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Second example for the heterocomplexation of chiral diols and complete disproportionation of enantiomers for non-racemic 2,3-*O*-cyclohexylidene-1,1,4,4-tetraphenylthreitols

Xiaoyun Hu, Zixing Shan *, Wei Li

Department of Chemistry, Wuhan University, Luojia Mountain, Wuhan 430072, China

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ABSTRACT

Inclusion complexation of a tricyclic dipeptide derived from (*S*)-proline toward several chiral diols was examined, and observed that inclusion complexation behavior depended strongly on the composition of diol. For 2,3-*O*-alkylidene-1,1,4,4-tetraphenylthreitols, the derivatives of cyclohexanone and acetone reacted with the dipeptide to generate a 1:2 inclusion complex; however, the former is achiroselective, affording the second heterocomplex known to date. Based on the heterocomplexation, complete disproportionation of enantiomers of non-racemic 2,3-*O*-cyclohexylidene-1,1,4,4-tetraphenylthreitol was successfully realized, leading to highly effective separation of the excess enantiomer from the racemate. On the other hand, inclusion complexation did not occur between the dipeptide and *rac*-pinanediol or (4*R*,5*R*)-4-diphenylhydroxymethyl-5-hydroxy-2,6,6-triphenyl-1,3,2-dioxaborolane.

1. Introduction

It is well known, a racemate is very difficult to experience enantiomeric separation in achiral environment, while enantiomeric purity of non-racemic compound can be frequently upgraded through recrystallization in suitable solvent. However, in general, the optical purification technology can only offer enantiomer-enriched sample or enantiomerically pure species in lower yield; furthermore, the search for practical solvents frequently is very time consuming. Since 1980s, it has been continuously observed that some non-racemic chiral compounds could offer species with different enantiomeric purity through chromatography on an achiral stationary phase. In 2006, Soloshonok [1–3] first proposed the concept of enantiomer self-disproportionation (or self-disproportionation of enantiomers) based on the observation on chromatographic separation in an achiral silica gel for non-racemic fluoroorganic compounds. Fig. 1 is a model for self-disproportionation of enantiomers. In the cases of self-disproportionation of enantiomers (SDEs) [4–5], cumulation of the excess enantiomer would occur; in certain cases, the enantiomer cumulation may be achieved in a great degree, even species of up to >99% ee was obtained; however, practical yield of the enantiomerically pure species is not acceptably satisfactorily. If under a certain condition, disproportionation of enantiomer is complete, theoretically, quantitative separation of the excess enantiomer from the racemate should be achieved; that is to say, it should afford the excess enantiomer of 100% ee and the racemate in calculated amount (Fig. 2).

In the course of our investigation on interaction between chiral host and racemic guest, we observed that a tricyclic dipeptide (3*S*,6*S*)-**1** [6–10] generated from (*S*)-proline was refluxed with *rac*-1,1′-bi-2-naphthol (BINOL) in benzene, then cooled to afford a 1:2:3 heterocomplex [11] consisting of the dipetide, *rac*-**BINOL** and benzene, possessing an indefinite chain structure (Scheme 1). This is the first observation on heterocomplexation phenomenon in chiral supramolecular chemistry. "Heterocomplexation" means achiroselective complexation between chiral host and racemic guest, where both the enantiomers of a racemic guest are synchronously bound to a chiral host. The heterocomplexation strategy has been successfully applied to quantitative separation [11] of the excess enantiomer from the racemate. In order to explore the universality of heterocomplexation phenomenon, interaction between some racemic diols and (3*S*,6*S*)-**1** was examined, finding that occurrence of the heterocomplexation

* Corresponding author.
E-mail address: zxshan@whu.edu.cn (Z. Shan).

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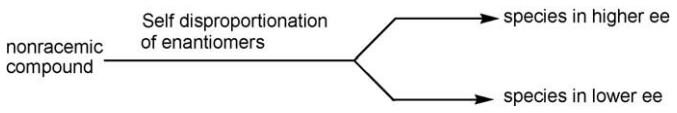


Fig. 1. Model for self-disproportionation of enantiomer (SDE).

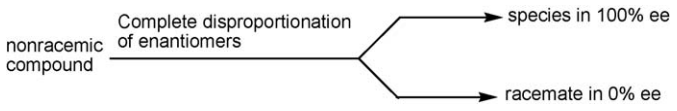


Fig. 2. Model for complete disproportionation of enantiomers (CDE).

depends strongly on the composition of reactants and solvents used. In the present paper, we report intermolecular interaction between (3*S*,6*S*)-**1** and several chiral 1,4-, 1,3- and 1,2-diols (Fig. 3), including *rac*- and (4*R*,5*R*)-2,3-*O*-cyclohexylidene-1,1,4,4-tetraphenylthreitol (CHTTOL), *rac*- and (4*R*,5*R*)-2,3-*O*-isopropylidene-1,1,4,4-tetraphenylthreitol (IPTTOL), (4*R*,5*R*)-4-diphenylhydroxymethyl-5-hydroxy-2,6,6-triphenyl-1,3,2-dioxaborolane (DHTDB) or *rac*-pinanediol (PADOL), the second example for heterocomplexation of chiral diols and complete disproportionation of enantiomers in non-racemic **CHTTOL**.

2. Results and discussion

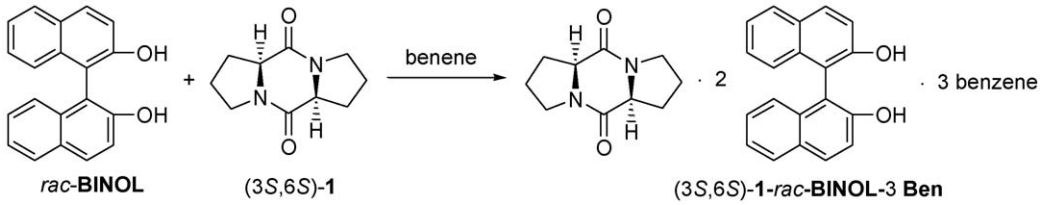
(3*S*,6*S*)-**1** was allowed to reflux with racemic 2,3-*O*-cyclohexylidene-1,1,4,4-tetraphenylthreitol (CHTTOL) [12–14] in benzene or toluene in a 1:1–3 molar ratio to form a homogeneous solution; cooled to room temperature, a white solid was isolated out of the system; after recrystallization in the same solvent as used in the reaction, a colorless crystal was obtained, respectively. The spectral analyses indicate that they are all a 1:2 supramolecular complex consisting of the dipetide and **CHTTOL**. The complex was worked up in a mixture of water and ethyl acetate to offer (3*S*,6*S*)-**1** and *rac*-**CHTTOL** from the water phase and the organic phase, respectively, revealing that a heterocomplexation occurred between (3*S*,6*S*)-**1** and *rac*-**CHTTOL** (Scheme 2). This is the second example for heterocomplexation of chiral diols known to date.

Attempts for obtaining single crystal suitable for X-ray crystallographic analysis *via* recrystallization in benzene or toluene have not met with success.

Interestingly, complexation reaction between enantiomerically pure (4*R*,5*R*)-2,3-*O*-cyclohexylidene-1,1,4,4-tetraphenylthreitol and (3*S*,6*S*)-**1** can also take place in toluene, but furnished a 1:1 supramolecular complex (Scheme 3).

The above facts show that between (3*S*,6*S*)-**1** and *rac*-**CHTTOL**, enantioselective inclusion complexation cannot occur, though (3*S*,6*S*)-**1** can form inclusion complex with an enantiomer of **CHTTOL**. It appears that existent form of chiral diols influences considerably its complexation property.

Taking into account of the previous result [11], heterocomplexation of (3*S*,6*S*)-**1** to *rac*-**CHTTOL** has been also attempted to apply to separation of the excess enantiomer from the racemate in non-racemic **CHTTOL**s. For a non-*rac*-**CHTTOL**, the amount of the *rac*-**CHTTOL** included can be readily calculated based on the ee value of the non-*rac*-**CHTTOL**, thus the appropriate (3*S*,6*S*)-**1** loading requested for the formation of a 1:2 complex with the *rac*-**CHTTOL** can be readily determined. When a stoichiometric (3*S*,6*S*)-**1** was added to a benzene or toluene solution of the non-*rac*-**CHTTOL**, refluxed, and then cooled, the *rac*-**CHTTOL** contained in the non-*rac*-**CHTTOL** was isolated out of the solution as a crystalline inclusion complex, while the excess enantiomer remained in benzene or toluene solution. The mother liquor removed from the inclusion complex was concentrated and



Scheme 1. Heterocomplexation of (3*S*,6*S*)-**1** to *rac*-**BINOL** in benene.

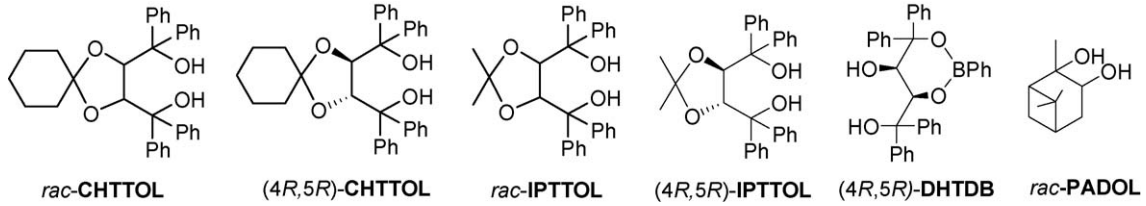
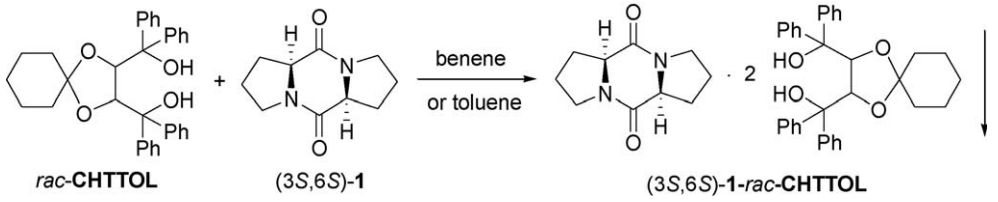
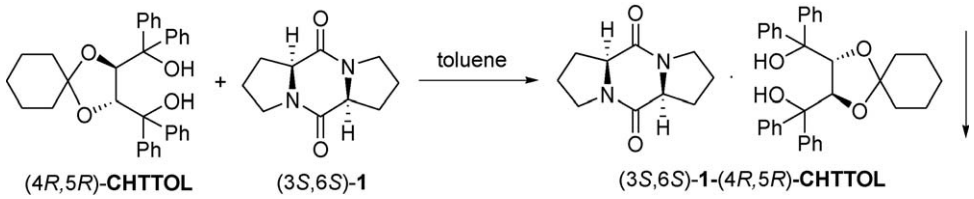


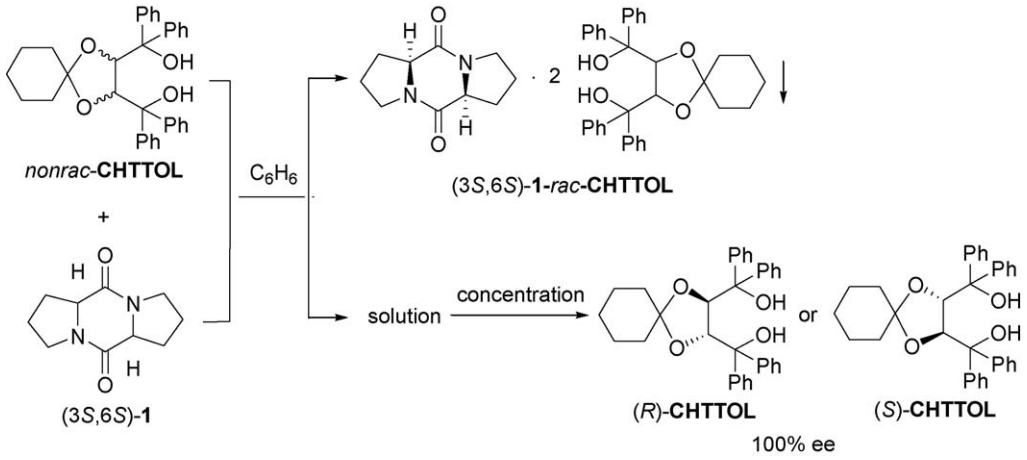
Fig. 3. Chiral diols examined in the present work.



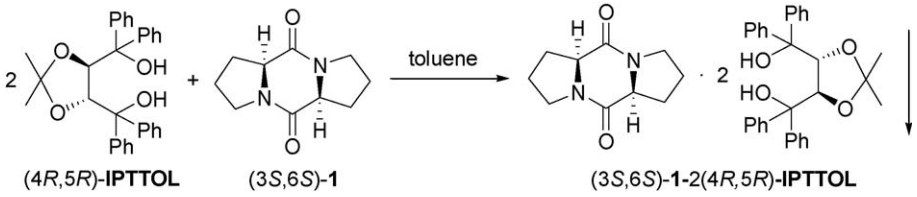
Scheme 2. Heterocomplexation of (3*S*,6*S*)-**1** to *rac*-**CHTTOL** in benzene or toluene.



Scheme 3. Inclusion complexation of (3*S*,6*S*)-**1** to (4*R*,5*R*)-**CHTTOL** in toluene.



Scheme 4. Complete disproportionation of enantiomers of non-racemic **CHTTOL***s via* heterocomplexation.



Scheme 5. Inclusion complexation between (3*S*,6*S*)-**1** and (4*R*,5*R*)-**IPTTOL**.

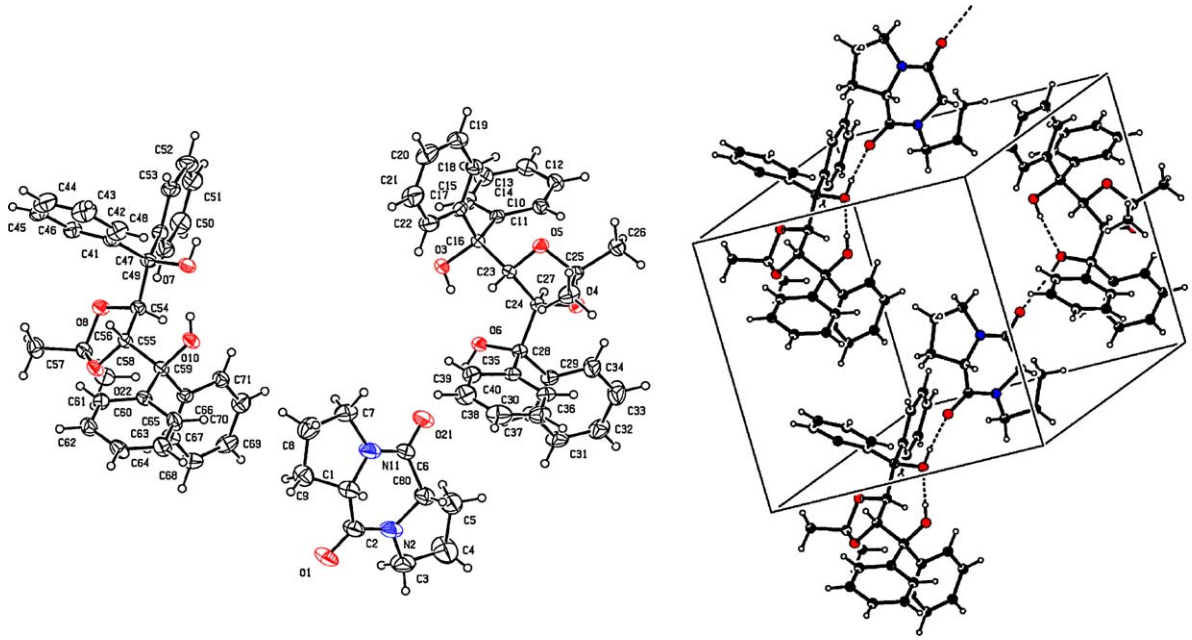


Fig. 4. Numbering scheme and molecular assembly for the inclusion complex of (3*S*,6*S*)-**1** and (4*R*,5*R*)-**IPTTOL**. Hydrogen bonding: O10 H10 O7, 0.82 1.82 2.635(2) 174.5; O6 H6 O21, 0.82 2.08 2.891(3) 172.2; O3 H3 O6, 0.82 1.92 2.709(2) 162.4.

crystallized to furnish enantiomerically pure (4*R*,5*R*)- or (4*S*,5*S*)-**CHTTOL** (Scheme 4). For example, a mixture of (4*R*,5*R*)-**CHTTOL** of 80% ee and 0.1 equivalent of (3*S*,6*S*)-**1** was dissolved in benzene or toluene (20 mL) under heating and refluxed for 2 h, and then cooled to ambient temperature to isolate a 1:2 colorless crystalline complex of (3*S*,6*S*)-**1** and *rac*-**CHTTOL**, *ca.* 60% yield. The solution removed from the crystal was evaporated to *ca.* half of the original volume to afford second crop, combined with the above together, *ca.* 85% yield. The mother liquor separated from the above inclusion complex was further concentrated to isolate a colorless crystal of enantiomerically pure (4*R*,5*R*)-**CHTTOL** in more than 80% yield. Finally, the solution was evaporated to dryness to furnish (4*R*,5*R*)-**CHTTOL** contaminated by the heterocomplex.

It presents a striking contrast to the above, an analog of *rac*-**CHTTOL**, *rac*-2,3-*O*-isopropylidene-1,1,4,4-tetraphenylthreitol (IPTTOL) [13] did not undergo heterocomplexation under similar condition to the above. However, between enantiomerically pure (4*R*,5*R*)-**IPTTOL** and (3*S*,6*S*)-**1**, an inclusion complexation took place and furnished a 1:2 crystalline complex (Scheme 5), which has been characterized by the single crystal X-ray diffraction analysis. The perspective view of the inclusion complex of (3*S*,6*S*)-**1** and (4*R*,5*R*)-**IPTTOL** showing the numbering scheme were shown in Fig. 4. The data [15] showed that only an inclusion complex molecule was included in a unit cell, where the configuration of the dipeptide is retentive, namely it still is *cis*-(3*S*,6*S*). It was also observed that in this supramolecular assembly, there are two types of H bonding, including an internal H bond between both the hydroxyl groups in per diol molecule and an intermolecular H bond between the hydroxyl group of the diol and the carbonyl group of (3*S*,6*S*)-**1**, and one carbonyl group of the dipeptide merely bonded to one diol molecule.

Similar investigation indicated that no inclusion complexation occurred between (3*S*,6*S*)-**1** and chiral pinanediol [16] or (4*R*,5*R*)-4-diphenylhydroxylmethyl-5-hydroxy-2,6,6-triphenyl-1,3,2-dioxa-borolane [17].

3. Conclusion

In summary, intermolecular interaction between (3*S*,6*S*)-**1** and some chiral diols has been examined, finding that the composition of diols is one of the most important factors influencing complexation property of the diols to (3*S*,6*S*)-**1**. Formation of the complex between (3*S*,6*S*)-**1** and (4*R*,5*R*)-2,3-*O*-cyclohexylidene-1,1,4,4-tetraphenylthreitol or (4*R*,5*R*)-2,3-*O*-isopropylidene-1,1,4,4-tetraphenylthreitol does not mean that enantioselective inclusion complexation can take place between (3*S*,6*S*)-**1** and the racemic diols. For the chiral diols examined here, only *rac*-2,3-*O*-cyclohexylidene-1,1,4,4-tetraphenylthreitol can undergo heterocomplexation to (3*S*,6*S*)-**1**, and realized highly effective separation of the excess enantiomer from the racemate in non-racemic 2,3-*O*-cyclohexylidene-1,1,4,4-tetraphenylthreitol *via* complete disproportionation of enantiomers.

4. Experimental

4.1. General

All the reagents and solvents are purchased (CP or AR grade). (3*S*,6*S*)-**1** was prepared according to the literature [10], mp 144–146 °C $[\alpha]_D^{25} = -44.5$ (*c* 1, in CH_3OH). IR: 1650 s. ^1H NMR ($CDCl_3$, 300 MHz): 1.82–2.37 (*m*, 8H), 3.51–3.55 (*dd*, *J* = 4.8 Hz, *J* = 7.8 Hz, 4H); 4.17 (*t*, *J* = 9.0 Hz, 2H). MS: 389 (6, $[M_{dimer}+1]^+$), 195 (100, $[M+1]^+$). *rac*- and (4*R*,5*R*)-**CHTTOL**s as well as *rac*- and (4*R*,5*R*)-**IPTTOL**s were synthesized referring to the literature [13], (4*R*,5*R*)-**DHTDB** was prepared according to the literature [16], and *rac*-**PADOL** were formed through mixing (+)- and (−)-**PADOL**, which was prepared by an improved Weber and Shepherd method [17]. Non-racemic (4*R*,5*R*)-**CHTTOL** was formed through mixing stoichiometrically *rac*- and (4*R*,5*R*)-**CHTTOL**. IR spectra were record on a Testscan Shimadzu FTIR 8000 in KBr. ^1H and ^{13}C NMR spectra were taken in $CDCl_3$ solutions at 300 or 400 MHz and 75 or 100 MHz, respectively, on a Varian Mercury VX 300 or Bruker AV 400, and all chemical shifts were reported as δ values (ppm) relative to Me_4Si. Melting points were determined on a VEB Wägetechnik Rapido PHMK 05 instrument and were not corrected. Optical rotations were measured in $CHCl_3$ on a PerkinElmer 341 Mc polarimeter.

4.2. Heterocomplexation of (3*S*,6*S*)-1 to rac-CHTTOL

A mixture of *rac*-**CHTTOL** (0.304 g, 0.6 mmol) and (3*S*,6*S*)-**1** (0.058 g, 0.3 mmol) was dissolved in benzene (10 mL) with heating and refluxed for 2 h, and then cooled to ambient temperature to isolate a 1:2 colorless crystalline complex (0.337 g) of (3*S*,6*S*)-**1** and *rac*-**CHTTOL**, yield: 93%. mp 215–228 °C, $[\alpha]_D^{25} = -21.2$ (*c* 1.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 1.11–1.29 (*m*, 12H, cyclohexylidene of diol), 1.37–1.47 (*m*, 8H, cyclohexylidene of diol), 1.87–2.36 (*m*, 8H, $2CH_2CH_2$ of dipeptide), 3.52–3.55 (*dd*, *J* = 8.8 Hz, *J* = 5.6 Hz, 4H, $2NCH_2$ of dipeptide), 4.11 (*s*, 4H, OH, disappeared after adding D_2O), 4.16 (*t*, *J* = 8.4 Hz, 2H, NCHC=O of dipeptide), 4.56 (*s*, 4H, CH, framework of diol), 7.22–7.35 (*m*, 24H, Ph-H), 7.37–7.41 (*m*, 8H, Ph-H), 7.50–7.55 (*m*, 8H, Ph-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.1, 142.7, 128.5, 128.1, 127.7, 127.2, 109.9, 80.5, 78.1, 60.5, 45.2, 36.5, 27.7, 23.9.

The spectra of a 1:2 inclusion complex isolated in toluene are very similar to those in benzene. ^1H NMR (400 MHz, $CDCl_3$): δ 1.14–1.27 (*m*, 12H, cyclohexylidene of diol), 1.40–1.44 (*m*, 8H, cyclohexylidene of diol), 1.83–2.36 (*m*, 8H, $2CH_2CH_2$ of dipeptide), 3.49–3.53 (*dd*, *J* = 8.8 Hz, *J* = 5.6 Hz, 4H, $2NCH_2$ of dipeptide), 4.14 (*t*, *J* = 8.0 Hz, 2H, NCHC=O of dipeptide), 4.22 (*s*, 4H, OH, disappeared after adding D_2O), 4.54 (*s*, 4H, CH, framework of diol), 7.20–7.33 (*m*, 24H, Ph-H), 7.35–7.40 (*m*, 8H, Ph-H), 7.49–7.54 (*m*, 8H, Ph-H).

The mother liquor was concentrated to offer second crop of the inclusion complex, combined with the above together, 0.55 g, 85% yield. The above obtained crystalline complex was worked up with a mixture of water and diethyl acetate to afford (3*S*,6*S*)-**1** [mp 143–145 °C $[\alpha]_D^{25} = -44.2$ (*c* 1, in CH_3OH)] and *rac*-**CHTTOL** [mp 211–214 °C $[\alpha]_D^{25} = 0$ (*c* 1, in $CHCl_3$)] from water phase and the organic phase, respectively.

4.3. A representative procedure for complete disproportionation of enantiomers for non-racemic CHTTOL

According to similar procedure to the above, *rac*-**CHTTOL** (0.525 g, 1.04 mmol)) of 80% ee was allowed to mix with (3*S*,6*S*)-**1** (0.03 g, 0.104 mmol) in benzene or toluene (20 mL), dissolved, refluxed, then cooled to isolate a 1:2 colorless crystalline inclusion complex of (3*S*,6*S*)-**1** and *rac*-**CHTTOL**. The solution removed from the inclusion complex crystal was concentrated to afforded crystals of (4*R*,5*R*)-**CHTTOL** (0.32 g, 75% yield), mp 195–197 °C, $[\alpha]_D^{25} = -75$ (*c* 1, $CHCl_3$). ^1H and ^{13}C NMR spectra are in conformance with those of the authorized sample. The mother liquor was further concentrated to furnish the second crystalline crop of (4*R*,5*R*)-**CHTTOL**, combined with the first crop, over 80% yield.

4.4. Inclusion complexation of (3*S*,6*S*)-1 to (4*R*,5*R*)-CHTTOL

Similar to the above, a mixture of (4*R*,5*R*)-**CHTTOL** (0.304 g, 0.6 mmol) and (3*S*,6*S*)-**1** (0.058 g, 0.3 mmol) was treated in toluene under reflux and then cooled to isolate a 1:1 colorless crystalline

complex (0.332 g, 92% yield) of (3*S*,6*S*)-**1** and (4*R*,5*R*)-**CHTTOL**. Mp 205–212 °C, $[\alpha]_D^{25} = -99.1$ (*c* 0.22, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 1.08–1.26 (*m*, 12H, cyclohexylidene of diol), 1.35-1.44 (*m*, 8H, cyclohexylidene of diol), 1.84–2.38 (*m*, 8H, $2CH_2CH_2$ of dipeptide), 3.49–3.53 (*dd*, *J* = 8.8 Hz, *J* = 5.2 Hz, 4H, $2NCH_2$ of dipeptide), 4.12 (*s*, 4H, OH, disappeared after adding D_2O), 4.14 (*t*, *J* = 8.0 Hz, 2H, NCHC=O of dipeptide), 4.52 (*s*, 4H, CH, framework of diol), 7.20–7.32 (*m*, 24H, Ph-H), 7.34–7.37 (*m*, 8H, Ph-H), 7.48–7.52 (*m*, 8H, Ph-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 142.4, 128.3, 127.8, 127.4, 127.2, 126.9, 109.6, 80.2, 77.9, 60.3, 44.9, 36.2, 27.4, 23.7, 23.1.

4.5. Inclusion complexation of (3S,6S)-1 to (4R,5R)-IPTTOL

Similar to the above, a mixture of (4*R*,5*R*)-**IPTTOL** (0.935 g, 2.0 mmol) and (3*S*,6*S*)-**1** (0.295 g, 1.0 mmol) was dissolved in toluene, refluxed for 2 h, and then cooled to isolate a 1:2, colorless crystalline complex (0.487 g, 93% yield) of (3*S*,6*S*)-**1** and (4*R*,5*R*)-**IPTTOL**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.06 (s, 12H, methyls of the diol), 2.34–1.91 (m, 8H, $2CH_2CH_2$), 3.55–3.51 (m, 4H, $2NCH_2$), 4.14 (t, *J* = 8.0 Hz, 2H, 2NCHC=O), 4.27 (s, 4H, OH of the diol, disappeared after adding D_2O), 4.61 (s, 4H, framework C–H of the diol), 7.39–7.32 (m, 32H, Ph-H of the diol), 7.57–7.55 (m, 8H, Ph-H of the diol). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 146.0, 142.7, 128.6, 128.1, 127.7, 127.5, 127.3, 127.2, 109.5, 81.0, 78.1, 60.5, 45.2, 27.7, 27.1, 23.3. After treatment with a mixture of water and diethyl acetate, (4*R*,5*R*)-**IPTTOL** was obtained from the organic phase, mp 192–194 °C, $[\alpha]_D^{25} = -60.5$ (*c* 1, $CHCl_3$); Lit. [12]: $[\alpha]_D^{25} = -60.6$ (*c* 1, $CHCl_3$), 100% ee. ^1H and ^{13}C NMR spectral data are identical to those cited in Ref. [13].

After standing for 3 months at ambient temperature (25–38 °C), the toluene solution of the inclusion complex of (3*S*,6*S*)-**1** and (4*R*,5*R*)-**IPTTOL** furnished a colorless single crystal suitable for X-ray diffraction analysis.

Crystallographic data of (3*S*,6*S*)-**1**·2 (4*R*,5*R*)-**IPTTOL**: empirical formula, $C_{72}H_{74}N_2O_{10}$; formula weight, 1127.33; calculated density, 1.253 g/cm^3; volume (V), 1493.6 (2) Å^3; crystal system, triclinic; space group, P1; *Z* = 1; unit cell dimensions, *a* = 9.2916 (9), *b* = 11.7937(11), *c* = 14.2641 (13), α = 87.127 (2)°, β = 76.0290 (10)°, γ = 79.9710 (10)°; absorption coefficient (μ), 0.083 mm^{-1}; index ranges, $-11 \le h \le 11$, $-14 \le k \le 14$, $-17 \le l \le 10$; *F*(000), 600; GOF, 1.025.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2009.10.017.

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