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ORIGINAL ARTICLE

Synthesis and amines enantiomeric recognition ability of binaphthyl-appended 22-crown-6 ethers derived from rosin acid

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Abstract Novel chiral 22-crown-6 ethers (**5a–b**) bearing methoxycarbonyl side groups derived from rosin acid and 2,2′-dihydroxy-1,1′-binaphthyl (BINOL) were prepared in optically pure forms, and their enantiodiscriminating abilities toward protonated primary amines and amino acid methyl ester salts were examined by the UV–vis titration method. These receptors exhibit good chiral recognition towards the isomers (up to $K_L/K_D = 5.23$, $\Delta\Delta G_0 = 4.10$ kJ mol^{-1}) in $CHCl_3$:MeOH = 2:1 at 25 °C.

Keywords Rosin acid · BINOL · Chiral crown ethers · Enantiodiscriminating abilities · UV–vis spectroscopy

Introduction

Enantiomeric recognition and separation of amine compounds are among the main topics of supramolecular chemistry since these compounds are basic building blocks of biological molecules and a number of them are known to possess potent biological activities [1, 2]. Among the numerous types of host molecules studied, chiral 18-crown-6 derivatives have been recognized as the most successful for the enantiodiscrimination of protonated primary amines [3–8] and high effectiveness of chiral 18C6 compounds in enantiomeric separations have been demonstrated by chromatographic methods [9–17]. Despite the well-established supramolecular system, there is still a strong requirement for novel types of host molecules in order to improve the enantioselectivity and performance in the enantiomer separation.

To prepare optically active crown ethers, especially the chiral host molecular without C_2-symmetric, natural products such as amino acids and carbohydrates [1, 18, 19] were often used as chiral starting material. However, the use of terpenoids as chiral pools has received fewer acceptances [20]. Naturally occurring enantiomeric abietic acid, the major diterpenoid components of rosin acid, promises to be an excellent starting material for preparing chiral reagents for enantiomeric separations because of its absolute optical purity and very stable stereochemistry structure. Maleopimaric acid, the Diels–Alder adduct of levopimaric acid with maleic anhydride [21], has been applied in catalytic asymmetric reaction [22]. In our prior works, we have reported using maleopimaric acid in the separations of D/L amino acids by CE [23–26]. Our interest has been focused on the developing of the chiral crown ether for the chromatographic uses, by using structural feature of maleopimaric acid. We report here an efficient and short-step synthesis of two optically pure crown ethers containing methoxycarbonyl groups, using maleopimaric acid and BINOL as start materials, and the result of enantiomeric recognition.

Results and discussion

Synthesis

The *Diels–Alder* addition product of rosin acid with maleic acid anhydride (**2** in Scheme 1) contain three functional

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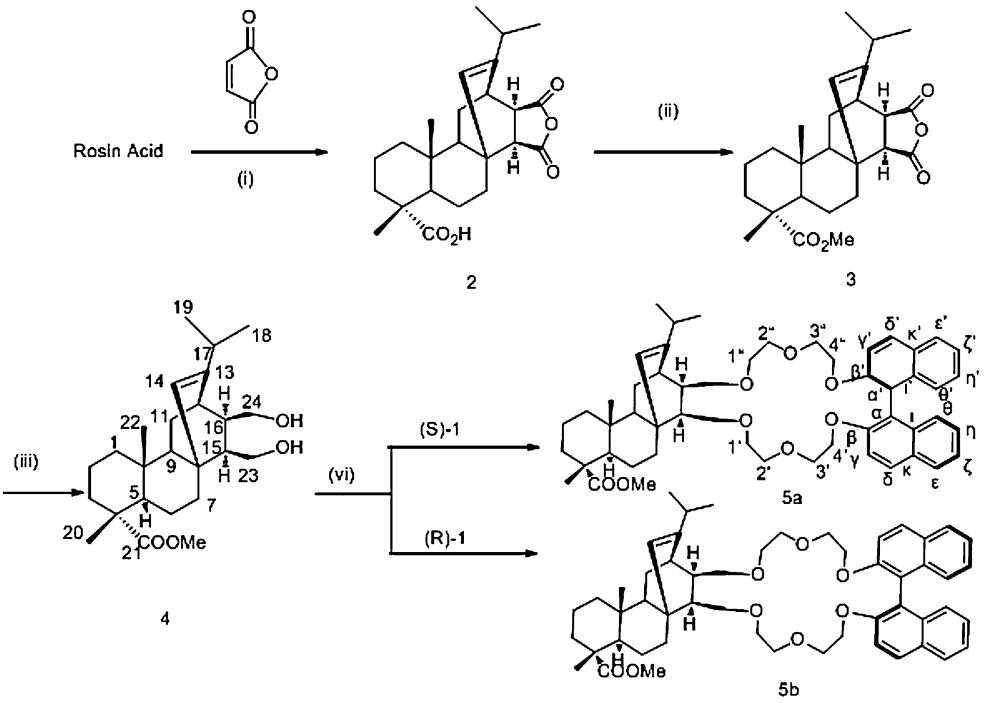
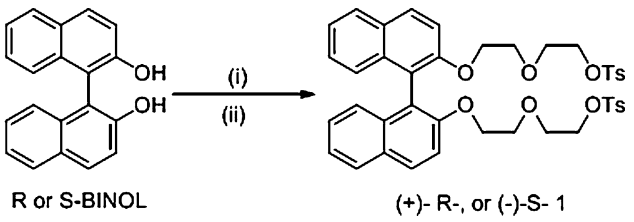


Scheme 1 Reagents and conditions: (i) no solvent, 140 °C; (ii) PCl_3, then MeOH, reflux, 4 h; (iii) $NaBH_4$ dioxane, reflux, 0.5 h; (vi) NaH, **1**, THF, reflux, 50 h

groups in their multiple cyclic chiral structures, and their reduction products **4** possessing two hydroxyl groups served as linkage part of host molecular in present crown ether synthesis. Introduction of a 2,2′-dihydroxy-1,1′-binaphthyl (BINOL) unit on these crown ethers may result in some interesting features: (i)formation of dual *chiral architectures* with rosin terpenoid structure *to control the shape and the cavity of the crown*, for observing special selectivity to different guests (ii) *providing supplementary* rigid *steric and chiral barriers*, which may allow different enantioselective interactions with chiral guests enantiomers, (iii) facilitate *photophysical studies* involving intramolecular by UV–vis spectroscopy, because of the presence of the photoactive 1,1′-binaphthyl chromophore [27].

The ditosylate **1** was prepared according to the reported procedure [28] in 27.2% overall yield, as shown in Scheme 2. Maleopimaric acid **2** and its methyl ester were prepared according to the reported procedure [21, 29]. The conversion of methyl esters **3** to diol **4** was carried out by the reported procedure [30] in 53% yield and followed by



Scheme 2 Synthesis of the ditosylate (+)–(*R*)– or (−)–(S)–**1**: (i) K_2CO_3/KI, 2-(2-chloroethoxy)ethanol, DMF, 150 °C, 48 h; (ii) Et_3N, TsCl, dichloromethane, rt., 24 h

the ring closure with (R) or (S) ditosylate **1** in the presence of NaH in THF under high dilution conditions [31]. The resulted host compound bears a methoxycarbonyl group in the side chain, which can easily be used as linkage group covalently bound to silica gel in the preparing chiral stationary phases or membranes [15].

The structures purposed for these new chiral macrocycles are consistent with the data obtained from NMR, MS and IR spectra. Structural assignment was further confirmed by compare with the NMR data (including ^1H, ^{13}C, COSY, HSQC, HMBC and ROESY) of its methoxycarbonyl reduction products.

UV–vis

In the UV spectroscopic titration experiments, addition of varying concentrations of guest molecules resulted in gradual increase or decrease of characteristic absorptions of the host molecules, the difference in the UV–vis spectra of its free and complexed states is sufficient for the estimation of molecular recognition thermodynamics.

Under the conditions employed herein, two primary amines and two amino acid methyl ester hydrochlorides salts were selected as the guest molecules. Absorption increased upon addition of the selected guests to all the hosts in $CHCl_3$: MeOH (2:1) at 25 °C. Under this condition, the absorption intensity at 327 nm for **NEA–HCl** and 281 nm for other guests were collected. The behavior of crown ethers (**6a–b, 7a–b**) and the selected guests during the titration indicated 1:1 complexation. The association constants (K_a) all the

supramolecular system formed were determined by titration, and analyzed by the Rose–Drago method [32]. The results of Ka and free-energy changes ($-\Delta G_0$) of these hosts with guest molecules are summarized in Table 1.

Taking into account the data in Table 1, it was shown that crown ethers **5a–b** formed complexes of appreciable stability constants towards isomers of all the ammonium ions hydrochloride ($Ka = 2.81 \times 10^3$–1.69×10^4 dm^3 mol^{-1}; $G_0 = 24.13$–19.68 kJ $\times$ mol^{-1}). The data presented herein are competitively to those obtained with chiral Eighteen member receptors [3–8], which implied that these 22-membered crown ethers coordinate the cation in a similar fashion as that for 18-crown-6, and founded the basis of chiral recognition.

However, the extent of enantiomeric recognition varies greatly, depending on different host–guest systems. It was mainly affected by the variation of their structure complementarity and displayed by the complex formed between the guest and the given ligand. The main structural feature governing effective enantiomeric recognition of the two crown ethers are broaden cavity of the 22-crown-6 and the special configurational characteristics of the ether chain with different diasteretopic faces, which formed by the combination of the dissimilar chiral units of the rosin and BINOL side chain.

It was shown from the data of K_D/K_L in Table 1, these receptors exhibit good chiral recognition towards most of the isomers excepted **5a** to NEA-HCl and **5b** to PhenG-OMe HCl ($K_D/K_L = 1.01$; entry 3 and 15). Encouragingly, there were two cases of host–guest chiral recognition in which the binding constants of the favorite enantiomer is more than five times of the other ($K_D/K_L = 5.23$ and 5.22, respectively; entry 1 and 13). That may be resulted from the huge barrier provided by the multiple cyclic chiral structures of rosin terpenoid and a combination of rigid *steric* effect and π–π noncovalent interactions provided by BINOL moiety. The chiral nature of crown ether and the rigidity of microenvironment of its cavity are all expected to play an important role in enantioselective induction. Moreover, a broaden cavity of the 22-crown-6 can also be expected have important recognition effects to aromatic amines and some of the amino acid methyl ester hydrochlorides.

The data in Table 1 show that important differences in the enantiomeric recognition of crown ethers towards the different guest. The different structural complementarity of chiral crown ethers with different configuration in the side chain to the guests with varies structure can be observed. Comparing the K_D/K_L values of NEA HCl (1.01 for **5a**; 1.40 for **5b**; see in Table 1, entry, 3; 11) with that of PEA HCl, PhenG-OMe HCl and PhenA-OMe HCl (5.23, 1.39

Table 1 Binding constants (*Ka*), free-energy changes ($-\Delta$Go), enantioselectivities K_L/K_D and $\Delta\Delta G_0$ calculated from $-\Delta$Go, for complexation for 1:1 complexes between L/D- amines salts and chiral host **5a** and **5b** in $CHCl_3$:MeOH (2:1) at 25 °C

Entry	Host	Guest	K_a (L mol^{-1})	K_D/K_L	$-\Delta G_0$ (KJ mol^{-1})	$\Delta\Delta G_0$ (KJ mol^{-1})
1	**5a**	*R*-PEA-HCl	$(1.69 \pm 0.61) \times 10^4$	5.23	24.13	4.10
2		*S*-PEA-HCl	$(3.23 \pm 0.9) \times 10^3$		20.03	
3		*R*-NEA-HCl	$(1.17 \pm 0.18) \times 10^4$	1.01	23.21	0.02
4		*S*-NEA-HCl	$(1.15 \pm 0.34) \times 10^4$		23.19	
5		*D* -PhenA-OMe·HCl	$(1.17 \pm 0.17) \times 10^4$	1.03[c]	23.22	−0.69
6		*L*-PhenA-OMe·HCl	$(1.55 \pm 0.75) \times 10^4$		23.91	
7		*D*-PhenG-OMe·HCl	$(5.88 \pm 0.87) \times 10^3$	1.39	21.51	0.82
8		*L*-PhenG-OMe·HCl	$(4.23 \pm 0.74) \times 10^3$		20.70	
9	**5b**	*R*-PEA-HCl	$(7.40 \pm 0.96) \times 10^3$	1.65	22.09	1.24
10		*S*-PEA-HCl	$(4.50 \pm 0.70) \times 10^3$		20.85	
11		*R*-NEA-HCl	$(1.40 \pm 0.18) \times 10^4$	1.40	23.67	0.84
12		*S*-NEA-HCl	$(1.00 \pm 0.06) \times 10^4$		22.84	
13		*D*-PhenA-OMe·HCl	$(1.47 \pm 0.20) \times 10^4$	5.22	23.78	4.10
14		*L*-PhenA-OMe·HCl	$(2.81 \pm 0.81) \times 10^3$		19.68	
15		*D*-PhenG-OMe·HCl	$(4.08 \pm 0.69) \times 10^3$	1.06	20.61	0.14
16		*L*-PhenG-OMe·HCl	$(3.86 \pm 0.81) \times 10^3$		20.47	

PEA-HCl 1-phenylethylamine hydrochloride salts, *NEA-HCl* 1-(1-naphthyl)ethylamine hydrochloride salts, *PhenA-OMe·HCl* phenylalanine methyl ester hydrochloride salts, *PhenG-OMe·HCl* phenylglycine methyl ester hydrochloride salts

[a] Concentration of the receptor (**5a**, **5b**: 5×10^{-5})

[b] K_R/K_S

[c] K_L/K_D

[d] $\Delta\Delta G_0 = \Delta G_0(D/R) - \Delta G_0(L/S)$

and 1.32 for **5a**; 1.65, 1.06 and 5.22 for **5b**; see in Table 1, entry 1, 7, 5; 9, 15, 13), it was shown that **5a** and **5b** showed better enantiomeric discrimination in average to the selected guests with relatively small group than to those with large group, crown ether with S-form of 1,1′-binaphthyl group (**5a**) showed better enantiomeric discrimination to the small-sized molecules, while the crown ether with R-form of 1,1′-binaphthyl group (**5b**) have advantage in recognition of middle-sized molecules. It may be result of the deferent configurational characteristics of the ether chain between **5a** and **5b**[1]. The highest enantioselectivity was achieved in the case of **5a** to PEA HCl. Since the crown ethers possess two diasteretopic, non equivalent faces, it is essential that the complexation for an efficient enantiodiscrimination should occur in such a manner that two guest enantiomers selectively complex to one of the different faces or to the same faces of the crown ether with different steric interaction and stability. The attitude of macrocycle **5a** to the small-sized molecules and **5b** to middle-sized molecules deserves a special consideration in its application.

Experimental

General information

Optical pure primary amines and amino acid methyl ester salts and 2, 2′-dihydroxy-1, 1′-binaphthyl were purchased from Sigma-Aldrich Chemicals (St. Louis, MO, USA). Gum rosin was purchased from Wuzhou Pine Chemicals (Wuzhou, China). All the other chemicals and organic solvents used in this work were of analytical grade unless otherwise specified. Optical rotations were measured using a Perkin Elmer Model 341polarimeter at ambient temperature and $[\alpha]_D$-values were given in units of 10^{-1} deg cm^2 g^{-1}. NMR spectra were measured in $CDCl_3$ on a BRUKER AVANCE AV500 spectrometer using TMS as the internal standard. IR spectra were recorded on a Nicolet ESP 360 FT-IR instrument. The mass spectra were obtained on a BRUKER ESQUIRE HCT spectrometer. Elemental analyses were performed on a Carlo Erba model 1106 elemental analyzer. HR–ESI–MS was recorded in Agilent 6210LC/MSD TOF. UV–vis absorption spectra were recorded with a CARY 100 spectrophotometer.

UV spectral measurements

The abilities of crown ethers to coordinate to amines and amino acid methyl ester hydrochlorides salts were investigated using UV spectroscopic titration [12] The UV–vis spectra were measured at 25 ± 0.1 °C with thermostated cell compartment by CARY 100 spectrophotometer. The same concentration of guest solution was added to the sample cell and reference cell. The maximum wavelengths are 327 nm for **5a** and **5b** to NEA HCl and 281 nm for other host–guest systems. $CHCl_3$:MeOH (2:1) was used as the solvent. The concentration of the hosts is 5.0×10^{-5} mol dm^{-3} with the increasing concentration of the added guest.

4-Methyl-13-(1-methylethyl)-4-methoxycarbonyl-16αH-atis-13-ene-23, 24-diol

4.04 g (0.01 mmol) **3** were dissolved in 100 mL dry dioxane; this mixture was added dropwise to 1.51 g (0.0376 mmol, 98%) $NaBH_4$ under cooling with ice. This mixture was stirred and heated at refluxing temperature for 30 min, and then the reaction mixtures was poured into ice water and conc. HCl were added before the mixture was extracted five times with CH_2Cl_2. The organic phase was dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography (petroleum ether:ethyl acetate = 3:1) to give pure product (2.6 g) as a colourless needle. Yield 53%. m.p. 163–165 °C (Ref. [30]: m.p. 163–164 °C), $[\alpha]_D^{25}$ + 33.1 (*c* 1.50, EtOH); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.59 (s, 3H, CH_3-22), 0.92–0.98 (m, 1H, H-1), 0.99 (d, J = 6.7 Hz, 3H, CH_3-18), 1.00 (d, J = 6.7 Hz, 3H, CH_3-19), 1.07–1.15(m, 5H, H-2, H-11 and CH_3–20), 1.35–1.55 (m, 7H, H-1, H-3, H-5, CH_2-6, H-7 and H-9), 1.62–1.73 (m, 3H, H-2, H-3 and H-11), 1.84 (dt, J = 9.8, 2.7 Hz, 1H, H-15), 1.98 (m, 1H, H-7), 2.20 (m, 2H, H-16, H-17), 2.37 (s, 1H, H-12), 3.43 (t, J = 10.4 Hz, 1H, H-23), 3.49–3.60 (m, 2H, H-23, H-24), 3.67 (s, 3H, OCH_3), 3.71–3.81 (m, 2H, H-24, OH-23 or OH-24), 5.33 (s, 1H, H-14). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.78 (C-22), 16.86 (C-20), 17.17(C-2), 20.48 (C-18), 21.16 (C-19), 22.34 (C-6), 30.13(C-11), 33.21 (C-17), 36.14 (C-3), 36.88 (C-7), 37.69 (C-4), 38.16 (C-12), 38.24 (C-10), 40.26 (C-1), 45.84 (C-8), 47.22(C-16), 49.41 (C-5), 51.96 (OCH_3), 54.08 (C-15), 55.20 (C-9), 61.10(C-23), 65.50 (C-24), 124.81 (C-14), 148.10 (C-13), 179.58(C-21); IR (KBr, ν, cm^{-1}): 3224(OH), 2928, 2867(CH_2), 1719(C=O); MS (APCI) *m/z*: 405(M + H^+).

General experimental procedure for the preparation of chiral 22-crown-6 derivatives (**5a–b**)

Compound 3 (1.26 g, 3 mmol), dissolved in anhydrous THF (80 mL) was treated with NaH (60% dispersion in paraffin oil, 0.96 g, 24 mmol); after 10 min, (S)- or (R)- 1 (2.4 g, 3 mmol) in dry THF (80 mL) was added and the reaction mixture was left under stirring at room temperature within 2 h. Then the suspension was stirred for another

[1] See in the Supplementary Data for the calculated structure of **5a** and **5b** by MMFF94 Minimization

48 h at refluxing temperature. After cooling to room tempetature, 10 mL water was add to the mixture in order to deactivate the excess NaH and the mixture was filtered and concentrated in vacuo. Water (20 mL) was added to the residue, and then extracted with dichloromethane (20 mL × 3). The combined organic layer was dried over $MgSO_4$ and the dichloromethane was evaporated off. The residue was purified by chromatography over silica (petroleum ether:acetone = 12:1) to give **4a** or **4b** as a colourless powder.

Compound **5a**. Yield: 10.3%, $[\alpha]_D^{25}$ −84.8 (*c* 1.12, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.58 (s, 3H, CH_3-22), 0.85–0.93 (m, 1H, H-1), 1.00 (d, J = 6.8 Hz, 3H, CH_3-18), 1.03 (d, J = 6.9 Hz, 3H, CH_3-19), 1.08–1.14 (m, 4H, H-11, CH_3-20), 1.34–1.59 (m, 9H, H-1, CH_2-2, H-10, H-5, CH_2-6, H-7 and H-9), 1.67–1.77 (m, 3H, H-3, H-11, and H-15), 1.90–1.93 (m, 1H, H-7), 2.10–2.14 (m, 1H, H-16), 2.19 (sept. d, J = 6.5, 1.2 Hz, 1H, H-17), 2.66 (s, 1H, H-12), 2.86 (t, J = 9.3 Hz, 1H, H-23), 2.95 (t, J = 9.1 Hz, 1H, H-24), 3.11–3.73 (m, 17H, H-23, H-24, OCH_3, CH_2-1′, CH_2-1″, CH_2-2′, CH_2-2″, CH_2-3″, CH_2-3′), 3.98–4.22 (m, 4H, CH_2-4′ and CH_2-4″), 5.31 (s, 1H, H-14), 7.13 (d, J = 8.5 Hz, 2H, H-θ or H-θ'), 7.20(t, J = 7.6 Hz, 2H, H-η and H-η'), 7.32 (dd, J = 11.5, 7.2 Hz, 2H, H-ζ and H-ζ'), 7.42 (d, J = 9.0 Hz, 1H, H-γ or H-γ'), 7.46 (d, J = 9.0 Hz, 1H, H-γ or H-γ'), 7.85(t, J = 9.2 Hz, 2H, H-ε and H-ε'), 7.90 (d, J = 9.0 Hz, 1H, H-δ or H-δ'), 7.95 (d, J = 9.0 Hz, 1H, H-δ or H-δ'); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.81 (C-22), 16.80 (C-20), 17.14 (C-2), 19.55 (C-19), 20.26 (C-18), 20.97 (C-6), 29.03 (C-11), 33.37 (C-17), 35.82 (C-12), 35.90 (C-7), 36.83 (C-3), 37.71 (C-9), 38.18 (C-1), 40.08 (C-8), 42.38 (C-16), 47.26 (C-4), 49.46 (C-5), 49.55 (C-15), 51.85 (OCH_3), 55.94 (C-9), 69.57(C-4″), 69.63 (C-4′), 69.63 (C-3″), 70.00 (C-23), 70.19 (C-3′), 70.19 (C-2″), 70.35 (C-2′), 70.70 (C-1″), 70.87 (C-1′), 71.42 (C-24), 115.17, 117.72(C-γ and C-γ'), 120.15, 121.44(C-α and C-α'), 123.58, 123.79(C-θ and C-θ'), 124.89(C-14), 125.42, 125.55(C-ζ and C-ζ'), 126.15, 126.29 (C-η and C-η'), 127.78, 127.87(C-ε and C-ε'), 129.13, 129.38(C-δ and C-δ'), 129.30, 129.71(C-κ and C-κ'), 134.08, 134.11(C-ι and C-ι'), 147.52(C-12), 154.27, 154.93(C-β and C-β'), 179.54(C-21); IR (KBr, ν, cm^{-1}): 2923, 2870(CH_2), 1593, 1508, 1464 (Ar), 1724 (C=O), 1622 (C = C), 1107 (C–O-C); MS (APCI) *m/z*: 831 [M-H] $^+$. Anal. Calcd for $C_{53}H_{68}O_8$: C 76.41 H 8.23 found: C 76.38 H 8.61

Compound **5b**. Yield: 10.7%, $[\alpha]_D^{25}$ +56.2 (*c* 1.12, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.58 (s, 3H, CH_3-22), 0.92–0.98 (m, 1H, H-1), 1.00 (d, J = 6.8 Hz, 3H, CH_3-18), 1.01 (d, J = 6.9 Hz, 3H, CH_3-19), 1.08–1.15 (m, 4H, H-11, CH_3-20), 1.34–1.55 (m, 9H, H-1, CH_2-2, H-10, H-5, CH_2-6, H-7 and H-9), 1.67–1.75 (m, 2H, H-10 and H-11), 1.82 (dt, J = 9.7, 2.7 Hz, 1H, H-15), 1.89–1.90 (m, 1H, H-7), 2.09 (dt, J = 9.9, 4.9 Hz, 1H, H-16), 2.22 (sept. d, J = 6.5, 1.2 Hz, 1H, H-17), 2.62 (s, 1H, H-12), 2.88 (t, J = 9.4 Hz, 1H, H-23), 3.04 (t, J = 9.6 Hz, 1H, H-24), 3.16–3.66 (m, 17H, H-23, H-24, OCH_3, CH_2-1′, CH_2-1″, CH_2-2′, CH_2-2″, CH_2-3′, CH_2-3″), 3.97–4.16 (m, 4H, CH_2-4′ and CH_2-4″), 5.31 (s, 1H, H-14), 7.11 (t, J = 8.9 Hz, 2H, H-θ or H-θ'), 7.20(dd, J = 8.3, 6.9 Hz, 2H, H-η and H-η'), 7.27–7.36 (m, 2H, H-ζ and H-ζ'), 7.42 (d, J = 8.9 Hz, 1H, H-γ or H-γ'), 7.47 (d, J = 8.8 Hz, 1H, H-γ or H-γ'), 7.85(t, J = 6.9 Hz, 2H, H-ε and H-ε'), 7.92 (d, J = 9.0 Hz, 1H, H-δ or H-δ'), 7.94 (d, J = 8.9 Hz, 1H, H-δ or H-δ'); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.81 (C-22), 16.82 (C-20), 17.15 (C-2), 20.19 (C-19), 21.04 (C-18), 22.30 (C-6), 29.23 (C-11), 33.23 (C-17), 35.87 (C-12), 35.87 (C-7), 36.80 (C-3), 37.72 (C-10), 38.22 (C-1), 40.08 (C-8), 42.15 (C-16), 47.25 (C-4), 49.51 (C-5), 50.74 (C-15), 51.82 (OCH_3), 55.92 (C-9), 69.44 (C-4″), 69.69 (C-4′), 69.74(C-3″), 69.74 (C-23), 69.87 (C-3′), 70.02 (C-2″), 70.17 (C-2′), 70.47 (C-1″), 70.96 (C-1′), 71.47 (C-24), 115.83, 116.78 (C-γ and C-γ'), 120.63, 120.87 (H-α and H-α'), 123.62, 123.67 (C-θ and C-θ'), 124.65 (C-14), 125.45, 125.50 (C-ζ and C-ζ'), 126.17, 126.23 (C-η and C-η'), 127.79, 127.85 (C-ε and C-ε'), 129.19, 129.32 (C-δ and C-δ'), 129.40, 129.57 (C-κ and C-κ'), 134.10, 134.15 (C-ι and C-ι'), 147.89 (C-13), 154.42, 154.69 (C-β and C-β'), 179.53 (C-21); IR (KBr, ν, cm^{-1}): 2929 (CH_2), 1593, 1507, 1464 (Ar), 1723 (C=O), 1622 (C = C), 1107 (C–O-C); MS (APCI) *m/z*: 832 $[M]^+$. HRMS (ESI) m/z calcd for $C_{53}H_{66}O_8Na$: 853.4656 found: 853.4662 $[M–2H + Na]^+$. Anal. Calcd for $C_{53}H_{68}O_8$: C 76.41 H 8.23 found: C 76.36 H 8.68

Conclusions

We have synthesized two 22-crown-6 ethers possessing methoxycarbonyl side groups comprising 1, 1′-binaphthyl and rosin acid moieties in the crown ring. These receptors showed strong affinity and different complementarity to various amines salts, and exhibit excellent enantiodiscriminating abilities toward protonated primary amines and amino acid methyl ester salts isomers in chiral recognition. Practically, through a short-step synthesis, the methoxycarbonyl side groups in the resulted host molecular will facilitate the crown ether covalently bound to silica gel in the preparing chiral stationary phases.

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