Electronic Supporting Information

(*S*)-BINOL-based boronic ester fluorescence sensors for enantioselective recognition of α-phenyl ethylamine and phenylglycinol

Jiemin Jiao, Guo Wei, Fei Li, Xuerong Mao, Yixiang Cheng*, Chengjian Zhu*

Key Lab of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

E-mail: yxcheng@nju.edu.cn and cjzhu@nju.edu.cn

Contents:

1. Enantioselective Recognition of (*S*)-L1, and (*S*)-L2 with α-phenyl ethylamine and phenylglycinol.

1.0×10^{-5} M solution of host compounds **(*S*)-L1** and **(*S*)-L2** in toluene, 0.01 M solution of (*R*)/(*S*)-phenyl ethylamine and (*L*)/(*D*)-phenylglycinol in THF were freshly prepared for each measurement. The resulting solution was allowed to stand at room temperature for 4 h before the fluorescence measurement.

1.1 Investigation of (*S*)-L1 with (*R*)/(*S*)-phenyl ethylamine

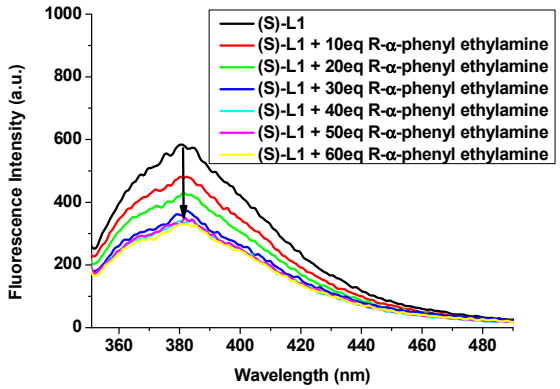


Figure S1. Fluorescence spectra of (*S*)-**L1** with different molar ratio of (*R*)-α-phenyl ethylamine

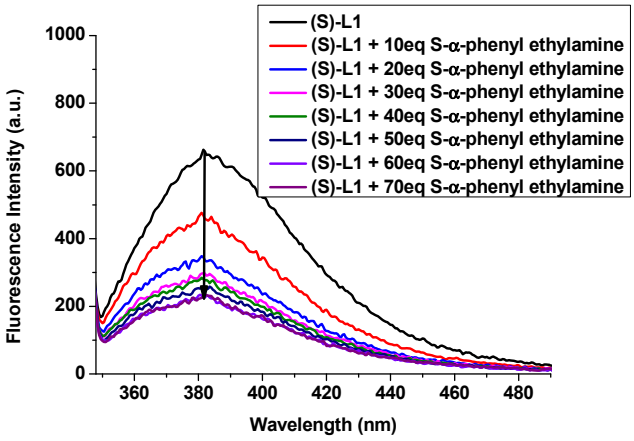


Figure S2. Fluorescence spectra of (*S*)-**L1** with different molar ratio of (*S*)-α-phenyl ethylamine

1.2 Investigation of (*S*)-L1 with (*L*)/(*D*)-phenylglycinol

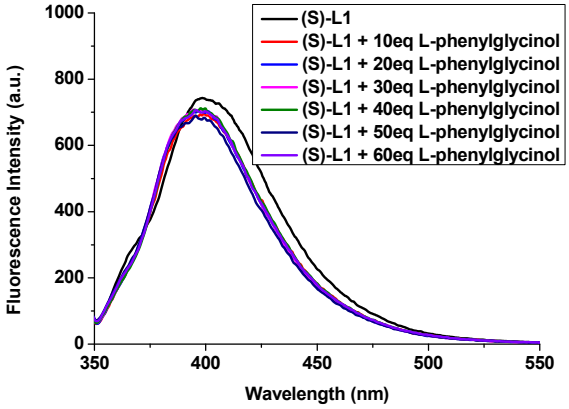


Figure S3. Fluorescence spectra of (*S*)-**L1** with different molar ratio of (*L*)-phenylglycinol.

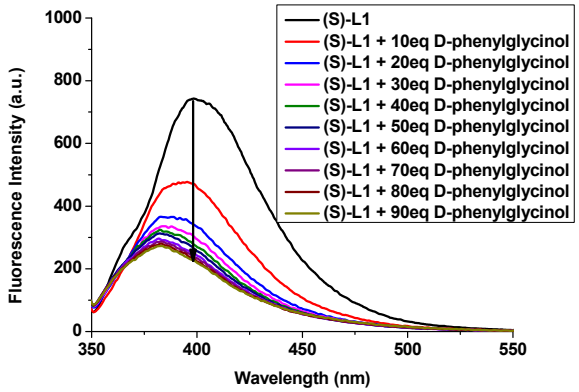


Figure S4. Fluorescence spectra of (*S*)-**L1** with different molar ratio of (*D*)-phenylglycinol.

1.3 Investigation of (*S*)-L2 with (*R*)-α-phenyl ethylamine

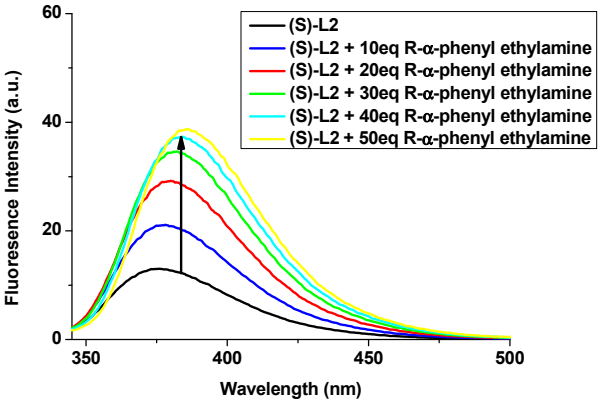


Figure S5. Fluorescence spectra of (*S*)-**L2** with different molar ratio of (*R*)-α-phenyl ethylamine

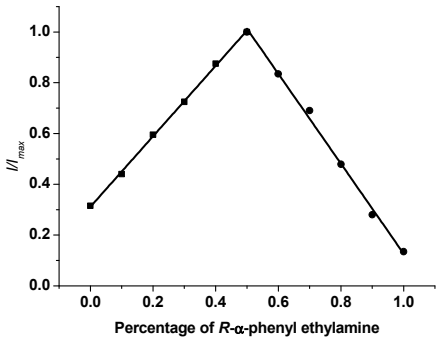


Figure S6. Fluorescence Jobs plot of (*S*)-**L2** and (*R*)-α-phenyl ethylamine. Total concentration of (*S*)-**L2** and (*R*)-phenyl ethylamine is 5.0×10^{-5} M.

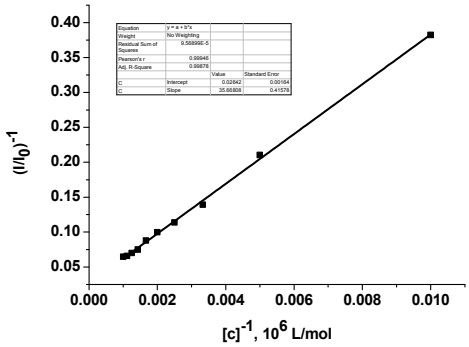


Figure S7. Relationship between $(I-I_0)^{-1}$ and $[c]^{-1}$. I: fluorescence intensity of **(*S*)-L2** with (*R*)-α-phenyl ethylamine. I_0: fluorescence intensity of **(*S*)-L2** without (*R*)-α-phenyl ethylamine (1.0×10^{-5} M in toluene); [c]: concentration of (*R*)-α-phenyl ethylamine in mixed solution.

Table S1. Parameter of the fitting curve in **Fig S7**

Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	9.56899E-5		
Pearson's r	0.99946		
Adj. R-Square	0.99878		
		Value	Standard Error
C	Intercept	0.02642	0.00164
C	Slope	35.66808	0.41578

1.4 Investigation of (*S*)-L2 with (*S*)-α-phenyl ethylamine

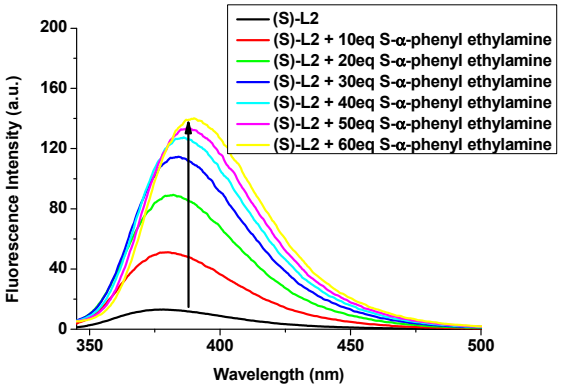


Figure S8. Fluorescence spectra of (*S*)-**L2** with different molar ratio of (*S*)-α-phenyl ethylamine

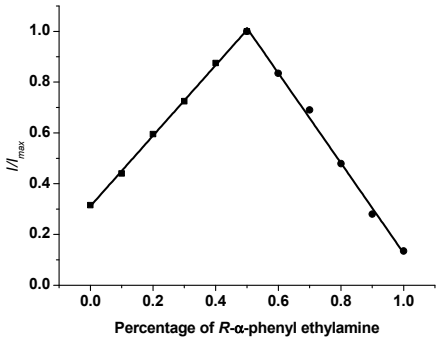


Figure S9. Fluorescence Jobs plot of (*S*)-**L2** and (*S*)-α-phenyl ethylamine. Total concentration of (*S*)-**L2** and (*S*)-α-phenyl ethylamine is 5.0×10^{-5} M.

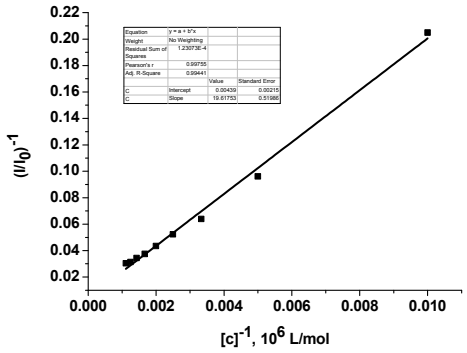
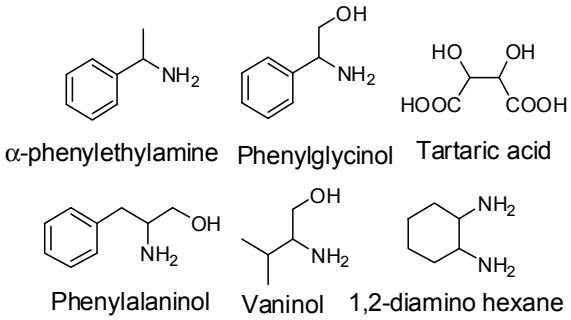


Figure S10. Relationship between $(I-I_0)^{-1}$ and $[c]^{-1}$. I: fluorescence intensity of (*S*)-**L2** with (*S*)-α-phenyl ethylamine. I_0: fluorescence intensity of (*S*)-**L2** without (*S*)-α-phenyl ethylamine (1.0×10^{-5} M in toluene); [c]: concentration of (*S*)-α-phenyl ethylamine in mixed solution.

Table S2: Parameters of the fitting curve in **Fig. S10**.

Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	1.23073E-4		
Pearson's r	0.99755		
Adj. R-Square	0.99441		
		Value	Standard Error
C	Intercept	0.00439	0.00215
	Slope	19.61753	0.51986

2. Fluorescence spectrum of (*S*)-L1 with other guest molecules.



Scheme1. Chiral guests used in the investigation of enantioselective recognition

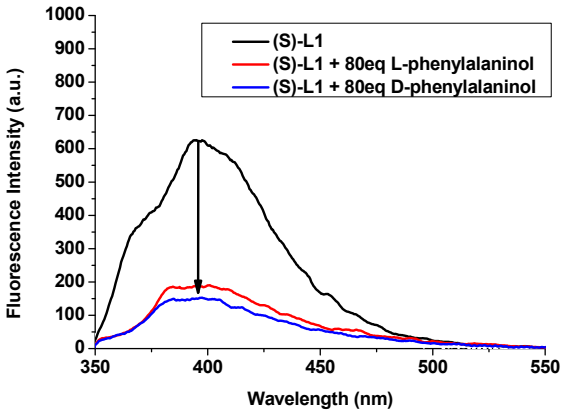


Figure S11. Fluorescence emission spectra of (*S*)-**L1**(1.0×10^{-5} mol/L in toluene) towards (*L*)/(*D*)-phenylalaninol (1.0×10^{-2} mol/L in THF)

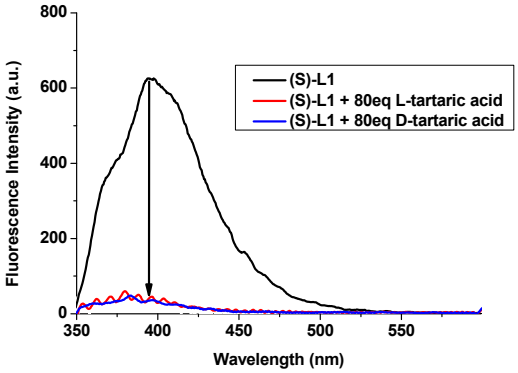


Figure S12. Fluorescence emission spectra of (*S*)-**L1** (1.0×10^{-5} mol/L in toluene) towards (*L*)/(*D*)-tartaric acid (1.0×10^{-2} mol/L in THF)

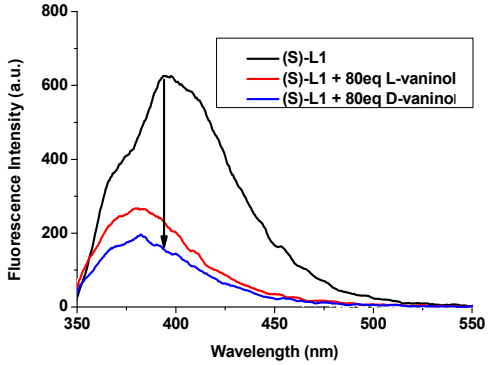


Figure S13. Fluorescence emission spectra of (*S*)-**L1** (1.0×10^{-5} mol/L in toluene) towards (*L*)/(*D*)-vaninol (1.0×10^{-2} mol/L in THF)

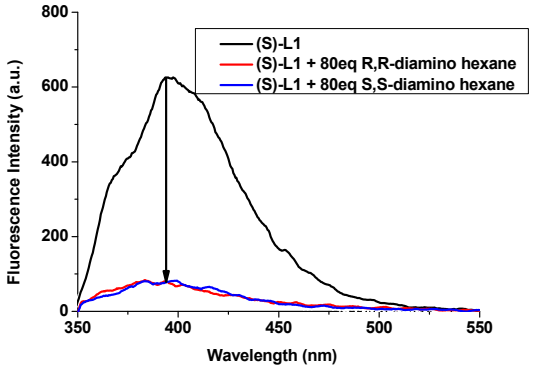


Figure S14. Fluorescence emission spectra of (*S*)-**L1** (1.0×10^{-5} mol/L in toluene) towards (*R*,*R*)/(*S*,*S*)-diaminol hexane (1.0×10^{-2} mol/L in THF)

3. Fluorescence spectrum of (*S*)-L2 with other guest molecules.

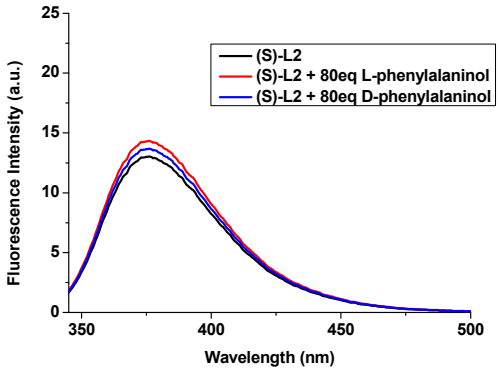


Figure S15. Fluorescence emission spectra of (*S*)-**L2** (1.0×10^{-5} mol/L in toluene) towards (*L*)/(*D*)-phenylalaninol (1.0×10^{-2} mol/L in THF)

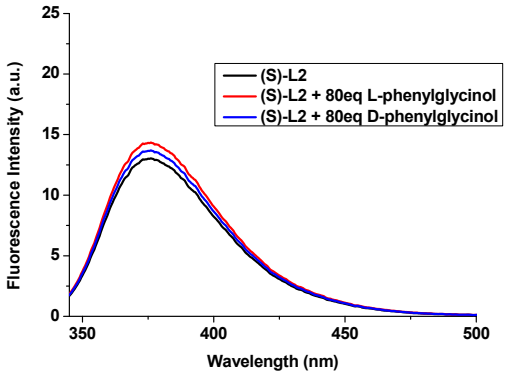


Figure S16. Fluorescence emission spectra of (*S*)-**L2** (1.0×10^{-5} mol/L in toluene) towards (*L*)/(*D*)-phenylglycinol (1.0×10^{-2} mol/L in THF)

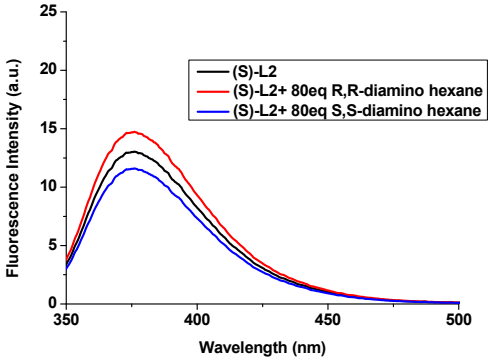


Figure S17. Fluorescence emission spectra of (*S*)-**L2** (1.0×10^{-5} mol/L in toluene) towards (*R*,*R*)/(*S*,*S*)-diamino hexane (1.0×10^{-3} mol/L in THF)

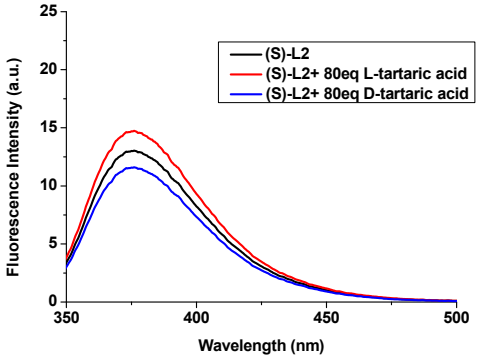


Figure S18. Fluorescence emission spectra of (*S*)-**L2** (1.0×10^{-5} mol/L in toluene) towards (*L*)/(*D*)-tartaric acid (1.0×10^{-2} mol/L in THF)

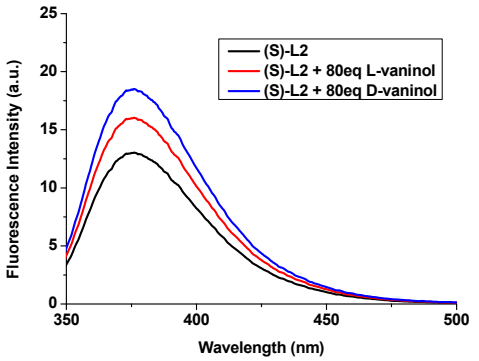


Figure S19. Fluorescence emission spectra of (*S*)-**L2** (1.0×10^{-5} mol/L in toluene) towards (*L*)/(*D*)-vaninol (1.0×10^{-2} mol/L in THF)

4. NMR spectra.

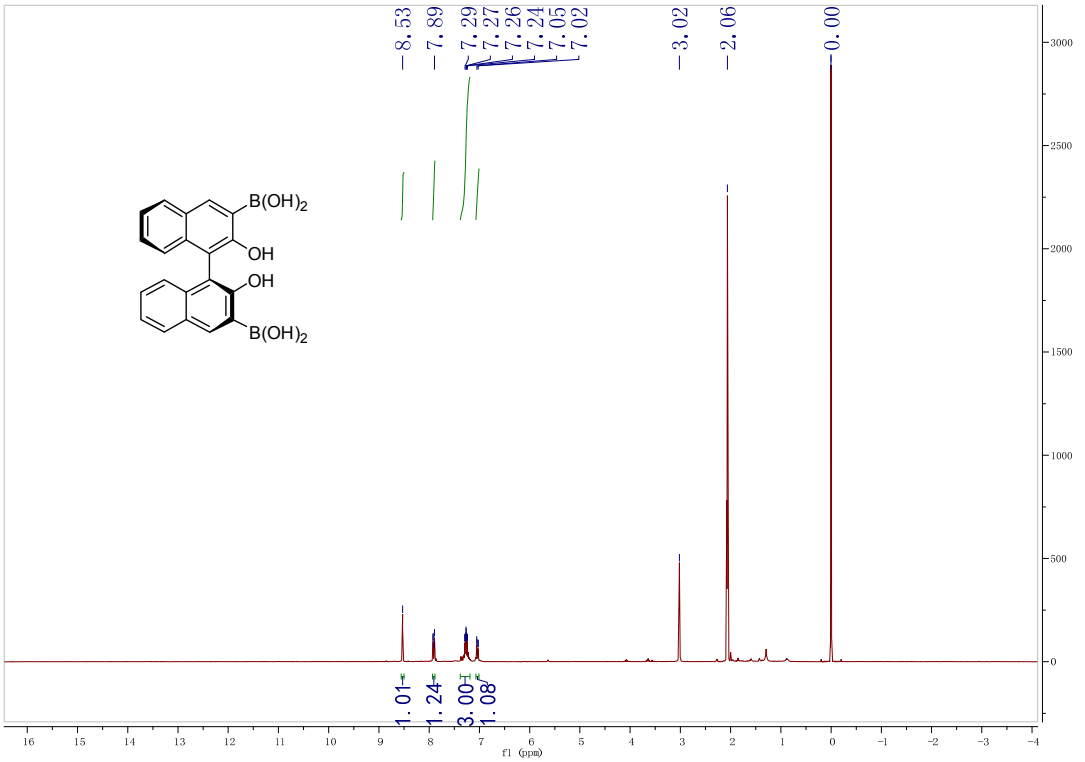


Figure S20. ^{1}H NMR of **3** (d_6-Acetone)

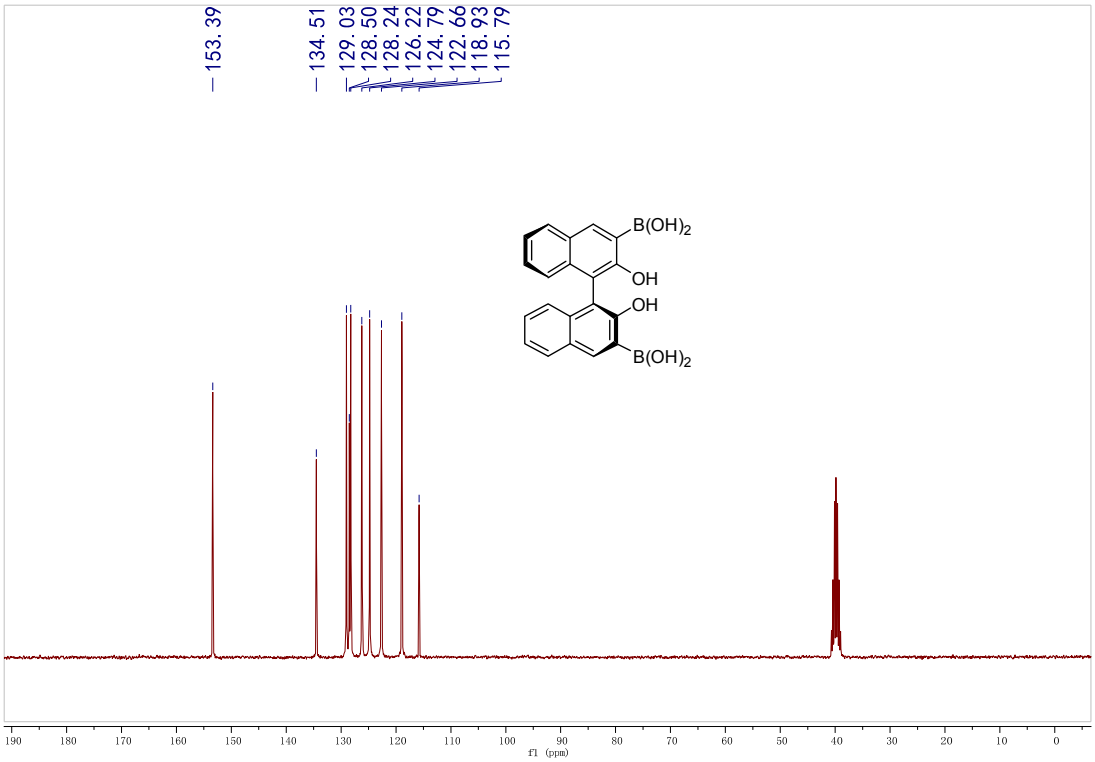


Figure S21. ^{13}C NMR of **3** (d_6-DMSO)

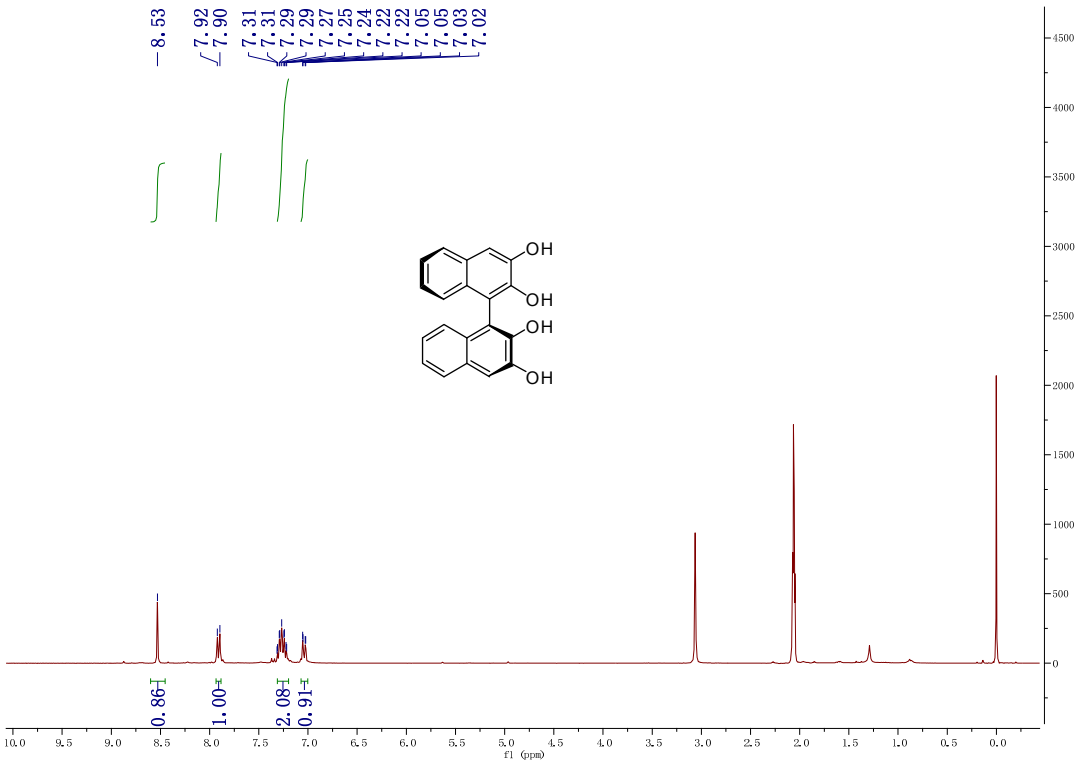


Figure S22. ^{1}H NMR of **4** (d_6-DMSO)

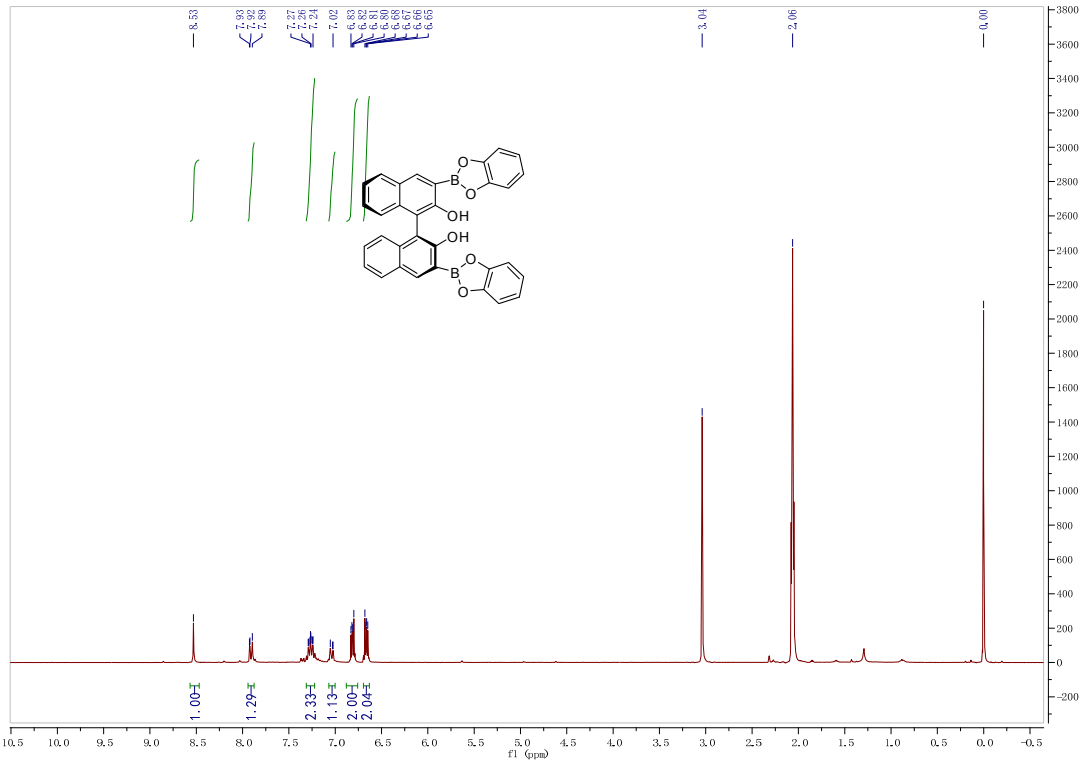


Figure S23. ^{1}H NMR of (*S*)-**L1** (d_6-Acetone)

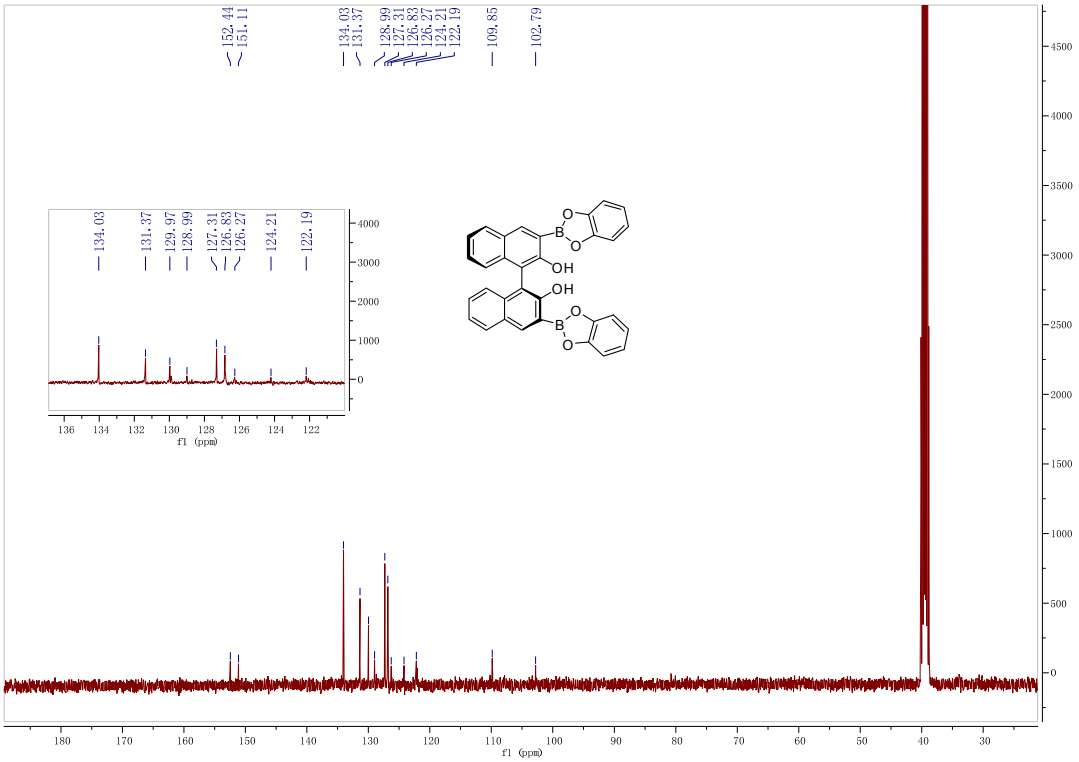


Figure S24. ^{13}C NMR of (*S*)-**L1** (d_6-DMSO)

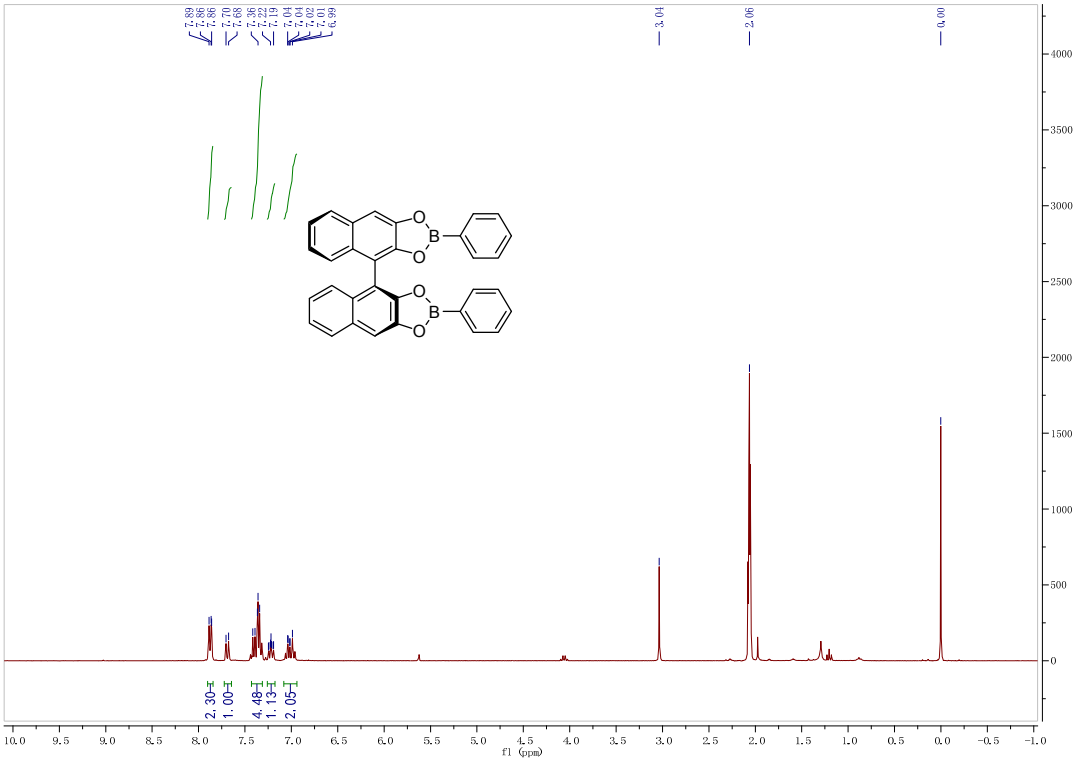


Figure S25. ^{1}H NMR of (*S*)-**L2** (d_6-Acetone)

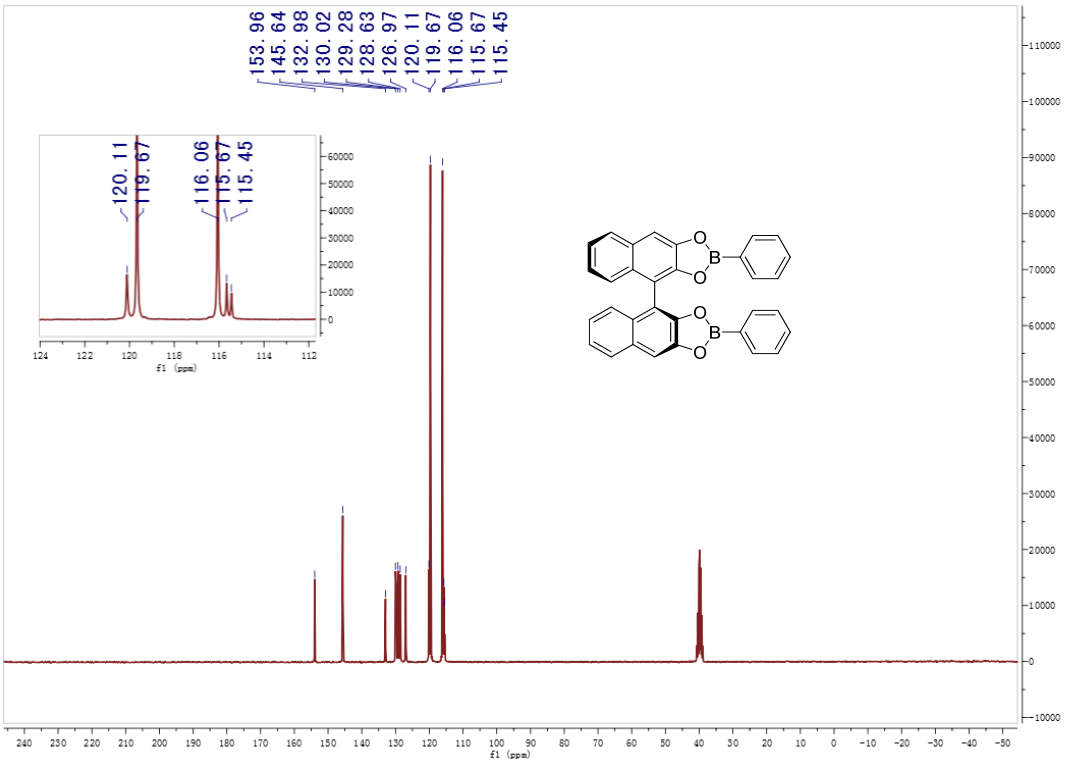


Figure S26. ^{13}C NMR of (*S*)-**L2** (d_6-DMSO)

5. IR spectra

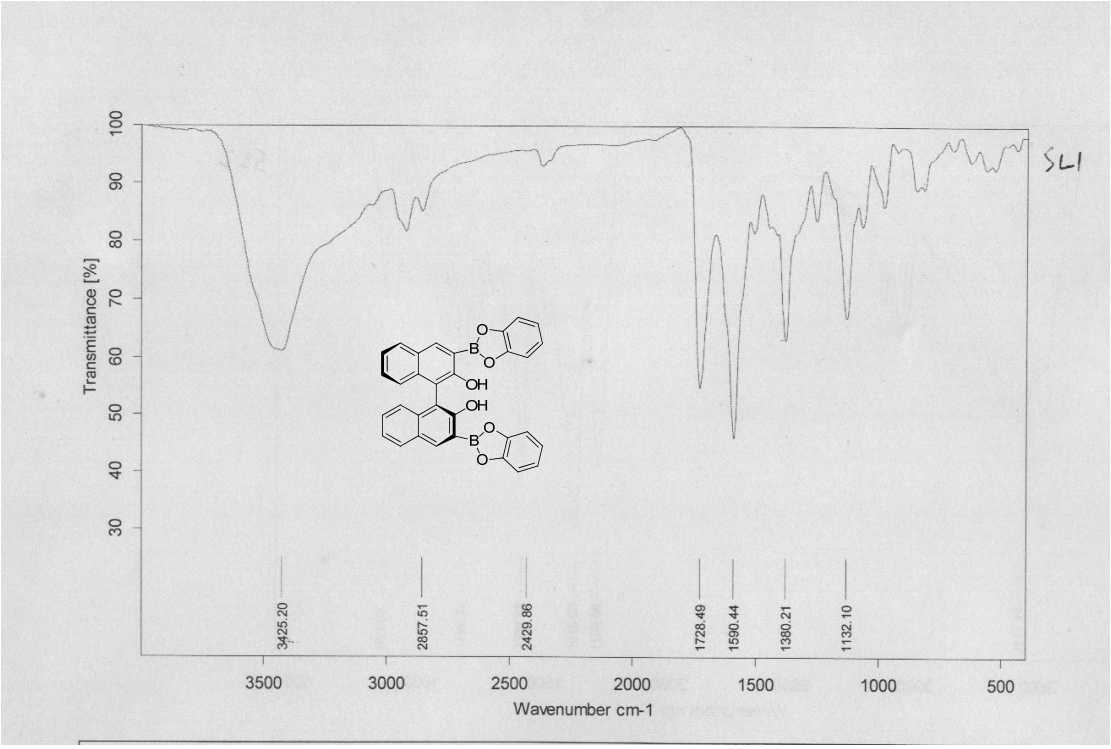


Figure S27. IR spectrum of (S)-**L1**

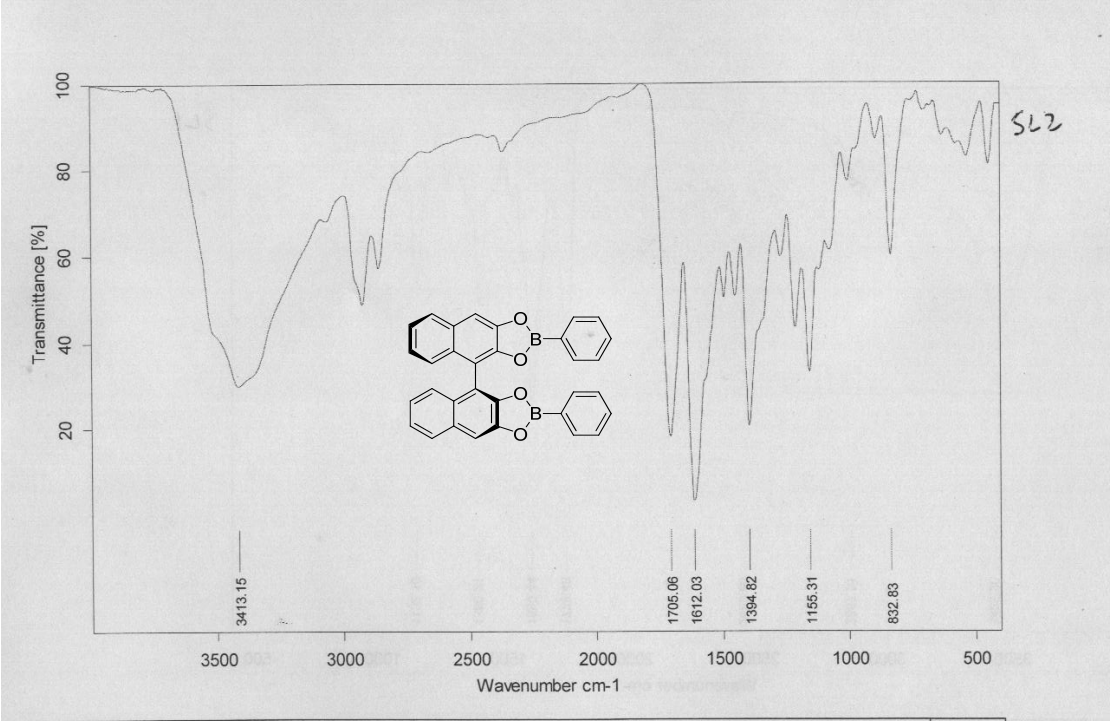


Figure S28. IR spectrum of (S)-**L2**

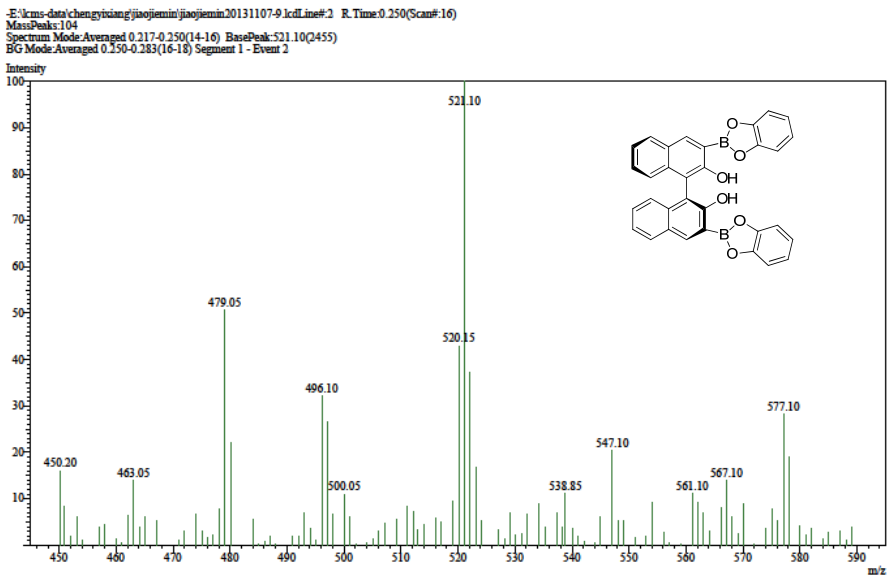


Figure S29. ESI-MS of (S)-**L1**，$[C_{32}H_{20}B_2O_6 - H]^-$ calcd 521.14; found 521.10.

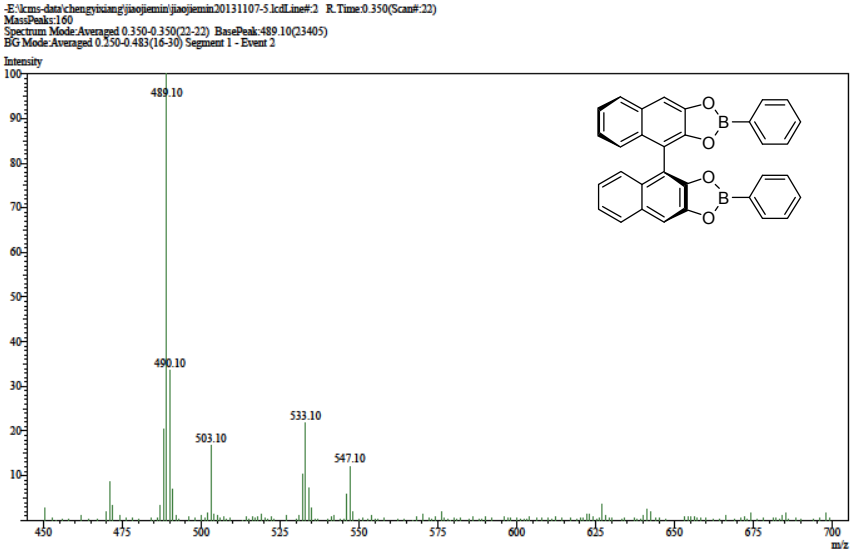


Figure S30. ESI-MS of (S)-**L2**，$[C_{32}H_{20}B_2O_4 - H]^-$ Calcd 489.15; found 489.10.

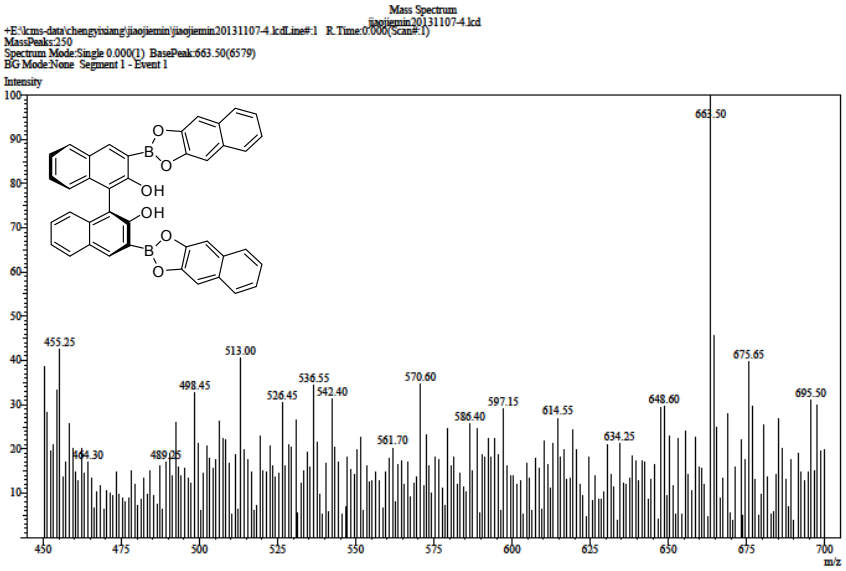


Figure S31. ESI-MS of (S)-**L3**，$[C_{40}H_{24}B_2O_6 + H_2O + Na]^+$ Calcd 663.18; found 663.50.

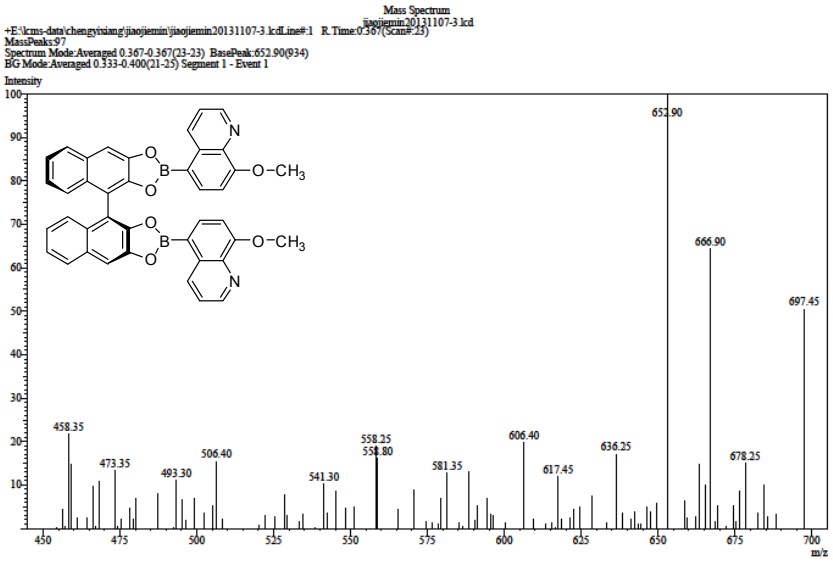
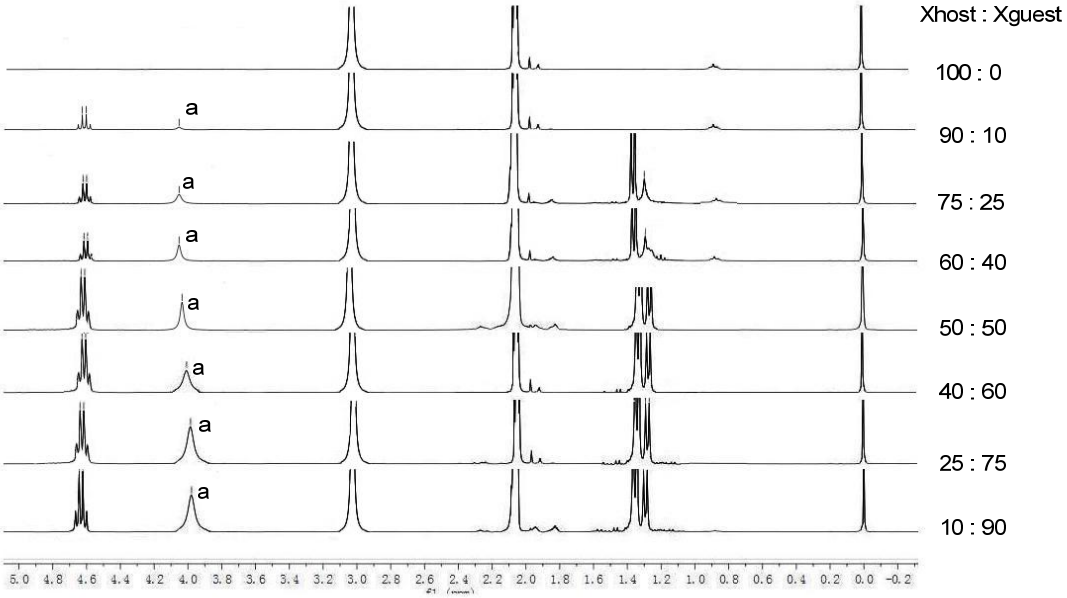
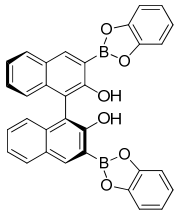


Figure S32. ESI-MS of (S)-**L4**, $[C_{40}H_{26}B_2N_2O_6 + H]^+$ Calcd 653.08; found 652.90.

6. ^{1}H NMR study of (*S*)-L1 and (*S*)-L2



Host =



Guest =

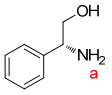


Figure S33. Partial ^{1}H NMR spectrum of (*S*)-**L1** + (*D*)-phenylglycinol (in d_6-Acetone). The total concentration of (*S*)-**L1** and (*D*)-phenylglycinol remains at 2.0×10^{-4} mol/L.

The ^{1}H NMR spectra of (*S*)-**L1** was determined as addition of (*D*)-phenylglycinol in different molar ratios. The H signal of amino group of guest compound (labeled as **a**) was shifted upfield upon addition of host compound from $\delta = 3.98$, and reached largest value at $\delta = 4.06$. This could be attributed to that B atom of host molecule played its role as electron acceptor, and amino group of guest played it role as electron donor.

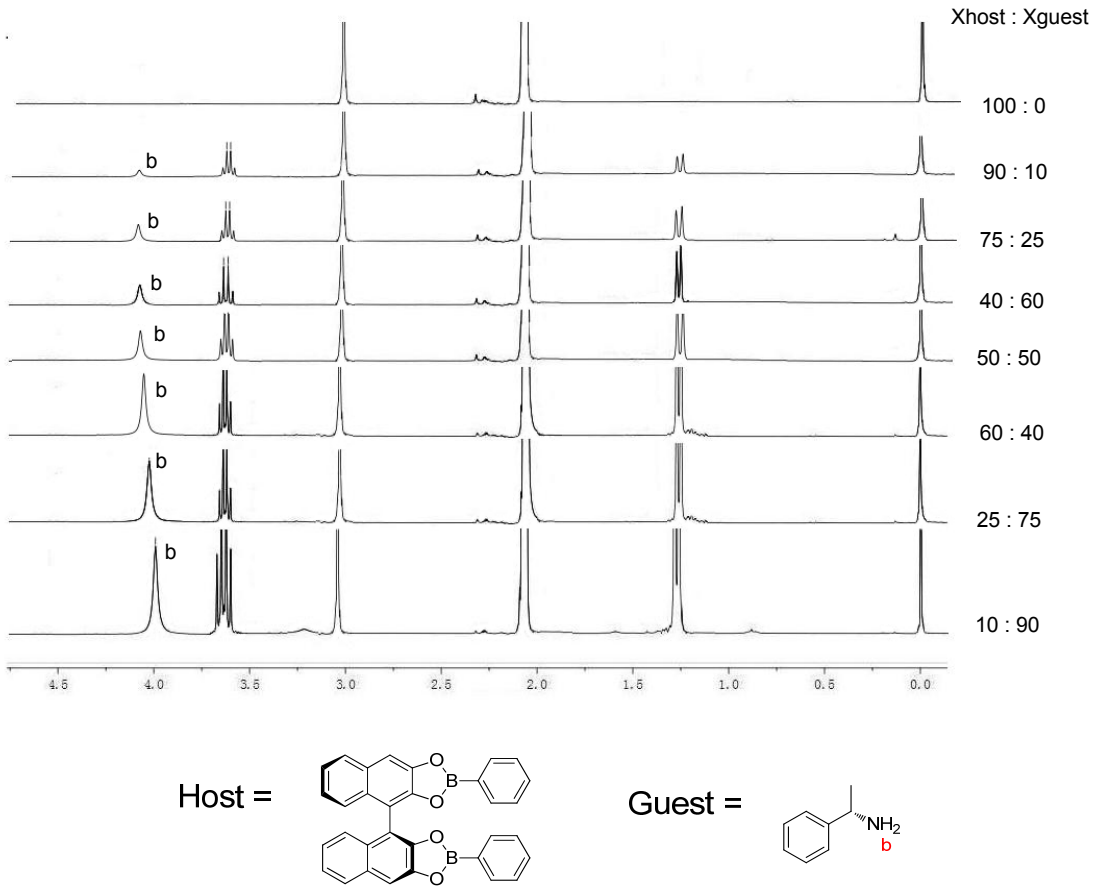


Figure S34. Partial ^{1}H NMR spectrum of (*S*)-**L2** + (*S*)-α-phenyl ethylamine (in d_6-Acetone). The total concentration of (*S*)-**L2** and (*S*)-α-phenyl ethylamine remains at 1.0×10^{-4} mol/L.

The ^{1}H NMR spectra of (*S*)-**L2** was also determined as addition of (*S*)-α-phenyl ethylamine in different molar ratios. The H signal of amino group of guest compound (labeled as **b**) was shifted upfield upon addition of host compound from δ = 4.01, and reached largest value at δ = 4.13. This could be attributed to the similar mechanism in (*S*)-**L1**.

7. UV-vis spectrum of (*S*)-L2 with phenyl amine

Herein, we further investigated UV-vis study of (*S*)-**L2** towards both enantiomers of phenyl ethylamine. As demonstrated in Figure **S29**, we found that UV-vis spectrum of sensor (*S*)-**L2** exhibits two absorption peaks situated at 288 nm and 322 nm, respectively. No obvious UV-vis absorbance change could be observed upon addition of (*R*)-phenyl ethylamine. However, the absorption peak at long wavelength region of 322 nm shows a little enhancement while sensor (*S*)-**L2** was treated with (*S*)-phenyl ethylamine, indicating that sensor (*S*)-**L2** exhibited higher coordinative effect upon (*S*)-phenyl ethylamine rather than (*R*)-phenyl ethylamine, which is coincident with fluorescence enantioselective recognition behavior.

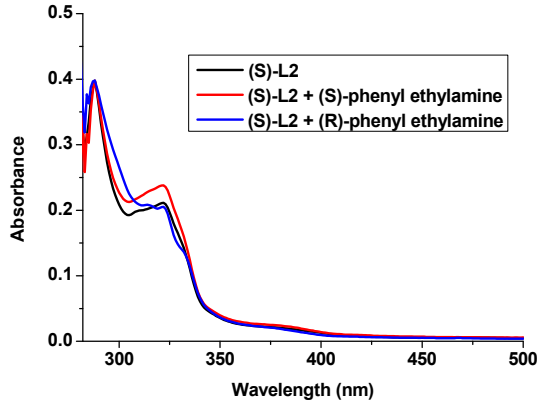


Figure **S35**. UV-vis spectra of (*S*)-**L2** (0.5×10^{-6} mol/L in $CHCl_3$) towards (*R*)- and (*S*)-α-phenyl ethylamine (1.0×10^{-2} mol/L in THF) at 1:100 molar ratio.