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A novel and effective chiral phosphoramide catalyst for the borane-mediated asymmetric reduction of prochiral α-halo ketones

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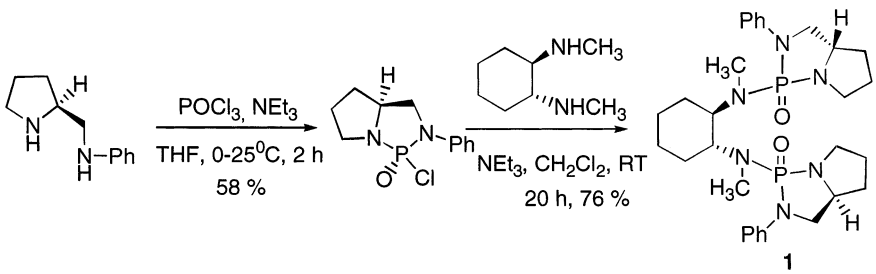
Abstract—The novel chiral phosphoramide, 1,4-bis[(5*S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl]piperazine, was synthesised and successfully employed as a catalyst in the borane-mediated asymmetric reductions of prochiral α-halo ketones, providing the corresponding α-halo alcohols in 90–95% enantiomeric purities. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The asymmetric reduction of prochiral ketones to provide secondary alcohols in high enantiomeric purity is a fundamental reaction in chiral chemistry and the applications of various borane-based chiral reducing agents in this reaction have been well documented.[1–4] After the ingenious utilisation of proline-based oxazaborolidines as catalysts by Corey, for the borane-mediated enantioselective reductions of prochiral ketones, a plethora of oxazaborolidines and related catalysts based on various chiral pool sources have been developed and their applications have been well studied.[2–8] Wills et al. recently introduced a novel class of catalysts containing the N-P=O structural framework for the borane-mediated asymmetric reductions of prochiral ketones[9–15] and they also developed interesting chiral phosphinamide catalysts for highly enantioselective borane-mediated asymmetric reductions.[11–13]

Recently, we turned our attention to chiral phosphoramides as part of our ongoing research program and in this direction we have synthesised the novel chiral phosphoramides **1** and **2** from (*S*)-2-anilinomethylpyrrolidine. The elegant work of Wills[9–15] on catalysts containing the N-P=O structural framework prompted us to examine the possible applications of catalysts **1** and **2** in borane-mediated asymmetric reductions. Herein, we report the reductions of α-halo ketones under the catalytic influence of 1,4-bis[(5*S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl]piperazine **2**, thus providing a convenient methodology for synthesis of 2-halo-1-arylethanols in 90–95% enantiomeric purities.



Scheme 1.

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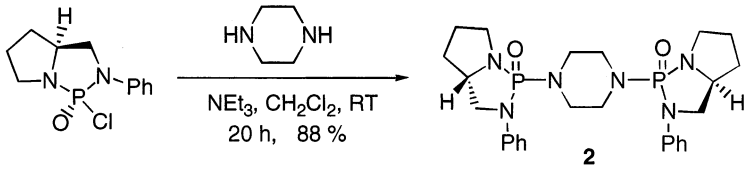
2. Results and discussion

The chiral phosphoramide (1*R*,2*R*)-1,2-bis[{(5*S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl}methylamino]cyclohexane **1** was synthesised by the reaction of (5*S*)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane (obtained from (*S*)-2-anilinomethylpyrrolidine, which, in turn, was synthesised from inexpensive and commercially available (*S*)-glutamic acid according to the known procedure[16–18]) with (1*R*,2*R*)-1,2-di(methylamino)cyclohexane in 76% yield. This route is shown in Scheme 1.

Similarly the chiral phosphoramide, 1,4-bis[(5*S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl]piperazine **2**, was prepared by the reaction of (5*S*)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo-(3.3.0)octane with piperazine as shown in Eq. (1).

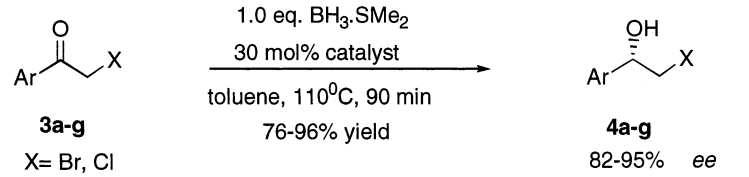


(1)

We first directed our studies towards the possible application of (1*R*,2*R*)-1,2-bis[{(5*S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl}methylamino]cyclohexane **1** as a catalyst in the borane-mediated asymmetric reductions of α-halo ketones. The reduction of phenacyl chloride **3a** by borane–dimethyl sulphide under the catalytic influence of molecule **1** was first examined under various conditions. The best results were obtained when the reduction was carried out using 30 mol% of catalyst **1** in refluxing toluene, providing the desired alcohol (*S*)-2-chloro-1-phenylethanol **4a** with 82% e.e. and in 94% yield.

We also examined the borane–dimethyl sulphide-mediated reduction of phenacyl chloride using catalytic phosphoramide **2** in toluene. Encouraging results were obtained when we carried out the reduction using 30 mol% of catalyst **2** in toluene, thus providing the desired 2-chloro-1-phenylethanol **4a** in 90% e.e. with (*S*)-configuration in 91% yield. Similarly the stereoselective borane–dimethyl sulphide reduction of phenacyl bromide **3b** in toluene with catalysts **1** and **2** was examined. These reactions afforded (*S*)-2-bromo-1-phenylethanol **4b** in 89% e.e. (88% yield) and 94% e.e. (92% yield), respectively.

Since the phosphoramide **2** offered better selectivities in these initial reductions than the catalyst **1**, we extended its use to the reductions of various prochiral α-halo ketones. These reactions afforded α-halo alcohols in high 76–96% yields and excellent e.e.s of 90–95% (Eq. (2), Table 1). Enantiomeric purities of the chiral alcohols **4a–4e** were determined by HPLC analysis using



(2)

Table 1. Asymmetric reduction of α-halo ketones[a]

Substrate	Ar	X	Catalyst (30 mol%)	Product	Yield (%)[b]	$[\alpha]_D^{25}$	Conf.[c]	E.e. (%)[d]
3a	Phenyl	Cl	**1**	**4a**	94	+39.7 (*c* 2.25)[e]	*S*	82
3b	Phenyl	Br	**1**	**4b**	88	+39.4 (*c* 2.0)[f]	*S*	89
3a	Phenyl	Cl	**2**	**4a**	91	+43.5 (*c* 2.4)[e]	*S*	90
3b	Phenyl	Br	**2**	**4b**	92	+42.45 (*c* 2.0)[f]	*S*	94
3c	4-Methylphenyl	Cl	**2**	**4c**	96	+47.2 (*c* 1.1)[f]	*S*[g]	92
3d	4-Ethylphenyl	Cl	**2**	**4d**	84	+41.0 (*c* 1.0)[f]	*S*[g]	92
3e	4-Methylphenyl	Br	**2**	**4e**	83	+41.8 (*c* 1.0)[f]	*S*[g]	95
3f	4-Chlorophenyl	Br	**2**	**4f**	90	+38.6 (*c* 1.15)[f]	*S*[g]	91[h]
3g	4-Bromophenyl	Br	**2**	**4g**	76	+32.75 (*c* 1.3)[f]	*S*	93[h]

[a] All reactions were carried out on 0.5 mM scale of α-halo ketone with 0.5 mM of $BH_3{\cdot}SMe_2$ in the presence of 30 mol% catalyst in toluene for 90 min at 110°C.

[b] Yield of pure alcohol after purification by column chromatography (silica gel, 5% ethyl acetate in hexanes).

[c] Absolute configuration was assigned by comparison of the sign of the specific rotation with that of reported molecules.[19,20]

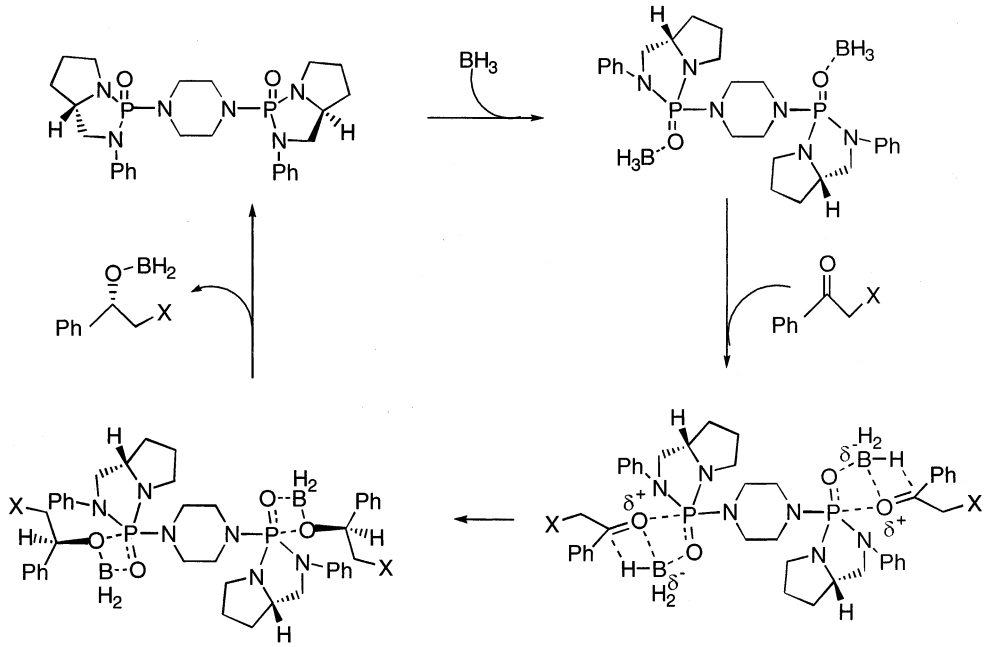
[d] Determined by HPLC analysis using the chiral column, Chiralcel-OD.

[e] Specific rotations were obtained in cyclohexane.

[f] Specific rotations were obtained in chloroform.

[g] Absolute configuration was tentatively assigned in analogy with **4a**, **4b** and **4g**.

[h] Enantiomeric purity was determined by ^1H NMR (200 MHz) analysis of the corresponding acetate in the presence of the chiral shift reagent, $Eu(hfc)_3$, with reference to the corresponding racemic acetate.



Scheme 2.

the chiral column Chiralcel-OD with reference to racemic alcohols. Enantiomeric purities of alcohols **4f** and **4g** were determined by ^{1}H NMR spectral analysis of the corresponding acetates in the presence of chiral shift reagent, Eu(hfc)$_3$, with reference to their racemic acetates.

A possible mechanism of the asymmetric reduction process is presented in Scheme 2. The first step of the catalytic cycle might involve the coordination of the phosphoramide oxygen to electron deficient boron, thereby generating a partial negative charge on boron. This renders the phosphoramide electron deficient, allowing it to act as a Lewis acid for coordination to the carbonyl functionality of the ketone. Subsequent hydride transfer from borane to ketone would then lead to the formation of an alkoxyborane, dissociation of which would release the chiral phosphoramide for further catalytic cycles (Scheme 2).

3. Conclusion

In conclusion, we have developed a new phosphoramide catalyst 1,4-bis[(5*S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl]piperazine **2** for borane-mediated reductions of prochiral α-halo ketones, thus providing a simple methodology for the highly enantioselective synthesis of α-halo alcohols.

4. Experimental

All melting points were recorded on a Superfit (India) capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Jasco-FT-IR model 5300 or a Perkin–Elmer model 1310 spectrometer. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded in deuterochloroform ($CDCl_3$) on a Bruker-AC-200 spectrometer using tetramethylsilane (TMS, $\delta = 0$) as internal standard. ^{31}P NMR (81 MHz) spectra were recorded on a Bruker-AC-200 spectrometer using 85% H_3PO_4 ($\delta = 0$ ppm) as external standard. Elemental analyses were recorded on a Perkin–Elmer 240C-CHN analyser. Liquid secondary ion mass spectrum of the compound **1** was obtained using an Autospec-M (Micromass, UK) mass spectrometer. Electrospray ionisation mass spectrum (EIMS) of the compound **2** was obtained using a Quattro-LC (Micromass, UK) mass spectrometer. HPLC analyses of alcohols were carried out on a Shimadzu LC-10AD instrument using the chiral column, Chiralcel-OD. Optical rotations were measured on a Jasco DIP 370 digital polarimeter. Starting material (5*S*)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane was prepared by the reaction of (*S*)-2-anilinomethylpyrrolidine with $POCl_3$ according to the literature procedure.[18]

4.1. (1*R*,2*R*)-1,2-Bis[{(5*S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl}methylamino]cyclohexane 1

To a stirred solution of (5*S*)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo(3.3.0)octane (1.0 g, 3.92 mM) in CH_2Cl_2 (20 mL) were added triethylamine (0.793 g, 7.84 mM) and (*1R,2R*)-1,2-di(methylamino)cyclohexane (0.278 g, 1.96 mM) at room temperature. After 20 h (monitored by TLC) the mixture was diluted with water (10 mL). The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (3×25 mL). The combined organic extract was washed successively with water and brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue purified by column chromatography (silica gel, 35% ethyl acetate in hexanes) to afford (1*R*,2*R*)-

1,2-bis[{(5*S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl}methylamino]cyclohexane as a crystalline solid (0.863 g, 76%); mp 260–262°C; $[\alpha]_D^{25}=+35.0$ (*c* 1.40, $CHCl_3$); IR (KBr): 2934, 1601, 1502, 1305, 1215 cm^{-1}; ^1H NMR: δ 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); ^{13}C NMR: δ 25.52, 26.00, 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: δ 23.37; MS (FAB) (*m*/*z*): 583 $(M+H)^+$. Anal. calcd for $C_{30}H_{44}N_6O_2P_2$: C, 61.84; H, 7.61; N, 14.42. Found: C, 61.75; H, 7.64; N, 14.52%.

4.2. 1,4-Bis[(5*S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl]piperazine 2

Compound **2** was prepared by reaction of (5*S*)-1,3-diaza-2-phospha-2-oxo-2-chloro-3-phenylbicyclo-(3.3.0)octane (1 g, 3.92 mM) with piperazine (0.169 g, 1.96 mM) at room temperature for 20 h following the procedure for (1*R*,2*R*)-1,2-bis[{(5*S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl}methylamino]cyclohexane **1**, as a crystalline solid (0.91 g, 88%) (after purification by column chromatography, silica gel, 1% methanol in ethyl acetate); mp 260°C (dec.); $[\alpha]_D^{25}=-59.4$ (*c* 1.4, $CHCl_3$); IR (KBr): 2957, 1602, 1500, 1300, 1224 cm^{-1}; ^1H NMR: δ 1.51–2.12 (m, 8H), 2.73–3.85 (m, 18H), 6.83–7.29 (m, 10H); ^{13}C NMR: δ 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 $(M+H)^+$. Anal. calcd for $C_{26}H_{36}N_6O_2P_2$: C, 59.30; H, 6.89; N, 15.96. Found: C, 59.42; H, 6.91; N, 15.85%.

4.3. General procedure for the asymmetric reduction of phenacyl chloride: synthesis of (*S*)-2-chloro-1-phenylethanol 4a

1,4-Bis[(5*S*)-1,3-diaza-2-phospha-2-oxo-3-phenylbicyclo(3.3.0)octan-2-yl]piperazine **2** (0.15 mM, 79 mg) was first dried by azeotropic drying with anhydrous toluene (2×3 mL) under nitrogen. The phosphoramide was then diluted with toluene (5 mL) and to this stirred solution borane–dimethyl sulphide (0.5 mM, 38 mg) was added and the reaction mixture heated to 110°C. Once the temperature was stable at 110°C, phenacyl chloride (0.5 mM, 77 mg) in toluene (1 mL) was added dropwise. After completion of the addition, the mixture was stirred for a further 90 min (monitored by TLC). The reaction mixture was allowed to cool to room temperature and quenched with saturated NH_4Cl solution. The organic layer was separated and the aqueous layer were extracted with ether (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_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 **4a** in 91% yield (71 mg), as a colourless oil. $[\alpha]_D^{25}=+43.5$ (*c* 2.4, cyclohexane) [Lit.[19] $[\alpha]_D^{25}=-48.1$ (*c* 1.73, cyclohexane), (*R*)-configuration, 100% e.e.]; 90% e.e., the enantiomeric purity was determined by HPLC using a chiral column [Chiralcel-OD, 95:5 hexanes:*i*-PrOH, 0.5 mL/min, 254 nm, retention times: 20.90 min (*S*) and 23.63 min (*R*)]; IR (neat): 3408 cm^{-1}; ^1H NMR: δ 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}C NMR: δ 50.77, 74.11, 126.11, 128.45, 128.67, 140.10.

4.4. (*S*)-2-Bromo-1-phenylethanol 4b

Colourless oil; yield: 92%; $[\alpha]_D^{25}=+42.45$ (*c* 2.0, $CHCl_3$) [Lit.[19] $[\alpha]_D^{25}=-39$ (*c* 8.00, $CHCl_3$), (*R*)-configuration, 93% e.e.]; 94% e.e., the enantiomeric purity was determined by HPLC using a chiral column [Chiralcel-OD, 95:5 hexanes:*i*-PrOH, 0.5 mL/min, 254 nm, retention times: 20.48 min (*S*) and 23.91 min (*R*)]; IR (neat): 3387 cm^{-1}; ^1H NMR: δ 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: δ 40.08, 73.84, 126.03, 128.47, 128.70, 140.43.

4.5. (*S*)-2-Chloro-1-(4-methylphenyl)ethanol 4c

Colourless oil; yield: 96%; $[\alpha]_D^{25}=+47.2$ (*c* 1.10, $CHCl_3$); 92% e.e., the enantiomeric purity was determined by HPLC using a chiral column [Chiralcel-OD, 95:5 hexanes:*i*-PrOH, 0.5 mL/min, 254 nm, retention times: 21.49 min (*S*) and 23.54 min (*R*)]; IR (neat): 3414 cm^{-1}; ^1H NMR: δ 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: δ 21.14, 50.74, 73.94, 126.02, 129.32, 137.11, 138.20.

4.6. (*S*)-2-Chloro-1-(4-ethylphenyl)ethanol 4d

Colourless oil; yield: 84%; $[\alpha]_D^{25}=+41.0$ (*c* 1.0, $CHCl_3$); 92% e.e., the enantiomeric purity was determined by HPLC using a chiral column [Chiralcel-OD, 95:5 hexanes:*i*-PrOH, 0.5 mL/min, 254 nm, retention times: 19.00 min (*S*) and 20.88 min (*R*)]; IR (neat): 3408 cm^{-1}; ^1H NMR: δ 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: δ 15.48, 28.58, 50.76, 74.00, 126.11, 128.14, 137.35, 144.58.

4.7. (*S*)-2-Bromo-1-(4-methylphenyl)ethanol 4e

Colourless oil; yield: 83%; $[\alpha]_D^{25}=+41.8$ (*c* 1.0, $CHCl_3$); 95% e.e., the enantiomeric purity was determined by HPLC using a chiral column [Chiralcel-OD, 95:5 hexanes:*i*-PrOH, 0.5 mL/min, 254 nm, retention times: 26.05 min (*S*) and 28.58 min (*R*)]; IR (neat): 3375 cm^{-1}; ^1H NMR: δ 2.35 (s, 3H), 2.54 (b, 1H), 3.49–3.68 (m, 2H), 4.90 (1H, dd, $J=8.6$, 3.8 Hz), 7.18 (d, 2H, $J=8.0$ Hz), 7.27 (d, 2H, $J=8.0$ Hz); ^{13}C NMR: δ 21.19, 40.14, 73.70, 125.93, 129.36, 137.46, 138.25.

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

Colourless oil; yield: 90%; $[\alpha]_D^{25}=+38.6$ (*c* 1.15, $CHCl_3$); 91% e.e., the enantiomeric purity was determined by ^1H NMR spectral analysis of the corresponding acetate in the presence of the chiral shift reagent,

$Eu(hfc)_3$, with reference to the racemic acetate; IR (neat): 3242 cm^{-1}; ^1H NMR: δ 2.64 (bs, 1H), 3.43–3.68 (m, 2H), 4.91 (1H, dd, $J=8.6$, 3.6 Hz), 7.22–7.47 (m, 4H); ^{13}C NMR: δ 39.64, 73.05, 127.39, 128.81, 134.15, 138.86.

4.9. (*S*)-2-Bromo-1-(4-bromophenyl)ethanol 4g

White solid; yield: 76%; mp: 70–72°C; $[\alpha]_D^{25}=+32.75$ (*c* 1.3, $CHCl_3$) [Lit.[20] $[\alpha]_D^{25}=-31$ (*c* 2.9, $CHCl_3$), *R*-configuration, 94% e.e.]; 93% e.e., the enantiomeric purity was determined by ^1H NMR spectral analysis of the corresponding acetate in the presence of chiral shift reagent, $Eu(hfc)_3$, with reference to the racemic acetate; IR (KBr): 3242 cm^{-1}; ^1H NMR: δ 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); ^{13}C NMR: δ 39.65, 73.10, 122.34, 127.71, 131.79, 139.35.

4.10. General procedure for acetylation: synthesis of (*S*)-1-acetoxy-2-bromo-1-(4-bromophenyl)ethane

Prepared according to the literature procedure described for the synthesis of (*R*)-1-acetoxy-2-bromo-1-phenylethane.[19]

A solution of (*S*)-2-bromo-1-(4-bromophenyl)ethanol (0.34 mM, 95 mg) and pyridine (4 mL) in acetic anhydride (20 mL) was stirred at room temperature. After 10 h, the reaction mixture was diluted with water (80 mL) and the reaction mixture was extracted with ether (3×20 mL). The combined organic layers were washed successively with aqueous 5% HCl and 10% sodium bicarbonate solution and the organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue obtained was purified by column chromatography (silica gel 5% ethyl acetate in hexanes) to provide the desired (*S*)-1-acetoxy-2-bromo-1-(4-bromophenyl)ethane (76 mg) in 70% yield; colourless oil; $[\alpha]_D^{25}=+42.2$ (*c* 2.50, $CHCl_3$); IR (neat): 1743 cm^{-1}; ^1H NMR: δ 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.

4.11. (*S*)-1-Acetoxy-2-bromo-1-(4-chlorophenyl)ethane

Colourless oil; yield: 80%; $[\alpha]_D^{25}=+54.1$ (*c* 1.35, $CHCl_3$); IR (neat): 1745 cm^{-1}; ^1H NMR: δ 2.13 (s, 3H), 3.53–3.69 (m, 2H), 5.90–5.99 (m, 1H), 7.23–7.40 (m, 4H); ^{13}C NMR: δ 20.89, 33.88, 74.10, 128.06, 128.93, 134.73, 136.22, 169.69.

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