenyl)ethanol [(S)-167d]:**

This product was obtained as a colorless liquid via the asymmetric reduction of 4-chlorophenacyl bromide (166d) with BH₃·SMe₂ in the presence of 4 mol% chiral source 188, following the similar procedure described for the molecule (S)-167b.

Yield: 92%

Enantiomeric purity: 89% [determined by ¹H NMR spectral analysis of the corresponding acetate (S)-171 in the presence of chiral shift reagent, Eu(hfc)3, with reference to racemic acetate (+)-171].
(S)-1-Acetoxy-2-bromo-1-(4-chlorophenyl)ethane [(S)-171]:

This molecule was prepared as a colorless liquid via the treatment of (S)-2-bromo-1-(4-chlorophenyl)ethanol [(S)-167d] with acetic anhydride in presence of pyridine following the similar procedure as described for the molecule (S)-171 (page no. 143).

Yield: 67%

$[\alpha]_D^{25} +53.0$ (c 1.0, CHCl$_3$).

**Determination of enantiomeric purity:**

The $^1$H NMR spectrum of chiral acetate (S)-171 (5 mg) (for similar $^1$H NMR spectral analysis of racemic acetate see page no. 143) was recorded in the presence of $\text{Eu(hfc)}_3$ (20 mg). The original singlet (at $\delta$ 2.13) of acetoxy methyl (OCOMe) protons splits into two distinct singlets in 94.5:5.5 ratio indicating that the enantiomeric purity of the alcohol (S)-167d is 89%.

(S)-2-Bromo-1-(4-bromophenyl)ethanol [(S)-167e]:

This product was obtained via the borane-mediated asymmetric reduction of 4-bromophenacyl bromide (166e) in the presence of 4 mol% chiral source 188, following the similar procedure described for the molecule (S)-167b, as white solid.

Yield: 89%

Mp: 71-72 °C
fa ), ]$^2_{25}$: +33.8 (c 2.4, CHCl$_3$) [Lit.$^{165}$ ]$^2_{25}$: -31.0 (c 2.9, CHCl$_3$), $R$-configuration, 94% ee).

Enantiomeric purity: 96% [determined by $^1$H NMR spectral analysis of the corresponding acetate ($S$)-172 in the presence of chiral shift reagent, Eu(hfc)$_3$, with reference to racemic alcohol ($\pm$)-172].

$(S)$-1-Acetoxy-2-bromo-1-(4-bromophenyl)ethane ([($S$)-172]:

This molecule was prepared as a colorless liquid via the treatment of ($i$S)-2-bromo-1-(4-bromophenyl)ethanol ([($S$)-167e] with acetic anhydride in presence of pyridine following the similar procedure as described for the molecule ($S$)-7\(^{88}\) (page no. 143).

Yield: 87%

[$\alpha$]$^2_{25}$: +48.27 (c 1.16, CHCl$_3$).

Determination of enantiomeric purity:

The $^1$H NMR spectrum of chiral acetate ($S$)-172 (5 mg) (for similar $^1$H NMR spectral analysis of racemic acetate see page no. 156) was recorded in the presence of Eu(hfc)$_3$ (20 mg). The original singlet (at 5 2.13) of acetoxy methyl protons (OCOMe) splits into two distinct singlets in the ratio of 98:2 indicating the enantiomeric purity of alcohol is 96%.

$(S)$-2-Chloro-1-(4-methylphenyl)ethanol ([($S$)-167f]:

This molecule was prepared via the asymmetric reduction of 4-methylphenacyl chloride
with BH$_3$SMe$_2$ in the presence of 4 mol% chiral source 188, as a colorless liquid, following the similar procedure described for the molecule (S)-167b.

\[
\text{Yield: 92%} \\
\text{[\(\alpha\)]}_D^{25} \quad +44.0 \text{ (c 1.0, CHCl}_3\text{).}
\]

Enantiomeric purity: 88% (determined by HPLC using chiral column, Chiralcel-OD).

**Determination of enantiomeric purity:**

HPLC analysis (solvent system, hexanes: IPA / 97.50:2.50; flow rate: 1.0 mL / min) of the racemic alcohol (+)-167f showed two peaks at 14.60 min (S) and 17.05 min (R) in 1:1 ratio on chiral column, Chiralcel-OD. The chiral alcohol (S)-167f showed two peaks at 14.64 min (S) and 16.80 min (R) in the ratio of 94:6 on similar HPLC analysis, indicating that its enantiomeric purity is 88%.

(S)-2-Bromo-l-(4-nitrophenyl)ethanol [(S)-167h]:

This compound was obtained via the asymmetric reduction of 4-nitrophenacyl bromide (166h) with BH$_3$SMe$_2$ in the presence of 4 mol% chiral source 188, as a white solid, following the similar procedure described for the molecule (S)-167b.

\[
\text{Yield: 90%} \\
\text{Mp: 78-80 °C} \\
\text{[\(\alpha\)]}_D^{25} \quad +33.2 \text{ (c 1.0, CHCl}_3\text{).}
\]
Enantiomeric purity: 92% [determined by $^1$H NMR spectral analysis of the corresponding acetate (S)-173 in the presence of chiral shift reagent, Eu(hfc)$_3$, with reference to racemic acetate (+)-173].

(S)-1-Acetoxy-2-bromo-1-(4-nitrophenyl)ethane [(S)-173]:

This compound was prepared as a colorless liquid by the reaction of (S)-2-bromo-1-(4-nitrophenyl)ethanol [(S)-167h] with acetic anhydride in presence of pyridine following the similar procedure described for the molecule (S)-171 (page no. 143).

Yield: 75 %

Mp: 102-105 °C

$[a]_D^{25}$: +46.60 (c 0.9, CHCl$_3$)

Determination of enantiomeric purity:

The $^1$H NMR spectrum of chiral acetate (S)-173 (5 mg) (for similar $^1$H NMR spectral analysis of racemic acetate see page no. 159) was recorded in the presence of Eu(hfc)$_3$ (20 mg). The original singlet (at 8 2.18) of acetoxy methyl (OCOMe) protons splits into two distinct singlets in 96:4 ratio indicating that the enantiomeric purity of the alcohol is 92%.

(R)-1-Phenylethanol [(R)-176a]:

This compound was obtained by the asymmetric reduction of acetophenone (175a) with BH$_3$.SMe$_2$ in the presence of 4 mol% catalyst 188 following the similar procedure described for the molecule (S)-167b, as a colorless liquid.
Yield: 80%

\[ \alpha \]_D^{25}: +29.0 \text{ (c 1.0, MeOH)} \] [Lit.\textsuperscript{167} \[ \alpha \]_D^{25}: +37.7 \text{ (c 3.81, MeOH), R-configuration, 84% ee}].

Enantiomeric purity: 63% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (\(\pm\)-176a).

**Determination of enantiomeric purity:**

HPLC analysis using chiral column, Chiralcel OD (solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL / min) of the chiral alcohol (\(\text{R}\))-176a (for similar HPLC analysis of racemic alcohol see page no. 171) showed two peaks at 8.76 min (\(\text{R}\)) and 10.72 min (\(\text{S}\)) in the ratio of 81.5:18.5 indicating that its enantiomeric purity is 63 %.

(\(\text{R}\))-1-Phenylpropan-1-ol [(\(\text{R}\))-176b]:

This compound was obtained as a colorless liquid via the asymmetric reduction of propiophenone (175b) with BH\textsubscript{3}\textcdot SMet in the presence of 4 mol% chiral source 188, following the similar procedure described for the molecule (\(\text{S}\))-167b.

Yield: 85%

\[ \alpha \]_D^{25}: +30.7 \text{ (c 1.9, CHCl}_3) \] [Lit.\textsuperscript{169} \[ \alpha \]_D^{25}: +43.03 \text{ (c 5.1, CHCl}_3), R-configuration, 96% ee].

Enantiomeric purity: 67% (determined by HPLC using chiral column, Chiralcel-OD).

IR (neat): \( v \) 3373 cm\textsuperscript{-1}
\( ^1H \) NMR: 

6 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: 

8 10.12, 31.85, 75.93, 126.02, 127.41, 128.35, 144.66.

**Determination of enantiomeric purity:**

HPLC analysis of the racemic alcohol (\( \pm \)-**176b** showed two peaks at 8.10 min (\( R \)) and 9.84 min (\( S \)) in 1:1 ratio on chiral column, Chiralcel-OD (solvent system, hexanes: 1\( \text{Pr} \)/\( \text{A} \) / 95:05; flow rate: 1.0 mL / min). The chiral alcohol (\( R \)-**176b** showed two peaks at 8.32 min \( R \) and 10.05 min \( S \) in the ratio of 83.5:16.5 on similar HPLC analysis, indicating that its enantiomeric purity is 67%.

\( \pm \)-1-Phenypropan-1-ol [(\( \pm \)-**176b**):

To a solution of propiophenone (**175b**) (2 mM, 268 mg) in toluene (5 mL) was added \( \text{BH}_3\text{SMe}_2 \) (152 mg, 2 mM) and stirred for 12 h. Then the reaction mixture was allowed to cool to 0 °C and quenched with methanol. The solvent was removed under reduced pressure and the residue, thus obtained was purified by column chromatography (silica gel, 5% ethyl acetate in hexanes) to provide the desired \( \pm \)-1-phenylpropan-1-ol [(\( \pm \)-**176b**] as a colorless oil.

Yield: 90% (245 mg)

This molecule has identical IR, \( ^1H \) & \( ^{13}C \) NMR spectral data as that of the chiral molecule (\( S \)-**176b**).
(R)-1-Phenylbutan-1-ol [(R)-176c]:

This compound was obtained as a colorless liquid by the asymmetric reduction of butyrophenone (175c) with BH$_3$SMe$_2$ in the presence of 4 mol% chiral source 188, following the similar procedure described for the molecule (S)-167b.

Yield: 83%

$[\alpha]_D^{25}$: +28.0 (c 0.7, benzene) [Lit.$^{23}$ $[\alpha]_D^{25}$: -45.2 (c 4.81, benzene). V-configuration, 100% ee].

Enantiomeric purity: 59% (determined by HPLC using chiral column, Chiralcel-OD-H).

IR (neat): ν 3300 cm$^{-1}$

$^1$H 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.

Determination of enantiomeric purity:

HPLC analysis of the racemic alcohol (+)-176c showed two peaks at 12.39 min (R) and 12.98 min (S) in 1:1 ratio on chiral column, Chiralcel-OD-H (solvent system, hexanes: IPA / 95:05; flow rate: 0.7 mL / min). The chiral alcohol (R)-176c showed two peaks at 12.30 min (R) and 13.10 min (S) in the ratio of 79.5:20.5 on similar HPLC analysis, indicating that the reaction is 59% enantioselective.
(+)-1-Phenylbutan-1-ol [(+)-176c]:

This compound was obtained as a viscous liquid via the reduction of butyrophenone (175c) with BH₃·SMe₂, following the similar procedure described for the molecule (+)-176b.

Yield: 83%

This compound has identical IR, ¹H & ¹³C NMR data as that of the chiral molecule (/?)-176c.

(R)-1,2,3,4-Tetrahydronaphth-1-ol [(R)-176d]:

This product was obtained as a colorless liquid via the asymmetric reduction of α-tetralone (175d) with BH₃·SMe₂ in the presence of 4 mol% chiral source 188 following the similar procedure described for the molecule (S)-167b.

Yield: 71%

[α]D²⁵: -16.4 (c 0.75, MeOH) [Lit.¹⁶⁹ [α]D²⁵: -23.14 (c 1.3, MeOH). R-configuration, 94% ee].

Enantiomeric purity: 70% (determined by HPLC using chiral column, Chiralcel-OD)

IR (neat): ν 3356 cm⁻¹

¹H NMR: 5 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).

¹³C NMR: 5 18.84, 29.19, 32.21, 67.96, 126.02, 127.38, 128.60, 128.84, 137.00, 138.86.
Determination of enantiomeric purity:

HPLC analysis (solvent system, hexanes: IPA / 97.5:2.5; flow rate: 0.4 mL / min) of the racemic alcohol (±)-176d showed two peaks at 35.42 min (S) and 39.44 min (R) in 1:1 ratio. Similar HPLC analysis of the chiral alcohol (S)-176d showed two peaks at 35.50 min (S) and 39.52 min (R) in the ratio of 15:85 indicating that its enantiomeric purity is 70%.

(+)-1,2,3,4-Tetrahydronaphth-1-ol [(+)-176d]:

This product was obtained as a colorless liquid via the reduction of α-tetralone (175d) with BH₃-SMe₂, following the similar procedure described for the molecule (+)-176b. Yield: 81%

The spectral data (IR, ¹H & ¹³CNMR) of this molecule are in full agreement with that of the chiral molecule (R)-176d.

(R)-1-(Naphth-1-yl)ethanol [(R)-176e]:

This compound was prepared by the asymmetric reduction of 1-acetonaphthone (175e) with BH₃-SMe₂ in the presence of 4 mol% catalyst 188, as a colorless liquid, following the similar procedure described for the molecule (S)-167b. Yield: 76%

[α]D²⁵: +50.3 (c 1.08, ether) [Lit.¹⁷⁰ [α]D²⁵: +82.1 (c 1.0, ether). R-
configuration, >99% ee].

Enantiomeric purity: 63% (determined by HPLC using chiral column, Chiralcel-OD).

IR (neat): \( \nu 3368 \text{ cm}^{-1} \)

\(^1\text{H NMR}: \) \( \delta 1.64 \text{ (d, 3H, J=6.0 Hz)}, 2.65 \text{ (bs, 1H)}, 5.59 \text{ (q, 1H, J=6.0 Hz)}, 7.36-8.20 \text{ (m, 7H)}. \)

\(^{13}\text{C NMR}: \) \( \delta 24.41, 67.04, 122.11, 123.28, 125.57, 126.04, 127.89, 128.94, 130.36, 133.89, 144.51. \)

**Determination of enantiomeric purity:**

HPLC analysis of the racemic alcohol (±)-176e showed two peaks at 24.68 min (R) and 37.82 min (S) in 1:1 ratio on chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL / min). Similar HPLC analysis of the chiral alcohol (R)-176e showed two peaks at 24.44 min (R) and 37.72 min (S) in the ratio of 81.5:18.5 indicating that its enantiomeric purity is 63 %.

**(±)-1-(Naphth-1-yl)ethanol [(±)-176e]:**

This compound was obtained as a viscous liquid via the reduction of 1-acetonaphthone (175e) with BH₃.SMe₂, following the similar procedure described for the molecule (±)-176b.

Yield: 78%

This compound has identical IR, \(^1\text{H} \& \(^{13}\text{C NMR} \) spectral data as that of the chiral molecule (R)-176e.
(5S)-1,3-Diaza-2-(benzylamino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (190):

To a stirred solution of (2S,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane [(2S,5S)-165] (0.5 mM, 128 mg) in CH₂Cl₂ (5 mL) were successively added triethylamine (1 mM, 0.14 mL) 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 CH₂Cl₂ (3 × 15 mL). The combined organic layer was washed successively with water and brine and was dried over anhydrous Na₂SO₄. 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,V)-1,3-diaza-2-(benzylamino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (190) as a crystalline solid (98 mg) in 60% yield.

Mp: 117-120 °C

[α]D²⁵: -42.28 (c 1.05, CHCl₃)

IR (KBr): ν 3190, 1599, 1207 cm⁻¹

¹H NMR: 5.1 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).

¹³C NMR: 6.26 26.27, 32.23, 44.95 (d, J=10.4 Hz), 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).

³¹P NMR: 521.16
Mass (m/z): 327 (M⁺)

Analysis cald. for C₁₈H₂₂N₃OP: C, 66.04; H, 6.77; N, 12.84.

Found: C, 66.29; H, 6.75; N, 12.75.

Asymmetric reduction of prochiral ketones in the presence of 5 mol% (5S)-1,3-diaza-2-(benzylamino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (190):

Spectral data (IR, ¹H & ¹³C NMR) of the chiral alcohols (S)-167a, (S)-167b and (R)-176a (prepared using chiral catalysts 190-192 or 193A or 193B or mixture of 193A and 193B) are in full agreement with that of the chiral alcohols (S)-167a, (S)-167b and (R)-176a prepared via the asymmetric reduction of corresponding prochiral ketones 166a, 166b and 175a using the catalysts 159 or (2S,5S)-165. Therefore, we have not presented their spectral data again in this section.

General procedure for the asymmetric reduction of prochiral ketones using 5 mol% (5S)-1,3-diaza-2-(benzylamino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (190):

(S)-2-Bromo-1-phenylethanol [(S)-167b]:

To a stirred solution of (5S)-1,3-diaza-2-(benzylamino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (190) (0.05 mM, 16.3 mg) in toluene (5 mL) was added...
borane-dimethyl sulphide (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 (166b) (1.0 mM, 199 mg) in toluene (2 mL) was added dropwise over 10 min and stirring was continued for further 45 min (monitored by TLC) at the same temperature (110 °C). 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, thus obtained was purified by column chromatography (silica gel, 5% ethyl acetate in hexanes) to provide the desired (S)-2-bromo-1-phenylethanol [(S)-167b] as a colorless oil.

Yield: 82% (165 mg)

$\left[\alpha\right]_{D}^{25}$: +39.66 (c 0.9, CHCl$_3$) [Lit.$^{162}$ $\left[\alpha\right]_{D}^{25}$: -39.0 (c 8.00, CHCl$_3$), R-configuration, 93% ee].

Enantiomeric purity: 89% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (±)-167b].

**Determination of enantiomeric purity:**

HPLC analysis (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min) of the chiral alcohol (S)-167b (for similar HPLC analysis of racemic alcohol see page no. 152) using chiral column, Chiralcel-OD showed two peaks at 8.38 min (S) and 10.14 min (R) in the ratio of 94.5:5.5 indicating that its enantiomeric purity is 89%.
(S)-2-Chloro-1-phenylethanol [(S)-167a]:

This alcohol was prepared by the borane-mediated asymmetric reduction of phenacyl chloride (166a) in the presence of 5 mol% (5S)-1,3-diaza-2-(benzylamino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (190), following the similar procedure described for the molecule (S)-167b, as a colorless liquid.

Yield: 82 %

\[ [\alpha]_D^{25} = +39.52 \ (c \ 2.75, \ \text{cyclohexane}) \] [Lit.\(^{162}\) \[ [\alpha]_D^{25} = -48.10 \ (c \ 1.73, \ \text{cyclohexane}), \ R\text{-configuration, 100\% ee}. \]

Enantiomeric purity: 84% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (+)-167a].

**Determination of enantiomeric purity:**

HPLC analysis of the chiral alcohol (S)-167a (for similar HPLC analysis of racemic alcohol see page no. 153) using chiral column, Chiralcel-OD, (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min) showed two peaks at 7.69 min (S) and 9.47 min (R). The peaks are in the ratio of 92:08 indicating that its enantiomeric purity is 84%.

(R)-1-Phenylethanol [(R)-176a]:

This compound was prepared via the asymmetric reduction of acetophenone (175a) with BH\(_3\).SMe\(_2\) in the presence of 5 mol% (5S)-1,3-diaza-2-(benzylamino)-2-phospha-
2-oxo-3-phenylbicyclo(3.3.0)octane (190), as a colorless liquid, following the similar procedure described for the molecule (S)-167b.

Yield: 74%

\[ \text{[\(\alpha\)}_D^{25} : +29.82 \ (c \ 0.86, \text{MeOH}) \ [\text{Lit.}^{167} \ [\text{[\(\alpha\)}_D^{25} : +37.7 \ (c \ 3.81, \text{MeOH}), \text{R-configuration}, 84\% \text{ ee}]. \]

Enantiomeric purity: 62\% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (+)-176a].

**Determination** of enantiomeric purity:

HPLC analysis (solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL / min) of chiral alcohol (R)-176a (for similar HPLC analysis of racemic alcohol see page no. 171) showed two peaks at 8.87 min (R) and 10.96 min (S) in the ratio of 81:19 indicating that the reduction is 62\% enantioselective.

**(5S)-1,3-Diaza-2-(\(t\)-butylamino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (191):**

This product was obtained as a white solid via the treatment of (2S,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane [(2S,5S)-165] with \(t\)-butylamine in the presence of triethylamine at 45 °C, following the similar procedure described for 190.

Time: 12 h

Yield: 55%
Mp: 129-132 °C

[α]D25: -36.84 (c 1.05, CHCl3)

IR(KBr): v 3171, 1601, 1224 cm⁻¹

1H NMR: 6 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).

13C NMR: 5 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, 120.61, 128.86, 142.05.

31P NMR: 8 17.17

Mass (m/z): 293 (M⁺)

Analysis calcd. for C13H24N3OP: C, 61.42; H, 8.25; N, 14.32.

Found: C, 61.26; H, 8.30; N, 14.35.

Asymmetric reduction of prochiral ketones with (5S)-1,3-diaza-2-(t-butyramino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (191)

(S)-2-Bromo-1-phenylethanol [(S)-167b]:

This molecule was obtained as a colorless liquid via the borane-mediated asymmetric reduction of phenacyl bromide (166b) in the presence of 5 mol% (5S)-1,3-diaza-2-(t-butyramino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (191), following the similar procedure described for the molecule (S)-167b using chiral catalyst 190.
Yield: 86 %

fa].)\textsuperscript{25}: +37.12 (c 1.84, CHCl\textsubscript{3}) \textnormal{[Lit.\textsuperscript{162} [\alpha]_D}\textsuperscript{25}: -39.0 (c 8.00, CHCl\textsubscript{3}), R-configuration, 93% ee].

Enantiomeric purity: 85% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (\(\pm\))-167b].

**Determination of enantiomeric purity:**

The chiral alcohol (\(S\))-167b (for similar HPLC analysis of racemic alcohol see page no. 152) showed two peaks at (retention times) 8.12 min (\(S\)) and 9.77 min (\(R\)) in the ratio of 92.50:7.50 on HPLC analysis using chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min) indicating that the reaction is 85% enantioselective.

(**S**)-2-Chloro-1-phenylethanol [(**S**)-167a]:

This compound was prepared by the asymmetric reduction of phenacyl chloride (166a) with BH\textsubscript{3}.SMe\textsubscript{2} in the presence of 5 mol\% (5\text{S})-1,3-diaza-2-(\(t\)-butylamino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (191), as a colorless liquid, following the similar procedure described for the molecule (\(S\))-167b using chiral catalyst 190.

Yield: 81%
[\alpha]_D^{25}: +31.93 \ (c \ 0.88, \ \text{cyclohexane}) \ [\text{Lit.}^{162} \ [\alpha]_D^{25}: -48.10 \ (c \ 1.73, \ \text{cyclohexane}), \ R\text{-configuration, 100\% ee}].

Enantiomeric purity: 65\% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (±)-167a].

**Determination of enantiomeric purity:**

HPLC analysis (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min) of the chiral alcohol (S)-167a (for similar HPLC analysis of racemic alcohol see page no. 153) showed two peaks at 7.95 min (S) and 9.23 min (R) on chiral column, Chiralcel-OD, in the ratio of 82.5:17.5 indicating that the reaction is 65\% enantioselective.

**(R)-1-Phenylethanol [(R)-176a]:**

This molecule was obtained as a colorless liquid by the asymmetric reduction of acetophenone (175a) with BH$_3$.SMe$_2$ in the presence of 5 mol\% (5S)-1,3-diaza-2-(t-butylamino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (191), following the similar procedure described for the molecule (S)-167b using chiral catalyst 190.

Yield: 84\%

[\alpha]_D^{25}: +20.58 \ (c \ 0.51, \ \text{MeOH}) \ [\text{Lit.}^{167} \ [\alpha]_D^{25}: +37.7 \ (c \ 3.81, \ \text{MeOH}), \ R\text{-configuration, 84\% ee}].

Enantiomeric purity: 44\% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (±)-176a].
**Determination of enantiomeric purity:**

HPLC analysis of the chiral alcohol (R)-176a (for similar HPLC analysis of racemic alcohol see page no. 171) using chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL /min) showed two peaks at 8.92 min (R) and 10.85 min (S). The peaks are in the ratio of 72:28 indicating that its enantiomeric purity is 44%.

(5S)-1,3-diaza-2-(allylamino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (192):

This compound was prepared via the reaction of (2S,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane [(2S,5S)-165] with allylamine in the presence of triethylamine, as a white solid, following the similar procedure described for the molecule 190.

<table>
<thead>
<tr>
<th>Time:</th>
<th>12 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield:</td>
<td>58%</td>
</tr>
<tr>
<td>Mp:</td>
<td>70-72 °C</td>
</tr>
<tr>
<td>[α]d^25:</td>
<td>-33.18 (c 1.1, CHCl3)</td>
</tr>
<tr>
<td>IR (KBr):</td>
<td>ν 3190, 1599, 1201 cm⁻¹</td>
</tr>
<tr>
<td>^1H NMR:</td>
<td>5 1.59-2.18 (m, 4H), 2.72-3.09 (m, 2H), 3.22-3.51 (m, 3H), 3.63-3.94 (m, 3H), 4.92-5.15 (m, 2H), 5.60-5.82 (m, 1H), 6.90-7.01 (m, 1H), 7.14-7.37 (m, 4H).</td>
</tr>
</tbody>
</table>
$^{13}$C NMR: 8 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).

$^{31}$P NMR: δ 21.38

Mass (m/z): 277 (M$^+$)

Analysis cald. for C$_{14}$H$_{20}$N$_3$OP: C, 60.64; H, 7.27; N, 15.15.

Found: C, 60.84; H, 7.30; N, 15.18.

Asymmetric reduction of prochiral ketones with (5S)-1,3-diaza-2-(allylamino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (192)

(S)-2-Bromo-1-phenylethanol [(S)-167b]:

This molecule was obtained as a colorless liquid via the asymmetric reduction of phenacyl bromide (166b) with BH$_3$.SMe$_2$ in the presence of 5 mol% (5S)-1,3-diaza-2-(allylamino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (192), following the similar procedure described for the molecule (S)-167b using the chiral catalyst 190.

Yield: 84 %

$[\alpha]_D^{25}$: +34.91 (c 1.10 CHCl$_3$) [Lit.$^{162}$ $[\alpha]_D^{25}$: -39.0 (c 8.00, CHCl$_3$), R-configuration, 93% ee].

Enantiomeric purity: 81% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (+)-167b].
Determination of enantiomeric purity:

HPLC analysis of the chiral alcohol (S)-167b (for similar HPLC analysis of racemic alcohol see page no. 152) showed two peaks at 8.12 min (S) and 9.76 min (R) in the ratio of 90.5:9.5 on chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min) indicating that its enantiomeric purity is 81%.

(S)-2-Chloro-l-phenylethanol [(S)-167a]:

This compound was prepared by the borane-mediated asymmetric reduction of phenacyl chloride (166a) in the presence of 5 mol% (5S)-1,3-diaza-2-(allylamino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (192), as a colorless liquid, following the similar procedure described for the molecule (S)-167b using the chiral catalyst 190.

Yield: 83%

$[\alpha]_{D}^{25}$: +29.82 (c 0.93, cyclohexane) [Lit. $[\alpha]_{D}^{25}$: 48.10 (c 1.73, cyclohexane), R-configuration, 100% ee].

Enantiomeric purity: 61% [determined by HPLC using chiral column Chiralcel-OD, with reference to racemic alcohol (±)-167a].

Determination of enantiomeric purity:

HPLC analysis (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min) of the chiral alcohol (S)-167a (for similar HPLC analysis of racemic alcohol see page no. 153) showed two peaks at 8.12 min (S) and 9.67 min (R) on chiral column, Chiralcel-OD, in the ratio of 80.5:19.5 indicating that the reduction is 61% enantioselective.
(R)-1-Phenylethanol

This molecule was obtained as a colorless liquid by the asymmetric reduction of acetophenone (175a) with BH$_3$.SMe$_2$ in the presence of 5 mol% (55)-1,3-diaza-2-(allylamino)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (192), following the similar procedure described for the molecule (5)-167b using the chiral catalyst 190.

Yield: 82%

$[\alpha]_D^{25}$: +17.2 (c 2.75, MeOH) [Lit.$^{167}$ $[\alpha]_D^{25}$: +37.7 (c 3.81, MeOH), R-configuration, 84% ee].

Enantiomeric purity: 37% (determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (+)-176a).

Determination of enantiomeric purity:

The alcohol (R)-176a (for similar HPLC analysis of racemic alcohol see page no. 171) showed two peaks at (retention times) 8.78 min (R) and 10.77 min (5) in the ratio of 68.50:31.50 on HPLC analysis using chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL / min) indicating that the reaction is 37% enantioselective.

(5S)-1,3-Diaza-2-[(5S)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo-(3.3.0)octane (193A):

This molecule was prepared as a white solid via the reaction between (2S,5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane [(2S,5S)-165] and (5)-1-meth-
ylbenzylamine [(S)-194] in the presence of triethylamine, following the similar procedure described for the molecule 190.

Time: 2 days
Yield: 90%
Mp: 148-150°C
[α]D25: -26.0 (c 1.0, CHCl₃)
IR (KBr): v 3211, 1601, 1205 cm⁻¹
¹H NMR: 5 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, 4H), 3.97-4.18 (m, 1H), 6.91-7.02 (m, 1H), 7.15-7.39 (m, 9H).
¹³C NMR: 6 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.
³¹P NMR: 6 17.88
Mass(m/z): 342 (M⁺+1)
Analysis cald. for C₁₉H₂₄N₃OP: C, 66.85; H, 7.09; N, 12.31.
Found: C, 66.70; H, 7.12; N, 12.25.
Asymmetric reduction of prochiral ketones with 5 mol% (5S)-1,3-diaza-2-[(5S)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane(193A):

(S)-2-Bromo-1-phenylethanol [(S)-167b]:

Borane-dimethyl sulphide (1.0 mM, 76 mg) was added, to a stirred solution of (5S)-1,3-diaza-2-[(S)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193A) (0.05 mM, 17.19 mg) in toluene (5 mL) at room temperature and the reaction mixture was heated to 110 °C. A solution of phenacyl bromide (166b) (1.0 mM, 199 mg) in toluene (2 mL) was added dropwise over 10 min and stirring was continued for further 45 min (monitored by TLC) at 110 °C. 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, thus obtained was purified by column chromatography (silica gel, 5% ethyl acetate in hexanes) to provide the pure (S)-2-bromo-1-phenylethanol [(S)-167b] as a colorless oil.

Yield: 80 % (161 mg)

[α]D$^{26}$: +39.41 (c 1.0, CHCl₃) [Lit.$^{162}$ [α]$D^{25}$: -39.0 (c 8.00, CHCl₃), R-configuration, 93% ee].

Enantiomeric purity: 89% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (+)-167b].

Determination of enantiomeric purity:

HPLC analysis (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min) of the chiral alcohol (S)-167b (for similar HPLC analysis of racemic alcohol see page no.
showed two peaks at 9.08 min (S) and 11.29 min (R) on chiral column, Chiralcel-OD, in the ratio of 94.5:5.5 indicating that its enantiomeric purity is 89%.

\((\mathcal{S})\)-2-Chloro-1-phenylethanol \((\mathcal{S})\)-167a:

This compound was obtained via the asymmetric reduction of phenacyl chloride \((\mathcal{S})\)-166a with BH3.SMe2 in the presence of 5 mol\% \((\mathcal{S})\)-1,3-diaza-2-[(\mathcal{S})-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane \((\mathcal{A})\), as a colorless liquid, following the similar procedure described for the molecule \((\mathcal{S})\)-167b.

Yield: 85%

\([\alpha]_D^{25}\): +42.3 (c 1.5, cyclohexane) [Lit.\(^{162}\) \([\alpha]_D^{25}\): -48.10 (c 1.73, cyclohexane), \(R\)-configuration, 100% ee].

Enantiomeric purity: 87% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol \((\pm)\)-167a].

**Determination of enantiomeric purity:**

The chiral alcohol \((\mathcal{S})\)-167a (for similar HPLC analysis of racemic alcohol see page no. 153) showed two peaks at 8.08 min (S) and 9.58 min (R) in the ratio of 93.5:6.5 on HPLC analysis using chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min), indicating that its enantiomeric purity is 87%.

\((\mathcal{R})\)-1-Phenylethanol \((\mathcal{R})\)-176a

This compound was obtained as a colorless liquid by the asymmetric reduction of acetophenone \((\mathcal{S})\)-175a with BH3.SMe2 in the presence of 5 mol\% \((\mathcal{S})\)-1,3-diaza-2-[(\mathcal{S})-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane \((\mathcal{A})\), as a colorless liquid, following the similar procedure described for the molecule \((\mathcal{S})\)-167b.

Yield: 85%

\([\alpha]_D^{25}\): +42.3 (c 1.5, cyclohexane) [Lit.\(^{162}\) \([\alpha]_D^{25}\): -48.10 (c 1.73, cyclohexane), \(R\)-configuration, 100% ee].

Enantiomeric purity: 87% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol \((\pm)\)-167a].

**Determination of enantiomeric purity:**

The chiral alcohol \((\mathcal{R})\)-167a (for similar HPLC analysis of racemic alcohol see page no. 153) showed two peaks at 8.08 min (S) and 9.58 min (R) in the ratio of 93.5:6.5 on HPLC analysis using chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min), indicating that its enantiomeric purity is 87%.

\((\mathcal{R})\)-1-Phenylethanol \((\mathcal{R})\)-176a

This compound was obtained as a colorless liquid by the asymmetric reduction of acetophenone \((\mathcal{S})\)-175a with BH3.SMe2 in the presence of 5 mol\% \((\mathcal{S})\)-1,3-diaza-2-[(\mathcal{S})-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane \((\mathcal{A})\), as a colorless liquid, following the similar procedure described for the molecule \((\mathcal{S})\)-167b.

Yield: 85%

\([\alpha]_D^{25}\): +42.3 (c 1.5, cyclohexane) [Lit.\(^{162}\) \([\alpha]_D^{25}\): -48.10 (c 1.73, cyclohexane), \(R\)-configuration, 100% ee].

Enantiomeric purity: 87% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol \((\pm)\)-167a].

**Determination of enantiomeric purity:**

The chiral alcohol \((\mathcal{R})\)-167a (for similar HPLC analysis of racemic alcohol see page no. 153) showed two peaks at 8.08 min (S) and 9.58 min (R) in the ratio of 93.5:6.5 on HPLC analysis using chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min), indicating that its enantiomeric purity is 87%.
1-phenylethlamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193A), following the similar procedure described for the molecule (S)-167b.

Yield: 87%

$\left[\alpha\right]_D^{25}$: $+32.60 \ (c \ 1.60, \text{MeOH}) \ [\text{Lit.} \ 167 \ [\alpha\]_D^{25} : +37.7 \ (c \ 3.81, \text{MeOH})], \ R$-configuration, 84% ee.

Enantiomeric purity: 72% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (±)-176a].

Determination of enantiomeric purity:

The chiral alcohol $(R)$-176a (for similar HPLC analysis of racemic alcohol see page no. 171) showed two peaks at (retention times) 9.08 min $(R)$ and 10.50 min $(S)$ in the ratio of 86:14 on HPLC analysis using chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL / min) indicating that the reaction is 72% enantioselective.

(5S)-1,3-diaza-2-[(R)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo-(3.3.0)octane (193B):

This compound was prepared via the reaction of $(2S,5S)$-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane $(2S,5S)$-165 with $(R)$-1-methylbenzylamine $(R)$-194 in the presence of triethylamine, as a viscous liquid, following the similar procedure described for the molecule 190.

Time: 2 days
Yield: 91%

$[\alpha]_D^{25}$: -22.90 (c 1, CHCl$_3$)

IR(neat): v 3211, 2966, 1601, 1201 cm$^{-1}$

$^1$H NMR: 5 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).

$^{13}$C NMR: 5 25.04 (d, J=8.1Hz), 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.

$^{31}$P NMR: 5 20.14

Mass(m/z): 341 (M$^+$)

Analysis cald. for C$_{19}$H$_{24}$N$_3$OP: C, 66.85; H, 7.09; N, 12.31.

Found: C, 66.66; H, 7.15; N, 12.35.

Asymmetric reduction of prochiral ketones with (5S)-1,3-diaza-2-[(R)-1-phenylethlamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193B)

(S)-2-Bromo-1-phenylethanol [(S)-167b]:

This compound was obtained as a colorless liquid via the borane-mediated asymmetric reduction of phenacyl bromide (166b) in the presence of 5 mol% (5S)-1,3-diaza-2-[(R)-1-phenylethlamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193B) following the similar procedure described for the molecule (S)-167b using chiral catalyst 193A.
Yield: 81%

\([\alpha]_D^{25} = +39.2 \ (c \ 1.25, \ \text{CHCl}_3) \) [Lit.\textsuperscript{162} \([\alpha]_D^{25} = -39.0 \ (c \ 8.00, \ \text{CHCl}_3), R-\) configuration, 93\% ee].

Enantiomeric purity: 88\% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (\(\pm\))-167b].

**Determination** of enantiomeric purity:

The alcohol (\(\textit{S}\))-167b (for similar HPLC analysis of racemic alcohol see page no. 152) showed two peaks at (retention times) 9.13 min (\(S\)) and 11.41 min (\(R\)) in the ratio of 94:6.0 on HPLC analysis using chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min) indicating that the reaction is 88\% enantioselective.

**(S)-2-Chloro-1-phenylethanol [(S)-167a]:**

This molecule was prepared as a colorless liquid by the asymmetric reduction of phenacyl chloride (166a) with BH\textsubscript{3}.SMe\textsubscript{2} in the presence of 5 mol\% (SS)-1,3-diaza-2-[(\(R\))-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193B) following the similar procedure described for the molecule (\(\textit{S}\))-167b using the chiral catalyst 193A.

Yield: 83\%
Enantiomeric purity: 84% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (±)-167a].

Determination of enantiomeric purity:

HPLC analysis (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min) of the chiral alcohol (S)-167a (for similar HPLC analysis of racemic alcohol see page no. 153) showed two peaks at 7.99 min (S) and 9.27 min (R) in the ratio of 92:8.0 indicating that its enantiomeric purity is 84%.

(R)-1-Phenylethanol [(R)-176a]:

This compound was prepared as a colorless liquid via the asymmetric reduction of acetophenone (175a) with BH$_3$.SMe$_2$ in the presence of 5 mol% (5S)-1,3-diaza-2-[(R)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193B) following the similar procedure described for the molecule (S)-167b using the chiral catalyst 193A.

Yield: 82%

$[\alpha]_D^{25}$: +31.6 (c 1.70, MeOH) [Lit.$^{167}[\alpha]_D^{25}$: +37.7 (c 3.81, MeOH), R-configuration, 84% ee].

Enantiomeric purity: 70% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (±)-176a].
Determination of enantiomeric purity:

HPLC analysis of the chiral alcohol \((R)-176a\) (for similar HPLC analysis of racemic alcohol see page no. 171) using chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL / min) showed two peaks at 9.09 min \((R)\) and 10.55 min \((S)\). The peaks are in the ratio of 85:15 indicating that its enantiomeric purity is 70%.

Asymmetric reduction of prochiral ketones using 2.5 mol% \((SS)-1,3\text{-diaza-2-}[\((S)\text{-1-phenylethylamino}]\)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane \((193\ A)\) and 2.5 mol% \((SS)-1,3\text{-diaza-2-}[\((R)\text{-1-phenylethylamino}]\)-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane \((193B)\):

\((S)\)-2-Bromo-1-phenylethanol \([\((S)\)-167b\]:

This molecule was obtained as a colorless liquid by the borane-mediated asymmetric reduction of phenacyl bromide \((167b)\) using 2.5 mol% \(193A\) and 2.5 mol% \(193B\), following the similar procedure described for the molecule \((S)-167b\) using the chiral catalyst \(193A\).

Yield: 80%

\([\alpha]_D^{25}\): +37.8 \((c\ 1.0,\ CHCl_3)\) \([\text{Lit.}^{162} [\alpha]_D^{25}\;: -39.0 \((c\ 8.00,\ CHCl_3)\); \(R\)-configuration, 93% ee].

Enantiomeric purity: 85% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol \((+)-167b\).]
Determination of enantiomeric purity:

HPLC analysis of the chiral alcohol (S)-167b (for similar HPLC analysis of racemic alcohol see page no. 152) showed two peaks at 9.01 min (S) and 11.22 min (R) in the ratio of 92.5:7.5 on chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL/min) indicating that its enantiomeric purity is 85%.

(S)-2-Chloro-1-phenylethanol [(S)-167a]:

This molecule was prepared via the asymmetric reduction of phenacyl chloride (166a) with BH₃.SMe₂ in the presence of 2.5 mol% 193A and 2.5 mol% 193B, following the similar procedure described for the molecule (S)-167b using the chiral catalyst 193A.

Yield: 80%

[α]D²⁵: +40.36 (c 1.1, cyclohexane) [Lit.¹⁶² [α]D²⁵: -48.10 (c 1.73, cyclohexane), R-configuration, 100% ee].

Enantiomeric purity: 82% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (±)-167a].

Determination of enantiomeric purity:

The alcohol (S)-167a (for similar HPLC analysis of racemic alcohol see page no. 153) showed two peaks at (retention times) 7.98 min (S) and 9.26 min (R) in the ratio of 91:9 on HPLC analysis using chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL/min) indicating that the reaction is 82% enantioselective.
(R)-1-Phenylethanol [(R)-176a]:

This compound was obtained as a colorless liquid by the asymmetric reduction of acetophenone (175a) with BH₃.SMe₂ in the presence of 2.5 mol% 193A and 2.5 mol% 193B, following the similar procedure described for the molecule (S)-167b using the chiral catalyst 193A.

Yield: 72%

[α]D₂₅: +28.58 (c 0.88, MeOH) [Lit.¹⁶⁷ [α]D₂₅: +37.7 (c 3.81, MeOH), R-configuration, 84% ee].

Enantiomeric purity: 60% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (+)-176a].

**Determination of enantiomeric purity:**

HPLC analysis (solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL / min) of the chiral alcohol (R)-176a (for similar HPLC analysis of racemic alcohol see page no. 171) showed two peaks at 8.89 min (R) and 11.00 min (S) in the ratio of 80:20 indicating that its enantiomeric purity is 60%.

Asymmetric reduction of prochiral ketones using 5 mol% (SS)-1,3-diaza-2-[(S)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane(193A)

Spectral data (IR, ¹H & ¹³C NMR) of the chiral alcohols (S)-167c, (S)-167d, (S)-167e, (S)-167f, (S)-167h (R)-176b, (R)-176c and (R)-176d (prepared using the chiral catalyst...
193A) are in full agreement with that of the chiral alcohols (S)-167c, (S)-167d, (S)-167e, (S)-167f, (S)-167h (R)-176b, (R)-176c and (R)-176d prepared via the asymmetric reduction of corresponding prochiral ketones 166c-f, 166h, 175b-d using the catalysts 159 or 188 or (2S,5S)-165. Therefore, we have not presented their spectral data again in this section.  

Similarly, spectral data (IR, $^1$H & $^{13}$C NMR) of the acetates (S)-171, (S)-172 and (S)-173 of chiral alcohols (S)-167d, (S)-167e and (S)-167h (prepared using the chiral catalyst 193 A) are in complete agreement with that of the acetates (S)-171, (S)-172 and (S)-173 of chiral alcohols (S)-167d, (S)-167e and (S)-167h [obtained via the asymmetric reduction of corresponding prochiral ketones 166d, 166e and 166h using the catalyst 159 or (2S, 5S)-165]. Therefore, we have not presented their spectral data again in this section. 

(S)-2-Bromo-1-(4-methylphenyl)ethanol [(S)-167c]:

This molecule was obtained via the borane-mediated asymmetric reduction of 4-methylphenacyl bromide (166c) in the presence of 5 mol% (5S)-1,3-diaza-2-[(S)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193A), following the similar procedure described for the molecule (S)-167b, as a viscous liquid.

Though it looks repetitive, with a view to have better understanding and perspective the details of the determination of enantiomeric purities of the chiral alcohols [HPLC analysis and $^1$H NMR spectral analysis using chiral shift reagent, Eu(hfc)$_3$] have been presented in each case.
Yield: 84%

$[\alpha]_D^{25}$: +37.87 (c 1.08, CHCl$_3$)

Enantiomeric purity: 91% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (+)-167c].

**Determination of enantiomeric purity:**

HPLC analysis (solvent system, hexanes: IPA / 95:05; flow rate: 0.5 mL / min) of the chiral alcohol (S)-167c (for similar HPLC analysis of racemic alcohol see page no. 142) showed two peaks at 26.02 min (S) and 28.51 min (R) on chiral column, Chiralcel-OD, in the ratio of 95.5:4.5 indicating that the reaction is 91% enantioselective.

(S)-2-Bromo-1-(4-chlorophenyl)ethanol [(S)-167d]:

This compound was obtained as a colorless liquid via the asymmetric reduction of 4-chlorophenacyl bromide (166d) with BH$_3$.SMe$_2$ in the presence of 5 mol% (S)-1,3-diaza-2-[(S)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193A), following the similar procedure described for the molecule (S)-167b.

Yield: 87%

$[\alpha]_D^{25}$: +39.0 (c 1 CHCl$_3$)

Enantiomeric purity: 89% [determined by $^1$H NMR spectral analysis of the corresponding acetate (S)-171 in the presence of chiral shift reagent, Eu(hfc)$_3$, with reference to racemic acetate (+)-171].
(S)-1-Acetoxy-2-bromo-1-(4-chlorophenyl)ethane [(S)-171]:

This molecule was prepared as a colorless liquid via the treatment of (S)-2-bromo-1-(4-chlorophenyl)ethanol [(S)-167d] with acetic anhydride in presence of pyridine following the similar procedure as described for the molecule (S)-171 (page no. 143).

Yield: 80 %

\[\alpha\] _D_ 25°: +53.10 (c 1.05, CHCl₃)

**Determination of enantiomeric purity:**

The ¹H NMR spectrum of chiral acetate (S)-171 (5 mg) (for similar ¹H NMR spectral analysis of racemic acetate see page no. 143) was recorded in the presence of Eu(hfc)₃ (20 mg). The original singlet (at 8 2.13) of acetoxy methyl (OCOMe) protons splits into two distinct singlets in the ratio of 94.5:5.5 indicating that the enantiomeric purity of the alcohol is 89%.

(S)-2-Bromo-1-(4-bromophenyl)ethanol [(S)-167e]:

This chiral alcohol was obtained via the asymmetric reduction of 4-bromophenacyl bromide (166e) with BH₃.SMe₂ in the presence of 5 mol% (55)-1,3-diaza-2-[(S)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193A), as a white solid, following the similar procedure described for the molecule (S)-167b.

Yield: 80 %

M.P: 70-72 °C
(S)-1-Acetoxy-2-bromo-1-(4-bromophenyl)ethane [(S)-172]:

This molecule was prepared as a colorless liquid via the treatment of (S)-2-bromo-1-(4-bromophenyl)ethanol [(S)-167e] with acetic anhydride in presence of pyridine following the similar procedure described for the molecule (S)-III (page no. 143).

Yield: 70%

$\left[\alpha\right]_D^{25}: +42.55 \ (c \ 0.94, \ CHCl_3)$

**Determination of enantiomeric purity:**

The $^1$H NMR spectrum of chiral acetate (S)-172 (5 mg) (for similar $^1$H NMR spectral analysis of racemic acetate see page no. 156) was recorded in the presence of chiral shift reagent, Eu(hfc)$_3$ (20 mg). The original singlet (at 5 2.13) of acetoxy methyl (OCOMe) splits into two distinct singlets in the ratio of 97:03 indicating that the enantiomeric purity of the alcohol is 94%.

(S)-2-Chloro-1-(4-methylphenyl)ethanol [(S)-167f]:

This molecule was prepared by the borane-mediated asymmetric reduction of 4-
methylphenacyl chloride (166f) in the presence of 5 mol % (5S)-1,3-diaza-2-[(S)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193A), following the similar procedure described for the molecule (S)-167b as a colorless liquid.

Yield: 82%

\([\alpha]_D^{25} : +44.88 \text{ (c 1.0, CHCl}_3\text{)}\)

Enantiomeric purity: 89% [determined by HPLC using chiral column Chiralcel-OD, with reference to racemic alcohol (±)-167f].

**Determination of enantiomeric purity:**

HPLC analysis (Chiralcel-OD, solvent system, hexanes: IPA / 97.5:2.5; Flow rate: 0.8 mL / min) of the chiral alcohol (S)-167f (for similar HPLC analysis of racemic alcohol see page no. 157) showed two peaks at 16.38 min (S) and 18.42 min (R) in the ratio of 94.5:5.5 on similar HPLC analysis, indicating that its enantiomeric purity is 89%.

**((S)-2-Bromo-1-(4-nitrophenyl)ethanol [(S)-167h]:**

This compound was obtained via the asymmetric reduction of 4-nitrophenacyl bromide (166h) with BH$_3$SMe$_2$ in the presence of 5 mol% (5S)-1,3-diaza-2-[(S)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193A), as a white solid, following the similar procedure described for the molecule (S)-167b.

Yield: 82%

\([\alpha]_D^{25} : +32.1 \text{ (c 1.0, CHCl}_3\text{)}\)
Enantiomeric purity: 91% [\(^1\)H NMR spectral analysis of the corresponding acetate (S)-173 in the presence of chiral shift reagent, Eu(hfc)\(_3\), with reference to racemic alcohol (+)-173].

**(S)-1-Acetoxy-2-bromo-1-(4-nitrophenyl)ethane [(S)-173]**

This product was prepared as a colorless liquid by the reaction of (S)-2-bromo-1-(4-nitrophenyl)ethanol [(S)-167h] with acetic anhydride in presence of pyridine following the similar procedure as described for the molecule (S)-171 (page no. 143).

Yield: 75 %

Mp: 102-105 °C

\([\alpha]\)_D\(^{25}\): +47.35 (c 1.1, CHCl\(_3\))

**Determination of enantiomeric purity:**

The \(^1\)H NMR spectrum of chiral acetate (S)-173 (5 mg) (for similar \(^1\)H NMR spectral analysis of racemic acetate see page no. 159) was recorded in the presence of chiral shift reagent, Eu(hfc)\(_3\) (20 mg). The original singlet (at 5 2.18) of acetoxy methyl (OCOME) protons splits into two distinct singlets in 95.5:4.5 ratio indicating the enantiomeric purity of the alcohol is 91%.

**(R)-1-Phenylpropan-1-ol [(R)-176b]:**

This molecule was obtained as a colorless liquid via the asymmetric reduction of propiophenone (175b) with BH\(_3\).SMe\(_2\) in the presence of 5 mol % (5S)-1,3-diaza-2-
[(S)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193A), following the similar procedure described for the molecule (S)-167b.

Yield: 81%

$\text{lab}^{25}: \ +27.84 \ (c \ 0.79, \ \text{CHCl}_3) \ [\text{Lit.}^{169} [\alpha]_D^{25}: +43.03 \ (c \ 5.1, \ \text{CHCl}_3), \ R$-configuration, 96% ee].

Enantiomeric purity: 61% [determined by HPLC using chiral column, Chiralcel-OD, with reference to racemic alcohol (±)-176b].

**Determination of enantiomeric purity:**

HPLC analysis of the chiral alcohol $(R)$-176b (for similar HPLC analysis of racemic alcohol see page no. 190) showed two peaks at 8.11 min $(R)$ and 9.86 min $(S)$ in the ratio of 80.5:19.5 on chiral column, Chiralcel-OD (solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL / min) indicating that its enantiomeric purity is 61%.

$(R)$-1-Phenylbutan-1-ol [(R)-176c]:

This molecule was obtained as a colorless liquid via the asymmetric reduction of butyrophenone (175c) with BH$_3$.SMe$_2$ in the presence of 5 mol% (SS)-1,3-diaza-2-[(S)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193A), following the similar procedure described for the molecule (S)-167b.

Yield: 80%

$[\alpha]_D^{25}: +21.95 \ (c \ 1.5, \ \text{benzene}) \ [\text{Lit.}^{23} [\alpha]_D^{25}: -45.2 \ (c \ 4.81, \ \text{benzene}), \ S$-
Enantiomeric purity: 47% (determined by HPLC using chiral column, Chiralcel-OD).

**Determination of enantiomeric purity:**

HPLC analysis (solvent system, hexanes: IPA / 95:05; flow rate: 0.7 mL / min) of the racemic alcohol [(±)-176c] showed two peaks at 11.21 min (R) and 12.74 min (S) in 1:1 ratio on chiral column, Chiralcel-OD. Similar HPLC analysis of the chiral alcohol [(R)-176c] showed two peaks at 11.27 min (R) and 12.78 min (S) in the ratio of 73.5:26.5 indicating that its enantiomeric purity is 47%.

**(R)-1,2,3,4-Tetrahydronaphth-1-ol [(R)-176d]:**

This product was prepared as a colorless liquid by the asymmetric reduction of α-tetralone (175d) with BH$_3$.SMe$_2$ in the presence of 5 mol% (5S)-1,3-diaza-2-[(5S)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193A) following the similar procedure described for the molecule (S)-167b.

**Yield:** 72%

**[α]$_D$$^{25}$:** -11.56 (c 0.9, MeOH)) [Lit.$^{169}$ [α]$_D$$^{25}$: -23.14 (c 1.3, MeOH), R-configuration, 94% ee].

Enantiomeric purity: 43% [determined by HPLC using chiral column Chiralcel-OD, with reference to racemic alcohol (+)-176d].
Determination of enantiomeric purity:

HPLC analysis (solvent system, hexanes: IPA / 97.5:2.5; flow rate: 0.4 mL / min) of chiral alcohol \((R)-176d\) (for similar HPLC analysis of racemic alcohol see page no. 193) showed two peaks at 35.44 min \((S)\) and 39.47 min \((R)\) in the ratio of 28.5:71.5 on chiral column, Chiralcel-OD, indicating that its enantiomeric purity is 43 %.

\((R)-1-(4\text{-Methylphenyl})\text{ethanol}\ [(R)-195a]:\)

This molecule was obtained by the asymmetric reduction of 4-methylacetophenone (168) with BH\(_3\).SMe\(_2\) in the presence of 5 mol% \((5S)-1,3\text{-diaza-2-\[(S)-1\text{-phenylethyl-}\text{amino}\]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193A), as a colorless liquid, following the similar procedure described for the molecule \((S)-167b\).

Yield: 77%

\([\alpha]_D^{25}\): +22.87 \((c\ 0.6, \text{MeOH})\) [Lit.\(^{171}\) \([\alpha]_D^{25}\) -43.5 \((c\ 0.994, \text{MeOH}), S\)-configuration, \(>99\%\) ee].

Enantiomeric purity: 51% [determined by HPLC analysis of corresponding acetate using chiral column, Chiralcel-OJ-H, with reference to racemic acetate \((\pm)-196a\)].

IR(neat): v 3352 cm\(^{-1}\)

\(^1\text{H}\) NMR: 6 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).

\(^{13}\text{C} \) NMR: 6 21.10, 25.08, 70.17, 125.40, 129.15, 137.06, 142.97.
Determination of enantiomeric purity:

The racemic acetate (+)-196a showed two peaks at 7.70 min (R) and 10.87 min (S) in 1:1 ratio on HPLC analysis using chiral column, Chiralcel-OJ-H (solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL / min). The chiral acetate (R)-196a showed two peaks at 7.66 min (R) and 10.82 min (S) in the ratio of 75.5:24.5 on similar HPLC analysis, indicating that its enantiomeric purity is 51%.

(R)-1-Acetoxy-1-(4-methylphenyl)ethane [(R)-196a]:

This molecule was prepared as a colorless liquid via the treatment of (S)-1-(4-methylphenyl)ethanol [(S)-195a] with acetic anhydride in presence of pyridine following the similar procedure as described for the molecule (S)-171 (page no. 143).

Yield: 83 %

\([\alpha]_{D}^{25}\): +61.49 (c 1.0, CHCl$_3$)

IR(neat): ν 1739 cm$^{-1}$

$^1$H NMR: 6 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).

$^{13}$C NMR: 8 21.10, 21.32, 22.07, 72.22, 126.14, 129.16, 137.60, 138.77, 170.27.
(+)-1-(4-Methylphenyl)ethanol [(+)-195a]:
This compound was obtained as colorless liquid via the reaction of 4-methylacetophenone (168) with BH$_3$.SMe$_2$ in toluene following the similar procedure described for the molecule (+)-176b.
Yield: 74%
This compound has identical IR, $^1$H & $^{13}$C NMR spectral data as that of the chiral molecule (R)-195a

(+)-1-Acetoxy-1-(4-methylphenyl)ethane [(+)-196a]:
This compound was prepared as a colorless liquid via the treatment of (+)-1-(4-methylphenyl)ethanol [(+)-195a] with acetic anhydride in presence of pyridine, according to the procedure described for the compound (S)-171 (page no. 143).
Yield: 83%
The spectral data (IR, $^1$H & $^{13}$C NMR) of this molecule are in full agreement with that of the chiral molecule (R)-196a

(R)-1-(4-Chlorophenyl)ethanol [(R)-195b]:
This molecule was obtained as a colorless liquid by the asymmetric reduction of 4-chloroacetophenone (169) with BH$_3$.SMe$_2$ in the presence of 5 mol% (S$^5$)-1,3-diaza-2-[(S$^5$)-1-phenylethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193A), following the similar procedure described for the molecule (S)-167b.
Yield: 70%
$[\alpha]_D^{25}$: +38.4 ($c$ 1.25, Et$_2$O) [Lit.$^{171}$ $[\alpha]_D^{25}$: -49.0 ($c$ 1.84, Et$_2$O), S-configuration, >99% ee].

Enantiomeric purity: 76% [determined by HPLC analysis of corresponding acetate using chiral column, Chiralcel-OJ-H, with reference to racemic acetate (+)-196b].

IR (neat): $\nu$ 3352 cm$^{-1}$

$^1$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).

$^{13}$C NMR: $\delta$ 25.13, 69.54, 126.78, 128.49, 132.92, 144.25.

Determination of enantiomeric purity:

HPLC analysis of the racemic acetate (+)-196b showed two peaks at 6.90 min ($R$) and 8.13 min ($S$) in 1:1 ratio on chiral column, Chiralcel-OJ-H (solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL / min). Similar HPLC analysis of the chiral acetate ($R$)-196b showed two peaks at 6.83 min ($R$) and 8.06 min ($S$) in the ratio of 88:12 indicating that its enantiomeric purity is 76%.

$(R)$-1-Acetoxy-1-(4-chlorophenyl)ethane/(R)-196b:

This molecule was prepared as a colorless liquid via the treatment of ($S$)-1-(4-chlorophenyl)ethanol [(R)-195b] with acetic anhydride in presence of pyridine following the similar procedure as described for the molecule ($S$)-171 (page no. 143).
Yield: 89 %

[a],)\textsuperscript{25}: +74.68 (c 0.39, CHCl\textsubscript{3})

IR(neat): ν 1738 cm\textsuperscript{-1}

\textsuperscript{1}H NMR: δ 1.52 (d, 3H, J=6.8 Hz), 2.07 (s, 3H), 5.85 (q, 1H, J=6.8 Hz).

\textsuperscript{13}C NMR: δ 21.31, 22.18, 71.64, 127.59, 128.74, 133.71, 140.32, 170.21.

(±)-1-(4-Chlorophenyl)ethanol [(±)-195b]:

This product was prepared by treatment of 4-chloroacetophenone (169) with BH\textsubscript{3}.SMe\textsubscript{2} following the similar procedure described for the molecule (+)-176b, as a colorless liquid.

Yield: 84%

The spectral data (IR, \textsuperscript{1}H & \textsuperscript{13}C NMR) of this molecule are in full agreement with that of the chiral molecule (R)-195b.

(±)-1-Acetoxy-1-(4-chlorophenyl)ethane [(±)-196b]:

This molecule was prepared as a colorless liquid via the treatment of (±)-1-(4-chlorophenyl)ethanol [(±)-195b] with acetic anhydride in presence of pyridine, according to the procedure described for the compound (S)-171 (page no. 143).

Yield: 86%
This alcohol has identical IR, $^1$H & $^{13}$C NMR spectral data as that of the chiral molecule ($R$)-196b.

($R$)-1-(4-Bromophenyl)ethanol [(R)-195c]:

This compound was prepared via the borane-mediated asymmetric reduction of 4-bromoacetophenone (170) in the presence of 5 mol% (5S)-1,3-diaza-2-[(S)-1-phenyl-ethylamino]-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octane (193A), as a colorless liquid, following the similar procedure described for the molecule (S)-167b.

Yield: 90%

$[\alpha]_D^{25}$: +30 (c 1.0, CHCl$_3$)[Lit.$^{171}$ [$[\alpha]_D^{25}$: -37.90 (c 1.13, CHCl$_3$), S-configuration, >99% ee].

Enantiomeric purity: 74% [determined by HPLC analysis of corresponding acetate using chiral column, Chiralcel-OJ-H, with reference to racemic acetate (±)-196c].

IR (neat): $\nu$ 3358 cm$^{-1}$

$^1$H NMR: 5 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).

$^{13}$C NMR: 6 25.09, 69.51, 121.00, 127.13, 131.43, 144.75.
Determination of enantiomeric purity:

HPLC analysis (solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL / min) of the racemic acetate (±)-196c showed two peaks at 7.13 min (R) and 8.38 min (S) in 1:1 ratio. Similar HPLC analysis of the chiral acetate (R)-196c showed two peaks at 7.13 (R) min and 8.39 min (S) in the ratio of 87:13 indicating that its enantiomeric purity is 74%.

(R)-1-Acetoxy-1-(4-bromophenyl)ethane [(R)-196c]:

This molecule was prepared as a colorless liquid via the treatment of (R)-(4-bromophenyl)ethanol [(R)-195c] with acetic anhydride in presence of pyridine following the similar procedure as described for the molecule (S)-171 (page no. 143).

Yield: 80%

[α]D 25: +60.24 (c 1.23, CHCl3)

IR (neat): ν 1736 cm⁻¹

¹H NMR: δ 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).

¹³C NMR: 6 21.15, 22.03, 71.54, 121.71, 127.83, 131.62, 140.82, 169.95.

(+)-1-(4-BromophenyI)ethanol[(+)-195c]:

This compound was prepared by the treatment of 4-bromoacetophenone (170) with BH₃.SMe₂ following the similar procedure described for the molecule (+)-176b, as a
colorless liquid.

**Yield:** 92%

This alcohol has identical IR, $^1$H & $^{13}$C NMR spectral data as that of the chiral molecule $(R)$-195c.

**(+)-1-Acetoxy-1-(4-bromophenyl)ethane [(±)-196c]:**

This compound was prepared as a colorless liquid *via* the treatment of (±)-1-(4-bromophenyl)ethanol [(±)-195c] with acetic anhydride in presence of pyridine, according to the procedure described for the compound $(S)$-171 (page no. 143).

**Yield:** 80%

The spectral data (IR, $^1$H & $^{13}$C NMR) of this molecule are in full agreement with that of the chiral molecule $(R)$-196c.
$^1$H NMR spectrum of 158
$^{13}$C NMR spectrum of 159

Spectrum 4
HPLC analysis of 167a (A) Chromatogram of (+)-167a, (B) Chromatogram of (S)-167a, 82% ee (obtained via the asymmetric reduction of 166a using 30 mol% catalyst 158), (C) Chromatogram of (S)-167a, 90% ee (obtained via the asymmetric reduction of 166a using 30 mol% catalyst 159).
HPLC analysis of 167b (A) Chromatogram of (+)-167b, (B) Chromatogram of (S)-167b, 89% ee (obtained via the asymmetric reduction of 166b using 30 mol% catalyst 158)

Solvent system, hexanes: IPA / 90:10; flow rate: 0.5 mL / min.
HPLC analysis of 167b (A) Chromatogram of (+)-167b, (B) Chromatogram of (S)-167b, 94% ee (obtained via the asymmetric reduction of 166b using 30 mol% catalyst 159).

Solvent system, hexanes: IPA / 95:05; flow rate: 0.5 mL / min.
$^1$H NMR spectrum of 172 (A) splitting of acetoxy methyl protons (OCOCH$_3$) of the molecule (±)-172 in the presence of Eu(hfc)$_3$ (B) splitting of acetoxy methyl protons (OCOCH$_3$) of the molecule (S)-172 [acetate of alcohol (S)-167e, obtained via the asymmetric reduction of 166e using 30 mol% catalyst 159] in the presence of Eu(hfc)$_3$, 93% ee.
\[ \text{H NMR spectrum of (2S, 5S)-165} \]
$^{13}$C NMR spectrum of (2S, 5S)-165

Spectrum 8
HPLC analysis of 167b (A) Chromatogram of (+)-167b, (B) Chromatogram of (S)-167b, 87% ee Chromatogram 4
[obtained via the asymmetric reduction of 166b using 5 mol% chiral source (2S, 5S)-165].
Solvent system, hexanes: IPA / 90:10; flow rate: 1.0 mL / min.
$^1$H NMR spectrum of 173 (A) splitting of acetoxyl methyl protons (OCOCH$_3$) of the molecule $(\pm)$-173 in the presence of Eu(hfc)$_3$ (B) splitting of acetoxyl methyl protons (OCOCH$_3$) of the molecule $(S)$-173 [acetate of alcohol $(S)$-167h, obtained via the asymmetric reduction of 166h using 5 mol% catalyst (2S, 5S)-165] in the presence of Eu(hfc)$_3$, 91% ee.
$^{13}$C NMR spectrum of recovered chiral catalyst 165A [from the (2S, 5S)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane ((2S, 5S)-165)] (5 mol%) catalyzed asymmetric reduction of phenacyl bromide (166b) with BH$_3 \cdot$SMe$_2$. 

*Spectrum 10*
HPLC analysis of 167b (A) Chromatogram of (±)-167b, (B) Chromatogram of (S)-167b, 85% ee (obtained via the asymmetric reduction of 166b using 12.8 mg catalyst 165A), (C) Chromatogram of (S)-167b, 82% ee (obtained via the asymmetric reduction of 166b using 12.8 mg catalyst 165B). Solvent system, hexanes: IPA / 95:05; flow rate: 1.0 mL / min.
HPLC analysis of 167b (A) Chromatogram of (±)-167b, (B) Chromatogram of (S)-167b, 55% ee [obtained via the asymmetric reduction of 166b using 20 mol% catalyst (2S, 5S)-177].
$^1$H NMR spectrum of (2R, 5S)-178

Spectrum 14
$^{13}$C NMR spectrum of (2$R$, 5$S$)-178

*Spectrum 15*
HPLC analysis of 167b (A) Chromatogram of (+)-167b, (B) Chromatogram of (S)-167b, 65% ee [obtained via the asymmetric reduction of 166b using 10 mol% catalyst (2R, 5S)-178].
Spectrum 19

$^{31}$P NMR spectrum of 188
HPLC analysis of 167b (A) Chromatogram of (+)-167b, (B) Chromatogram of (S)-167b, 91% ee (obtained via the asymmetric reduction of 166b using 4 mol% catalyst 188).
HPLC analysis of 167c (A) Chromatogram of (±)-167c, (B) Chromatogram of (S)-167c, 91% ee (obtained via the asymmetric reduction of 166c using 4 mol% catalyst 188).
HPLC analysis of 176b (A) Chromatogram of (+)-176b, (B) Chromatogram of (R)-176b, 67% ee (obtained via the asymmetric reduction of 175b using 4 mol% catalyst 188).
HPLC analysis of 167b (A) Chromatogram of (+)-167b, (B) Chromatogram of (S)-167b, 89\% ee (obtained via the asymmetric reduction of 166b using 5 mol\% catalyst 190).
$^1$H NMR spectrum of 192

Spectrum 24
(A) $^3\text{P}NMR$ spectrum of 190
(B) $^3\text{P}NMR$ spectrum of 191
(C) $^3\text{P}NMR$ spectrum of 192
HPLC analysis of 167b (A) Chromatogram of (±)-167b, (B) Chromatogram of (S)-167b, 85% ee (obtained via the asymmetric reduction of 166b using 5 mol% catalyst 191), (C) Chromatogram of (S)-167b, 81% ee (obtained via the asymmetric reduction of 166b using 5 mol% catalyst 192).
$^1$H NMR spectrum of 193A

Spectrum 27
(A) $^{31}\text{P}$ NMR spectrum of 193A (B) $^{31}\text{P}$ NMR spectrum of 193B
HPLC analysis of 167b (A). Chromatogram of (±)-167b. (B) Chromatogram of (S)-167b, 89% ee (obtained via the asymmetric reduction of 166b using 5 mol% catalyst 193A). (C) Chromatogram of (S)-167b, 88% ee (obtained via the asymmetric reduction of 166b using 5 mol% catalyst 193B). (D) Chromatogram of (S)-167b, 85% ee (obtained via the asymmetric reduction of 166b using 5 mol% catalyst (1:1 mixture of catalysts 193A and 193B)).
HPLC analysis of 167f (A) Chromatogram of (+)-167f, (B) Chromatogram of (S)-167f, 89% ee (obtained via the asymmetric reduction of 166f using 5 mol% catalyst 193A).
HPLC analysis of 196b (A) Chromatogram of (Z)-196b, (B) Chromatogram of (R)-196b, 76% ee