Supplementary Information for

Rational Design of a Fluorescent Sensor to Simultaneously Determine Both the Enantiomeric Composition and Concentration of Chiral Functional Amines

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I. Preparation of Samples for Fluorescence Measurement.

For the interactions with the diamine: A 2 mM stock solution of (*R*)-**4** in CH_2Cl_2 and 2 mM $Zn(OAc)_2 \cdot 2H_2O$ in CH_3OH were freshly prepared for each measurement. For the fluorescence enhancement study, a sensor solution of (*R*)-**4**+Zn^{2+}(2 equiv) (2 mM) was mixed with various equiv of the diamine solution (15 mM in CH_3OH) in a 10 mL test tube. The resulting solution was allowed to stand at room temperature for 3 h, then was diluted to the desired concentration (0.02 mM) for 0.5 h before measurements. All the fluorescence spectra were taken within 2 h.

For the interactions with the amino alcohols: A 2 mM stock solution of (*R*)-**4** in CH_2Cl_2 and 2 mM $Zn(OAc)_2 \cdot 2H_2O$ in CH_3OH were freshly prepared for each measurement. For the fluorescence enhancement study, a sensor solution of (*R*)-**4**+Zn^{2+}(2 equiv) (2 mM) was mixed with various equiv of an amino alcohol solution (15 mM in CH_3OH) in a 10 mL test tube. The resulting solution was allowed to stand at room temperature for 3.5 h and be diluted to the desired concentration (0.02 mM) before measurements. All the fluorescence spectra were taken within 2 h.

For the interactions with the amino acids: A 2 mM stock solution of (*R*)-**4** in CH_2Cl_2, 2 mM $Zn(OAc)_2 \cdot 2H_2O$ in CH_3OH and a solution of an amino acid (15 mM) mixed with n-Bu_4NOH (16.5 mM) in CH_3OH were freshly prepared for each measurement. For the fluorescence enhancement study, a sensor solution of (*R*)-**4**+Zn^{2+}(2 equiv) (2 mM) was mixed with various equiv of the n-Bu_4NOH-amino acid mixed solution in a 10 mL test tube. The resulting solution was allowed to stand at room temperature for 3.5 h and be diluted to the desired concentration (0.02 mM) before measurements. All the fluorescence spectra were taken within 2 h.

II. Supplementary Fluorescence Spectra, UV/vis Absorption Spectra, TOF Mass Spectra and NMR Titration Plots

Time Dependence Fluorescence Responses

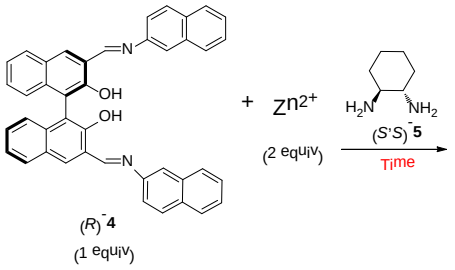


Figure S1. Fluorescence kinetics spectra of (*R*)-**4** (2.0×10^{-3} M) with 25 equiv (*S*,*S*)-**5** in the presence of 2 equiv $Zn(OAc)_2 \cdot 2H_2O$. (Solvent: CH_3OH/2% CH_2Cl_2. λ_{exc} = 370 nm, slit = 5/5 nm.).

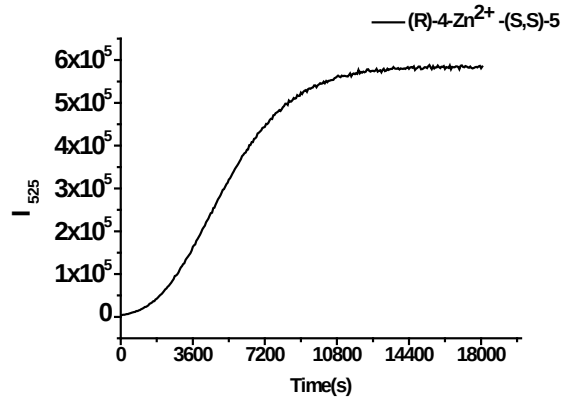


Figure S2. Fluorescence spectra of 2-naphthylamine (4.0×10^{-5} M) without/with the $Zn(OAc)_2 \cdot 2H_2O$ (4.0×10^{-5} M). (Solvent: CH_3OH/2% CH_2Cl_2. λ_{exc} = 370 nm, slit = 5/5 nm.).

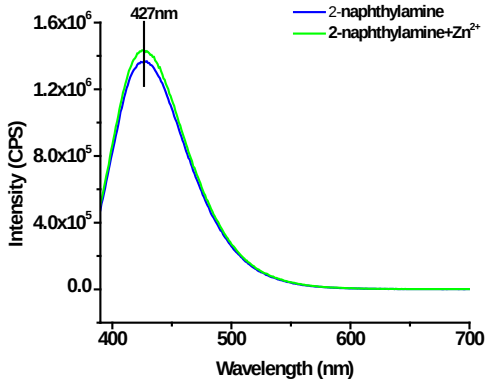
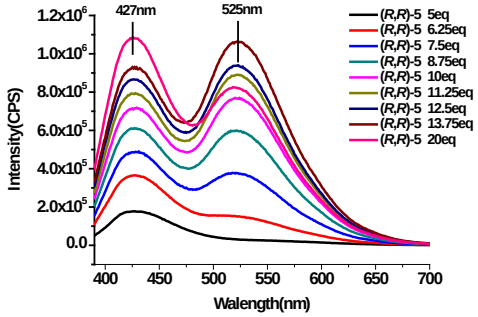
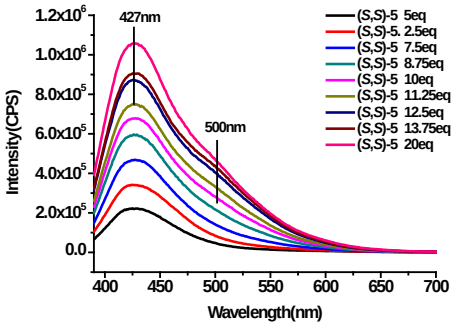


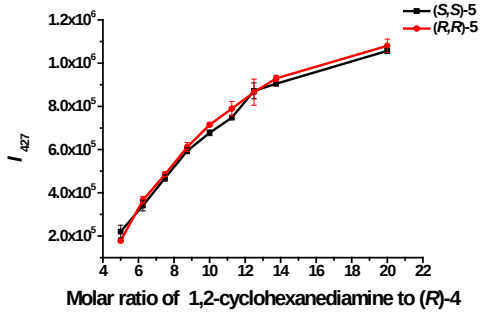
Figure S3. Fluorescent response of (*S*)-**4** (2.0× 10^{-5} M in CH_3OH/2% CH_2Cl_2) + Zn^{II} (2 equiv) to 5 – 20 eq (*R*,*R*)-**5** (a) and (*S*,*S*)-**5** (b). Plots of I_{427} (c), I_{525} (d), I_{525}/I_{500} (e) for (*S*)-**4** (2.0 × 10^{-5} M in CH_3OH/2% CH_2Cl_2) + Zn^{II} (2 equiv) in the presence of varying concentrations of (*S*,*S*)-**5** and (*R*,*R*)-**5**. (λ_{exc} = 370 nm, slit: 5/5nm)



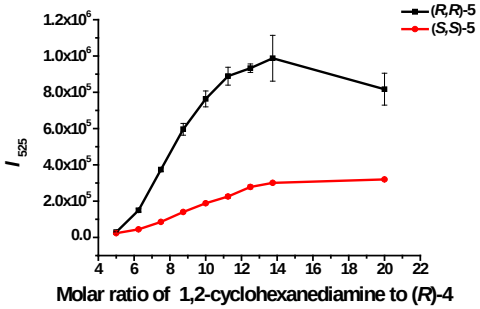
(a)



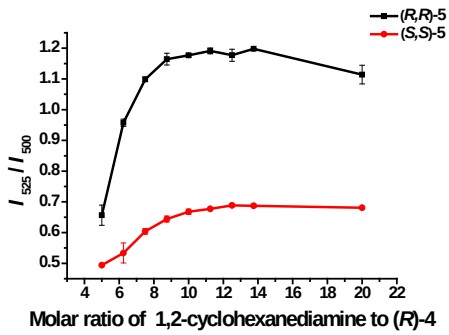
(b)



(c)



(d)



(e)

Figure S4. Excitation spectra of (*R*)-**4** (2.0×10^{-5} M CH_3OH/2% CH_2Cl_2) + Zn^{II}(2 equiv) toward 40 equiv *L*-**7** when the emission wavelengths are at 527 and 427 nm respectively.

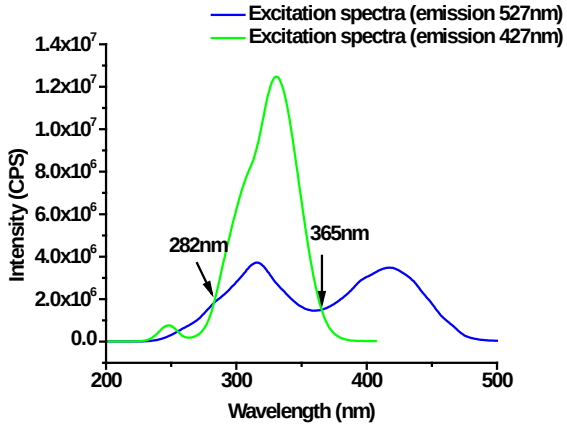
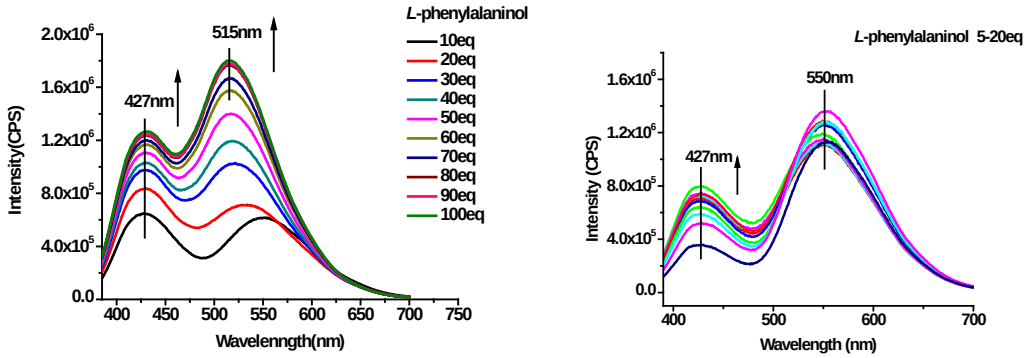
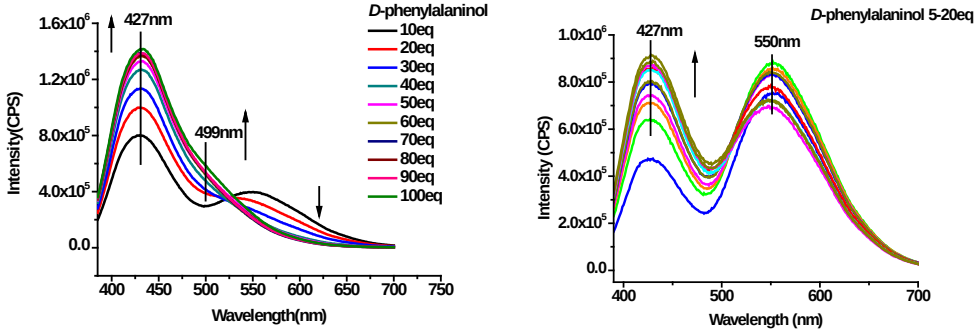


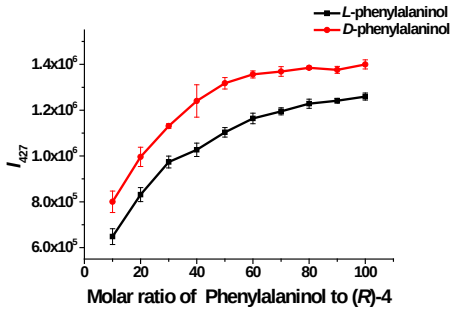
Figure S5. Fluorescence spectra of (*R*)-**4** (2.0×10^{-5} M) + Zn^{II}(2 equiv) to 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 equiv *L*-**8** (a) and *D*-**8** (b). Plots of I_{427} (c), I_{515} (d), I_{515}/I_{499} (e) for (*R*)-**4** (2.0×10^{-5} M) + Zn^{II}(2 equiv) in the presence of varying concentrations of *L*-**8** and *D*-**8**. (Solvent: CH_3OH/2% CH_2Cl_2. λ_{exc} = 365 nm, slit = 4/4 nm.).



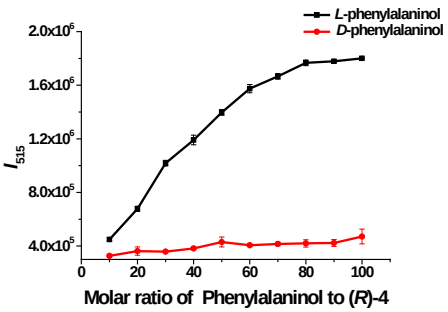
(a)



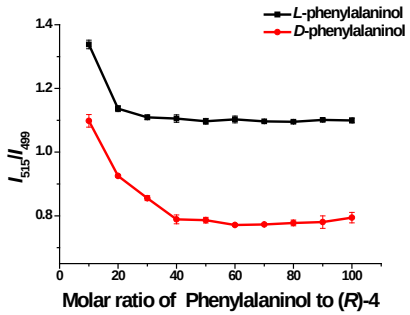
(b)



(c)



(d)



(e)

Figure S6. Excitation spectra of (*R*)-**4** (2.0×10^{-5} M CH_3OH/2% CH_2Cl_2) + Zn^{II} (2 equiv) toward 40 equiv *L*-**9** when the emission wavelengths are at 521 and 427 nm respectively.

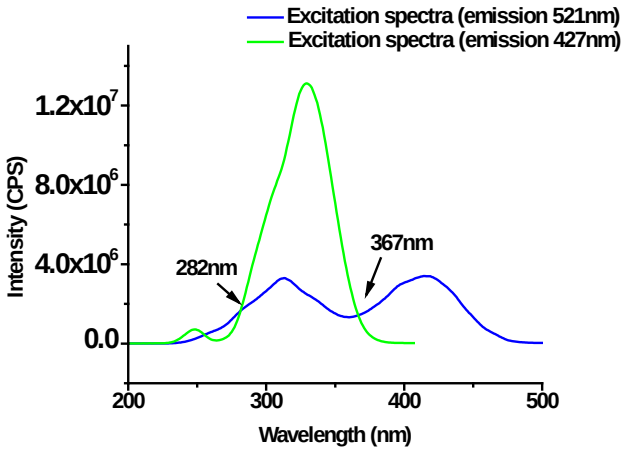
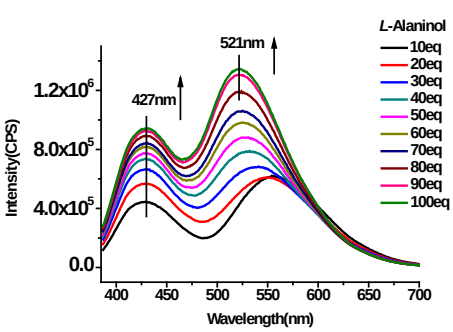
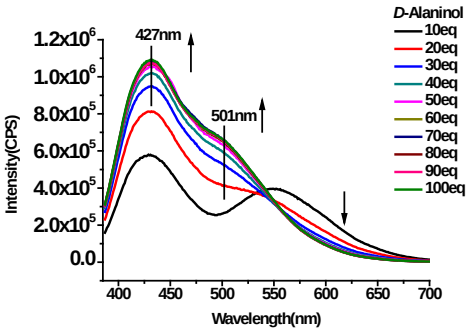


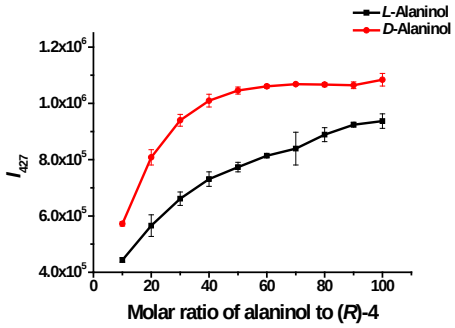
Figure S7. Fluorescence spectra of (*R*)-**4** (2.0×10^{-5} M) + Zn^{II} (2 equiv) toward 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 equiv *L*-**9** (a) and *D*-**9** (b). Plots of I_{427} (c), I_{521} (d), I_{521}/I_{501} (e) for (*R*)-**4** (2.0×10^{-5} M) + Zn^{II} (2 equiv) in the presence of varying concentrations of *L*-**9** and *D*-**9**. (Solvent: CH_3OH/2% CH_2Cl_2. λ_{exc} = 367 nm, slit = 4/4 nm.).



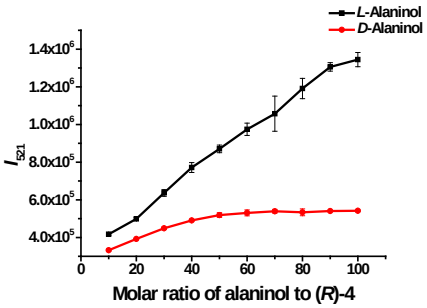
(a)



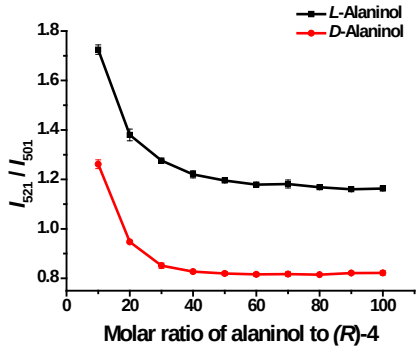
(b)



(c)

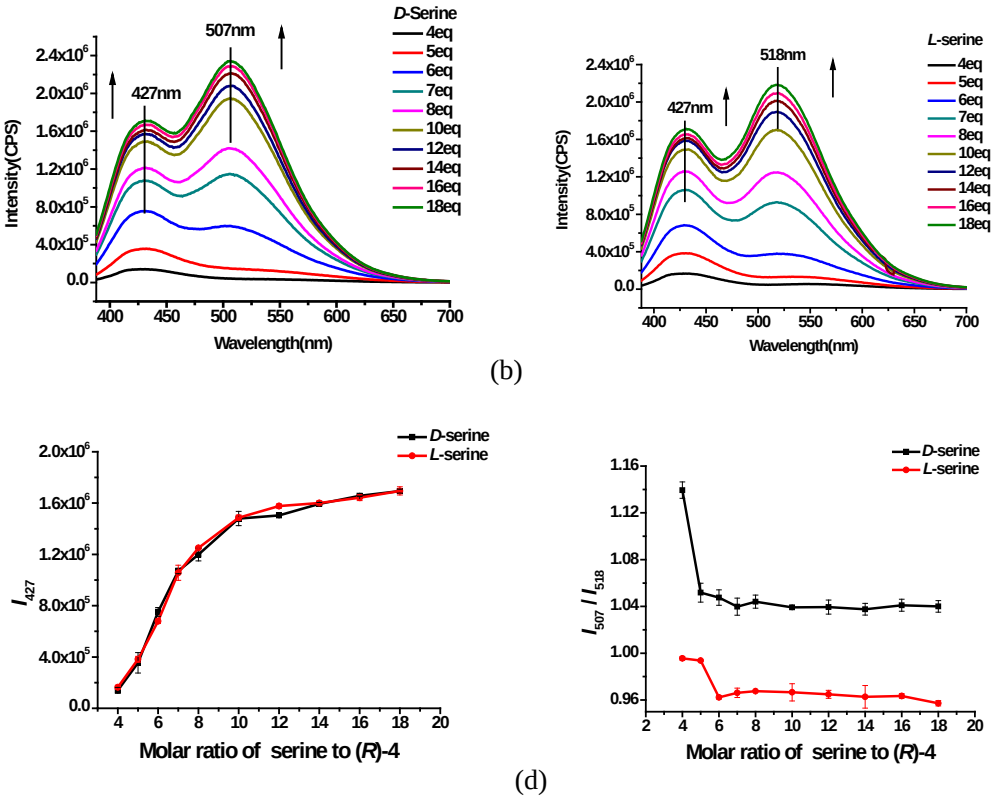


(d)



(e)

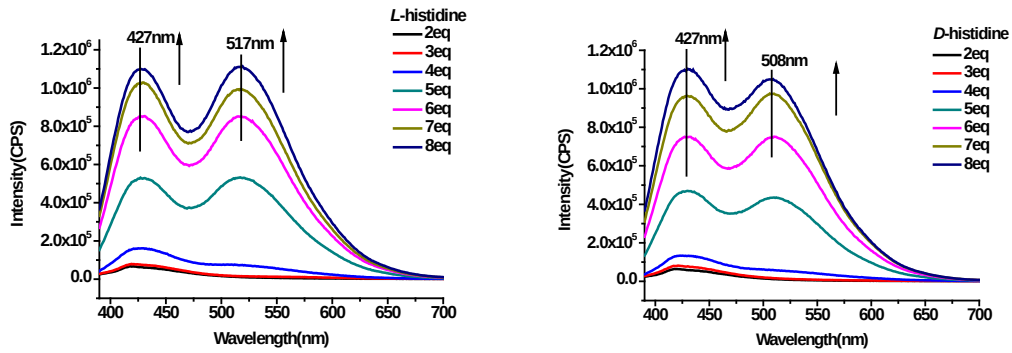
Figure S8. Fluorescence spectra of (*R*)-**4** (2.0×10^{-5} M) + Zn^{II}(2 equiv) toward 16, 20, 24, 28, 32, 40, 48, 56, 64 and 72 μL of *L*-**14** (15.0×10^{-3} M)+n-Bu_4NOH (16.5×10^{-3} M) (a) and of *D*-**14** (15.0×10^{-3} M)+n-Bu_4NOH (16.5×10^{-3} M) (b). Plots of I_{427} (c), I_{518}/I_{507} (d) for (*R*)-**4** (2.0×10^{-5} M) + Zn^{II}(2 equiv) in the presence of varying concentrations of *L*-**14**+n-Bu_4NOH and *D*-**14**+n-Bu_4NOH. (Solvent: CH_3OH/2% CH_2Cl_2. λ_{exc} = 368 nm, slits = 5/5 nm.).



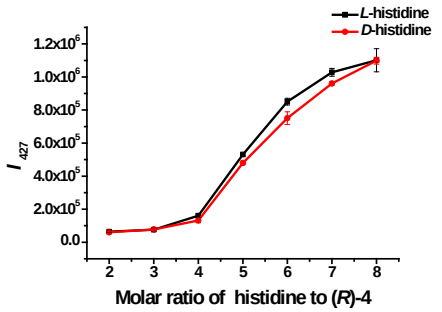
(a) (b)

(c) (d)

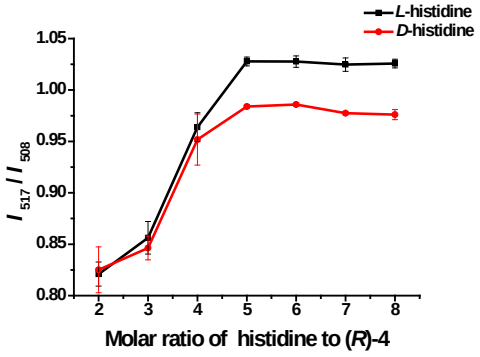
Figure S9. Fluorescence spectra of (*R*)-**4** (2.0×10^{-5} M) + Zn^{II}(2 equiv) toward 8, 12, 16, 20, 24, 28 and 32 μL of *L*-**13** (15×10^{-3} M)+n-Bu_4NOH (16.5×10^{-3} M) (a) and of *D*-**13** (15×10^{-3} M)+n-Bu_4NOH (16.5×10^{-3} M) (b). Plots of I_{427} (c), I_{517}/I_{508} (d) for (*R*)-**4** (2.0×10^{-5} M) + Zn^{II}(2 equiv) in the presence of varying concentrations of *L*-**13**+n-Bu_4NOH and *D*-**13**+n-Bu_4NOH. (Solvent: CH_3OH/2% CH_2Cl_2. λ_{exc} = 370 nm, slit = 5/5 nm.).



(a) (b)

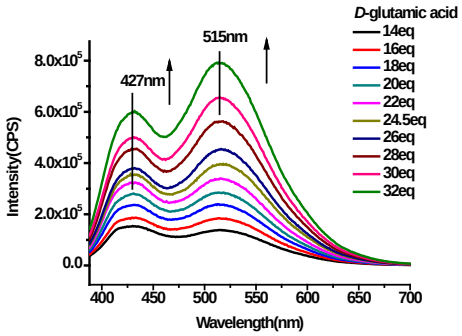


(c)

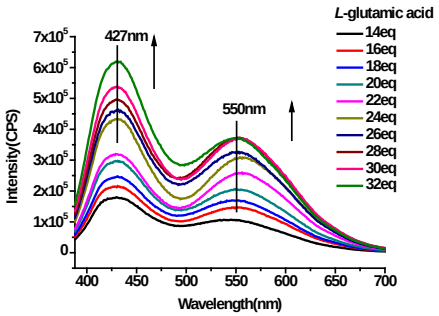


(d)

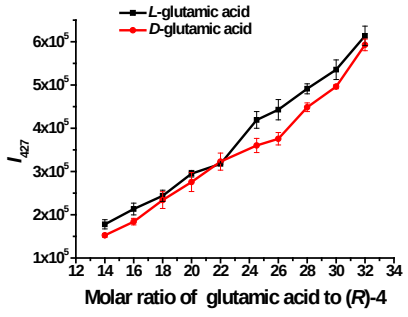
Figure S10. Fluorescence spectra of (*R*)-**4** (2.0 × 10^{-5} M) + Zn^{II}(2 equiv) toward 56, 64, 72, 80, 88, 98, 104, 112, 120 and 128 μL of *D*-**12** (15 × 10^{-3} M) + n-Bu_4NOH (16.5×10^{-3} M) (a) and of *L*-**12** (15 × 10^{-3} M) + n-Bu_4NOH (16.5 × 10^{-3} M) (b). Plots of I_{427} (c), I_{515} (d), I_{515}/I_{550} (e) for (*R*)-**4** (2.0 × 10^{-5} M) + Zn^{II}(2 equiv) in the presence of varying concentrations of *D*-**12** (15 × 10^{-3} M) + n-Bu_4NOH (16.5 × 10^{-3} M) and *L*-**12** (15 × 10^{-3} M) + n-Bu_4NOH (16.5×10^{-3} M). (Solvent: CH_3OH/2% CH_2Cl_2. λ_{exc} = 368 nm, slit = 5/5 nm.).



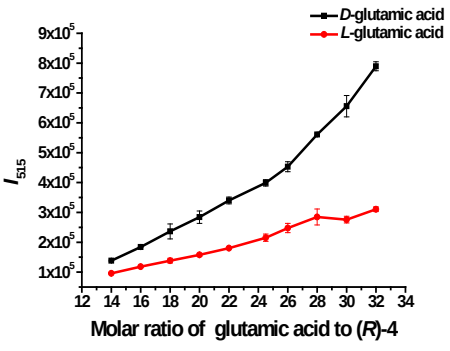
(a)



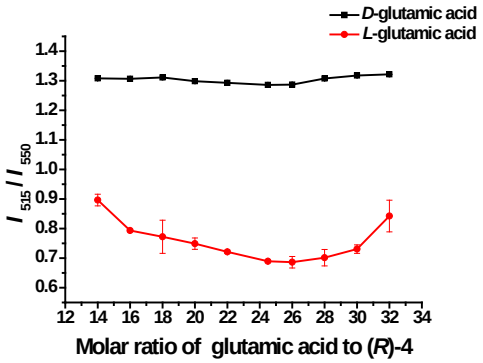
(b)



(c)

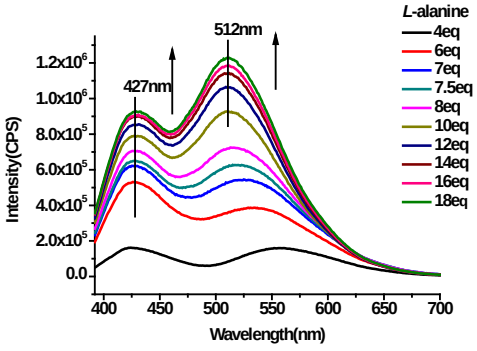


(d)

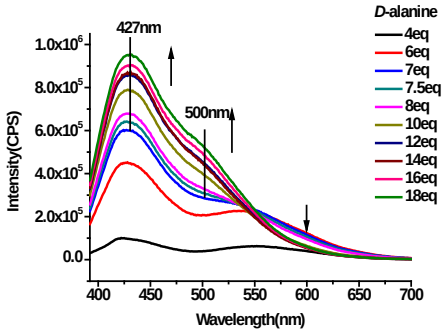


(d)

Figure S11. Fluorescence spectra of (*R*)-**4** (2.0×10^{-5} M) + Zn^{II} (2 equiv) toward 16, 24, 28, 30, 32, 40, 48, 56, 64 and 72 μL of *D*-**11** (15×10^{-3} M) + n-Bu4NOH (16.5×10^{-3} M) (a) and of *L*-**11** (15×10^{-3} M) + n-Bu4NOH (16.5×10^{-3} M) (b). Plots of I_{427} (c), I_{512} (d), I_{512}/I_{550} (e) for (*R*)-**4** (2×10^{-5} M) + Zn^{II} (2 equiv) in the presence of varying concentrations of *D*-**11** (15×10^{-3} M) + n-Bu4NOH (16.5×10^{-3} M) and *L*-**11** (15×10^{-3} M) + n-Bu4NOH (16.5×10^{-3} M). (Solvent: CH_3OH/2% CH_2Cl_2. λ_{exc} = 372 nm, slit = 5/5 nm.).



(a)



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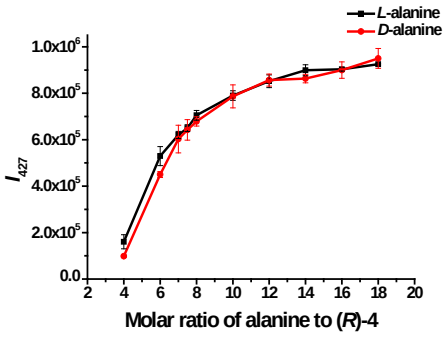

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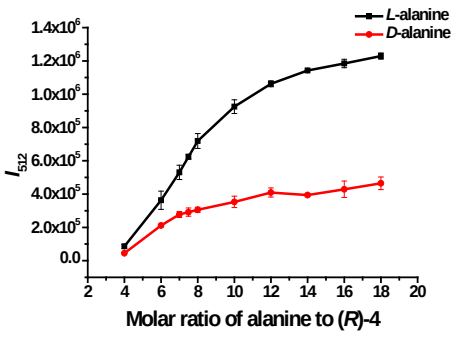

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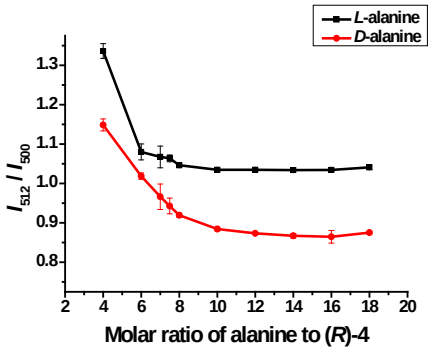
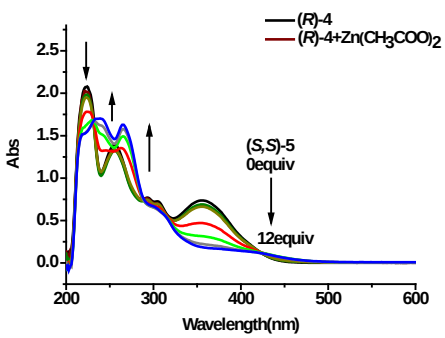
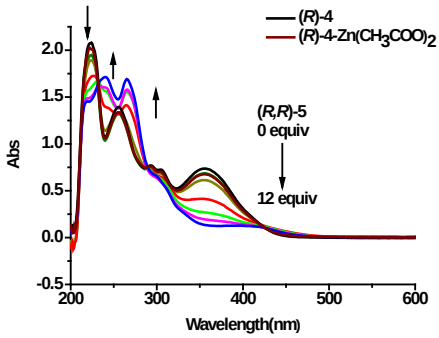


(e)

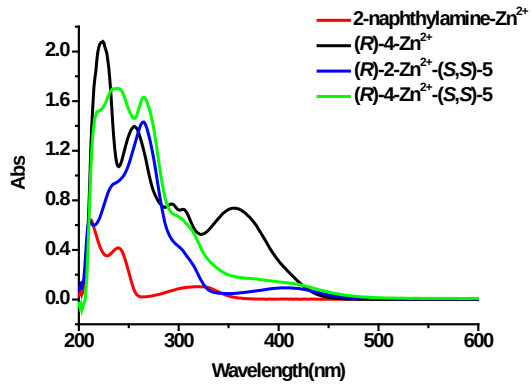
Figure S12. UV/ vis absorption titration of (*R*)-**4** with 2, 4, 6, 8, 10 and 12 equiv (*S*,*S*)-**5** (a) and (*R*,*R*)-**5** (b) in the presence of Zn^{II}. (c) UV/vis absorption spectra of (*R*)-**2** and (*R*)-**4** with (*S*,*S*)-**5** in the presence of Zn^{II}.



(a)



(b)



(c)

Figure S13. TOF mass spectra of (*R*)-**4** + $Zn(OAc)_2 \cdot 2H_2O$ (2 equiv) + (*S*,*S*)-**5** (7 equiv).

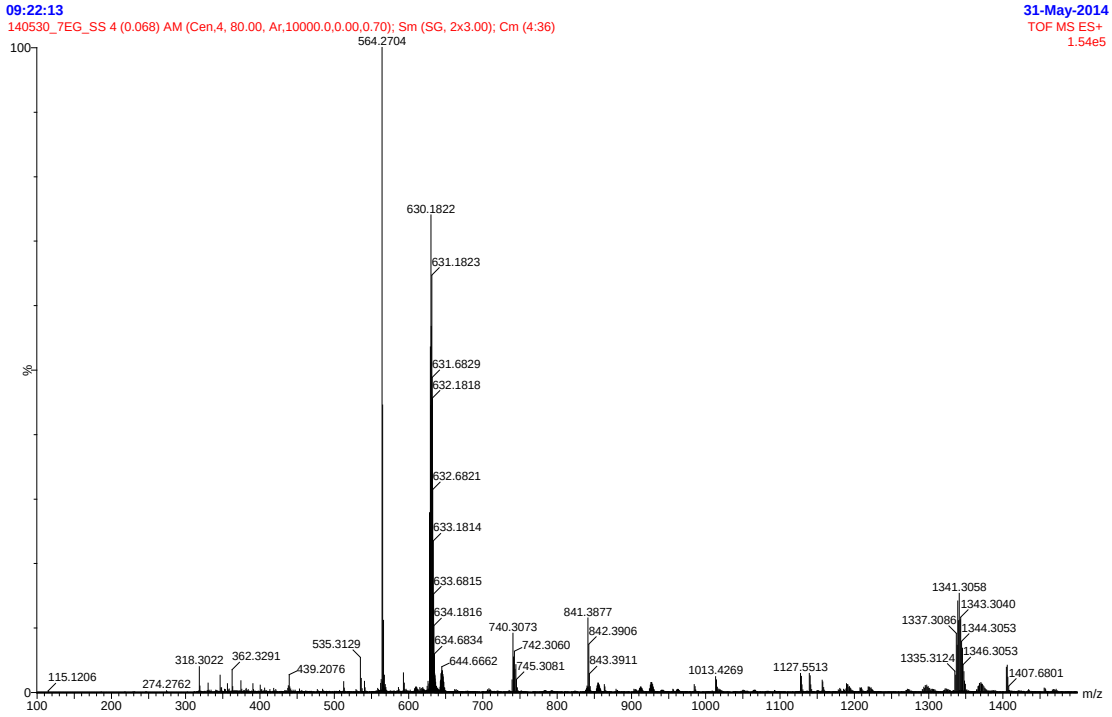


Figure S14. TOF mass spectra of (*R*)-**4** + $Zn(OAc)_2 \cdot 2H_2O$ (2 equiv) + (*R*,*R*)-**5** (7 equiv).

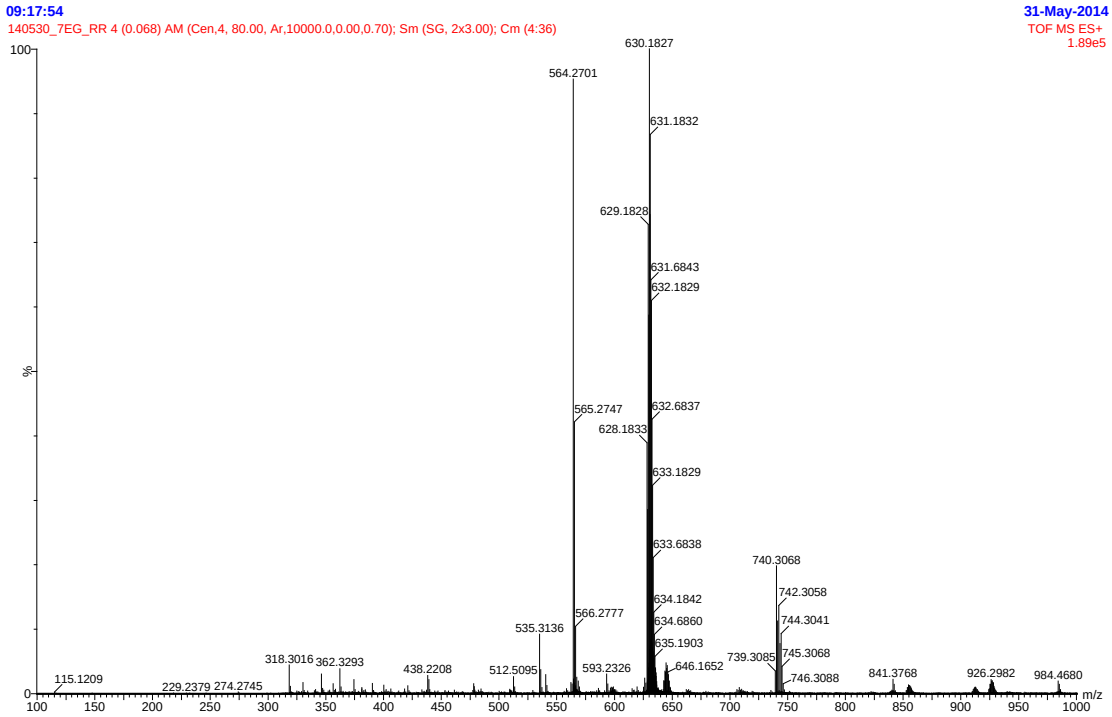


Figure S15. ^{1}H NMR titration of (*R*)-**4** (5mM) + $ZnBr_2$ (2 equiv) with (*S*,*S*)-**5** in $CDCl_3$: CD_3OD (2: 1) in comparison with the naphthalene-2-amine + $ZnBr_2$ (10 mM). (The ^{1}H NMR spectra were taken after the solution was allowed to stand at room temperature for 3 h).

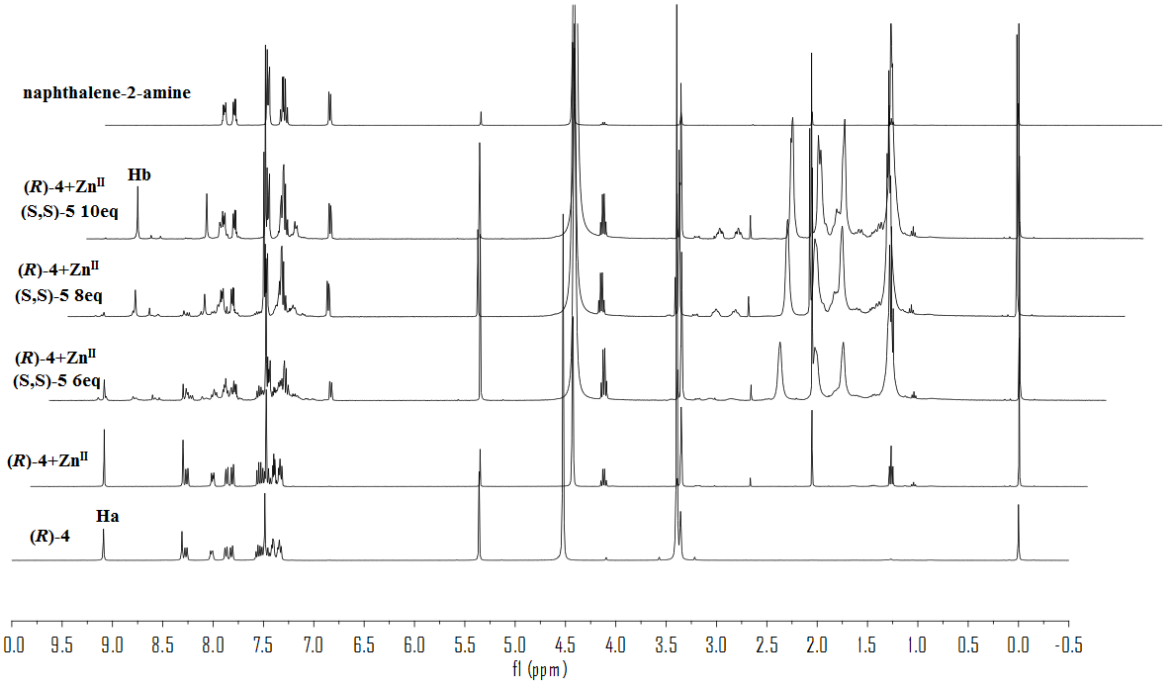


Figure S16. ^{1}H NMR titration of (*R*)-**4** (5 mM) + $ZnBr_2$ (2 equiv) with (*R*,*R*)-**5** in $CDCl_3$: CD_3OD (2: 1) in comparison with the **2**-naphthylamine + $ZnBr_2$ (10 mM). (The ^{1}H NMR spectra were taken after the solution was allowed to stand at room temperature for 3 h).

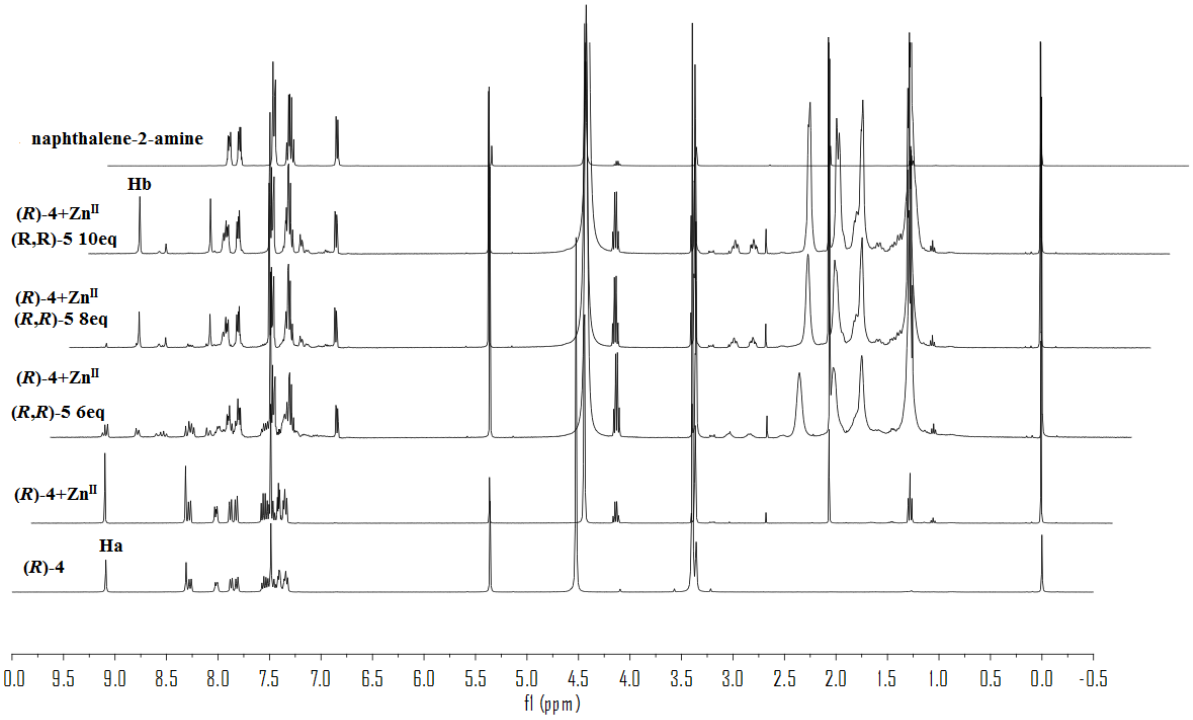


Figure S17. ^{1}H NMR spectrum of (*R*)-**4** (5mM) with $ZnBr_2$ (2 equiv) toward (*S*,*S*)-**5** and (*R*,*R*)-**5** (10 equiv) in $CDCl_3$: CD_3OD (2: 1) in comparison with the (*R*)-**4** (5mM) without $ZnBr_2$ (1 equiv) toward (*S*,*S*)-**5** and (*R*,*R*)-**5**. (The ^{1}H NMR spectra were taken after the solution was allowed to stand at room temperature for 3 h).

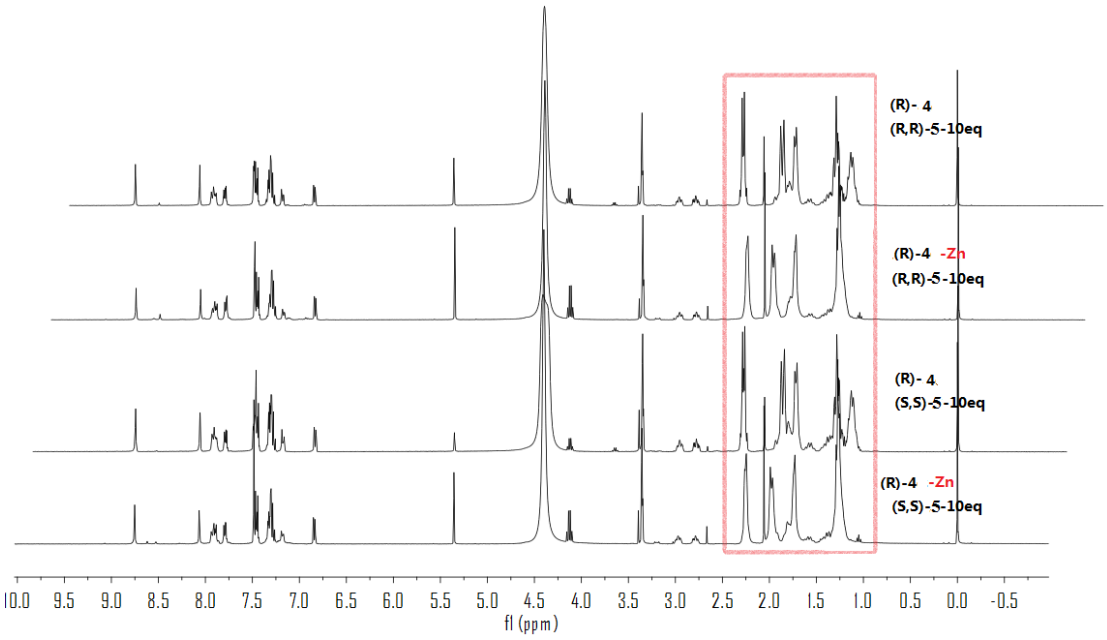
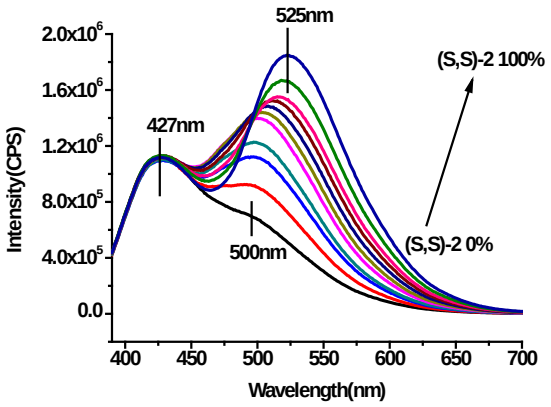
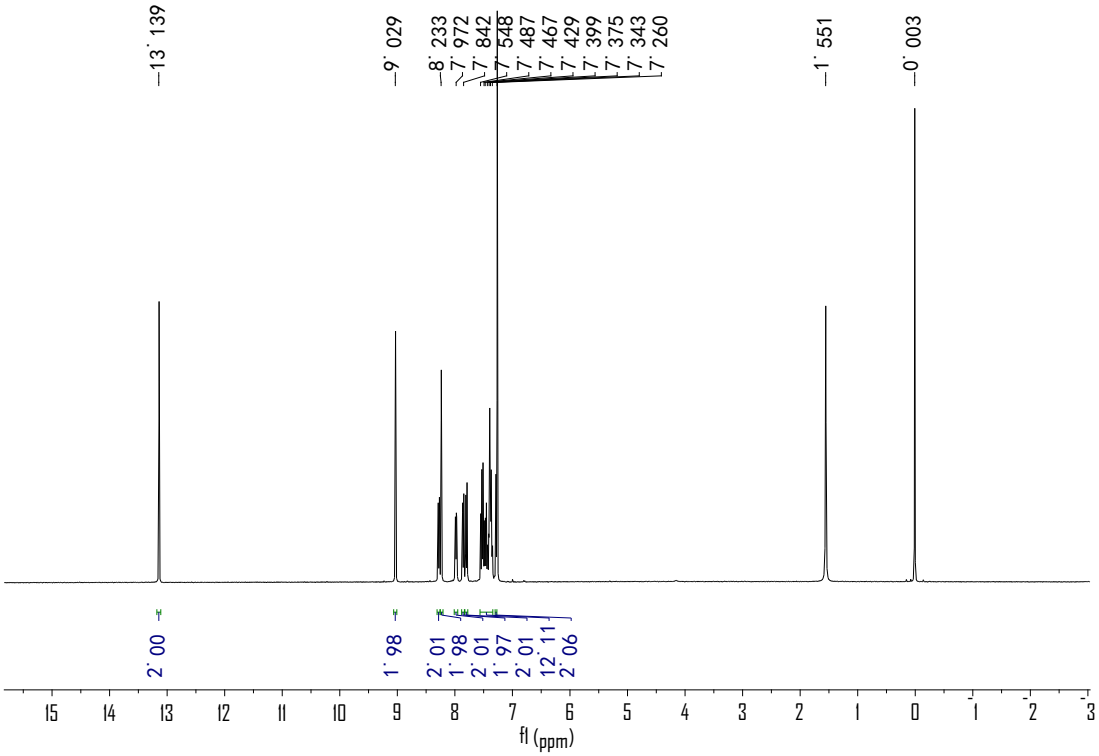


Figure S18. Fluorescence spectra of (*R*)-**4** (2.0×10^{-5} M) + Zn^{2+} (2 equiv) in the presence of the enantiomeric mixture of *trans*-1,2-cyclohexanediamine [from 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% to 100% (*S*,*S*)-**5**] at a total concentration of 22.5×10^{-5} M. (Solvent: CH_3OH with 2% CH_2Cl_2. λ_{exc} = 370 nm, slit = 5/5 nm.).

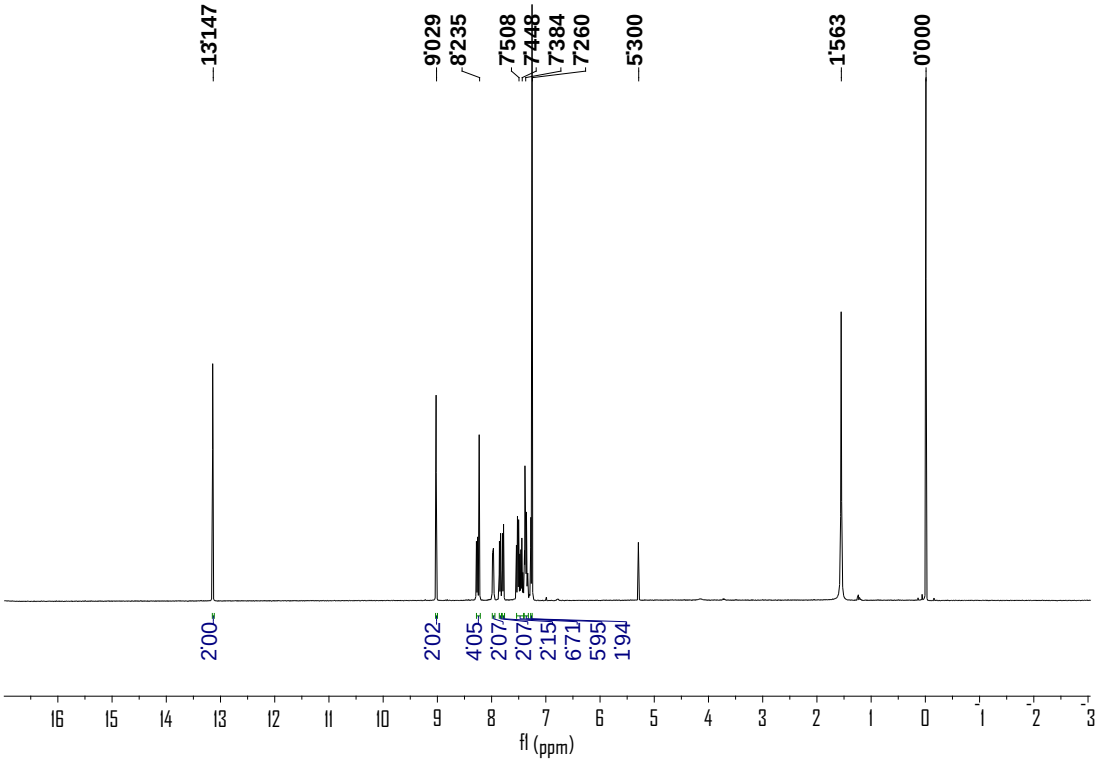


III. Preparation and Characterization of the (*R*)-4 and (*S*)-4

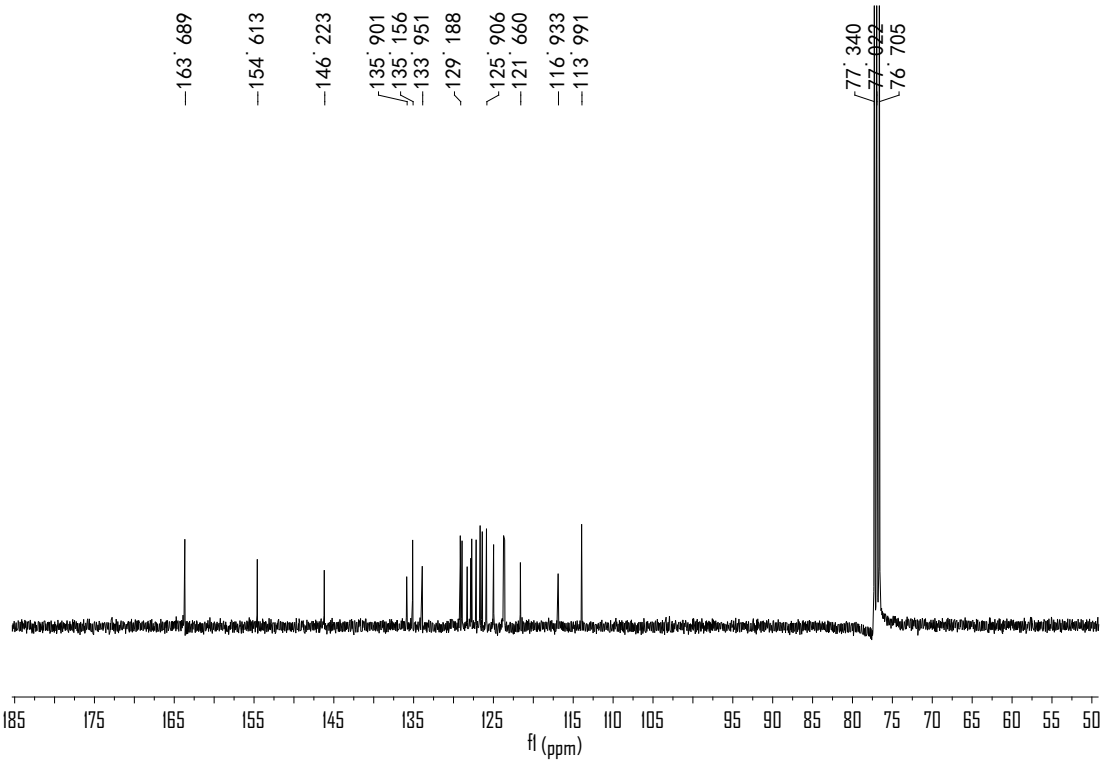
^{1}H-NMR of the (*R*)-4 ($CDCl_3$, 400 MHz)



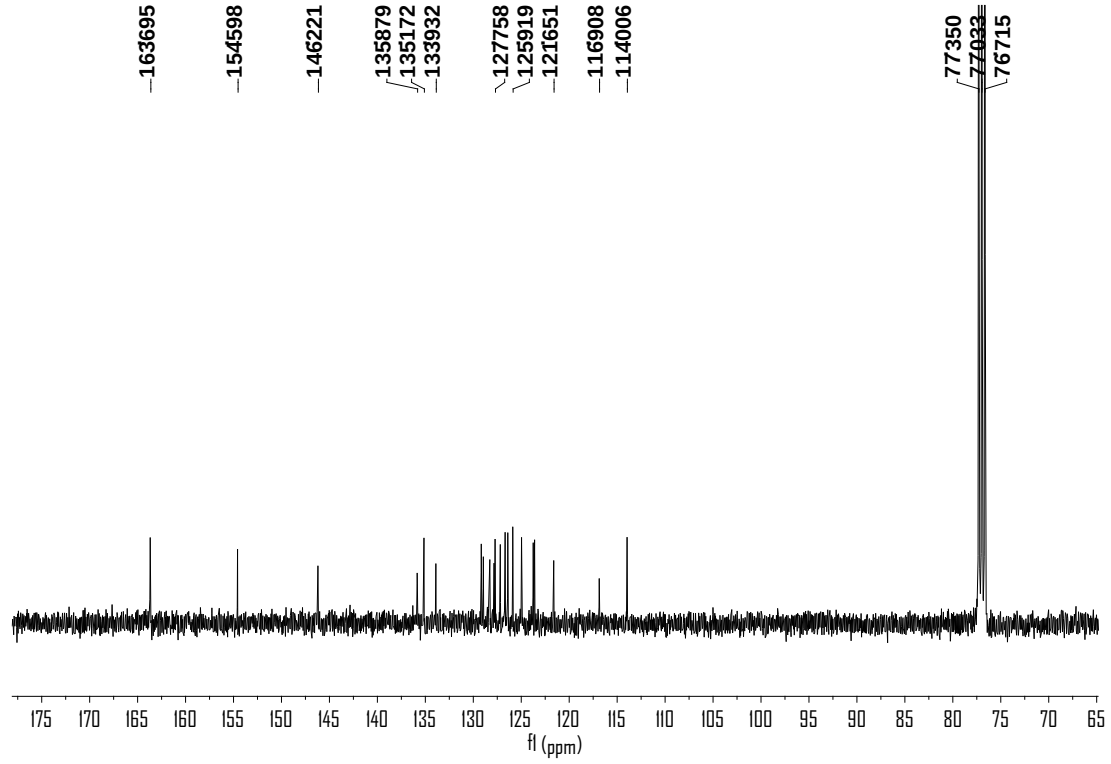
^{1}H-NMR of the (*S*)-4 ($CDCl_3$, 400 MHz)



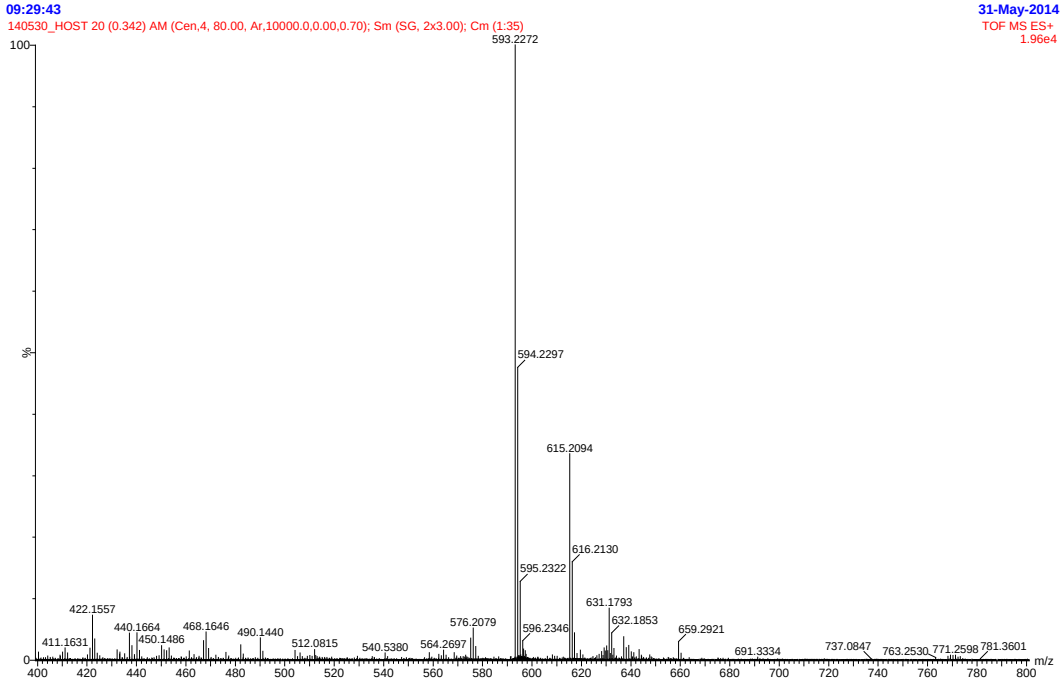
^{13}C-NMR of the (*R*)-4 ($CDCl_3$, 100 MHz)



^{13}C-NMR of the (*S*)-4 ($CDCl_3$, 100 MHz)



HRMS of the (*R*)-4



HRMS of the (*S*)-4