

C₂-Symmetric chiral diamine ligands for enantiomeric recognition of amino acid esters and mandelic acid by proton NMR titration method

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Received: 25.07.2012 • Accepted: 11.03.2013 • Published Online: 10.06.2013 • Printed: 08.07.2013

Abstract: Two novel C₂-symmetric chiral diamines containing α -phenylethyl and α -(1-naphthyl)ethyl chiral subunits were prepared with quantitative yields. Enantiomeric recognition properties of these simple structured diamine ligands towards D- and L-amino acid esters and D- and L-mandelic acid were examined by the ¹H NMR titration method. These ligands exhibited strong complexation (with K_f up to 2481 M⁻¹) and good enantioselectivity (up to K_L/K_D = 4.08) towards the mandelic acid enantiomers. The results show that simple structured and easily accessible acyclic C₂-symmetrical compounds can also be used for enantiomeric recognition of racemic amino acids and mandelic acid in addition to complex molecules such as crown ethers and other cyclic molecules.

Key words: Enantiomeric recognition, C₂ symmetric, chiral diamines, amino acids, mandelic acid, NMR titration

1. Introduction

Amino acids and their derivatives are chiral organic molecules involved in a wide variety of biological processes. They play an important role in the area of design and preparation of pharmaceuticals, as they are part of the synthesis process in the production of drug intermediates and protein-based drugs. Therefore, the study of the enantiomeric recognition of these compounds is of particular significance for understanding the interactions between biological molecules and the design of asymmetric catalysis systems, new pharmaceutical agents, and separation materials.¹

Molecular recognition is a fundamental property of various natural systems, based on the ability of a molecular receptor to form a complex preferentially with one of the enantiomers of a chiral molecule by noncovalent interaction such as hydrogen bonding, electrostatic interaction, and hydrophobic interaction.^{2–5} Therefore, the chemical or biological activity of a compound often depends upon its stereochemistry in living organisms. The study of synthetic model systems could contribute new perspectives for the development of pharmaceuticals, enantioselective sensors, catalysts, and other molecular devices.⁶

The rational design of receptors with a chiral recognition ability for chiral amino acids and carboxylic acids is still receiving considerable attention, although numerous chiral macrocyclic receptors have been developed for amino acids and related compounds.^{7–13} In particular, C₂-symmetric ligands have been widely used in chiral recognition and asymmetric synthesis.^{14,15} The C₂-symmetry is of great interest to the organic chemist as it

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opens up the possibility of the parallel synthesis of multiple parts of the molecule, thus increasing the convergence of retrosynthetic strategies.^{16,17} Interestingly, the number of targets found to possess such symmetry seems to exceed that expected to arise from pure chance. A literature survey involving theoretical calculations and comparisons of the energy of monomers, dimers, trimers, and tetramers was recently been published by Greer and colleagues.¹⁸

C_2 -symmetric enantiopure diamines are recognized as important structural elements of many biologically active compounds and have been widely employed in asymmetric transformations including epoxidation,¹⁹ allylic substitution,²⁰ hydrogenation reactions,²¹ and many other catalytic asymmetric transformations.²² Pena et al. synthesized a series of C_2 -symmetrical and nonsymmetrical chiral diamines and used them as chiral solvating agents for NMR enantiodiscrimination of chiral carboxylic acid.²³ Ghosh and Masanta reported the synthesis and photophysical behavior of an anthracene-labeled receptor bearing an amine group to use in recognition of α -keto and hydroxy acids.²⁴

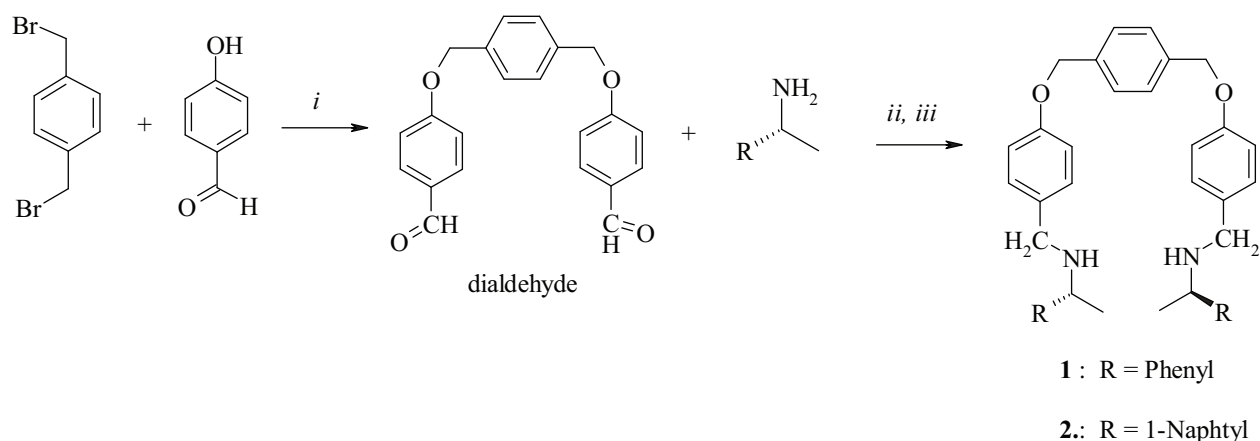
Since the pioneering work of Cram and colleagues, numerous chiral macrocyclic and complex structured ligands have been synthesized and studied for enantiomeric recognition of racemic compounds.²⁵ However, the use of acyclic and simple structured ligands as hosts for enantiomeric recognition of the racemic compounds is limited. We report herein a practice synthesis of 2 novel simple structured C_2 -symmetric chiral diamines (**1**, **2**) and evaluation of enantiomeric recognition properties of these ligands toward amino acid esters and mandelic acid by ^1H NMR titration method.

2. Results and discussion

2.1. Synthesis

The simple structured and easily obtained organic compounds are very important in synthetic chemistry. In this study, we synthesized 2 novel, easily obtained C_2 -symmetric chiral diamine ligands bearing N - α -phenylethyl (**1**) and N - α -(1-naphthyl)ethyl (**2**) chiral subunits. The host-guest interactions of these chiral ligands with chiral amino acid methyl ester hydrochlorides and mandelic acid were characterized. K_f values for these host-guest interactions are reported.

The syntheses of chiral diamines **1** and **2** were accomplished in 2 steps. Initially, C_2 -symmetric di-



Scheme 1. Reagents and conditions: *i*, CH_3CN , K_2CO_3 , reflux, 15 h. *ii*, MeOH , reflux, 5 h. *iii*, MeOH , NaBH_4 , room temperature, 2 h.

aldehyde was prepared according to the procedure described in the literature.²⁶ The 2 chiral amines, (*R*)- α -phenylethylamine and (*R*)- α -(1-naphthyl)ethylamine, were used as chiral sources for synthesis of diamines **1** and **2** (Scheme 1). The reactions of the dialdehyde with the 2 chiral amines in MeOH following by treatment of reactions mixtures with NaBH₄ gave C₂-symmetric chiral diamines (**1** and **2**) with quantitative yields. All compounds were characterized with ¹H NMR, ¹³C NMR, IR and elemental analysis.

2.2. Enantiomeric recognition by ¹H NMR titration method

The molecular recognition can be characterized by various spectroscopic methods such as UV-Vis, NMR, fluorescence, and IR.^{27,28} The NMR titration method has proven to be effective in determining the bonding constant value for host–guest interaction. The advantages of the ¹H NMR method are that the experiment can be carried out in a wide variety of solvents and that useful structural information can often be obtained.

To determine the equilibrium constant for the simple reaction requires knowledge of the equilibrium concentrations of the species H, G, and H.G. When H and G are host and guest species that form an H.G complex that is held together by weak intermolecular forces (e.g., hydrogen bonding and van der Waals forces), the equilibrium constant is usually referred to as a binding constant or association constant to indicate that the product has chemical characteristics that still strongly resemble the unassociated ('free') molecules. The appearance of the NMR spectrum of the mixture represented by Eq. (1) would depend on K_f and on the rate of the reaction.²⁹



In this study, the association constants of the host–guest systems formed were calculated according to the modified Benesi–Hildebrand equation,³⁰ i.e. Eq. (2), the basis of the ¹H NMR spectra data using the same methyl peak of the chiral hosts.

$$H + G \rightleftharpoons H \cdot G$$

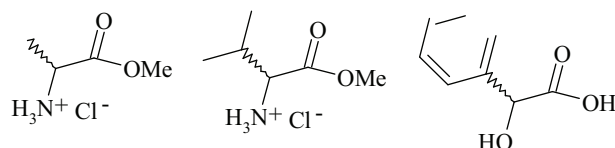
$$1/\Delta\delta = 1/(K_f\Delta\delta_{\max}[H_o]) + 1/\Delta\delta_{\max}. \quad (2)$$

The enantiomeric recognitions for the hydrogen chloride salts of D-, L-AlaOMe; D-, L-ValOMe; and D-, L-mandelic acid (Scheme 2) by chiral hosts **1** and **2** have been characterized by ¹H NMR titration method. In all association experiments, 1:1 binding stoichiometry was observed. Figure 1 shows 1:1 complexation between host **1** and mandelic acid by Job plots based on ¹H NMR shifts of methine proton's signal of the guest. Figure 2 shows the spectroscopic changes of the ¹H NMR methylene (Ar-CH₂O-) protons signals of chiral host **1** (1 mM) in the absence and presence of L- and D-mandelic acid (0.167–5 mM) in CDCl₃ at 298 K. The experimental data and ¹H NMR chemical shifts of the methylene signal are given in Table 1 for L-mandelic acid and host **1**. Figure 3 shows a typical plot of the host–guest complexation of **1** and L-mandelic acid based on data given Table 1. Binding constants (K_f) were calculated using data given in Figure 3. Before adding the guest, the methylene protons of host **1** showed a singlet at around 5.09 ppm. When the host and guest interacted in a solution forming a 1:1 complex, this peak was shifted upfield and showed an AB system. The binding constant of the complex was obtained using these peaks. Other guests showed similar behavior with different amounts of chemical shifts. The estimated structures of complexes formed between hosts and guests are given in Scheme 3. Probably, while amino acids preferred hydrogen bonding interaction in complexation, mandelic acid preferred π – π and hydrogen bonding interaction. Thus, the greater enantioselectivity of mandelic acid may be explained by forming a rigid structured complex between L-mandelic acid by appropriate π – π stacking interaction of the

2 aromatic rings of the host and 1 of the guest and the hydrogen bonding interaction between amine groups of the host and –OH groups of the guest. The shifting ArCH₂O-methylene protons show that the complexation of the guest occurred in the cavity of the host and near these groups (ArCH₂O-). Nevertheless, we do not have enough consistent data for precise information or stronger proposition.

Table 1. Experimental data of ¹H NMR titration of L-mandelic acid and host **1**. [H]_o: concentration of the host and [G]_o: concentration of the guest in each NMR tube.

[H] _o (× 10 ⁻³)	[G] _o (× 10 ⁻³)	1 / [G] _o (× 10 ²)	δ (ppm)	Δδ (× 10 ⁻²)	(1/[G] _o) / 1000	1 / Δδ
1.00	0		5.0953			
1.00	0.176	59.9	5.1157	2.04	5.99	49.0
1.00	0.333	30.0	5.1268	3.15	3.00	31.7
1.00	0.666	15.0	5.1316	3.63	1.50	27.5
1.00	1.000	10.0	5.1394	4.41	1.00	22.7
1.00	2.000	5.00	5.1444	4.91	0.50	20.4
1.00	3.000	3.33	5.1625	6.72	0.33	14.9
1.00	4.000	2.50	5.1823	8.70	0.25	11.5
1.00	5.000	2.00	5.1831	6.74	0.20	14.8



Scheme 2. AlaOMe.HCl, ValOMe.HCl, and mandelic acid used as guests.

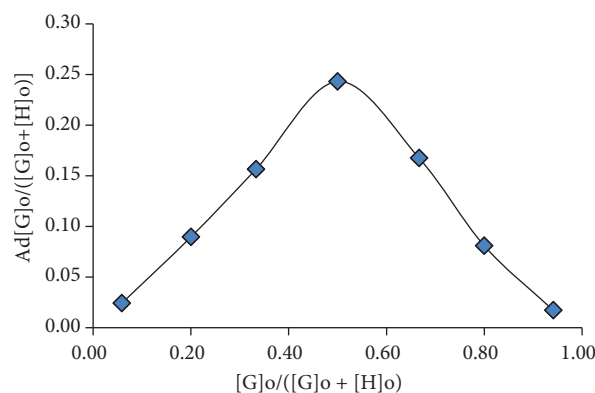


Figure 1. Job plots for mandelic acid and host **1** based on ¹H NMR shifts of guest's methine signal. [G]_o/([G]_o + [H]_o) = 0.50; [H]_o: [G]_o = 1:1.

The binding constants (K_f) and enantioselectivities (K_L/K_D) for the complexation of L-/D-guests with the hosts (**1**, **2**) in CDCl₃ are given in Table 2. All guests form a stable complex with chiral host **1** and **2**, as shown in Table 2. The association constants of the chiral host **1** with the L- and D-enantiomers of mandelic acid were found to be 2481.95 and 607.80, respectively. The L-form is 4.08 times more stable than the D-form ($K_L/K_D = 4.08$). In the same way, host **2** exhibited chiral recognition toward the enantiomers of a mandelic acid by $K_L/K_D = 1.73$. It was shown that host **1** exhibited stronger complexation and enantioselectivity than host **2** toward mandelic acid.

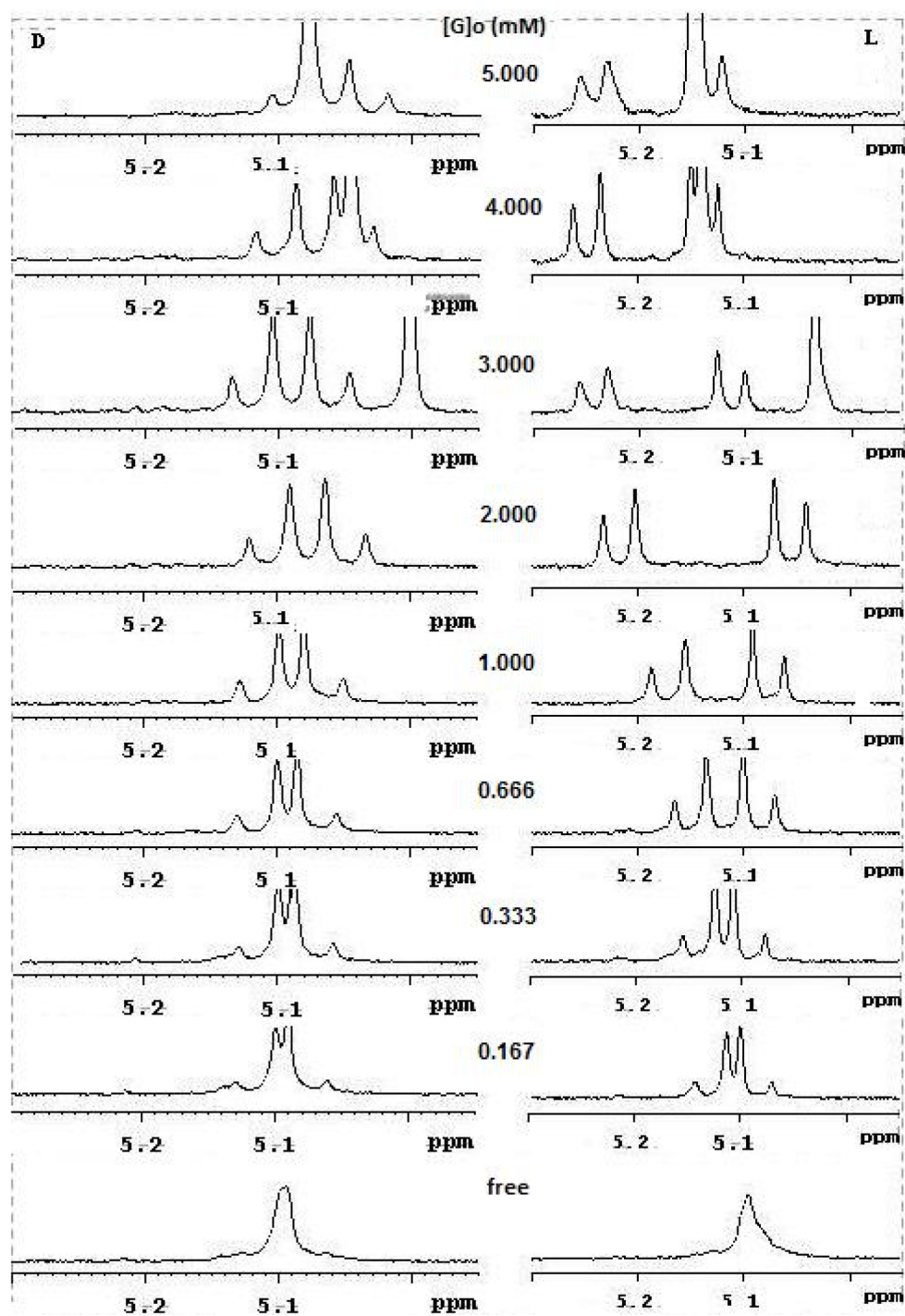


Figure 2. ^1H NMR spectral changes of chiral host **1** in the presence of D- and L-mandelic acid (methylene signal of host **1**) in CDCl_3 .

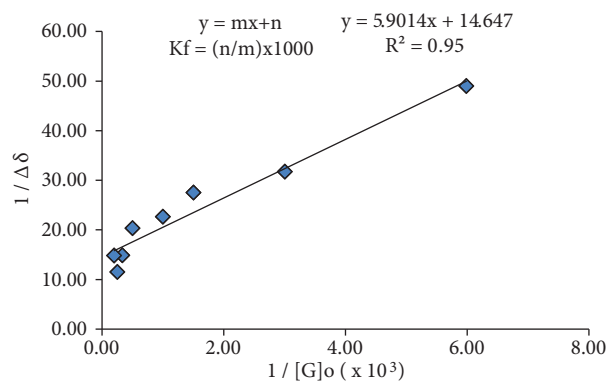
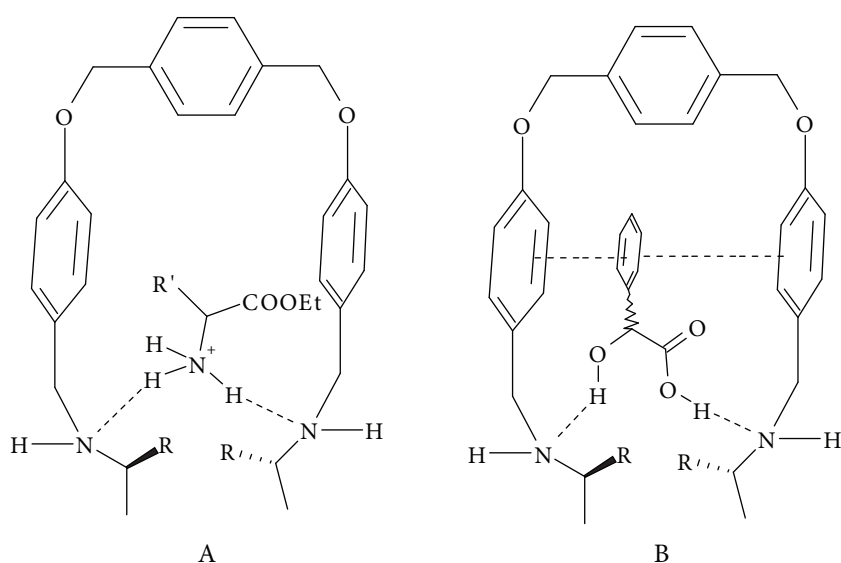


Figure 3. Typical plot of $1 / \Delta\delta$ versus $1 / [G]_0$ for the host-guest complexation of **1** and L-mandelic acid in CHCl_3 .



Scheme 3. General structures estimated for the complexes formed between hosts and guests (A: amino acids, B: mandelic acid).

Table 2. Binding constants (K_f) and enantioselectivities K_L/K_D for the complexation of L-/D-guests with the hosts (**1**, **2**) in CDCl_3 .

Host	Guest	K_f (dm^3/mol)	K_L/K_D (K_D/K_L)
1	L-Val	300.44	0.93 (1.08)
	D-Val	324.44	
	L-Ala	406.29	0.88 (1.14)
	D-Ala	462.95	
	L-Mandelic acid	2481.9	4.08 (0.25)
	D-Mandelic acid	607.80	
2	L-Val	85.520	0.43 (2.31)
	D-Val	197.83	
	L-Ala	421.69	0.89 (1.12)
	D-Ala	470.35	
	L-Mandelic acid	199.61	1.73 (0.58)
	D-Mandelic acid	115.50	

In the case of amino acid methyl ester guests, higher binding constants and enantioselectivities were obtained for D-enantiomers. Host **2** exhibited enantioselectivity toward D- and L-valine methyl ester by $K_D/K_L = 2.33$, while host **1** exhibited low enantioselectivity toward same guest ($K_D/K_L = 1.1$). Both hosts **1** and **2** also exhibited low enantioselectivity toward L- and D-alanine methyl ester by $K_D/K_L = 1.36$ and 1.12, respectively. This result shows that the presence of the naphtho unit on the stereogenic center of the host gives rise to enantioselectivities but decreases the complexation abilities toward amino acid methyl esters. This may be due to the steric enhancing of the naphtho unit on the stereogenic center of host **2**. In the case of the mandelic acid guest, steric enhancing of the naphtho unit decreases both enantioselectivity and complexation ability. This may be due to the fact that the steric repulsions of the naphtho unit are very high for complexation with mandelic acid, which bears a phenyl unit in the stereogenic center.

These results demonstrate that the substituent on the stereogenic center plays a very important role in the chiral recognition. It is also shown that the steric effect or repulsion between the substituent on the stereogenic center (e.g., alkyl or aryl group) of the host and the guest has been found to be an important factor. More steric repulsions decrease complexation but give rise to enantioselectivity when guests are amino acids, but higher steric repulsions decrease both complexation and enantioselectivity when guests are mandelic acid.

3. Experimental

3.1. Materials and methods

All chemicals were of reagent grade unless otherwise specified. R/S 1-phenylethylamine and 1-(1-naphthyl)ethylamine, D- and L-amino acid methyl ester hydrochlorides, and D- and L-mandelic acids were purchased from Fluka or Merck. Silica gel 60 (Merck, 0.040–0.063 mm) and silica gel/TLC-cards (F254) were used for flash column chromatography and thin layer chromatography. Melting points were determined with a Gallenkamp Model apparatus with open capillaries. Infrared spectra were recorded on a Mattson 1000 FTIR model spectrometer. Elemental analyses were performed with a Carlo-Erba 1108 model apparatus. Optical rotations were taken on a PerkinElmer 341 model polarimeter. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker DPX-400 High Performance Digital FT-NMR Spectrometer. The chemical shifts (δ) and coupling constants (J) are expressed in parts per million and hertz.

3.2. NMR experiments

3.2.1. Job plots

The stoichiometry of the complex between hosts **1** and **2** and the guests was determined using spectroscopic changes of the same methine proton that is on the stereogenic center of the guest by continuous variation plot (Job plot) according to the method described in the literature (Figure 1).³¹

3.2.2. NMR titrations

The host compound was dissolved in an appropriate amount of solvent and the resulting solution was evenly distributed among 9 NMR tubes. The first tube was sealed only with the host compound. The guest solution was added in increasing amounts to the NMR tubes so that the following solutions had relative amounts of guest versus host compound. The concentration of the host was constant (1 mM) with the increasing concentrations of the added guest (Table 1).

3.3. Synthesis

3.3.1. 4,4'-[benzene-1,4-diylbis(oxy)]dibenzaldehyde

This compound was prepared according to the procedure described in the literature.²⁶ Mp: 164–165 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 5.10 (s, 4H), 7.14 (s, 4H), 7.47 (d, *J* = 8.04 Hz, 4H), 7.85 (d, *J* = 8.04 Hz, 4H), 9.91 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): 69.92, 115.17, 127.50, 130.32, 131.98, 136.02, 163.43, 190.73; IR: m 3080, 2941, 2882, 2820, 2810, 2735, 1680, 1614, 1577, 1512, 1420, 1256, 1169, 990, 891, 822, 800, 651, 619, 561, 500; Anal. Calcd for C₂₂H₁₈O₄: C, 76.29; H, 5.24. Found: C, 76.30; H, 5.29.

3.4. (R,R)-(1-Phenylethyl)-[4-(4-{4-[(1-phenylethyl amino)methyl]phenoxy)methyl} -benzyloxy) benzyl amine (1)

To a solution of dialdehyde (500 mg, 1.45 mmol) in 30 mL of EtOH was added (*R*)-1-phenylethylamine (375 mg, 3.1 mmol). The reaction mixture was heated at reflux for 16 h. The mixture was then cooled to room temperature and NaBH₄ (74 mg, 1.96 mmol) was added slowly. The reaction mixture was stirred for 2 h. The EtOH was removed and 5 mL water was added to the residue. The mixture was then extracted with CH₂Cl₂ (3 × 10 mL) and the organic extracts were combined, dried over MgSO₄, and evaporated in vacuo to give a viscous oil with quantitative yield (800 mg). [α]_D²⁰ = +5 (c 1, CHCl₃); ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 1.39 (d, *J* = 6.4 Hz, 6H), 2.16 (bs, 2H), 3.72 (d, *J* = 13.2 Hz, 2H), 3.82–3.88 (m, 4H), 5.09 (s, 4H), 6.99–7.03 (m, 4H), 7.27–7.47 (m, 18H); ¹³C NMR (CDCl₃, 400 MHz) δ (ppm): 24.6, 47.6, 57.4, 70.0, 113.12, 120.9, 126.3, 127.0, 128.3, 128.45, 128.9, 129.1, 130.3, 137.6, 145.7, 156.9; IR (cm⁻¹): 3333, 3061, 3026, 2962, 2924, 2864, 1600, 1492, 1452, 1370, 1287, 1235, 1116, 1049, 1018, 777, 701; Anal. Calcd. for C₃₈H₄₀N₂O₂: C, 81.98; H, 7.24; N, 5.03. Found: C, 81.55; H, 7.33; N, 4.95.

3.4.1. (R,R)-(1-(1-Naphthyl ethyl)-[4-(4-{4-[(1-(1-naphthylethyl amino)methyl] phenoxy)methyl} benzyloxy)benzyl amine (2)

To a solution of dialdehyde (500 mg, 1.45 mmol) in 30 mL of EtOH was added (*R*)-1-(1-naphthyl)ethylamine (520 mg, 3.1 mmol). The reaction mixture was heated at reflux for 16 h. The mixture was then cooled to room temperature and NaBH₄ (74 mg, 1.96 mmol) was added slowly. The reaction mixture was stirred for 2 h. The EtOH was removed and 5 mL water was added to the residue. The mixture was then extracted with CH₂Cl₂ (3 × 10 mL) and the organic extracts were combined, dried over MgSO₄, and evaporated to give a viscous oil with quantitative yield (950 mg). [α]_D²⁰ = +45.4 (c 1, CHCl₃); ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 1.49 (d, *J* = 6.4, 6H), 2.17 (bs, 2H), 3.78 (d, *J* = 12.8 Hz, 2H), 3.90 (d, *J* = 12.8 Hz, 2H), 4.60–4.70 (m, 2H), 5.01 (s, 4H), 6.93–6.98 (m, 4H), 7.24–7.32 (m, 8H), 7.39–7.49 (m, 6H), 7.73–7.75 (m, 4H), 7.85–7.88 (m, 2H), 8.05–8.07 (m, 2H). ¹³C NMR (CDCl₃, 400 MHz) δ (ppm): 23.5, 47.6, 52.5, 69.8, 113.16, 120.9, 123.1, 125.2, 125.8, 126.3, 126.9, 127.1, 128.3, 128.9, 130.4, 131.4, 133.9, 137.4, 141.1, 156.9. IR (cm⁻¹): 3343, 3058, 3040, 2961, 2923, 2864, 1599, 1493, 1452, 1370, 1288, 1235, 1117, 1050, 1015, 779, 753. Anal. Calcd. for C₄₆H₄₄N₂O₂: C, 84.11; H, 6.75; N, 4.26. Found: C, 84.32; H, 6.84; N, 4.19.

4. Conclusion

We have developed 2 novel simple structured C₂-symmetric chiral diamines (**1**, **2**) and studied their enantiomeric recognition properties toward D- and L-amino acid methyl ester hydrochlorides and D- and L-mandelic acid

using the ^1H NMR titration method. The highest enantioselectivity was obtained by host **1** toward L-mandelic acid up to $K_f = 2481\text{ M}^{-1}$ with K_L/K_D equal to 4.08. These results show that simple structured and easily accessible acyclic C_2 -symmetrical compounds can be used for enantiomeric recognition of racemic amino acids and mandelic acids. The secondary amine groups of the ligands used in this study allow them to covalently bond with several polymeric structures for enantioseparation of racemic compounds (especially mandelic acid). These ligands can also be derived to several structurally complex compounds to give rise to their effect on enantioselectivity.

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