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Facile Synthesis of the Uryl Pendant Binaphthol Aldehyde and Its Selective Fluorescent Recognition of Tryptophan

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An easy and convenient synthetic route to (*S*)-2-hydroxy-2'-(3-phenyluryl-benzyl)-1,1'-binaphthyl-3-carboxaldehyde (**1**), capable of recognizing tryptophan by fluorescence has been developed. The binol carboxaldehyde **1** exhibited a high selectivity to L-tryptophan over other examined L-α-amino acids such as alanine, phenylalanine, glutamine, arginine, lysine, serine, threonine, aspartat, valine, histidine and cysteine, with a fluorescence "turn-on" signal. In addition, **1** displayed chiral discrimination with good enantioselectivity toward L-tryptophan over D-tryptophan through different fluorescence enhancement factors.

Key Words : Tryptophan, Recognition, Enantioselectivity, Fluorescence, Binaphthol

Introduction

Molecular recognition is the key step in a wide range of controlled separation and chemical transformation processes, with enzymes performing this task with an unsurpassed degree of selectivity. As a consequence, chiral recognition has emerged as one of the significant processes for diverse chemical and biological phenomena.[1] Among the basic chiral compounds, enantiomerically pure α-amino acids are of particular importance as they are widely used as chiral pool in ligand design and are also investigated as precursors of chiral catalysts.[2] As an essential naturally occurring amino acid, tryptophan (Trp) plays a pivotal role in biological processes such as protein biosynthesis, animal growth, and plant development.[3] Therefore, the selective recognition of tryptophan is of great importance for its biochemical study.[4] Although considerable attention has been paid to the enantioselective recognition of unprotected α-amino acids,[5] during the past decade, only a few studies on the recognition and separation of tryptophan by steroid-based receptor[6] and molecularly imprinted polymers[7] have been documented. On the other hand, most reports on amino acid recognition mainly employ non-covalent interactions such as hydrogen bonding, metal coordination, and hydrophobic interactions. Nevertheless, receptors that are capable of recognizing α-amino acids through reversible bond formation are still rare.[8]

Recent studies demonstrated that uryl pendant binol derivative, (*S*)-2-hydroxy-2'-(3-phenylurylbenzyl)-1,1'-binaphthyl-3-carbxaldehyde (**1**), has versatile utilities such as chiral recognition of 1,2-amino alcohols[9] and as a chirality conversion reagent (CCR) for a wide range of L-amino acids to D-amino acids.[8b] Both of these applications are based on the reversible imine bond formation associated with resonance-assisted hydrogen bond (RAHB) between **1** and the amino compounds as NMR was used as the monitoring tool. On continuation of our interest in the development of fluorescent chemosensors, we speculated that the fluorescence properties of **1** and its Schiff bases with amino acids should be different; thereby **1** may act as an efficient receptor for fluorescent recognition of α-amino acids.

Herein, we report a high yield and an expedient synthetic route to receptor **1** and its fluorescent recognition of unprotected α-amino acids. Receptor **1** exhibited a high selectivity toward tryptophan among the tested α-amino acids by fluorescence "turn-on" signal, and most importantly, it also displayed a good enantioselectivity to L-Trp over D-Trp.

Experimental Section

General Methods and Materials. Compounds **2** and **3** were prepared according to the previously described method.[9] All other reagents were purchased from commercial sources and used without further purification. Amino acids were used as their tetrabutyl ammonium carboxylate salts. ^{1}H NMR spectra and ^{13}C NMR spectra were obtained on a Varian INOVA-400 MHz Spectrometer with tetramethylsilane (TMS) as internal standard. Elemental analysis was performed on a PE-2400 elemental analyzer. Melting points were measured on a Mel-Temp capillary melting point apparatus and are uncorrected. Fluorescence spectra were measured using 970 CRT fluorescence spectrophotometer made by Shanghai Analytical Instrument Factory.

(*S*)-2,2-Dihydroxy-3-hydroxymethyl-1,1-binaphthyl (5): To an ice-cooled solution of **2** (2.5 g, 7.96 mmol) in methanol, $NaBH_4$ (0.363 g, 9.55 mmol) was added and allowed to stir overnight at RT. Then, the reaction mixture was quenched with H_2O, and after evaporation of methanol, 100 mL of ethyl acetate was added into the residue. Finally, the obtained solution was filtered and washed with water several

times and the organic layer was collected, dried over sodium sulfate and evaporated to give compound **5**. Yield: 97%, mp 206-207 °C; IR (KBr) ν/cm^{-1}: 3100, 3020, 1250, 750, 690; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.93 (m, 4H, ArH), 7.37-7.33 (m, 7H, ArH), 5.03 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 133.4, 131.4, 129.5, 128.4, 127.5, 124.2, 124.1, 117.8, 110.8; Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.70; H, 5.11.

(*S*)-2-Hydroxy-1-(2,2,-dimethyl-1,3-dioxa-1,2,3,4-tetrahydroanthracen-9-yl)-naphthalene (6): Compound **5** (0.5 g, 1.58 mmol) in dry acetone was added to a solution of 2,2-dimethoxypropane (0.1 mL, 15 mmol) in dry acetone (10 mL) containing a few drops of concentrated sulfuric acid at 18-20 °C. After stirring at 20 °C overnight, the reaction mixture was neutralized by saturated sodium carbonate solution and extracted with ethyl acetate. The organic layer was washed with water, dried over sodium sulfate and removed under reduced pressure. The crude product was chromatographed on silica gel with ethyl acetate/petroleum ether as eluent (1:6, v/v) to give **6**. Yield: 83%, mp 130-132 °C; IR (KBr) ν/cm^{-1}: 3120, 2900, 1465, 1250, 751, 698; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.05-7.91 (m, 11H, ArH), 5.17 (s, 2H, CH_2), 5.00 (s, 1H, OH), 1.44 (s, 6H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.1, 135.3, 133.6, 127.8, 123.6, 115.7, 97.9, 58.2; MALD-Tof-MS (*m/z*): 357, $[M+H]^+$, 379, $[M+Na]^+$; Anal. Calcd. for $C_{24}H_{20}O_3$: C, 80.88; H, 5.66. Found: C, 80.83; H, 5.68.

(*S*)-2-(3-Phenyluryl-benzyloxy)-1-(2,2,-dimethyl-1,3-dioxa-1,2,3,4-tetrahydroanthracen-9-yl)-naphthalene (7): Compound **6** (2.42 g, 6.75 mmol) in DMF (20 mL) was added dropwise to a slurry of NaH (0.30 g, 7.43 mmol) in DMF (50 mL) with stirring under ice-cooled conditions. After 1 h of stirring, 3-phenyluryl-benzyl bromide (**3**) (2.26 g, 7.42 mmol) was added, and the stirring was continued at room temperature. After an additional 5 h of stirring, the reaction mixture was extracted with ethyl acetate and washed with water. The crude product was purified by silica column chromatography with ethyl acetate/petroleum ether as eluent (1:7, v/v) to furnish the product **7** as a yellow solid. Yield: 95%, mp 108-109 °C; IR (KBr) ν/cm^{-1}: 3300, 3010, 2900, 1680, 1465, 1250, 750, 690; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15-7.57 (m, 20H, ArH), 6.73 (s, 1H, NH), 6.71 (s, 1H, NH), 5.30 (s, 2H, CH_2), 4.81 (s, 2H, CH_2), 1.42 (s, 3H, CH_3), 1.50 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 149.8, 131.1, 128.8, 124.5, 123.9, 122.9, 120.8, 70.1, 65.6, 19.1; MALD-Tof-MS (*m/z*): 580, $[M+H]^+$; Anal. Calcd. for $C_{38}H_{32}N_2O_4$: C, 78.60; H, 5.55; N, 4.82. Found: C, 78.62; H, 5.53; N, 4.85.

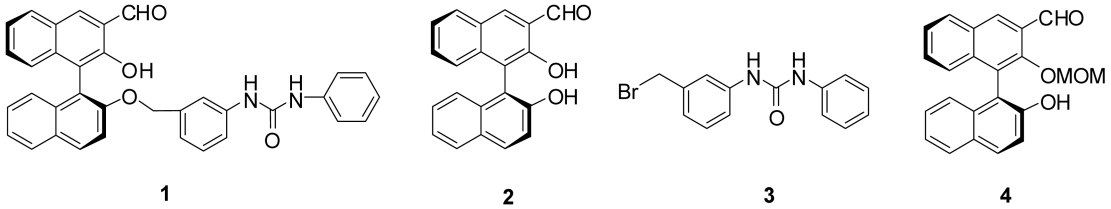
(*S*)-2-Hydroxy-3-hydroxymethyl-2'-(3-phenyluryl-benzyloxy)-1,1'-binaphthyl (8): To a stirred solution of **7** (0.27 g, 0.76 mmol) in glycol (5 mL) and THF (50 mL) was added *p*-$MeC_6H_4SO_3H$ (0.13 g, 0.91 mmol). After refluxing for 3 h, the reaction mixture was quenched with saturated sodium carbonate and extracted with ethyl acetate. The organic layer was washed with water and dried over sodium sulfate. The solution was concentrated and dried *in vacuo*. Yield: 91%, mp 96-97 °C. IR (KBr) ν/cm^{-1}: 3350, 3150, 3010, 1679, 1465, 749, 693; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15-7.39 (m, 20H, ArH), 6.73 (s, 2H, NH), 5.29 (s, 2H, CH_2), 5.07 (s, 2H, CH_2), 4.84 (s, 1H, OH), 2.03 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 148.2, 129.8, 128.1, 127.8, 126.2, 124.8, 123.1, 117.5, 76.6, 61.2; MALD-Tof-MS (*m/z*): 579, $[M+K]^+$; Anal. Calcd. for $C_{35}H_{28}N_2O_4$: C, 77.76; H, 5.22; N, 5.18. Found: C, 77.78; H, 5.19; N, 5.21.

(*S*)-2-Hydroxy-2'-(3-phenylurylbenzyl)-1,1'-binaphthyl-3-carbxaldehyde (1): To a stirred solution of **8** (0.67 g, 1.24 mmol) in methylene dichloride (40 mL) was added PCC (0.536 g, 2.48 mmol) and 0.4 g of crushed 4 Å molecular sieves at room temperature. After 12 h of stirring at RT, the mixture was diluted with methylene chloride and passed through a short pad of celite. The filtrate was washed with aqueous NaOH solution, concentrated and the product was purified by column chromatography with methanol-triethylamine (10:1, v/v) as eluent to give 0.598 g (91%) of **1** as yellow solids. Structure of **1** was confirmed by ^{1}H NMR and ESI-mass spectroscopy and the results are in full agreement with the previously reported data.[9]

Results and Discussion

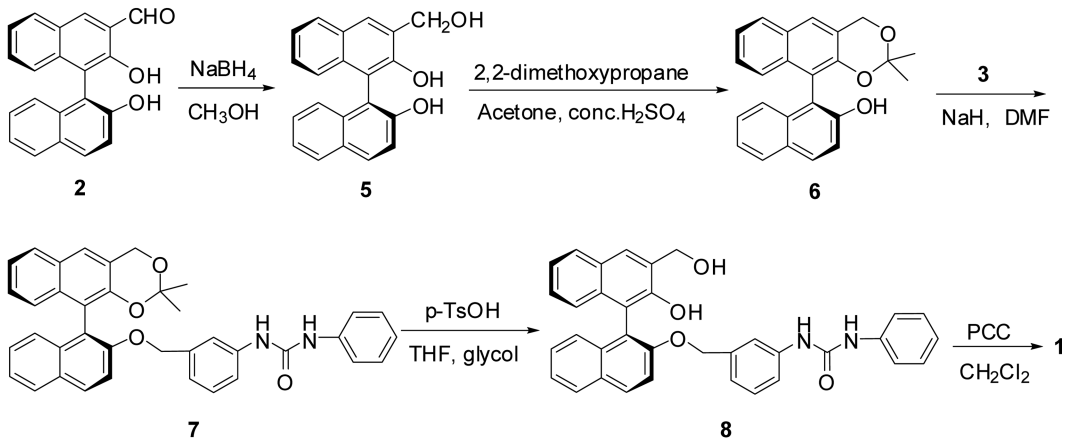
Receptor **1** has been prepared by the direct coupling of (*S*)-2,2'-dihydroxy-1,1'-binaphthyl-3-carboxaldehyde (**2**) and 3-phenyluryl-benzylbromide (**3**).[9] This reaction produces a mixture of products that are not easily separable and a time consuming one. However, Kim and co-workers developed a relatively more advantageous procedure,[10] where a mono MOM protected intermediate **4** is involved. Though the synthesis of the receptor **1** is achieved in good yield, the synthesis of the intermediate **4**, is associated with certain drawbacks such as difficult separation and relatively low yield. Therefore, there is an urgent need to design and synthesize a more convenient and high yield route to receptor **1**.

Having designed a facile synthetic route, we applied this methodology to obtain the receptor **1**. Compound **5** was obtained in almost quantitative yield by reduction of **2** with



1 **2** **3** **4**

Structures of compounds **1**-**4**.



Scheme 1. Synthesis of receptor **1**.

$NaBH_4$ in methanol, which was followed by reaction with 2,2-dimethoxypropane in dry acetone in the presence of catalytic amount of sulfuric acid afforded the protected compound **6** in high yield.[11] Reaction of **6** and **3** in dry DMF afforded the urea-based binol derivative **7**, which was followed by acid hydrolysis and Pyridinium chlorochromate (PCC) oxidation gave the target receptor **1** in a good yield (Scheme 1).

To evaluate the selectivity of **1** to α-amino acids, the fluorescence intensity changes of **1** in ethanol upon addition of 14 equiv of various L-amino acids were firstly explored (Figure 1). Receptor **1** in ethanol exhibited a weak fluorescence emission at 361 nm and upon addition of 14 equiv of L-Trp, it showed a significant increase in fluorescence intensity at 351 nm with 10 nm of blue shift. It is noteworthy that the addition of L-tyrosine resulted in a distinct fluorescence enhancement at 309 nm, which blue shifted 52 nm compared to receptor **1**, and the emission at 351 nm did not change too much. Nevertheless, addition of other L-amino acids such as alanine, phenylalanine, cysteine, glutamine, arginine, lysine, serine, threonine, aspartate, valine, histidine and cysteine do not induce remarkable fluorescence intensity changes. These results indicate that the receptor **1** performs a selective fluorescent recognition of L-Trp.

In addition, the enantioselective recognition ability of receptor **1** to D,L-tryptophan was also examined. As shown in Figure 2, when L- and D-Trp are added to the solution of **1** in ethanol (10 μM) separately, the fluorescence emission intensities at 351 nm are all increased. The enhancing efficiency (I/I_0) is about 7 folds with the addition of 14 equiv of D-Trp, while it is 18 folds with 14 equiv of L-Trp (Figure 2). In order to examine the fluorescence influence of Trp on the fluorescence intensities of the tested solutions, the fluorescence of L-Trp and D-Trp were also checked in the absence of **1** under the identical conditions (Figure 2). The results indicate that Trp itself (140 μM) exhibits very weak fluorescence intensity at 351 nm, therefore, the fluorescence influence of Trp (0 to 14 equiv) on the fluorescence of host-guest binding can be negligible under the adopted conditions. These results demonstrate that **1** acts as a good enantioselective receptor for the enantiomers of tryptophane.

To get some insight into the origin of the enantioselectivity of **1** to L-Trp, the energy minimizing of the two imines formed, namely **1**-L-Trp and **1**-D-Trp (Scheme 2) were

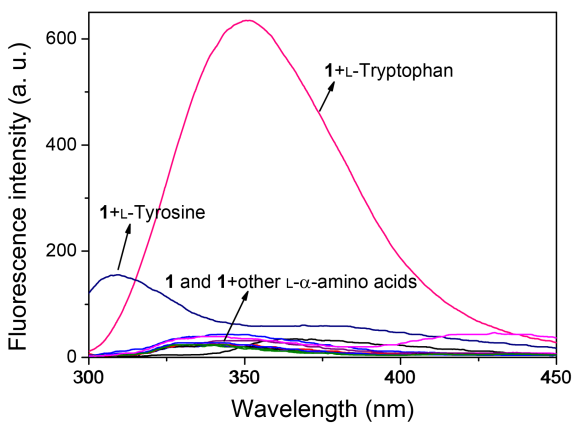


Figure 1. Fluorescence spectra of solution **1** (10 μM in ethanol) upon addition of 14 equiv of various L-α-amino acids. Each sample was checked after 5 h of the addition of amino acid at room temperature (excited at 298 nm).

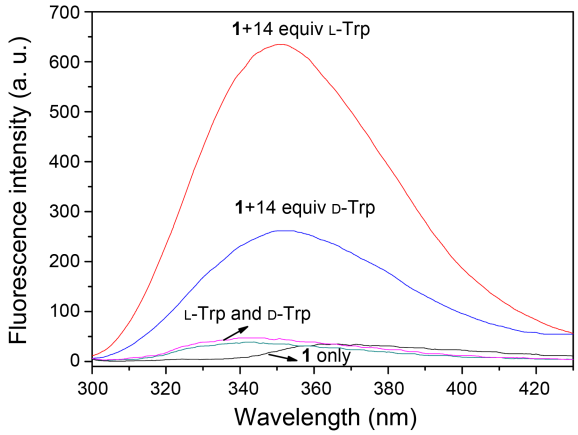
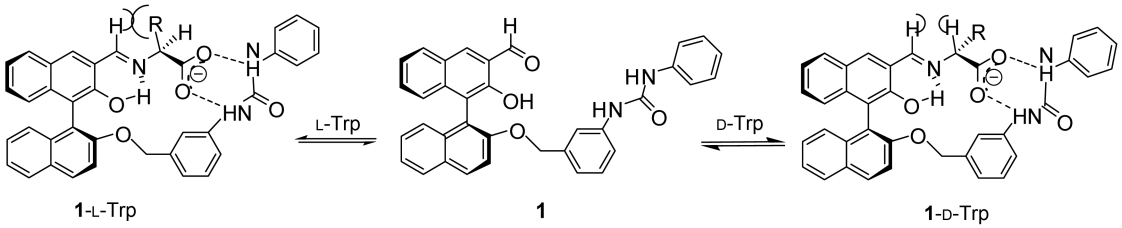


Figure 2. Fluorescence spectra of solution **1** (10 μM in ethanol) upon addition of L- and D-Trp (14 equiv of each). Each sample was checked after 5 h of the addition of amino acid at room temperature (excited at 298 nm).



Scheme 2. Schematic representation of the different steric repulsions of **1**-L-Trp and **1**-D-Trp.

carried out using Density Functional Theory (B3LYP/STO-3G in the Gaussian03 program) (molecular modelling structures were shown in supporting information Figure S1). The calculation results showed that **1**-D-Trp is more stable than **1**-L-Trp by about 3.5 kJ/mol, this result is in assistance with Kim's previous prediction.[8b] The discrepancy between thermodynamic calculation results and experimental observations inspired us to speculate that the **1**-L-Trp imine formation may undergoes a kinetic control process, whereas, the formation of "**1**-D-Trp" may undergoes a thermodynamic control process. To support our hypothesis, typical reactions were carried out as follows: 5 equiv of L-Trp and D-Trp were added into an ethanol solution of **1**, respectively, both of the reactions were kept for 1 h at room temperature and monitored intermittently by TLC. The TLC monitoring showed that reaction of **1** with L-Trp is more quickly than the reaction of **1** with D-Trp. TLC sample of the one hour reaction mixture "**1**+L-Trp" showed **1** is almost disappeared and a new spot corresponding to imine product clearly appeared, whereas, **1** in the reaction mixture of "**1**+D-Trp" still left much. Time-dependent fluorescence of **1** solution (10 μM in ethanol) in the presence of 14 equiv. of L-Trp and D-Trp, respectively, were also examined (supporting information Figure S2). The more stronger fluorescence intensity of reaction mixture "**1**+L-Trp" also demonstrate that reaction rate of **1** and L-Trp is faster than that of **1** and D-Trp at room temperature. Whereas, when the reaction mixtures were heated to reflux, the formation of **1**-D-Trp is faster than that of **1**-L-Trp. The opposite reaction rates of **1** with L-Trp and D-Trp at low and high temperature can support, to some extent, the formation of **1**-L-Trp undergoes a kinetic control process and the formation of **1**-D-Trp undergoes a thermodynamic control process. Combination of the abovementioned experiment results, the good enantioselectivity of **1** toward Trp enanotiomers can be attributed to the relative faster formation of **1**-L-Trp imine under adopted experiment conditions.

Subsequently, fluorescence titrations of solution **1** (10 μM) by using a series amount of L-Trp and D-Trp were carried out. Figure 3(a) shows that, upon incremental addition of L-Trp into solution **1**, the fluorescence intensity at 351 nm increases accordingly. Similarly, incremental addition of D-Trp into solution **1** also induces a gradual fluorescence enhancement at 351 nm, but the increasing degree is smaller compared to L-Trp (Figure 3(b)). These results reveal that the receptor **1** has a good enantioselectivity to L-Trp over D-Trp.

To further understand the enantioselectivity of **1** to L- and D-Trp, their binding constants were calculated by Benesi-Hildebrand plot method. Linear fitting of the fluorescence titration profiles using Benesi-Hildebrand plot based on a 1:1 binding mode were examined. The equation used is as follow.[12]

$$\frac{1}{I-I_0} = \frac{1}{K_s[\mathrm{L}][\mathrm{A}]} + \frac{1}{[\mathrm{L}]}$$

where I and I_0 are the fluorescence intensities at 351 nm in the presence and absence of L-Trp/D-Trp, respectively. [A] represents the concentration of L-Trp or D-Trp. K_s is the binding constant, and [L] is the concentration of **1**. Plotting of $1/(I-I_0)$ versus 1/[L-Trp] and 1/[D-Trp], respectively, showed satisfactory linear relationships (correlation coeffi-

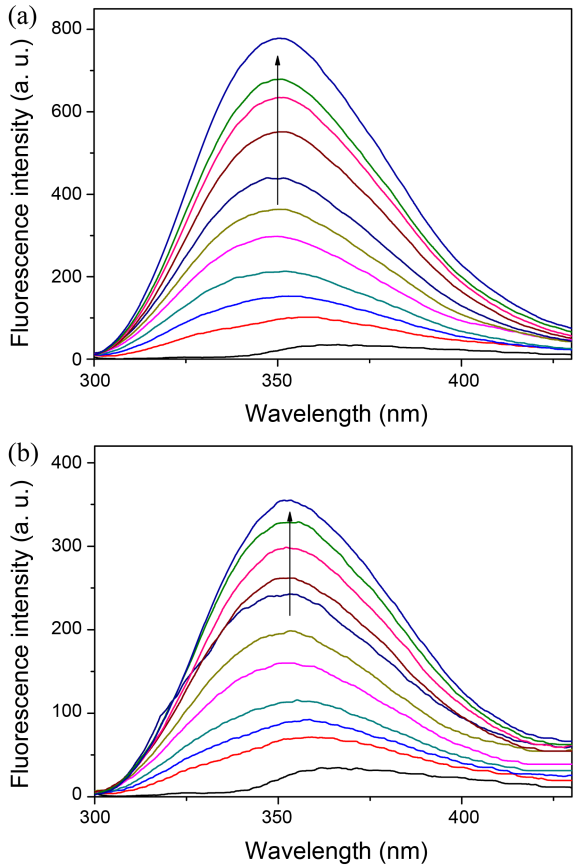


Figure 3. Fluorescence changes of solution **1** (10 μM in ethanol) upon addition of different amount of (a) L-Trp (0-20 equiv) and (b) D-Trp (0-20 equiv). Each sample was checked after 5 h of the addition of amino acid at room temperature (excited at 298 nm).

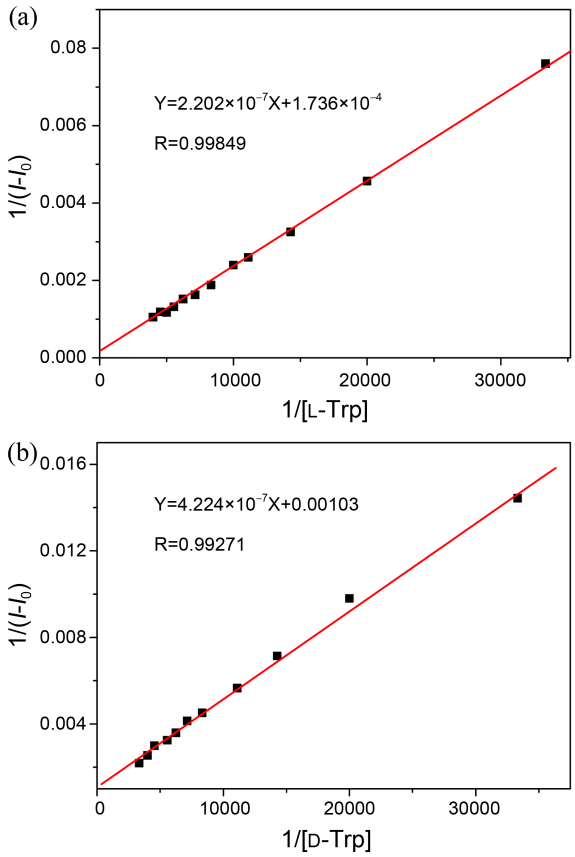


Figure 4. Benesi-Hildebrand plot (emission at 351 nm) of solution **1** (10 μM in ethanol) with (a) L-Trp and (b) D-Trp.

cient are all over 0.99) (Figure 4(a) and Figure 4(b)). The binding constant of **1** with L-Trp is calculated to be $K_{s[L]}$ = 4.54 × 10^{11} M^{-1}, while the binding constant of **1** with D-Trp is $K_{s[D]}$ = 2.36 × 10^{11} M^{-1}, thus the enantioselectivity is $K_{s[L]}/K_{s[D]}$ = 1.91:1. The greater $K_{s[L]}$ value is in good agreement with the fact that formation of imine **1**-L-Trp is easier than the formation of imine **1**-D-Trp. These results demonstrate that receptor **1** exhibits a good fluorescence enantioselectivity toward tryptophane enantiomers.

Conclusion

In conclusion, we described a novel and facile synthesis (*S*)-2-hydroxy-2'-(3-phenyluryl-benzyl)-1,1'-binaphthyl-3-carbxaldehyde (**1**) and its fluorescent recognition of *α*-amino acids. Receptor **1** displayed a high selectivity to L-tryptophan over the other examined L-*α*-amino acids including alanine, phenylalanine, cysteine, glutamine, arginine, lysine, serine, threonine, aspartate, valine, histidine and cysteine, with a significant fluorescence enhancement. Moreover, receptor **1** exhibits a good enantioselectivity toward L-Trp over D-Trp through different fluorescence enhancement factors. As far as we are aware, this is the first example of amino acid recognition based on reversible imine formation, and receptor **1** has a potential application in enantioselective fluorescent recognition of tryptophan enantiomers.

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