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Synthesis and resolution of new cyclohexyl fused spirobiindane 7,7′-diol

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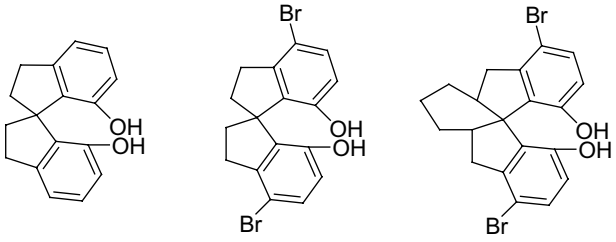
Abstract—A new type of spiro biindane derived chiral ligand has been synthesized and resolved into its enantiomeric pure forms with its crystal structure also established.

1. Introduction

Asymmetric catalysis of an organic reaction provides a powerful tool for multi-amplification of chirality to obtain enantiomerically pure compounds.[1] Thus the designing and subsequent development of a variety of new chiral ligands have become an ongoing process for synthetic chemists to apply to various enantioselective reactions.[2] To some extent, the relationship between structure–activity has been exploited by carrying out structural modifications, which lead to the most efficient chiral ligands.

Of all the chiral ligands, 1,1′-binaphthalene derivatives,[3] which possess C_2 symmetry, occupy a prominent position as chiral auxiliaries and ligands for asymmetric synthesis. Recently spiranes, another class of molecules with axial chirality, are receiving much attention.[4] Since 1,1′-spirobiindane[5] offers promising chemical robustness and conformational rigidity, it is indeed worthwhile to explore its utility in asymmetric synthesis. A literature survey reveals that only a limited number of publications have appeared using this class of ligands in asymmetric synthesis.[6] 1,1′-Spirobiindane-7,7′-diols **1** and **2** were recently reported[7] and their backbone used to prepare various phosphoramidites chiral ligands,[8] which were found to be useful for rhodium catalyzed asymmetric hydrogenation reactions.[9]

Even minor modifications of the chiral ligands have been found to enhance manifold functional capability of these ligands in asymmetric catalysis.[10] Thus we are interested in the modifications of spirobiindanes by increasing the rigidity of the spiro ring as well as the bulkiness. The other possibility is to substitute the aromatic ring with an electronegative atom like bromine. We herein report the synthesis of the chiral ligand 2,2′-cyclohexyl-4,4′-dibromo-1,1′-spirobiindane-7,7′-diol **3**, its separation and the single crystal XRD of both enantiomers.



1 **2** **3**

2. Results and discussion

It was envisaged that spiro chiral ligand **3** having a cyclohexyl moiety connecting the two positions of the biindane ring, would provide a highly hindered steric environment. The rigidity thus obtained would support the necessary prerequisites for a chiral ligand and promote the performance in a better way. Ligand **3** was prepared as shown in Scheme 1. Reaction of cyclohexanone with *m*-anisaldehyde in the presence of ethanolic sodium hydroxide solution resulted in the formation of the

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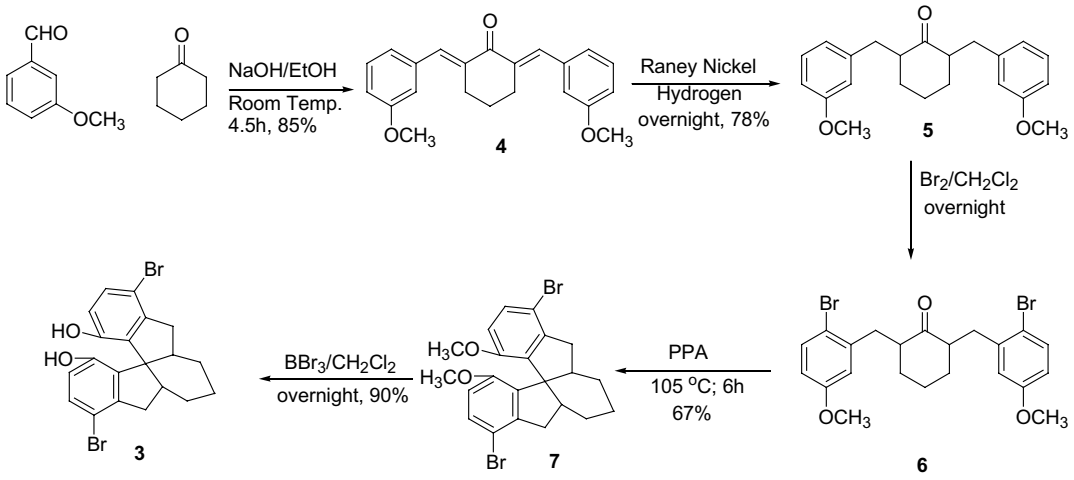


Scheme 1.

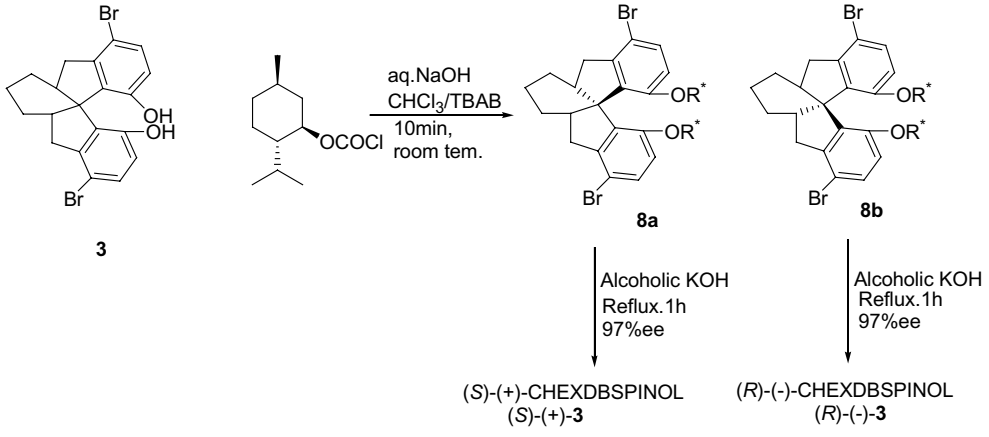
condensed product 2,6-bis(3-methoxy benzylidene)-cyclohexanone **4** in 85% yield.

Catalytic hydrogenation of the double bond in **4** was achieved with Raney nickel within 12 h to give 2,6-bis(3-methoxy benzyl)cyclohexanone **5** in 78% yield against palladium on charcoal or platinum on carbon forming some side products. Selective ring bromination of **5** took place yielding 2,6-bis(6-bromo-3-methoxy benzyl)cyclohexanone **6**. The intramolecular ring closure of **6** was effected using polyphosphoric acid to form 7,7′-dimethoxy-4,4′-dibromo,2,2′-cyclohexyl-1,1′-biindane **7**. Products **6** and **7** were obtained in a combined yield of 67%. NMR analysis of **7** clearly showed only one set of peaks indicating that only one diastereomer had been obtained. We believe that a high degree of rigidity favors the cyclization to occur with only two forms. This observation was further substantiated by HPLC analysis using a chiral column (DAICEL, Chiralcel ODR-H), which showed only two peaks in an equal ratio (retention time 27.8 and 29.2 in CH_3CN/H_2O = 80:20).

Demethylation of **6** was carried out using BBr_3 to afford the free diol as a racemic mixture, namely 7,7′-dihydroxy-4,4′-dibromo,2,2′-cyclohexyl-1,1′-biindane **3** in 90% yield.

2.1. Chiral separation

The enantiomeric separation of the racemic ligand **3** was attempted by two different methods. First we tried chiral phase transfer catalyzed complexation method using *N*-benzyl chinchonidinium chloride in either toluene or a mixture of hexane and toluene. In both the cases, only partial resolution was achieved. We next tried, as shown in Scheme 2, the chiral derivatization method using (−)-menthyl chloroformate as a derivatizing agent. (−)-Menthyl chloroformate was prepared in our laboratory using a known method[6] and used as such without any further purification. Reacting racemic ligand **3** in an aqueous $NaOH/CH_2Cl_2$ solution in the presence of tetrabutylammonium bromide (TBAB) with (−)-menthyl chloroformate quickly yielded two diastereomers **8a** and **8b** in 81% and 83%, respectively. The two diastereomers were separated by crystallizing in hexane. One of the diastereomers was crystallized out and the other diastereomer still present in the mother liquor. The deprotection of the hydroxyl groups in **8a** and **8b** was



Scheme 2.

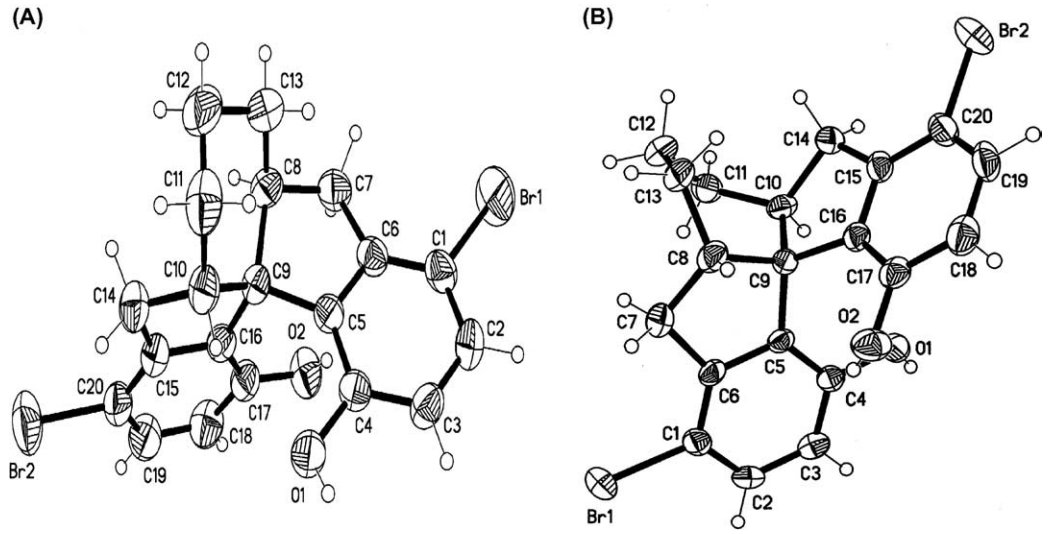


Figure 1.

carried out by refluxing in aqueous KOH/EtOH to yield (*S*)-(+)-**3** and (*R*)-(−)-**3**.

We were able to obtain single crystals of the (*S*)-(+)-CHEXDBSPINOL (*S*)-(+)-**3** and (*R*)-(−)-CHEXDBSPINOL (*R*)-(−)-**3** from hexane, which were suitable for X-ray crystallography.[11] The ORTEP view of the crystal structures is shown in Figure 1A and B.

3. Experimental

3.1. General

All the reagents were used as received. Raney nickel was purchased from Acros chemicals. Flash column chromatography was performed over silica gel (230–400 mesh). Melting points were measured on a Buchi melting point B-540 and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-400 spectrometer. The chemical shifts are reported as δ values (ppm) relative to TMS. Infrared spectra were recorded on a BIORAD Excalibur Series (FTS 3000mx). Optical rotations were measured on Jasco J-810 spectropolarimeter (Na lamp). HPLC analysis was done by using a chiral column (DAICEL, Chiralcel OD-H) with hexane/isopropanol.

3.2. 2,6-Bis(3-methoxybenzylidene)cyclohexanone 4

A solution of *m*-methoxybenzaldehyde (20 g, 147 mmol) and cyclohexanone (7.21 g, 73.5 mmol) in 20 mL of ethanol was added to a solution of 15 g of NaOH in 270 mL of 50% aqueous ethanol over a period of 30 min and stirred for 4 h at room temperature. The reaction mixture was then allowed to settle overnight. The solid obtained was filtered and washed with water and the product vacuum dried (20.90 g, 85%). Mp 77–79 °C. ^{1}H NMR: ($CDCl_3$ δ) 1.73–1.79 (m, 2H), 2.89–2.92 (m, 4H), 3.8 (s, 2H), 6.874 (dd, 2H, $J = 8$ Hz, $J = 2.4$ Hz), 6.97 (d, 2H, $J = 2$ Hz), 7.03 (d, 2H, $J = 8$ Hz), 7.34 (s, 2H): ^{13}C NMR: ($CDCl_3$ δ) 22.95, 28.48, 55.29, 114.23, 115.74, 122.84, 129.35, 136.43, 136.86, 137.29, 159.44, 190.37. IR (KBr pellet, cm^{-1}): 1633, 1602, 1575, 1169; MS *m/z* (%) 334.1 (M^+, 90), 303 (100), 275 (10), 213 (10), 115 (15), 91 (10); HRMS calcd for $C_{22}H_{22}O_3$ 334.1568. Found 334.1563.

3.3. 2,6-Bis(3-methoxybenzyl)cyclohexanone 5

A solution of 2,6-bis(3-methoxybenzylidene)cyclohexanone (3 g, 9 mmol) in 30 mL of acetone was stirred with Raney nickel (6 g) under an atmosphere of hydrogen at room temperature with the progress of the reaction monitored by TLC. A further 3 g of Raney nickel was needed if the reaction had not gone to completion. Upon disappearance of the starting material in TLC, the reaction mixture was carefully filtered off without allowing the Ra-Ni to become dry by washing with acetone and the filtrate was concentrated in a rotary evaporator. The crude product was column chromatographed using EA/Hex (5:95) as eluent. (2.36 g, 78% yield). Mp 81–82.6 °C. ^{1}H NMR: ($CDCl_3$ δ) 1.22–1.38 (m, 2H), 1.52–1.57 (m, 1H), 1.73–1.79 (m, 1H), 2.03–2.06 (m, 2H), 2.34–2.40 (m, 2H), 2.53–2.56 (m, 2H), 3.193 (dd, 2H, $J = 14$ Hz, $J = 4.8$ Hz), 3.76 (s, 6H), 6.68–6.73 (m, 6H), 7.16 (t, 2H, $J = 8$ Hz). ^{13}C NMR: ($CDCl_3$ δ) 25.33, 34.91, 35.53, 52.31, 55.13, 111.13, 114.92, 121.56, 129.21, 142.24, 159.54, 212.78. IR (KBr pellet, cm^{-1}): 1698 (C=O), 1254, 1150; MS *m/e* (%) 338 (M^+, 95), 320 (15), 295 (10), 217 (85), 199 (45), 161 (30), 147 (20), 122 (100), 91 (40); HRMS calcd for $C_{22}H_{26}O_3$ 338.1881. Found 338.1888.

3.4. 2,6-Bis(6-bromo-3-methoxybenzyl)cyclohexanone 6

2,6-Bis(3-methoxybenzyl)cyclohexanone 3 g, (8.9 mmol) was dissolved in methylene chloride (15 mL) containing pyridine (3 mL) and the reaction mixture cooled to −10 °C after which bromine in methylene chloride solution (8 mL, 10% v/v) was added dropwise. After completing the addition, the reaction mixture was brought

to room temperature and stirred for 12 h during which time the reaction was completed as shown by TLC. The reaction mixture was then diluted with CH_2Cl_2 (25 mL) and the organic layer washed with aqueous $NaHSO_3$ solution to remove excess bromine, followed by dilute HCl. It was then dried over magnesium sulfate and removing solvent to get the product **6** as yellow solid (3.98 g). Mp 167–168 °C. ^{1}H NMR: ($CDCl_3$ δ) 2.024–2.062 (m, 2H), 2.558 (dd, 2H, J = 13.8 Hz, J = 8 Hz), 2.66–2.69 (m, 2H), 2.65 (dd, 2H, J = 16. Hz, J = 5.2 Hz), 6.603 (dd, 2H, J = 8.8 Hz, J = 3.2 Hz), 6.776 (d, 2H, J = 3.2 Hz), 7.36 (d, 2H, J = 8.8 Hz). ^{13}C NMR: ($CDCl_3$ δ) 25.34, 34.92, 35.53, 52.81, 55.13, 111.14, 114.93, 121.21, 142.25, 159.55, 212.74. IR (KBr pellet, cm^{-1}): 602, 1240, 1697 (C=O); MS *m/e* (%): 494 (M^+ 9), 414 (100), 336 (95), 278 (15), 198 (85), 161 (20), 137 (80), 91 (10); HRMS calcd $C_{22}H_{24}Br_2O_3$ 494.0092. Found 494.0116.

3.5. 7,7′-Dimethoxy-4,4′-dibromo-2,2′-cyclohexyl-1,1′-biindane 7

Compound **6** (3.98 g) was stirred with polyphosphoric acid (30 g) at 105 °C for 6 h. The mixture was poured into water (more dilution with 300 mL of water was needed in order to prevent the formation of emulsion during extraction) and extracted with methylene chloride (2 × 100 mL). The organic layer was washed with water, dried, and concentrated. The crude product was purified by column chromatography with EA/Hex (2:98) as eluent to give product **7** (2.83 g, 67% yield for two steps). Mp 168–170.4 °C. ^{1}H NMR: ($CDCl_3$ δ) 1.42–1.46 (m, 2H), 1.52–1.54 (m, 4H), 2.715 (dd, 2H, J = 15.8 Hz, J = 6.6 Hz), 2.87–2.90 (m, 2H), 3.068 (dd, 2H, J = 15.8 Hz, J = 7.8 Hz), 3.44 (s, 6H), 6.49 (d, 2H, J = 8 Hz), 7.23 (d, 2H, J = 8 Hz). ^{13}C NMR: ($CDCl_3$ δ) 17.92, 26.21, 39.50, 41.98, 55.58, 111.15, 111.54, 130.35, 136.79, 145.96, 156.32. IR (KBr pellet, cm^{-1}): 669, 2361; MS *m/e* (%) 476 (M^+ 60), 399 (80), 355 (10), 318 (25), 276 (80), 239 (15), 198 (58), 159 (34), 138 (33), 101 (12); HRMS calcd for $C_{22}H_{22}Br_2O_2$ 475.9986. Found 475.9971.

3.6. *rac*-7,7′-Dihydroxy-4,4′-dibromo-2,2′-cyclohexyl-1,1′-biindane 3

Compound **7** (2.38 g, 5 mmol) was dissolved in dry methylene chloride (25 mL) in a flame-dried flask under an argon atmosphere. The solution was then cooled down to −75 °C and treated with 1 M $BBr_3CH_2Cl_2$ solution (11.5 mL, 2.3 equiv). Upon completing the addition, the reaction mixture was allowed to warm up to room temperature and stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (25 mL) and washed with water until the washings were neutral. The organic layer was dried and concentrated and the crude product obtained, crystallized from hexane to yield compound **3** (2.02 g, 90% yield). Mp 187–192.4 °C. ^{1}H NMR: ($CDCl_3$ δ) 1.53–1.55 (m, 8H), 1.60–1.68 (m, 2H), 2.75–2.85 (m, 4H), 2.95–3.03 (m, 2H), 4.47 (b, 2H), 6.47 (d, 2H, J = 8 Hz), 7.21 (d, 2H, J = 8 Hz). ^{13}C NMR: ($CDCl_3$ δ) 16.10, 22.99, 38.50, 42.68, 62.80, 111.36, 116.94, 132.20, 132.25, 145.43, 152.52. IR (KBr pellet, cm^{-1}): 3460 (–OH), 2361, 1337, 667; MS *m/e* (%) 449 (M^+ 100) 368 (80), 290 (30), 263 (82), 248 (28), 184 (75), 145 (40), 124 (45), 77 (10); HRMS calcd for $C_{20}H_{18}Br_2O_2$ 447.9657. Found 447.9673.

3.7. Resolution of 7,7′-dihydroxy-4,4′-dibromo-2,2′-cyclohexyl-1,1′-biindane (CHEXDBSPINOL) and 7,7′-bis-(L-menthyloxy-carbonyloxy)-4,4′-dibromo-2,2′-cyclohexyl-1,1′-biindane 8a and 8b

A racemic mixture of CHEXDBSPINOL (1.575 g, 3.5 mmol) was taken in aqueous solution of sodium hydroxide (0.6 g in 10 mL of H_2O, 15 mmol) and to this added a solution of chloroform (10 mL) containing 0.50 g (1.56 mmol) of tetrabutylammonium bromide after which (−)-menthyl chloroformate 3.47 g (11.1 mmol, 70% w/w) was added under rapid stirring. After the solution had been stirred at room temperature for 10 min, the two phases were separated. The aqueous phase was extracted two times with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and evaporation of the solvent in a rotary evaporator afforded a crude product, which was passed through a column packed in hexane to collect the two diastereomers. The mixture was then dissolved in hot hexane (30 mL) and allowed to cool to room temperature slowly wherein one of the diastereomers crystallized out. The mother liquid was decanted and left out at room temperature overnight to afford a second crop of crystals. The combined white crystals were washed with hexane (2 × 2 mL) and dried in vacuo (1.15, 81% yield). (*S*)-(+)-menthyl CHEXDBSPINOL. Mp 142.8–143.7 °C; $[\alpha]_D$ = +33.1 (*c* 2, $CHCl_3$). ^{1}H NMR: ($CDCl_3$ δ) 0.64 (d, 6H, J = 7.2 Hz), 0.83–1.0 (m, 14H), 1.28–1.69 (m, 20H), 1.84–1.88 (m, 2H), 2.74–2.82 (m, 4H), 3.09–3.12 (m, 2H), 4.31–4.37 (m, 2H), 6.83 (d, 2H, J = 8.4 Hz), 7.30 (d, 2H, J = 8.8 Hz). ^{13}C NMR: ($CDCl_3$ δ) 16.22, 17.67, 20.75, 21.95, 23.21, 26.12, 26.24, 31.22, 31.58, 34.03, 40.17, 42.91, 46.75, 63.75, 79.15, 116.85, 122.59, 131.22, 138.94, 146.42, 147.26, 152.27. IR (KBr pellet, cm^{-1}): 1755, 1258, 1230.

The mother liquid was evaporated to dryness and the residue passed through a short column of silica gel packed in hexane to afford the other diastereomer of (*R*)-(−)-menthyl CHEXDBSPINOL (1.18 g, 83% yield). Mp 61–62.5 °C. ^{1}H NMR: ($CDCl_3$ δ) 0.75 (d, 6H, J = 6.8 Hz), 0.84–0.91 (m, 12H), 0.91–1.00 (m, 2H), 1.28–1.64 (m, 18H), 1.70–1.73 (m, 2H), 1.84–1.88 (m, 2H), 2.74–2.82 (m, 4H), 3.09–3.14 (m, 2H), 4.31–4.37 (m, 2H), 6.82 (d, 2H, J = 8.4 Hz), 7.29 (d, 2H, J = 8.8 Hz). ^{13}C NMR: ($CDCl_3$ δ) 16.22, 17.66, 20.75, 21.96, 23.20, 26.12, 26.22, 31.28, 34.03, 39.19, 40.17, 42.91, 46.75, 63.74, 79.16, 116.86, 122.60, 131.22, 138.94, 146.42, 147.26, 152.28. IR (KBr pellet, cm^{-1}): 1758, 1734, 1260, 1230.

3.8. Hydrolysis of menthyl esters 8a and 8b

To a solution of KOH (8.7 g, 155 mmol) in 10% degassed water/ethanol (10 mL) was added 1.06 g of **8a** (1.3 mmol) and the mixture refluxed for 1 h after which time no **7a** remained (TLC). The reaction mixture was then cooled

and rotary evaporated. To the residue, 20 mL of water was added and extracted with hexane. The aqueous layer was separated and acidified with 6 M HCl to produce a white precipitate, which was extracted with a mixture (20 mL) of hexane and ethyl acetate (9:1). The organic layer was dried and concentrated under reduced pressure to give a crystalline material of (*S*)-(+)-CHEXDBSPINOL, (*S*)-(+)-**3**, 97.5% ee, Mp 120–122 °C. $[\alpha]_D$ = +111.7 (*c* 2, $CHCl_3$). ^1H NMR: ($CDCl_3$ δ) 1.57–1.61 (m, 6H), 1.76–1.72 (m, 2H), 2.80–2.84 (m, 2H), 2.88–2.90 (m, 2H), 4.48 (b, 2H), 6.52 (d, 2H, *J* = 8.4 Hz), 7.26 (d, 2H, *J* = 8.4 Hz): ^{13}C NMR: ($CDCl_3$ δ) 16.07, 22.92, 38.49, 42.69, 62.78, 111.37, 116.95, 132.28, 145.44, 152.52. IR (KBr pellet, cm^{-1}): 3457, 1463; MS *m/e* (%): 447 (60), 371 (65), 290 (33), 265 (80), 248 (25), 189 (22), 184 (62), 145 (30), 124 (40); HRMS calcd for $C_{20}H_{18}Br_2O_2$ 447.9664. Found 447.9671.

Similar hydrolysis treatment of **8b** (1.0 g, 1.3 mmol) followed by crystallization in hexane afforded (*R*)-(−)-CHEXDBSPINOL, (*R*)-(−)-**3**, as white crystals 97% ee. Mp 190–192.6 °C.

$[\alpha]_D$ = −110.74 (*c* 2, $CHCl_3$) ^1H NMR: ($CDCl_3$ δ) 1.57–1.59 (m, 6H), 1.67–1.72 (m, 2H), 2.80–2.84 (m, 2H), 2.88–2.90 (m, 2H), 2.99–3.06 (m, 2H), 4.48 (b, 2H), 6.52 (d, 2H, *J* = 8.4 Hz), 7.25 (d, 2H, *J* = 8.8 Hz). ^{13}C NMR: ($CDCl_3$ δ) 16.07, 22.94, 38.48, 42.68, 62.78, 111.36, 116.94, 132.16, 132.26, 145.43, and 152.52. IR (KBr pellet, cm^{-1}): 3470, 1463; MS *m/e* (%): 447 (60), 371 (65), 290 (33), 265 (80), 248 (25), 189 (22), 184 (62), 145 (30), 124 (40); HRMS calcd for $C_{20}H_{18}Br_2O_2$ 447.9664. Found 447.9671.

3.9. X-ray investigation and crystal data

A pure sample of enantiomer (*S*)-(+)-**3** was crystallized from hexane and the resulting crystals examined by the single crystal X-ray analysis technique. This crystal was monoclinic in space group P2 (1)/n and has a unit cell with: volume 1785 Å^3; cell dimensions *a* = 8.94 Å, *b* = 22.04 Å, and *c* = 9.11 Å; and angles $\alpha = 90°$, $\beta = 96.36°$, and $\gamma = 90°$. The unit cell has one molecule with an empirical formula of $C_{20}H_{18}Br_2O_2$ and weight of 450.16 g/mol. The data was collected at 223 K with wavelength of 0.71073 Å. Density (cal.) 1.674 mg/m^3, *Z* = 4, absorption coefficient = 4.549 mm^{-1}, *F*(000) = 896, crystal size = 0.36 × 0.30 × 0.30 mm^3, theta range for data collection = 1.85–27.50°. Final *R* indices [*I* > sigma(*I*)] of *R*1 = 0.0469, *wR*2 = 0.1096, and *R* indices (all data) of *R*1 = 0.0811, *wR*2 = 0.1217.

Pure enantiomer (*R*)-(−)-**3** did not yield good quality crystals suitable enough for single crystal X-ray analysis. However, crystallization of Y from hexane in the presence of menthol led to a good quality crystalline material that after X-ray investigation gave the following data. The crystal was monoclinic P2 (1). The asymmetric unit contained two independent molecules of $C_{20}H_{18}O_2Br_2$ and a molecule of $C_{10}H_{20}O$ with a formula weight of 1056.59 g/mol. The crystal had a unit cell with: volume 2276 Å^3; cell dimensions *a* = 9.87 Å, *b* = 16.76 Å, and *c* = 13.94 Å; and angles $\alpha = 90°$, $\beta = 99.39°$, and $\gamma = 90°$. The data was collected at 223 K with wavelength of 0.71073 Å. Density (cal.) 1.541 mg/m^3, *Z* = 2, absorption coefficient = 3.582 mm^{-1}, *F*(000) = 1072, crystal size = 0.50 × 0.20 × 0.10 mm^3, theta range for data collection = 1.48–27.48°. Final *R* indices [*I* > sigma(*I*)] of *R*1 = 0.0412, *wR*2 = 0.0841, and *R* indices (all data) of *R*1 = 0.0601, *wR*2 = 0.0887.

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References

1. *Advance in Catalysis Process:* (a) *Asymmetric Transformation;* Doyle, M., Ed. JAI: Greenwich, CT, 1995; Vol. 1; (b) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994.
2. Seyden-Penn, J. *Chiral Auxiliaries and Ligands in Asymmetric Synthesis*; John Wiely: New York, 1995.
3. For review of C_2-symmetry in asymmetric synthesis see: Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581.
4. (a) Ramachary, D. B.; Naidu, S.; Barbas, C. F. *Synlett* **2003**, *12*, 1910; (b) Coles, S. J.; Davies, D. B.; Eaton, R. J.; Hursthouse, M. B.; Killic, A.; Shaw, R. A.; Uslu, A. *Eur. J. Org. Chem.* **2004**, 1881; (c) Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereo Chemistry of Organic Compounds*; Wiley: New York, 1994; p 1138.
5. (a) Brewster, J. H.; Prudence, R. T. *J. Am. Chem. Soc.* **1973**, *95*, 1217; (b) Hill, R. K.; Cullison, D. A. *J. Am. Chem. Soc.* **1973**, *95*, 1229.
6. Li, Z.; Liang, X.; Wu, F.; Wan, B. W. *Tetrahedron: Asymmetry* **2004**, *14*, 665.
7. (a) Birman, V. B.; Rheingold, A. L.; Lam, K.-C. *Tetrahedron: Asymmetry* **1999**, *10*, 125; (b) Zhang, J.-H.; Liao, J.; Cui, X.; Yu, K.-B.; Zhu, J.; Deng, J.-G.; Shu, S.-F.; Wang, L.-X.; Zhou, Q.-L.; Chung, L. W.; Te, T. *Tetrahedron: Asymmetry* **2002**, *13*, 1363.
8. (a) Fu, Y.; Xie, J.-H.; Hu, A.-G.; Zhou, H.; Wang, L.-X.; Zhou, Q.-L. *Chem. Commun.* **2002**, 480; (b) Zhou, H.; Wang, W.-H.; Fu, Y.; Xie, J.-H.; Shi, W.-J.; Wang, L.-X.; Zhou, Q.-L. *J. Org. Chem.* **2003**, *68*, 1582.
9. (a) Hua, J.; Wang, L.-X.; Fu, Y.; Zhu, S.-F.; Fan, B.-M.; Duan, H.-F.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2003**, *125*, 4404; (b) Hu, A.-G.; Fu, Y.; Xie, J.-H.; Zhou, H.; Wang, L.-X.; Zhou, Q.-L. *Angew. Chem., Int. Ed.* **2002**, *41*, 2348.
10. (a) Bandin, M.; Casolari, S.; Cozzi, P. G.; Proni, G.; Schmohel, E.; Spada, G. P.; Tagliavini, E.; Achille, U.-R. *Eur. J. Org. Chem.* **2000**, 491; (b) Hu, X.; Bai, C.; Dai, H.; Chen, H.; Zheng, Z. *J. Mol. Cat. A* **2004**, 107.
11. Crystallographic data has been deposited with Cambridge Crystallographic Data Center. Supplementary publication no. ccdc 249392 and 249393. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).