Supporting Information

Self-assembly Bamboo-Like Carbon Nanotubes Based on Chiral H_8BINOL Sensors to Recognize Cinchonidine Efficiently by Diastereoisomer Complexes

Contents

Synthesis

Synthesis of *S*-2, *S*-1

S-5,5',6,6',7,7',8,8'-octahydro[1,1'-binaphthalene]-2,2'-diol (2.00 g, 6.80 mmol) with a stirrer were put in a 100 mL eggplant-shaped bottle, and added dry DCM (10 mL) to fully dissolve *S*-H_8BINOL. Then, Br_2 (1.00 mL) dissolved in dry DCM (15 mL) was slowly added dropwise to the reaction system at -30°C. The mixture was stirred for 4 h. The reaction was intercepted, while thin layer chromatography detection proved the vanishing point of the start material and a new blot was generated. The temperature of the system was then reduced to ambient temperature, the reaction solution was recovered and filtered, washed three times with saturated sodium bisulfite solution to collect the yellow liquid, DCM extraction and dried with anhydrous Na_2SO_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 get 2.80 g (*S*-**2**) of white solid in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (*s*, 2H), 5.24 (*s*, 2H), 2.79 (*d*, J = 6.4 Hz, 4H), 2.46 – 1.96 (*m*, 4H), 2.07 – 1.52 (*m*, 8H). {1H}^{13}C NMR (101 MHz, $CDCl_3$) δ 147.28, 136.80, 132.06, 122.30, 107.25, 29.10, 26.90, 22.80. Put *S*-**2** (2.5 g, 5.45 mmol) solid into a 100 ml pressure resistant flask and add DME solution (20 ml) to dissolve *S*-**2** thoroughly. Continue adding K_2CO_3 (1.1 g, 8.76 mmol) and added 5 mL of deionized water to dissolve K_2CO_3. Continue to add phenylboronic acid (2.66 g, 21.8 mmol) $Pd(PPh_3)_4$ (0.52 g, 0.48 mmol) to the

pressure-resistant flask. The oil bath was heated to 100 °C and reacted for 13 hours under continuous reaction. Washed the reaction solution with saturated NaHSO3 and NaCl solution, extracted with dichloromethane, and dried with diatomaceous earth to remove moisture. Finally, 356 mg *S*- (3,3'-phenyl)-5,5'6,6',7',8,8'-octahydro-[1,1'-dinaphthalene]-2,2'-diol, *S*-**1**) white flocculent solid was obtained by silica gel column with the yield of 70%. ^{1}H NMR (400 MHz, DMSO) δ 7.60 – 7.43 (m, 4H), 7.45 – 7.01 (m, 8H), 6.92 (d, J = 4.1 Hz, 2H), 2.81 – 2.56 (m, 4H), 2.34 – 2.14 (m, 2H), 2.11 – 1.89 (m, 2H), 1.79 – 1.45 (m, 8H). {1H}^{13}C NMR (101 MHz, DMSO) δ 149.37, 139.74, 136.06, 130.64, 129.67, 128.75, 128.38, 127.09, 126.71, 124.51, 29.33, 27.32, 23.29, 23.19. M.p.126.7℃, $[\alpha]_D^{21} =$ 29.3 (c 1.07, $CHCl_3$).

Synthesis of *R*-2, *R*-1

R-5,5',6,6',7,7',8,8'-octahydro[1,1'-binaphthalene]-2,2'-diol (2.00 g, 6.80 mmol) with a stirrer were put in a 100 mL eggplant-shaped bottle, and added dry DCM (10 mL) to fully dissolve *R*-H_8BINOL. Then, Br_2 (1.00 mL) dissolved in dry DCM (15 mL) was slowly added dropwise to the reaction system at -30°C. The mixture was stirred for 4 h. The reaction was intercepted, while thin layer chromatography detection proved the vanishing point of the start material and a new blot was generated. The temperature of the system was then reduced to ambient temperature, the reaction solution was recovered and filtered, washed three times with saturated sodium bisulfite solution to collect the yellow liquid, DCM extraction and dried with anhydrous Na_2SO_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 get 2.80 g (*R*-**2**) of white solid in 90% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.33 (*d*, J = 11.4 Hz, 2H), 5.15 (*d*, J = 12.2 Hz, 2H), 3.27 – 2.63 (*m*, 4H), 2.25 (*m*, 4H), 1.90 – 1.42 (*m*, 8H). {1H}^{13}C NMR (101 MHz, Chloroform-d) δ 147.22, 136.79, 132.58, 131.54, 122.22, 107.22, 29.09, 26.94, 22.77.

Put *R*-**2** (2.5 g, 5.45 mmol) solid into a 100 mL pressure-resistant flask and add DME solution (20 mL) to dissolve *R*-**2** thoroughly. Continue adding K_2CO_3 (1.1 g, 8.76 mmol) and added 5 mL of deionized water to dissolve K_2CO_3. Continue to add phenylboronic acid (2.66 g, 21.8 mmol) $Pd(PPh_3)4$ (0.52 g, 0.48 mmol) to the pressure resistant flask. The oil bath was heated to 100 °C and reacted for 13 hours under continuous reaction. Washed the reaction solution with saturated $NaHSO_3$ and NaCl solution, extracted with dichloromethane, and dried with diatomaceous earth to remove moisture. Finally, 356 mg *R*- (3,3'-phenyl)-5,5'6,6',7',8,8'-octahydro-[1,1'-dinaphthalene]-2,2'-diol, *R*-**1**) white flocculent solid was obtained by silica gel column with the yield of 70%. ^{1}H NMR (400 MHz, DMSO) δ 7.50 (dd, J = 7.9, 4.2 Hz, 4H), 7.35 (t, J = 6.8 Hz, 4H), 7.25 (dd, J = 14.3, 7.9 Hz, 4H), 6.92 (d, J = 4.3 Hz,2H), 2.81 – 2.55 (m, 4H), 2.23 (d, J = 16.7 Hz, 2H), 2.00 (d, J = 17.2 Hz, 2H), 1.75 – 1.51 (m, 8H). {1H}^{13}C NMR (101 MHz, DMSO) δ 149.36, 139.73, 136.05, 130.63, 129.66, 128.74, 128.38, 127.08, 126.71, 124.51, 29.32, 27.31, 23.28, 23.18. M.p.191.1℃, $[\alpha]_D^{21} =$ -29.3 (c 1.07, $CHCl_3$).

In the NMR spectra of *R*-**1** and *S*-**1**, the signal peaks at 3.3 and 2.5 were caused by the water peak of DMSO

^{1}HNMR and {1H} ^{13}CNMR

^{1}HNMR and {1H}^{13}CNMR of *R*-2

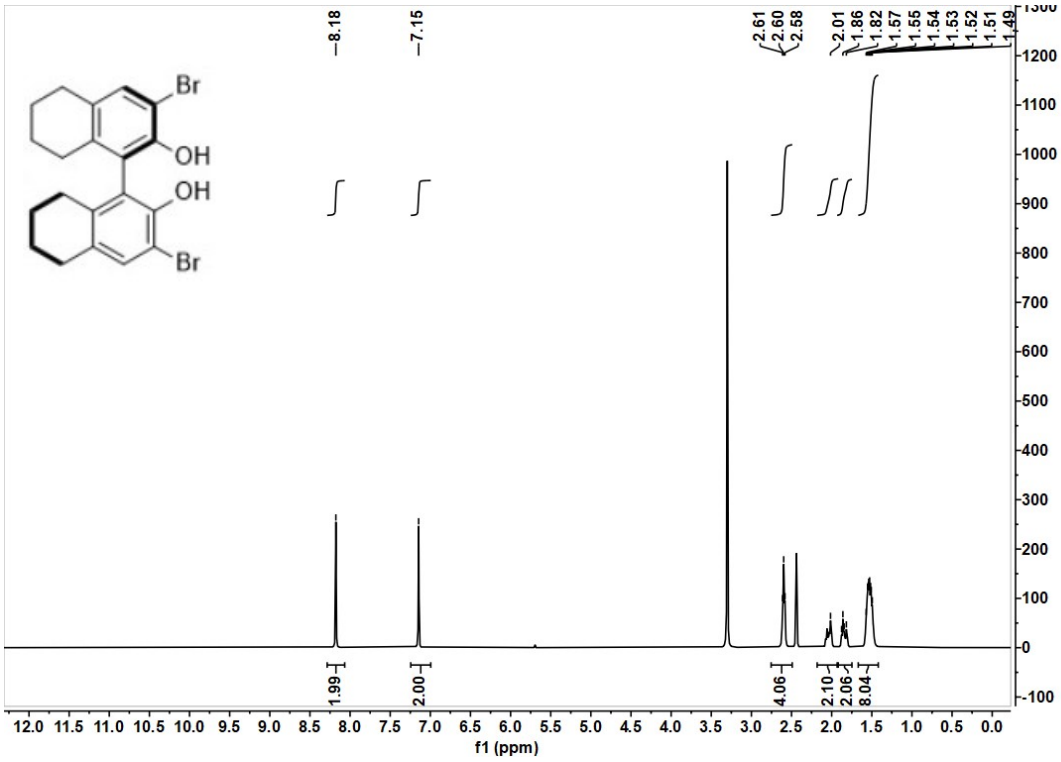

Figure S1. ^{1}HNMR of *R*-**2** (DMSO)

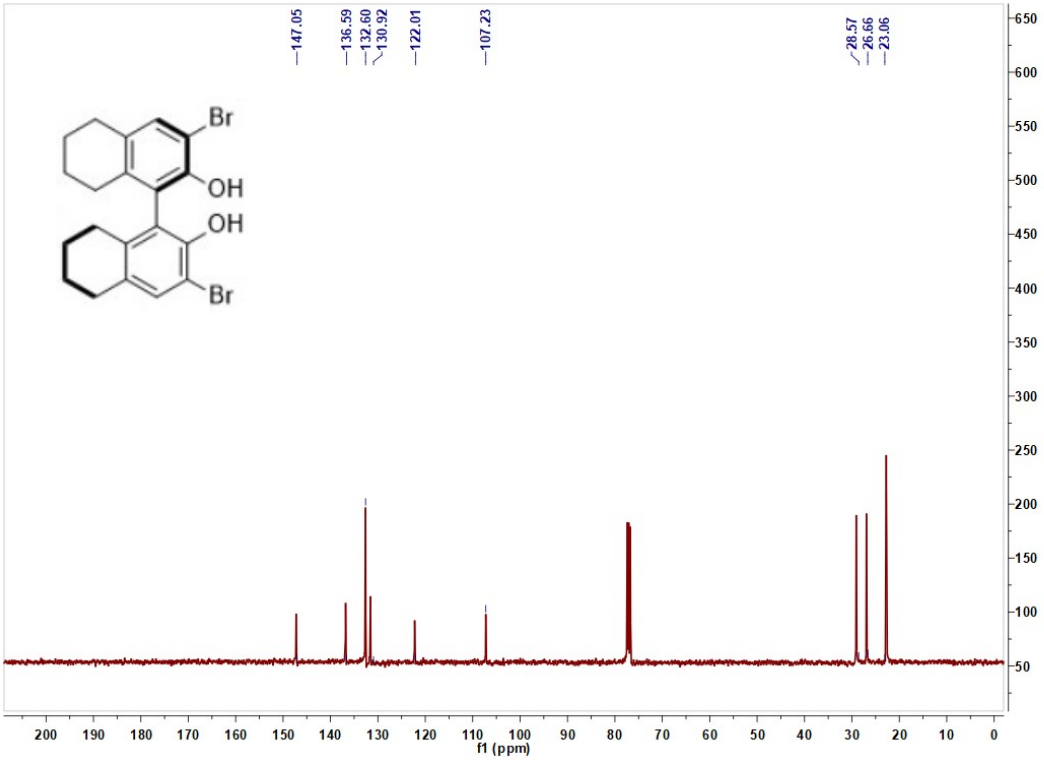

Figure S2. {1H}^{13}CNMR of *R*-**2** ($CDCl_3$)

[1]HNMR and {1H}[13]CNMR of *R*-1

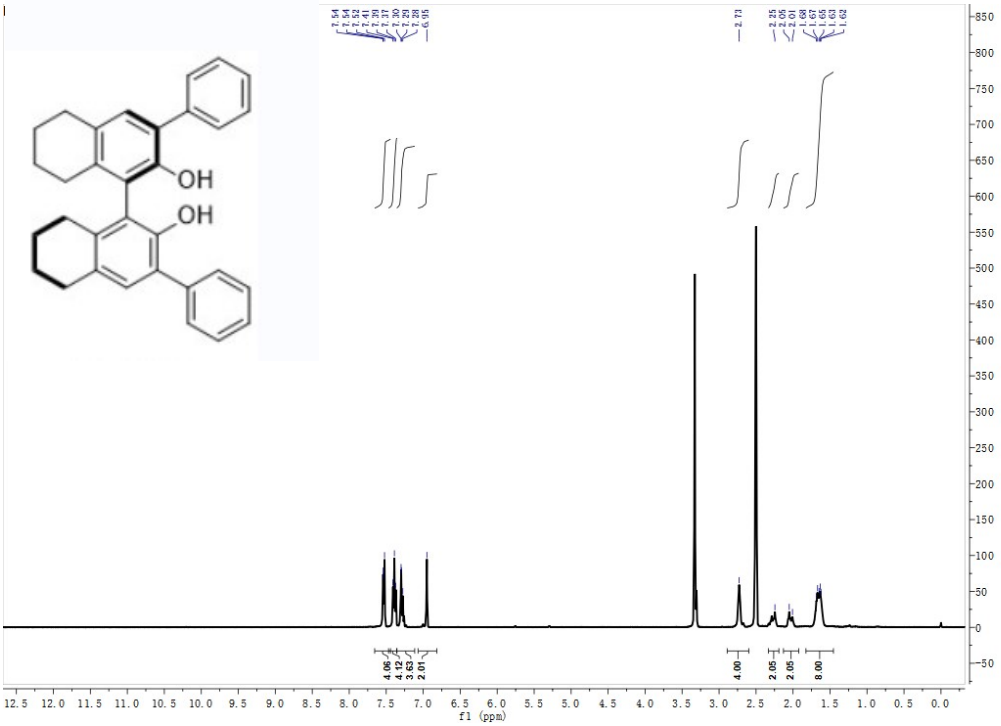

Figure S3. [1]HNMR of *R*-**1** (DMSO)

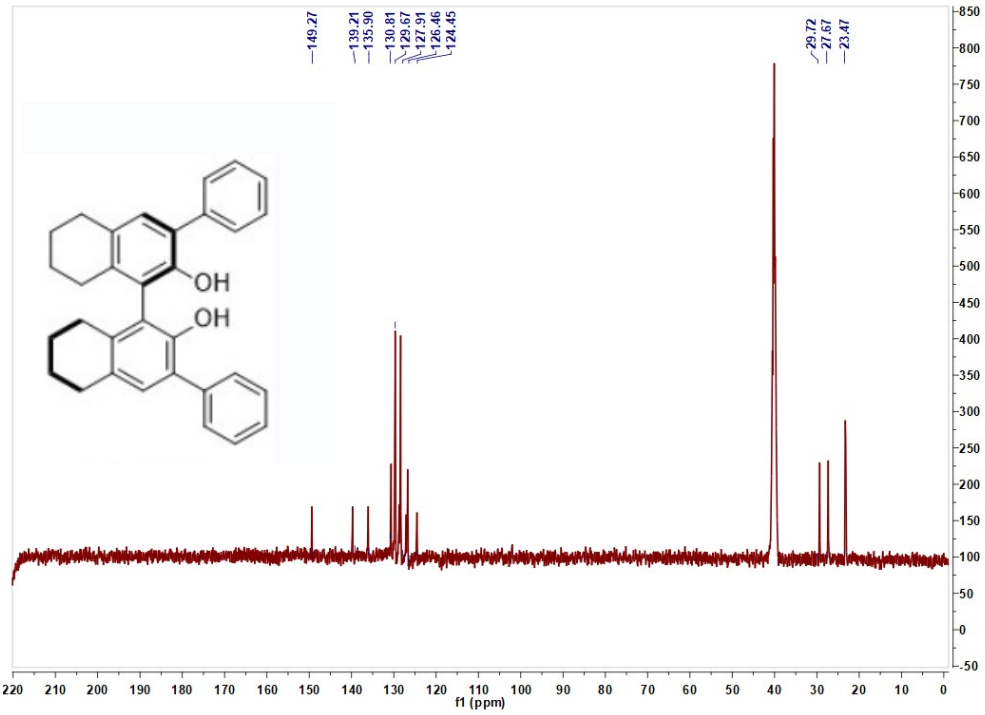

Figure S4. {1H}[13]CNMR of *R*-**1** (DMSO)

[1]HNMR and {1H}[13]CNMR of *S*-2

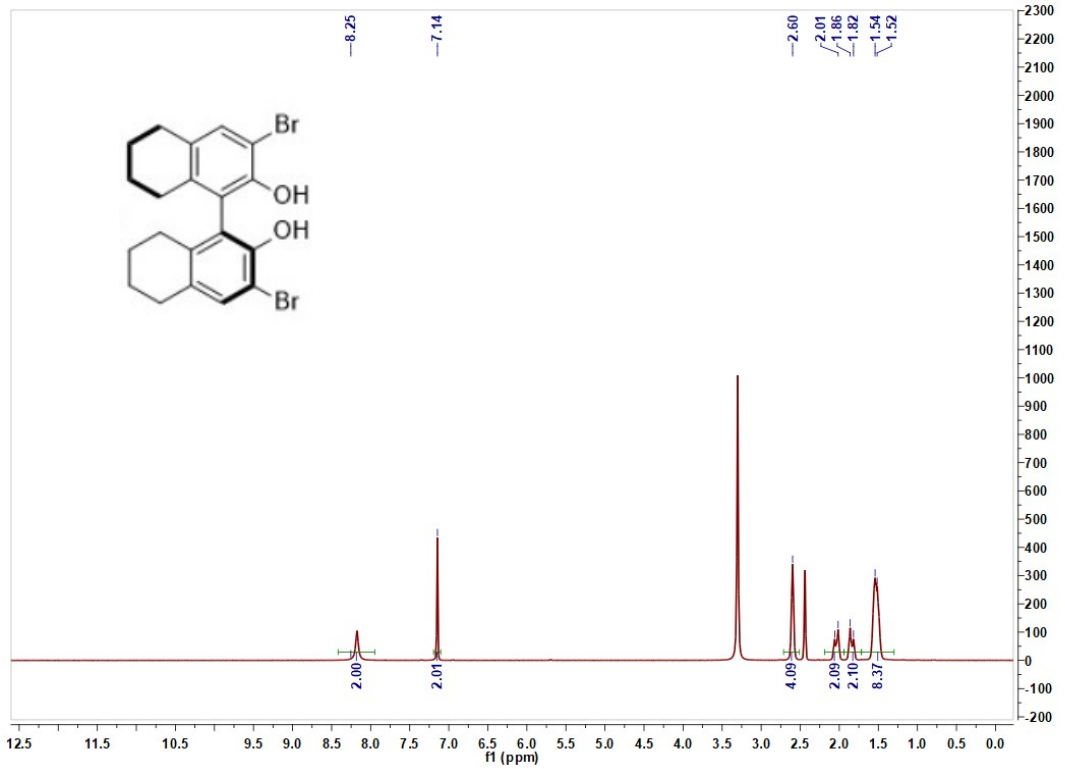

Figure S5. [1]HNMR of *S*-**2** (DMSO)

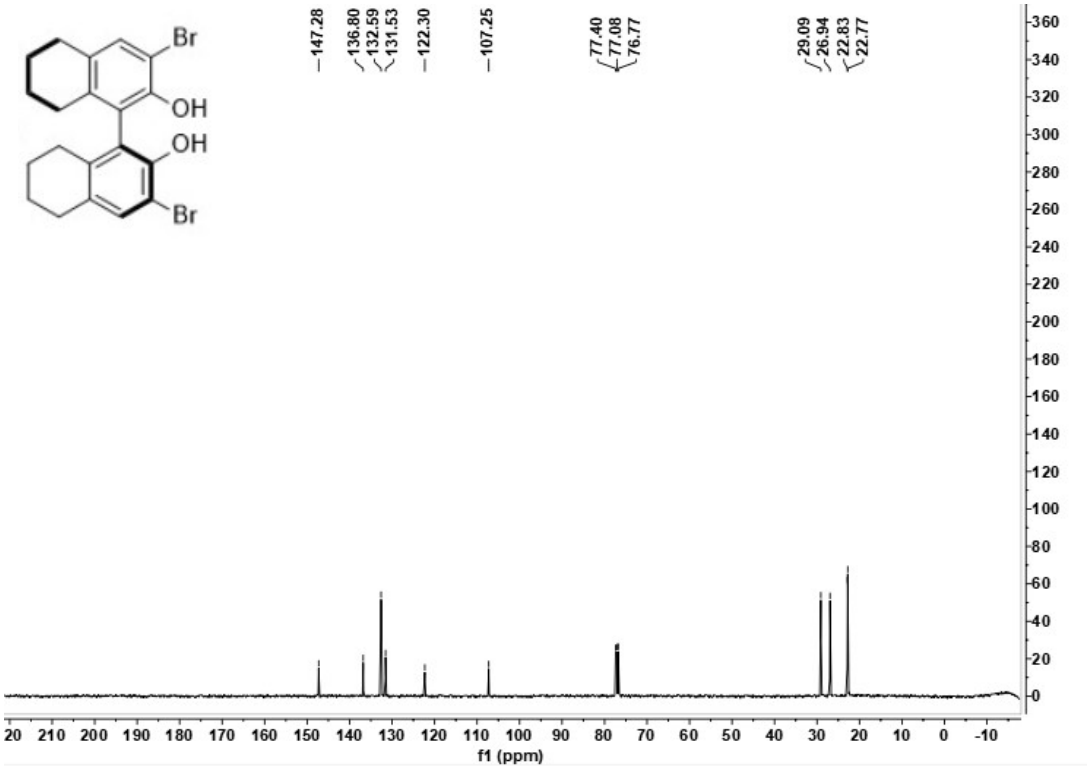

Figure S6. {1H}[13]CNMR of *S*-**2** ($CDCl_3$)

[1]HNMR and [13]CNMR of *S*-1

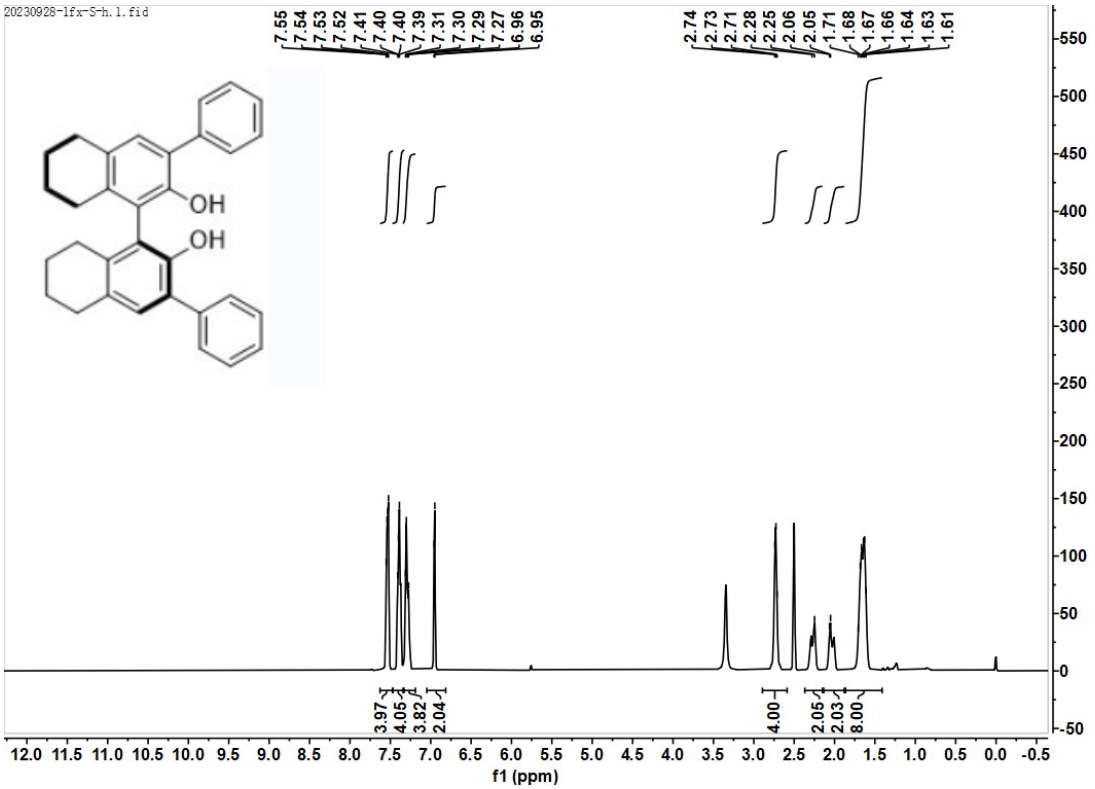

Figure S7. [1]HNMR of ***S*-1** (DMSO)

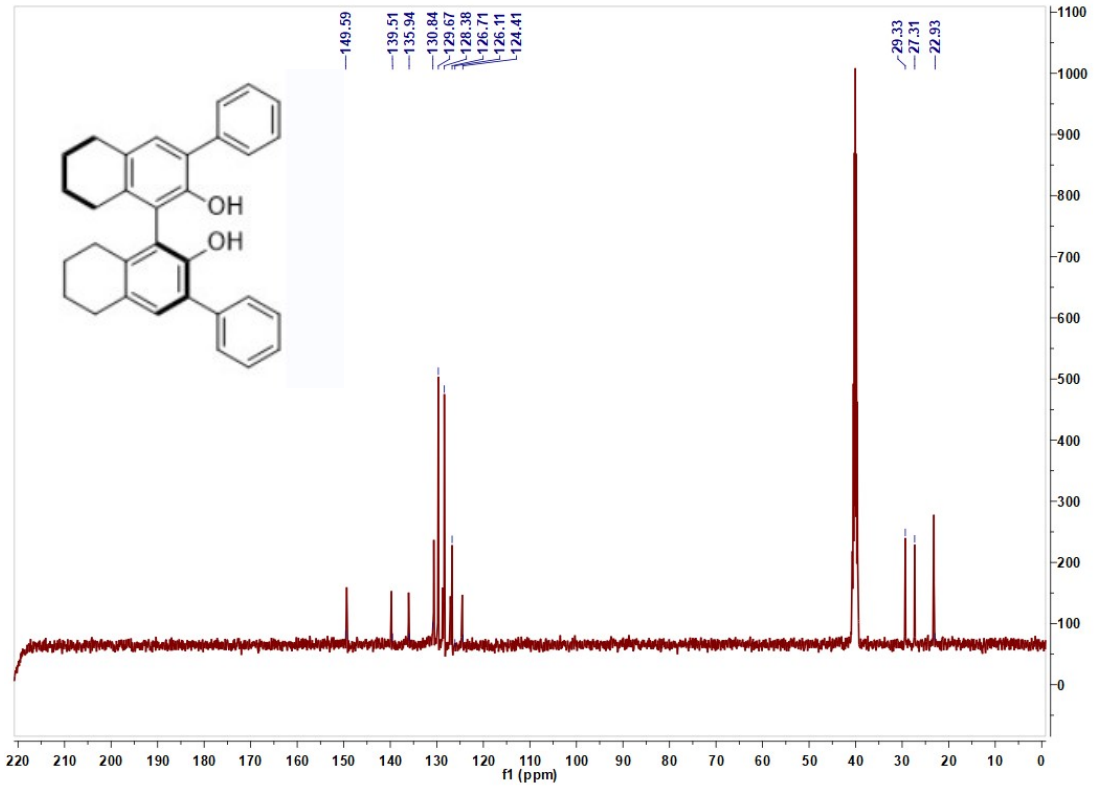

Figure S8. {1H}[13]CNMR of ***S*-1** (DMSO)

Fluorescence experiments of *S*-1 and *R*-1

The fluorescence response of *S*-**1** and *R*-**1** to seven different chiral splitting agents or chiral asymmetric catalytic species (*S*-Phenethylamine, D-2-Aminobutyric acid, (1*S*,2*S*)-1,2-Diphenylethylenediamine, (1*S*,2*S*)-1,2-Cyclohexanediamine, *S*-2-Amino-1-phenylethanol, D-tert-Leucinol, Cinchonidine) without any cations and an-ions was discussed in figure 6a and 6b. *S*-**1** and *R*-**1** were dissolved in chromatographic methanol with the probe concentration of 2.0×10^{-5} M, and analytes were dissolved in ethanol or deionized water at a concentration of 0.25 M. When 5 eq chiral species were added sequentially to probe *S*-**1**, *S*-**1** showed significant decrease in fluorescence to cinchonidine at λ_{exc}=270 nm, whereas other chiral reagents did not cause a significant fluorescence response and the wavelength hardly shifted. And the fluorescence recognition trend of *R*-**1** was consistent with that of *S*-**1**, indicating that both *S*-**1** and *R*-**1** had obvious fluorescence selectivity for cinchonidine. The changes suggested that *S*-**1** and *R*-**1** could obvious selective recognize cinchonidine.

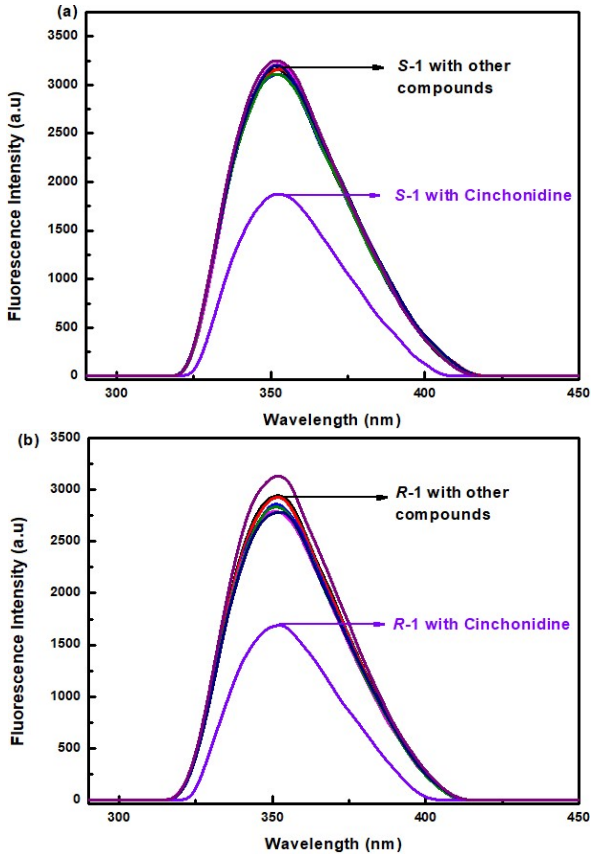

Figure S9. (a) Fluorescence spectra of *S*-**1** (2.0×10^{-5} M) with 5 eq chiral compounds in aqueous or ethanol solution. (λ_{exc}=270 nm, slits: 5.0/5.0 nm). (b) Fluorescence spectra of *R*-**1** (2.0×10^{-5} M) with 5 eq chiral compounds in aqueous or ethanol solution. (λ_{exc}=270 nm, slits: 5.0/5.0 nm).

Complex ratio diagram of cinchonidine with S-1

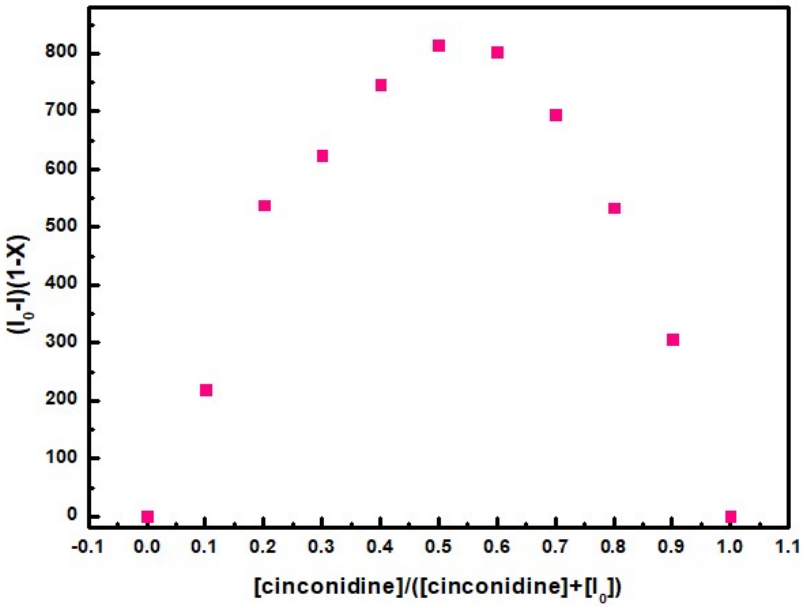

Figure S10. Fluorescence spectra of cinchonidine (in MeOH).

Binding model for the concluded binding ratio of 1:1

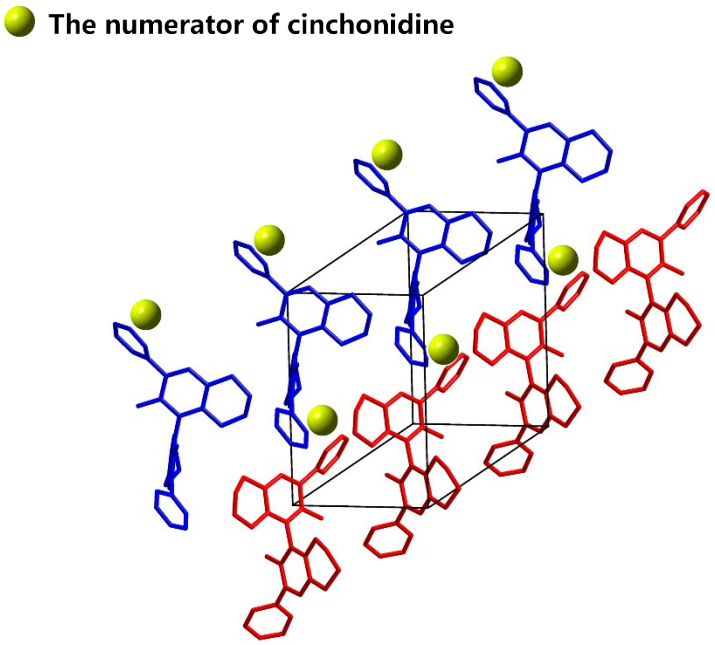

Figure S11. Binding model

The plot of $F_0/(F_0-F)$ versus 1/[cinchonidine](a) *S*-1 (b) *R*-1

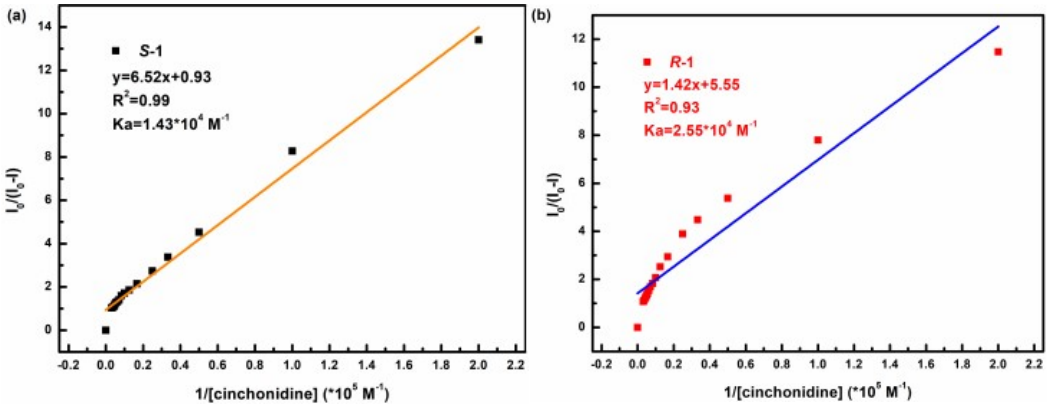

Figure S12 The plot of $F_0/(F_0-F)$ versus 1/[cinchonidine] (a) S-1 (b) R-1

The ^{1}HNMR titration of S-1 and cinchonidine

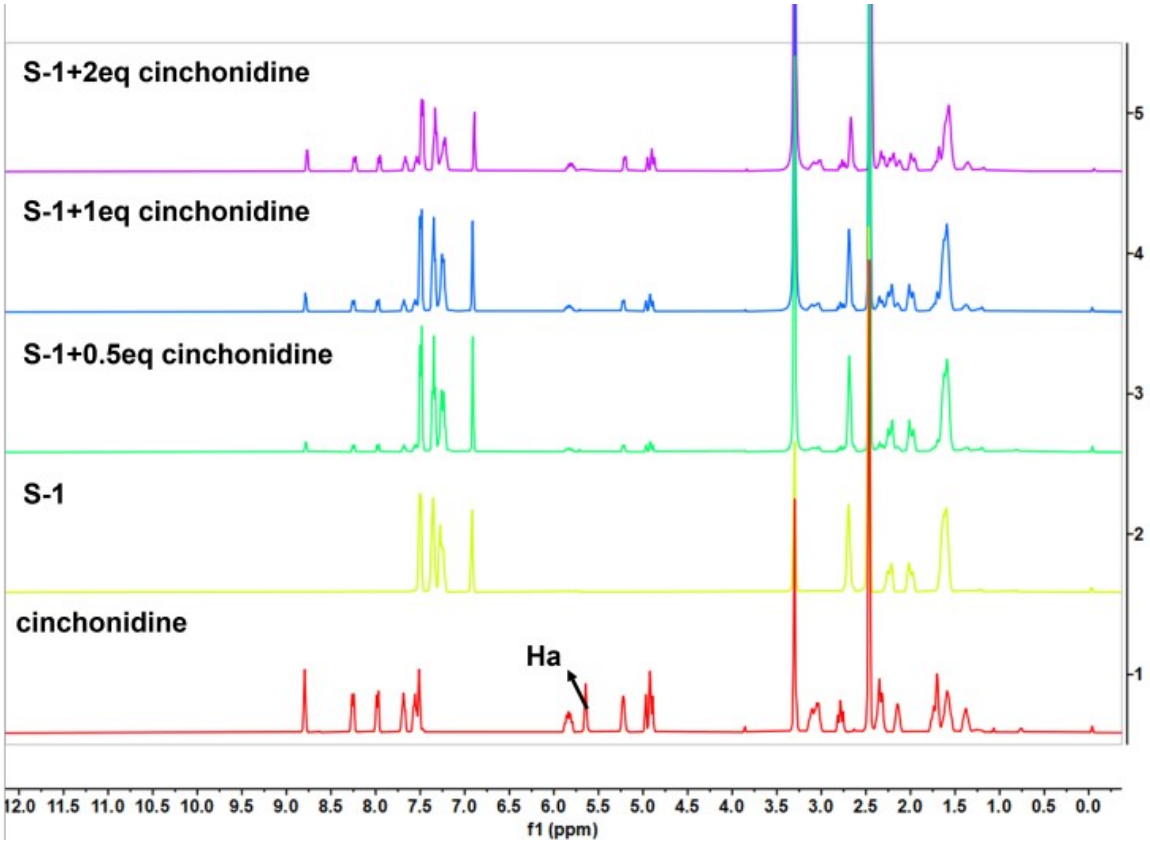

Figure S13 ^{1}H NMR spectra of S-1 and different equivalents of cinchonidine in deuterated DMSO (400 MHz).

UV absorption spectra of cinchonidine

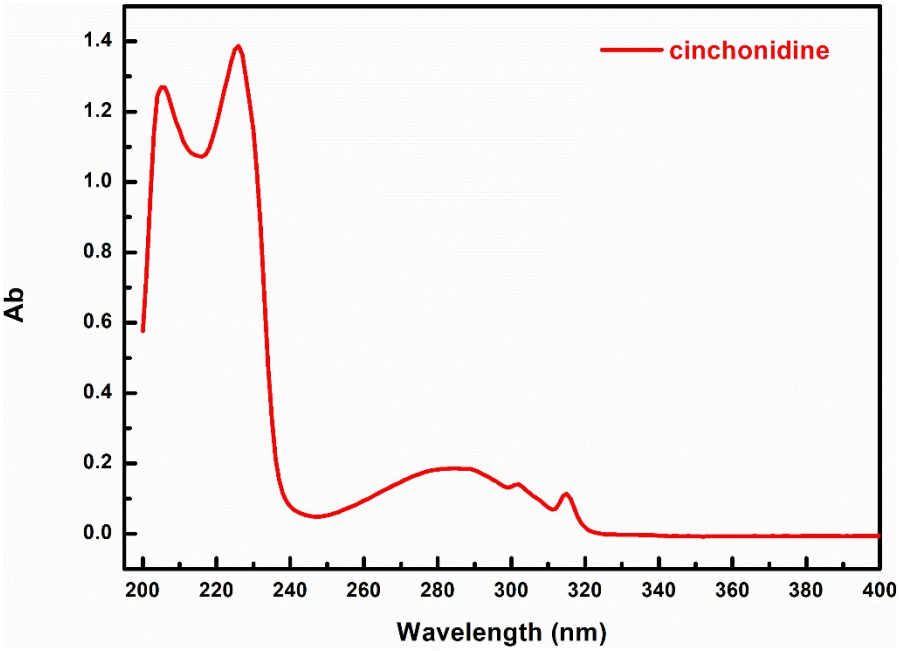

Figure S14. UV absorption spectra of cinchonidine (in MeOH).

Fluorescence spectra of cinchonidine

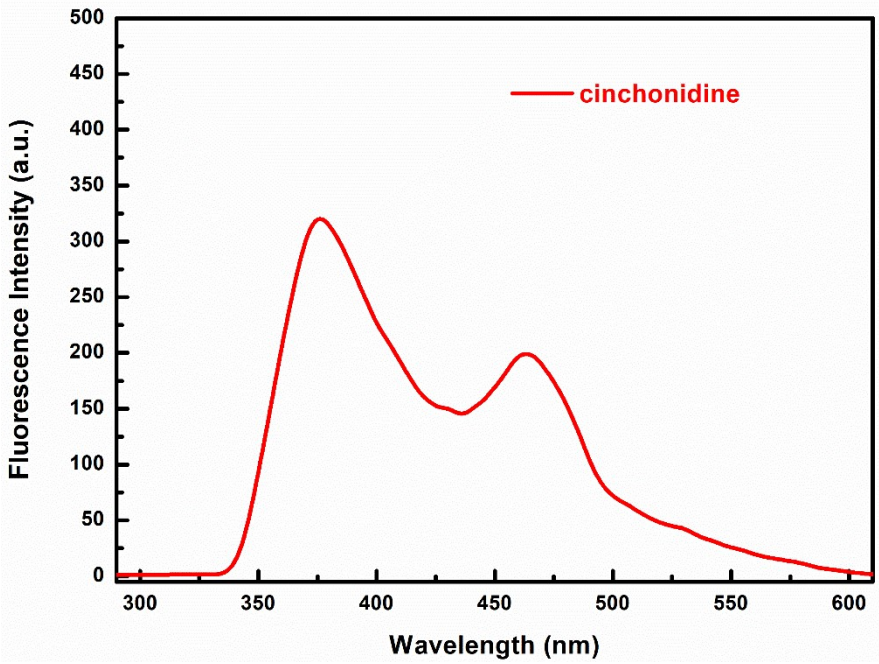

Figure S15. Fluorescence spectra of cinchonidine (in MeOH).