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Supporting Information

Chiral fluorescent sensor based on H_8-BINOL for high enantioselective recognition of D- and L-Phenylalanine†

Yafeng Zhang,[a] Huizhen Wang,[a] Hu Yu,[b] and Xiaoxia Sun*[a]

[a] Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang, 330013, China

[b] College of Chemistry, Nanchang University, Nanchang, China
Email: sunxiaoxia77@126.com

Content

Synthesis

Synthesis of *R*-2 probe

R-2,2'-alkynylmethoxy-5,5',6,6',7,7',8,8'-octahydrobinol (300 mg, 0.875 mmol) was put in a 100 mL aubergine flask, evacuated several times and protected by argon, 6 mL of tetrahydrofuran was added and stirred thoroughly to dissolve completely, to the system was appended methyl 2-azidoacetate (0.17 ml, 1.75 mmol) to the system. Sodium ascorbate (347 mg, 1.75 mmol) and copper sulphate pentahydrate (219 mg, 0.875 mmol) were then accurately weighed, dissolved in 5 ml of water after a few minutes and appended to the system. When the reaction is complete it is monitored by Thin Layer Chromatography and quenched by adding 15 ml of ice water to the reaction flask, It was then extracted three times with dichloromethane, collected, washed with prepared saturated brine, dried with anhydrous sodium sulphate for 30 minutes and separated by column chromatography (silica gel 200-300 mesh, eluting solvent CH_3OH: CH_2Cl_2 = 1: 2,v/v), white solid of 0.453 g was obtained with a yield of 93%. M.p. 64-67℃. $[\alpha]_D^{25}$-0.50 (c 0.2, CH_3OH). Elemental analysis results: C (experimental value: 63.74%, calculated value: 63.96%), H (experimental value: 5.78%, alculated value: 5.99%), N (experimental value: 13.53%, calculated value: 13.99%). O (experimental value: 16.75%, calculated value: 16.06%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.97 (s, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 5.20 (s, 1H), 5.09 – 4.81 (m, 8H), 3.66 (s, 6H), 2.66 (d, *J* = 3.9 Hz, 4H), 2.28 – 2.13 (m, 2H), 2.04 (dt, *J* = 17.2, 6.1 Hz, 2H), 1.95 (s, 1H), 1.58 (ddt, *J* = 18.7, 12.7, 6.6 Hz, 10H), 1.35 – 1.07 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.47 (d, *J* = 57.3 Hz), 152.55, 145.18, 136.59, 130.03, 128.15, 126.27, 123.34, 110.33, 62.44, 52.43, 50.08, 28.91, 26.74, 22.63 (d, *J* = 5.2 Hz).ppm. HRMS (ESI-): calcd for $[C_{32}H_{36}N_6O_6{}^+H^-]^-$ 601.2696; found 601.2835.

Synthesis of propargyl derivatives c

S-5,5',6,6',7,7',8,8'-octahydrobiol (1 g, 3.396 mmol) and K_2CO_3 (1.079 g, 7.813 mmol) were placed in a 100 ml single-necked flask and 20 ml of acetone was added to dissolve it, and eventually 3-bromopropyne (0.73 mL, 8.482 mmol) was added to the system lento. After stirring for 10 min, the response was heated to around 55°C for refluxing and the response was fulfilled overnight. This reaction was intercepted when thin layer chromatography confirmed the disappearance of the starting material and the creation of a new spot. The temperature of the system was then lowered to ambient temperature, the reaction solution was recovered and filtered, washed three times with acetone to collect the light yellow liquid and dried with anhydrous $MgSO_4$. Then the crude product was obtained by rotary concentration on a rotary evaporator, and later separated by column chromatography (silica gel 200-300 mesh, eluting solvent petroleum ether : ethyl acetate = 15:1, v/v) to obtain 0.512 g of white solid in 45% yield. M.p. 96-98℃. $[\alpha]_D^{25}$ -0.55 (c 0.2, CH_3OH). ^{1}H NMR(400 MHz, Chloroform-*d*) δ 7.05 (d, *J* = 8.5 Hz, 1H), 6.90 (dd, *J* = 17.7, 8.4 Hz, 2H), 6.69 (d, *J* = 8.3 Hz, 1H), 4.51 (s, 2H), 4.31 (s, 1H), 2.67 (q, *J* = 7.8, 7.1 Hz, 4H), 2.30 (t, *J* = 2.3 Hz, 1H), 2.25 – 1.87 (m, 4H), 1.60 (d, *J* = 22.9 Hz, 8H).

Synthesis of *S*-1 probe

S-2,2'-alkynylmethoxy-5,5',6,6',7,7',8,8'-octahydrobinol (200 mg, 0.603 mmol) was put in a 100 mL aubergine flask, evacuated several times and protected by argon, 6 mL of tetrahydrofuran was added and stirred thoroughly to dissolve completely, to the system was added methyl 2-azidoacetate(0.07 ml, 0.722 mmol) to the system. Sodium ascorbate (238 mg, 1.204 mmol) and copper sulphate pentahydrate (150 mg, 0.603 mmol)) were then accurately weighed, dissolved in 5 ml of water after a few minutes and added to the system. When the reaction is complete it is monitored by Thin Layer Chromatography and quenched by adding 15 ml of ice water to the reaction flask, It was then extracted three times with dichloromethane, collected, washed with prepared saturated brine, dried with anhydrous sodium sulphate for 30 minutes and separated by column chromatography (silica gel 200-300 mesh, eluting solvent CH_3OH:CH_2Cl_2=1:2,v/v) , a white solid of 0.266 g was obtained with a yield of 98%. M.p.92-94℃.$[\alpha]_D^{25}$ -0.80 (c 0.2, CH_3OH).

Elemental analysis results: C (experimental value: 69.68%, calculated value: 69.79%), H (experimental value: 6.32%, calculated value: 6.49%), N (experimental value: 9.24, calculated value: 9.40%), O (experimental value:14.76%, calculated value:14.32%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (s, 1H), 7.09 (d, J = 8.4 Hz, 1H), 7.01 (d, J = 8.2 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.77 (d, J = 8.2 Hz, 1H), 5.48 – 4.92 (m, 4H), 3.79 (s, 3H), 3.11 – 2.70 (m, 4H), 2.36 – 2.06 (m, 4H), 1.85 – 1.43 (m, 11H), 1.26 (td, J = 7.1, 2.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.26, 149.73, 145.06, 137.58, 135.84, 130.94, 129.77, 128.76, 123.23, 122.89, 111.76, 111.05, 62.45, 52.49, 50.20, 28.83, 26.81, 26.57, 22.64, 22.44. ppm. HRMS (ESI-): calcd for $[C_{26}H_{29}N_3O_4{}^+H^-]^-$ 448.2158; found 448.1769.

^{1}HNMR, ^{13}CNMR and ESI-MS

^{1}HNMR of propargyl derivatives b

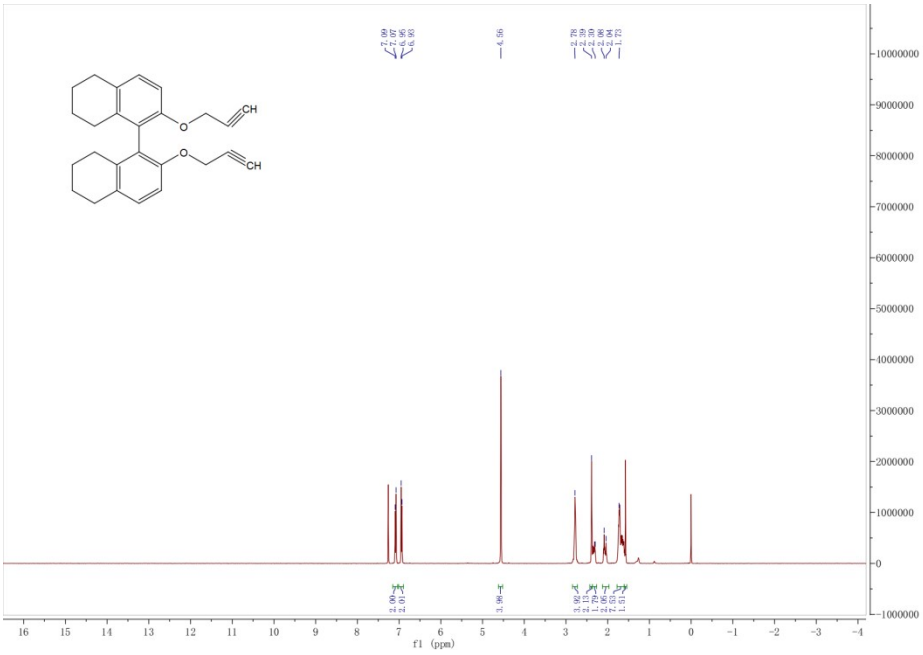


Figure S 1 ^{1}HNMR of propargyl derivatives b ($CDCl_3$)

[1]HNMR of propargyl derivatives a

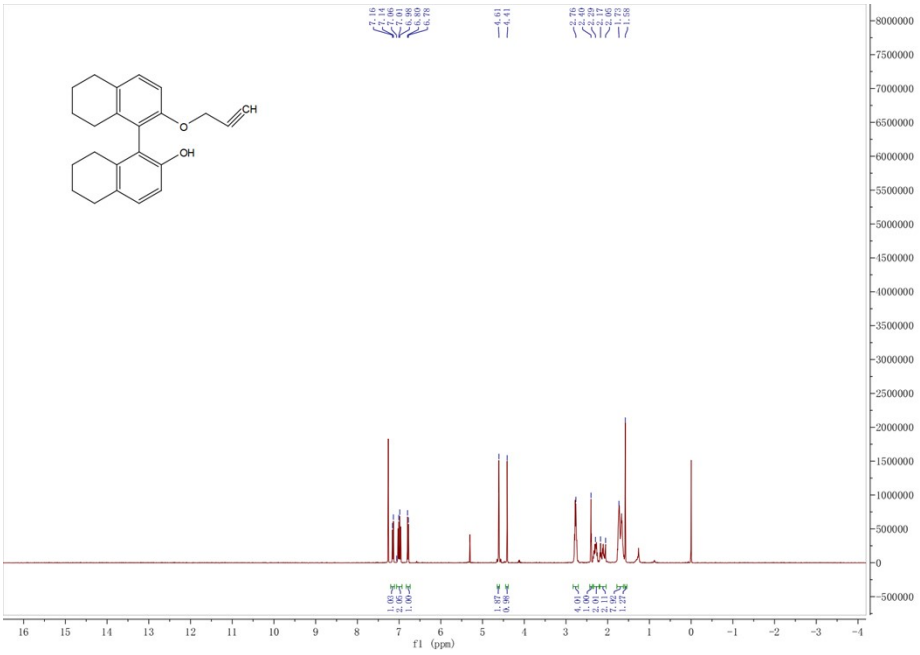


Figure S2 [1]HNMR of propargyl derivatives a ($CDCl_3$)

[1]HNMR of propargyl derivatives c

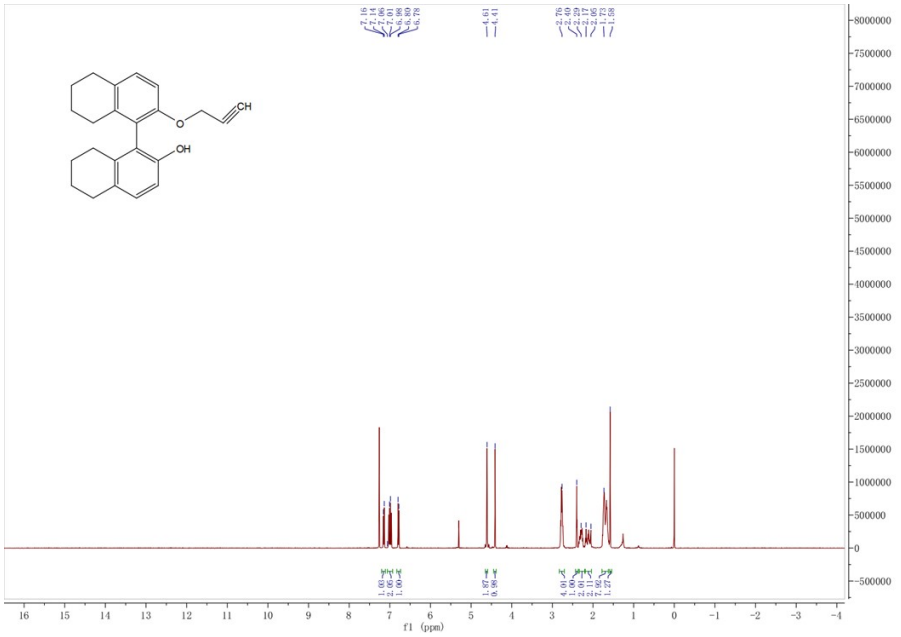
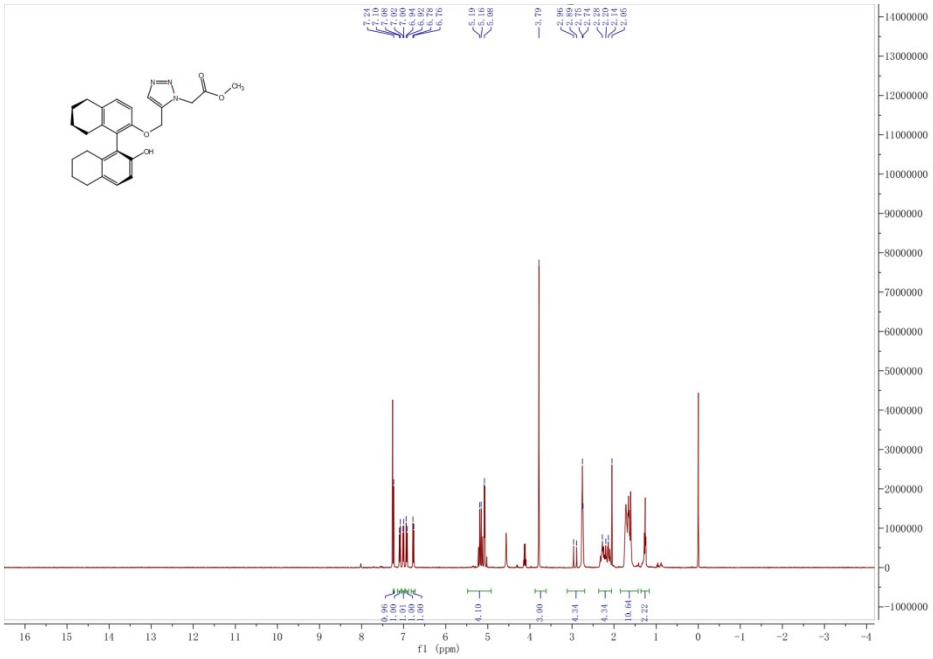
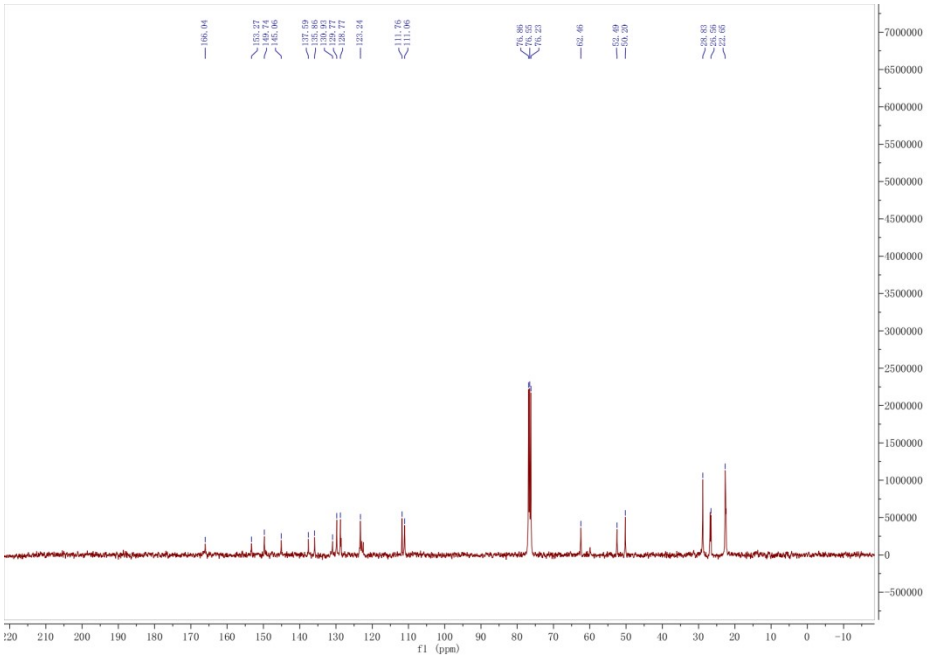


Figure S 3 [1]HNMRof propargyl derivatives **c** ($CDCl_3$)

^{1}HNMR, ^{13}CNMR and ESI-MS of *S*-1





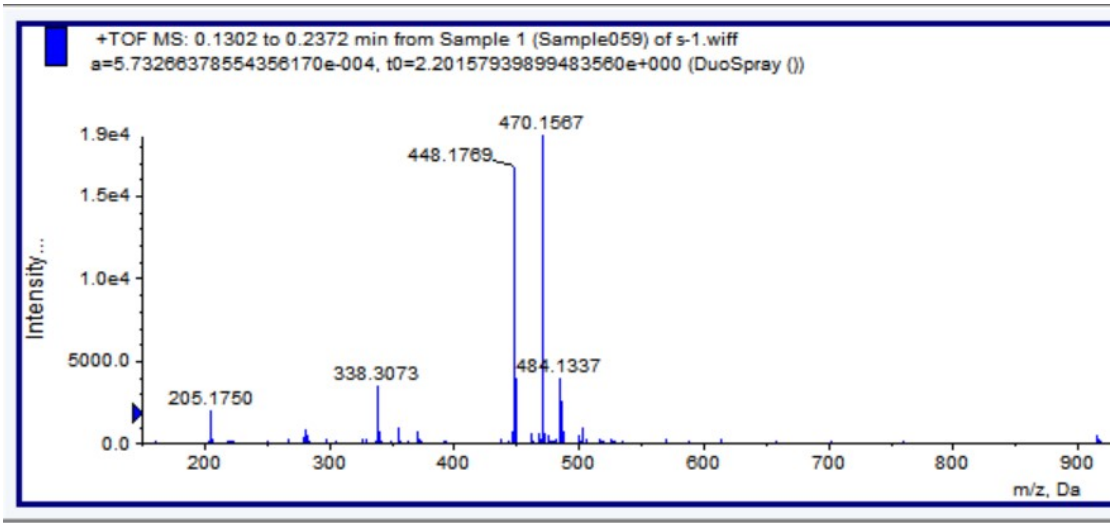
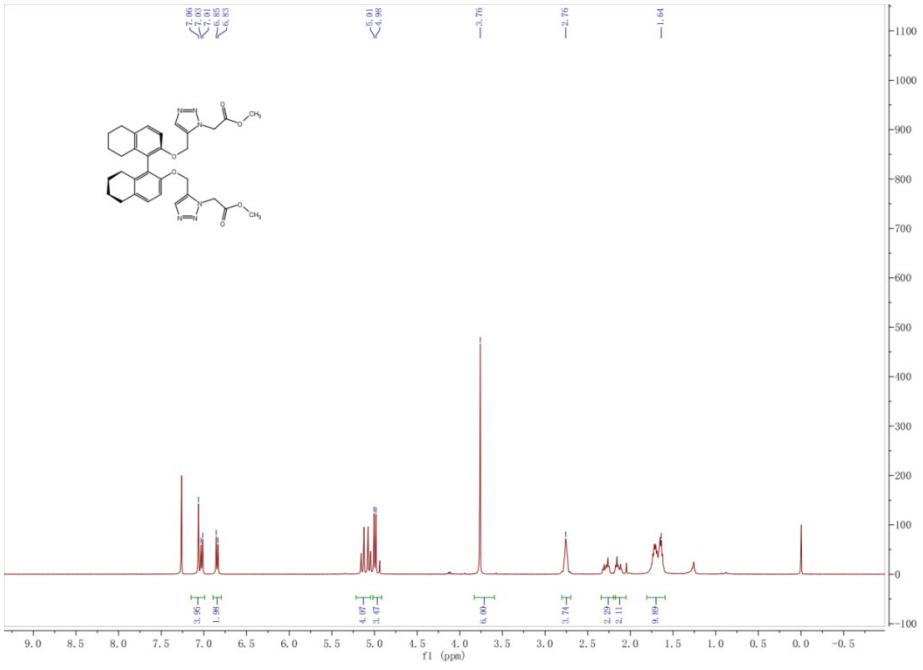


Figure S4 ^{1}HNMR, ^{13}CNMR of ***S*-1**($CDCl_3$)

^{1}HNMR, ^{13}CNMR and ESI-MS of *R*-2



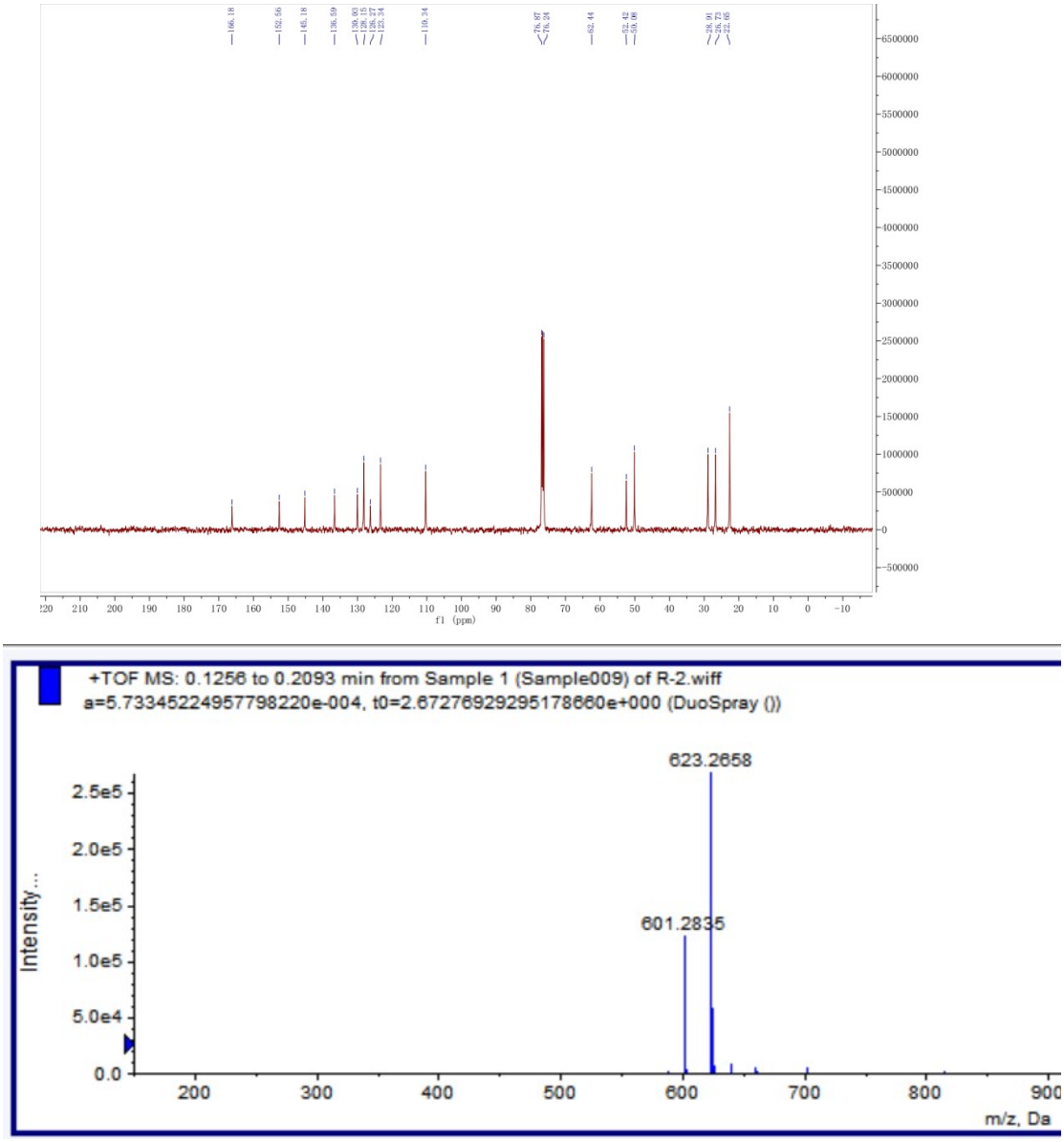
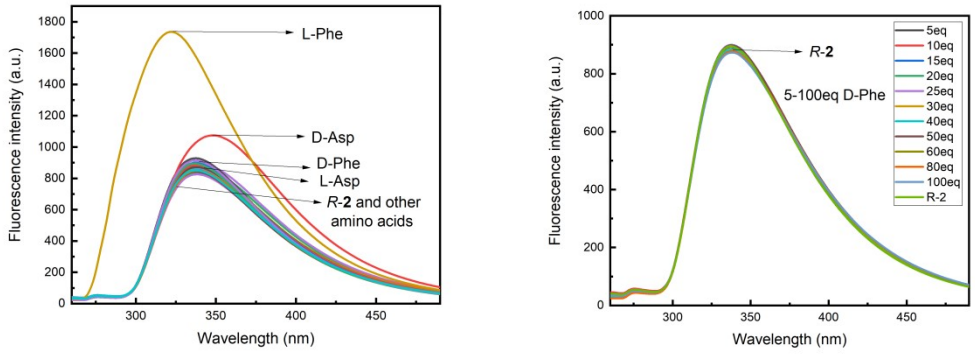


Figure S 5 ^{1}HNMR, ^{13}CNMR of ***R*-2**($CDCl_3$)

Fluorescence spectra

Fluorescence spectra of *R*-2



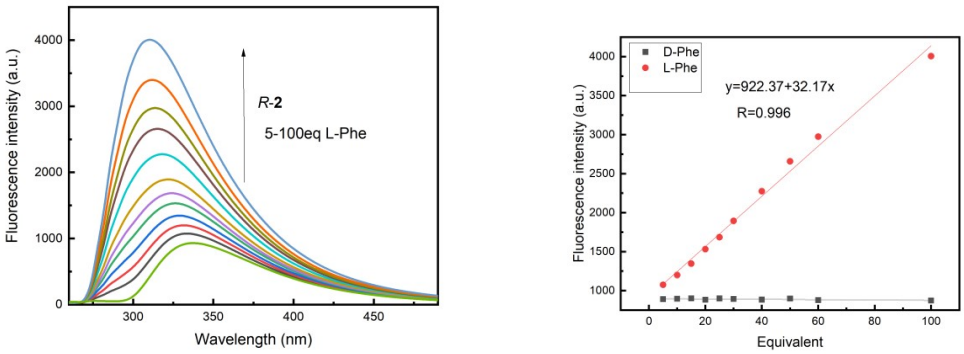


Figure S 6 (a) Fluorescence spectra of ***R*-2** (2.0 x 10^{-5} M in CH_3OH) with different enantiomers of 16 ordinary amino acids (20.0 equivalents) in the absence of metal ions(λex=260 nm, slits=2.5/2.5nm). (b) Fluorescence titration of ***R*-2** with D-Phenylalanine in CH_3OH. (c) Fluorescence titration of ***R*-2** with L-Phenylalaninein CH_3OH. (d) Fluorescence intensities at λ=315 nm versus the equivalents of Phenylalanine (λex=260 nm, slits=2.5/2.5 nm)

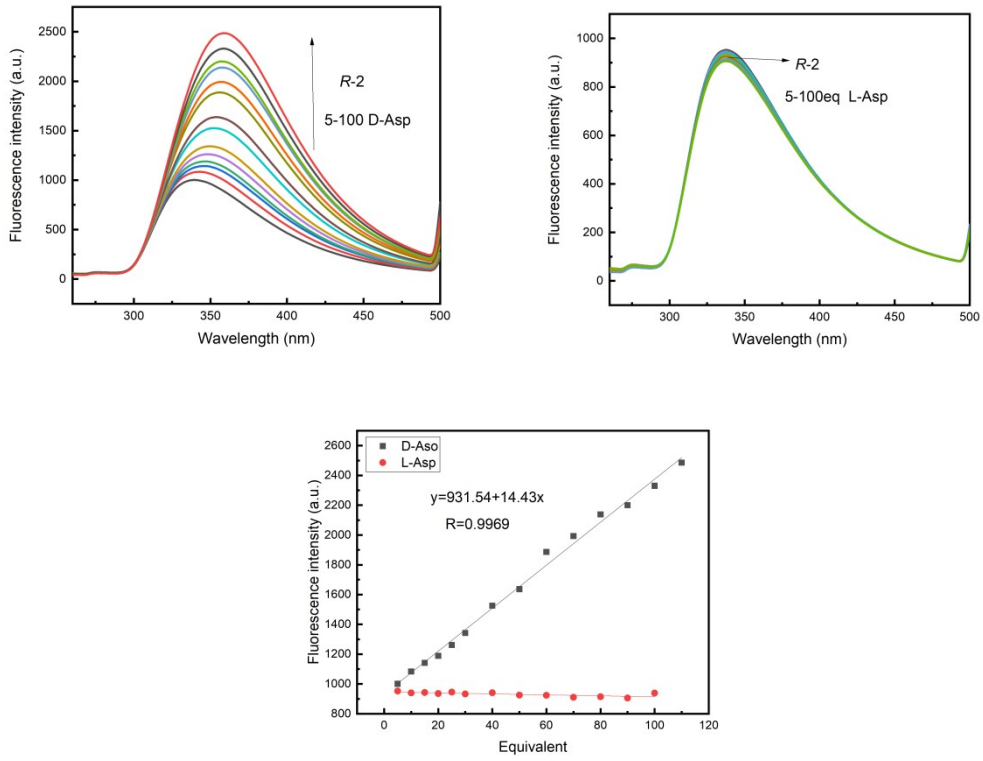


Figure S7 (a) Fluorescence titration of *R*-**2** with D-Asp in CH_3OH. (c) Fluorescence titration of *R*-**2** with L-Asp in CH_3OH. (c) The linear relationship between the fluorescence intensity of probe *R*-**2** and Asp at λ=350 nm (λex=260 nm, slits=2.5/2.5 nm)

Fluorescence spectra of *S*-1

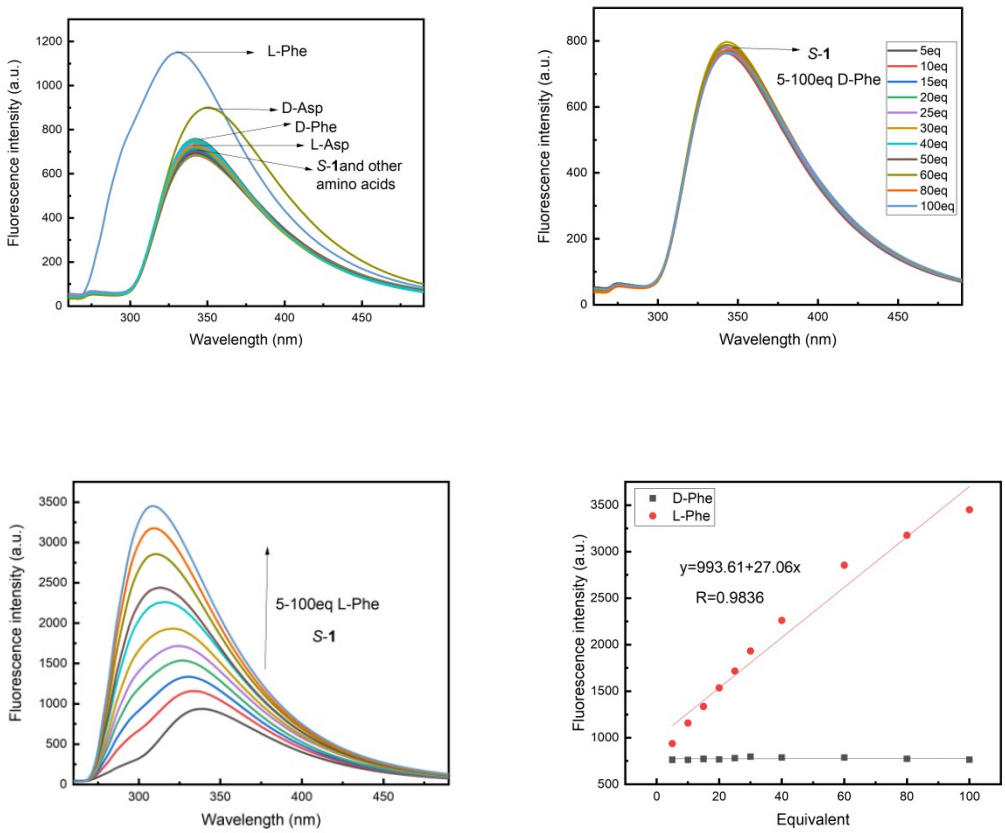
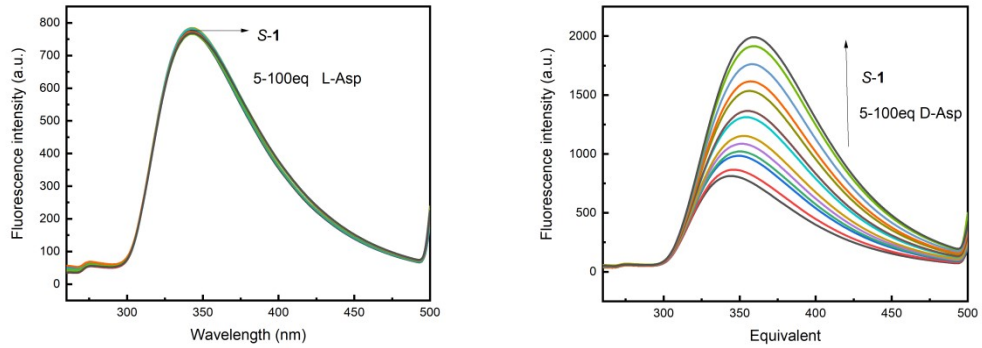


Figure S 8 (a) Fluorescence spectra of ***S*-1** (2.0 x 10^{-5} M in CH_3OH) with different enantiomers of 16 ordinary amino acids (20.0 equivalents) in the absence of metal ions (λex=260 nm, slits=2.5/2.5 nm). (b) Fluorescence titration of ***S*-1** with D- Phenylalanine in CH_3OH. (c) Fluorescence titration of ***S*-1** with L-Phenylalaninein CH_3OH. (d) Fluorescence intensities at λ=315 nm versus the equivalents of Phenylalanine (λex=260 nm, slits=2.5/2.5 nm)



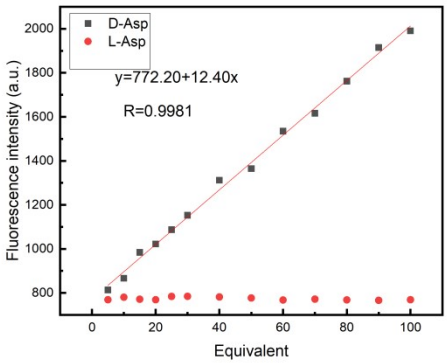
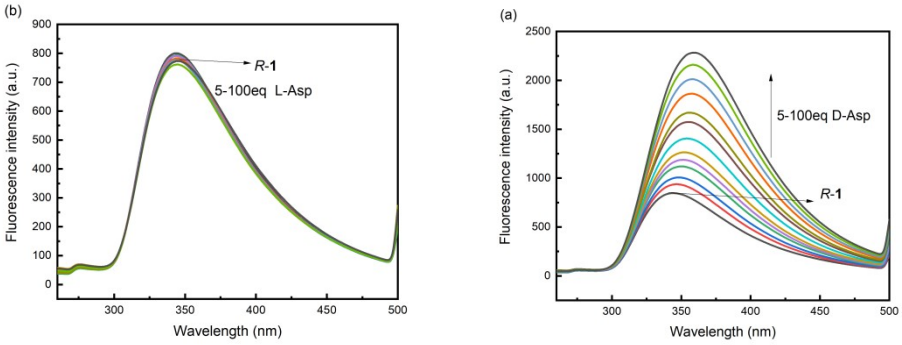


Figure S9 (a) Fluorescence titration of *S*-**1** with D-Asp in CH_3OH. (b) Fluorescence titration of *S*-**1** with L-Asp in CH_3OH. (c) The linear relationship between the fluorescence intensity of probe *S*-**1** and Asp at λ=350 nm (λex=260 nm, slits=2.5/2.5 nm)

Fluorescence spectra of *R*-1



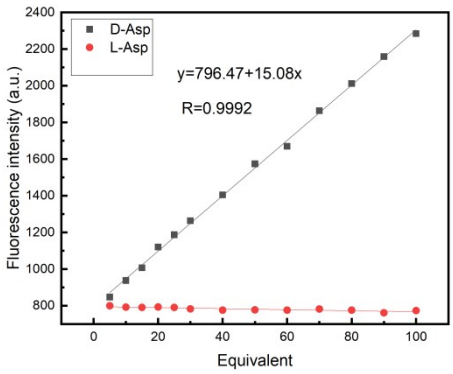


Figure S 10 (a) Fluorescence titration of *R*-**1** with D-Asp in CH_3OH. (b) Fluorescence titration of *R*-**1** with L-Asp in CH_3OH. (c) The linear relationship between the fluorescence intensity of probe *R*-**1** and Asp at λ=350 nm (λex=260 nm, slits=2.5/2.5 nm)