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Novel NMR chiral solvating agents derived from (1*R*,2*R*)-diaminocyclohexane: synthesis and enantiodiscrimination for chiral carboxylic acids

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Abstract—A series of new compounds, (1*R*,2*R*)-1-(1′,8′-naphthalimide)-2-aminocyclohexane **1** and its 4′-derivatives **2** and **3** derived from (1*R*,2*R*)-1,2-diaminocyclohexane have been synthesized conveniently and efficiently. ^{1}H NMR spectroscopy was employed to investigate their enantiodiscriminating ability. Compared with α-phenylethylamine, a commercially available chiral solvating agent (CSA), these compounds exhibited better enantiodiscriminating ability toward the chiral carboxylic acids we had chosen, distinguishing them as promising and practical CSAs.

1. Introduction

Chiral carboxylic acids are basic building blocks of many natural products, biological molecules, and drugs.[1–3] Although significant progress has been made for the asymmetric synthesis of chiral carboxylic acids, the search for highly enantioselective and practical catalysts has been continuously a very interesting topic.[1–6] The application of high throughput combinatorial techniques has greatly facilitated research in this field,[6] hence it has given rise to an increasing demand for rapid and accurate methods to measure the enantiomeric composition of chiral carboxylic acids. Apart from other analytical methods, such as HPLC[7] and GC[8] on chiral stationary phases, the use of chiral solvating agents (CSAs)[9–11] for NMR spectroscopy is a satisfactory and convenient method to meet this demand. The method only needs the preparation of a mixture of CSA with the chiral analyte in a suitable deuterated solvent and the recording of a routine NMR spectrum. Comparing with HPLC and GC, this method has another advantage that it can provide direct structural and dynamic information of host–guest complexes in solution.

In contrast to the CSAs for chiral amines and alcohols, there are less reports about CSAs for chiral carboxylic acids.[10–12] In particular, CSAs that can lead to clear baseline separation of the multiplet of the probe group in two enantiomers are rare.

In our previous work, we have already synthesized some chiral macrocyclic polyamines derived from natural amino acids and tartaric acid.[13–16] ^{1}H NMR spectroscopy was employed to investigate their enantiodiscriminating ability.[17,18] The results revealed that all these compounds exhibited good enantiodiscriminating ability toward the chiral carboxylic acids we had chosen.

Recently we have made another approach to obtain more effective and practically applicable CSAs for chiral carboxylic acids. A class of compounds (1*R*,2*R*)-1-(1′,8′-naphthalimide)- 2-aminocyclohexane **1** and its 4′-derivatives **2** and **3** derived from (1*R*,2*R*)-diaminocyclohexane (DACH) was designed and synthesized. The structure of **1**–**3** involves an amino group and a large aromatic system, attached to two chiral centers of (1*R*,2*R*)-diaminocyclohexane, respectively. It is expected that the formation of host–guest diastereomeric complexes,[19,20] will be achieved mainly through interaction of the amino group and the carboxyl group in the chiral carboxylic acid, but the π–π interaction may also play some important role if the chiral carboxylic acid also contains an aromatic moiety. The most important role of the aromatic systems is that its anisotropic influence may cause the chemical shift non-equivalences ($\Delta\Delta\delta$) of the

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probe groups of the two enantiomers of the chiral guests. The non-equivalence ($\Delta\Delta\delta$) is the difference of the chemical shifts of corresponding protons of two enantiomers of the guests in the presence of the CSAs. The cyclohexane block in the designed host molecules can stabilize the position of two substituted groups on the chiral centers, thus the fixed conformation is expected to benefit the formation of diastereomeric host–guest complexes, and improve the enantioselective recognition ability.

2. Results and discussion

Compounds **1**–**3** (Scheme 1) were synthesized by the reaction of (1*R*,2*R*)-DACH with the appropriate 1,8-naphthalic anhydride and characterized by MS, ^{1}H NMR, ^{13}C NMR, IR, and EA. The synthetic procedure was simple and convenient, and the yields for **1**–**3** were 93.5%, 95.0%, and 92.5% based on DACH, respectively.

The crystal structure of compound **1** was obtained via X-ray single crystal structure analysis.[21] The molecular structure is shown in Figure 1, which is consistent with the stable conformation we expected. It is noteworthy that the torsion angle of H–C13–N1–C11 is approximately 178°, which means that the naphthalene plane is almost parallel to the C13–H bond, also indicating that the naphthalene plane is perpendicular to the chair-like cyclohexane plane.

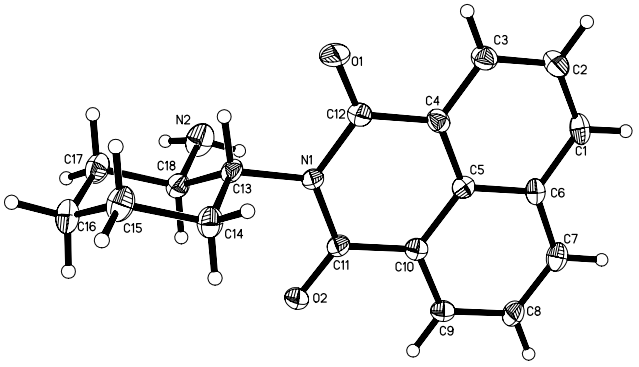


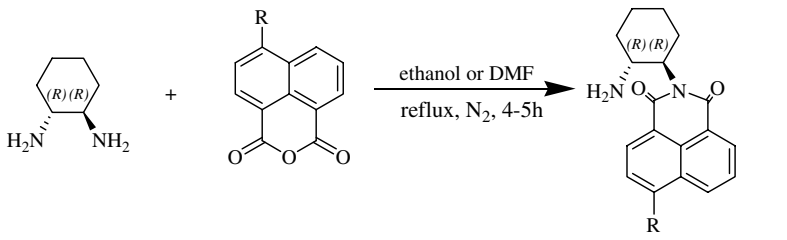
Figure 1. ORTEP drawing of the molecular structure of **1**.

^{1}H NMR spectroscopy was utilized to investigate the enantiodiscriminating ability of **1**–**3**, and the guests include racemic compounds of α-methoxyphenylacetic acid (MPAA), dibenzoyltartaric acid (DBTA), and some chiral drugs such as naproxen, ibuprofen, and ketoprofen. The N-derivatives of some amino acids, including phthalyl alanine, phthalyl leucine, *p*-tolylsulfonyl alanine (Ts-alanine), *p*-tolylsulfonyl valine (Ts-valine), *p*-nitrobenzenesulfonyl alanine (*p*-Nbs-alanine), and *o*-nitrobenzenesulfonyl alanine (*o*-Nbs-alanine), were also synthesized as guests to further investigate the relationship of the guest structure with recognition ability. To evaluate the enantiodiscriminating capabilities of **1**–**3**, (*S*)-α-phenylethylamine (PEA), a commercially available CSA,[11] was also utilized as the reference CSA to recognize those guests we chose.

Table 1 summarizes the chemical shift non-equivalences ($\Delta\Delta\delta$) of CH_3 and CH in the chiral carbon (or CH_3 in isopropyl group) of the chiral carboxylic acid guests in the presence of 1 equiv of **1**–**3** or PEA, respectively. From Table 1 we can see that any of compounds **1**–**3** has led to a clear baseline separation of the methine proton quartets of phthalyl alanine, *p*-tolylsulfonyl alanine (Ts-alanine), *p*-tolylsulfonyl valine (Ts-valine), *p*-nitrobenzenesulfonyl alanine (*p*-Nbs-alanine), and *o*-nitrobenzenesulfonyl alanine (*o*-Nbs-alanine). The $\Delta\Delta\delta$ of the methine proton of Ts-alanine was 58.8 Hz in the presence of compound **1** (see Fig. 2). The largest $\Delta\Delta\delta$ of the methine proton was up to 104.1 Hz with compound **2** as CSA. We further noticed that only compound **3** could enantiodiscriminate DBTA and phthalyl leucine.

Compounds **1**–**3** also show good enantiodiscriminating ability for some chiral drugs such as naproxen, ibuprofen, and ketoprofen. As for the $\Delta\Delta\delta$s of α-CH_3 of these guests, **1**–**3** could lead to the larger $\Delta\Delta\delta$s than PEA. Particularly, when ketoprofen was chosen as the guest, **1**–**3** could lead to clear separation of the methyl proton doublet peaks, based on which the enantiomeric composition could be determined (see Fig. 3). Although the $\Delta\Delta\delta$s of the CH of these guests were larger in the presence of PEA than in the presence of **1**–**3**, clear baseline separation of the proton signal still could not observed by using PEA.

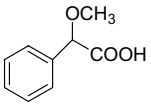
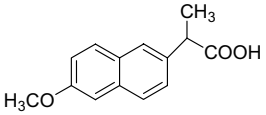
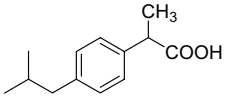
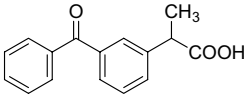
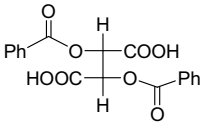
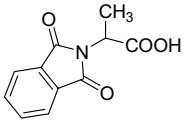
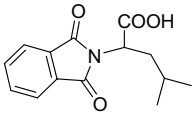
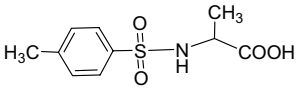
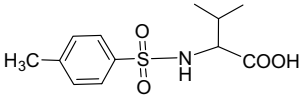
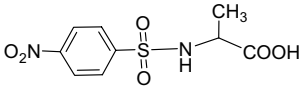
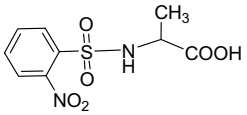
From the data in Table 1, it is clear that compared with PEA, **1**–**3** exhibited better chiral recognition ability (larger $\Delta\Delta\delta$) toward the derivatives of amino acids than the other guests in this work. For example, in the case of *p*-Nbs-alanine, PEA showed no enantiodiscrimination while **1**–**3** exhibited good enantioselective ability, the $\Delta\Delta\delta$s of CH



1 *(R,R)*- R=H
2 *(R,R)*- R=Br
3 *(R,R)*- R=$N(CH_3)_2$

Scheme 1. The synthetic route to **1**–**3**.

Table 1. Chemical shift non-equivalences ($\Delta\Delta\delta$, 300 MHz) for 1:1 diastereoisomeric complexes of **1**–**3** and PEA with racemic guests in $CDCl_3$ at 25 °C

Guests			$\Delta\Delta\delta$ (Hz)[b]			
			1	**2**	**3**	PEA
	MPAA	CH	15.3(*S*)	16.5(*S*)	47.1(*S*)	37.2
	Naproxen	CH CH_3	6.9 13.5	7.5 7.2	6.9 11.4	6.3 —[a]
	Ibuprofen	CH CH_3	6.6 11.7	4.5 6.6	3.0 8.7	18.6 6.9
	Ketoprofen	CH CH_3	7.2 15.9	4.5 18.0	7.2 25.2	18.6 3.3
	DBTA	CH	0.0	0.0	38.1(D)[c]	30.0
	Phthalyl alanine	CH CH_3	62.4(D) 10.2(D)	43.2(D) 0.0	38.4(D) 3.9(D)	17.7 —[a]
	Phthalyl leucine	CH	—[a]	—[a]	31.2(D)	3.9
	Ts-alanine	CH CH_3	58.8(D) 14.7(D)	104.1(D) 44.4(D)	—[a] 15.6(D)	6.3 3.0
	Ts-valine	CH CH_3	46.8(D) 45.6(L)	42.0(D) 46.5(L)	—[a] 35.7(L)	0.0 0.0
	*p*-Nbs alanine	CH CH_3	30.0 17.7	36.6 5.7	36.0 18.0	0.0 0.0
	*o*-Nbs alanine	CH CH_3	60.9 15.6	62.7 7.8	42.3 13.5	6.6 0.0

[a] The peaks of hosts overlapped with the peaks of the probe groups of guests.
[b] In brackets: configuration of the enantiomer corresponding to the signal at higher field.
[c] The mole ratio of CSA and guest is 2:1.

being 30.0, 36.6, and 36.0 Hz, for **1**–**3**, respectively. The results imply that the molecular structure of **1**–**3** fits the above guests better than that of PEA does. According to the crystallographic data for the structure of **1** and the data for PEA from a computer simulation (Hyperchem 7.0), the distance (4.5–7.0 Å) between the amino group and the aryl group in **1** is larger than that (2.4–5.0 Å) in PEA. It means that the larger distance between the amino group and the aryl group in **1**–**3** is more suitable to match the distance of the carboxyl group and the aryl group in any of the

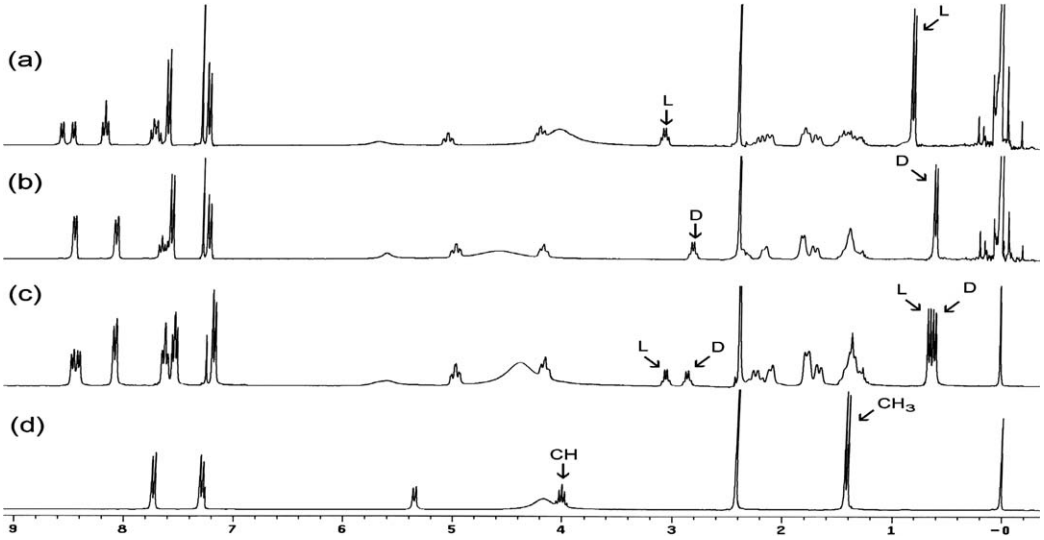


Figure 2. ^{1}H NMR spectra of equimolar mixtures (20 mM each) of Ts-alanine/**1**: (a) Ts-L-alanine and **1**; (b) Ts-D-alanine and **1**; (c) Ts-L/D-alanine and **1**; (d) Ts-L/D-alanine without **1**.

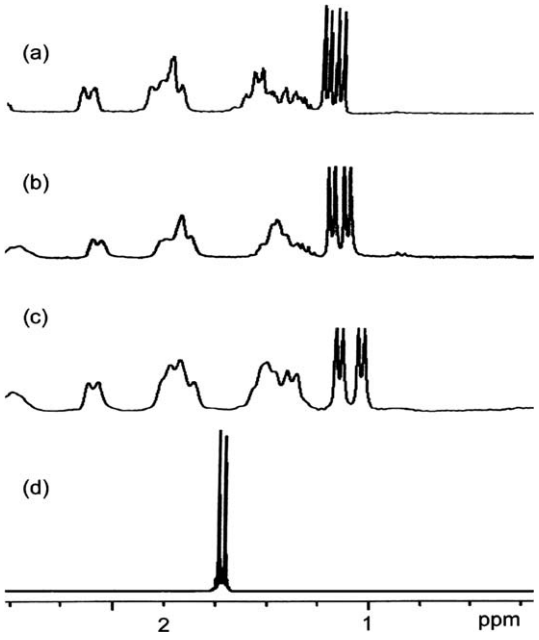


Figure 3. ^{1}H NMR (300 Hz, $CDCl_3$, 25 °C, ppm referred to TMS as external standard) spectral regions corresponding to CH_3 protons of racemic ketoprofen (20 mM): (a) equimolar mixture **1**/racemic ketoprofen; (b) equimolar mixture **2**/racemic ketoprofen; (c) equimolar mixture **3**/racemic ketoprofen; (d) free racemic ketoprofen.

above derivatives of amino acid, so it is favorable to the formation of the instantaneous complexes of **1**–**3** with these guests.

The ^{1}H NMR spectra of **1**–**3** with several enantiomerically pure guests in a variety of ratios in $CDCl_3$ at a constant total concentration of 3.0×10^{-3} M were obtained. The stoichiometric ratio of the host–guest complex was determined according to Job's method of continuous variations.[22] The Job plots of **1** with (*R*)-MPAA and (*S*)-MPAA were illustrated in Figure 4, showing a minimum of $\Delta\delta X$ at $X = 0.5$, which indicates that a 1:1 instantaneous complex was formed. The Job plots we have got indicated that **1**–**3** form 1:1 instantaneous complexes with all these enantiomerically pure guests, respectively.

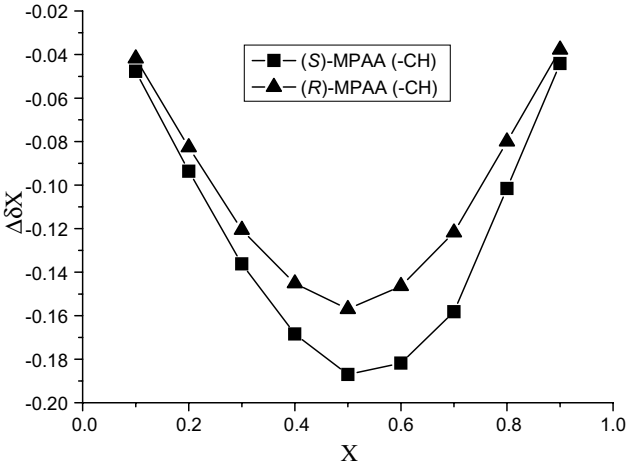


Figure 4. Job plots of **1** with (*R*)- and (*S*)-MPAA [X = molar fraction of MPAA, $\Delta\delta$ = chemical shift change of the methine of (*R*)- and (*S*)-MPAA].

We also performed the titration curves of **1**–**3** with these enantiomerically pure guests, respectively. The association constants with **1**–**3** were determined from the titration curves by a nonlinear least-squares fitting method (Table 2).[22] It showed that the (*S*)-MPAA was more strongly bound to **1**–**3** than the (*R*)-enantiomer was, and the D-enantiomer of Ts-alanine was more strongly bound to **1** and **3** than the L-enantiomer was. It is clear that the association constants of **1**–**3** to Ts-alanine are about 1 order of magnitude higher than those to MPAA, showing that the structure of **1**–**3** matched Ts-alanine much better than that of MPAA.

Table 2. Association constants K_a (mol/l)$^{-1}$of **1**–**3** with chiral carboxylic acids

Entry	CSAs	Guests	K_a (mol/l)$^{-1}$	K_a(*S* or D)/ K_a(*R* or L)
1	**1**	(*R*)-MPAA	$(1.6 \pm 0.1) \times 10^3$	2.75
2	**1**	(*S*)-MPAA	$(4.4 \pm 1.8) \times 10^3$	
3	**1**	Ts-D-Alanine	$(2.2 \pm 1.1) \times 10^4$	1.22
4	**1**	Ts-L-Alanine	$(1.8 \pm 0.5) \times 10^4$	
5	**2**	(*R*)-MPAA	$(1.6 \pm 0.1) \times 10^3$	1.81
6	**2**	(*S*)-MPAA	$(2.9 \pm 0.6) \times 10^3$	
7	**2**	Ts-D-Alanine	$(1.4 \pm 0.4) \times 10^4$	0.78
8	**2**	Ts-L-Alanine	$(1.8 \pm 0.6) \times 10^4$	
9	**3**	(*R*)-MPAA	$(2.0 \pm 0.3) \times 10^3$	2.40
10	**3**	(*S*)-MPAA	$(4.8 \pm 1.3) \times 10^3$	
11	**3**	Ts-D-Alanine	$(2.1 \pm 1.1) \times 10^4$	1.50
12	**3**	Ts-L-Alanine	$(1.4 \pm 0.8) \times 10^4$	
13	**3**	D-DBTA	$(1.6 \pm 0.3) \times 10^2$	0.76
14	**3**	L-DBTA	$(2.1 \pm 0.3) \times 10^2$	

3. Conclusion

Compounds **1**–**3**, which have a unique structure, were designed and synthesized conveniently and efficiently. The unique structure contains a cyclohexane block, making the substituent groups on the two chiral centers adopt a fixed dimensional position and constant distance. ^{1}H NMR spectroscopy was employed to investigate their enantiodiscriminating ability. Compared to α-phenylethylamine, a commercially available chiral solvating agent (CSA), all these compounds exhibited better enantiodiscriminating ability toward the chiral carboxylic acids studied in this work. The excellent enantioselectivity, simple synthetic procedure, and the high synthetic yields make them promising and practical CSAs.

4. Experimental

4.1. General methods

NMR spectra were recorded in $CDCl_3$ on Varian Mercury VX300 FT-NMR spectrometer (^{1}H at 300 MHz and ^{13}C at 75 MHz) operating at 298 K. IR spectra were performed on a Nicolet 170SX FT-IR spectrometer in KBr pellets. Mass spectra were recorded on a VJ-ZAB-3F-Mass Spectrometer using the FAB technique. The elemental analysis was performed on a Calo-Erba elemental analyzer (Model 1106). Optical rotations were measured with a Perkin Elmer polarimeter (Model 341) using the sodium D line at 589 nm.

(1*R*,2*R*)-1,2-Diaminocyclohexane (DACH) is available by resolution of the crude commercial racemate with tartaric acid.[23]

4.2. Preparation of 1–3

4.2.1. (1*R*,2*R*)-1-(1′,8′-Naphthalimide)-2-aminocyclohexane 1. To a solution of 1,8-naphthalic anhydride (3.96 g, 0.020 mol) in DMF (150 ml), refluxed under a nitrogen atmosphere, was added the solution of DACH (2.74 g, 0.024 mol) in DMF (50 ml). Refluxing was continued for 4 h. Then the solution was decanted into cold water (1400 ml) and left overnight. Then, the precipitates were collected and then recrystallized twice from ethanol to give pale yellow needle crystal **1**, yield 93.5%, mp: 230–233 °C; $[\alpha]_D^{20} = +2.3$ (*c* 2.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 7.75$–8.55 (m, 6H, 6Ar*H*), 4.72–4.81 (td, 1H, $^3J_{ae} = 3.3$ Hz, $^3J_{aa} = 10.8$ Hz, C*H*N), 3.71–3.80 (td, 1H, $^3J_{ae} = 3.6$ Hz, $^3J_{aa} = 11.1$ Hz, C*H*NH$_2$), 1.19–2.54 (m, 10H, 4CH_2, 2N*H*H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 165.7$, 164.6, 133.8, 131.7, 131.0, 128.5, 127.1, 123.5, 122.8, 61.2, 50.7, 37.6, 29.0, 26.5, 25.8; MS: *m*/*z* 295 (M^++1, 100%); Anal. Calcd (%) for $C_{18}H_{18}N_2O_2$: C, 73.45; N, 9.52; H, 6.16. Found (%): C, 73.14; N, 9.23; H, 6.21. IR (KBr, cm^{-1}): *v* 3436, 2933, 2859, 1690, 1657, 1625, 1588, 1342, 1238, 777.

4.2.2. (1*R*,2*R*)-1-(4′-Bromo-1′,8′-naphthalimide)-2-aminocyclohexane 2. To a solution of 4-bromo-1,8-naphthalic anhydride (2.77 g, 0.010 mol) in ethanol/DMF (1:2) (90 ml), refluxed under a nitrogen atmosphere, was added the solution of DACH (1.37 g, 0.012 mol) in ethanol/DMF (1:2) (30 ml). Refluxing was continued for 5 h. Then the solution was decanted into cold water (1000 ml) and left overnight. Then, the precipitates were collected and then recrystallized twice from ethanol to give pale yellow solid **2**, yield 95.0%, mp: 211–213 °C; $[\alpha]_D^{20} = -12.8$ (*c* 0.065, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 7.78$–8.59 (m, 5H, 5Ar*H*), 4.69–4.77 (td, 1H, $^3J_{ae} = 3.3$ Hz, $^3J_{aa} = 11.1$ Hz, C*H*N), 3.68–3.77 (td, 1H, $^3J_{ae} = 3.9$ Hz, $^3J_{aa} = 10.8$ Hz, C*H*NH$_2$), 1.20–2.53 (m, 10H, 4CH_2, 2N*H*H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 165.1$, 164.0, 133.1, 132.6, 131.9, 131.2, 130.6, 130.1, 129.3, 128.3, 123.3, 122.8, 61.3, 50.7, 37.8, 29.0, 26.5, 25.8; MS: *m*/*z* 375 (M^++1 100%); Anal. Calcd (%) for $C_{18}H_{17}BrN_2O_2$: C, 57.92; N, 7.51; H, 4.59. Found (%): C, 58.37; N, 7.66; H, 4.61. IR (KBr, cm^{-1}): *v* 3436, 3089, 3070, 2932, 2854, 1700, 1661, 1587, 1405, 1344, 1237, 1186, 780.

4.2.3. (1*R*,2*R*)-1-[4′-(*N*,*N*-Dimethylamino)-1′,8′-naphthalimide]-2-aminocyclohexane 3. 4-Bromo-1,8-naphthalic anhydride was converted to 4-*N*,*N*-dimethylamino-1,8-naphthalic anhydride as described in the literature.[24] To a solution of 4-*N*,*N*-dimethylamino-1,8-naphthalic anhydride (1.20 g, 0.0050 mol) in ethanol (100 ml), refluxed under a nitrogen atmosphere, was added the solution of DACH (0.68 g, 0.0060 mol) in ethanol (30 ml). Refluxing was continued for 5 h. Then the solution was decanted into cold water (500 ml) and left overnight. Then, the precipitates were collected and then recrystallized twice from ethanol to give yellow needle crystal **3**, yield 92.5%, mp: 183–184 °C; $[\alpha]_D^{20} = -16.0$ (*c* 0.025, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 7.10$–8.55 (m, 5H, 5Ar*H*), 4.73–4.80 (t, 1H, $^3J = 9.9$ Hz, C*H*N), 3.73–3.82 (td, 1H, $^3J_{ae} = 3.9$ Hz, $^3J_{aa} = 10.2$ Hz, C*H*NH$_2$), 3.09 (s, 6H, 2CH_3) 1.19–2.54 (m, 10H, 4CH_2, 2N*H*H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 166.2$, 165.5, 133.3, 132.5, 131.6, 131.2, 130.9, 130.6, 125.3, 125.1, 113.5, 60.9, 50.7, 45.1, 37.3, 29.0, 26.5, 25.8; MS: *m*/*z* 338 (M^++1, 100%); Anal. Calcd (%) for $C_{20}H_{23}N_3O_2$: C, 71.19; N, 12.45; H, 6.87. Found (%): C, 70.83; N, 12.41; H, 7.15. IR (KBr,

cm^{-1}): ν 3381, 3078, 2926, 2852, 2798, 1690, 1643, 1587, 1389, 1359, 1241, 1132, 1082, 1002, 784, 760.

4.3. NMR shift experiments

Samples for analysis were obtained by mixing equimolar amounts of **1**–**3** with the guests in $CDCl_3$, making the concentrations of the hosts (or guests) normally 20 mM.

4.4. Evaluation of the stoichiometric ratio of the host–guest complex (Job plots)

The stoichiometric ratio of the host–guest complex was determined according to Job's method of continuous variations. Equimolar amounts of host and guest compounds were dissolved in $CDCl_3$. These solutions were distributed among nine NMR tubes, with the molar fractions X of host and guest in the resulting solutions increasing (or decreased) from 0.1 to 0.9 (and vice versa). The complexation induced shifts ($\Delta\delta$) were multiplied by X and plotted against X itself (Job plot).

4.5. NMR host–guest titrations

The resulting solution of the guest compound, dissolved in the appropriate amount of solvent with a concentration of 3.0×10^{-3} M, was evenly distributed among 10 NMR tubes. The host compound was also dissolved in the appropriate amount of solvent and added in increasing amounts to the NMR tubes, so that the ratio of the host to the guest of the 10 tubes was 0, 0.13, 0.40, 0.80, 1.33, 2.00, 2.67, 4.00, 5.33, 8.00, respectively. K_a was calculated by a nonlinear least-squares fitting method from the observed $\Delta\delta$ values and the respective host and guest concentrations.

A representative example is given below: compound **1** versus (*S*)-MPAA in $CDCl_3$. Weighed amounts: compound **1**: 29.40 mg in 1.00 ml; (*S*)-MPAA: 4.15 mg in 5.00 ml. $K_a(S)$ $[M^{-1}] = (4.4 \pm 1.8) \times 10^3$.

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21. Crystallographic data for the structure of compound **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 267790. 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]. Crystal data of **1**: $C_{18}H_{18}N_2O_2$, $M = 294.35$, orthorhombic, space group $P2(1)2(1)2(1)$, $a = 7.2900(15)$ Å, $b = 16.646(3)$ Å, $c = 24.201(5)$ Å, $V = 2936.8(10)$ Å^3, $D = 1.331$ g/cm^3, $\mu = 0.088$ mm^{-1}, $F(000) = 1240$, $Z = 8$, $R_1 = 0.0571$, $\omega R_2 = 0.1056$. Data collection for the crystal structure determination was carried out on a R-AXIS-IV diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) at a temperature of 291 (2) °C. Of the 7048 reflections measured in the $2.15 \leqslant \theta \leqslant 23.50°$ range, 4231 reflections were unique and 2717 reflections with $I > 2\sigma(I)$ were used in structure solution and refinement. $R_{int} = 0.0776$. $w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$. The structure was solved by direct method using SHELXL-97. All of the non-hydrogen atoms were refined by full-matrix least-squares methods using anisotropic displacement parameters.
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