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# Resolution of (±)-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxylic acid using (1*R*,2*R*)-*trans*-cyclohexane-1,2-diamine

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ABSTRACT

A simple and efficient method has been developed to resolve (±)-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxylic acid [(±)-BINOL-3,3′-dicarboxylic acid] (±)-**1** using inexpensive and readily accessible chiral resolving agent (1*R*,2*R*)-*trans*-cyclohexane-1,2-diamine **2**. Enantiomers of BINOL-3,3′-dicarboxylic acid were obtained in good yields and enantiomeric purity, for example, (*S*)-(−)-**1** was isolated in 34% yield with >99% ee and (*R*)-(+)-**1** was obtained in 36% yield with >99% ee. The formation of diastereomeric salt **A** between (*S*)-BINOL-3,3′-dicarboxylic acid and (1*R*,2*R*)-*trans*-cyclohexane-1,2-diamine was ascertained by using IR, single crystal X-ray crystallography, and HRMS.



## 1. Introduction

Enantiomerically pure $C_2$-symmetric 2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxylic acid (BINOL-3,3′-dicarboxylic acid) and its derivatives have been employed as chiral inducers in asymmetric catalysis.[1] Some of the derivatives have been used as chiral discriminators for α-amino acids in addition to being used as chiral hosts in host–guest chemistry.[2,5a] Further utility of this molecule is hampered because of the non-availability of a simple method to prepare enantiomerically pure BINOL-3,3′-dicarboxylic acid. There are three distinct protocols available for the synthesis of optically active BINOL-3,3′-dicarboxylic acid; (i) α-lithiation of enantiomerically pure BINOL followed by carboxyl group introduction;[1e,f] (ii) asymmetric oxidative coupling of a chiral auxiliary attached to a β-naphthol derivative[4] or homo coupling of methyl 3-hydroxy-2-naphthoate with chiral diamine copper complexes;[3,8a,b] (iii) resolution of racemic BINOL-3,3′-dicarboxylic acid using either L-leucine methyl ester or L-brucine.[5] Although these methods are promising, they are associated with intrinsic drawbacks such as the use of sensitive reagents, multiple steps, and several recrystallization steps to give enantiomerically pure compounds. Racemic BINOL was successfully resolved using optically active *trans*-1,2-diaminocyclohexane through inclusion complex formation,[9a] whereas the optically active (1*R*,2*R*)-*trans*-cyclohexane-1,2-diamine **2** was obtained through classical resolution using L-(+)-tartaric acid via diastereomeric salt formation.[10] The presence of two –OH groups in BINOL and two –COOH groups in tartaric acid prompted us to examine the feasibility of using optically active (1*R*,2*R*)-*trans*-cyclohexane-1,2-diamine, (1*R*,2*R*)-**2** for the resolution of racemic BINOL-3,3′-dicarboxylic acid (±)-**1**. Herein, we report our findings on the successful resolution of racemic BINOL-3,3′-dicarboxylic acid (±)-**1** using (1*R*,2*R*)-*trans*-cyclohexane-1,2-diamine **2** (Fig. 1).[6]

## 2. Results and discussion

Racemic 2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxylic acid (BINOL-3,3′-dicarboxylic acid) (±)-**1** was prepared in three simple steps from commercially available 3-hydroxy-2-naphthoic acid using reported procedures.[7,8] Esterification of 3-hydroxy 2-naphthoic acid with MeOH in presence of conc $H_2SO_4$ furnished methyl 3-hydroxy-2-naphthanoate **4**. Oxidative coupling of **4** using a Cu catalyst generated the dimethylester of BINOL-3,3′-dicarboxylic acid **5**. Saponification of diester **5** with methanolic KOH gave the racemic BINOL-3,3′-dicarboxylic acid in 72% overall yield (Scheme 1).

The presence of phenolic –OH and –COOH groups in the BINOL-3,3′-dicarboxylic acid **1** rendered the opportunity to separate the enantiomers using a chiral base via a classical resolution protocol. Accordingly, we screened basic resolving agents such as (*R*)-(+)-α-methylbenzylamine, (+)-cinchonine, (*S*)-proline, (*R*)-(+)-1-(*N*-pyrrolidine)-1-phenyl ethane, etc., for the resolution of (±)-BINOL-3,3′-dicarboxylic acid **1**. All of these reagents failed to furnish the non-racemic BINOL-3,3′-dicarboxylic acid. The successful resolution of *trans*-1,2-diaminocyclohexane using L-(+)-tartaric acid and subsequent utility of optically active 1,2-diaminocyclohexane, that is, (1*R*,2*R*)-*trans*-cyclohexane-1,2-diamine **2** in the

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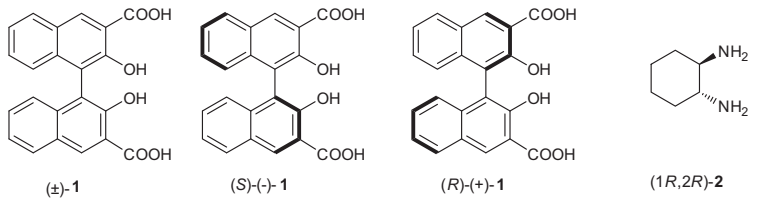
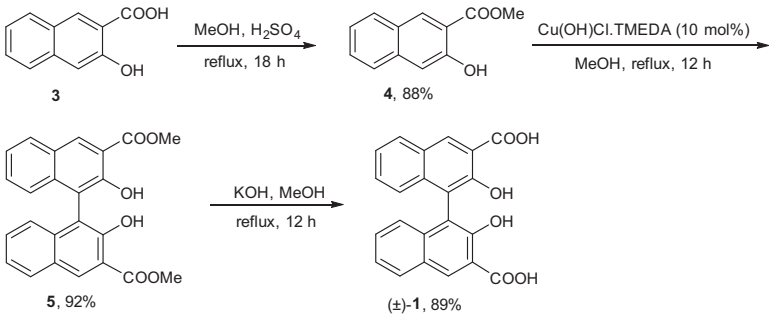



**Figure 1.** Representative diagrams of (±)-**1**, (*S*)-(−)-**1**, (*R*)-(+)-**1**, and (1*R*,2*R*)-**2**.




**Scheme 1.** Preparation of (±)-BINOL-3,3′-dicarboxylic acid **1**.

resolution of racemic BINOL[9a] allowed us to use (1*R*,2*R*)-*trans*-cyclohexane-1,2-diamine **2** for the resolution of racemic BINOL-3,3′-dicarboxylic acid **1**. Hence, the resolution experiments were carried out with (±)-**1** using 0.5 equiv of (1*R*,2*R*)-*trans*-cyclohexane-1,2-diamine **2** as a chiral resolving agent in solvents such as MeOH, EtOH, *i*-PrOH, $H_2O$ at room temperature. Although the experiments with MeOH and EtOH as solvents at room temperature produced the diastereomeric salt, the BINOL-3, 3′-dicarboxylic acid **1** obtained from this salt was found to be racemic. In order to separate the enantiomers, the experiments were carried out in MeOH and EtOH at an elevated temperature for 12 h in the presence of 0.5 equiv of chiral resolving agent (1*R*,2*R*)-**2**. Encouraging results were obtained. For example, the diastereomeric salt was precipitated out while (±)-**1** was dissolved in methanol by stirring at 70 °C (oil bath temperature) followed by adding 0.5 equiv of (1*R*,2*R*)-**2**, and refluxed the mixture for 12 h. The precipitate was decomposed by stirring with 6 M HCl/EtOAc to furnish (*S*)-(−)-**1** in 44% yield with 47% ee. The filtrate, upon evaporation and decomposition with 6 M HCl/EtOAc, afforded (*R*)-(+)-**1** in 52% yield with 68% ee (Scheme 2). While using, EtOH as a solvent, (*S*)-(−)-**1** was obtained in 45% yield with 27% ee from precipitate while (*R*)-(+)-**1** was obtained in 50% yield with 18% ee from filtrate.

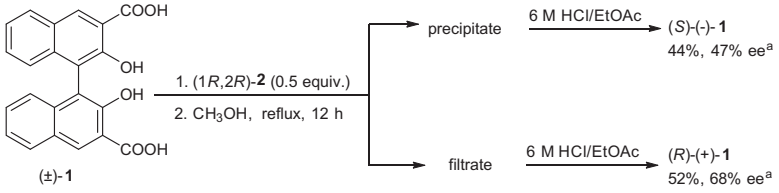
It has been proven in some instances[9a] that a mixture of MeOH and $H_2O$ furnishes better yields and enantiopurities of both isomers in resolution processes. Thus, resolution experiments were carried out with (±)-**1** using 0.5 equiv of (1*R*,2*R*)-**2** in different ratios of MeOH and $H_2O$ (from 9:1 to 7:3). The results are summarized in Table 1. It is interesting to note that the resolution of (±)-**1** using 0.5 equiv of (1*R*,2*R*)-**2** in 9:1 mixture of MeOH and $H_2O$ furnished (*S*)-(−)-**1** in 41% yield with 81% ee from precipitate and (*R*)-(+)-**1** was obtained in 44% yield with 90% ee from the filtrate (Table 1, entry 5). Increasing the $H_2O$ composition in MeOH/$H_2O$ from 9:1 to 7:3 decreased the enantiomeric excess of both enantiomers of **1** in this resolution process (Table 1, entries 6 and 7). Based on these observations, the optimum solvent ratio of MeOH and $H_2O$ was found to be 9:1 for the resolution of (±)-**1** using 0.5 equiv of (1*R*,2*R*)-**2**.

Further optimization experiments were carried out with various equivalents of (1*R*,2*R*)-**2** (0.5–1 equiv) in a MeOH and $H_2O$ (9:1) mixture. An increase in equivalents of chiral resolving agent (1*R*,2*R*)-**2** did not have any beneficial effect. The best result was

**Table 1**
Effect of solvent and solvent ratio on the resolution of (±)-**1**[a]

| Entry | Solvent | Precipitate | | Filtrate | |
|---|---|---|---|---|---|
| | | % yield[b] | % ee[c,d] | % yield[b] | % ee[c,d] |
| 1 | MeOH | 44 | 47 (*S*) | 52 | 68 (*R*) |
| 2 | EtOH | 45 | 27 (*S*) | 50 | 18 (*R*) |
| 3 | *i*-PrOH | — | — | — | — |
| 4 | $H_2O$ | — | — | — | — |
| **5** | **MeOH/$H_2O$ (9:1)** | **41** | **81 (*S*)** | **44** | **90 (*R*)** |
| 6 | MeOH/$H_2O$ (8:2) | 45 | 77 (*S*) | 42 | 81 (*R*) |
| 7 | MeOH/$H_2O$ (7:3) | 43 | 58 (*S*) | 44 | 43 (*R*) |

[a] In all experiments, (±)-**1** (374 mg, 1 mmol) and (1*R*,2*R*)-**2** (57 mg, 0.5 mmol) were dissolved in solvent (22 mL) and refluxed for 12 h.
[b] Yields are of isolated products.
[c] Enantiomeric excess was determined by Chiral HPLC analysis.
[d] Absolute configuration assigned by comparing with literature data.[1e]




[a] Enantiomeric excess was determined by chiral HPLC analysis of the corresponding methyl ester derivative

**Scheme 2.** The resolution of (±)-**1** using (1*R*,2*R*)-**2** in MeOH.

obtained when 0.5 equiv of (1*R*,2*R*)-**2** was used in the resolution process. In order to improve the enantiomeric purity and yield of the isomers of BINOL-3,3′-dicarboxylic acid, the experiments were carried out with BINOL-3,3′-dicarboxylic acid (±)-**1** using 0.5 equiv of (1*R*,2*R*)-**2** in a 9:1 mixture of methanol and water by refluxing in different time intervals (Table 2). Increasing the time interval from 12 h to 24 h led to the enantiomeric excess of (*S*)-BINOL-3,3′-dicarboxylic acid from precipitate fraction increasing from 81% to 90% ee; however the enantiomeric excess of (*R*)-BINOL-3,3′-dicarboxylic acid from the filtrate fraction decreased from 90% to 74% ee. The yields of the isomers from both the precipitate and the filtrate did not change much with time.

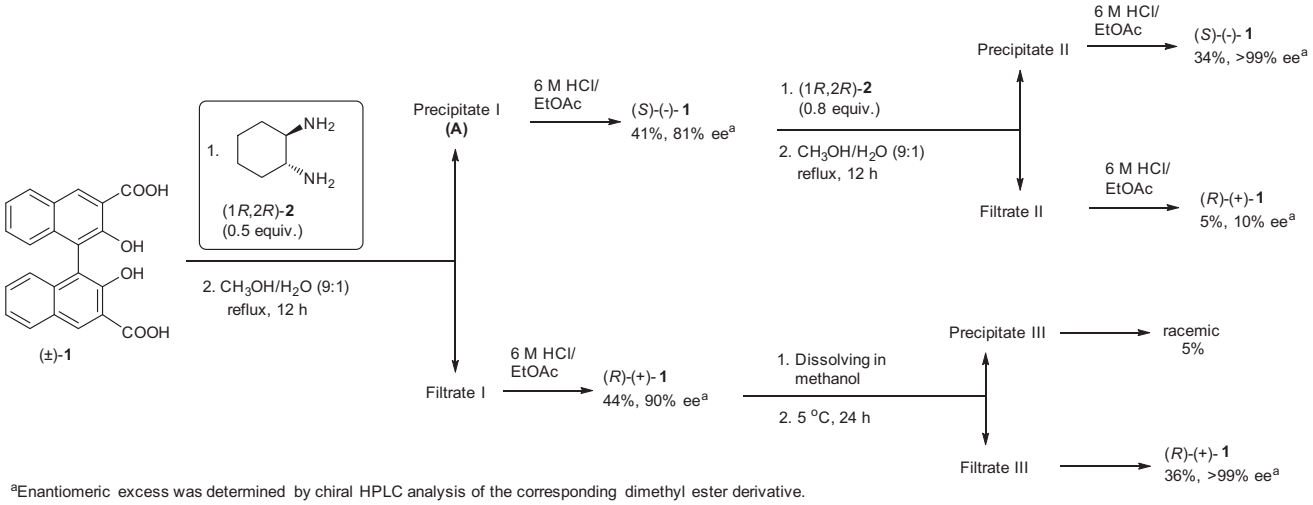
Hence the optimized conditions based on the variables such as solvent ratio, time, equivalents of (1*R*,2*R*)-**2**, for the resolution of (±)-BINOL-3,3′-dicarboxylic acid **1** were found to be refluxing (±)-**1** with 0.5 equiv of (1*R*,2*R*)-**2** in a 9:1 mixture of methanol and water for 12 h. The precipitated diastereomeric salt **A** afforded (*S*)-BINOL-3,3′-dicarboxylic acid in 41% yield with 81% ee and the filtrate afforded (*R*)-BINOL-3,3′-dicarboxylic acid in 44% yield with 90% ee (Scheme 3). The formation of diastereomeric salt **A** was confirmed by FT-IR spectroscopic analysis of the precipitate fraction (precipitate-I, Scheme 3). The C=O stretching frequency in (±)-BINOL-3,3′-dicarboxylic acid **1** was found to be 1680 $cm^{-1}$. IR spectra of the precipitate-I (**A**) showed a strong band at 1640 $cm^{-1}$, a typical stretching frequency observed for carboxylate anions. This was further confirmed through single crystal X-ray crystallographic analysis as well as using HRMS data (Fig. 2). In order to improve the enantiomeric purity of (*S*)-BINOL-3,3′-dicarboxylic acid, the reaction was carried out with scalemic (*S*)-(−)-**1** (>81% ee) and 0.8 equiv of (1*R*,2*R*)-**2** in a 9:1 mixture of solvent methanol and water at an elevated temperature.

After 12 h, the diastereomeric salt possessing low solubility in methanol/water mixture was precipitated out (precipitate-II, Scheme 3) from the reaction mixture. Next, (*S*)-(−)-**1** was isolated in 34% yield with >99% ee after decomposing precipitate-II with 6 M HCl (Scheme 3). The mother liquor from the first resolution step (filtrate-I) was evaporated using rotary evaporator to give a residue. This residue was dissolved in ethyl acetate and washed with 6 M HCl to remove trace amounts of (1*R*,2*R*)-*trans*-cyclohexane-1,2-diamine **2**, which was used in the resolution process. After concentrating the mother liquor, (*R*)-(+)-**1** was isolated in 45% yield with 90% ee. It was decided to increase the enantiomeric purity of scalemic (*R*)-(+)-**1** (90% ee) through recrystallization in methanol. Accordingly, the scalemic (*R*)-(+)-**1** (90% ee) was dissolved in methanol by heating and then allowed to stand at 5 °C for 24 h. The precipitated material was found to be racemic. The isomer

**Table 2**
Effect of time on resolution of (±)-**1**[a]

| Entry | Time (h) | Precipitate | | Filtrate | |
|---|---|---|---|---|---|
| | | % yield[b] | % ee[c,d] | % yield[b] | % ee[c,d] |
| **1** | **12** | **41** | **81 (*S*)** | **44** | **90 (*R*)** |
| 2 | 18 | 40 | 86 (*S*) | 45 | 82 (*R*) |
| 3 | 24 | 44 | 90 (*S*) | 48 | 74 (*R*) |

[a] In all experiments, (±)-**1** (374 mg, 1 mmol) and (1*R*,2*R*)-**2** (57 mg, 0.5 mmol) were dissolved in a mixture of methanol (20 mL) and water (2 mL) and refluxed for different time intervals.
[b] Yields are of isolated products.
[c] Enantiomeric excess was determined by Chiral HPLC analysis.
[d] Absolute configuration assigned by comparing with literature data.[1e]




**Scheme 3.** The resolution of (±)-**1** using (1*R*,2*R*)-**2**.

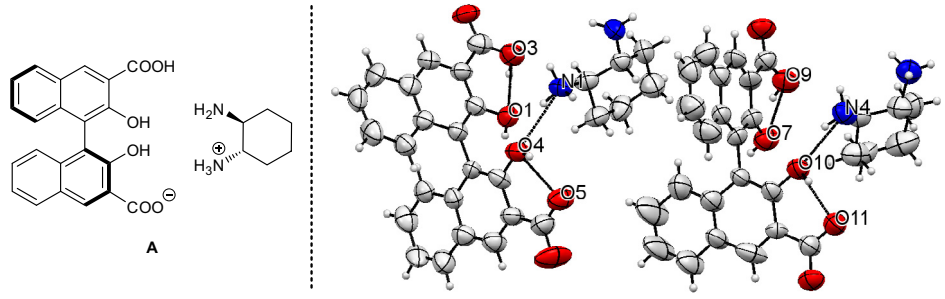



**Figure 2.** ORTEP diagram of diastereomeric salt **A** with 50% probability.

(*R*)-(+)-**1**, obtained from methanol after evaporation, was found to be >99% ee with 36% yield (Scheme 3).

## 3. Conclusion

In conclusion, we have established a simple and convenient method for the resolution of racemic BINOL-3,3′-dicarboxylic acid (±)-**1** using (1*R*,2*R*)-*trans*-cyclohexane-1,2-diamine (1*R*,2*R*)-**2** in methanol and water mixture. The IR and single crystal X-ray analysis were used to prove the formation of diastereomeric salt **A**. This resolution method can be used for the large scale production of both isomers of BINOL-3,3′-dicarboxylic acids in enantiomerically pure form.

## 4. Experimental

### 4.1. General

Melting points reported are uncorrected and were measured using a BUCHI M-560, Buchi Labortechnik AG, Switzerland. Infrared spectra were recorded on a Thermo Nicolet 6700 FT-IR Spectrophotometer and are reported in frequency of absorption ($cm^{-1}$). Mass spectra were measured with micro mass Q-TOF (ESI-HRMS), $^1H$ and $^{13}C$ NMR were recorded on Bruker AVANCE 400 spectrometer. NMR spectra for the samples were measured in DMSO-$d_6$ using TMS as an internal standard. The chemical shifts are expressed in $\delta$ ppm down field from the signal of internal TMS. Optical rotations were determined by a Rudolph Polarimeter AUTOPOL IV. All solvents used in the reactions were distilled using standard procedures. Racemic 2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxylic acid (BINOL-3,3′-dicarboxylic acid) (±)-**1** was prepared in three steps from 3-hydroxy-2-naphthoic acid using reported procedures.[7,8] The chiral resolving agent (1*R*,2*R*)-*trans*-cyclohexane-1,2-diamine was obtained via classical resolution of a *cis*- and *trans*-mixture of cyclohexane-1,2-diamine using L-(+)-tartaric acid.[10] Yields are given for isolated products showing homogeneity on a TLC plate and no impurities detectable in the NMR spectrum. The 2-hydroxy-3-naphthoic acid, TMEDA and CuCl, a mixture of *cis*- and *trans*-cyclohexane-1,2-diamine, L-(+)-tartaric acid were purchased from Sigma–Aldrich and used without further purification. Analytical thin layer chromatographic tests were carried out using precoated silica gel GF254 plates purchased from Merck Specialties Private Ltd, India and the spots were visualized by $KMnO_4$ solution or UV light. Column chromatography was carried out using Merck silica gel (100–200 mesh). All the glassware were pre-dried at 120 °C for at least 6 h and assembled while hot and cooled under a stream of dry nitrogen gas. In all experiments, round bottom flasks and reaction tube of appropriate size were used. Enantiomeric excess of corresponding dimethyl ester derivative of samples was determined on Shimadzu HPLC systems using the Daicel Chiralpak AD-H column. The absolute configuration of sample was assigned by comparing the sign of optical rotation.[1e]

Full crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1407947. These data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 (1223)336033; or e-mail: deposit@ccdc.cam.ac.uk.

#### 4.1.1. Resolution of (±)-2,2′-dihydroxy-(1,1′-binaphthalene)-3,3′-dicarboxylic acid (BINOL-3,3′-dicarboxylic acid) (±)-1 using (1*R*,2*R*)-*trans*-cyclohexane-1,2-diamine (1*R*,2*R*)-2

In a 500 mL two necked round bottom flask equipped with reflux condenser, the racemic BINOL-3,3′-dicarboxylic acid (±)-**1** (3.74 g, 10 mmol) was dissolved in a mixture of methanol (180 mL) and water (21 mL). The resulting mixture was stirred at 70 °C for 5 min and then a solution of (1*R*,2*R*)-**2** (570 mg, 5 mmol) in methanol (8 mL) was added dropwise. The overall proportion of methanol and water was 9:1. The solution was refluxed for 12 h and then cooled to room temperature. The precipitated diastereomeric salt (precipitate-I) was filtered and washed with cold methanol (3 × 20 mL) and dried in vacuo. The precipitate-I was decomposed with 6 M HCl and extracted with ethyl acetate (3 × 100 mL). The combined organic layers were washed with saturated sodium chloride solution and dried over anhydrous $Na_2SO_4$, filtered and the solvent was evaporated in vacuo to afford the scalemic (*S*)-(−)-**1** with >81% ee (1.53 g, 41%).

In order to enrich the enantiomeric purity of (*S*)-(−)-**1**, scalemic (*S*)-(−)-**1** (1.53 g, 4.1 mmol, >81% ee) was dissolved in a mixture of methanol (74 mL) and water (9 mL) by heating the reaction mixture at 70 °C for 5 min. To the clear solution, (1*R*,2*R*)-**2** (373 mg, 3.28 mmol, 0.8 equiv) in methanol (4 mL) was added dropwise, the resulting reaction mixture was stirred at reflux. After 12 h, the reaction mixture was cooled down to room temperature. Precipitate-II thus obtained was filtered and washed with cold methanol (3 × 20 mL) and dried in vacuo. The precipitate-II was decomposed with 6 M HCl and extracted with ethyl acetate (3 × 60 mL). The organic layers were combined, washed with saturated sodium chloride solution and dried over anhydrous $Na_2SO_4$, filtered and the solvent was evaporated using rotary evaporator under reduced pressure. The isomer (*S*)-(−)-**1** was obtained as a pale yellow solid (1.27 g, 34%, >99% ee) and it was characterized by $^1H$ NMR and $^{13}C$ NMR. Mp >290 °C; $[\alpha]_D^{25} = -189$ (*c* 1.08, pyridine), Lit. $[\alpha]_D^{25} = -189$ (*c* 1.06, pyridine).[1e] Chiral HPLC analysis of the corresponding dimethyl ester derivative: Chiralcel AD-H column, hexanes/isopropanol 90:10, (flow rate: 1 mL/min, detection at 254 nm) major enantiomer $t_R = 8.27$ min, minor enantiomer $t_R = 15.12$ min.

The mother liquor (Filtrate-I, Scheme 3) was evaporated using a rotary evaporator to obtain the residue. The residue was dissolved in ethyl acetate and washed with 6 M HCl to remove trace amounts of (1*R*,2*R*)-*trans*-cyclohexane-1,2-diamine **2** that was used in the resolution. The solvent was removed under reduced pressure. The (*R*)-(+)-**1** was isolated as a pale yellow solid (1.68 g, 45%, >90% ee). The scalemic (*R*)-(+)-**1** (1.68 g, >90% ee) was dissolved in methanol (35 mL) and allowed to stand at 5 °C for 24 h. The solid material thus obtained was filtered off. The filtrate was concentrated using a rotary evaporator under reduced pressure. The (*R*)-(+)-**1** was obtained as a pale yellow solid (1.34 g, 36%, >99% ee) and it was characterized by $^1H$ NMR and $^{13}C$ NMR. Mp >290 °C; $[\alpha]_D^{25} = +189$ (*c* 1.08, pyridine), Lit. $[\alpha]_D^{25} = +189$ (*c* 1.06, pyridine).[1e] $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.01–6.98 (m, 2H), 7.37–7.35 (m, 4H), 8.10–8.08 (m, 2H), 8.74 (s, 2H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ = 114.72, 116.43, 123.73, 124.10, 126.79, 129.32, 129.91, 132.72, 136.55, 154.17, 172.22. Chiral HPLC analysis of the corresponding dimethyl ester derivative: Chiralcel AD-H column, hexanes/isopropanol 90:10, (flow rate: 1 mL/min, detection at 254 nm) minor enantiomer $t_R = 8.27$ min, major enantiomer $t_R = 15.12$ min.

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## References


1. (a) Pu, L. *Chem. Rev.* **1998**, *98*, 2405–2494; (b) Pu, L.; Yu, B. H. *Chem. Rev.* **2001**, *101*, 757–824; (c) Yang, X. W.; Sheng, J. H.; Da, C. S.; Wang, H. S.; Su, W.; Wang, R.; Chan, A. S. C. *J. Org. Chem.* **2000**, *65*, 295–296; (d) Yang, X. W.; Su, W.; Liu, D. X.; Wang, H. S.; Shen, J. H.; Da, C. S.; Wang, R.; Chan, A. S. C. *Tetrahedron* **2000**, *56*, 3511–3516; (e) Kitajima, H.; Ito, K.; Aoki, Y.; Katsuki, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 207–217; (f) Kitajima, H.; Aoki, Y.; Ito, K.; Katsuki, T. *Chem. Lett.* **1996**, 1113–1114; (g) Casas, J.; Najera, C.; Sansano, J. M.; Gonzalez, J.; Saa, J. M.; Vega, M. *Tetrahedron: Asymmetry* **2001**, *12*, 699–702.
2. Sambasivan, S.; Kim, D.-S.; Ahn, K. H. *Chem. Commun.* **2010**, 541–543.
3. (a) Li, X. L.; Yang, J.; Kozlowski, M. C. *Org. Lett.* **2001**, *3*, 1137–1140; (b) Kim, K. H.; Lee, D.-W.; Lee, Y.-S.; Ko, D.-H.; Ha, D.-C. *Tetrahedron* **2004**, *60*, 9037–9042.
4. Xin, Z.-Q.; Da, C.-S.; Dong, S.-L.; Liu, D.-X.; Wei, J.; Wang, R. *Tetrahedron: Asymmetry* **2002**, *13*, 1937–1940.
5. (a) Cram, D. J.; Helgeson, R. C.; Peacock, S. C.; Kaplan, L. J.; Domeier, L. A.; Moreau, P.; Koga, K.; Mayer, J. M.; Chao, Y.; Siegel, M. G.; Hoffman, D. H.; Sogah, G. D. Y. *J. Org. Chem.* **1978**, *43*, 1930–1946; (b) Stanley, W. M.; Adams, R. *Red. Trav. Chim. Pays-Bas* **1929**, *48*, 1035–1040.
6. Ramanathan, C. R.; Someshwar, N. Provisional Indian Patent Appl. 2418/del/2014, 2014.
7. Miller, L. E.; Hanneman, W. W.; Jhon, W. L.; Smeby, R. R. *J. Am. Chem. Soc.* **1954**, *76*, 296–298.
8. (a) Nakajima, M.; Miyoshi, I.; Kanayama, K.; Noji, M.; Koga, K. *J. Org. Chem.* **1999**, *64*, 2264–2271; (b) Noji, M.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* **1994**, *35*, 7983–7984; (c) de Jong, C. R. H. I. In *Organic Syntheses by Oxidation with Metal Compounds*; Mijs, W. J., de Jong, C. R. H. I., Eds.; Plenum Press: New York, 1986; pp 423–443.
9. (a) Schanz, H. J.; Linseis, M. A.; Gilheany, D. G. *Tetrahedron: Asymmetry* **2003**, *14*, 2763–2769; (b) Mucha, P.; Mloston, G.; Jasinski, M.; Linden, A.; Heimgartner, H. *Tetrahedron: Asymmetry* **2008**, *19*, 1600–1607.
10. Larrow, J. F.; Jacobsen, E. N.; Gao, Y.; Hong, Y.; Nie, X.; Zepp, C. M. *J. Org. Chem.* **1994**, *59*, 1939–1942.