# A New and Practical Method for Preparing Enantiomerically Pure [1,1′-Binaphthalene]-2,2′-diol: Resolution of Racemic [1,1′-Binaphthalene]-2,2′-diol with *threo*-(1*S*,2*S*)-2-Amino-1-(4-nitrophenyl)propane-1,3-diol–Cyclohexanone Condensate

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An economic and practical method for preparing enantiomerically pure [1,1′-binaphthalene]-2,2′-diols is reported. Thus, a condensate of *threo*-(1*S*,2*S*)-2-amino-1-(4-nitrophenyl)propane-1,3-diol and cyclohexanone (CHANP) was used as a resolving agent. A 2:1:1 mixture of racemic [1,1′-binaphthalene]-2,2′-diol, boric acid, and CHANP was refluxed for several hours in THF or MeCN to give a white precipitate of bis{(*R*)-[1,1′-binaphthalene]-2,2′-diol}boric acid CHANP derivative, from the precipitate, and a filtrate separated from the precipitate, (*R*)- and (*S*)-[1,1′-binaphthalene]-2,2′-diol of 100% ee were obtained in *ca*. 65% yield, respectively.

**1. Introduction.** – Artificial chiral-pool compounds, (−)-(*S*)- and (+)-(*R*)-[1,1′-binaphthalene]-2,2′-diols possessing a $C_2$-symmetric axis are very important chiral ligands and auxiliaries, and they have been extensively used in stoichiometric and catalytic asymmetric reactions [1]. For the preparation of the optically active [1,1′-binaphthalene]-2,2′-diol [2], fractional recrystallization of diastereoisomers, resolution with enzymes or microorganisms, enantioselective inclusion complexation, and asymmetric oxidative coupling have become important approaches. However, these preparations utilize expensive resolving agents or chiral inductors [3–14], or are not easy to carry out[1]), or the time required for preparation is long[2]). From the practical point of view, they are not all economical.

*threo*-(1*S*,2*S*)-2-Amino-1-(4-nitrophenyl)propane-1,3-diol (ANP), a 'chiral waste' in the production of chloromycetin, is one of the least expensive artificial chiral materials available. However, application of ANP and its derivatives to the preparation of optically active [1,1′-binaphthalene]-2,2′-diols has never been reported. In consideration that reactions of 1,1′-biaryl-2,2′-diol, and $B(OH)_3$ or its ester tend to form an ionic spirocyclic boron complex in the presence of an amine [15][11c], and that we have been able to prepare conveniently and chemoselectively ketone condensates of ANP [16], we recently attempted to resolve racemic [1,1′-binaphthalene]-2,2′-diol with ANP ketone condensates *via* the formation of an ionic spiro-borate salt and found an economic, practical preparative method for both enantiomers of [1,1′-binaphthalene]-

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[1]) In all methods for preparation of the enantiomerically pure [1,1′-binaphthalene]-2,2′-diol *via* a cyclophosphoric acid ester, preparation of diastereoisomers and separation of the enantiomers from the diastereoisomers must be carried out under anhydrous conditions, and $LiAlH_4$ was required in the later step.

[2]) In most cases, preparation requires several days; in certain cases, it takes more than ten days.

2,2′-diol. Here, we report the new procedure for preparation of enantiomerically pure (−)-(*S*)- and (+)-(*R*)-[1,1′-binaphthalene]-2,2′-diol.

**2. Results and Discussion.** – 2.1. *Preparation of Enantiomerically Pure [1,1′-Binaphthalene]-2,2′-diols* via *the Formation of an Ionic Spiro-Borate Salt*. Previously, we have observed that [1,1′-biphenyl]-2,2′-diol reacted easily with $B(OH)_3$ to give a *Mulenhoff*'s acid with a boron spirocyclic structure, and the acid could be stabilized by an amine [15]. Similar to [1,1′-biphenyl]-2,2′-diol, [1,1′-binaphthalene]-2,2′-diol should also be able to form a spiro-borate salt in the presence of an amine. If a spiro-borate salt can be stereo-selectively produced from one enantiomer of racemic [1,1′-binaphthalene]-2,2′-diol in the presence of a chiral amine, it is possible to separate efficiently both enantiomers of racemic [1,1′-binaphthalene]-2,2′-diol. Thus, we examined reactions of racemic [1,1′-binaphthalene]-2,2′-diol, $B(OH)_3$, and ANP ketone condensates. We are fortunate to observe that ANP-cyclohexanone condensate (CHANP; *i.e.* 3-(hydroxymethyl)-2-(4-nitrophenyl)-1-oxa-4-azaspiro[4.5]decane) could be used as a resolving agent for racemic [1,1′-binaphthalene]-2,2′-diol under appropriate conditions. For example, a 2:1:1 mixture of racemic [1,1′-binaphthalene]-2,2′-diol ((*rac*-**1**), $B(OH)_3$ (**2**), and CHANP (**3**) was allowed to reflux in THF or MeCN for several hours to give a white precipitate of bis{(*R*)-[1,1′-binaphthalene]-2,2′-diol}-boric acid CHANP derivative, which has been characterized by IR, $^1$H-NMR, and MS. The precipitate gave massy, colorless transparent crystals of (*R*)-**1** of 100% ee in *ca*. 65% yield after acidification and kinetic crystallization from toluene[3]). The solution separated from the precipitate was evaporated, and the residue was recrystallized from toluene to give (*S*)-**1** of 100% ee in almost the same yield. It can be seen that a kinetic resolution occurred under the experimental conditions. However, the efficiency of resolution strongly depended on the reaction conditions; changing the reactant ratio, reaction medium, and the period of reaction would result in a decrease in yield of the enantiomerically pure products and even led to failure of resolution. The procedure for preparing enantiomerically pure [1,1′-binaphthalene]-2,2′-diols from CHANP *via* the formation of an ionic boron complex is shown in the *Scheme*.

2.2. *Influence of Reactant Ratio on Resolution*. To form a spiro-borate salt from the reactants **1**, **2**, and **3**, their molar ratio should be 2:1:1. This has been established by our experiments (*Table 1*). It can be seen in *Table 1* that only the 2:1:1 molar ratio could provide enantiomerically pure (*R*)-**1** and (*S*)-**1** in high yield (*Entries 2* and *3*). Under the experimental conditions, the reaction occurred stereoselectively and furnished a large amount of white precipitate of diastereoisomeric bis {(*R*)-[1,1′-binaphthalene]-2,2′-diol}-boric acid-CHANP derivative. When an excess of the reactant **1** or **3** was used, enantiomerically pure [1,1′-binaphthalene]-2,2′-diols were obtained in very low yield; meanwhile, a large amount of *rac*-**1** was recovered. We observed that the amount of bis{(*R*)-[1,1′-binaphthalene]-2,2′-diol}-boric acid-CHANP derivative was decreased with increasing amount of *rac*-**1** used. In *Entry 3*, 2.11 g of solid bis{(*R*)-[1,1′-binaphthalene]-2,2′-diol}-boric acid-CHANP derivative precipitated from the reac-

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[3]) *Smrcina et al*. proposed that the excess enantiomer in a nonracemic [1,1′-binaphthalene]-2,2′-diol could be enriched *via* kinetic crystallization in benzene. We found that toluene is a better solvent than benzene for kinetic crystallization.

Scheme. *Resolution of* rac-*[1,1′-Binaphthalene]-2,2′-diol with* threo-*(1*S*,2*S*)-2-Amino-1-(4-nitrophenyl)propane-1,3-diol–Cyclohexanone Condensate* (CHANP)

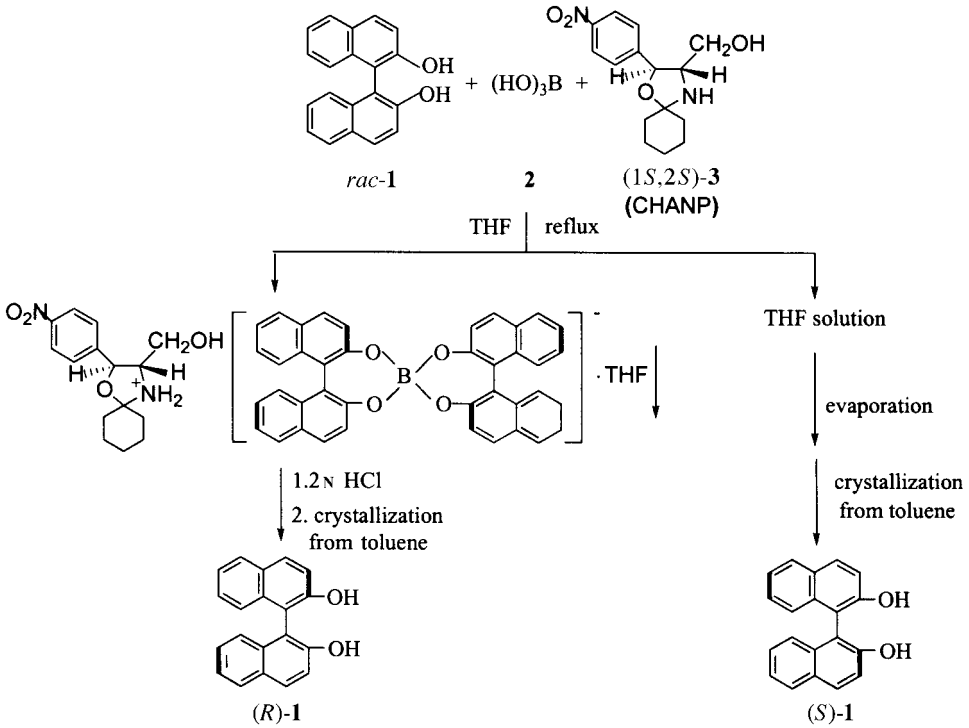


Table 1. *Influence of Reactant Ratio on Resolution*[a])

| *Entry* | Reactant ratio | Product yield [%] | |
|---|---|---|---|
| | **1/2/3** | (*R*)-form | (*S*)-form |
| *1* | 1 : 1 : 1 | 0 | 0 |
| *2* | 2 : 1 : 1 | 68.4 | 61.5 |
| *3* | 2 : 1 : 1 | 64.4 | 54.5 |
| *4* | 3 : 1 : 1 | 35.7 | 18.2 |
| *5* | 4 : 1 : 1 | 0 | 0 |
| *6* | 2 : 1 : 2 | – | 3.5 |

[a]) All reactions were carried out in 40 ml of THF under reflux for 6 h and the amount of $B(OH)_3$ used was 5 mmol. In *Entry 2*, the (*R*)-isomer was obtained after acidification in $Et_2O$ of the resulting white precipitate in the reaction, evaporation of the $Et_2O$ solution, washing the residue with petroleum ether, and then recrystallization from toluene. In the other reactions, the (*R*)-isomer was obtained after treatment according to the above procedure, except without washing the residue obtained by evaporation of the $Et_2O$ solution with petroleum ether.

tion system; in *Entry 4*, the reaction gave 1.66 g of precipitate of the derivative mentioned; and, in *Entry 5*, no precipitation occurred. The residue obtained after evaporation was treated with hot toluene to give a large amount of a white precipitate, but this precipitate, could not provide either of the enantiomerically pure

[1,1′-binaphthalene]-2,2′-diols after treatment. In *Entry 6*, although 2.4 g of precipitate was isolated, after treatment of the solid and evaporation, a large amount of *rac*-**1** was obtained. It is obvious that the use of excess *rac*-**1** and the resolving agent is not favorable for stereoselective formation of a spiro-borate salt, indicating that excess *rac*-**1** and resolving agent promote the reaction to form a spiro-borate salt from (*S*)-**1**.

2.3. *Influence of Reaction Medium on the Resolution.* A 2:1:1 mixture of the reactants **1**, **2**, and **3** was allowed to reflux for 5–6 h in different solvents. The results are shown in *Table 2*. It can be seen that only the reactions performed in THF and MeCN furnished the desired products in high yield. When benzene or toluene was used as a reaction medium (*Entries 4* and *5*), no precipitation of bis{(*R*)-1,1′-binaphthalene]-2,2′-diol}boric acid CHANP derivative occurred. In *Entry 3*, the reaction performed in 70 ml of $Et_2O$ gave 3.6 g of white precipitate, which was stirred in a large amount of $Et_2O$ to give an insoluble solid (a mixture of diastereoisomeric spiro-borate salts) and an etheral solution from which a large amount of *rac*-**1** was obtained after treatment. It seems that THF and MeCN are suitable solvents for the resolving reaction; a nonpolar or a less-polar solvent is not favorable for the resolution.

Table 2. *Influence of Reaction Medium on Resolution*[a])

| *Entry* | Reaction medium | Product yield [%] | |
|---|---|---|---|
| | | (*R*)-form | (*S*)-form |
| *1* | THF | 64.4 | 54.5 |
| *2* | MeCN | 63.0 | 59.0 |
| *3* | $Et_2O$ | – | 5.6 |
| *4* | Benzene | trace | |
| *5* | PhMe | trace | |

[a]) All reactions were carried out in a 2:1:1 molar ratio under reflux for 5–6 h, and the amount of $B(OH)_3$ used was 5 mmol. The (*R*)-isomer in the *Entry 2* was obtained after acidification in $Et_2O$ for the white precipitate resulting from the reaction, evaporation of the $Et_2O$ solution, and then direct recrystallization from toluene.

2.4. *Influence of Reaction Time on the Resolution*. A 2:1:1 mixture of the reactants **1**, **2** and **3** was allowed to reflux in MeCN and benzene, respectively, the resolution results are shown in *Table 3*. We observed that the reactions performed in benzene, regardless of the reaction time, did not give a precipitate (*Entries 4–6*); after evaporation of the solution, a viscous residue was obtained. Although addition of $Et_2O$ led to precipitation, it could not provide enantiomerically pure products from either the precipitate or the ethereal solution, and only *rac*-**1** was obtained. When the reaction was performed in MeCN, a long reaction time resulted in decrease of the yield of enantiomerically pure [1,1′-binaphthalene]-2,2′-diol (*Entry 3*). The result implies that, after over 6 h, (*S*)-**1** in the reaction system participated in the salt-forming reaction, and amount of the spiro-borate salt from the (*S*)-isomer increased with prolongation of the reaction time. On the other hand, the reaction for less than 4 h (*Entry 1*) merely led to an enantiomerically pure product in low yield, indicating that it probably takes more than 3 h for the efficient formation of bis{(*R*)-[1,1′-binaphthalene]-2,2′-diol}boric acid.

Table 3. *Influence of Reaction Time on Resolution*[a])

| *Entry* | Reaction medium | Reaction time [h] | Product yield [%] | |
|---|---|---|---|---|
| | | | (*R*)-form | (*S*)-form |
| *1* | MeCN | 3 | – | 7.0 |
| *2* | MeCN | 6 | 63.0 | 59.0 |
| *3* | MeCN | 11 | – | 21.7 |
| *4* | Benzene | 0.5 | – | – |
| *5* | Benzene | 6 | trace | |
| *6* | Benzene | 15 | – | – |

[a]) All reactions were carried out in a 2 : 1 : 1 molar ratio under reflux, and the amount of $B(OH)_3$ used was 5 mmol. The (*R*)-isomer was obtained after acidification in $Et_2O$ for the white precipitate resulting from the reaction, evaporation of the $Et_2O$ solution, and then direct recrystallization from toluene

2.5. *The Diastereoselectivity of the Formation of the Spiro-Borate.* In the presence of CHANP, both enantiomers of *rac*-**1** can stereoselectively react with $B(OH)_3$ to form a spiro-borate, and they can be isolated as salts. This has been established by our experiments. We observed that the diastereoselectivity of the reaction depended mainly upon the medium used. Only in THF or MeCN do (*R*)-**1** and (*S*)-**1** show a large difference in the rate of formation of the spiro-borate, and only (*R*)-**1** can react at an appropriate rate and give a white precipitate of bis{(*R*)-[1,1′-binaphthalene]-2,2′-diol}-boric acid CHANP derivative under appropriate conditions. The parallel experiments performed with enantiomerically pure (*R*)-**1** and (*S*)-**1** indicated that the (*S*)-isomer did not yield a precipitate of a spiro-borate salt in these solvents within 6 h. We also observed that the amount of bis{(*R*)-[1,1′-binaphthalene]-2,2′-diol}boric acid CHANP derivative precipitated from the reaction mixture is an important measure of resolution efficiency. It appears that highly stereoselective formation of bis{(*R*)-[1,1′-binaphthalene]-2,2′-diol}-boric acid-CHANP derivative is the key to efficient resolution of *rac*-**1** with CHANP.

It can be seen from the above discussion that factors affecting the resolution efficiency are complicated. When resolution was carried out in a 2 : 1 : 1 molar ratio in THF or MeCN for 5 – 6 h, diastereoisomeric bis{(*R*)-[1,1′-binaphthalene]-2,2′-diol}-boric acid – CHANP derivative precipitated and enantiomerically pure (*R*)-**1** and (*S*)-**1** were obtained in *ca.* 65% yield from the precipitate and the mother liquor. However, the resolutions showed a poor diastereoselectivety when resolution was not performed in a 2 : 1 : 1 molar ratio or carried out in a nonpolar or less polar solvent or for a longer time.

**3. Conclusions.** – We have developed a novel and practical method for preparing enantiomerically pure (+)-(*R*)- and (−)-(*S*)-[1,1′-binaphthalene]-2,2′-diols, (*R*)-**1** and (*S*)-**1**, respectively, through the reaction of *rac*-**1**, $B(OH)_3$, and *threo*-(1*S*,2*S*)-2-amino-1-(4-nitrophenyl)propane-1,3-diol-cyclohexanone condensate. Our method is technologically simple and easy to carry out (one-pot reaction, conventional operation without special conditions). Morever, the time required for the preparation is short ([1,1′-binaphthalene]-2,2′-diol of 100% ee can be obtained within 24 h) and preparative cost is low. It is perhaps one of the most economical and practical methods for

preparing enantiomerically pure (+)-(*R*)- and (−)-(*S*)-[1,1′-binaphthalene]-2,2′-diols at present.

## Experimental Part

*General*. M.p.: *VEB Wagetechnik Rapio PHMK05* instrument; not corrected. Optical rotations: *WZZ-1S* (Shanghai, China) polarimeter. IR Spectra: *Testscan Shimadzu FTIR 8000*, in KBr. $^1$H-NMR Spectra: *Varian Mercury VS 300*, $\delta$ values [ppm] relative to $Me_4Si$. MS: *VG ZAB-HF-3F* spectrometer.

*Reagents. threo*-(1*S*,2*S*)-2-Amino-1-(4-nitrophenyl)propane-1,3-diol-cyclohexanone condensate was prepared according to the method described in [16]. *rac*-[1,1′-Binaphthalene]-2,2′-diol (*rac*-**1**) was purchased from *Beijing Xizhong* chemical factory, and used without special treatment.

*Preparation of (+)-(*R*)- and (−)-(*S*)-[1,1′-Binaphthalene]-2,2′-diols* ((*R*)-**1** and (*S*)-**1**, resp.) *of 100% ee*. To a 100-ml round-bottom flask, 2.86 g (10 mmol) of *rac*-**1**, 0.31 g (5 mmol) of $B(OH)_3$, 1.46 g (5 mmol) of *threo*-(1*S*,2*S*)-2-amino-1-(4-nitrophenyl)propane-1,3-diol−cyclohexanone condensate, and THF (40 ml) were added. Then, the flask was fitted successively with a 50-ml pressure-equalized additive funnel charged with an appropriate amount of anh. $CaCl_2$, a reflux condenser, and an oil bubbler with a stopcock. The mixture was refluxed with magnetic stirring for 6 h to form a large amount of white precipitate. After cooling to ambient temp., the precipitate was separated by filtration, washed with a small amount of THF, and then dried under reduced pressure to give 2.21 g of solid bis{(*R*)-[1,1′-binaphthalene]-2,2′-diol}-boric acid 1-oxa-4-azaspiro[4.5]-decane derivative as a solvate of THF; the solid was stirred in 30 ml $Et_2O$ for 0.5 h at ambient temp., filtered, and the insoluble solid was collected, dried, and weighed; 2.11 g. M.p. 222–225°. IR (KBr): 3436*m* (O−H), 3053*m* (Ar−H), 2965 (sh.), 2942*m-s*, 2873*m* (C−H), 2780–2400*m-w* ($NH_2^+$), 1612*m*, 1589*m-s* (C=C−C), 1521*s* ($NO_2$), 1510 (sh., C=C−C), 1462*s* ($CH_2$), 1360 (sh., $CH_2$), 1339v*s* (br., $NO_2$ + B−O), 1268*m* (C−N), 1244v*s* (Ar−O), 1072v*s* (B−O), 1010vv*s*, 973v*s*, 909*m-s* (C−O−C or C−O), 819*m-s* (Ph−H), 752*m-s* (napht.-H). $^1$H-NMR ((D$_6$)DMSO, 300 MHz): 1.30–1.80 (*m*, 10 H of cyclohexane and $CH_2$(3), $CH_2$(4) of THF); 2.98 (*m*, NCH); 3.58 (*m*, $CH_2O$ and $CH_2$(2), $CH_2$(5) of THF); 4.66 (*d*, *J* = 7.5, ArC*H*C); 5.03 (*t*, $CH_2OH$); 6.93 (*d*, *J* = 8.7, 4 H of napht.); 7.07–7.34 (*m*, 12 H of napht.); 7.62 (*d*, *J* = 8.7, H−C(2), H−C(6) of Ph); 7.77–7.98 (*m*, 8 H of napht.); 8.11 (*d*, *J* = 8.7, H−C(3), H−C(5) of Ph); 9.25 (*s*, $NH^{2+}$). FAB-MS: 580 (17, [*M* − $C_{15}H_{20}N_2O_4$ (CHANP)]$^+$; 292 (18, [*M* − $C_{40}H_{25}BO_4$]$^+$), 286 (22, $C_{20}H_{14}O_2$). This solid is hard to dissolve in $H_2O$, petroleum ether, $Et_2O$, benzene, PhMe, THF, MeCN, MeOH, EtOH, i-PrOH, $CHCl_3$, AcOEt, $Me_2CO$, *etc.*, except DMSO and DMF. To the solid product, 2M HCl and $Et_2O$ were added, and the mixture was stirred until complete dissolution occurred. The $Et_2O$ layer was separated, and the $H_2O$ phase was extracted with $Et_2O$. The org. phases were combined and dried ($Na_2SO_4$); the $Et_2O$ soln. was evaporated, and the residue was washed with petroleum ether. Then, an appropriate amount of toluene was added for recrystallization to give 0.98 g of massy, colorless transparent crystals of (+)-(*R*)-**1** in 68.5% yield. M.p. 208–210°. $[\alpha]_D^{22} = +35.2$ (*c* = 1, THF). 100% ee.

The THF mother liquor removed from the solid was evaporated to give a solid residue, which was essentially the enriched (*S*)-isomer. The residue was crystallized from toluene to furnish 0.88 g of massy, transparent crystals of (−)-(*S*)-**1** in 61.5% yield. M.p. 208–210°. $[\alpha]_D^{22} = -35.3$ (*c* = 1, THF). 100% ee.

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