Enantioselective Fluorescent Recognition of β-Amino Alcohols by a Stereoselective Cyclization

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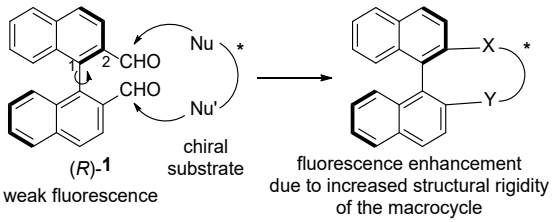
ABSTRACT: 2,2'-Diformyl-1,1'-binaphthyl is found to exhibit highly enantioselective fluorescence enhancement in the presence of various β-amino alcohols and base. It provides a new method to determine the enantiomeric composition of those substrates and has potential for high throughput analysis. On the basis of detailed spectroscopic analyses, it is proposed that a stereoselective cyclization of a β-amino alcohol with the probe should occur to form a rigid macrocyclic intermediate, contributing to the greatly enhanced fluorescence.

Introduction

Nucleophilic amine addition to aldehydes followed by dehydration to form imines has been extensively used in materials synthesis[1] and molecular recognition[2-5] including fluorescent sensing because of the reversibility of the reaction and the mild reaction conditions. Recently, we proposed to use the dialdehyde-based compound (*R*)-2,2'-diformyl-1,1'-binaphthyl [(*R*)-**1**] as a novel molecular probe for fluorescent recognition of functional amines. It was postulated that the reaction of the two electrophilic aldehyde groups of (*R*)-**1** with the two functional groups of a substrate might lead to restricted rotation around the 1,1'-bond of (*R*)-**1** which should increase the structural rigidity and thus enhance the fluorescence (Scheme 1). The chirality of the probe could also allow differentiation of the two enantiomers of a chiral substrate due to a potentially stereoselective reaction. However, when the enantiomer of (*R*)-**1**, (*S*)-**1**, was amine group to an aldehyde group of (*S*)-**1** was observed without the concomitant addition of the carboxylate group to another aldehyde except when the dicarboxylic acid derivatives, that is, glutamic and aspartic acids,

Scheme 1. A proposed double nucleophilic addition to the dialdehyde probe.



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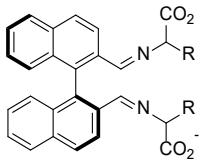
were used.[6] Condensation of (*S*)-**1** with excess amount of an α-amino acid can form a diimine product like **2** which did not generate significant fluorescence enhancement.



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In order to further explore the application of the molecular probe (*R*)- or (*S*)-**1**, we studied their interaction with β-amino alcohols that can generate a more nucleophilic alkoxide group under basic conditions than the carboxylate group of α-amino acids. It is discovered that compound (*R*)-**1** exhibits highly enantioselective fluorescence enhancement in the presence of various chiral β-amino alcohols under basic conditions. It can be used to determine the enantiomeric composition of these substrates.[7,8] Our mechanistic study has demonstrated that unlike most α-amino acids, a β-amino alcohol can undergo stereoselective cyclization with (*R*)-**1** to form a macrocyclic intermediate which contributes to the greatly enhanced fluorescence. Herein, these results are reported.

Results and Discussion

We examined the fluorescence response of (*R*)-**1** toward D- and L-alaninol in various solvents in the presence of a base (See Figure S1 in SI). Highly enantioselective fluorescence responses were observed. Figure 1 gives an example of the fluorescence spectra of (*R*)-**1** with D- and L-alaninol (2.0 equiv) and NaOH (2.0 equiv) in CH_3OH/CH_3CN (99/1). It shows that D-alaninol greatly enhanced the fluorescence of (*R*)-**1** at λ = 383 nm (I_R/I_0 = 101) but the fluorescence enhancement by L-alaninol was much smaller. The enantioselective fluorescence enhancement ratio [*ef* = $(I_R-I_0)/(I_S-I_0)$] was found to be 7.3. We examined the fluorescent response of (*R*)-**1** toward L- and D-alaninol in the *absence* of base (see Figure S2 in SI) and found

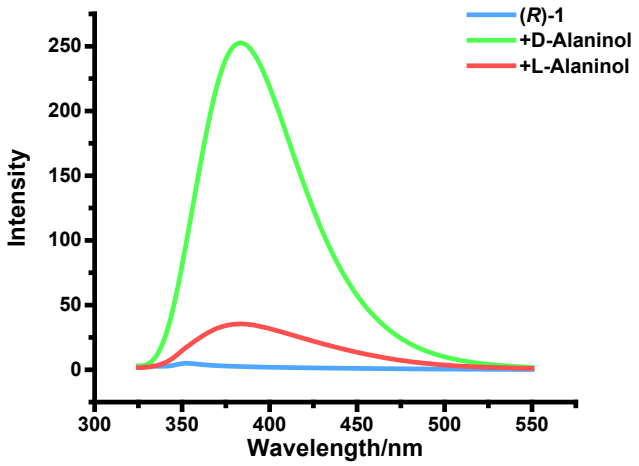


Figure 1. Fluorescence spectra of (*R*)-**1** (2.0×10^{-5} M) with L- and D-alaninol (2.0 equiv) and NaOH (2.0 equiv). (Solvent: CH_3OH/CH_3CN = 99/1, v/v. λ_{exc} = 314 nm, slits: 5/5 nm)

much weaker fluorescence responses. The fluorescence response of (*R*)-**1** with L- and D-alaninol in the presence of various bases was also examined. It was found that the common organic bases (pyridine, N-methylpiperidine and triethylamine) cannot cause fluorescence enhancement, but other bases such as tetramethylguanidine, tetrabutylammonium hydroxide, potassium carbonate, sodium hydroxide, potassium hydroxide and potassium tert-butoxide can all cause fluorescence enhancement (see Figure S29 in SI).

A detailed investigation on the fluorescent response of (*R*)-**1** toward D- and L-alaninol was then conducted. In these measurements, (*R*)-**1** (2.0 mM) in CH_3CN was mixed with D- or L-alaninol (2.0 equiv) and NaOH (2.0 equiv) in methanol at 30 °C and then diluted with methanol to 2.0×10^{-5} M. We studied the influence of the reaction time before dilution on the fluorescent response. As shown in Figure S3 in SI, the fluorescence enhancement of (*R*)-**1** by D-alaninol (2.0 equiv) became stable after 150 min, and much weaker fluorescence enhancement was observed with the addition of L-alaninol. Therefore, all the subsequent fluorescence measurements were conducted after 180 min of reaction. As shown in Figure 2 and Figure S4 in SI,

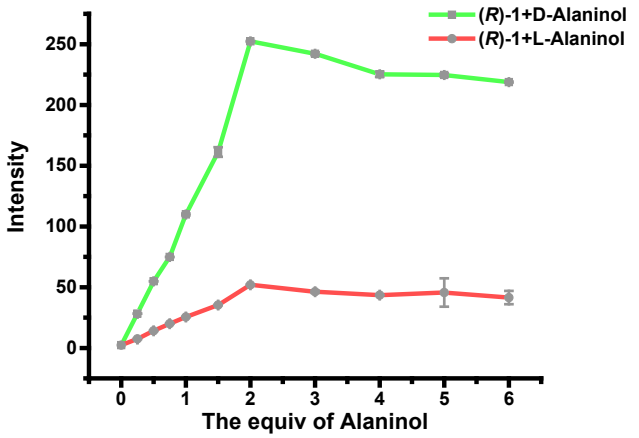


Figure 2. Fluorescence intensity of (*R*)-**1** (2.0×10^{-5} M) at λ = 383 nm versus varying equivalence of L- and D-alaninol. (Solvent: CH_3OH/CH_3CN = 99/1, v/v. Error bars from three independent experiments. λ_{exc} = 314 nm, slits: 5/5 nm)

while the concentration of D-alaninol increased, there was large increase of the fluorescence intensity of (*R*)-**1** at 383 nm which reached maximum at 2.0 equiv D-alaninol. When more than 2.0 equiv of D-alaninol was added, the fluorescence started to decrease. A similar trend was observed when L-alaninol was used, but the fluorescence intensities were much smaller.

The fluorescent response of (*S*)-**1**, the enantiomer of (*R*)-**1**, toward L- and D-alaninol was also studied under the same conditions. As shown in Figure S5 in SI, a close to mirror image relation was observed between the fluorescent responses of (*R*)- and (*S*)-**1** toward the enantiomers of this amino alcohol, which confirms the inherent chiral recognition process. We examined the interaction of (*R*)- and (*S*)-**1** with alaninol at various enantiomeric compositions and plotted the fluorescence intensities of each enantiomeric probe versus the enantiomeric excess of the amino alcohol in Figure 3. A mirror image relationship was observed between the fluorescent responses of this pair of enantiomeric sensors. Thus, using these figures, the enantiomeric composition of this amino alcohol can be determined.

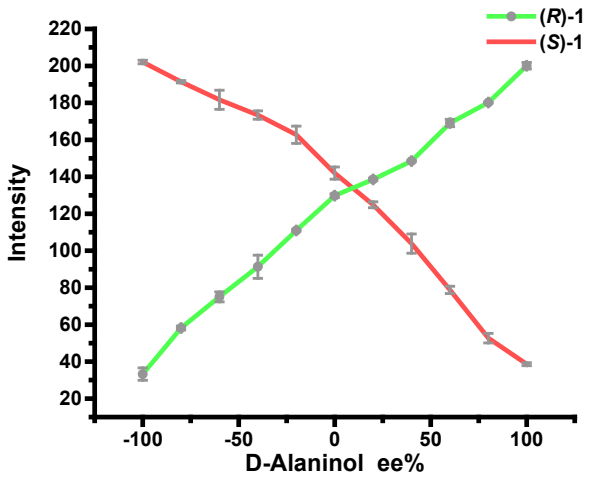


Figure 3. Fluorescence intensity of (*R*)- and (*S*)-**1** (2.0×10^{-5} M) at λ = 383 nm versus [D-alaninol] % (2.0 equiv) (Solvent: CH_3OH/CH_3CN = 99/1, v/v. Error bars from three independent experiments. λ_{exc} = 314 nm. Slit: 5/5 nm).

The CD spectra of (*R*)-**1** show significant changes especially at 229 and 260 nm when treated with L- or D-alaninol (see Figure S24 and S25). At those wavelengths, the CD responses of (*R*)-**1** toward L-alaninol are different from those toward D-alaninol. This indicates that the reaction of (*R*)-**1** with L-alaninol should be very different from the reaction with D-alaninol. The UV spectra in Figure S26 and S27 in SI also show significant differences between the reactions of (*R*)-**1** with L- and D-alaninol. The fluorescence quantum yield of (*R*)-**1** was found to be <0.01% which increased to 1.22% upon reaction with D-alaninol (2 equiv) (see Table S3 in SI).

In order to gain further understanding on the reaction of (*R*)-**1** with D- and L-alaninol, we conducted NMR spectroscopic studies. (*R*)-**1** (50.0 mM) was dissolved in CD_3CN, and D- and L-alaninol (100.0 mM) were dissolved in CD_3OD together with 2.0 equiv of NaOH.

An aliquot of the above (*R*)-**1** solution (50 μL) was added to each NMR tube together with varying equivalents of alaninol. Then, CD_3OD was added to reach a volume of 500 μL and the concentration of (*R*)-**1** in each NMR tube was 5.0 mM. After each reaction mixture was allowed to stand at 30 °C for 2 h, its ^1H NMR spectrum was obtained at room temperature (Figure 4a,b). As shown in Figure 4a,b, compound (*R*)-**1** in the mixed solvent of CD_3CN/CD_3OD (1/9) before the addition of the amino alcohols gave multiple aldehyde signals around δ 9.5 as well as two signals at δ 4.87 and 4.90. These can be attributed to the formation of two diastereomeric hemiacetal compounds from the addition of methanol to one of the aldehyde groups of (*R*)-**1**. Figure 4a,b further show that when (*R*)-**1** was treated with an excess amount of D- or L-alaninol (up to 6 equiv), it was almost completely converted to a symmetric product. Both products from the two reactions were isolated and characterized as the diimine compounds $\mathbf{5}_{\text{D-alaninol}}$ (Scheme 2) and $\mathbf{5}_{\text{L-alaninol}}$ which showed only weak fluorescence (See Figure S6 in SI).

The main difference between the reaction of D- and L-alaninol with (*R*)-**1** is that in the presence of 1 - 2 equiv of D-alaninol, a significant new ^1H NMR signal at δ 5.33 appeared (Figure 4a), but under the same conditions L-alaninol generated much weaker signals in this region (Figure 4b). We conducted detailed 1D and 2D ^1H and ^{13}C NMR spectroscopic analyses for the reaction products of (*R*)-**1** with 1.0 equiv D-alaninol in the presence of base (see Figure S7 in SI). On the basis of this study, formation of a mixture of compounds **3** and **4** is proposed for the reaction of (*R*)-**1** in the presence of 1.0 equiv alaninol and base (Scheme 2). Although this mixture cannot be separated to allow isolation of **3** and **4**, we are able to identify the NMR signals for each compound to establish their structures.

The ^1H NMR signal at δ 5.33 is assigned to H_β on the hemiacetal group of **4** and the corresponding C_d signal is at δ 88. The H_α signal of **4** is at δ 3.56 and the CH_3 proton signal is at δ 1.14 (d, J = 5.9 Hz). A NOE effect between H_β and the CH_3 proton was observed in the NOESY spectrum which has established the *R* configuration at C_d (see Figure S7d in SI). A small signal at δ 5.25 can be attributed to the H_β NMR signal of the stereoisomer with a *S* configuration at C_d and its integration ratio with the signal at δ 5.33 is 1:8. This indicates the formation of **4** is highly stereoselective.

The cross peak between H_β and C_C (δ 74) in the 2D ^1H-^{13}C HMBC spectrum supports the macrocyclic structure of **4** (See Figure S7e in SI). The two diastereotopic protons on C_C of **4** are well separated at δ 3.63 (m) and 4.43 (t, J = 6.4 Hz), consistent with a rigid cyclic structure, but for the non-macrocyclic compound **3**, the two diastereotopic protons on C_C give only a multiplet at δ 3.41 because of the flexible imine unit. The aldehyde signal of **3** gives a weak and broad signal at δ 9.51.

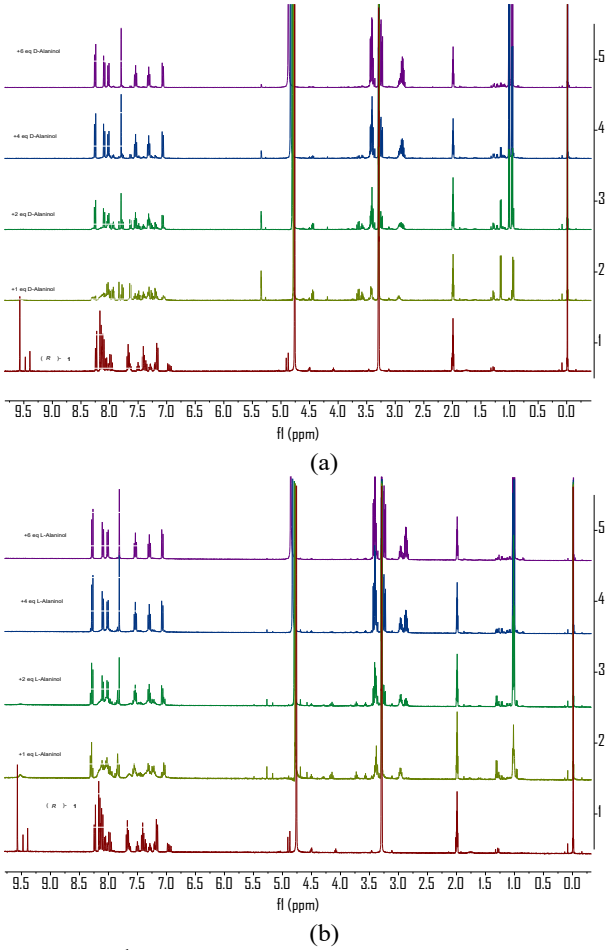
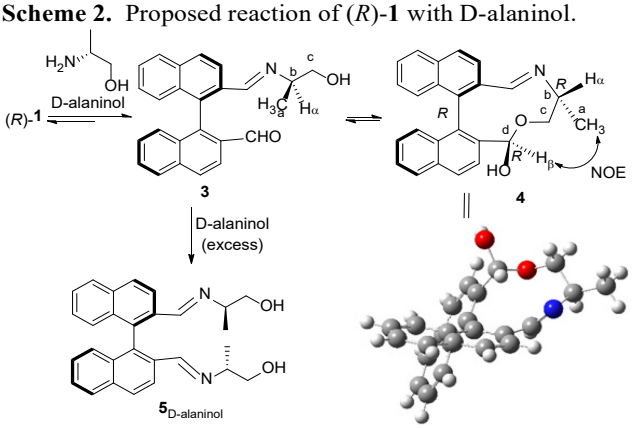
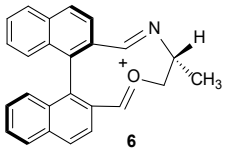


Figure 4. ^1H NMR spectra of the reaction mixture of (*R*)-**1** (5.0 mM) with varying equiv. of (a) D-alaninol and (b) L-alaninol in a mixed solvent of CD_3CN/CD_3OD (1/9). (Reaction time: 2 h.)

Scheme 2. Proposed reaction of (*R*)-**1** with D-alaninol.



We have conducted TOF mass spectroscopic analysis (ESI) for the product mixture of **3** and **4** formed from the reaction of (*R*)-**1** with 1.0 equiv D-alaninol and base (see Figure S8 in SI). A peak at m/z 368.1656 (calcd for $M+H^+$: 368.1651) can be assigned to the molecular ions of both **3** and **4**. An intense signal at m/z 350.1543 (the base peak) is observed for the fragment ion **6** formed from **4**+H^+-H_2O (calcd for M-OH: 350.1545).



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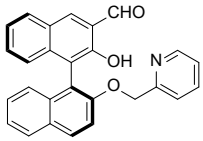
We have conducted DFT calculation (B3LYP, 6-31G*) by using Gaussian 09 serials software on the four diastereomers of **4** containing a (*R*)-binaphthyl unit (See Figure S18-S23 in SI). It is found that the stereoisomer **4** containing two *R* carbon centers is the most stable one. The energy-minimized molecular modelling structure of **4** is given in Scheme 2.

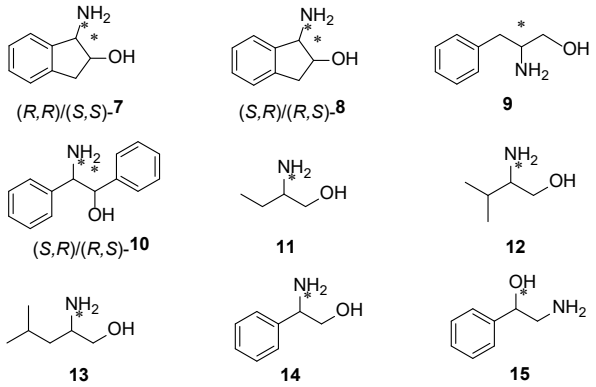
The reactions shown in Scheme 2 can be used to explain the observed enantioselective fluorescent response of (*R*)-**1** toward D- and L-alaninol. At lower concentration of D-alaninol, the monoimine compound **3** is generated which can then undergo a stereoselective intramolecular nucleophilic addition to form the macrocyclic hemiacetal compound **4**. The increased structural rigidity of **4** restricts rotation of the 1,1'-binaphthyl unit which should account for the observed greatly enhanced fluorescence. When L-alaninol is used to react with (*R*)-**1**, however, it is more difficult for the corresponding monoimine compound to undergo an intramolecular nucleophilic addition to the aldehyde group due to the formation of a less stable macrocyclic stereoisomer as shown by DFT calculation (see Figure S23 in SI), thus giving much smaller fluorescence enhancement. The isolated $\mathbf{5}_{\text{D-alaninol}}$ exhibits the same emission wavelength as **4** but has much lower fluorescence intensity. This indicates that the fluorophore of **4** should be its naphthyl-imine unit which is the same as that of $\mathbf{5}_{\text{D-alaninol}}$. That is, there should be energy migration from the less conjugated naphthyl unit of **4** to its more conjugated naphthyl-imine unit.

Previously, a 1,1'-binaphthyl-based monoaldehyde (*S*)-**7** in combination with Zn^{2+} was found to show enantioselective fluorescence enhancement in the presence of chiral *β*-amino alcohols.[8g,h] Without coordination of Zn^{2+}, (*S*)-**7** cannot form a rigid cyclic structure like **4** with an amino alcohol, and thus cannot give fluorescence enhancement.



(*S*)-**7**

We have further studied the fluorescence response of (*R*)-**1** toward additional *β*-amino alcohols under similar conditions (Figure 5). In general, while the amino alcohol stereoisomers with *S* configuration at the amine carbon cannot cause much change on the fluorescence of the probe, those with *R* configuration at the amine carbon can greatly enhance the fluorescence of (*R*)-**1** at 383 nm. As shown in Figure 6 and S9-S17 in SI, high enantioselectivity has been observed for the compounds **7** – **15**. Figure 6 gives several examples of the observed highly enantioselective fluorescent responses with the following *ef* values: 6.0 for **8**, 7.2 for **9**, 4. 2 for **11,** and 32.7 for **15**. Compound **15** containing a chiral alcohol carbon rather than a chiral amine carbon also showed high enantioselectivity in fluorescent response.



(*R,R*)/(*S,S*)-**7** (*S,R*)/(*R,S*)-**8** **9**

(*S,R*)/(*R,S*)-**10** **11** **12**

13 **14** **15**

Figure 5. Additional *β*-amino alcohols that have shown highly enantioselective fluorescence response with (*R*)-**1**.

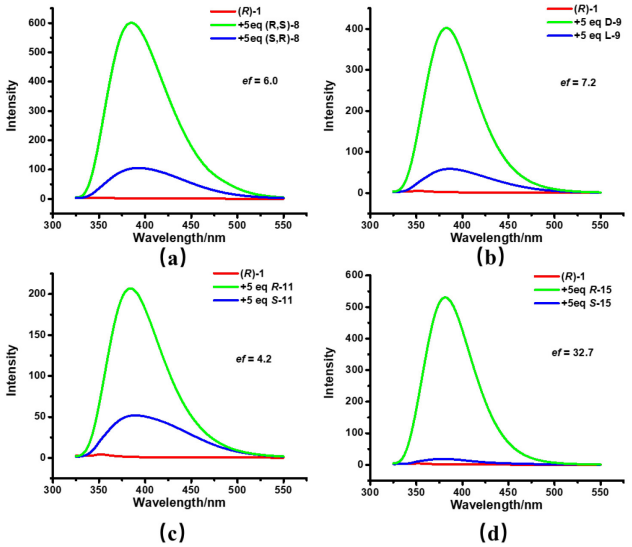


Figure 6. Fluorescence spectra of (*R*)-**1** (2.0×10^{-5} M) with (a) (*R,S*)/(*S,R*)-**8**; (b) D/L-**8**; (c) (*R*)/(*S*)-**11**; (d) (*S*)/(*R*)-**15**. (Substrate: 5.0 equiv. NaOH: 2.0 equiv. Solvent: CH_3OH/CH_3CN = 99/1, v/v. λ_{exc} = 314 nm, slits: 5/5 nm)

We have also studied the interaction of (*R*)-**1** with *γ*-, *δ*- and *ε*-amino alcohols which gave much weaker fluorescence response than those observed for the *β*-amino alcohols (see Figure S28 in SI).

In conclusion, we have discovered that the chiral dialdehyde (*R*)-**1** is a highly enantioselective fluorescent probe for chiral *β*-amino alcohols in the presence of base. We have conducted detailed 1D and 2D NMR and mass spectroscopic investigations which have revealed a stereoselective cyclization mechanism for the reaction of a *β*-amino alcohol with the probe. Formation of a structurally rigid macrocycle between the chirality-matched substrate and the probe is proposed to account for the greatly enhanced fluorescence. This work provides a new method to determine the enantiomeric compositions of various *β*-amino alcohols which has

potential for high throughput analysis.

Experimental Section

General Information

Unless otherwise indicated, all reagents were purchased from commercial sources and used without further purification. In the optical spectroscopic studies, all the solvents were HPLC grade purchased from Thermo Fisher (China) CO., Ltd. NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). Fluorescence spectra were obtained using Hitech F-7000 spectrofluorometer at 298 K. The theoretical calculations of the proposed intermediate **4** were performed using Gaussian 09 serials software. The ground-state structures were obtained by B3LYP density functional method with basis set 6-31G*. The molecular models were visualized with Gaussview 6.0 software.

Sample preparation for fluorescence measurement. A stock solution (2.0 mM) of (*R*)-**1** in a solvent such as CH_3CN was prepared. Stock solutions (4.0 mM) of the amino alcohols in methanol were prepared by mixing the amino alcohols and NaOH (2.0 equiv). For optical analysis, solutions of (*R*)-**1** (25 μL each) were added to several test tubes. A solution of an amino alcohol was added to each test tube and the resulting solution was allowed to stand at 30 °C. After 3 h, the mixture in each test tube was diluted with methanol to obtain 2.0×10^{-5} M solutions of (*R*)-**1** for fluorescence measurements. Fluorescence spectra were recorded within 1 h of the sample preparation.

Synthesis and Characterization of $\mathbf{5}_{\text{D-alaninol}}$. A mixture of D-alaninol (0.0532 g, 0.71 mmol, 2.2 equiv), (*R*)-**1** (0.1000 g, 0.032 mmol) in MeOH was stirred at room temperature for 12 h. Then the solvent was removed under reduced pressure, and the solid was washed with ice methanol to give $\mathbf{5}_{\text{D-alaninol}}$ as a pale-yellow product in 76% yield (0.1039 g). ^{1}H NMR (400 MHz, CD_3OD) δ 8.25 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 8.7 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.79 (s, 1H), 7.53 (ddd, J = 8.3, 7.0, 1.4 Hz, 1H), 7.29 (ddd, J = 8.4, 7.0, 1.4 Hz, 1H), 7.06 (d, J = 8.5 Hz, 1H), 3.40 (t, J = 5.6 Hz, 2H), 2.95 – 2.87 (m, 1H), 0.94 (d, J = 6.3 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_3OD) δ 160.30, 136.28, 134.52, 132.98, 132.87, 128.60, 128.07, 127.25, 126.80, 126.13, 122.95, 68.07, 65.66, 16.93. HRMS: m/z calcd. for $C_{28}H_{28}N_2O_2H$, $M+H^+$ = 425.2229; found: 425.2197.

Synthesis and Characterization of $\mathbf{5}_{\text{L-alaninol}}$. $\mathbf{5}_{\text{L-alaninol}}$ was prepared in the same way as $\mathbf{5}_{\text{D-Alaninol}}$ by starting with L-alaninol in 72% yield (0.0985 g). ^{1}H NMR (400 MHz, CD_3OD) δ 8.28 (d, J = 8.7 Hz, 1H), 8.09 (d, J = 8.8 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.81 (s, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 7.7 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H), 3.40 (s, 2H), 2.95 (q, J = 6.4 Hz, 1H), 1.02 (d, J = 6.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_3OD) δ 159.98, 136.33, 134.56, 132.93, 132.78, 128.64, 128.02, 127.31, 126.80, 126.38, 122.96, 68.07, 65.90, 17.41. HRMS: m/z calcd. for $C_{28}H_{28}N_2O_2Na$, $M+Na^+$=447.2048; found: 447.2002.

Acknowledgement: This work was financially supported by the National Natural Science Foundation of China (22171195) and Sichuan Science and Technology Program (2021YJ0398). LP thanks the partial support of this project by the US National Science Foundation (CHE-1855443). We also thank Jing Li from the Comprehensive Training Platform of Specialized Laboratory in College of Chemistry at Sichuan University for sample analysis.

Supplementary Information Available: Additional spectroscopic data are provided.

Keywords: Aldehydes, Amino alcohols, 1,1'-Binaphthyl, Fluorescent Probes, Enantioselective

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