Improved resolution methods for (*R*,*R*)- and (*S*,*S*)-cyclohexane-1,2-diamine and (*R*)- and (*S*)-BINOL

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Abstract—Starting from inexpensive L-(+)-tartaric acid, it was possible to resolve and obtain pure both enantiomers of *trans*-cyclohexane-1,2-diamine **1** and thence both enantiomers of BINOL **2**, two of the most powerful, chiral inducing backbones in asymmetric catalysis. The modified method is very economic, not only due to an almost doubling of the overall yields of enantiomerically pure compounds (86% **1**, 83% **2**) but also due to the easy recovery of resolving agent **1** [66% (*R*,*R*)-**1**, 79% (*S*,*S*)-**1**] in the BINOL resolution. An improvement in the yield of the preparation of racemic BINOL is also recorded.
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1. Introduction

trans-Cyclohexane-1,2-diamine **1** forms the backbone of many useful chiral ligands in asymmetric catalysis[1] and can also be used for the resolution[2] of (±)-2,2′-dihydroxy-1,1′-binaphthyl (racemic BINOL) **2** itself arguably an even more important backbone (vide infra).

Enantiopure (*R*,*R*)-**1** can be straightforwardly obtained from the relatively inexpensive racemic mixture as the L-(+)-tartrate salt (Scheme 1).[3] However, as originally reported by Galsbol, Steenbol and Sorensen,[3a] this method lacks the possibility to easily and cheaply obtain the other enantiomer during the separation process. This is because their method for obtaining the (*S*,*S*)-isomer calls for the addition of a large excess of L-(+)-tartaric acid to the mother liquor after the separation of the (*R*,*R*)-derivative in order to precipitate the (*S*,*S*)-**1**·[L-(+)-tartrate]₂ salt.[3a] However, it is doubtful that this procedure gives the enantiopure (*S*,*S*)-diamine salt since the yields of (*R*,*R*)-diamine after separation usually do not exceed 85% and therefore contamination of the undesired diamine salt ought to be left in the
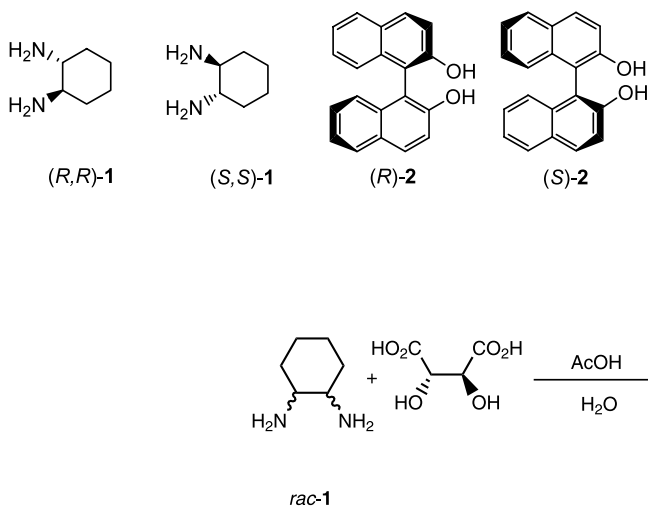
Scheme 1.

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precipitate. Indeed, in common with Larrow and Jacobsen,[3b] we found that the (S,S)-diamine could not be obtained without a substantial number of purification steps. This unavailability of the (S,S)-isomer not only results in an economic setback by wasting precious material but also forces the use of the unnatural and relatively more expensive D-(−)-tartaric acid[3b] whenever the (S,S)-isomer is needed, a common requirement in asymmetric catalysis work.

Enantiopure BINOL **2** is another extremely useful backbone from which a large variety of powerful, chiral inducing ligands can be accessed which are widely used in asymmetric catalysis.[4] Two resolving methods for racemic BINOL **2** have commonly been used, the more recent[5] utilizing the moderately expensive cinchonidine (as its quaternary ammonium salt with benzyl chloride), the other one utilizing (R,R)-cyclohexanediamine.[2] It was reported that both enantiomers of **2** could be accessible from one racemic batch using the latter method in which two inclusion complexes are formed with the diamine, one of which contains a solvent molecule and is less soluble than the other containing no solvent (Scheme 2). However, lacking detailed experimental data for this procedure we could not reproduce those findings after several attempts. This increases the appeal of the use of the *N*-benzylcinchonidinium chloride, since both enantiomers are obtained in very high yields and enantiomeric excess in a straightforward manner, thus outweighing the cost disadvantage.

Herein we report an improved method for the resolution of *trans*-cyclohexane-1,2-diamine (*rac*-**1**). Both enantiomers could be isolated in good to excellent yields and were obtained in enantiopure form (>99.8% ee) as chemically inert bis-ammonium salts. Racemic BINOL *rac*-**2** was prepared in significantly higher yields by a modified work up protocol and resolved using (R,R)- and (S,S)-cyclohexanediamine to give both isomers in enantiopure form (>99.8% ee) in very good yields. Moreover, the precious and enantiopure diamines were easily recovered as their corresponding monotartrate salts in 66% and 79% yields respectively.

2. Results and discussion

In our efforts to obtain enantiopure diamine (S,S)-**1**, we tried to separate as much of the (R,R)-derivative from the racemic mixture as possible. Therefore, we started out by employing the same method as described by Larrow and Jacobsen[3b] using L-(+)-tartaric acid in a mixture of water and acetic acid and isolated the pure (R,R)-**1** tartrate (>99.8% ee [HPLC of derived toluamide[3b]]) in 41% yield (of a theoretical 50%) after filtration. The filtrate now still contained significant amounts of (R,R)-**1** tartrate salt. By removing water under reduced pressure and addition of methanol, a slurry was formed, filtration of which afforded another fraction of (R,R)-**1** tartrate (19% yield, 88% ee [HPLC]) also containing (S,S)-**1** acetate. Addition of 2.5 equiv. of concentrated HCl and the same overall volume of acetone afforded the (S,S)-**1**2HCl salt (96% ee [HPLC]) as a microcrystalline precipitate, which was filtered and purified by reprecipitation from water/methanol with acetone to give an isolated yield of 24% (of a theoretical 50%, >99.8% ee [HPLC]). Both derivative salts are chemically inert and can be stored for months at room temperature without loss of purity.

A setback in practicality, however, lies in the time consuming removal of water from the mother liquor after the first separation. In order to simplify the resolution, instead of water, we tried refluxing methanol as a polar and more easily removable solvent. Since the solubility of the (R,R)-**1** tartrate salt in methanol is very low, the initial precipitate was obtained as a viscous, dirty white glue which contained significant amounts of trapped (S,S)-**1** acetate which we then tried to re-dissolve by increasing the reflux time to 16 h before filtration. By then the precipitate was transformed into a white, microcrystalline powder. This method gave 49% yield (of a theoretical 50%) and 96% ee [HPLC] of the desired compound. Addition of conc. HCl and acetone afforded the (S,S)-**1** dihydrochloride in 40% yield and 98% ee [HPLC] after filtration. A prolonged reflux time in order to extract more of the soluble (S,S)-**1** acetate from the insoluble (R,R)-**1** tartrate, however, did not improve enantioselectivities.
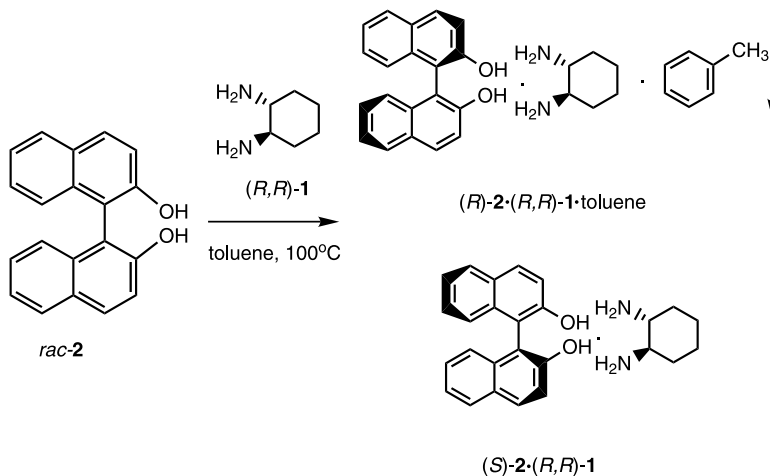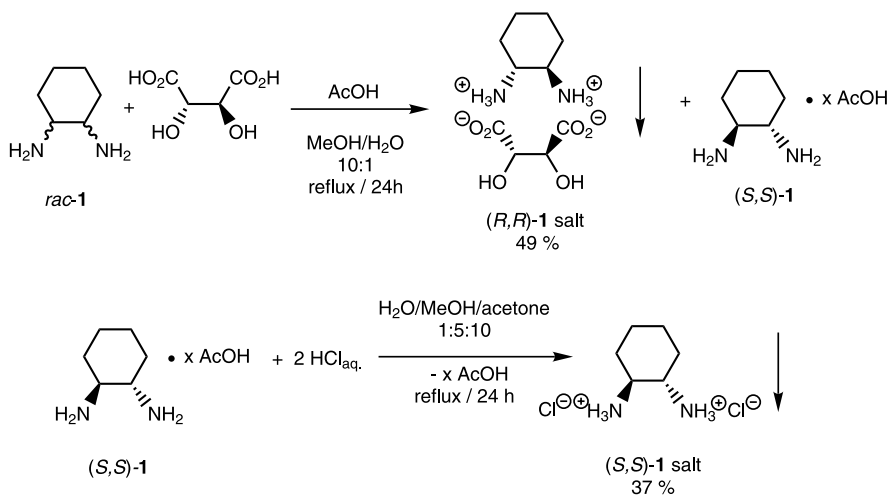

Scheme 2.

With these results in mind we were able to construct an optimised procedure. We chose to use a methanol/water (10:1) mixture to carry out the resolution with the idea of slightly improving the solubility of the (R,R)-**1** tartrate salt. This resulted in the desired effect of re-dissolving virtually all of the (S,S)-**1** acetate. After 24 h reflux of the diamine tartrate/acetate mixture, we were able to separate by filtration the (R,R)-**1** tartrate salt as nicely crystallized, colorless material in 49% yield (of a theoretical 50%) and >99.8% ee [HPLC]. Then we added conc. HCl and acetone to the mother liquor and refluxed for further 24 h. Over this time period a nicely crystallized material precipitated and was easily removed by filtration, after cooling to room temperature, to give 37% (of a theoretical 50%) of the (S,S)-**1**(HCl)$_2$ salt (>99.8% ee [HPLC]).[6] Therefore by this method, enantiomerically pure material was obtained in an overall yield of 86% (Scheme 3). The free diamines are readily available from their respective tartrate and hydrochloride salt by dissolution in 4 M aqueous NaOH and extraction of the diamine with CH$_2$Cl$_2$.

With both enantiomers of *trans*-cyclohexane-1,2-diamine easily available, we attempted to find an improved and more reliable method for the resolution of BINOL **2**. Kawashima and Hirata described in their method[2] that, in toluene, the more soluble inclusion complex, (S)-**2**·(R,R)-**1**, can be obtained from the mother liquor in 96% ee (measured by HPLC of the liberated BINOL) after separation of the less soluble (R)-**2**·(R,R)-**1**·toluene complex. We also made this observation. However, in contrast to the described procedure, after removal of volatiles, we were not able to increase further the ee by simply washing the residue with toluene. Recrystallisation of the liberated (S)-BINOL also did not give an improved ee. Also the reported procedure does not give details for the recovery of the precious, enantiopure diamine, which also is a valid factor for economic feasibility. There are actually two points in the procedure at which the relevant diamine has to be recovered: (i) in the formation of the inclusion complex, an excess of diamine is used which should be recovered if possible; (ii) when the BINOL is liberated from the inclusion complex, the diamine is also liberated and may be recovered.

With the other hand of the diamine more readily available we found that we were able to use it to improve the isolation of the more soluble BINOL isomer, Scheme 4. Thus we followed Kawashima and Hirata's protocol[2] initially and were able to separate the (R)-**2**·(R,R)-**1**·toluene inclusion complex which, after recrystallisation from toluene, gave a 45% yield (of a theoretical 50%) and 99.8% ee [HPLC]). We then added L-(+)-tartaric acid to the mother liquor to remove as much as possible of the excess (R,R)-**1** (we got about 46% of it back) and employed the enantiopure (S,S)-**1** to form the corresponding (S)-**2**·(S,S)-**1**·toluene complex. This crystallized from hot toluene in the same fashion as (R)-**2**·(R,R)-**1**·toluene complex and was easily separated by filtration in 43% yield (of a theoretical 50%). The product already was optically pure without further recrystallisation (>99.8% ee, after liberation of BINOL, [HPLC]). Finally the mother liquor from the formation of this inclusion complex was treated with DL-(±)-tartaric acid to recover the small amount of excess (S,S)-diamine used.

In order to increase the feasibility of the new protocol we aimed for the best possible recovery of the diamines (R,R)-**1** and (S,S)-**1** from the inclusion complexes. After trying various acids for the liberation of BINOL we found that the tartaric acids were the most suitable for our purposes. Thus after dissolution of complex (R)-**2**·(R,R)-**1**·toluene in methanol/water (10:1) and addition 1.1 equiv. of tartaric acid the corresponding (R,R)-**1**·tartrate salt precipitated almost quantitatively and could be separated by filtration. (R)-BINOL precipitated from the filtrate during the removal of methanol from the solution and was filtered and after

Scheme 3.
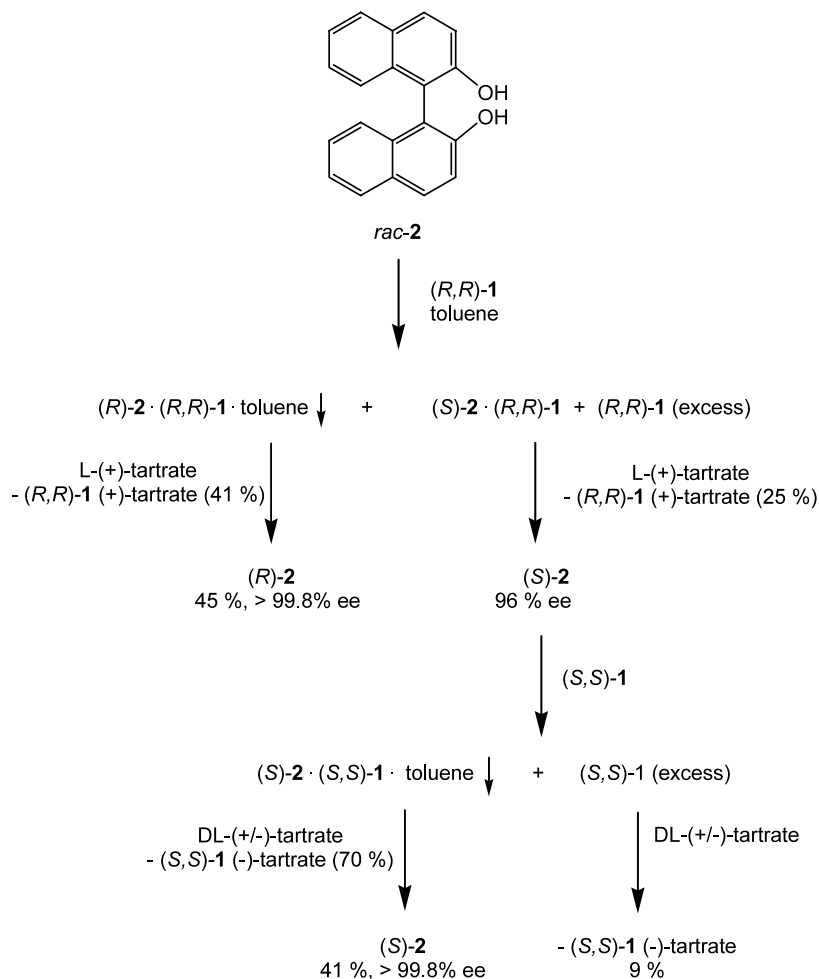
Scheme 4.

purification by dissolution in CH_2Cl_2 and washing with aqueous Na_2CO_3 gave a 94% yield of enantiomerically pure material, corresponding to a 42.4% yield overall. Complex (S)-**2**·(S,S)-**1**·toluene was treated in a similar fashion using 2.2 equiv. of racemic DL-tartaric acid, which is significantly less expensive than enantiopure D-(−)-tartaric acid, and the (S,S)-**1**·D-(−)-tartrate salt was recovered again almost quantitatively. (S)-BINOL was obtained enantiomerically pure in 95% yield (40.4% overall) after the same washing procedure with Na_2CO_3. The overall yield of enantiopure BINOL for the resolution is therefore 83%.

The total recovery of the diamines used was as follows: 25% (R,R)-**1** (+)-tartrate was recovered from the formation step and 41% (R,R)-**1** (+)-tartrate from the liberation procedure to give a total recovery of (R,R)-**1** (+)-tartrate = 66%. Similarly 9% (S,S)-**1** (−)-tartrate (formation step) and 70% of (S,S)-**1** (−)-tartrate (liberation procedure) was recovered to give total recovery of 79% of S,S-**1** (−)-tartrate. The lower recovery from the inclusion complex formation step may be due to the low air-stability of the non-complexed diamine. Scheme

4 comprehends all manipulations conducted during the resolution procedure for *rac*-BINOL.

3. Conclusions

For the first time an inexpensive and straightforward method has been developed for the resolution of both enantiomers of *trans*-cyclohexanediamine. The new method not only more than doubles the yields over previously reported methods and thus proves to be significantly more economic, it thereby also provides easier access to a larger variety of catalytic experiments. Both enantiomers also can be used for a reliable resolution of racemic BINOL, also doubling the overall yield for the same reasons. This method becomes even more attractive due to good and simple recovery of the diamines, which further improves its economic aspects.

4. Experimental

In all experiments, solvents and reagents were used as provided by the Aldrich Chemical Company and water was double distilled before use. Enantiopurities for

(*R*,*R*)- and (*S*,*S*)-cyclohexane-1,2-diamine (as *m*-toluoyl amide derivatives)[3b] as well as (*R*)- and (*S*)-BINOL were determined via HPLC using a Chiralpak AD column (250 mm length) with hexane/*i*-PrOH as eluting solvent (94/6 for **1**, 88/12 for **2**) with detection at $\lambda = 254$ nm: retention times: 8 min (*S*,*S*)-**1**; 24 min (*R*,*R*)-**1**; 20 min (*R*)-**2**; 25 min (*S*)-**2** all at 1 mL min^{-1}.

4.1. Resolution of racemic 1

4.1.1. Method A. Racemic diamine (11.41 g, 100 mmol) was dissolved in water (20 mL) and stirred. L-(+)-Tartaric acid (7.50 g, 50 mmol) was added in portions under continuous stirring and the solution was then heated to 90°C. When all material had dissolved, glacial acetic acid (10 mL, ~170 mmol) was added dropwise and the temperature maintained under stirring at 90°C for 1 h. After cooling to room temperature, the precipitate was filtered and the filtrate retained. The precipitate was washed with ice-cooled water (2×10 mL) and methanol (3×10 mL) and oven-dried (12 h at 80°C) to give (*R*,*R*)-**1**·tartrate (10.92 g, 41.30 mmol, 41%, >99.8% ee [HPLC of the liberated diamine toluamide]). ^{1}H NMR (300.1 MHz, D$_2$O, 20°C): $\delta = 4.29$ (s, 2H, **CH** [tartrate]), 3.32 (m, 2H, **H$_3$N$^+$–CH**), 2.11 (m, 2H) 1.77 (m, 2H), 1.46–1.26 (m, 4H, **CH$_2$**).

Water was removed from the initial filtrate under reduced pressure at 50°C until the residue solidified. Methanol (50 mL) was added and the slurry was filtered again, washed with methanol (2×20 mL) and oven-dried (12 h at 80°C) to give an intermediate fraction containing mostly (*R*,*R*)-**1** tartrate (1.57 g, 88% ee [HPLC]). Conc. aqueous HCl (10 mL, ~130 mmol) was added to the mother liquor and stirred for 10 min before acetone (150 mL) was added. The precipitated formed was filtered, washed with acetone (3×20 mL) and oven-dried (12 h at 80°C) to yield (*S*,*S*)-**1**·(HCl)$_2$ (8.16 g, 43.6 mmol; 43.6%, 96.4% ee). Recrystallisation was conducted by dissolving the material in boiling water (6 ml) followed by addition of methanol (30 ml). After refluxing for 10 min, acetone (48 ml) was added and the slurry was refluxed for another 2 h. The precipitate was filtered and dried in the oven (12 h at 80°C) to yield enantiomerically pure (*S*,*S*)-**1**·(HCl)$_2$[6] (4.47 g, 23.90 mmol, 24%, >99.8% ee [HPLC]). ^{1}H NMR (300.1 MHz, D$_2$O, 20°C): $\delta = 4.73$ (s, 6H, **HDO** from 2NH$_3$$^+$), 3.41 (m, 2H, **H$_3N^+$–CH**), 2.18 (m, 2H), 1.83 (m, 2H), 1.55 (m, 2H), 1.39 (m, 2H, **CH$_2$**).

The overall yield of enantiomerically pure material therefore was 65%.

4.1.2. Method B. Glacial acetic acid (7.50 mL, ~130 mmol) was added to a solution of diamine **1** (11.41 g, 100 mmol) in methanol (180 mL) in a two-necked round-bottomed flask equipped with magnetic stirring bar. Then a solution of L-(+)-tartaric acid (7.50 g, 50 mmol) in methanol (40 mL) was added dropwise with vigorous stirring over a period of 30 min and a white solid precipitated from the solution. The slurry was heated to reflux and stirred at this temperature for 16 h. After cooling to room temperature, the slurry was

filtered. The crystalline precipitate was washed with methanol (2×20 mL) and dried in the oven (12 h at 80°C) to give (*R*,*R*)-**1**·tartrate (15.71 g, 49.4 mmol; 49% yield, 97.1% ee [HPLC]). Conc. aqueous HCl (10 ml, ~130 mmol) was added to the mother liquor and heated to reflux for 1 h. The precipitate formed was filtered and washed twice with cold methanol (20 mL) to give (*S*,*S*)-**1**·(HCl)$_2$ salt (7.42 g, 39.6 mmol, 39.6% yield, 97.6% ee [HPLC]).

4.1.3. Optimised method C. In a 500 ml two-necked round-bottomed flask equipped with reflux condenser, dropping funnel and magnetic stirring bar, racemic diamine **1** (11.4 g, 100 mmol) was dissolved in a solvent mixture of water (20 mL) and methanol (160 mL). Then glacial acetic acid (7.5 mL, 7.8 g, ~130 mmol) was added dropwise with stirring. A solution of L-(+)-tartaric acid (7.51 g, 50.0 mmol) in methanol (30 mL) was added dropwise and the dropping funnel was rinsed with methanol (10 mL). The overall proportion of methanol to water was therefore 10:1. The solution was refluxed for 24 h and, after cooling to room temperature, the slurry was filtered. The precipitate was washed with methanol (3×20 mL) and oven-dried (12 h at 80°C). Thereby (*R*,*R*)-**1**·tartrate was obtained as an enantiomerically pure, crystalline powder (12.80 g, 48.5 mmol, 49% yield, >99.8% ee [HPLC]). The mother liquor (including the various washes) was transferred into a 1000 mL round-bottomed flask equipped with a stirring bar and a reflux condenser. Concentrated HCl (10 mL, ~130 mmol) was added in one portion with stirring and the mixture was heated under reflux. Acetone (500 mL) was added in portions of 50 ml over a period of 1 h under continuous reflux and reflux was continued for another 24 h. A white precipitate was formed and, after cooling to room temperature, the slurry was filtered. The precipitate was washed with acetone (3×20 mL) and dried in the oven (12 h at 80°C). Thereby (*S*,*S*)-**1**·(HCl)$_2$ was obtained as a white, crystalline powder (6.85 g, 36.6 mmol, 37% yield, >99.8% ee [HPLC]).

The overall yield of enantiomerically pure material was therefore 86%.

4.2. Derivatisation of 1 for HPLC[3b]

Aqueous NaOH (4 M, 1 mL) was added to a slurry of *trans*-cyclohexane-1,2-diamine tartrate salt (25 mg) in CH$_2$Cl$_2$ (1.5 mL) in a scintillation vial and the vessel was shaken for approximately 30 s until all the solid material had dissolved. Then *m*-toluoyl chloride (50 μL) was added via syringe and the mixture shaken for another 30 s. After the separation of the layers, a portion (0.2 mL) was removed from the organic layer and added to *i*-PrOH (2 mL). Samples (20 μL) of this solution were used for HPLC analysis.

4.3. Preparation of racemic 2

Racemic BINOL was prepared according to a modified version of a literature procedure.[7] 2-Naphthol (15.00 g, 104 mmol) and water (600 mL) were heated under

reflux in a 1000 ml round-bottomed flask equipped with a dropping funnel and reflux condenser. A solution of FeCl$_3$·6H$_2$O (30.00 g, 111 mmol) in water (60 mL) was added dropwise with vigorous stirring and the mixture heated under reflux for another 30 min after completion of the addition. Racemic 2,2′-dihydroxy-1,1′-binaphthyl precipitated during the procedure and the hot slurry was filtered through a preheated Buchner funnel. After washing with boiling water until the filtrate became colorless, the brownish residue was dried by sucking air through the funnel for another 1.5 h. Two recrystallisation procedures were performed from refluxing toluene (180 mL) with cooling to 40°C in a water bath of that temperature and filtration through a preheated filtration funnel. The mother liquors were combined, the solvent removed and the residue twice recrystallised in the same fashion from toluene (2×80 mL). Both sets of crystals were combined and dried under vacuum in the desiccator (16 h at 20 mbar). The product was obtained as colorless needles (11.81 g, 41.11 mmol, 79%; mp: 219°C, lit 218°C[6]).

4.4. Resolution of racemic 2—formation of the inclusion complexes

4.4.1. Formation of (R)-BINOL-(R,R)-cyclohexanediamine·toluene inclusion complex. Racemic **2** (5.73 g, 20.03 mmol) was added to a solution of (R,R)-**1** [2.514 g, 22.05 mmol, 2.2 equiv. with respect to (R)-**2**] in toluene (60 mL) and the solution was stirred for 30 min at room temperature, heated to 100°C for 10 min and then slowly cooled to room temperature. A precipitate was formed which was filtered and washed with cold toluene (2×10 mL). The mother liquor was kept for further manipulations (vide infra). Recrystallisation of the precipitate from hot toluene (20 mL) afforded enantiomerically pure (R)-**2**·(R,R)-**1**·toluene (4.47 g, 9.06 mmol, 45%, 99.8% ee [HPLC of the liberated BINOL-vide infra]) as colorless needles which were dried in the desiccator under vacuum (16 h at 20 mbar).

4.4.2. Liberation of crude (S)-BINOL and recovery of excess (R,R)-cyclohexanediamine. The mother liquor (vide supra) was transferred into a round-bottomed flask, the solvent was evaporated and the pale-yellow, gluey residue {(S)-**2**·(R,R)-**1**: 4.28 g, 96% ee [HPLC]} was dissolved in a mixture of methanol (90 mL) and water (10 mL). L-(+)-Tartaric acid (1.875 g, 12.5 mmol, 1.1 equiv. of calculated excess diamine) was added in one portion and the mixture heated to reflux for 16 h. During the procedure a crystalline precipitate {(R,R)-**1** (+)-tartrate: 1.43 g, 5.43 mmol, 25% of total (R,R)-diamine employed, 99.8% ee [HPLC]} was formed and, after cooling to room temperature, it was filtered, washed with methanol (2×20 mL) and dried in the oven (12 h at 80°C). The filtrate was transferred into a round-bottomed flask, water (30 mL) was added and the methanol was removed at the rotary evaporator. During the procedure, the crude (S)-BINOL precipitated almost quantitatively and was filtered, washed with water (5×20 mL) and dried in the desiccator under reduced pressure (16 h at 20 mbar) to give (S)-**2** (2.90 g, 10.14 mmol, 51%, 96% ee [HPLC]).

4.4.3. Formation of (S)-BINOL-(S,S)-cyclohexanediamine·toluene inclusion complex. The crude BINOL was dissolved in toluene (50 ml) and the solution added to (S,S)-**1** (1.39 g, 12.20 mmol, 1.2 equiv.). The mixture was stirred for 30 min at room temperature and then heated to reflux for 5 min. Upon slow cooling to room temperature, a precipitate was formed which was filtered, washed with ice-cold toluene (2×10 mL) to give colorless needles of (S)-**2**·(S,S)-**1**·toluene (4.20 g, 8.51 mmol, 43%, >99.8% ee) after removal of solvent traces in the desiccator under reduced pressure (16 h at 20 mbar). The filtrate was kept for further manipulations.

4.4.4. Recovery of excess (S,S)-cyclohexanediamine. The filtrate was transferred into a round-bottomed flask, the solvent was evaporated and the residue was dissolved in a mixture of methanol (45 mL) and water (5 mL). DL-(+/−)-Tartaric acid (0.751 g, 5.00 mmol, ~2.3 equiv. of calculated excess diamine) was added in one portion and the mixture heated to reflux for 16 h. During the procedure a crystalline precipitate (S,S-**1**·D-(−)-tartrate: 0.302 g, 1.14 mmol, 9% of total S,S-diamine employed, >99.8% ee [HPLC]) was formed and, after cooling to room temperature, it was filtered, washed with methanol (2×10 mL) and dried in the oven (12 h at 80°C).

4.5. Liberation of enantiopure (R)-2 and (S)-2 from their inclusion complexes

4.5.1. Liberation of (R)-BINOL and recovery of (R,R)-1 (+)-tartrate. The inclusion complex (R)-**2**·(R,R)-**1**·toluene (4.47 g, 9.06 mmol) was dissolved in a mixture of water (9 mL) and methanol (80 mL) and L-(+)-tartaric acid (1.136 g, 9.97 mmol, 1.1 equiv.) was added in one portion. The reaction was heated under reflux for 16 h and after cooling the precipitate {(R,R)-**1** (+)-tartrate: 2.38 g, 9.02 mmol, >99% recovery for the reaction, 41% of total (R,R)-diamine employed, >99.8% ee [HPLC]} was removed by filtration, washed with methanol (2×20 mL) and dried in the oven (12 h at 80°C). Water (30 mL) was added to the filtrate and the methanol was removed under reduced pressure affording the precipitation of the (R)-BINOL. The precipitate was filtered, washed with water (5×20 mL) and transferred into a separatory funnel charged with CH$_2$Cl$_2$ (50 mL) and saturated aqueous Na$_2$CO$_3$ solution (20 mL). After vigorous shaking, the organic layer was separated, dried over MgSO$_4$ and after solvent removal under reduced pressure (R)-**2** (2.43 g, 8.50 mmol, 94%, >99.8% ee) was obtained in enantiomerically pure form.

4.5.2. Liberation of (S)-BINOL and recovery of (S,S)-1 (−)-tartrate. In an almost identical procedure (S)-**2**·(S,S)-**1**·toluene (4.20 g, 8.51 mmol) was dissolved in a mixture of water (9 mL) and methanol (80 mL) and DL-(±)-tartaric acid (2.70 g, 18.0 mmol, 2.2 equiv.) was added in one portion. The reaction was heated under reflux for 16 h and after cooling the precipitate {(S,S)-**1** (−)-tartrate: 2.24 g, 8.48 mmol, >99% for the reaction, 70% of total (S,S)-diamine employed, >99.8% ee [HPLC]} was removed by filtration, washed with methanol (2×20 mL) and dried in the oven (12 h at

80°C). Water (30 mL) was added to the filtrate and the methanol was removed under reduced pressure affording the precipitation of the (*S*)-BINOL. The precipitate was filtered, washed with water (5×20 mL) and transferred into a separatory funnel charged with CH_2Cl_2 (50 mL) and saturated aqueous Na_2CO_3 solution (20 mL). After vigorous shaking, the organic layer was separated, dried over $MgSO_4$ and after solvent removal under reduced pressure (*S*)-**2** (2.322 g, 8.12 mmol, 95%, >99.8% ee) was obtained in enantiomerically pure form.

In summary, starting from *rac*-**2**, enantiomerically pure BINOL was obtained in an overall yield of 83% and an overall recovery for the diamines as their corresponding tartrate salts of 66% for (*R*,*R*)-**1** and 79% for (*S*,*S*)-**1** was achieved.

Acknowledgements

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