Supporting information

Chiral Couramin-based Fluorescence Sensor for Highly Enantioselective Recognition of Phenylalaninol

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Contents:

1. Material and Methods

NMR spectra were recorded on Bruker-300 spectrometer 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR and reported as parts per million (ppm) from the internal standard TMS. Electrospray ionization mass spectra (ESI-MS) were measured on a Thermo Finnigan LCQ Fleet system. FT-IR spectra were taken on a Nexus 870 FT-IR spectrometer. Fluorescence spectra were obtained from a RF-5310 PC spectrometer. C, H, and N of elemental analyses were performed on an Elementar Vario MICRO analyzer. Specific rotation was determined with a Ruololph Research Analyfical Autopol I. All solvents and reagents were commercially available A.R. grade. All the solvents were dried using standard percedures immediatly before usage.

2. Enantioselective Recognition of L1 with phenylalaninol

2.1 General Procedures

1.0×10^{-6} mol/L solution of host compounds **L1** in different kinds of solvents and 0.01 mol/L solution of (*L*)-/(*D*)-phenylalaninol 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.

2.2. Investigation of solvents

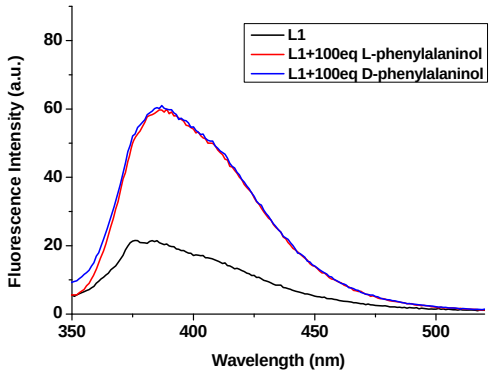

Figure S1. Fluorescence spectra of **L1** (1.0×10^{-6} mol/L in toluene) with and without (*L*)-/(*D*)-phenylalaninol (1.0×10^{-2} mol/L in THF) at 1:110 molar ratio (λ_{ex} = 337 nm, λ_{em} = 387 nm).

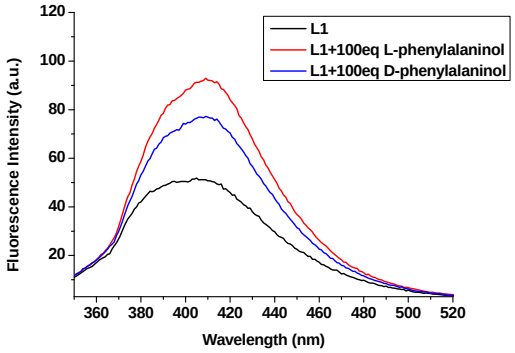

Figure S2. Fluorecence spectra of **L1** (1.0×10^{-6} mol/L in CH_2Cl_2) with and without (*L*)-/(*D*)-phenylalaninol (1.0×10^{-2} mol/L in THF) at 1:110 molar ratio (λ_{ex} = 338 nm, (λ_{em} = 409 nm).

2.3. Fluorescence investigation of L1 with phenylalaninol

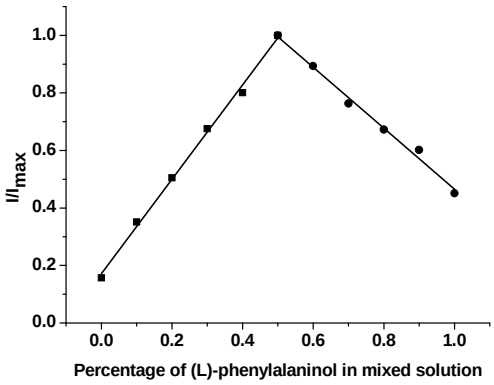

Figure S3. Fluorescence Jobs plot of **L1** and (*L*)-phenylalaninol. Total concentration of **L1** and (*L*)-phenylalaninol is 5.0×10^{-6} mol/L in THF, measured at λ = 409 nm.

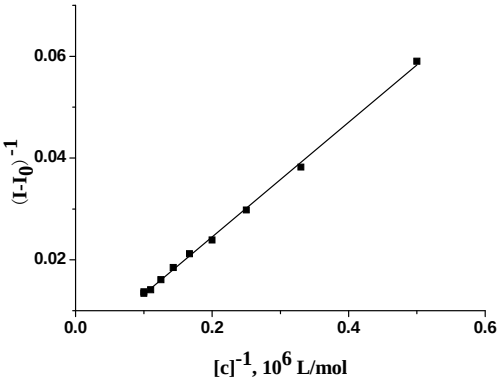

Figure S4. Relationship between $(I-I_0)^{-1}$ and $[c]^{-1}$. I: fluorescence intensity of **L1** with (*L*)-phenylalaninol; I_0: fluorescence intensity of **L1** without (*L*)-phenylalaninol; [c]: concentration of (*L*)-phenylalaninol in mixed solution.

Table S1: Parameters of the fitting curve in **Figure S4**

Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	2.52416E-6		
Pearson's r	0.99933		
Adj. R-Square	0.99848		
		Value	Standard Error
B	Intercept	0.00199	3.4544E-4
	Slope	0.11259	0.00146

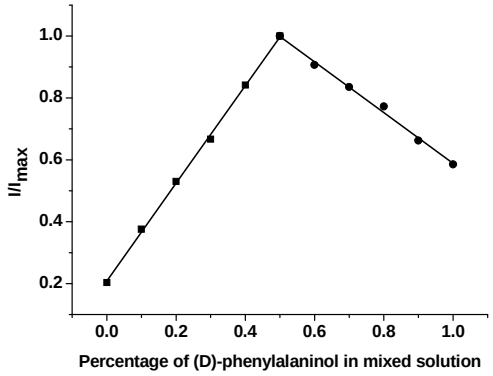

Figure S5. Fluorescence Jobs plot of **L1** and (*D*)-phenylalaninol. Total concentration of **L1** and (*D*)-phenylalaninol is 5.0×10^{-6} mol/L in THF, measured at $\lambda = 409$ nm.

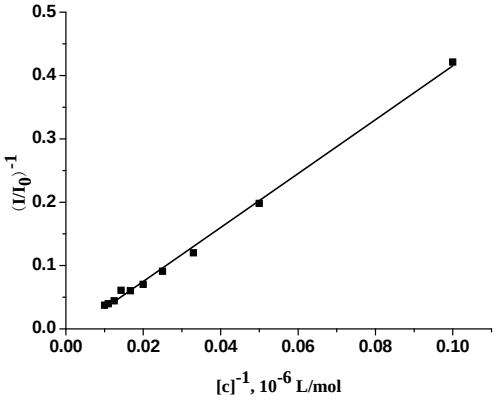

Figure S6. Relationship between $(I-I_0)^{-1}$ and $[c]^{-1}$. I: fluorescence intensity of **L1** with (*D*)-phenylalaninol; I_0: fluorescence intensity of **L1** without (*D*)-phenylalaninol; [c]: concentration of (*D*)-phenylalaninol in mixed solution.

Table S2: Parameters of the fitting curve in **Figure S6**

Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	3.51278E-4		
Pearson's r	0.9986		
Adj. R-Square	0.99686		
		Value	Standard Error
B	Intercept	0.01028	0.00313
	Slope	4.25758	0.07966

2.4 ^{1}H NMR studies on the interaction of L1 with (*L*)-phenylalaninol

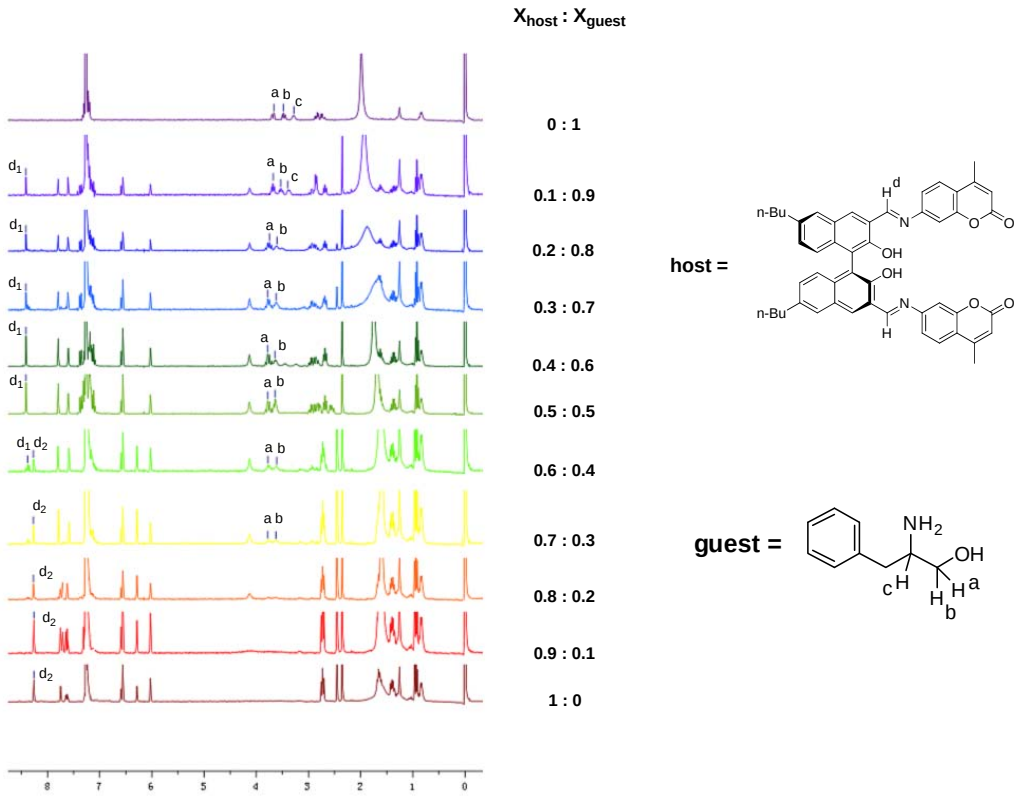

Figure S7. Partial ^{1}H NMR spectra of **L1**+(L)-phenylalaninol (in $CDCl_3$). The total concentration of **L1**+(L)-phenylalaninol was maintained at 2.0×10^{-3} mol/L

The ^{1}H NMR spectra of **L1** (1.0×10^{-6} mol/L in THF) were determined as addition of (*L*)-/(*D*)-phenylalaninol (1×10^{-2} mol/L in THF) in different molar ratio, as the following figures. The signals of H of guest compound at δ = 3.48(b), 3.66(a) are shifted downfield, and δ reached maximum at δ = 3.64(b), 3.78(a) respectively, while the molar ratio of host/guest is 0.5:0.5. $\Delta_{\delta a}$= 0.12, $\Delta_{\delta b}$ = 0.16. Meanwhile hydrogen atom at c position also shifts downfield, demonstrating that hydroxyl and amino groups of guest are engaged in recognition process. In addition, low Δ_δ value indicates that the interaction of host and guest molecular is not quite strong, thus high molar ratio of guest is required in recognition process. It can be also observed that the signal of H of imine group in host compound at δ = 8.26(d_2) is shifted to 8.26(d_1) at the 1:1 molar ratio of host/guest, which indicates that imine group of chiral host also interacts with guest through H-bonding.

3. Fluorescence spectrum of L1 with other amino alcohols.

3.1 Fluorescence investigation of L1 with phenylglycinol

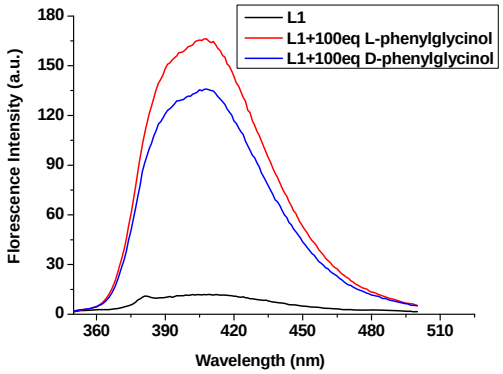

Figure S8. Fluorecence spectra of **L1** (1.0×10^{-5} mol/L in THF) with and without (*L*)-/(*D*)-phenylglycinol (1.0×10^{-2} mol/L in THF) at 1:110 molar ratio (λ_{ex} = 409 nm).

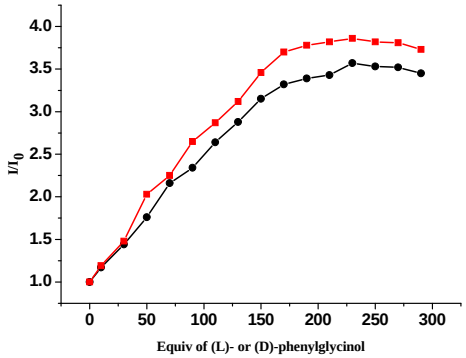

Figure S9. Fluorecence enhancement of **L1** (1.0×10^{-6} mol/L in THF) with different molar ratio of (*L*)-/(*D*)-phenylglycinol (1.0×10^{-2} mol/L in THF), from 1:10 to 1:300, λ_{ex} = 409 nm.

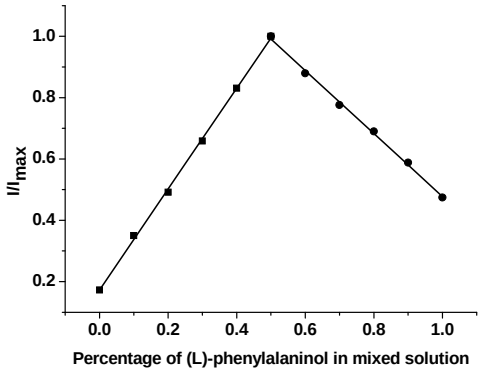

Figure S10. Fluorescence Jobs plot of **L1** and (*L*)-phenylglycinol. Total concentration of **L1** and (*L*)-phenylglycinol is 5.0×10^{-6} mol/L in THF, measured at λ = 409 nm.

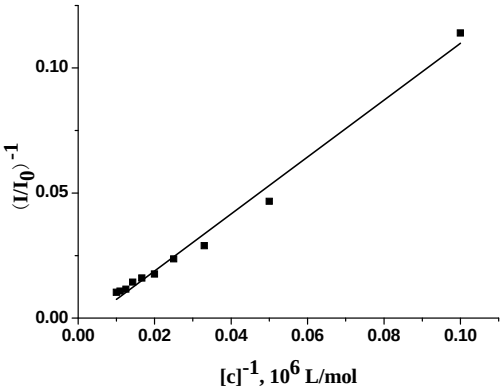

Figure S11. Relationship between $(I-I_0)^{-1}$ and $[c]^{-1}$. I: fluorescence intensity of **L1** with (*L*)-phenylglycinol; I_0: fluorescence intensity of **L1** without (*L*)-phenylglycinol; [c]: concentration of (*L*)-phenylglycinol in mixed solution.

Table S3: Parameters of the fitting curve in **Figure S10**.

Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	1.00657E-4		
Pearson's r	0.99443		
Adj. R-Square	0.9875		
		Value	Standard Error
B	Intercept	0.00389	0.00168
	Slope	1.13797	0.04264

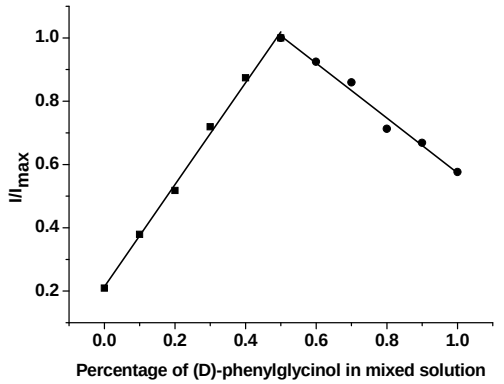

Figure S12. Fluorescence Jobs plot of **L1** and (*D*)-phenylglycinol. Total concentration of **L1** and (*D*)-phenylglycinol is 5.0×10^{-6} mol/L in THF, measured at $\lambda = 409$ nm.

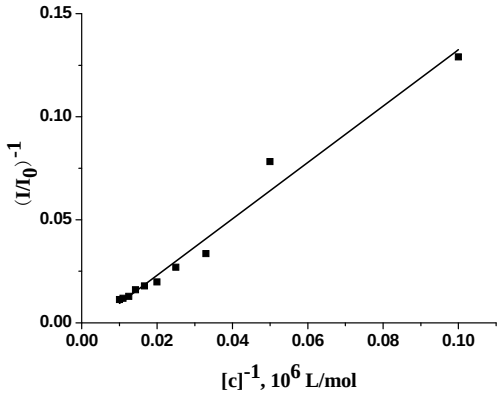

Figure S13. Relationship between $(I-I_0)^{-1}$ and $[c]^{-1}$. I: fluorescence intensity of **L1** with (*D*)-phenylglycinol; I_0: fluorescence intensity of **L1** without (*D*)-phenylglycinol; [c]: concentration of (*D*)-phenylglycinol in mixed solution.

Table S4: Parameters of the fitting curve in **Figure S12**

Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	2.89999E-4		
Pearson's r	0.98898		
Adj. R-Square	0.97535		
		Value	Standard Error
B	Intercept	0.00427	0.00285
	Slope	1.36785	0.07238

3.2 Fluorescence spectrum of L1 with alaninol and valinol

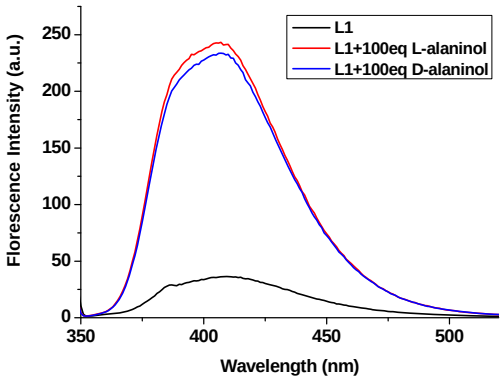

Figure S14. Fluorecence spectra of **L1** (1.0×10^{-6} mol/L in THF) with and without (*L*)-/(*D*)-alaninol (1.0×10^{-2} mol/L in THF) at 1:110 molar ratio (λ_{ex} = 409 nm).

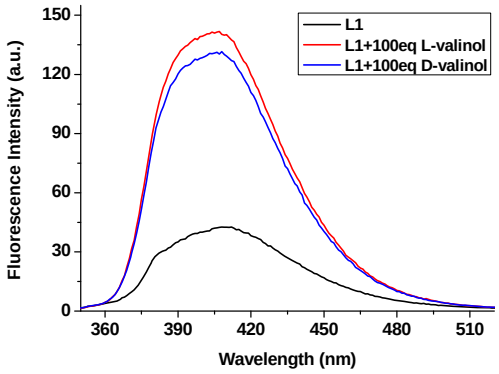

Figure S15. Fluorecence spectra of **L1** (1.0×10^{-6} mol/L in THF) with and without (*L*)-/(*D*)-valinol(1.0×10^{-2} mol/L in THF) at 1:110 molar ratio (λ_{ex} = 409 nm).

4. Fluorescence spectrum of L2 with four kinds of amino alcohol.

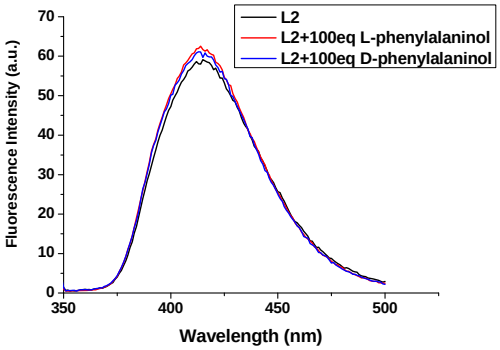

Figure S16. Fluorecence spectra of **L2** (1.0×10^{-6} mol/L in THF) with and without (*L*)-/(*D*)-phenylalaninol (1.0×10^{-2} mol/L in THF) at 1:110 molar ratio (λ_{ex} = 409 nm).

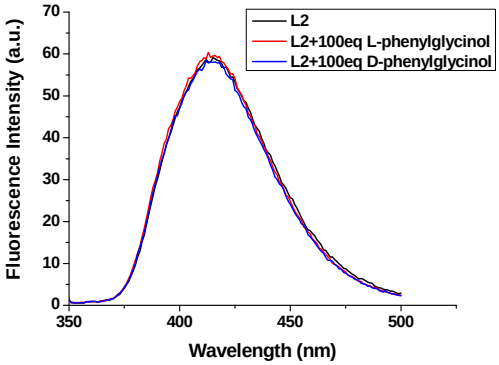

Figure S17. Fluorecence spectra of **L2** (1.0×10^{-6} mol/L in THF) with and without (*L*)-/(*D*)-phenylglycinol (1.0×10^{-2} mol/L in THF) at 1:110 molar ratio (λ_{ex} = 409 nm).

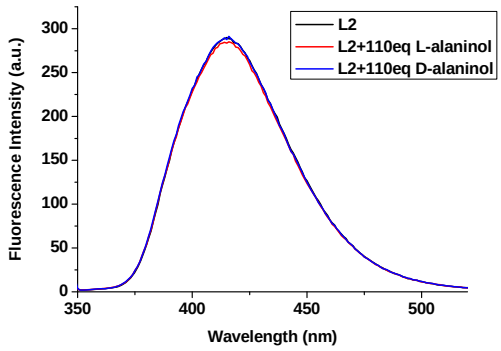

Figure S18. Fluorecence spectra of **L2** (1.0×10^{-6} mol/L in THF) with and without (*L*)-/(*D*)-alaninol (1.0×10^{-2} mol/L in THF) at 1:110 molar ratio (λ_{ex} = 409 nm).

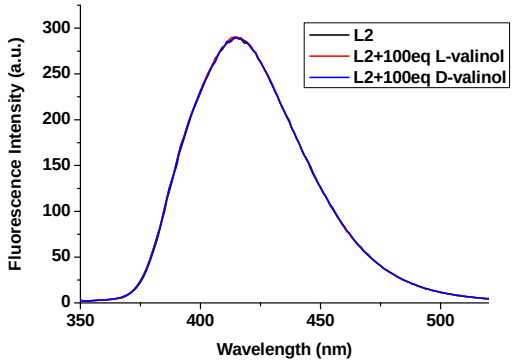

Figure S19. Fluorecence spectra of **L2** (1.0×10^{-6} mol/L in THF) with and without (*L*)-/(*D*)-valinol(1.0×10^{-2} mol/L in THF) at 1:110 molar ratio (λ_{ex} = 409 nm).

5. NMR, IR and MS Spectrum

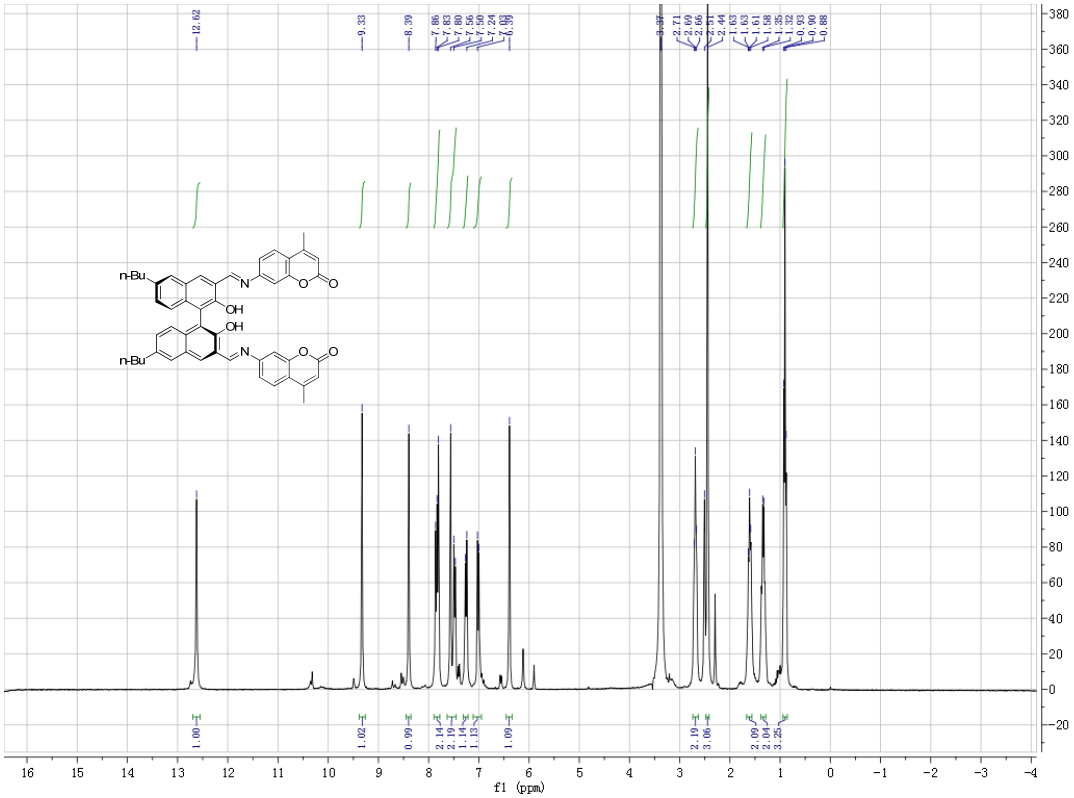

Figure S20. ^{1}H NMR of **L1**

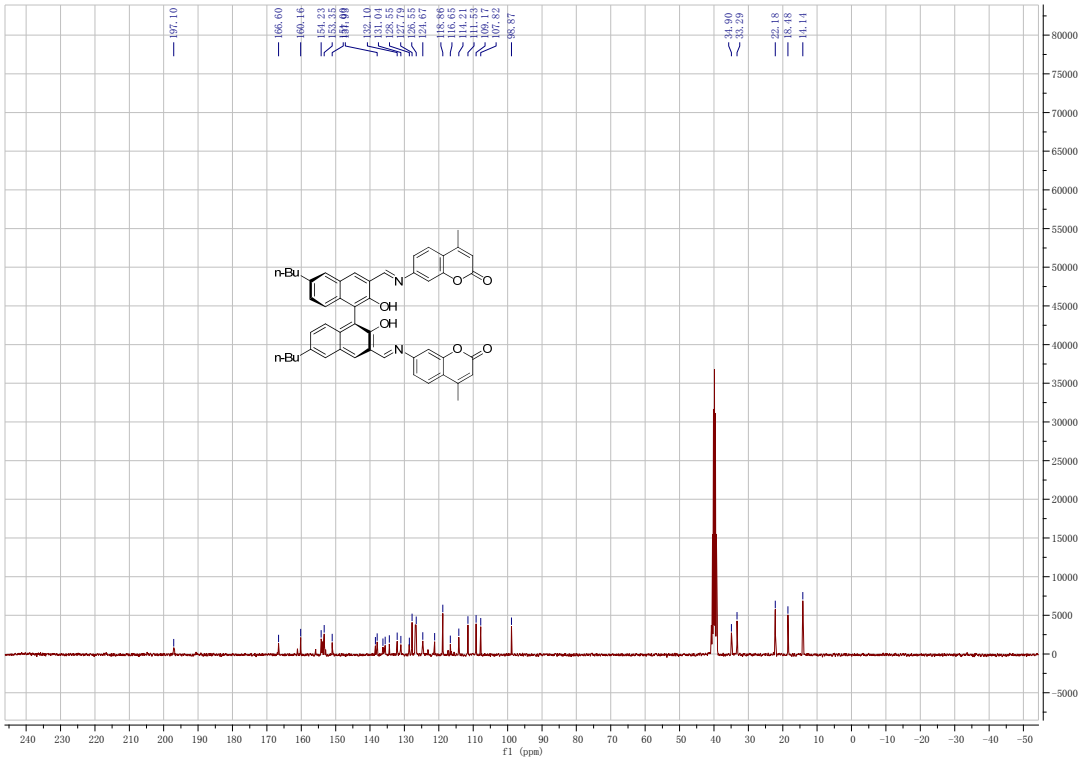

Figure S21. ^{13}C NMR of **L1**

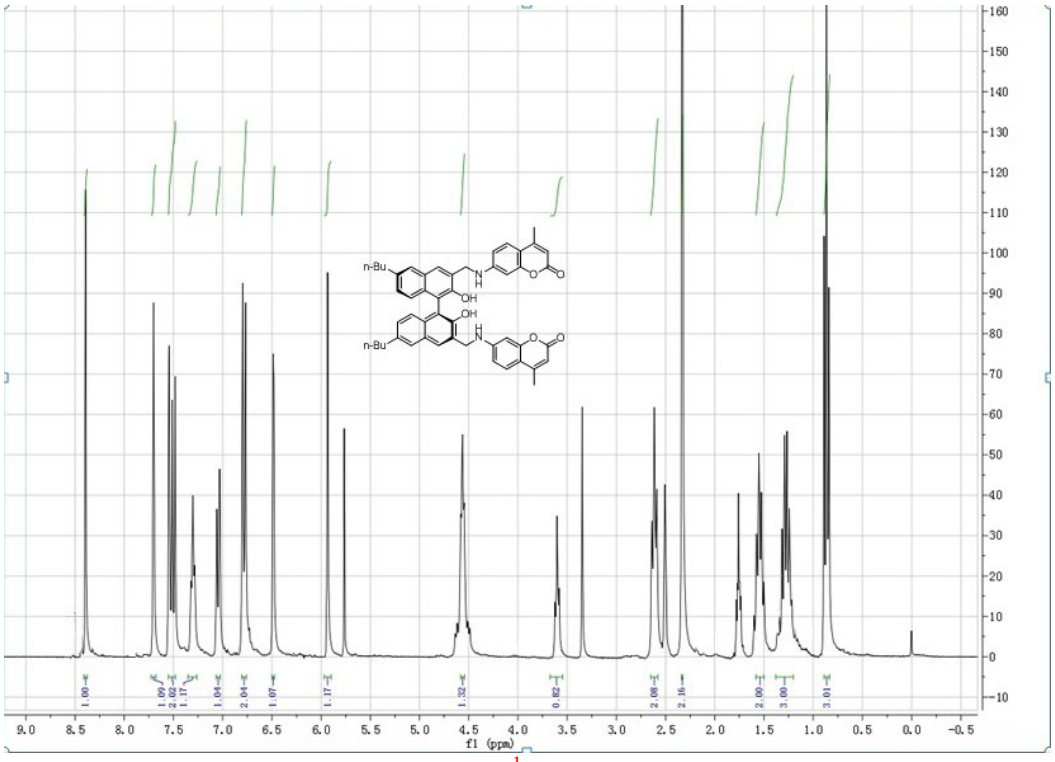

Figure S22. ^{1}H NMR of **L2**

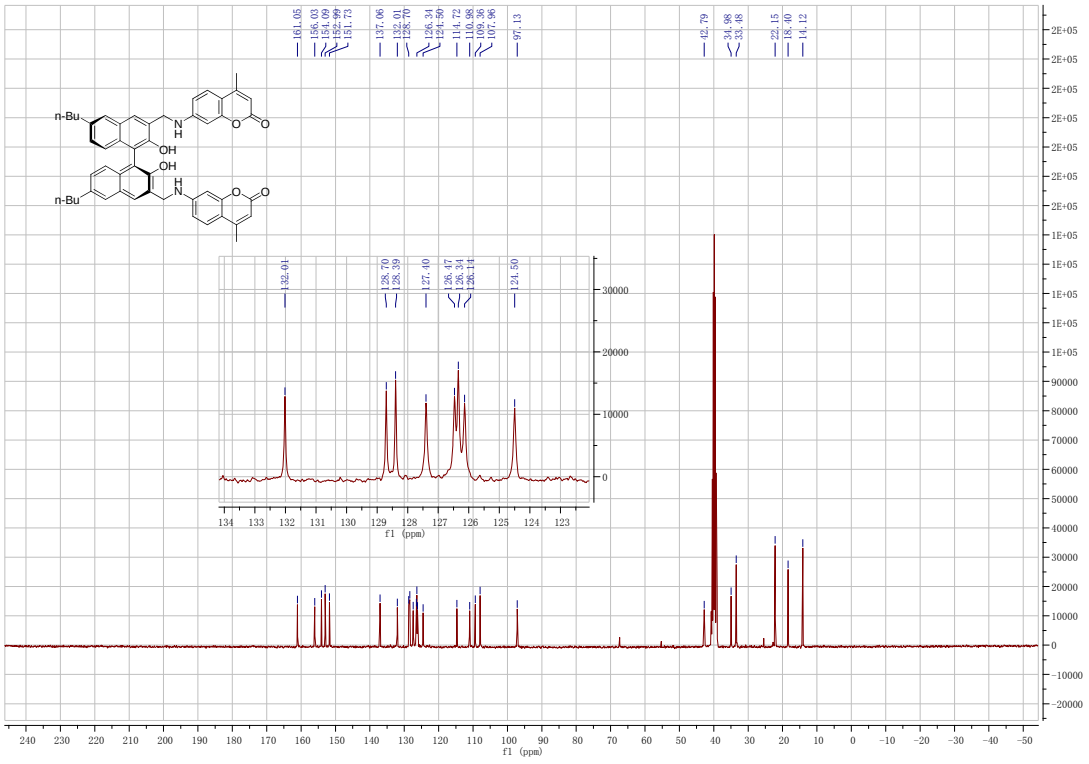

Figure S23. ^{13}C NMR of **L2**

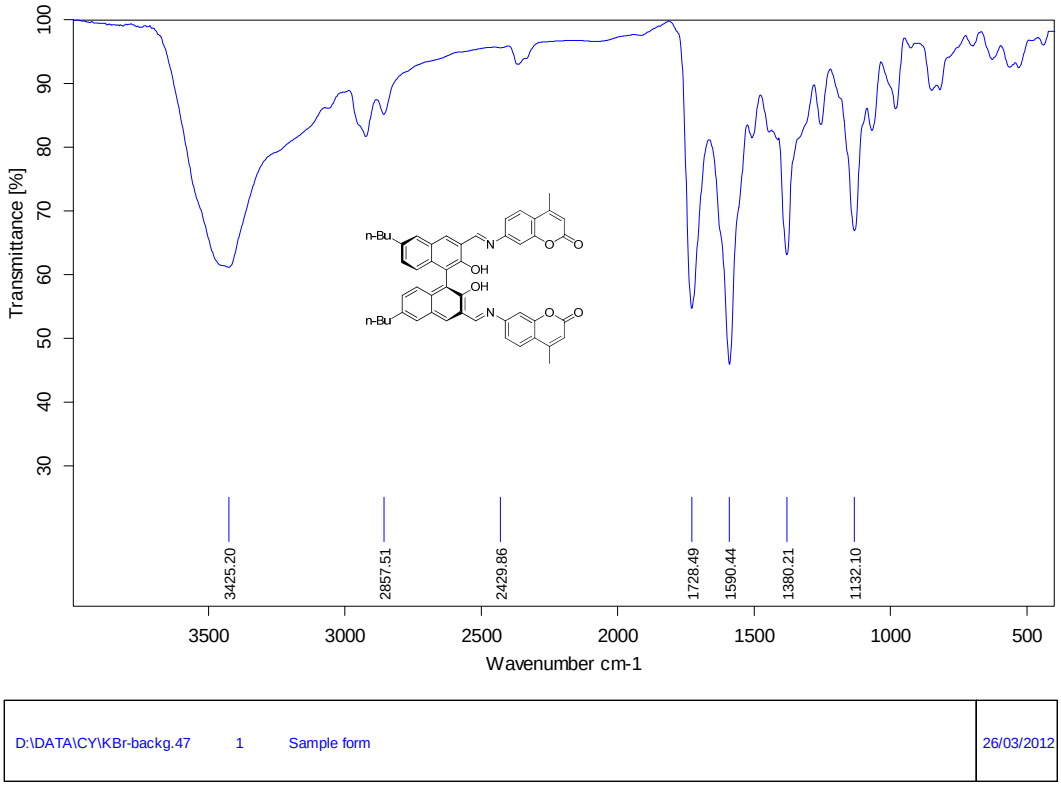

Figure S24. IR spectrum of **L1**

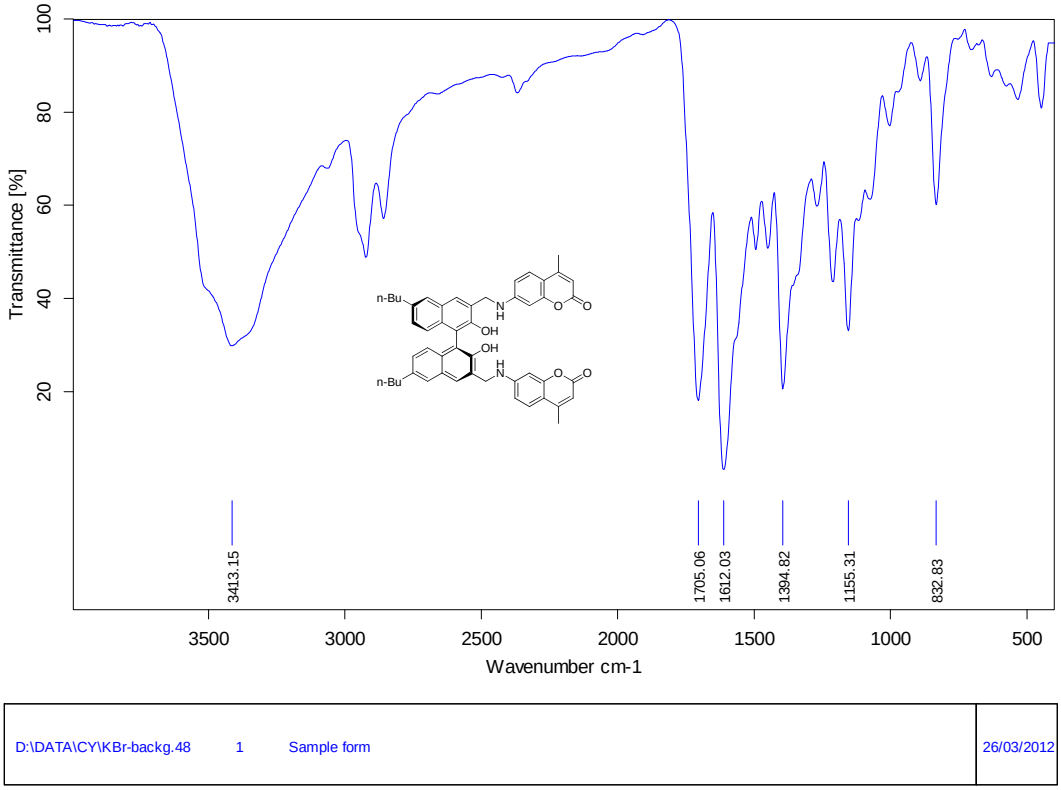

Figure S25. IR spectrum of **L2**

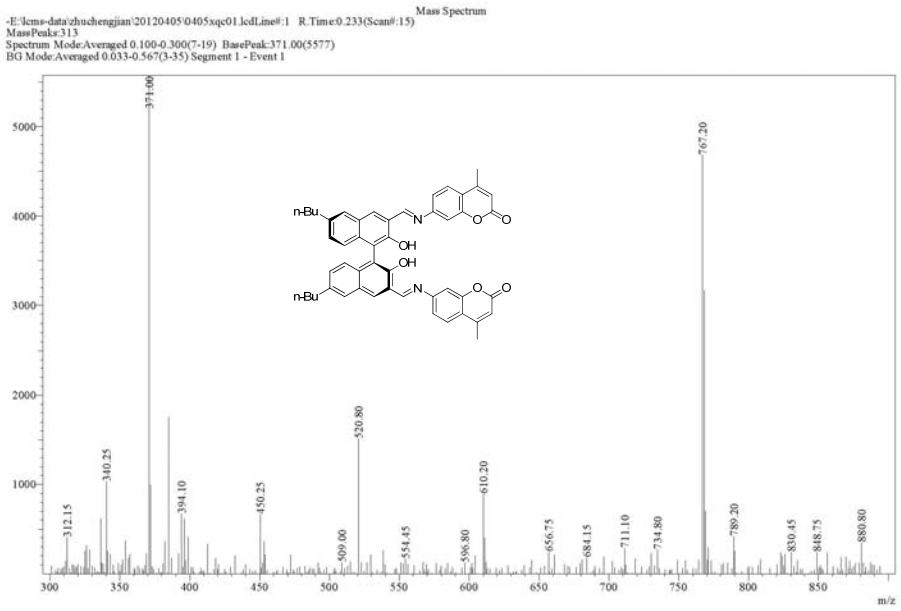

Figure S26. MS $[M-1]^-$ spectrum of **L1**

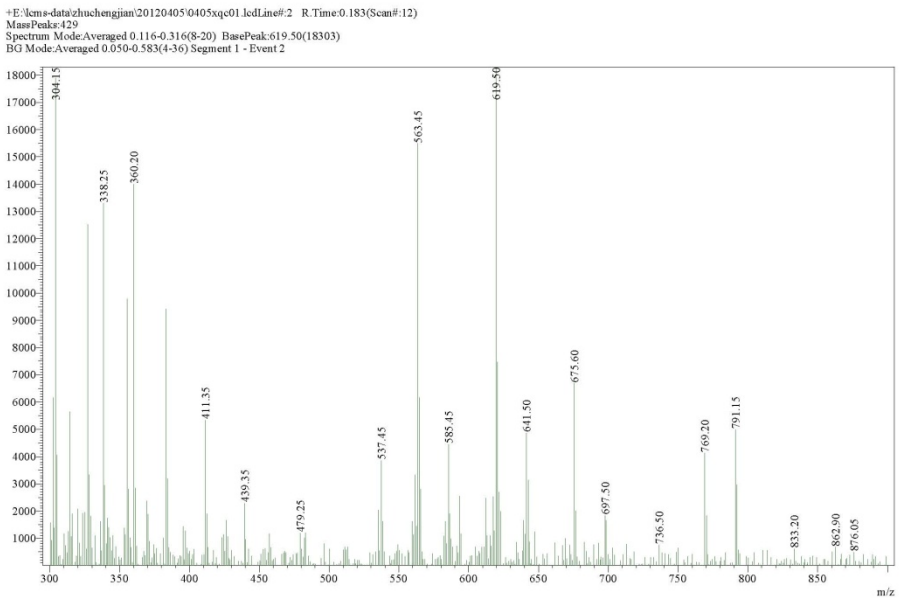

Figure S27. MS $[M+1]^+$ spectrum of **L1**

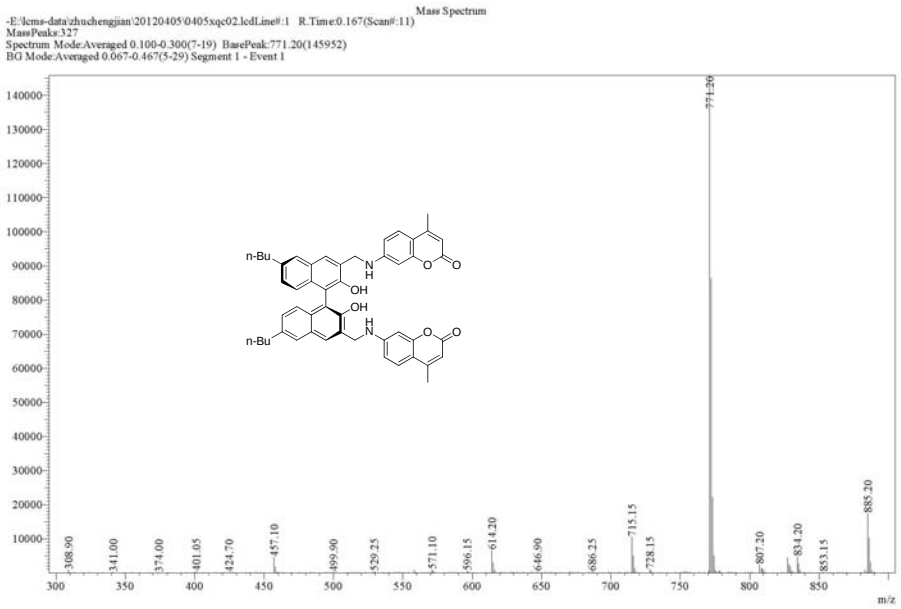

Figure S28. MS $[M-1]^-$ spectrum of **L2**

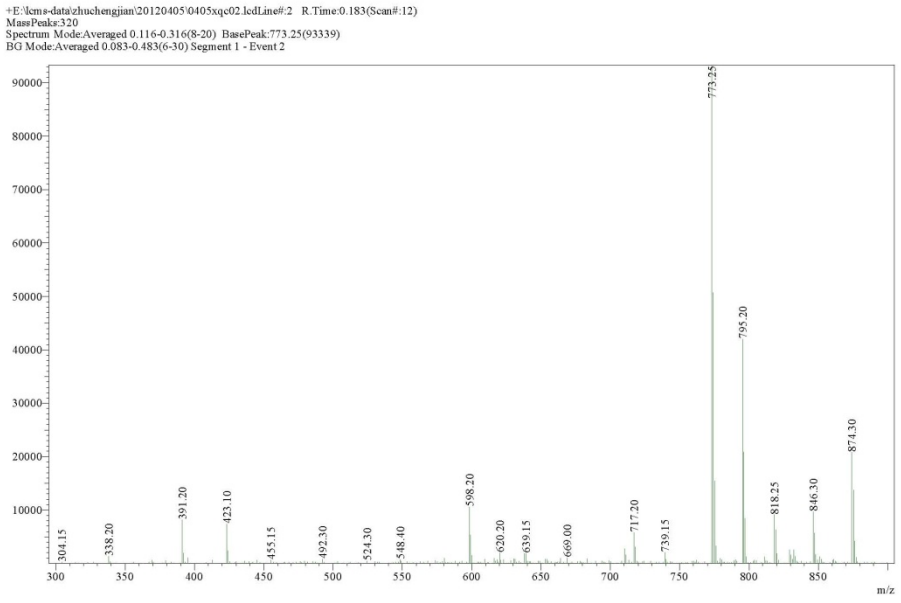

Figure S29. MS $[M+1]^+$ spectrum of **L2**