JOC The Journal of Organic Chemistry

ARTICLE

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Study of the Fluorescent Properties of Partially Hydrogenated 1, 1′-Bi-2-naphthol-amine Molecules and Their Use for Enantioselective Fluorescent Recognition

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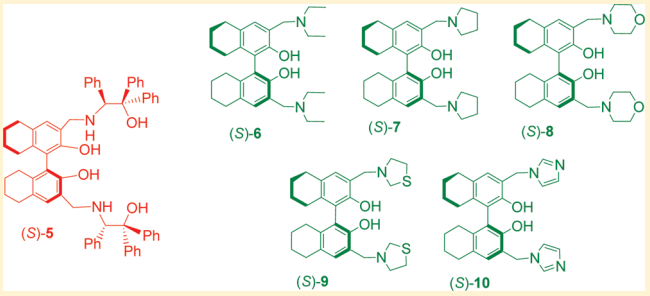
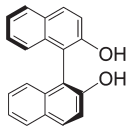
Supporting Information

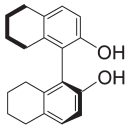
ABSTRACT: The fluorescent properties of a series of H_8BINOL-amine compounds are investigated. It is revealed that the intramolecular hydrogen bonds of these compounds contribute to the shift of the emission of their H_8BINOL unit to a much longer wavelength. That is, the emission of H_8BINOL is at λ = 323 nm, but that of the H_8BINOL-amino alcohol (*S*)-**5** is at λ = 390 nm. Binding of (*S*)-**5** with mandelic acid suppresses its intramolecular hydrogen bonding and restores the short wavelength emission of the H_8BINOL unit. When (*S*)-**5** (1.0×10^{-4} in CH_2Cl_2) was treated with (*R*)-mandelic acid (4.0×10^{-3}), a large fluorescence enhancement at the short wavelength (λ_{emi} = 330 nm) was observed with I_R/I_0 = 11.7. When (*S*)-MA was used under the same conditions, the enhancement at the short wavelength emission was much smaller. Thus, a good enantioselective fluorescent response was observed with ef =3.5 [ef: enantioselective fluorescence enhancement ratio = $(I_R - I_0)/(I_S - I_0)$]. This study demonstrates that the H_8BINOL-based molecules are promising as a new class of enantioselective fluorescent sensors.

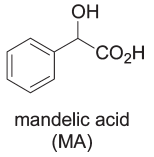


INTRODUCTION

Fluorescent chemical sensors have been applied to the detection of metal cations, pH, anions, proteins, and DNAs.[1−3] Enantioselective fluorescent sensors are also receiving increasing attentions because they can provide real time analysis for the enantiomeric composition of chiral compounds and enhance the sensitivity in the detection of chiral substrates.[4,5] Among the enantioselective fluorescent sensors developed, those based on the chiral structure of 1,1′-bi-2-naphthol (BINOL) have been actively investigated, and a few highly enantioselective fluorescent sensors have been discovered for the recognition of α-hydroxycarboxylic acids, amines, amino alcohols, and amino acids.[6] H_8BINOL is a partially hydrogenated derivative of BINOL. The increased steric bulkiness of H_8BINOL due to the sp^3 carbons and the increased electron density on the aromatic rings make this compound both sterically and electronically quite different from BINOL. The use of H_8BINOL and its derivatives in asymmetric catalysis has been actively pursued and a number of efficient catalysts have been developed.[7] However, no study on using H_8BINOL to build enantioselective fluorescent sensor was reported before. In our laboratory, we have synthesized a series of H_8BINOL-amine compounds and have explored their application in the fluorescent recognition of mandelic acid (MA), a representative of α-hydroxycarboxylic acids. This investigation demonstrates that although the H_8BINOL-based compounds do not have the extended conjugation as those derived from BINOL, they still exhibit very interesting fluorescent properties and have opened a new window in the fluorescence spectrum for the enantioselective fluorescent recognition. Herein, these results are reported.[8]

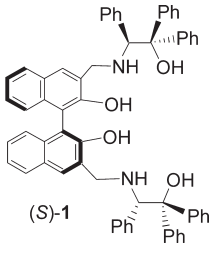






RESULTS AND DISCUSSION

Synthesis of the H_8BINOL-Amine Molecules and Study of Their Fluorescent Properties.

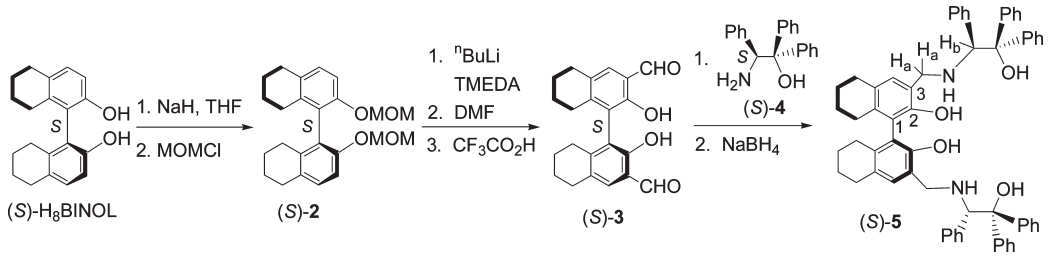


Recently, we reported that the BINOL-amino alcohol molecule (*S*)-**1** is a highly enantioselective fluorescent sensor for the structurally

Received: January 30, 2011
Published: March 15, 2011

   dx.doi.org/10.1021/jo200226k | *J. Org. Chem.* 2011, 76, 2814–2819

Scheme 1. Synthesis of the H_8BINOL-Amino Alcohol (*S*)-5



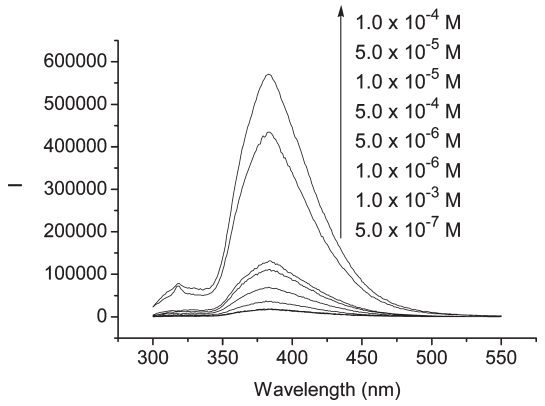


Figure 1. Fluorescence spectra of (*S*)-**5** in CH_2Cl_2 at various concentrations (λ_{exc} = 290 nm, slit = 3.0/3.0 nm).

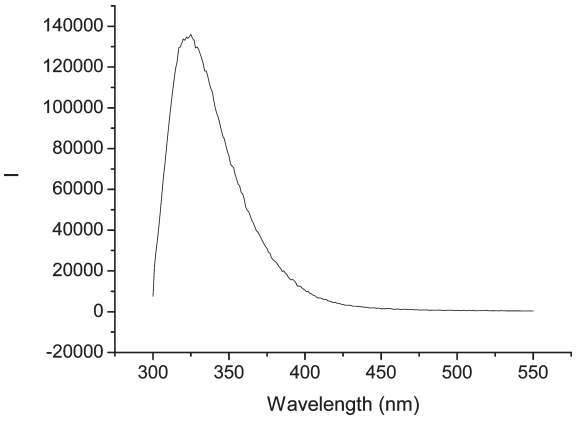


Figure 2. Fluorescence spectrum of (*S*)-H_8BINOL (2.0×10^{-4} M in CH_2Cl_2) (λ_{exc} = 288 nm, slit = 4.0/4.0 nm).

diverse α-hydroxycarboxylic acids.[9] In order to explore the application of H_8BINOL in fluorescent recognition, we have prepared a H_8BINOL analogue of (*S*)-**1**. As shown in Scheme 1, protection of (*S*)-H_8BINOL with methoxymethyl (MOM) group gave (*S*)-**2**. Ortho-lithiation followed by addition of DMF and hydrolysis gave the H_8BINOL dialdehyde (*S*)-**3**.[10] Condensation of (*S*)-**3** with the amino alcohol (*S*)-**4** followed by reduction produced the H_8BINOL-amino alcohol (*S*)-**5** in 71% yield. The specific optical rotation of this compound is $[\alpha]_D = -119.9$ (*c* 0.865, $CHCl_3$), greater than that of (*S*)-**1** {$[\alpha]_D = -93.7$ (*c* 0.80, CH_2Cl_2)}. The ^{1}H NMR spectrum of (*S*)-**5** in $CDCl_3$ shows two doublets at δ 3.59 (d, J = 13.5 Hz, 2H) and 3.77 (d, J = 13.5 Hz, 2H) for the two diastereotopic protons (H_a) of the 3,3′-methylene substituents, which are significantly more upfield than those observed for (*S*)-**1** at δ 3.78 (d, J = 13.8 Hz, 2H) and 4.16 (d, J = 13.8 Hz, 2H). This is consistent with the more electron rich aromatic rings of (*S*)-**5**.

The UV spectrum of (*S*)-**5** in CH_2Cl_2 gives absorptions at λ_{max} (ε) = 232 (2.6×10^4) and 290 (7.4×10^3) nm, without the long wavelength absorption of (*S*)-**1** at λ_{max} = 334 nm due to the reduced conjugation system in (*S*)-**5**. The peak position and shape of the absorption signals of (*S*)-**5** do not change while the concentration changes. The fluorescence spectra of (*S*)-**5** in CH_2Cl_2 at various concentrations are shown in Figure 1. Compound (*S*)-**5** gives a major emission at λ_{emi} = 390 nm whose shape and position also do not change with concentration. This emission wavelength of (*S*)-**5** is much longer than that observed for (*S*)-H_8BINOL at λ_{emi} = 323 nm as shown in Figure 2. Compound (*S*)-**5** gives only a very weak short wavelength emission signal at λ_{emi} = 318 nm close to where (*S*)-H_8BINOL emits. The concentration independence of both the absorption and emission of (*S*)-**5** indicates that the long wavelength fluorescence signal of (*S*)-**5** is not due to the formation of either excimer or ground state aggregate. The fluorescence spectrum of (*S*)-**5** is also very different from that of (*S*)-**1** which exhibits dual emission signals at λ_{emi} = 372 and 448 nm in CH_2Cl_2.[9] The fluorescence quantum yield of (*S*)-**5** is estimated to be 0.36% by using 2-aminopyridine as the standard.[11,12]

We have studied the solvent effect on the fluorescence property of (*S*)-**5**. Changing the solvent from CH_2Cl_2 to CH_3OH caused little change on the absorption as well as the fluorescence spectra of (*S*)-**5** at various concentrations. This indicates that the intermolecular hydrogen bonding interaction of (*S*)-**5** has little influence on its electronic properties. Similarly, the use of acetonitrile as the solvent also maintains the absorption and fluorescence properties of (*S*)-**5**.

In order to gain further understanding on the fluorescent properties of (*S*)-**5**, we have prepared the H_8BINOL-amine molecules (*S*)-**6**−(*S*)-**10** by using our recently developed one-step reaction of H_8BINOL with an in situ generated aminomethanol (Scheme 2).[10] These H_8BINOL-amine compounds such as (*S*)-**7** and (*S*)-**8** have exhibited excellent enantioselectivity in the asymmetric arylzinc and vinylzinc additions to aldehydes.[10,13] The fluorescence spectra of these compounds in CH_2Cl_2 (2.0×10^{-4} M) are obtained. As shown in Figure 3, compounds (*S*)-**6**, (*S*)-**7**, and (*S*)-**8** give a major emission peak at about 380 nm, similar to (*S*)-**5**. No change in peak position and shape is observed when the concentrations of these compounds are varied. However, (*S*)-**9** gives dual emissions at λ_{emi} = 329 and 370 (sh) nm, and (*S*)-**10** gives only a short wavelength emission at λ_{emi} = 324 nm. The fluorescence signal of (*S*)-**10** is very similar to that of (*S*)-H_8BINOL.

In the ^{1}H NMR spectra of compounds (*S*)-**6**, (*S*)-**7**, and (*S*)-**8**, their H_8BINOL hydroxyl proton signals appeared at δ 11.13,

dx.doi.org/10.1021/jo200226k |*J. Org. Chem.* 2011, 76, 2814–2819

11.91, and 10.38, respectively.[10] These greatly downfield-shifted ^{1}H NMR signals indicate strong intramolecular hydrogen bonds between the hydroxyl protons and the basic nitrogen atoms. The chemical shift of the hydroxyl proton signal of (*S*)-**9** (δ 9.52) is about 2 ppm less downfield than that of (*S*)-**7**. This may imply a weaker hydrogen bond in (*S*)-**9** probably because of the reduced basicity of the nitrogen atom adjacent to the sulfur atom. The H_8BINOL hydroxyl proton signal of (*S*)-**10** is observed at δ 3.48, greatly upfield-shifted in comparison with those of (*S*)-**6**−(*S*)-**9**. This is attributed to the nonbasic α nitrogen atoms of the imidazole rings of (*S*)-**10** that cannot form intramolecular hydrogen bond with the H_8BINOL hydroxyl protons at all. The more basic γ nitrogen atom in each of the imidazole rings of (*S*)-**10** is not sterically feasible to form an intramolecular hydrogen bond.

On the basis of the above analysis, we propose that the difference between the fluorescence spectra of the H_8BINOL-amine compounds (*S*)-**6**−(*S*)-**10** could arise from the different capability of their nitrogen atoms to form intramolecular hydrogen bonds. Compound (*S*)-**10** cannot form an intramolecular hydrogen bond and thus exhibits only the emission of its H_8BINOL unit. Compounds (*S*)-**6**, (*S*)-**7**, and (*S*)-**8** have strong intramolecular hydrogen bonds and thus show emission of either the intramolecually hydrogen-bonded complex or its subsequent excited-state proton transfer complex.[14] Compound (*S*)-**9** forms a weaker intramolecular hydrogen bond and shows the emissions contributed by both the H_8BINOL unit and the intramolecually hydrogen-bonded complex.

The study of compounds (*S*)-**6**−(*S*)-**10** has revealed the nature of the emission of the H_8BINOL-amino alcohol (*S*)-**5** as a contribution from its intramolecularly hydrogen-bonded complex. It explains why the fluorescence spectrum of (*S*)-**5** is very different from that of H_8BINOL. Unlike that observed in the ^{1}H NMR spectra of compounds (*S*)-**6**−(*S*)-**10**, the H_8BINOL hydroxyl proton signals of (*S*)-**5** are invisible probably because of fast exchange in solution.

Study of the Interaction of (*S*)-5 with Mandelic Acid. We have investigated the interaction of (*S*)-**5** with the enantiomers of MA. As shown in Figure 4a, when (*S*)-**5** (1.0×10^{-4} in CH_2Cl_2) was treated with (*R*)-MA (4.0×10^{-3}), a large enhancement at the short wavelength emission (λ_{emi} = 330 nm) was observed with I_R/I_0 = 11.7. When (*S*)-MA was used under the same conditions, the enhancement at the short wavelength emission was much smaller. Thus, a good enantioselective fluorescent response was observed with ef =3.5 [ef: enantioselective fluorescence enhancement ratio = $(I_R - I_0)/(I_S - I_0)$]. The fluorescence enhancement at the long wavelength emission of (*S*)-**5** is much smaller and also with little enantioselectivity. Figure 4b displays the results of three independent measurements for the fluorescence enhancement of (*S*)-**5** at the short wavelength emission while the concentration of the acid is varied. We have prepared (*R*)-**5**, the enantiomer of (*S*)-**5**, from (*R*)-H_8BINOL and (*R*)-**4** and studied its interaction with (*R*)- and (*S*)-MA. It is found that (*S*)-MA causes much greater fluorescence enhancement for (*R*)-**5** at the short wavelength emission than (*R*)-MA does. This confirms the enantioselective nature of the observed different fluorescence enhancements for the sensor in the presence of the two enantiomers of the acid.

The greatly enhanced short wavelength emission of (*S*)-**5** in the presence of (*R*)-MA demonstrates that protonation of the nitrogen atoms of (*S*)-**5** by the acidic proton of (*R*)-MA should have suppressed the intramolecular hydrogen bonding between the H_8BINOL hydroxyl protons of (*S*)-**5** and its amine nitrogens and restored the emission of the H_8BINOL unit. The overall fluorescence enhancement should be generated from the formation of the structurally more rigid intermolecular complex between (*S*)-**5** and (*R*)-MA.

When (*S*)-H_8BINOL is treated with (*R*)- or (*S*)-MA, there is almost no fluorescence enhancement and enantioselectivity (Figure 5). Thus, the intermolecular hydrogen bonding between the amino alcohol units of (*S*)-**5** and (*R*)-MA is important for the observed enantioselective fluorescent enhancement.

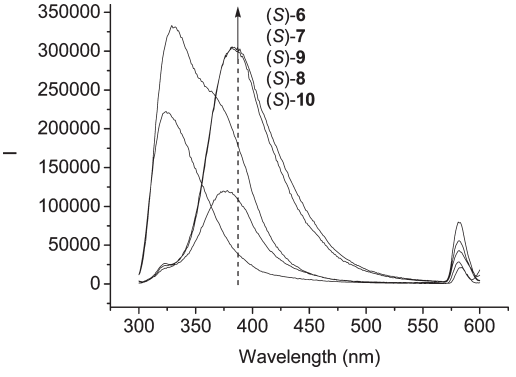
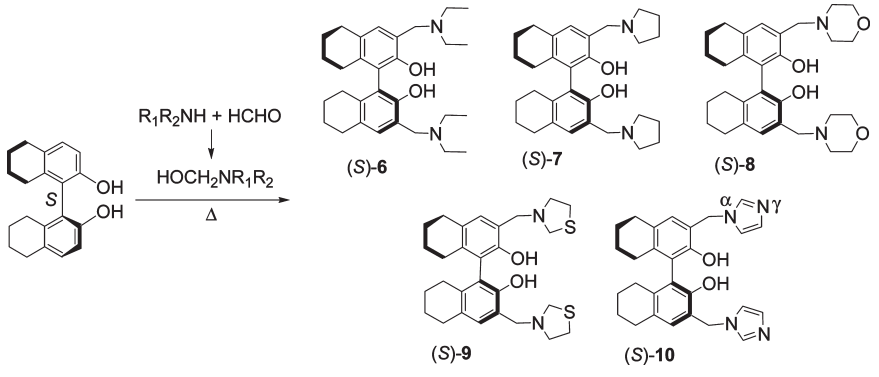


Figure 3. Fluorescence spectra of compounds (*S*)-**6**−(*S*)-**10** [2.0×10^{-4} M in CH_2Cl_2. λ_{exc} = 292 nm for (*S*)-**6**−(*S*)-**9** and 291 nm for (*S*)-**10**. Slit: 5.0/5.0 nm for (*S*)-**6**, (*S*)-**7**, and (*S*)-**9** and 4.0/4.0 nm for (*S*)-**8** and (*S*)-**10**].

Scheme 2. Synthesis of the H_8BINOL-Amine Compounds (*S*)-6−(*S*)-10



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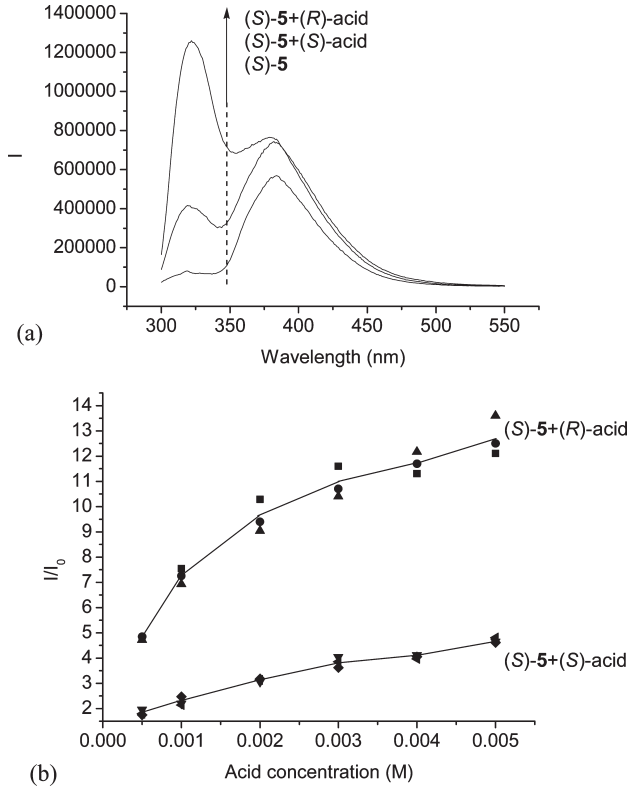

Figure 4. (a) Fluorescence spectra of (*S*)-**5** (1.0×10^{-4} M, CH_2Cl_2) with/without (*R*)- and (*S*)-MA (4.0×10^{-3} M). (b) Three independent measurements of fluorescence enhancement of (*S*)-**5** (1.0×10^{-4} M, CH_2Cl_2) at λ_{em} = 330 nm with varying acid concentrations. (λ_{exc} = 290 nm, slit = 3.0/3.0 nm).

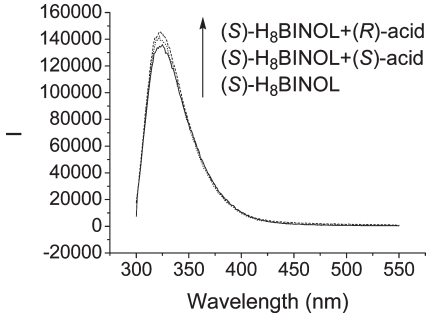

Figure 5. Fluorescence spectra of (*S*)-H_8BINOL (2.0×10^{-4} M in CH_2Cl_2) in the presence of (*R*)- and (*S*)-mandelic acid (4.0×10^{-3} M) [λ_{exc} = 288 nm, slit = 4.0/4.0 nm].

A ^{1}H NMR spectroscopic investigation on the interaction of (*S*)-**5** with (*R*)-MA in $CDCl_3$ was conducted while the total concentration was maintained at 6.0×10^{-3} M. Addition of (*S*)-**5** to the solution of (*R*)-MA caused the α proton signal of (*R*)-MA to undergo upfield shift from δ 5.26 to δ 4.20 as the ratio of (*S*)-**5** relative to (*R*)-MA reached 2:3. This large upfield shift indicates that the complexation between (*S*)-**5** and (*R*)-MA might have placed the α proton of the acid in the electronically shielded region of the sensor. Further increasing the ratio of (*S*)-**5** versus (*R*)-MA to 5:1 shifted the α proton signal of (*R*)-MA downfield to δ 4.53. Thus, the structure of the complex probably changes as the amount of (*S*)-**5** versus (*R*)-MA further increases. In the ^{1}H NMR spectrum, the two doublet signals of the diastereotopic protons H_a of (*S*)-**5** began to move toward each other with the addition of (*R*)-MA and then merged into a singlet at δ 3.74 when the ratio of (*R*)-MA relative to (*S*)-**5** reached 0.43:1 (= 1:2.3). However, when the amount of (*R*)-MA was further increased, the singlet split back into two doublets, which were then moving away from each other with increasing (*R*)-MA. When the ratio of (*R*)-MA relative to (*S*)-**5** reached 9:1, the H_a signals of (*S*)-**5** were observed at δ 4.24 (d, *J* = 12.3 Hz) and 3.63 (d, *J* = 12.0 Hz). We propose the following hypothesis to explain the above observed changes in the NMR signals of (*S*)-**5**. The intramolecular hydrogen bonds between the amine nitrogens and the core H_8BINOL hydroxyl protons in (*S*)-**5** should generate a rigid cyclic structure giving the two well-resolved diastereotopic proton signals for H_a. Addition of acid should protonate the amine group and allow free rotation of the 3,3′-substituents of (*S*)-**5**, resulting in the merged signal of the H_a protons. As the amount of (*R*)-MA increases, a structurally rigid intermolecular complex between (*S*)-**5** and (*R*)-MA should be produced to give the well separated signals for the H_a protons.

On the basis of the above NMR study, the Job plots for the interaction of (*S*)-**5** with (*R*)-MA were produced.[15] Figure 6a is obtained by monitoring the change of the α proton signal of (*R*)-MA, and Figure 6b by monitoring the change of the H_b signal of (*S*)-**5**. Both plots indicate that (*S*)-**5** and (*R*)-MA form a 1:2 complex in the ground state. Because the fluorescence response of (*S*)-**5** toward (*R*)-MA at a constant total concentration of 1.0×10^{-4} M is very small, the Job plot could not be used to determine the excited state binding stoichiometry of (*S*)-**5** with (*R*)-MA.

Interaction of the H_8BINOL-Amine Compounds (*S*)-6−(*S*)-10 with MA. The fluorescent responses of the H_8BINOL-amine compounds (*S*)-**6**−(*S*)-**10** in the presence of (*R*)- and (*S*)-MA are studied. As shown in Figure 7, when compounds (*S*)-**6**, (*S*)-**7**, and (*S*)-**8** were treated with MA, large fluorescence enhancements at the short wavelength were observed similar to that observed for (*S*)-**5**. This is consistent with the suppressed intramolecular hydrogen bonding interaction of these compounds when their amine nitrogens are interacting with the carboxylic acid proton of the acid. However, almost no enantioselectivity was observed. When compound (*S*)-**9** was treated with MA, little fluorescence enhancement was observed. This indicates that the intermolecular interaction of (*S*)-**9** with MA should be much weaker than that of compounds (*S*)-**5**−(*S*)-**8** because of the weaker basicity of the nitrogens in (*S*)-**9**. Although the α nitrogen atoms of (*S*)-**10** are not basic at all, there is significant fluorescence enhancement in the presence of (*R*)-MA with I_R/I_0 = 3.2. It is proposed that the much more basic γ nitrogens of (*S*)-**10** should have participated in the complexation with (*R*)-MA to form a structurally more rigid fluorophore, leading to the observed fluorescence enhancement. When (*S*)-**10** was treated with the enantiomeric acid (*S*)-MA, the fluorescence enhancement was smaller, giving a good enantioselectivity of ef =2.1. This indicates that (*S*)-**10** is a promising candidate for the enantioselective fluorescent recognition of MA.

Summary. We have investigated the fluorescent properties of a series of H_8BINOL-amine compounds. This study reveals that the intramolecular hydrogen bonds of these compounds can shift the emission of their H_8BINOL unit to a much longer wavelength. In spite of the much shorter conjugation in the H_8BINOL-based fluorophore of (*S*)-**5** than that in the BINOL-based compound (*S*)-**1**, (*S*)-**5** has exhibited very efficient fluorescent response toward an α-hydroxycarboxylic acid. Binding of (*S*)-**5** with the acid suppresses its intramolecular hydrogen bonding and restores the short wavelength emission of the H_8BINOL unit, giving high sensitivity and good enantioselectivity. Thus, with appropriate design of the structure

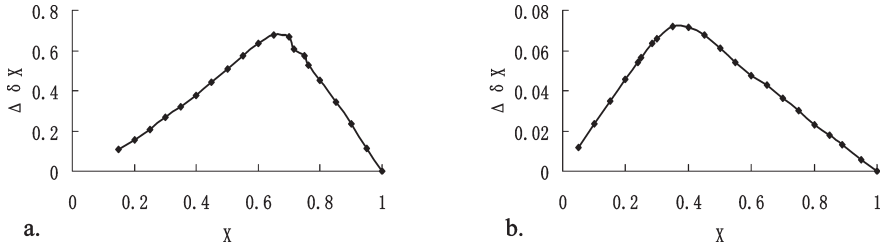

Figure 6. Job plots of (*S*)-**5** with (*R*)-MA obtained by using the ^{1}H NMR signal change ($\Delta\delta = \delta_0 - \delta$) of (a) the H_α of (*R*)-MA {*X* = [acid]/([acid] + [sensor]} and (b) the H_b of (S)-**5** {X = [sensor]/([sensor] + [acid])}.

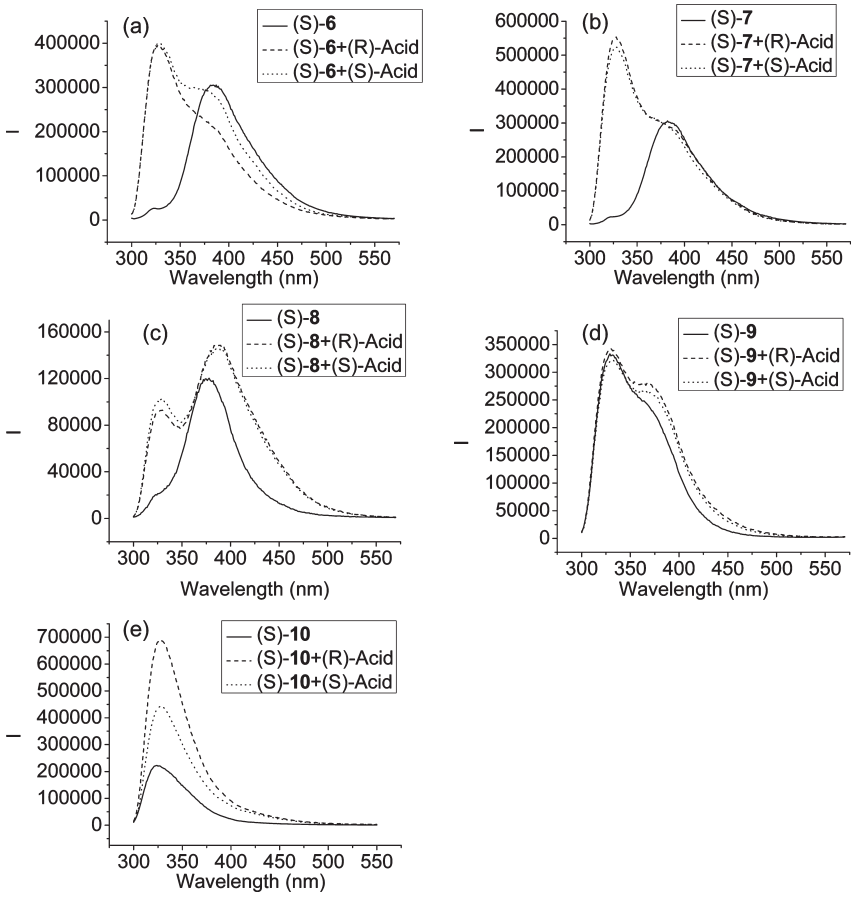

Figure 7. Fluorescence spectra of (*S*)-**6**−(*S*)-**10** (2.0×10^{-4} M in CH_2Cl_2) in the presence of (*R*)- and (*S*)-MA (4.0×10^{-3} M) [λ_{exc} = 292 nm for (*S*)-**6**−(*S*)-**9** and 291 nm for (*S*)-**10**. Slit: 5.0/5.0 nm for (*S*)-**6**, (*S*)-**7**, and (*S*)-**9** and 4.0/4.0 nm for (*S*)-**8** and (*S*)-**10**].

and functional groups, the H_8BINOL-based molecules are promising as a new class of enantioselective fluorescent sensors. In comparison with their BINOL analogues, the H_8BINOL-based compounds have opened a new window in the shorter emission wavelength to observe the enantioselective fluorescent recognition. This has allowed the use of (*R*)-**5** together with (*S*)-**1** as a pseudoenantiomeric fluorescent sensor pair to simultaneously determine both the concentration and the enantiomeric composition of an α-hydroxycarboxylic acid.[8]

EXPERIMENTAL SECTION

Synthesis and Characterization of Sensor (*S*)-5. (1) (*S*)-3,3′-DiformylH_8BINOL, (*S*)-**3** (245 mg, 0.70 mmol), was dissolved in CH_2Cl_2 (22 mL) in the presence of 4 Å molecular sieves and combined with (*S*)-2-amino-1,1,2-triphenylenthanol, (*S*)-**4** (607 mg, 2.10 mmol). The reaction mixture was heated at reflux for 30 h and monitored by using ^{1}H NMR spectroscopy. When the reaction was complete, the reaction mixture was cooled to room temperature and filtered. The filtrate was concentrated under vacuum and passed through a silica gel column eluted with CH_2Cl_2 to give the corresponding Schiff base. (2) The Schiff base was dissolved in methanol (28 mL) and cooled down to 0 °C. $NaBH_4$ (106 mg, 2.80 mmol) was added in small portions. The reaction temperature was maintained at 0 °C until the solution became colorless and transparent. Then, it was allowed to proceed at room temperature for additional 30 min. Methanol was removed, and the residue was dissolved in ethyl acetate (50 mL) and washed with water (15 mL). The aqueous layer after separation was extracted with ethyl acetate (3 × 30 mL). The combined organic layer was washed with brine (15 mL) and dried over anhydrous Na_2SO_4. After evaporation of the

dx.doi.org/10.1021/jo200226k |*J. Org. Chem.* 2011, 76, 2814–2819

solvent, the residue was purified by flash column chromatography on silica gel eluted with hexanes/ethyl acetate (3/1) to afford (*S*)-**5** as a white solid in 71% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.72 (m, 8H), 2.17 (m, 2H), 2.34 (m, 2H), 2.66 (m, 4H), 3.59 (d, J = 13.5 Hz, 2H), 3.77 (d, J = 13.5 Hz, 2H), 4.63 (s, 2H), 6.58 (s, 2H), 7.02−7.31 (m, 28H), 7.59 (d, J = 7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.5, 23.6, 27.5, 29.5, 49.4, 69.0, 80.5, 121.8, 122.0, 126.4, 126.7, 126.9, 127.6, 127.7, 127.8, 127.9, 128.7, 128.8, 130.1, 130.4, 136.4, 137.4, 144.5, 145.4, 151.4. HRMS calcd for $C_{62}H_{61}N_2O_4$ (MH^+): 897.4631. Found: 897.4653. Mp 124−125 °C. $[\alpha]_D$ = −119.9 (c 0.865, $CHCl_3$). The enantiomer (*R*)-**5** was obtained in the same way by using (*R*)-3,3′-diformylH$_8$BINOL and (*R*)-2-amino-1,1,2-triphenylenthanol. $[\alpha]_D$ = 119.3 (c 0.470, $CHCl_3$).

Preparation of Samples for Fluorescence Measurement. *Materials.* Sensors were purified by column chromatography and then stored in a refrigerator. The commercially obtained enantiomers of MA were recrystallized from methanol. They were then passed through a short column of silica gel (eluted with diethyl ether) and dried under vacuum. All of the solvents were either HPLC or spectroscopic grade. The stock solutions of the sensors were freshly prepared for each measurement. A 0.01 M stock solution of MA in methylene chloride was freshly prepared. For the fluorescence enhancement study, a sensor solution was mixed with the MA solution at room temperature in a 5 mL volumetric flask and diluted to the desired concentration. The resulting solution was allowed to stand at room temperature for 2−3 h before the fluorescence measurement.

■ ASSOCIATED CONTENT

Supporting Information. Additional UV, fluorescence, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We are grateful for partial support of this work from the U.S. National Science Foundation (CHE-0717995 and ECCS-0708923).

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