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Macrocyclic compounds as chiral solvating agents for phosphinic, phosphonic, and phosphoric acids

Fengnian Ma,[a] Xiumin Shen,[a] Jie Ou-Yang,[b] Zhiwei Deng[b] and Cong Zhang[a,*]

[a]*College of Chemistry, Beijing Normal University, Beijing 100875, China*
[b]*Analytical and Testing Center, Beijing Normal University, Beijing 100875, China*

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Abstract—Novel macrocyclic compounds, synthesized and used as chiral solvating agents for phosphinic, phosphonic, and phosphoric acids, are reported in this article. NMR (^{1}H NMR and/or ^{31}P NMR) studies demonstrate that these acids have large nonequivalent chemical shifts in the presence of these macrocyclic compounds. Quantitative analyses of a series of the selected phosphinic acids with different enantiomeric purities show the high accuracy of this method.

1. Introduction

The phosphinic and phosphonic acids, such as phosphinic peptides[1,2] and fosfomycin,[3–5] are chiral organic molecules involved in a wide variety of biological processes. In addition, the chiral phosphoric acids play an important role in organic synthesis as chiral organocatalysts,[6–12] as resolving agents[13–15] and as chiral solvating agents (CSAs).[16] Simple methods for determining the enantiomeric purities of these chiral compounds are in high demand. NMR spectroscopy, employed CSA, might even be considered a facile and environmentally benign tool.[17,18]

Some chiral amines, such as α-phenylethylamine,[19] α-(1-naphthyl)-ethylamine,[19,20] and ephedrine,[19,20] have been used as CSAs for α-aminophosphonic and α-hydroxylphosphonic acids, but the peaks are not often baseline separated, because their chemical shift differences are generally too small. Some better examples[21–23] have been reported by Kafarshi and co-workers, employing cyclodextrins as CSAs for α-aminophosphonic and α-aminophosphinic acids.

Previously, we demonstrated that[24] the macrocyclic compound **1a** is an effective CSA for carboxylic acids. The nonequivalent chemical shifts ($\Delta\Delta\delta$) of enantiomeric acids are up to 0.80 ppm in the presence of **1a** in ^{1}H NMR (500 MHz) spectra. Herein, we report that the macrocyclic compounds **1a** and **1b** (see Fig. 1), using (*S*)-α-(2-naphthyl)-ethylamine instead of (*S*)-α-phenylethylamine as the chiral source to increase the size of the anisotropic group, can be used as chiral solvating agents for the determination of ee values of phosphinic, phosphonic, and phosphoric acids by ^{1}H NMR and/or ^{31}P NMR.

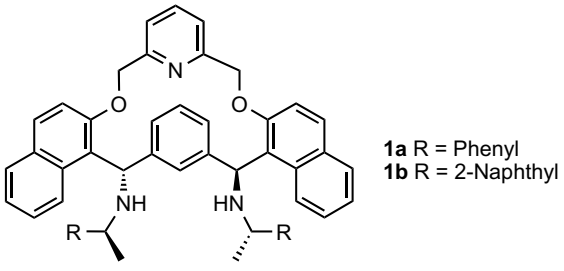

Figure 1. The structures of macrocyclic compounds **1a** and **1b**.

2. Results and discussion

The new macrocyclic compound **1b** was synthesized in a similar manner to **1a**.[24] First, a Mannich reaction was undergone, using (*S*)-α-(2-naphthyl)-ethylamine **2b**, β-naphthol, and *m*-benzenedialdehyde as starting materials, to yield aminonaphthol **3b**. Then, coupling of **3b** with

* Corresponding author. Tel.: +86 13825661820; fax: +86 10 58210397; e-mail: czhang@bnu.edu.cn

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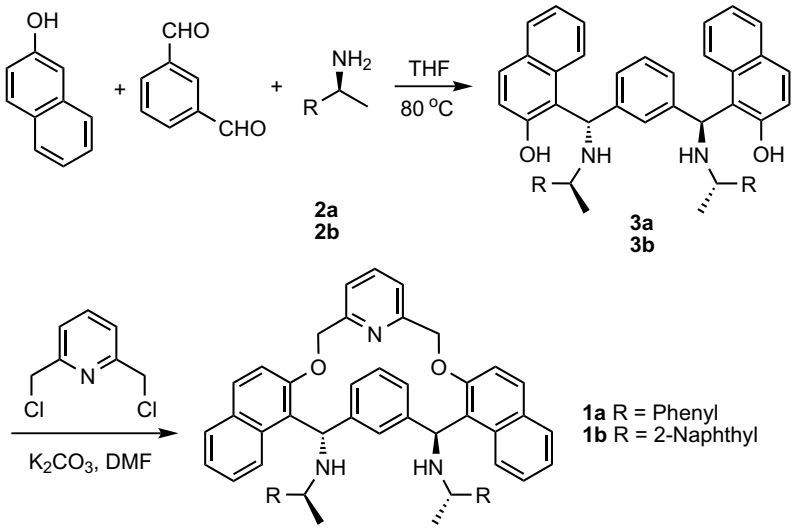


Scheme 1. Synthesis of macrocyclic compounds **1a** and **1b**.

2,6-bischloromethylpyridine leads to the formation of the target molecule **1b** in a high yield (see Scheme 1).

The crystal structure[25] of **1b** indicates that it is a 16-membered ring product, and the absolute configuration is (*S*,*S*,*S*,*S*) (see Fig. 2), which demonstrates that the newly formatted stereogenic centers of **3b** are also of (*S*)-configurations.

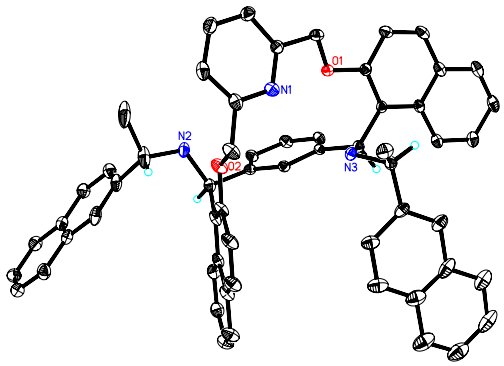


Figure 2. X-ray structure of the new macrocyclic compound **1b**.

We previously reported that in less polar solvents, **1a** exhibited better chiral recognition ability (larger $\Delta\Delta\delta$) toward carboxylic acids.[24] However, for racemic phosphinic acid **4**, the ^{1}H NMR spectra exhibited broad signals in the presence of **1a** in less polar solvents, such as benzene-d_6 and $CDCl_3$. The signals of the two isomers of **4** cannot be split in DMSO-d_6 and a better result was obtained in MeOD-d_4 (see Fig. 3). This can be explained because the strong intermolecular hydrogen bond between **1a** and acid **4** may decrease the rate of exchange between **4** in the free and bound state to the intermediate rate of the ^{1}H NMR timescale, which could lead to spectral broadening. Proper weakening of the hydrogen bond by increasing the polarity of the solvent will give a better result. Finally, we found that in the mixed solvent of $CDCl_3$ and MeOD-d_4 (containing 5% volume of MeOD-d_4), the signals were resolved better and the $\Delta\Delta\delta$ increased to 0.35 ppm (500 MHz) for the α-proton of **4** (10 mM) as 1 equiv of **1a** was added, compared to that in MeOD-d_4 (0.07 ppm).

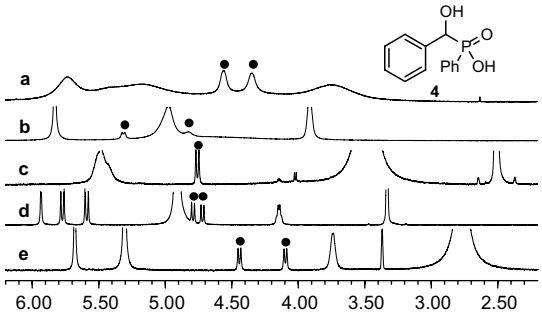


Figure 3. The overlaid ^{1}H NMR spectra of **1a** and **4** in various solvents. The dots indicate the signals of the methine proton of **4**. (a) $CDCl_3$; (b) benzene-d_6; (c) DMSO-d_6; (d) MeOD-d_4; (e) $CDCl_3$/MeOD-d_4 (5%).

The stoichiometry was determined according to Job's method of continuous variation.[26,27] The Job plots of $\Delta\delta X$ versus the mole fraction (X) of (*R*)- or (*S*)-**4** in the mixture were obtained, which all showed maxima at $X = 0.6$ (see Fig. 4). This indicates that **1a** or **1b** forms a '1:1.5' complex with (*R*)-**4** or (*S*)-**4**. Probably the acid interacts with the two aliphatic nitrogen atoms of **1a** or **1b** in a stepwise manner and, a 1:1 complex and a 1:2 complex may exist at the same time under the experimental conditions. However, we have no direct evidences for these complexes.

The large nonequivalent ^{1}H chemical shifts of (*R*)-**4** and (*S*)-**4** in the presence of **1a** inspired us to explore the enantiomeric discriminating ability of **1a** and **1b** with that of other acids. A wide variety of racemic acids, including α-hydroxy phosphinic acids **4**–**8**, *N*-tosyl-α-amino phosphinic acids **9** and **10**, *N*-tosyl-α-amino phosphonic acids **11** and **12**, cyclic phosphoric acids **13** and **14**, were chosen as guests

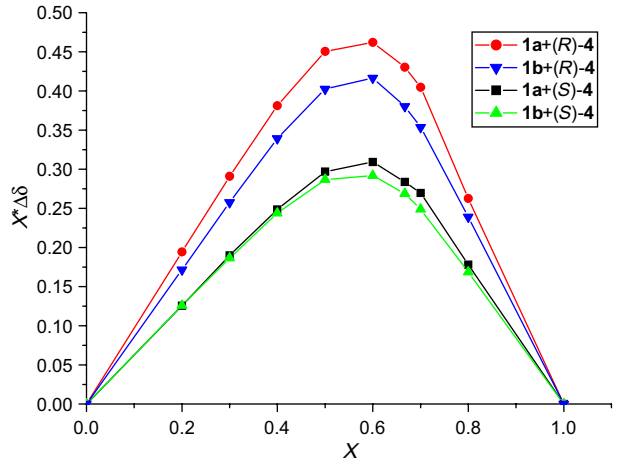


Figure 4. Job plots for the complexation of **1a** and **1b** with (*R*)-**4** and (*S*)-**4** ($X = [\mathbf{1}]/([\mathbf{1}] + [\mathbf{4}])$, $\Delta\delta$ = variation of the chemical shift of the α-proton of **4**).

to screen the potential of **1a** and **1b** as CSAs. The results are summarized in Table 1.

As shown in Table 1, in the presence of **1a** or **1b**, the methine protons (**4**–**7**, **9**–**11**, **14**) and the methyl protons (**8**, **12**) are all split into two peaks due to the different interactions of the two enantiomers of the acids with the CSA. For most of the examples, the ^{1}H chemical shift nonequivalences are large enough to afford baseline resolution for accurate integration, especially for α-hydroxy phosphinic acids and cyclic phosphoric acids; the $\Delta\Delta\delta$ are up to 173.1 Hz (for **4** in the presence of **1a**) and 194.3 Hz (for **14** in the presence of **1b**). For phosphonic acids **11** and **12**, the $\Delta\Delta\delta$ are generally equal to or smaller than the coupling constants, which are not suitable for the determination of the enantiomeric compositions. However, this problem can be solved as ^{31}P NMR spectroscopy was employed. In the ^{31}P NMR spectra, the signals of **11** and **12** were split into two peaks at the baseline in the presence of **1a** or **1b**. For other acids, the ^{31}P NMR tests were also done (see Table 1). The results are quite different from that of the ^{1}H NMR tests. The two enantiomeric isomers of most α-hydroxy phosphinic acids cannot be distinguished in ^{31}P NMR spectra under the experimental conditions, while a baseline separation of the ^{31}P NMR signals was achieved for all the phosphonic and cyclic phosphoric acids. From a comparison of the chemical shift nonequivalences in the ^{1}H and ^{31}P spectra of the chosen acids in the presence of **1a** and **1b**, it appears that the change of the anisotropic group from phenyl to naphthyl does not improve the chiral discrimination. Perhaps the side chain is not a key functional group for the discrimination. Unfortunately, we failed to observe intermolecular NOEs in the 2D NOESY spectra to get even more convincing evidence.

To explore the quantitative analysis ability of **1a** and **1b** as a CSA, six samples containing **4** with 0%, 25%, 45%, 60%, 85% and 90% ee were prepared, and the enantiomeric compositions were determined by the ^{1}H NMR method in the presence of 1 equiv of **1a**. The results (see Fig. 5), which were calculated based on the integrations of the NMR signals, are within ±2% of the actual enantiopurity of the samples and demonstrate the high accuracy of this method.

3. Conclusion

In conclusion, we have discovered macrocyclic compounds **1a** and **1b**, which show excellent ability to discriminate the enantiomers of a broad variety of phosphinic, phosphonic, and phosphoric acids by ^{1}H NMR and ^{31}P NMR spectroscopy. All the acids chosen, except **8**, have a baseline separation of NMR signals in ^{1}H NMR and/or ^{31}P NMR spectra under the experimental conditions.

4. Experimental

4.1. General

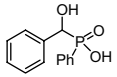
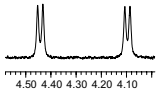
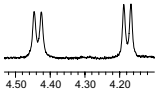
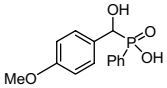
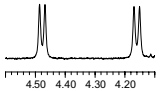
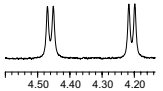
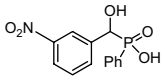
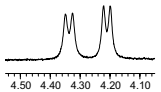
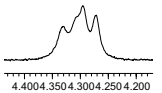
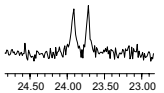
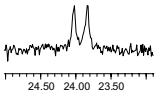
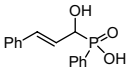
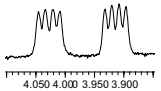
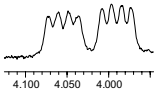
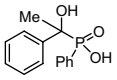
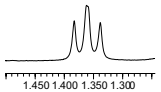
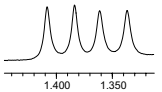
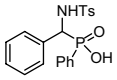
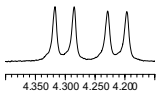
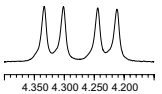
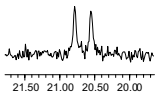
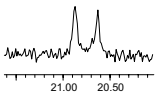
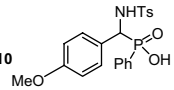
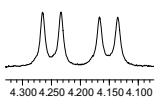
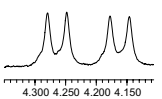
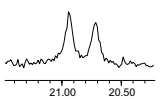
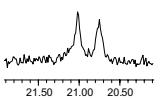
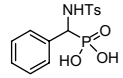
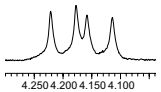
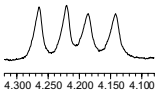
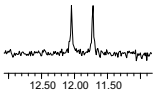
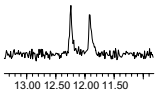
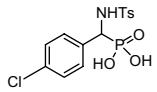
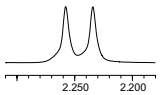
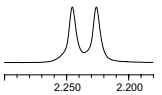
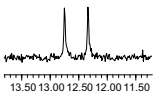
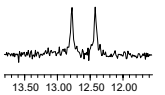
IR spectra were obtained on a Nicolet 360 Avatar IR spectrometer as KBr pellets. NMR spectra were recorded on Avance 500 Bruker spectrometer at 500 MHz for ^{1}H, 125 MHz for ^{13}C and 202 MHz for ^{31}P. Mass spectra were recorded on Trace MS 2000-Mass Spectrometer using the EI technique. Elemental analysis was performed on Vario E1 elemental analyzer. Optical rotations were measured with a Perkin–Elmer Model 343 polarimeter using the sodium D line at 589 nm.

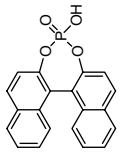
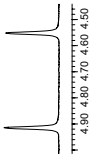
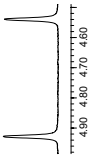
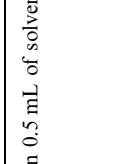
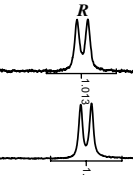
4.2. Synthesis of aminonaphthol 3b

(*S*)-α-(2-Naphthyl)-ethylamine (3.80 g, 22 mmol) in 1 mL THF was added to a solution of *m*-benzenedialdehyde (1.34 g, 10 mmol), 2-naphthol (4.00 g, 27 mmol) in 4 mL of hot THF. The mixture was stirred at 80 °C under a nitrogen atmosphere for 3d and then purified by flash chromatography (acetone–petrol ether = 1:8) affording a crude product, which was purified by flash chromatography once again (ethyl acetate–petrol ether = 1:5) affording **3b** as a white solid (1.83 g, 25.1% yield).

Mp 143–144 °C, $[\alpha]_{D}^{20} = +280.0$ (*c* 0.51, THF). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ: 1.58 (d, $J = 7.9$ Hz, 6H), 2.36 (d, $J = 12.0$ Hz, 2H), 4.02 (dd, $J = 11.0$, 7.0 Hz, 2H), 5.38 (s, 2H), 6.96 (d, $J = 7.6$ Hz, 2H), 7.04 (t, $J = 7.5$ Hz, 2H), 7.05 (t, $J = 7.5$ Hz, 1H), 7.11 (d, $J = 9.0$ Hz, 2H), 7.12 (s, 1H), 7.20 (t, $J = 7.4$ Hz, 2H), 7.27 (d, $J = 9.0$ Hz, 2H), 7.38 (d, $J = 8.5$ Hz, 2H), 7.46 (s, 2H), 7.51 (t, $J = 6.9$ Hz, 2H), 7.55 (t, $J = 6.7$ Hz, 2H), 7.70 (d, $J = 7.9$ Hz, 2H), 7.75 (d, $J = 8.1$ Hz, 2H), 7.78 (d, $J = 8.9$ Hz, 2H), 7.90 (d, $J = 8.1$ Hz, 2H), 7.93 (d, $J = 8.7$ Hz, 2H), 13.50 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ: 23.03, 56.57, 59.41, 112.88, 120.08, 121.14, 122.42, 123.25, 126.08, 126.34, 126.41, 126.54, 126.79, 127.22, 127.76, 127.92, 128.70, 129.27, 129.85, 132.59, 133.04, 133.30, 139.98, 142.04, 157.35; IR (KBr): 3459, 3304, 3044, 1621, 1600, 1270, 1236 cm^{-1}. Elemental Anal. Calcd for $C_{52}H_{44}N_2O_2$: C, 85.68; H, 6.08; N, 3.84. Found: C, 85.31; H, 6.44; N 3.57.

Table 1. Measurements of ^{1}H and ^{31}P chemical shift nonequivalences ($\Delta\Delta\delta$) of the acids in the presence of macrocyclic compounds **1a** or **1b** by ^{1}H NMR (500 MHz) and ^{31}P NMR (202 MHz) in $CDCl_3$/MeOD-d_4 (5%) at 25 °C[a]

Acids	^{1}H NMR[b]				^{31}P NMR			
	1a		**1b**		**1a**		**1b**	
	$\Delta\Delta\delta$ (Hz)	Spectra	$\Delta\Delta\delta$ (Hz)	Spectra	$\Delta\Delta\delta$ (Hz)	Spectra	$\Delta\Delta\delta$ (Hz)	Spectra
4 	173.1		129.2		0.0		0.0	
5 	158.2		126.4		0.0		0.0	
6 	64.1		17.5[d]		39.8		38.7	
7 	56.8		31.8		0.0		0.0	
8 	11.8[c,d]		23.5[c]		0.0		0.0	
9 	44.1		44.8		41.7		49.5	
10 	49.2		51.0		45.4		58.0	
11 	31.6[e]		39.3[e]		65.6[e]		65.4[e]	
12 	11.8[c,e]		9.7[c,e]		83.3[e]		71.8[e]	

13		—[f,g]	181.2		194.3		120.5[g]		136.3[g]	
14		—[f,g]					79.2		106.3	

[a] All samples were prepared by mixing 1 equiv of **1a** or **1b** and 1 equiv of acids in NMR tubes, the final concentrations were 10 mM in 0.5 mL of solvent.
[b] ^{1}H chemical shift nonequivalences of the methine protons on the chiral centers of the acids unless otherwise indicated.
[c] ^{1}H chemical shift nonequivalences of the methyl protons of the acid.
[d] The ^{1}H chemical shift nonequivalences are similar or equal to the coupling constants of the protons.
[e] Using $CDCl_3$/MeOD-d_4 (10%) as the solvent.
[f] The signals of the acid overlap with **1a** and **1b**.
[g] 0.5 equiv of **1a** or **1b** was used.

Figure 5. Determination of the enantiomeric purity of (α-hydroxybenzyl)phenylphosphinic acid **4** (ee% = R% − S%), the (R) and (S) in the spectra stand for the α-proton of the corresponding isomer of (α-hydroxybenzyl)phenylphosphinic acid **4**.

4.3. Synthesis of macrocyclic compound 1b

A mixture of 1.46 g (2 mmol) aminonaphthol **3b**, 0.35 g (2 mmol) 2,6-dichloromethylpyridine and 2.76 g (20 mmol) K_2CO_3 in 40 mL dry DMF was stirred at room temperature for 36 h. Then it was poured into 100 mL water and extracted with toluene (20 mL × 3), washed with water (20 mL) and brine (20 mL). The organic phase was dried with Na_2SO_4, filtrated, and concentrated. The residue was recrystallized with dichloromethylene and acetone affording **1b** as colorless crystals (1.44 g, 86.7%).

Mp 172–174 °C, $[\alpha]_D^{20} = +19.6$ (c 0.23, THF). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ: 1.26 (d, $J = 5.4$ Hz, 6H), 3.76 (q, $J = 6.2$ Hz, 2H), 4.37 (d, $J = 11.4$ Hz, 2H), 5.23 (d, $J = 8.5$ Hz, 2H), 5.30 (d, $J = 8.5$ Hz, 2H), 5.49 (d, $J = 11.9$ Hz, 2H), 6.82 (d, $J = 7.0$ Hz, 2H), 6.87 (d, $J = 7.2$ Hz, 1H), 7.19 (t, $J = 7.2$ Hz, 2H), 7.22–7.41 (stack, 14H), 7.52 (d, $J = 7.7$ Hz, 2H), 7.56 (d, $J = 7.5$ Hz, 2H), 7.60 (d, $J = 7.4$ Hz, 2H), 7.73–7.64 (m, 1H), 7.77 (d, $J = 7.5$ Hz, 2H), 7.92 (d, $J = 8.0$ Hz, 2H), 7.98 (d, $J = 8.1$ Hz, 2H), 8.57 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ: 24.97, 55.65, 57.11, 71.54, 114.56, 121.57, 123.07, 123.52, 125.07, 125.83, 126.57, 127.15, 127.46, 127.69, 127.87, 128.55, 129.04, 129.50, 132.79, 133.38, 134.04, 137.19, 143.13, 144.03, 155.0, 155.68; IR (KBr): 3455, 3051, 1621, 1595, 1260, 1239 cm^{-1}; MS (EI): 831 (M^+). Elemental Anal. Calcd for $C_{59}H_{49}N_3O_2$: C, 85.17; H, 5.94; N, 5.05. Found: C, 84.81; H, 5.78; N, 4.86.

4.4. Resolution of (α-hydroxybenzyl)phenylphosphinic acid 4

A mixture of 7.44 g (30 mmol) of (α-hydroxybenzyl)phenylphosphinic acid **4**, 5.28 g (18 mmol) of cinchonidine, 45 mL of EtOH and 45 mL of H_2O was heated until a clear

solution took place. The heating mantle is removed, and the solution is allowed to cool to room temperature. After 24 h the product is collected and washed with 20 mL of EtOH–H_2O (1:1) to give 4.65 g of salt with $[\alpha]_D^{20} = -46.2$ (*c* 0.71, CH_3OH).

Then 4 g of the salt is stirred with 20 mL of EtOH–H_2O (1:1) and 3 mL of concentrated hydrochloric acid, then filtered, washed with water, and dried to give 1.32 g of (*S*)-**4** with $[\alpha]_D^{20} = +56.5$ (*c* 0.75, CH_3OH), 92% ee. Recrystallization from ethanol (1 g/10 mL) gave 0.85 g of enantiomerically pure (*S*)-(+)-**4**. $[\alpha]_D^{20} = +61.3$ (*c* 0.61, CH_3OH).

The mother liquid was acidified with 10 mL of concentrated hydrochloride acid to give 3.13 g of (*R*)-(−)-**4** with $[\alpha]_D^{20} = -34.6$ (*c* 0.88, CH_3OH), 56% ee. Recrystallization from ethanol (1 g/10 mL) three times gave 0.78 g of enantiomerically pure (*R*)-(−)-**4** $[\alpha]_D^{20} = -61.5$ (*c* 1.1, CH_3OH).

The absolute configuration of (*S*)-(+)-**4**, $[\alpha]_D^{20} = +61.3$ (*c* 0.61, CH_3OH), has been reported by Cai et al.[28] determined by X-ray diffraction. ^1H NMR method using **1a** as CSA also affirmed the enantiopurities of the resolved products.

4.5. Determination of stoichiometry by ^1H NMR titrations (Job plots)

The host **1a** or **1b** and guest (*R*)- or (*S*)-(α-hydroxybenzyl)phenylphosphinic acid **4** were separately dissolved in $CDCl_3/CD_3OD$-5% with a concentration of 10 mM. These solutions were distributed among 9 NMR tubs, with various amounts of host **1a** or **1b** and guest (*R*)- or (*S*)-(α-hydroxybenzyl)phenylphosphinic acid **4**, and the total concentration of host and guest was 10 mM. The ^1H NMR spectrum of each sample was recorded on a 500 MHz spectrometer. All recorded Job plots were found to exhibit maxima at 0.6. This indicates that **1a** and **1b** forms a '1:1.5' complex with the (α-hydroxybenzyl)phenylphosphinic acid **4**.

4.6. Study of the discrimination ability of 1a and 1b toward guests 4–14

The samples were prepared by adding 1 equiv of **1a** or **1b** to a $CDCl_3/CD_3OD$-5% solution of the guests (10 mM), for guest **13**, 0.5 equiv of **1a** or **1b** was used, and for guests **11** and **12**, $CDCl_3/CD_3OD$-10% was used as a solvent. The ^1H NMR and ^{31}P NMR spectra were registered at room temperature using a 500 MHz instrument.

4.7. Evaluation of the accuracy of this determining method

To evaluate the accuracy of our determining method, we prepared six samples containing (*R*)-(α-hydroxybenzyl)phenylphosphinic acid **4** with 0%, 25%, 45%, 60%, 85% and 90% ee, respectively (all samples were prepared by adding 1 equiv (not exactly) of host **1a** in the solutions of (α-hydroxybenzyl)phenylphosphinic acid **4** (10 mM in $CDCl_3/CD_3OD$-5%)), and determined their enantiomeric purities in the presence of host **1a** by using ^1H NMR method. The results, which were calculated based on the integrations of the NMR signals, are shown in Figure 5.

Acknowledgment

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25. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary

publication numbers CCDC 652314. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].
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