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Synthesis of novel chiral Schiff base and amino alcohol derivatives of calix[4]arene and chiral recognition properties

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ABSTRACT

In the present study, the synthesis and liquid phase extraction properties towards some amino acid methylesters and amino alcohols of Schiff base and amino alcohol substituted calix[4]arene are reported. The Schiff base substituted calix[4]arene **5** has been synthesized via condensation reaction involving 5,17-diformyl-11,23-di-*tert*-butyl-25,27-di[3-(4-formylphenoxy)propoxy]-26,28 dihydroxycalix[4]arene **4** and (*R*)-(−)-2-phenylglycine methyl ester in $CHCl_3$:MeOH. To give the amino alcohol substituted calix[4]arene **6**, the synthesized chiral compound **5** was reduced by $LiAlH_4$. The new chiral Schiff base and amino alcohol derivatives of calix[4]arene have been characterized by a combination of FT-IR, ^1H NMR, ^{13}C NMR, FAB-MS and elemental analysis. Also, the extraction behaviors of **5** and **6** towards some selected amino acid methylesters and amino alcohols have been studied by liquid–liquid extraction.

1. Introduction

Calixarenes, cyclic oligomers of phenolic units linked through the ortho positions, are a fascinating class of macrocycles. They are synthetic macrocycles readily available by condensation of *p*-*tert*-butylphenol with formaldehyde under alkaline conditions. From these starting materials, a large number of sophisticated compounds have been prepared. To date, various calixarenes that possess ketone, amine, ester, amide, carboxylic acid or other functional groups have been synthesized for separation, recognition, discrimination and catalysis. A number of books were published concerning synthesis, structural features and host–guest interactions [1]. More specifically, the subject of chemical recognition and separation of ions was addressed in several publications [2]. On the other hand, only few reviews concerning calixarenes for biochemical recognition are available, e.g. on peptido- and glycoconjugates and the role of hydrogen-bonding interactions [3], on neoglyco conjugates with large rigidified cavities [4] and on synthetic receptors [5]. Among them, chiral recognition, the process in which an enantiomerically pure host molecule, such as a chiral calixarene, selectively binds one of the enantiomers, is one of the most essential reaction processes occurring in living systems [6]. Therefore chiral calixarenes [7] have attracted increasing research interest because of their potential in enantio discrimination processes. They can be obtained either by attaching chiral moieties at one of the calix rims (upper or lower) [1] or by synthesizing inherently chiral derivatives [8] in which an asymmetric substitution of the macrocycle is associated to its intrinsic three-dimensional nature. From a practical point of view, the first approach appears to be preferable because inherent chirality always requires a difficult resolution on an appropriate scale [9]. Therefore, a large number of chiral calixarenes have been prepared by using chiral units, such as single amino acids [10], peptides [11], amino alcohols [12], sugars [13], tartaric acid esters [14], binaphthyl [15], glycidyl [16], menthone [17], and guanidinium groups [18].

Herein we report the synthesis of novel chiral calix[4]arene platform with Schiff base and amino alcohol derivatives on their lower and upper rim for quantitative extraction of some amino acid methylesters and amino alcohols in a liquid–liquid extraction system.

2. Experimental

2.1. Materials and general methods

Melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer in $CDCl_3$. FT-IR spectra were recorded on a Perkin Elmer spectrum 100. UV–vis spectra were obtained on a Shimadzu 160A UV–visible recording spectrophotometer. FAB-MS spectra were taken on a Varian MAT 312 spectrometer. Elemental analyses were performed on a Leco CHNS-932 analyzer. Optical rotations were measured on an Atago AP-100 digital polarimeter. Analytical TLC was performed on precoated silica gel plates (SiO_2, Merck PF254), while silica gel 60

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(Merck, particle size 0.040–0.063 mm, 230–240 mesh) was used for preparative column chromatography. Generally, solvents were dried by storing them over molecular sieves (Aldrich; 4 Å, 8–12 mesh). Acetone and $CHCl_3$ were distilled from $CaSO_4$ and $CaCl_2$, respectively. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

The following amino acid methylester hydrochlorides and amino alcohols obtained from Aldrich or Merck at the highest commercially available purity were used in this study: L-phenylalanine methylester hydrochloride (L-Phe-OMe), D-phenylalanine methylester hydrochloride (D-Phe-OMe), L-alanine methylester hydrochloride (L-AlaOMe), D-alanine methylester hydrochloride (D-AlaOMe), L-tryptophan methylester hydrochloride (L-TrpOMe), D-tryptophan methylester hydrochloride (D-TrpOMe), L-phenylglycinol (L Phegly), D-phenylglycinol (L-Phegly), (R)-(5)-(hydroxymethyl)-2-pyrolidinone [(R)-Hyd-Me-Pyr], (S)-(5)-(hydroxymethyl)-2-pyrolidinone [(S)-Hyd-Me-Pyr] (Figs. 1 and 2).

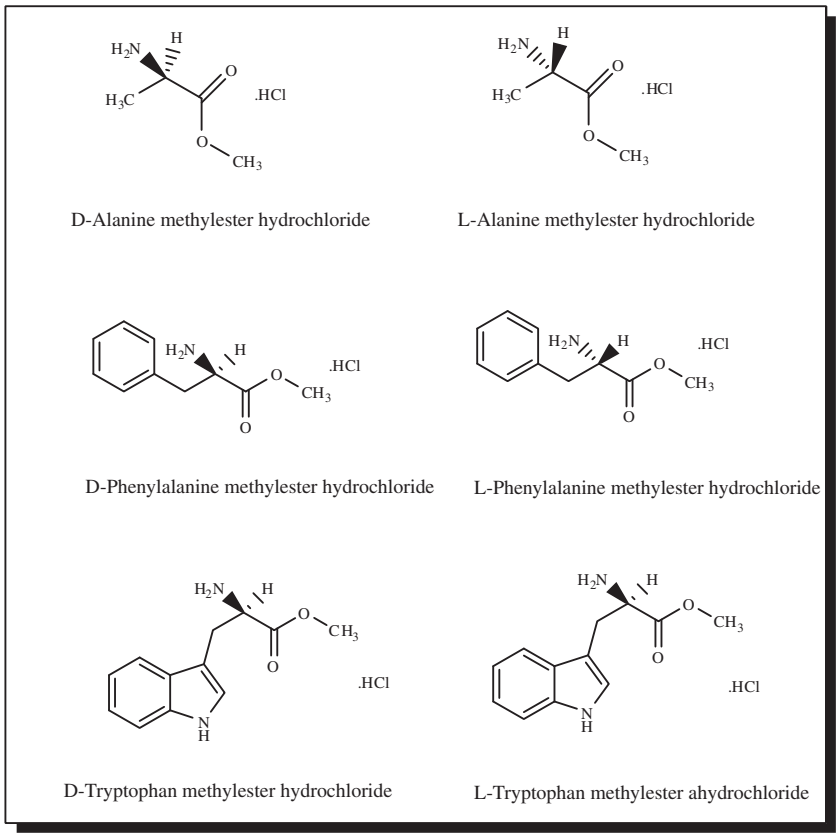


Fig. 1. The chemical structures of amino acid methylesters used in experiments.

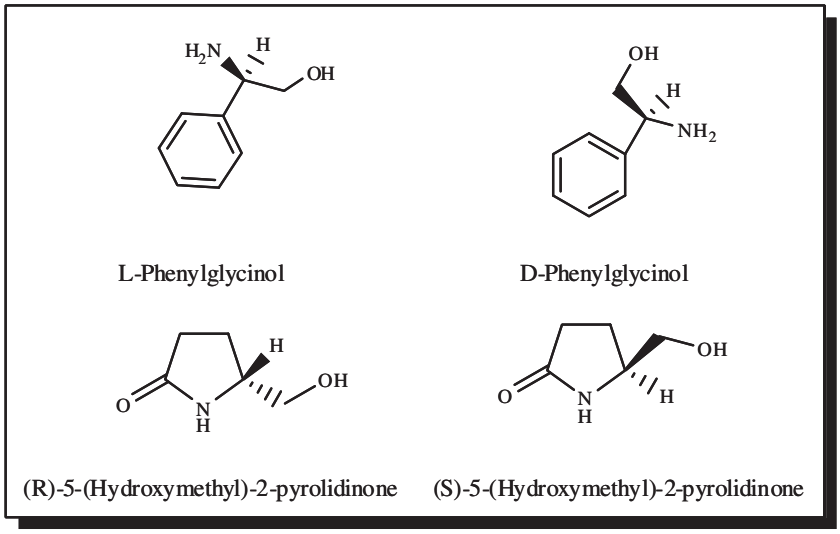


Fig. 2. The chemical structures of amino alcohols used in experiments.

2.2. Syntheses

Compounds **1** and **2** were prepared according to the literature methods [19,20]. Other compounds (**3**–**6**) were synthesized by adapting known synthetic procedures.

2.2.1. Compound 3

To a mixture of **2** (1 g, 1.12 mmol) and K_2CO_3 (0.34 g, 2.47 mmol) in acetonitrile (100 mL), *p*-hydroxybenzaldehyde (0.30 g, 2.46 mmol) was added and the reaction mixture was stirred at reflux for 2.5 days. After cooling, the solvent was removed under reduced pressure. The remaining solid was taken up CH_2Cl_2 (100 mL) and washed with 1 M HCl (2 × 50 mL) and water (50 mL). The organic layer was dried over $MgSO_4$ and evaporated to give a white powder. The product was crystallized from CH_2Cl_2:hexane (1:3) to obtain pure **3** (85%). mp: 198–201 °C. FT-IR: 1678 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 1.00 (s, 18H, $C(CH_3)_3$), 1.29 (s, 18H, $C(CH_3)_3$), 2.36 (p, 4H, J = 6.2 Hz, $CH_2CH_2CH_2$), 3.34 (d, 4H, J = 13.1 Hz, $ArCH_2Ar$), 4.13 (t, 4H, J = 6.2 Hz, $OCH_2CH_2CH_2$), 4.24 (d, 4H, J = 13.1 Hz, $ArCH_2Ar$), 4.48 (t, 4H, J = 6.2 Hz, $CH_2CH_2CH_2O$), 6.86 (s, 4H, ArH), 7.04–7.09 (m, 8H, ArH), 7.61 (s, 2H, ArOH), 7.81 (d, 4H, J = 8.6 Hz, ArH), 9.85 (s, 2H, CHO). FAB-MS *m*/*z*: (996.10) $[M+Na]^+$. Anal. Calcd. for $C_{64}H_{76}O_8$ (973.28): C, 78.98; H, 7.87. Found: C, 79.01; H, 7.90.

2.2.2. Compound 4

Compound **3** (1.0 g, 1.03 mmol) and hexamethylenetetramine (HMTA, 5.94 g, 42.36 mmol) were taken in trifluoroacetic acid (TFA, 60 mL). The reaction mixture was refluxed until the starting material (compound **3**) had disappeared (TLC). On completion, the mixture was quenched with cold water and extracted with dichloromethane. The organic layer was washed with water and dried over Na_2SO_4. Evaporation of the solution gave a white solid residue, which was crystallized from a mixture of acetone:hexane (2:3) to give product **4** in 75% yield. mp: 155–158 °C. FT-IR: 1679 cm^{-1} (CH=O). ^1H NMR ($CDCl_3$): δ 0.98 (s, 18H, $C(CH_3)_3$), 2.42 (p, 4H, J = 6.2 Hz, $CH_2CH_2CH_2$), 3.47 (d, 4H, J = 13.3 Hz, $ArCH_2Ar$), 4.18 (t, 4H, J = 6.2 Hz, $OCH_2CH_2CH_2$), 4.22 (d, 4H, J = 13.3 Hz, $ArCH_2Ar$), 4.45 (t, 4H, J = 6.2 Hz, $CH_2CH_2CH_2O$), 6.86 (s, 4H, ArH), 7.03 (d, 4H, J = 8.6 Hz, ArH), 7.62 (s, 4H, ArH), 7.78 (d, 4H, J = 8.6 Hz, ArH), 8.62 (s, 2H, ArOH), 9.80 (s, 2H, CHO), 9.82 (s, 2H, CHO). FAB-MS *m*/*z*: (939.91) $[M+Na]^+$. Anal. Calcd. for $C_{58}H_{60}O_{10}$ (917.09): C, 75.96; H, 6.59. Found: C, 76.01; H, 6.61.

2.2.3. Compound 5

To a solution of **4** (0.8 g, 0.87 mmol) in $CHCl_3$ (50 mL) was added a solution of (*R*)-(−)-2-phenylglycine methyl ester hydrochloride and triethylamine (1 mL, excess) in MeOH (10 mL) and refluxed for 24 h. The reaction mixture was allowed to cool to room temperature, and filtered. Evaporation of the solvent and subsequent purification of the mixture by recrystallization from $CHCl_3$:MeOH (1:3) afforded pure **5**. Yield 78%. mp; 115–119 °C. $[\alpha]_D^{22} = -9.8$ (*c* 0.5, $CHCl_3$); FT-IR: 1686 and 1636 cm^{-1} (C=N), 1737 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 0.96–1.02 (m, 18H, $C(CH_3)_3$), 2.40 (p, 4H, J = 5.2 Hz, $CH_2CH_2CH_2$), 3.41–3.46 (m, 4H, $ArCH_2Ar$), 3.72 (s, 6H, OCH_3), 3.74 (s, 6H, OCH_3), 4.14 (m, 4H, $OCH_2CH_2CH_2$), 4.17–4.23 (m, 4H, $ArCH_2Ar$), 4.45 (m, 4H, $CH_2CH_2CH_2O$), 5.13 (s, 2H, *CH*Ph), 5.15 (s, 2H, *CH*Ph), 6.85–6.95 (m, 8H, ArH), 7.25–7.37 (m, 12H, ArH), 7.48–7.50 (m, 8H, ArH), 7.57–7.61 (m, 4H, ArH), 7.71 (d, 4H, J = 8.2 Hz, ArH), 8.16 (s, 2H, CHN), 8.19 (s, 2H, CHN), 8.36 (s, 2H, ArOH). ^{13}C NMR ($CDCl_3$): δ 172.1, 171.9, 163.8, 163.2, 161.5, 156.5, 149.7, 149.6, 148.4, 148.2, 138.8, 138.7, 138.6, 132.2, 130.6, 129.8, 129.7, 128.8, 128.7, 128.2, 128.0, 127.8, 127.0, 126.3, 126.2, 126.1, 115.0, 114.7, 73.0, 64.8, 52.7, 52.6, 52.5, 45.8, 34.4, 31.4, 30.1. FAB-MS *m*/*z*: (1528.61) $[M+Na]^+$. Anal. Calcd. for $C_{94}H_{96}N_4O_{14}$ (1505.79): C, 74.98; H, 6.43. Found: C, 75.01; H, 6.46.

2.2.4. Compound 6

To a stirred suspension of compound **5** (0.7 g, 0.46 mmol) in THF (100 mL) under dry N_2 gas was added $LiAlH_4$ (0.172 g, 4.65 mmol) in three steps at room temperature. Then, the reaction mixture was refluxed for 3 h. The solution was filtrated and the filtrate was evaporated under reduce pressure. The residue was dissolved in CH_2Cl_2 (50 mL) and to the solution was added NaOH 1 M. The organic phase was separated and dried over $MgSO_4$. After evaporation of the solvent, the crude product was recrystallized in MeOH:CH_2Cl_2 (2:1). Yield 65%.%. mp; 126–129 °C. $[\alpha]_D^{22} = -13.3$ (*c* 0.5, $CHCl_3$); FT-IR: 3293 cm^{-1} (OH). ^1H NMR ($CDCl_3$): δ 1.02 (br s, 18H, $C(CH_3)_3$), 2.35–2.40 (m, 4H, $CH_2CH_2CH_2$), 3.28–3.82 (m, 28H, $ArCH_2Ar + CH_2CH_2CH_2O + CH_2OH + NHCH_2$), 4.18 (m, 4H, $OCH_2CH_2CH_2$), 4.23 (m, 4H, $ArCH_2Ar$), 4.38 (m, 4H, *CH*Ph), 6.85–6.97 (m, 12H, ArH), 7.11–7.13 (m, 4H, ArH), 7.28–7.37 (m, 22H, ArH + ArOH). ^{13}C NMR ($CDCl_3$): δ 161.6, 156.7, 149.8, 149.7, 148.5, 148.2, 138.9, 138.8, 138.7, 132.3, 130.6, 129.9, 129.7, 128.8, 128.6, 128.3, 128.1, 127.8, 127.2, 126.4, 126.3, 126.2, 115.0, 114.8, 73.2, 70.6, 69.2, 69.1, 67.8, 67.7, 53.4, 53.1, 45.9, 34.5, 31.5, 30.2. FAB-MS *m*/*z*: (1424.63) $[M+Na]^+$. Anal. Calcd. for $C_{90}H_{104}N_4O_{10}$ (1401.81): C, 77.11; H, 7.48. Found: C, 77.14; H, 7.50.

2.3. Analytical procedure

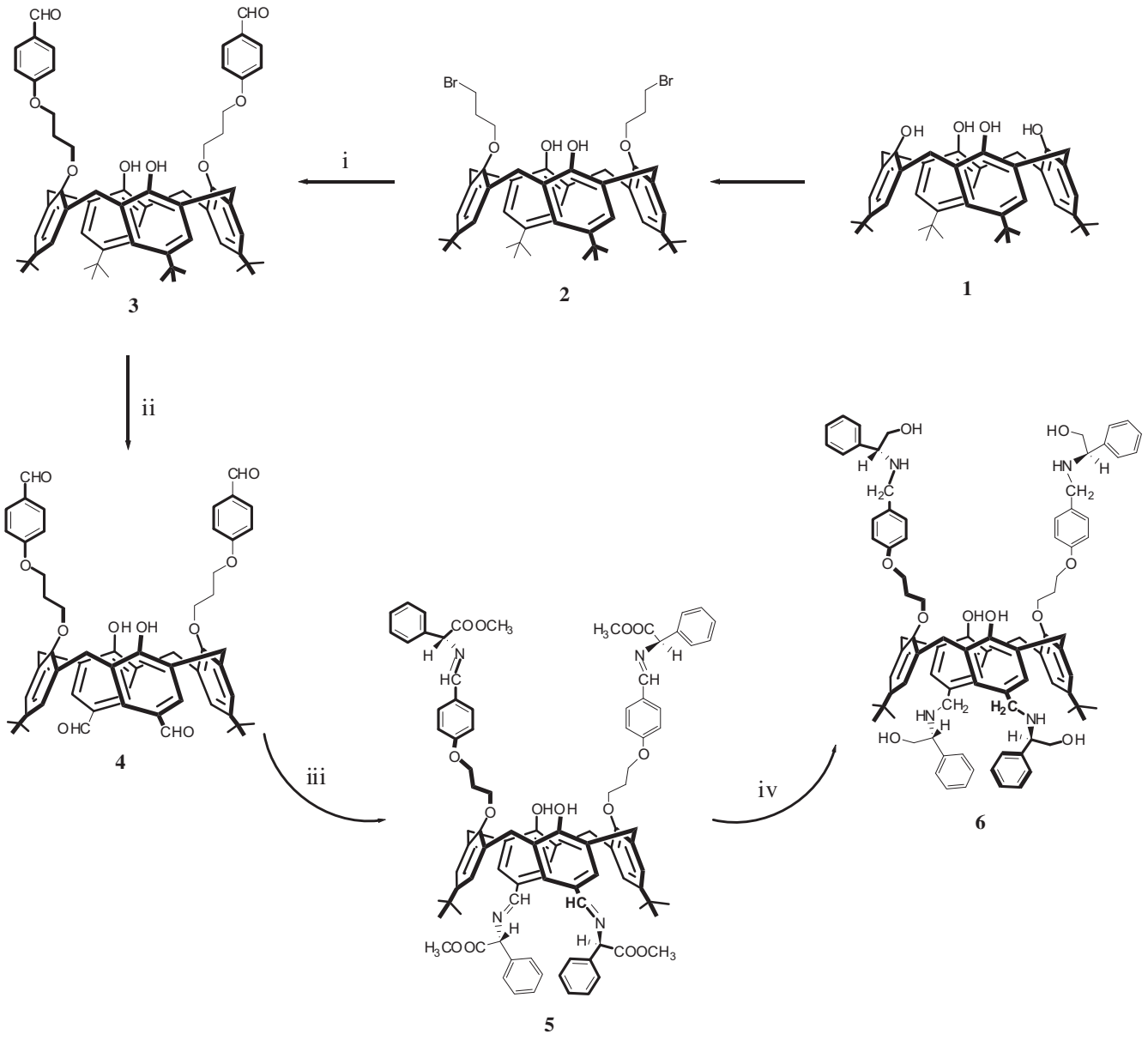
Picrate extraction experiments were performed following Pedersen's procedure [21]. A 10 mL of a 2.0×10^{-5} M aqueous picrate (the picrate solutions were prepared as our previous study [22]) and 10 mL of 1×10^{-3} M solution of calixarene **5** or **6** in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min, then magnetically stirred in a thermostated water-bath at 25 °C for 1 h, and finally left standing for an additional 30 min. The concentration of the picrate ion, which remained in the aqueous phase was then determined spectrophotometrically. Blank experiments showed that no picrate extraction occurred in the absence of calixarene. The percent extraction (E%) has been calculated as:

$$E\% = (A_0 - A)/A_0 \times 100 \quad (4)$$

where A_0 and A are the initial and final concentrations of the ammonium picrate before and after the extraction, respectively. All measurements were performed in triplicate and an average was taken as final result.

3. Results and discussion

We have interested in the synthesis of novel chiral calix[4]arene-based ionophores having Schiff base and amino alcohol moieties and also investigated the extraction properties of chiral calix[4]arene Schiff base **5** and amino alcohol **6** derivatives towards some selected α-amino acid methylesters and amino alcohols through the two-phase solvent extraction system. The synthesis of **1**–**6** depicted in Scheme 1 have been carried out as follows: After compounds **1** and **2** have been synthesized according to previous literature methods [19,20], compound **2** was reacted with *p*-hydroxybenzaldehyde in dry acetonitrile in the presence of potassium carbonate at reflux for 2.5 days in order to obtain **3** in 85% yield. The characterization of compound **3** was made by a combination of FT-IR, ^1H NMR and elemental analysis. The FT-IR spectra show an aldehyde band at 1678 cm^{-1}, and ^1H NMR exhibits singlet at 9.85 ppm corresponding to the aldehyde protons. To obtain the tetra aldehyde derivative **4** of calix[4]arene, compound **3** was reacted with hexamethylenetetramine (HMTA) in trifluoroacetic acid (TFA) and it afforded compound **4** in 75% yield. ^1H NMR spectra confirmed the composition of **4** due to observing peaks at 9.80 and 9.82 ppm, which correspond to the aldehyde protons and the



Scheme 1. Schematic representation of synthesis of chiral calix[4]arene derivatives **5** and **6**. Reagents and conditions: (i) *p*-hydroxybenzaldehyde, K_2CO_3, acetonitrile, 85%; (ii) HMTA, TFA, reflux, 75%; (iii) (*R*)-(−)-2-phenylglycine methyl ester hydrochloride, methanol: toluene, reflux, 78%; (iv) $LiAlH_4$, THF, reflux, 65%.

disappearance of *t*-butyl groups at 1.29 ppm belong to compound **3** (Fig. 3). The chiral Schiff base derivative of calix[4]arene **5** was prepared from the reaction of compound **4** with (*R*)-(−)-2-phenylglycine methyl ester in $CHCl_3$:MeOH. From ^1H NMR data, **5** exhibits two singlet at 8.16, 8.19 ppm, respectively, which indicates the presence of HC=N (Fig. 4) This conclusion has also been confirmed by strong C=N bands at 1686–1637 cm^{-1} and ester band at 1737 cm^{-1} in the FT-IR spectra of chiral Schiff base derivative. Subsequent reduction of these ester and Schif base groups of **5** by lithium aluminum hydride yielded amino alcohol derivative **6** in 65% yield. Completion of the reaction was followed by FT-IR spectroscopy, which showed the disappearance of the band due to C=N bands at 1686–1637 cm^{-1} and ester band at 1737 cm^{-1} and appearance of the band due to alcohol hydroxyl groups at 3293 cm^{-1}. Also, the formation of **6** was confirmed by the disappearance of the HC=N protons belong to compound **4** at 8.16 and 8.19 ppm in ^1H NMR spectra (Fig. 5). Compounds **5** and **6** are asymmetric due to the formation of chiral sub-units onto the lower and upper rim of calix[4]arene. The splitting patterns of protons (see Experimental) reflect the presence of the chiral moieties in the molecules [23].

Extraction studies were performed in order to examine the extraction behavior of α-amino acid methylesters and amino alcohols from the aqueous phase into the organic phase (CH_2Cl_2) by using novel chiral calix[4]arene derivatives **5** and **6**. The results of the picrate extraction studies are summarized in Tables 1 and 2. These data have been obtained by using dichloromethane solution of the ligands to extract ammonium picrates from aqueous solution. The equilibrium concentration of ammonium picrate in an aqueous phase was then determined spectrophotometrically. From the extraction data given Tables 1 and 2, it has been observed that compound **1** and **4** transfer all amino acid and amino alcohol species from aqueous phase into organic phase in trace amounts, and chiral calix[4]arene Schiff base **5** and amino alcohol **6** recognize all amino acid and amino alcohol species in high yields. According to our experience and knowledge from our previous

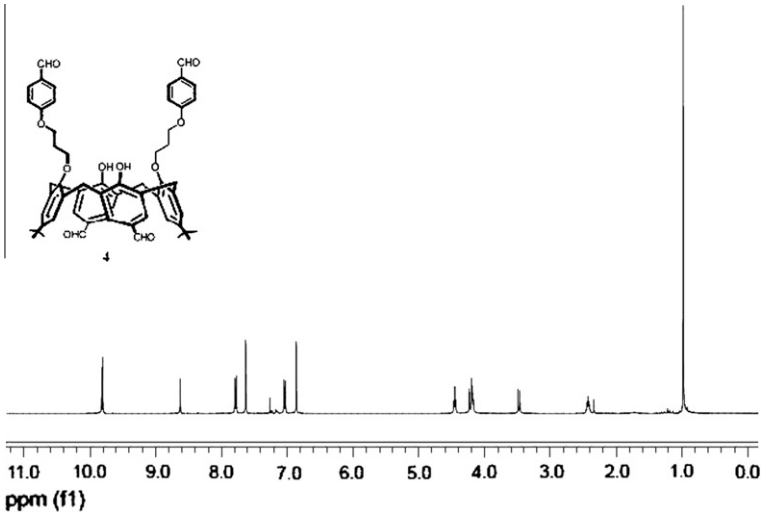


Fig. 3. The ^{1}H NMR spectra of compound **4**.

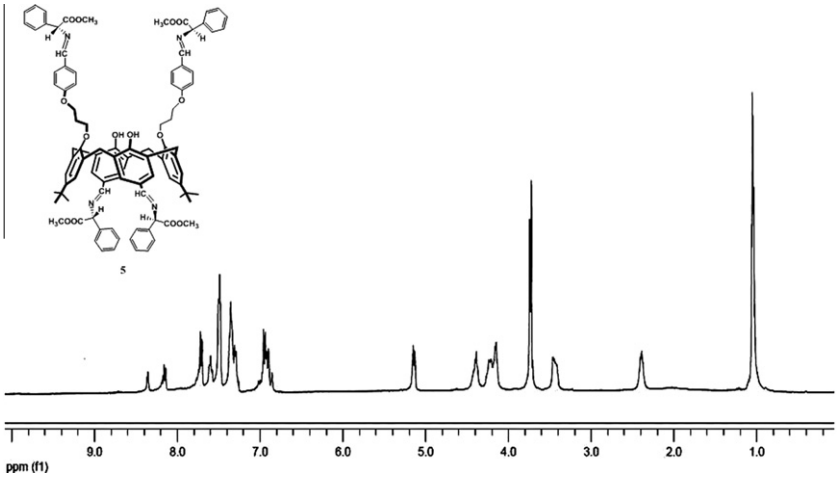


Fig. 4. The ^{1}H NMR spectra of compound **5**.

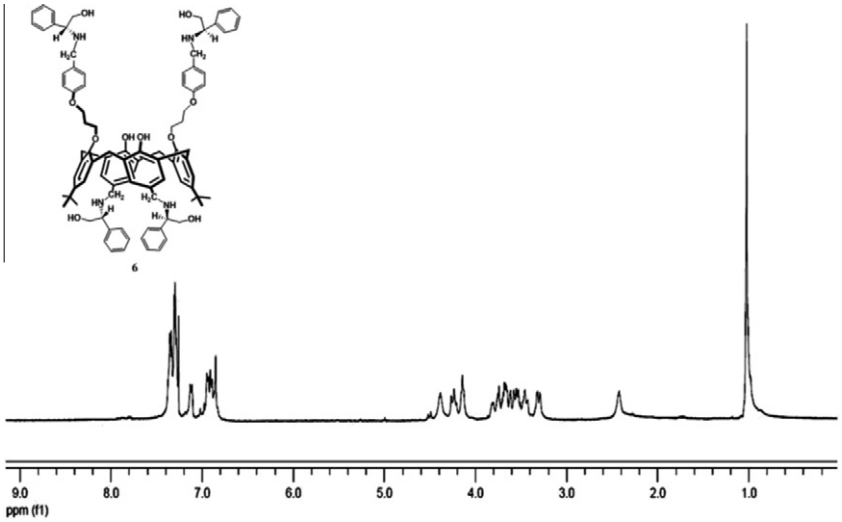


Fig. 5. The ^{1}H NMR spectra of compound **6**.

Table 1
Extraction percentage of selected amino acid methylesters with **4**, **5** and **6**.[a]

Ligand	L-AlaOMe	D-AlaOMe	L-PheOMe	D-PheOMe	D-TrpOMe	L-TrpOMe
1[b]	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
4	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
5	54.4 ± 1.1	57.2 ± 0.9	69.4 ± 1.4	76.4 ± 1.3	75.3 ± 1.1	77.1 ± 1.2
6	55.1 ± 0.8	56.8 ± 1.0	61.2 ± 1.2	57.4 ± 1.1	73.9 ± 1.4	72.5 ± 1.3

[a] Aqueous phase, [ammonium picrate] = 2.0×10^{-5} M; organic phase, dichloromethane, [ligand] = 1.0×10^{-3}; at 25 °C, for 1 h.
[b] Chloroform was used as organic phase.

Table 2
Extraction percentage of selected amino alcohols with **4**, **5** and **6**.[a]

Ligand	D-Phegly	L-Phegly	(R)-Hyd-Me-Pyr	(S)-Hyd-Me-Pyr
1[b]	<1.0	<1.0	<1.0	<1.0
4	<1.0	<1.0	<1.0	<1.0
5	66.5 ± 1.3	79.3 ± 1.4	65.2 ± 1.2	70.9 ± 1.3
6	69.5 ± 1.4	89.2 ± 1.5	68.9 ± 1.1	80.0 ± 1.2

[a] Aqueous phase, [ammonium picrate] = 2.0×10^{-5} M; organic phase, dichloromethane, [ligand] = 1.0×10^{-3}; at 25 °C, for 1 h.
[b] Chloroform was used as organic phase.

study and the other studies [22,24,25], increased extraction properties of chiral calix[4]arene Schiff base and amino alcohol (**5** and **6**) can be explained by multiple hydrogen bonding between **5**–**6** and amino acids or amino alcohols. In addition, the guests are stabilized by CH–π interactions with the aromatic walls of the hydrophobic cavity of the chiral calix[4]arenes (**5** and **6**). An expectation of this study is also to observe chiral discrimination between amino acids or amino alcohols by using these new chiral calix[4]arene derivatives as a ligand. From the results, this goal is relatively true, especially for phenylglycinols because of their extraction abilities being different according to each other, when compared to other species.

The extraction data for **6** has been analyzed by a classical slope analysis method. Assuming the extraction of an ammonium cation ($R{-}NH_3^+$) by the receptor **6** according to the following equilibrium:

$$[R{-}NH_3^+]_{aq} + [Pic^-]_{aq} + x[L]_{org} \rightleftharpoons [R{-}NH_3Pic(L)_x]_{org}$$

The extraction constant K_{ex} is defined by

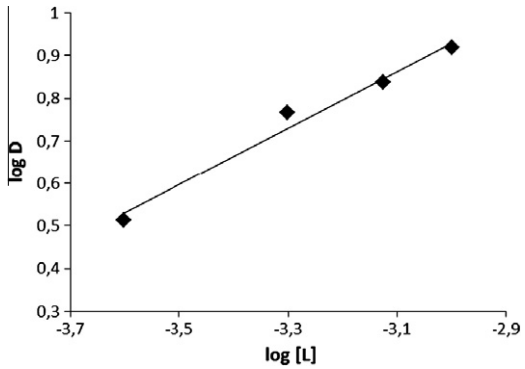


Fig. 6. Log D versus log[L] for the extraction of L-Phegly by **6** from an aqueous phase into dichloromethane phase at 25 °C.

$$K_{ex} = \frac{[R{-}NH_3Pic(L)_x]}{[R{-}NH_3^+][Pic^-][L]^x} \quad (1)$$

Eq. (1) can be rewritten as

$$\log D_A = \log K_{ex}[Pic^-] + x\log[L] \quad (2)$$

where the distribution ratio D_A is defined as ratio of the concentrations of the ammonium cation ($R{-}NH_3^+$) in the two phases:

$$D_A = [R{-}NH_3Pic(L)_x]_{org}/[R{-}NH_3^+]_{aq} \quad (3)$$

Consequently a plot of $\log D_A$ versus log[L] leads to a straight line, whose slope allows the stoichiometry of the extracted species to be determined.

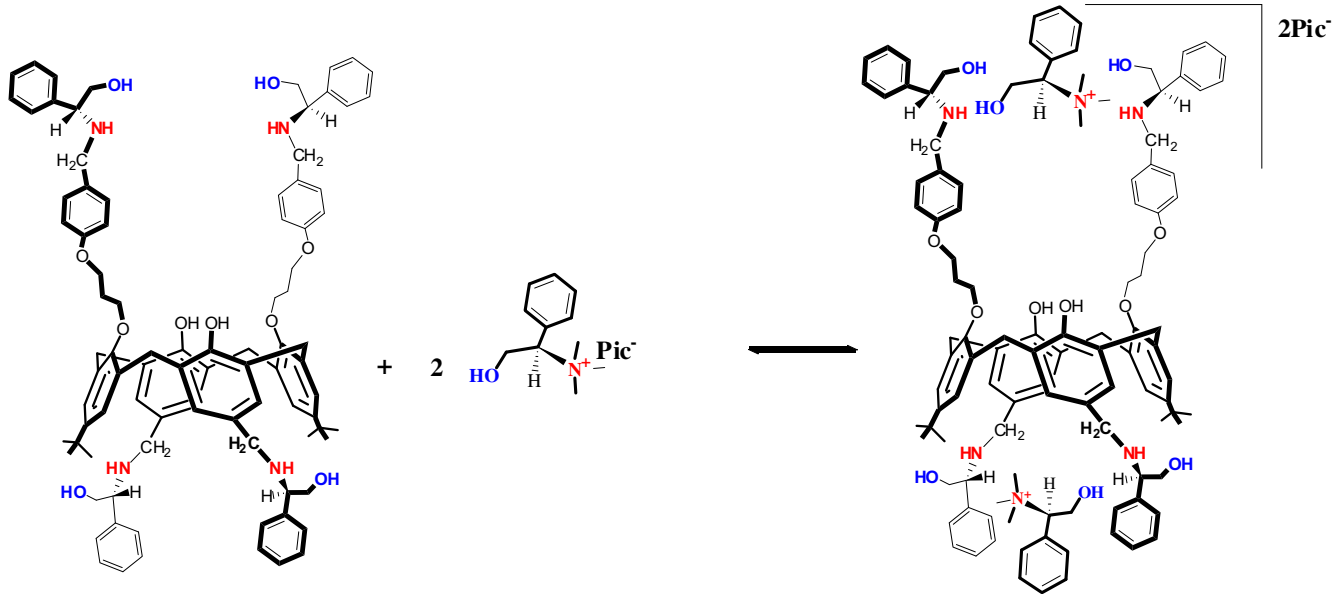


Fig. 7. Proposed interaction model between **6** and ammonium cation (L-Phegly).

Fig. 6 shows the extraction into dichloromethane at different concentrations of **6** for the ammonium ion. A linear relationship between $\log D_A$ versus log[L] is observed with a slope for ammonium ion by **6**, which equals 0.66, suggesting that **6** forms a 1:2 complex with an ammonium cation. According to these data, the proposed interaction model between **6** and L-Phegly is depicted in Fig. 7. The analytical data of **6** shows that the complexation reaction takes place according to the following equilibrium:

$$(L)_{org} + 2(R{-}NH_3^+Pic^-)_{aq} \overset{K_{ex}}{\rightleftharpoons} (L(R{-}NH_3^+Pic^-)_2)_{org}$$

According to the experimental data, if the Eq. (2) rearrangement for **6**, $\log K_{ex}$ has the value 2.92 ± 0.2.

4. Conclusions

Novel chiral Schiff base and amino alcohol derivatives of calix[4]arene were synthesized with convenient reactions in order to examine the extraction and chiral discrimination ability towards some selected amino acids and amino alcohols. The enantioselective recognition ability of the receptors was studied by UV/vis absorption spectroscopy. Although the chiral calix[4]arene Schiff base and amino alcohol derivatives (**5** and **6**) were excellent extractants for all used amino acid and amino alcohol species, the chiral discrimination between amino acid and amino alcohol molecules could not be obtained. It should be noted that the hydrophobic cavity of chiral calix[4]arenes and hydrogen bonding led us to recognize these amino acids and amino alcohols. This work should be useful with regards to the synthesis of chiral and enantioselective receptors.

Acknowledgment

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