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Novel ligands based on bromosubstituted hydroxycarbonyl [2.2]paracyclophane derivatives: synthesis and application in asymmetric catalysis

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ABSTRACT

New planar-chiral hydroxycarbonyl [2.2]paracyclophane derivatives, 4-acetyl-13-bromo-5-hydroxy [2.2]paracyclophane (Br-AHPC, 63%) and 4-benzoyl-13-bromo-5-hydroxy[2.2]paracyclophane (Br-BHPC, 53%), were synthesized and reacted with the enantiomers of α-phenylethylamine to form corresponding Schiff bases, 12-bromo-4-hydroxy-5[1-(1-phenyl-ethylimino)-ethyl]-[2.2]paracyclophane and 12-bromo-4-hydroxy-5[1-(1-phenyl-ethylimino)-(phenyl)methylen-[2.2]paracyclophane. The diastereomers of the imines were resolved and their absolute configurations and consequently the corresponding configurations of the enantiomers of Br-AHPC were determined by X-ray diffraction. Enantiomerically pure Schiff bases were applied as ligands to form catalysts for the enantioselective addition reaction of diethylzinc with benzaldehyde where 1-phenylpropanol was obtained with 77–91% ee.

1. Introduction

A number of planar chiral *ortho*-hydroxycarbonyl [2.2]paracyclophane derivatives have been successfully used in enantiomerically pure forms in asymmetric synthesis and catalysis. For example, 4-formyl-5-hydroxy[2.2]paracyclophane **1** (FHPC) has been used as a chiral auxiliary in the asymmetric synthesis of α-amino acids,[1] and the asymmetric trimethylsilylcyanation of benzaldehyde.[2] Asymmetric alkyl and alkenyl zinc complexes with Schiff's bases from a variety of hydroxycarbonyl [2.2]paracyclophane derivatives, such as FHPC **1**, 4-acetyl-5-hydroxy[2.2]paracyclophane **2** (AHPC), 4-benzoyl-5-hydroxy[2.2]paracyclophane **3** (BHPC) (Fig. 1), including salenes, have demonstrated high induction properties (>99 ee) in 1,2-addition reactions to aldehydes.[3,4]

Hydroxycarbonyl [2.2]paracyclophane derivatives containing bromine as an additional substituent at the pseudo-*ortho* position with respect to the carbonyl group were prepared by Ma et al. (Fig. 2, A) as well as its Schiff bases which, as ligands, demonstrated high selectivity in the copper-catalyzed asymmetric Henry reaction.[5] In a continuation of our studies on the asymmetric induction ability of different types of substituted paracyclophane backbones[6] we herein elaborate on the methods of synthesis and the resolution of novel hydroxycarbonyl [2.2]paracyclophane derivatives containing bromine at the pseudo-*geminal* position with respect to the carbonyl group (Fig. 2, B), and showed application of their Schiff bases as ligands in asymmetric diethylzinc addition to benzaldehyde.

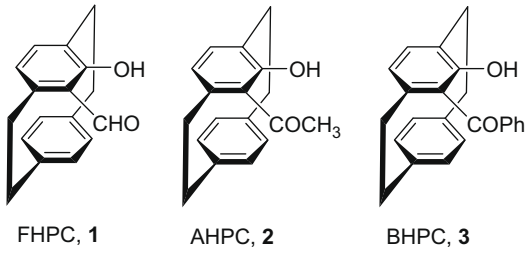

Figure 1. *ortho*-Hydroxycarbonyl [2.2]paracyclophane derivatives.

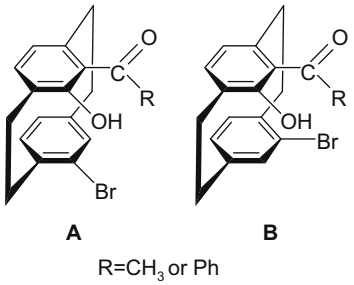

Figure 2. Tris-substituted bromine-containing *ortho*-hydroxycarbonyl [2.2]paracyclophane derivatives.

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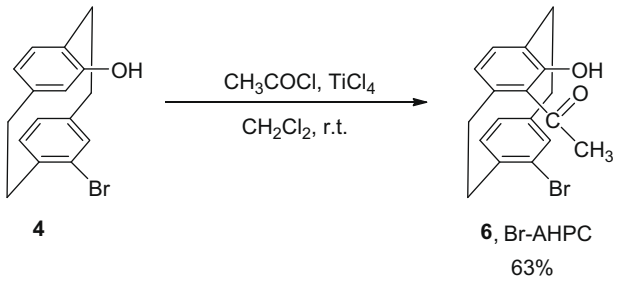
2. Results and discussion

12-Bromo-4-hydroxy[2.2]paracyclophane **4** was selected as the starting material and was obtained from 4,12-dibromo[2.2]paracyclophane.[7,8] We carried out several reactions of pseudo-*ortho*-bromophenol **4** with paraformaldehyde. Earlier, FHPC **1** was obtained by alkylation of 4-hydroxy[2.2]paracyclophane **5** with paraformaldehyde in the presence $SnCl_4$ and Bu_3N.[9] However, it was found that the alkylation of pseudo-*ortho*-bromophenol **4** does not occur under these conditions and starting bromophenol was recovered from the reaction mixture in quantitative yield. Increasing the reaction time, the addition of a triple excess of alkylating reagent, and a change of catalyst to $TiCl_4$ did not lead to the formation of product **1**. This is probably because of a bulky bromine atom at the pseudo-*gem*-position to the estimated place of attack not allowing alkylation of bromophenol **4**.

The possibility of preparing tris-substituted *ortho*-hydroxycarbonyl [2.2]paracyclophane derivatives by acylation of 12-bromo-4-hydroxy[2.2]paracyclophane **4** with acylchloride/$TiCl_4$ was studied under conditions analogous to those described for 4-hydroxy[2.2]paracyclophane (Scheme 1).[10]



Scheme 1. The preparations of Br-AHPC **6**.

The reaction of bromophenol **4** with acetyl chloride was carried out at various temperatures. A maximum yield of 1[13-bromo-5-hydroxy[2.2]paracyclophane-4-yl)]ethanon **6**, Br-AHPC, 63%) was achieved at 20 °C over 72 h. Our attempts to reduce the reaction time by increasing the temperature led to a decrease in yield of the target product. The formation of the acetylated product does not occur in boiling CH_2Cl_2, and starting pseudo-*ortho*-bromophenol **4** formed tars. Acetylation which was carried out at 30 °C afforded the target product **6** but the yield was low (30%). For the Br-AHPC **6**, an X-ray diffraction study was carried out (Fig. 3).

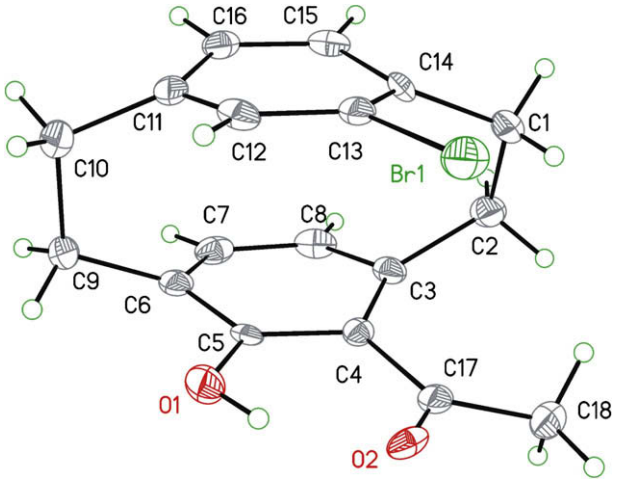


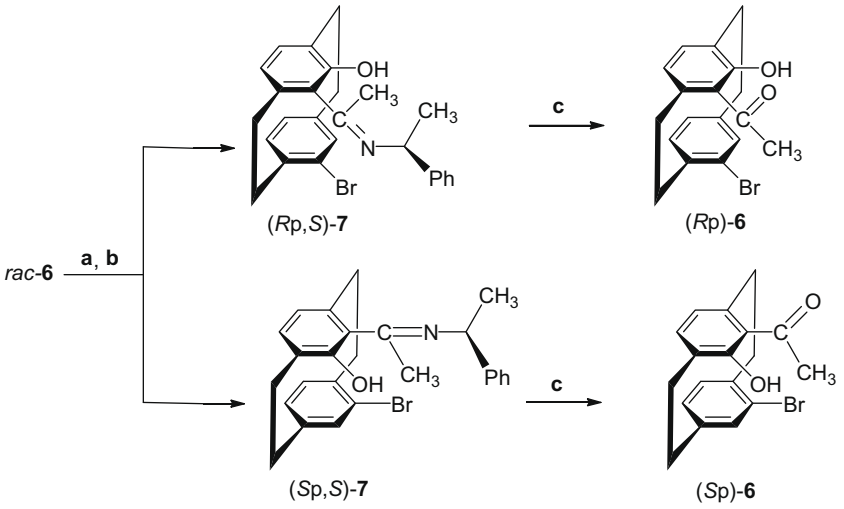
Figure 3. General view of one independent molecule of 4-acetyl-13-bromo-5-hydroxy[2.2]paracyclofane in the structure of **6** with the representation of atoms by thermal ellipsoids at the 50% probability level; (O1···O2) = 2.485(3) Å, (O1–H1–O2) = 146°, (O1′···O2′) = 2.493(3) Å, (O1′–H2–O2′) = 147°.

The standard method of preparing the enantiomers of the hydroxycarbonyl [2.2]paracyclophane derivatives involved resolution of their racemates via diastereomeric Schiff bases with (*S*)-phenylethylamine [(*S*)-α-PEA].[5,10]

We have elaborated on the procedure of the preparation of diastereomeric Schiff bases of Br-AHPC **6** with (*S*)-α-PEA. The transformation was carried out in refluxing toluene in the presence of Et_2SnCl_2 as a catalyst for 43 h in nearly quantitative yield leading to an equimolar mixture of two diastereomers, 12-bromo-4-hydroxy-5[1-(1-phenyl-ethylimino)-ethyl]-[2.2]paracyclophane **7** (Scheme 2).

The individual ketimines **7** were separated by preparative column chromatography on silica gel and then re-crystallized from heptane, to give (*Sp*,*S*)-**7** ($[\alpha]_D^{25} = -397.9$, toluene) and (*Rp*,*S*)-**7** ($[\alpha]_D^{25} = +872.0$, toluene) with diastereomeric purities exceeding 99% as determined by ^1H NMR spectroscopy.

The absolute configurations of diastereomeric Schiff bases **7** were established by X-ray diffraction analysis of crystalline



Scheme 2. Resolution of Br-AHPC **6** into its enantiomers. Reagents and conditions: (a) (*S*)-α-PEA, Et_2SnCl_2, toluene, 110 °C; (b) chromatography resolution SiO_2/CH_2Cl_2, than crystallization from hexane; (c) $Na_2S_2O_5$, $EtOH/H_2O$.

ketimine with R_f = 0.190 (SiO_2/CH_2Cl_2) obtained from a mixture pentane/heptane. The configuration of this diastereomer was determined as (*Rp*,*S*)-**7** (Fig. 4), the (*Sp*,*S*)-configuration was assigned to diastereomer **7** with R_f = 0.093.

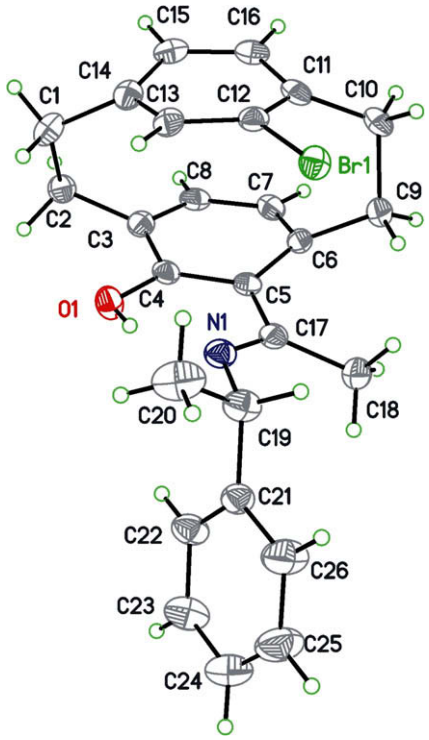


Figure 4. General view of (*Rp*,*S*)-12-bromo-4-hydroxy-5[1-(1-phenyl-ethylimino)-ethyl]-[2.2]paracyclophane in the structure of **7** with the representation of atoms by thermal ellipsoids at the 50% probability level; (O1···N1) = 2.484(4) Å, (O1–H1–N1) = 148°.

The procedure which was used for the hydrolysis of diastereomeric ketimines **7** was applied using a method previously reported for the diastereomeric Schiff bases of AHPC **2** with α-PEA.[10] Boiling of ketimines **7** with sodium metabisulfite $Na_2S_2O_5$ (3.7 eq.) in a mixture of C_2H_5OH/H_2O for 5 h, followed by acidification with 2 M HCl until pH 1 did not lead to the hydrolysis, and starting Schiff bases **7** were isolated quantitatively.

Effective hydrolysis **7** was achieved by the addition of a twofold excess of $Na_2S_2O_5$ to a boiling solution of (*Rp*,*S*)-**7** in 50% aqueous ethanol for 100 h. Enantiomer (*Rp*)-**6** ($[\alpha]_D^{25} = +363.3$, toluene) was obtained in 79% yield. Hydrolysis of (*Sp*,*S*)-**7** gave (*Sp*)-**6** ($[\alpha]_D^{25} = -361.5$, toluene) with 67% yield. Since the enantiomeric purity of the resolving agent (*S*)-α-PEA was greater than 99%, the ee of (*S*)-**6** and (*R*)-**6** obtained in this way must also have been close to this value.

The complications in the hydrolysis of ketimines **7** could be because of the presence of strong intramolecular hydrogen bonding –OH···N=, which was confirmed by X-ray investigations of (*Rp*,*S*)-**7** (Fig. 3), according to which the distance –OH···N= 1.7510 Å, –O···N= 2.4832 Å.

The acylation reaction of **4** with benzoyl chloride was carried out under conditions similar to those used for the synthesis of BHPC **3** [$TiCl_4$ (1.3 equiv), CH_2Cl_2, room temperature] (Scheme 3).

Unlike the benzoylation of unsubstituted phenol **5**, the same reaction with bromophenol **4** produced a mixture of two compounds, namely the *ortho*-regioselective C-acylated-[13-bromo-5-hydroxy[2.2]paracyclophane-4-yl)]phenylmetanon **8** (Br-BHPC, 26%) and the O-acylated product [12-bromo[2.2]paracyclophane-4-yl)]benzoate **9** (19%) (Table 1). The interaction time of bromophenol **4** with $TiCl_4$ was increased from 0.5 to 1.5 h. This resulted in a decrease of yield of the side product **9** from 19% to 7%, and thus an increase in the yield of the target Br-BHPC **8** from 26% to 53%, and a decrease in the reaction time from 28 to 7 days (Table 1).

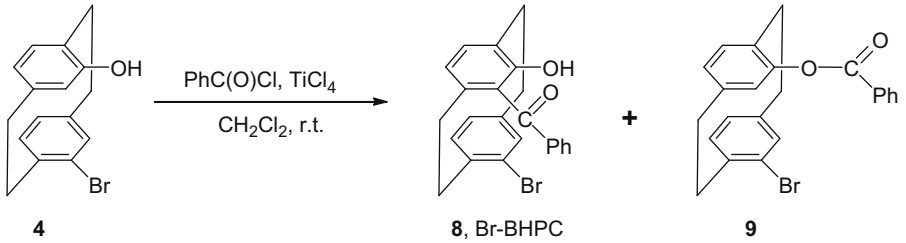
Table 1
Reaction of 12-bromo-4-hydroxy[2.2]paracyclophane with benzoylchloride

Run	Ratio of **4**/$TiCl_4$/PhC(O)Cl	Interaction time of **4** with $TiCl_4$ (h)	Reaction time (day)	Ratio of **8**/**9**	Yield of **8** (%)	Yield of **9** (%)
1	1/1.3/1	0.5	28	1.4/1	26	19
2	1/1.3/1	1.5	7	8.1/1	53	7

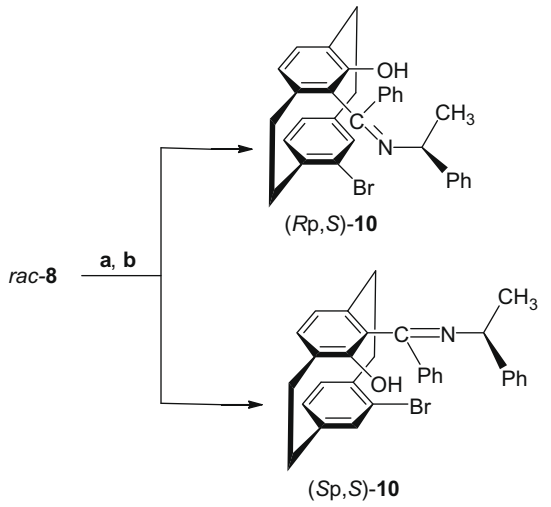
The reaction of Br-BHPC **8** with (*S*)-α-PEA gave an equimolar mixture of diastereomeric Schiff bases, 12-bromo-4-hydroxy-5[1-(1-phenyl-ethylimino)-(phenyl)methylen-[2.2]paracyclophane **10** (Scheme 4). A stronger Lewis acid, $TiCl_4$, was used as the catalyst, and thus was efficient for the synthesis of diastereomeric Schiff bases BHPC **3** with α-PEA.[10] The reaction was carried out nearly quantitative in refluxing toluene after 60 h, with water being removed by a Dean–Stark trap filled with $MgSO_4$.

For the separation of diastereomeric ketimines **10**, a combined method was used. The first stage of the procedure was based on the different solubility of Schiff base **10** in ethanol. Single-shot crystallization of the starting mixture gave the less soluble diastereomer **10** (R_f = 0.36, CH_2Cl_2) in 72% yield. The following column chromatography of the filtrate afforded both ketimines **10** in diastereomerically pure forms (de >99% by NMR). Single-crystal X-ray diffraction indicated an (*Sp*,*S*)-configuration for ketimine **10** with R_f = 0.36 ($[\alpha]_D^{25} = -549.2$, toluene) (Fig. 5). Diastereomer with R_f = 0.44 was given the configuration (*Rp*,*S*)-**10** ($[\alpha]_D^{25} = +555.0$, toluene).

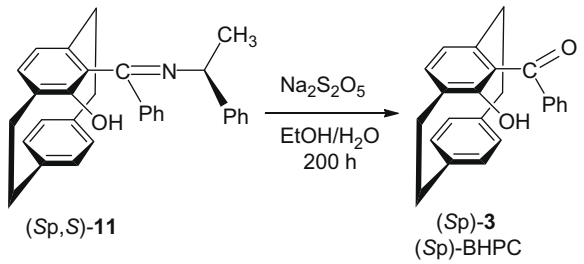
The nearest analogues of the Schiff bases of Br-BHPC **10** are those of BHPC **11**. To date, no successful procedure for the hydrolysis of **11** has been reported.[10] We were able to hydrolyze ketimines **11** using the technique described for the Schiff bases of Br-AHPC **7**. The hydrolysis of (*Sp*,*S*)-**11** was complete after 200 h, with the formation of enantiomerically pure (*S*)-BHPC **3** ($[\alpha]_D^{25} = -254.4$, benzene) in 42% yield (Scheme 5).



Scheme 3. Acylation of 12-bromo-4-hydroxy[2.2]paracyclophane **4** with benzoyl chloride.



Scheme 4. The preparations of diastereomeric Schiff bases **8** Br-BHPC with (S)-α-PEA. Reagents and conditions: (a) (*S*)-α-PEA, $TiCl_4$, toluene, 110 °C; (b) chromatography resolution SiO_2/CH_2Cl_2, then crystallization from hexane.



Scheme 5. Hydrolysis of the Schiff base of BHPC **3** with (*S*)-α-PEA.

However, our attempts to hydrolyze the Schiff base of Br-BHPC **10** using this method were unsuccessful. The reaction did not occur even after 200 h and starting ketimines **10** were recovered almost quantitatively.

In our opinion the difficulties of hydrolysis of the Schiff base derived from Br-BHPC **10** can be attributed to the presence of a strong intramolecular hydrogen bond –OH···N=, which was confirmed by X-ray diffraction investigations of (*Sp*,*S*)-**10** (Fig. 5), where the distance OH···N= 1.7478 Å, O···N 2.5040 Å, and by the presence of a bulky Br-substituent in a pseudo-*geminal* position to imino group.

The synthesized ketimines **7** and **10** were tested as chiral inductors in the asymmetric addition of Et_2Zn to benzaldehyde (Fig. 6). The standard experimental procedure included the addition of 2.2 equiv of Et_2Zn and 1 equivalent of benzaldehyde to a solution of 0.1 equiv of the chiral catalyst **7** or **10** in toluene at 0 °C. The mixture was stirred at room temperature for 15 h. Excessive Et_2Zn was destroyed by adding 1 M HCl and after standard work-up (see Section 4), the enantiomeric excess of the resulting 1-phenylpropanol **12** was determined by chiral HPLC chromatography. All reactions proceeded smoothly to give alcohol **12** with high conversion ratios (>95%). Both diastereomeric pairs (*Rp*,*S*)-**7**, (*Sp*,*S*)-**7** and (*Rp*,*S*)-**10**, (*Sp*,*S*)-**10** have shown high asymmetric induction. The results displayed in Figure 5 for the sake of comparison are obtained by the catalysis of this reaction with the corresponding Schiff base of AHPC (*Rp*,*S*)-**13**, (*Sp*,*S*)-**13** and BHPC (*Rp*,*S*)-**11**, (*Sp*,*S*)-**11**.[4]

The Schiff bases derived from Br-BHPC demonstrated better efficiency compared with those derived from Br-AHPC ((*Rp*,*S*)-**10**—85% (*S*)-**12**, (*Sp*,*S*)-**10**—91% (*S*)-**12**; and (*Rp*,*S*)-**7**—77% (*R*)-**12**, (*Sp*,*S*)-**7**—81% ee (*S*)-**12**, respectively). In comparison with Br-AHPC and Br-BHPC derivatives together with the analogous Schiff bases of AHPC and BHPC **7**, **10** and **13**, **11** the ketimines of Br-AHPC and AHPC display an approximately equal induction ability; however introducing a bromine atom led to an inversion of the absolute configuration of the resultant **12**, whereas both Br-BHPC Schiff bases gave an increase in enantioselectivity of **12** with the same configuration in the case of (*Rp*,*S*)-**10** and opposite configuration for (*Sp*,*S*)-**10**. The best result was observed for (*Sp*,*S*)-**10** (91% ee).

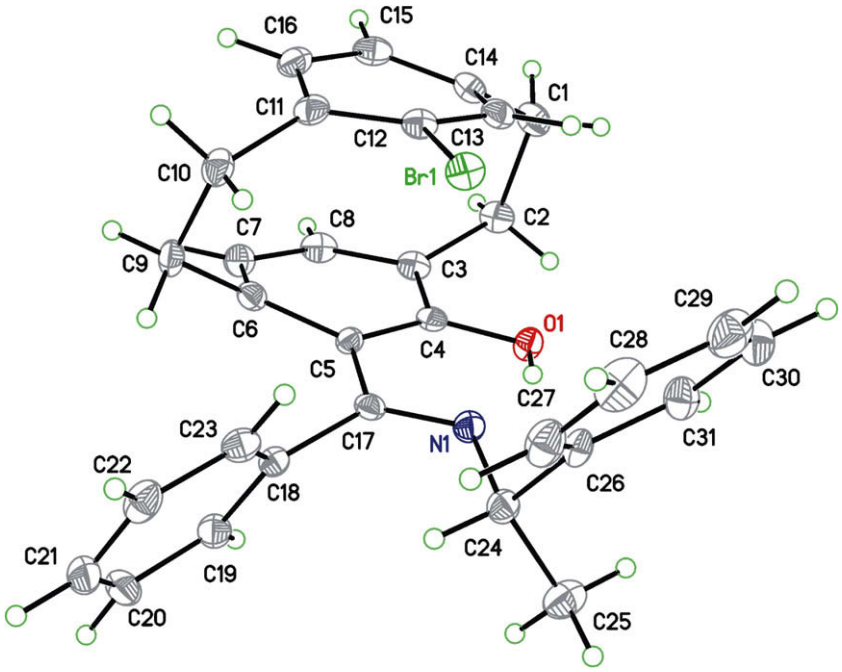


Figure 5. General view of (*Sp*,*S*)-12-bromo-4-hydroxy-5[(1-phenyl-ethylimino)-(phenyl)methylen]-[2.2]paracyclophane in the structure of **10** with the representation of atoms by thermal ellipsoids at the 50% probability level; (O1···N1) = 2.504(2) Å, (O1–H1–N1) = 149°.

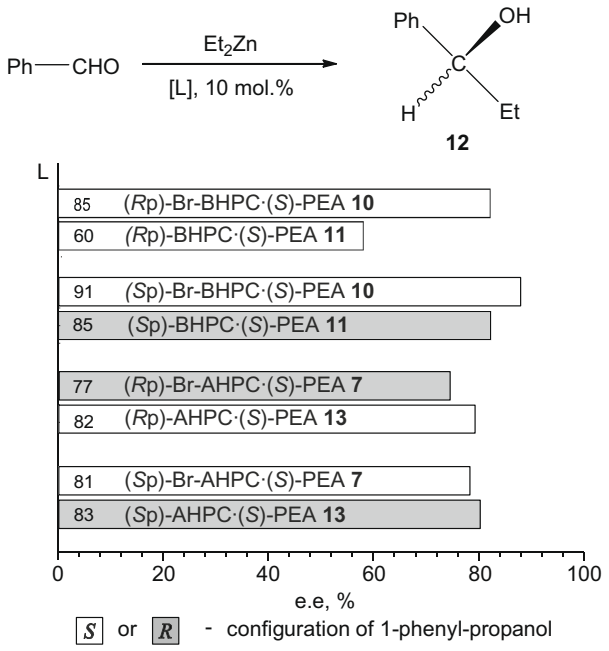


Figure 6. Enantioselective addition of diethylzinc to benzaldehyde catalyzed by bidentate iminophenol ligands.

Comparative analysis of the results of the X-ray investigations of compounds **6**, **7** and **10** has showed some specific features of the molecular structure of tris-substituted bromine-containing *ortho*-hydroxycarbonyl [2.2]paracyclophane derivatives. The solid state molecular structures of **6**, **7** and **10** are represented in Figures 3–5 and their main geometric parameters are listed in Table 2. All substances crystallize in chiral space groups ($P1$, $P6_1$ and $P2_12_12_1$, respectively) and contain heavy bromine atoms that allow us to obtain the absolute configurations of **7** and **10** via the anomalous X-ray dispersion technique. The crystals of **6** contain two symmetrically independent molecules which are enantiomeric forms of **6**

Table 2
Selected geometric parameters of molecules **6**, **7** and **10** (Å)

Bond	**6**	**7** 0.13(H_2O)	**10**
C–Br	1.903(3)–1.915(3)	1.901(4)	1.902(1)
C–O	1.343(4)–1.345(4)	1.343(4)	1.344(2)
C17=O2	1.138(4)–1.238(4)		
C17=N1		1.296(5)	1.293(2)
C4–C17 (or C5–C17)	1.480(4)–1.498(4)	1.473(5)	1.481(2)
C3–C4, C4–C5, C5–C6, C6–C7, C7–C8, C8–C3	1.369(5)–1.419(5)	1.382(5)–1.429(5)	1.382(2)–1.427(2)
C11–C12, C12–C13, C13–C14, C14–C15, C15–C16, C16–C11	1.383(5)–1.427(4)	1.388(5)–1.408(5)	1.388(2)–1.400(2)
C1–C2, C9–C10	1.571(5)–1.585(5)	1.582(6)–1.586(5)	1.577(2)–1.590(2)
σ1[a]	0.073(3)–0.079(3)	0.070(3)	0.071(2)
σ2[a]	0.071(3)–0.072(3)	0.077(3)	0.074(2)
d[a]	2.97	2.99	2.97

[a] σ1—average deviation of atoms from the least-squared plane (C3–C4–C5–C6–C7–C8); σ 2—average deviation of atoms from the least-squared plane (C11–C12–C13–C14–C15–C16); d—the distance between the centres of above-mentioned rings.

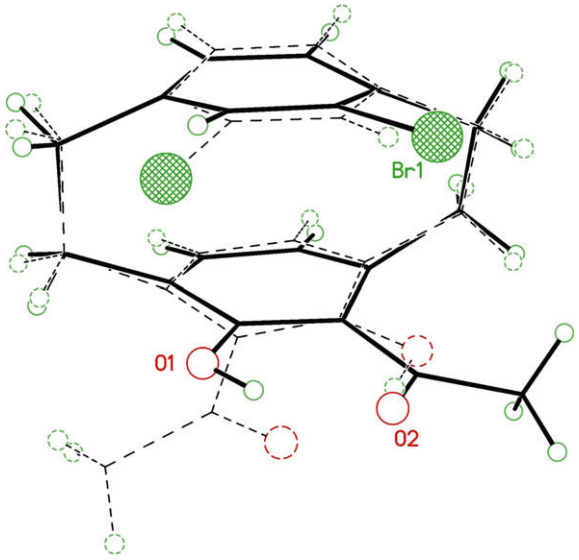


Figure 7. Projection of molecular view for two independent molecules of **6**. Superimposed atoms are C3, C6, C11, C14 and, respectively, C6′, C3′, C14′, C11′.

(Fig. 7), thus crystalline **6** is a racemic mixture of (*R*)- and (*S*)-4-acetyl-13-bromo-5-hydroxy[2.2]paracyclophanes.

The paracyclophane rings of **6**, **7** and **10** adopt boat conformation with average atom deviation from the least-squared planes (R_{ms}) equal to ca. 0.07 Å. The phenyl rings of **7** and **10** are almost planar (R_{ms} does not exceed 0.007(3) Å). The range of the C–C bond distances of the (C3–C4–C5–C6–C7–C8) ring of paracyclophane is more pronounced than that of the (C11–C12–C13–C14–C15–C16) ring (Table 2). Although C5–C17 bond is a single one, the orientation of the substituent at the C5 atom of the paracyclophane seems dictated by the presence of intramolecular hydrogen O–H···O **6** and O–H···N **7** and **10** bonds (Figs. 3–5). The planar orientation of O1–C5–C4–C17–O2 or O1–C4–C5–C17–N1 fragment ($R_{ms} \approx 0.03$Å) results from this hydrogen bonding. As all acidic hydrogen atoms are involved in intramolecular bonding only weak intermolecular bonds (C–H···C, C–H···O and C–H···Br) are present in the structures of **6**, **7** and **10**.

3. Conclusion

In conclusion, we have synthesized racemic Br-AHPC and Br-BHPC and described a simple and efficient procedure for the resolution of Br-AHPC into enantiomers. The application of enantiomerically pure ketimines Br-AHPC and Br-BHPC with (*S*)-α-PEA as chiral ligands in asymmetric Et_2Zn addition to benzaldehyde afforded the 1-phenylpropanol having 77–91% ee. Hydrolysis conditions for Schiff bases of BHPC with (*S*)-α-PEA **11** have been described and BHPC was obtained in enantiomerically pure form.

4. Experimental

4.1. General

Toluene was distilled from sodium ketyl benzophenone under argon. CH_2Cl_2 was passed from a column filled with Al_2O_3. Acetyl chloride and (*S*)-α-phenylethylamine were purchased from Merck and used without purification. Benzoyl chloride was distilled under reduced pressure. NMR: Bruker AVANCE-400 (400.13 and 100.61 MHz, for ^1H and ^{13}C, respectively); Bruker AVANCE-300 (300.13 and 75.47 MHz, for ^1H and ^{13}C, respectively); Bruker AVANCE-600 (600.22 and 150.93 MHz, for ^1H and ^{13}C, respec-

tively). For ^{1}H NMR, the residual signal of the solvent protons with the chemical shift δ 7.27 ($CDCl_3$) was used as the internal standard. Mass spectra were obtained on a KRATOS MS890A mass spectrometer (70 eV). TLC analyses were performed on silica gel pre-coated SORBFIL plates PTLC-A-UV (Sorbpolimer). Optical rotations were recorded on a Perkin–Elmer 241 instrument in a thermostated cell. Column chromatography was performed on Kieselgel 60, 230–400 mesh ASTM (Merck). Enantiomeric analyses were carried out by HPLC on Chiralpak AD-H analytical column using hexane/2-propanol (100/4) as an eluent (1 mL/min) detected at 254 nm.

4.2. *rac*-1[13-Bromo-5-hydroxy[2.2]paracyclophane-4-yl)]ethanon (Br-AHPC) 6

To a solution of **4** (0.50 g, 1.65 mmol) in CH_2Cl_2 (13 mL) was added $TiCl_4$ (0.23 mL, 2.13 mmol) at 0 °C. The resulting dark cherry-coloured solution was stirred at room temperature for 40 min, then acetyl chloride (0.12 mL, 1.65 mmol) was added. The reaction mixture was stirred at room temperature for 72 h. The resulting solution was quenched with 30 mL of H_2O and stirred for 10 min. The yellow organic layer was washed with H_2O (2 × 60 mL). The water layer was extracted with CH_2Cl_2 (3 × 30 mL). Organic layers combined were dried over anhydrous Na_2SO_4. The crude product was obtained after removal of the solvent in vacuo and purified by column chromatography (SiO_2, R_f = 0.40, eluent toluene) to yield **6** (0.357 g, 63%). Analytically pure **6** was obtained by crystallization from heptane. Mp 168–170 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.48–2.63 (m, 1H, –CH_2–CH_2–), 2.66 (s, 3H, –C(O)CH_3), 2.78–2.89 (m, 1H, –CH_2–CH_2–), 2.99–3.10 (m, 2H, –CH_2–CH_2–), 3.10–3.20 (m, 1H, –CH_2–CH_2–), 3.38–3.52 (m, 2H, –CH_2–CH_2–), 3.67–3.77 (m, 1H, –CH_2–CH_2–), 6.22 (d, ^3J = 7.8 Hz; 1H, H-15, or H-7, or H-8), 6.58 (dd, ^3J = 7.8 Hz; ^4J = 1.8 Hz, 1H, H-16), 6.61 (d, ^3J = 7.8 Hz; 1H, H-7, or H-8, or H-15), 6.64 (d, ^3J = 7.8 Hz; 1H, H-8, or H-7, or H-15), 6.97 (d, ^4J = 1.8 Hz; 1H, H-12), 7.27 (s, 1H, –OH); ^{13}C NMR ($CDCl_3$, 400 MHz): δ 30.7, 31.4, 33.1, 33.6, 35.8, 120.9, 126.4, 127.9, 128.4, 130.7, 132.7, 134.7, 137.1, 140.2, 142.7, 143.3, 162.8 C(OH), 204.3 C(O); MS (EI), *m*/*z* (rel): 344 (14, $[M\text{-}H]^+$), 265 (9, $[M-H-Br]^+$), 247 (7), 184 (6), 163 (6), 162 (34), 161 (100), 147 (6), 134 (12), 133 (16), 120 (15), 105 (6), 103 (9). Anal. Calcd for $C_{18}H_{17}BrO_2$: C, 62.62; H, 4.96.; Br, 23.14. Found: C, 62.89; H, 4.90; Br, 23.36.

4.3. 12-Bromo-4-hydroxy-5[1-(1-phenyl-ethylimino)-ethyl]-[2.2]paracyclophane, (*Rp*,*S*)-7 and (*Sp*,*S*)-7

A solution of racemic **6** (0.150 g, 0.44 mmol) with (*S*)-α-PEA (0.06 mL, 0.48 mmol) and a catalytic amount of Et_2SnCl_2 in 8 mL of toluene was refluxed in an apparatus equipped with a Dean–Stark trap filled with anhydrous $MgSO_4$ for 43 h. A diastereomeric mixture of ketimines **7** was obtained after removal of the solvent in vacuo with quantitative yield. The individual diastereomers was obtained by column chromatography (SiO_2, eluent CH_2Cl_2). Analytically pure (*R*p,*S*)-**7** and (*S*p,*S*)-**7** were obtained by crystallization from heptane. MS (EI), *m*/*z* (rel): 448 (10, $[M]^+$), 447 (23, $[M-H]^+$), 266 (20), 265 (100), 264 (34), 251 (5), 250 (22), 249 (5), 248 (6), 174 (6), 162 (11), 161 (94), 160 (100), 146 (10), 132 (17), 118 (5), 117 (7), 115 (7), 105 (30), 104 (5), 103 (13).

4.3.1. (*Sp*,*S*)-7

TLC R_f = 0.093 (eluent CH_2Cl_2); 0.100 g (51%); mp 107–109 °C; $[\alpha]_D^{25} = -397.9$ (*c* 0.33, toluene); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.78 (d, ^3J = 6.7 Hz; 3H, –CH_3), 2.32 (s, 3H, –CH_3), 2.44–2.57 (m, 1H, –CH_2–CH_2–), 2.74–2.89 (m, 1H, –CH_2–CH_2–), 2.99–3.21 (m, 3H, –CH_2–CH_2–), 3.34–3.56 (m, 3H, –CH_2–CH_2–), 4.86 (q, ^3J = 6.7 Hz; 1H, –CH–), 6.04 (d, ^3J = 7.8 Hz; 1H, H-7 or H-8), 6.46 (d, ^3J = 7.8 Hz; 1H, H-8 or H-7), 6.59 (dd, ^3J = 7.8, ^4J = 1.8 Hz; 1H, H-15), 6.68 (d, ^3J = 7.8 Hz; 1H, H-16), 7.11 (d, ^4J = 1.8 Hz; 1H, H-13), 7.20–7.26 (m, 1H, *p*-Ph); 7.29–7.35 (m, 4H, Ph); 17.26 (br s, 1H, –OH); ^{13}C NMR ($CDCl_3$, 300 MHz): δ 21.48, 25.52, 32.36, 33.86, 34.70, 36.55, 57.55, 120.37, 124.17, 126.82, 127.08, 127.83, 129.49, 130.70, 131.63, 132.73, 134.82, 137.64, 138.16, 142.22, 143.45, 143.99, 170.28, 171.63. Anal. Calcd for $C_{26}H_{26}BrNO$: C, 69.64; H, 5.84; N, 3.12; Br, 17.82. Found: C, 69.60; H, 5.77; N, 3.08; Br, 17.94.

4.3.2. (*Rp*,*S*)-7

TLC R_f = 0.190 (eluent CH_2Cl_2); 0.092 g (47%); mp 99–100 °C; $[\alpha]_D^{25} = +872.0$ (*c* 0.25, toluene); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.66 (d, ^3J = 6.7 Hz; 3H, –CH_3), 2.37 (s, 3H, –CH_3), 2.43–2.51 (m, 1H, –CH_2–CH_2–); 2.60–2.70 (m, 1H, –CH_2–CH_2–); 2.99–3.15 (m, 3H, –CH_2–CH_2–); 3.22–3.31 (m, 2H, –CH_2–CH_2–); 3.42–3.50 (m, 1H, –CH_2–CH_2–); 4.78 (q, ^3J = 6.7 Hz; 1H, –CH–); 5.96 (d, ^3J = 7.8 Hz; 1H, H-7 or H-8), 6.44 (d, ^3J = 7.8 Hz; 1H, H-8 or H-7), 6.61 (dd, ^3J = 7.8, ^4J = 1.8 Hz; 1H, H-15), 6.64 (d, ^3J = 7.8 Hz; 1H, H-16), 6.94 (dd, ^4J = 1.8; 1H, H-13); 7.31 (d, ^3J = 7.5 Hz; 1H, *p*-Ph); 7.42 (t, ^3J = 7.5 Hz; 2H, 2 *m*-Ph); 7.53 (d, ^3J = 7.5 Hz; 2H, 2 *o*-Ph); 17.14 (br s, 1H, –OH); ^{13}C NMR ($CDCl_3$, 600 MHz): δ 21.34, 25.34, 32.12, 33.85, 33.91, 37.04, 57.46, 120.35, 124.11, 127.05, 127.83, 128.08, 129.28, 130.36, 130.85, 133.23, 135.25, 137.91, 138.46, 142.54, 143.40, 143.51, 170.63, 170.91. Anal. Calcd for $C_{26}H_{26}BrNO$: C, 69.64; H, 5.84; N, 3.12; Br, 17.82. Found: C, 69.82; H, 5.70; N, 3.02; Br, 17.87.

4.4. (*Rp*)-Br-AHPC, (*Rp*)-6

To a solution of (*R*p,*S*)-**7** (0.215 g, 0.48 mmol) in EtOH (12.5 mL), H_2O (3.7 mL) and $Na_2S_2O_5$ (0.334 g, 1.76 mmol) were added. The resulting mixture was refluxed for 50 h. Then $Na_2S_2O_5$ (0.334 g, 1.76 mmol) was added and the resulting suspension was diluted with 50% aq EtOH until the reaction mixture became clear. The solution was then refluxed for 50 h. The mixture was cooled to room temperature and an excess of 2 M HCl was added to adjust to pH 5–7. The mixture was extracted with toluene (3 × 20 mL), and the organic layer was successively washed with H_2O (2 × 20 mL), saturated aq Na_2CO_3 (20 mL) and H_2O (20 mL), and dried with Na_2SO_4. After evaporation of the solvent in vacuo and purification of the solid residue on SiO_2 (eluent $CHCl_3$), 0.111 g (79%) of (*R*p)-**6** was isolated. An analytically pure sample of (*R*p)-**6** was obtained by recrystallization from hexane; mp 146–148 °C; $[\alpha]_D^{25} = +363.3$ (*c* 0.23, toluene). Anal. Calcd for $C_{18}H_{17}BrO_2$: C, 62.62; H, 4.96; Br, 23.14. Found: C, 62.81; H, 4.85; Br, 22.92. ^{1}H NMR data are identical to those of a racemic sample.

4.5. (*Sp*)-Br-AHPC, (*Sp*)-6

Compound (*S*p)-**6** was obtained by the same method from (*S*p,*S*)-**7** in 67% yield. An analytically pure sample of (*S*p)-**6** was obtained by recrystallization from hexane; mp 146–148 °C; $[\alpha]_D^{25} = -361.5$ (*c* 0.23, toluene). Anal. Calcd for $C_{18}H_{17}BrO_2$: C, 62.62; H, 4.96.; Br, 23.14. Found: C, 62.49; H, 4.80; Br, 23.00. ^{1}H NMR data are identical to those of a racemic sample.

4.6. Acylation of 12-bromo-4-hydroxy-[2.2]paracyclophane 4 with benzoyl chloride

To a solution of **4** (0.500 g, 1.65 mmol) in CH_2Cl_2 (13 mL) was added $TiCl_4$ (0.24 mL, 2.15 mmol). The resulting dark cherry-coloured solution was stirred at room temperature for 1.5 h; then benzoyl chloride (0.19 mL, 1.65 mmol) was added. The reaction mixture was stirred at room temperature for seven days. The resulting solution was quenched with 30 mL of H_2O and stirred for 10 min. The yellow organic layer was washed with H_2O

(2 × 60 mL). The water layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to obtain a mixture of two products: [13-bromo-5-hydroxy[2.2]paracyclophane-4-yl)]phenylmetanon **8** (Br-BHPC) and [12-bromo[2.2]paracyclophane-4-yl)]benzoate **9**. These were separated by column chromatography on silica gel using toluene as the eluent. Analytically pure **8** and **9** were obtained by crystallization from heptane.

4.6.1. [13-Bromo-5-hydroxy[2.2]paracyclophane-4-yl)]phenylmetanon 8 (Br-BHPC)

TLC R_f = 0.4; 0.355 g; 53% yield; mp 140–142 °C; MS (EI), *m*/*z* (rel): 408 (2, $[M]^+$), 406 (1, [M), 309 (5); 224 (26, $[M-C_8H_7Br]^+$); 223 (100, $[M-C_8H_8Br]^+$), 209 (12); 195 (15); 181 (8); 178 (5); 167 (6); 152 (5). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.51–2.64 (m, 2H, $-CH_2-CH_2-$); 2.64–2.79 (m, 2H, $-CH_2-CH_2-$); 3.05–3.21 (m, 3H, $-CH_2-CH_2-$); 3.45–3.58 (m, 1H, $-CH_2-CH_2-$); 6.25 (d, ^3J = 7.8 Hz; 1H, H-7 or H-8); 6.59–6.65 (m, 2H, H-15 or H-16); 6.69 (d, ^3J = 7.8 Hz; 1H, H-7 or H-8); 7.04 (d, ^4J = 1.8 Hz; 1H, H-12); 7.41–7.48 (m, 2H, *o*-Ph), 7.52–7.58 (m, 1H, *p*-Ph), 7.67–7.74 (m, 2H, *m*-Ph), 13.13 (s, 1H, –OH). ^{13}C NMR ($CDCl_3$): δ 31.8, 33.0, 33.8, 36.3, 119.1, 125.9, 127.4, 127.6, 128.2, 128.3, 129.6 (2C), 130.4, 132.0, 132.7, 135.0, 137.5, 141.1, 141.3, 142.6, 145.1, 163.2 (C(OH)), 200.4 (C(O)). Anal. Calcd for $C_{18}H_{17}BrO_2$: C, 67.82; H, 4.70; Br, 19.62. Found: C, 67.98; H, 4.98; Br, 19.54.

4.6.2. [12-Bromo[2.2]paracyclophane-4-yl)]benzoate 9

TLC R_f = 0.3; 0.044 g, 7% yield; mp 178–180 °C; MS (EI), *m*/*z* (rel): 408 (30, $[M]^+$), 407 (5, $[M]^+$), 406 (33, $[M]^+$), 400 (8), 328 (12, $[M-Br]^+$), 327 (42); 326 (5), 323 (5), 322 (21), 299 (7), 224 (28, $[M-C_8H_7Br]^+$), 223 (14), 222 (8), 221 (7), 207.(8), 193 (6), 185 (8), 182 (7), 180 (8), 179 (10), 178 (9), 167 (8), 165 (10), 149 (19), 139 (7), 125 (6), 121 (8), 120 (5), 111 (6), 109 (5), 106 (11), 105 (100); ^{1}H NMR ($CDCl_3$): δ 2.69–2.80 (m, 1H, $-CH_2-CH_2-$), 2.81–2.91 (m, 1H, $-CH_2-CH_2-$), 2.92–3.01 (m, 1H, $-CH_2-CH_2-$), 3.01–3.27 (m, 4H, $-CH_2-CH_2-$), 3.41–3.52 (m, 1H, $-CH_2-CH_2-$), 6.48–6.60 (m, 3H, H-8 or H-16, H-7, H-15), 6.61 (d, ^3J = 7.8 Hz; 1H, H-8 or H-16), 6.87 (d, ^4J = 1.8 Hz; 1H, H-5 or H-13), 7.11 (d, ^4J = 1.8 Hz; 1H, H-13 or H-5), 7.56–7.64 (m, 2H, *m*-Ph), 7.67–7.73 (m, 1H, *p*-Ph), 8.30 (d, ^3J = 7.8 Hz; 2H, *o*-Ph). Anal. Calcd for $C_{18}H_{17}BrO_2$: C, 67.82; H, 4.70; Br, 19.62. Found: C, 67.89; H, 4.58; Br, 19.55.

4.7. 12-Bromo-4-hydroxy-5[1-(1-phenyl-ethylimino)-(phenyl) methylen]-[2.2]paracyclophanes, (*Rp*,*S*)-10 and (*Sp*,*S*)-10

A solution of racemic **8** (0.247 g, 0.60 mmol), $TiCl_4$ (0.07 mL, 0.60 mmol) and (*S*)-α-PEA (0.1 mL, 0.79 mmol) in toluene (10 mL) was refluxed in a flask equipped with a Dean–Stark trap filled with anhydrous $MgSO_4$ for 43 h. The solvent was removed and the resulting mixture of diastereomeric (*Sp*,*Rc*)-**10** and (*Rp*,*Rc*)-**10** was separated by column chromatography on silica gel using CH_2Cl_2 as the eluent. Analytically pure diastereomers **10** were obtained by crystallization from hexane. MS (EI), *m*/*z* (rel): 511 (33, $[M]^+$), 510 (14, $[M]^+$), 509 (35, $[M-H]^+$), 510 (14, $[M]^+$), 405 (10), 328 (23, $[M-C_8H_9Br]^+$), 327 (78), 326 (44), 312 (20, $[M-C_8H_9Br-OH]^+$), 224 (16), 223 (76), 222 (100), 195 (13), 194 (24), 105 (36), 103 (11).

4.7.1. (*Sp*,*S*)-10

TLC R_f = 0.36 (eluent CH_2Cl_2); 0.100 g (51%); mp 150–152 °C; $[\alpha]_D^{25} = -549.2$ (*c* 0.20, toluene); ^{1}H NMR ($CDCl_3$): δ 1.42 (d, ^3J = 6.5 Hz; 3H, $-CH_3$), 1.92–2.01 (m, 1H, $-CH_2-CH_2-$), 2.19–2.25 (m, 1H, $-CH_2-CH_2-$); 2.43–2.61 (m, 2H, $-CH_2-CH_2-$); 2.84–2.95 (m, 1H, $-CH_2-CH_2-$); 3.00–3.09 (m, 1H, $-CH_2-CH_2-$); 3.12–3.22 (m, 1H, $-CH_2-CH_2-$); 3.49–3.58 (m, 1H, $-CH_2-CH_2-$); 4.56 (q, ^3J = 6.5 Hz; 1H, –CH–); 5.90 (d, ^3J = 7.3 Hz; 1H, H-7 or H-8), 6.50 (d, ^3J = 7.8 Hz; 1H, H-8 or H-7), 6.54–6.58 (m, 2H, H-15, H-16), 7.12 (br s, 1H, H-13), 7.06–7.15 (m, 1H, *p*-Ph–C=N), 7.30–7.37 (m, 1H, *p*-Ph), 7.37–7.54 (m, 8H, Ph), 17.54 (br s, 1H, –OH); ^{13}C NMR ($CDCl_3$, 600 MHz): δ 26.15 (Me), 30.78, 33.38, 33.40, 35.36, 57.88 (N–CH), 118.62 (C-6), 123.97 (C-7), 126.50 (1C, Ph), 126.73 (2C, *o*-Ph), 127.20 (*p*-Ph), 127.52 (1C, Ph–CN), 128.72 (2C, *m*-Ph), 128.84 (3C, PhC=N), 129.35 (o-Ph=CN), 129.47, 130.80 (C-16) 132.42 (C-13), 133.94 (C-15), 135.54, 137.26 (C-14), 138.24 (C-8), 142.50 (C-11), 143.91 (1C, PhC=N), 144.21 (C-3) 170.82 (C=N), 171.50 (C-4). Anal. Calcd for $C_{31}H_{28}BrNO$: C, 72.94; H, 5.53; N, 2.74; Br, 15.65. Found: C, 73.04; H, 5.64; N, 2.67; Br, 15.52.

4.7.2. (*Rp*,*S*)-10

TLC R_f = 0.44 (eluent CH_2Cl_2); 0.092 g (47%); mp 176–178 °C; $[\alpha]_D^{25} = +555.0$ (*c* 0.20, toluene); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.80 (d, ^3J = 6.5 Hz; 3H, $-CH_3$), 1.93–2.02 (m, 1H, $-CH_2-CH_2-$), 2.19–2.27 (m, 1H, $-CH_2-CH_2-$), 2.49–2.56 (m, 1H, $-CH_2-CH_2-$), 2.56–2.65 (m, 1H, $-CH_2-CH_2-$), 2.97–3.07 (m, 2H, $-CH_2-CH_2-$), 3.11–3.20 (m, 1H, $-CH_2-CH_2-$), 3.45–3.56 (m, 1H, $-CH_2-CH_2-$), 4.76–4.83 (m, 1H, –CH–), 5.89 (d, ^3J = 7.8 Hz; 1H, H-7 or H-8), 6.46 (d, ^3J = 7.8 Hz; 1H, H-8 or H-7), 6.51 (dd, ^3J = 7.8, ^4J = 1.8 Hz; 2H, H-15), 6.57 (d, ^3J = 7.8 Hz; 1H, H-16), 6.75 (br d, ^3J = 6.0 Hz; 1H, *o*-Ph–C=N), 6.95 (d, ^3J = 7.8 Hz; 2H, *o*-Ph), 7.07–7.12 (m, 1H, *p*-Ph–C=N), 7.12–7.17 (m, 1H, *m*-Ph), 7.20 (d, ^4J = 1.8 Hz; 1H, H-13), 7.23–7.31 (m, 1H, *m*-Ph–C=N), 7.42–7.49 (m, 1H, *o*-Ph), 7.53–7.62 (m, 1H, *m*-Ph–C=N), 7.91 (br d, ^3J = 6.0 Hz; 1H, *o*-Ph–C=N), 17.30 (s, 1H, –OH); ^{13}C NMR ($CDCl_3$, 600 MHz): δ 24.30 (1C, CH_3), 31.25, 34.10. 35.05, 35.63, 57.42, 119.27, 124.76, 126.90 (2C, Ph), 127.40, 127.67, 128.42 (br s, 2C, *Ph*–C=N), 129.17 (2C, Ph), 129.68 (br s, 1C, *Ph*–C=N), 129.84 (br s, 1C, *Ph*–C=N), 129.98, 130.61, 132.15, 132.86, 134.21, 136.40, 137.70, 138.57, 143.13, 144.09, 144.65, 171.52, 172.48. Anal. Calcd for $C_{31}H_{28}BrNO$: C, 72.94; H, 5.53; N, 2.74; Br, 15.65. Found: C, 73.03; H, 5.47; N, 2.59; Br, 15.70.

4.8. Hydrolysis of Schiff bases (*Sp*,*S*)-11

To a solution of (*Sp*,*S*)-**11** (0.400 g, 0.93 mmol) in EtOH (30 mL), $Na_2S_2O_5$ (1.000 g, 5.26 mmol) was added. The resulting suspension was refluxed and H_2O was added until the reaction mixture became clear. The solution was refluxed for 15 h. Then an additional portion of $Na_2S_2O_5$ (1.000 g, 5.26 mmol) was added and the resulting suspension was diluted with H_2O and EtOH until it fully dissolved after which the solution was refluxed for 15 h. The last procedure was repeated until the disappearance of starting (*Sp*,*S*)-**11** by TLC (11 times). The mixture was extracted with $CHCl_3$ (3 × 100 mL), and the organic layer was dried with Na_2SO_4. After evaporation of the solvent in vacuo and purification of the solid residue on SiO_2 (eluent $CHCl_3$), 0.130 g (42%) of (*Sp*)-**3** were isolated. An analytically pure sample of (*Sp*)-**3** was obtained by recrystallization from heptane; mp 149.0 °C; $[\alpha]_D^{25} = -254.4$ (*c* 0.25, benzene); lit. for (*Rp*)-**3**: mp 151.5–152.5 °C; $[\alpha]_D^{25} = +250.0$ (*c* 0.24, benzene).[10] Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.22; H, 6.04. The ^{1}H NMR data are in a good agreement with those of *rac*-**3**.[10]

4.9. Enantioselective addition of diethylzinc to benzaldehyde catalyzed by ketimines 7 and 10 typical procedure

To a solution of the respective Schiff base (0.01 mmol) in toluene (0.28 mL), 1.1 equiv of Et_2Zn in toluene (0.2 mL, 0.22 mmol) was added in one portion at 0 °C followed by the dropwise addition of benzaldehyde (0.1 mmol). The mixture was stirred for 15 h at room temperature and the reaction was quenched by the addition of HCl solution (1*N*, 0.45 mL), and the reaction mixture was diluted with Et_2O (2 mL) and H_2O (1 mL). The organic layer was separated

Table 3
Crystallographic data, details of data collection and structure refinement parameters for compounds **6**, **7** 0.13(H_2O) and **10**

	6	**7**	**10**
Chemical formula	$C_{18}H_{17}BrO_2$	$C_{26}H_{26}BrNO{\cdot}0.13(H_2O)$	$C_{31}H_{28}BrNO$
M_r	345.23	450.72	510.45
Crystal system, space group	Triclinic, $P1$	Hexagonal, $P6_1$	Orthorhombic, $P2_12_12_1$
Temperature (K)	100	120	100
a (Å)	7.8266 (7)	20.0931 (18)	10.5085 (4)
b (Å)	8.1061 (8)	20.0931 (18)	10.7928 (5)
c (Å)	12.1276 (11)	9.6513 (10)	20.8067 (9)
α (°)	81.048 (2)	90	90
β (°)	80.680 (2)	90	90
γ (°)	75.286 (2)	120	90
V (Å^3)	729.06 (12)	3374.5 (6)	2359.82 (17)
Z	2	6	4
μ (mm^{-1})	2.82	1.84	1.77
Crystal size (mm)	0.28 × 0.19 × 0.07	0.37 × 0.04 × 0.03	0.31 × 0.25 × 0.18
T_{min}, T_{max}	0.506, 0.827	0.890, 0.934	0.592, 0.731
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9321, 8008, 6959	25411, 4547,3992	41225, 6884,6651
R_{int}	0.018	0.060	0.025
No. of reflections	8008	4547	6884
No. of parameters	375	273	308
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.79, −0.48	0.45, −0.31	0.39, −0.27
Flack parameter	0.023 (6)	−0.041 (10)	0.001 (4)

and the aqueous fraction was extracted with Et_2O (3 × 3 mL). The combined organic fractions were washed with aq $NaHCO_3$ (3 mL) and dried with Na_2SO_4. After solvent removal, the oily residue was subjected to chiral HPLC analysis without further purification. Enantiomeric analysis of 1-phenylpropanol was performed by HPLC (Varian 5000 LC) on Chiracel OD (250 mm × 4.6 mm) with hexane/2-propanol 100/4 as eluent, flow parameters rate 1 mL/min, temperature 20 °C, detector UV 254 nm, the retention times were 8.2 (*S*) and 8.9 min (*R*), respectively.

4.10. X-ray diffraction of 6, 7 and 10

X-ray diffraction of **6**, **7** and **10** data were collected at 120(2) K with Bruker SMART 1000 CCD **7**[11] and at 100(2) K with Bruker Apex II CCD **6** and **10**[12] diffractometers using graphite monochromated Mo Kα radiation. The structures were solved by the direct method and refined by full-matrix least squares method against F^2 of all data, using SHELXTL PLUS software.[13] Non-hydrogen atoms were found on difference Fourier maps and refined with anisotropic displacement parameters. The residual peak (0.9 e A^{-3}) in the structure of **7** was attributed to a disordered water molecule. The population of the water molecules was found to be a free variable (FVAR instruction) and then fixed at 0.13. The positions of H(O) atoms were found on difference Fourier maps and of H(C) were calculated. All hydrogen atoms were included in refinement in isotropic approximation by the riding model with the U_{iso}(H) = 1.5U_{eq}(X_i) for methyl groups and water molecules and the U_{iso}(H) = 1.2U_{eq}(X_{ii}) for other atoms, where U_{eq}(C) are equivalent thermal parameters of parent atoms. Details of data collection and refinement parameters are given in Table 3. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 769546–769548. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 lEZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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