Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

A chiroptical chemodosimeter for fast and specific recognition of mercury(II) ions in aqueous media

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General information

Materials and instruments

All solvents were of analytical grade and were dried according to standard procedures if necessary. L-Phenylglycinol, methyl salicylate, and propargyl bromide were purchased from Aladdin Shanghai Reagent Co. and used without any further purification. Analytical grade $Hg(ClO_4)_2 \cdot 3H_2O$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Cd(NO_3)_2$, $Ni(NO_3)_2$, $Pb(NO_3)_2$, $Mn(NO_3)_2$, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Cr(NO_3)_3$, $Al(NO_3)_3$, $AgNO_3$, $NaNO_3$, KNO_3 and other reagents were obtained from commercial sources and used as received unless noted otherwise. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance AMX–400 spectrometer using $CDCl_3$ as a solvent; chemical shifts are represented in ppm with tetramethylsilane (TMS) as the internal reference. A Bruker Vector 22 Fourier Transform Infrared spectrometer was applied for recording spectra in KBr pellets. Electrospray ionization-mass spectrometry (ESI-MS) measurements were performed with a Varian 500 mass spectrometer. Steady-state fluorescence spectra were recorded on a Perkin–Elmer LS–55 fluorescence spectrometer in the right-angle geometry (90° collecting optics). CD spectra were obtained in a buffer solution on a Biologic MOS-450 CD spectropolarimeter (France) at ambient temperature (cell length: 1 cm, scanning speed: 10 nm/sec). UV-vis absorption spectra were recorded on the same spectrometer for CD.

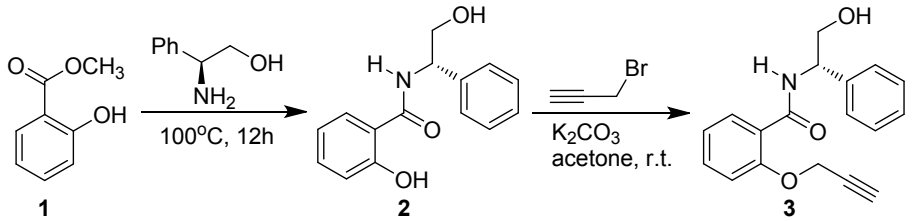
Preparation of stock solutions for UV-vis, CD, and fluorescence studies

Spectral titration experiments were performed on 10^{-4} M solution of probe **3** in HOAc-NaOAc buffer (containing 1% methanol) by adding aliquots of a solution of the selected salt at room temperature (~25°C). Stock solutions of the metal ions (10^{-2} M) were prepared in deionized water as their nitrate salts except for $Hg(ClO_4)_2$. In titration experiments, the stock solution of **3** was directly mixed with the metal ion solution in a 3 ml quartz cuvette (path length = 1 cm) and then the spectrum was recorded. For fluorescence spectrum measurements, excitation was provided at 350 nm, and emission was collected from 250 to 550 nm.

Table S1 Preparation of NaOAc-HOAc and NaH_2PO_4-Na_2HPO_4 buffer solutions

pH	ingredients	
3.6	NaOAc (0.02 M), 0.75 mL	HOAc (0.02 M), 9.25 mL
3.8	NaOAc (0.02 M), 1.20 mL	HOAc (0.02 M), 8.80 mL
4.0	NaOAc (0.02 M), 1.80 mL	HOAc (0.02 M), 8.20 mL
4.2	NaOAc (0.02 M), 2.65 mL	HOAc (0.02 M), 7.35 mL
4.4	NaOAc (0.02 M), 3.70 mL	HOAc (0.02 M), 6.30 mL
4.8	NaOAc (0.02 M), 5.90 mL	HOAc (0.02 M), 4.10 mL
5.0	NaOAc (0.02 M), 7.00 mL	HOAc (0.02 M), 3.00 mL
5.2	NaOAc (0.02 M), 7.90 mL	HOAc (0.02 M), 2.10 mL
5.4	NaOAc (0.02 M), 8.60 mL	HOAc (0.02 M), 1.40 mL
5.8	NaOAc (0.02 M), 9.40 mL	HOAc (0.02 M), 0.60 mL
7.0	Na_2HPO_4 (0.02 M), 6.10 mL	NaH_2PO_4 (0.02 M), 3.90 mL
8.0	Na_2HPO_4 (0.02 M), 9.47 mL	NaH_2PO_4 (0.02 M), 0.53 mL

Synthesis and characterization



Scheme S1. Synthetic route of probe **3**.

Synthesis of (*S*)-2-hydroxy-*N*-(2-hydroxy-1-phenylethyl)benzamide (2):

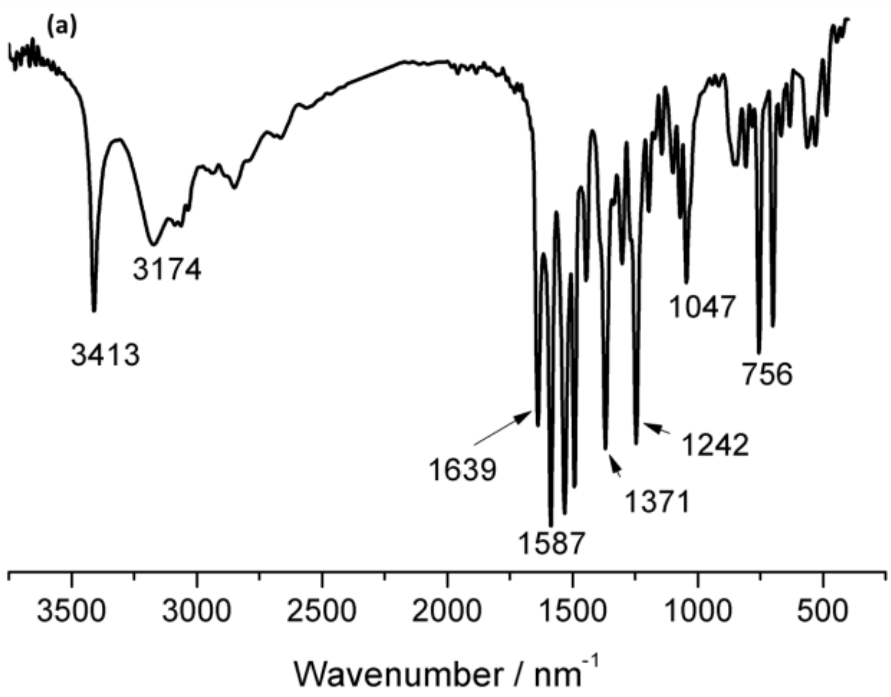
Both L-phenylglycinol (6.9 g, 50 mmol) and methyl salicylate (7.6 g, 50 mmol) were placed in a 100-mL three-necked flask fitted with a Dean-Stark trap and a reflux condenser. The mixture was heated to 100°C with violent magnetic stirring until ~1.5 mL of distillate was collected. The resulted residue was firstly purified via column chromatography using ethyl acetate : *n*-hexane (1:9) as the eluent afford 10.7 g of (*S*)-2-hydroxy-*N*-(2-hydroxy-1-phenylethyl)benzamide (**2**) (78%) as a white solid. Mp：95.4–96.2°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 11.95 (s, 1H, OH), 7.39 (d, 1H, NH), 7.23 (m, 7H, ArH), 6.85 (d, 1H, ArH), 6.72 (m, 1H, ArH), 5.10 (m, 1H, CH),

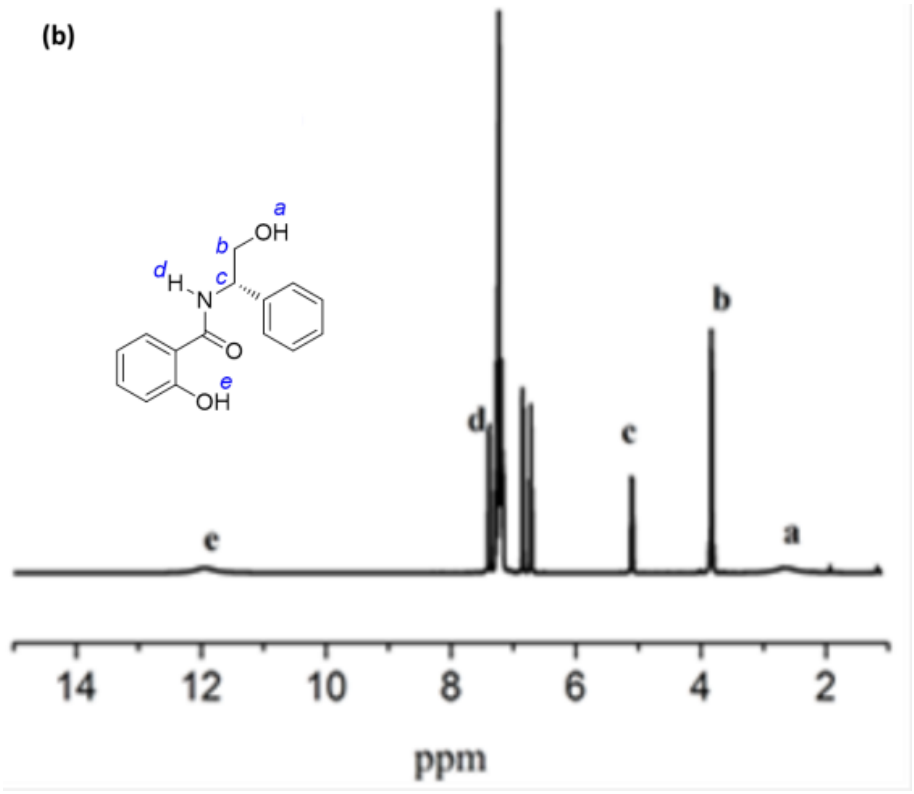
3.83 (m, 2H, CH_2), 2.71 (s, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 168.96, 160.27, 137.55, 133.43, 127.92, 126.99, 125.52, 124.86, 117.85, 117.50, 113.16, 76.36, 75.72, 64.79, 54.30; IR (cm^{-1}, KBr): 3413, 3174, 1639, 1587, 1371, 1242, 1047, 756; MS (ESI): *m/z* 257.11 ($M + H^+$).

Synthesis of *N*-(*o*-propargyloxybenzoyl)-L-phenylglycinol (3):

Into a solution of the intermediate **2** (5.14 g, 20 mmol) in acetone (20 mL) were added propargyl bromide (2.62 g, 22 mmol) and K_2CO_3 (9.7 g, 70 mmol). After stirring the reaction mixture at room temperature for 10 h, the solvent was removed *in vacuo*. The resulting solid matter was recrystallized from ethyl acetate : hexane (1:5) to give the target product *N*-(*o*-propargyloxybenzoyl)-L-phenylglycinol (**3**) in yield 73 % (4.58 g, white solid). Mp: 101.3–101.8°C; ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.46 (d, 1H, NH), 8.14 (d, 1H, ArH), 7.32 (m, 6H, ArH), 7.07 (m, 1H, ArH), 6.95 (d, 1H, ArH), 5.26 (m, 1H, CH), 4.74 (s, 2H, CH_2), 3.91 (m, 2H, CH_2), 2.56 (s, 1H, OH), 2.50 (s, 1H, C≡H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 164.1, 154.3, 137.9, 131.6, 131.1, 127.4, 126.3, 125.5, 120.9, 120.5, 111.3, 76.0, 75.7, 75.5, 75.4, 65.9, 55.7, 55.3; IR (cm^{-1}, KBr): 3386, 2129, 1639, 1529, 1300, 1219, 756; MS (ESI): *m/z* 296.3 ($M + H^+$).

Spectroscopic data

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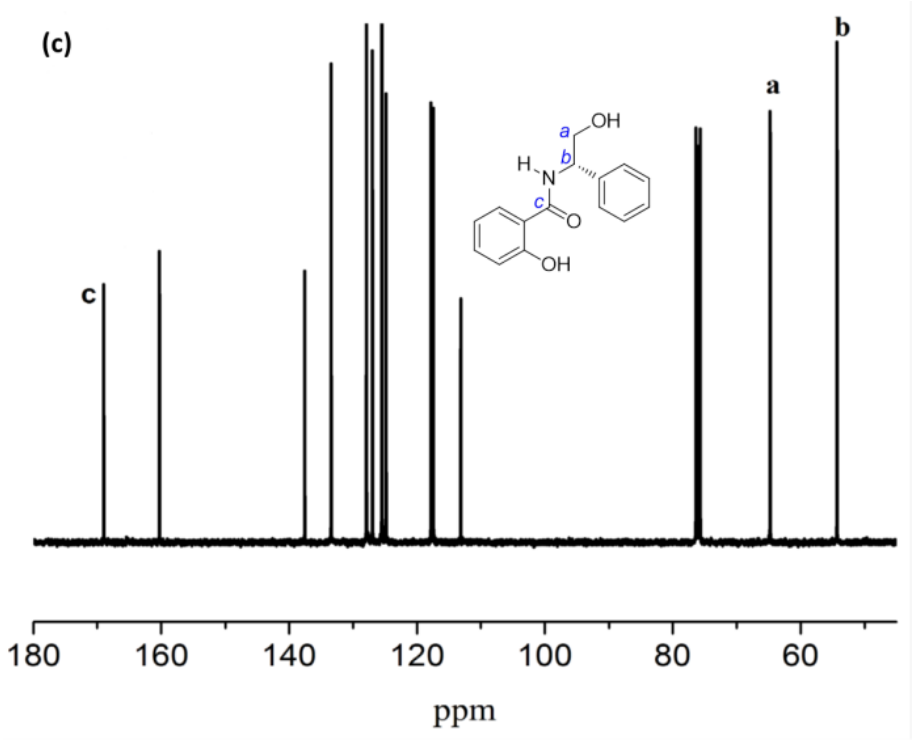
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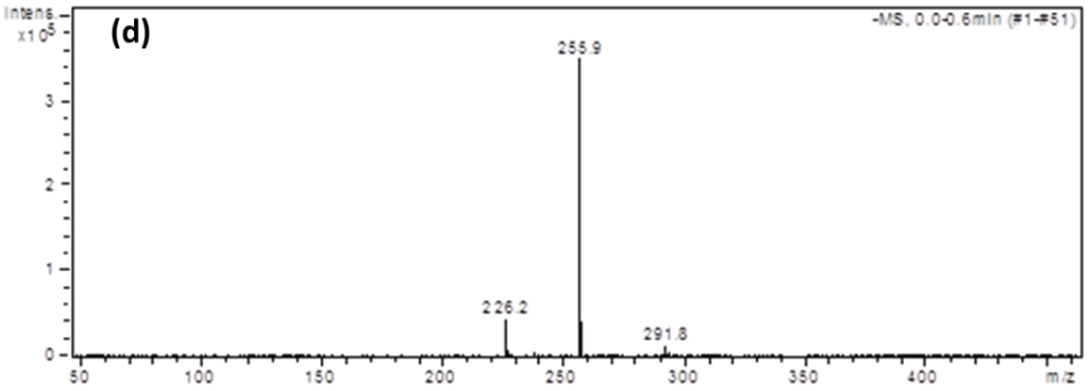
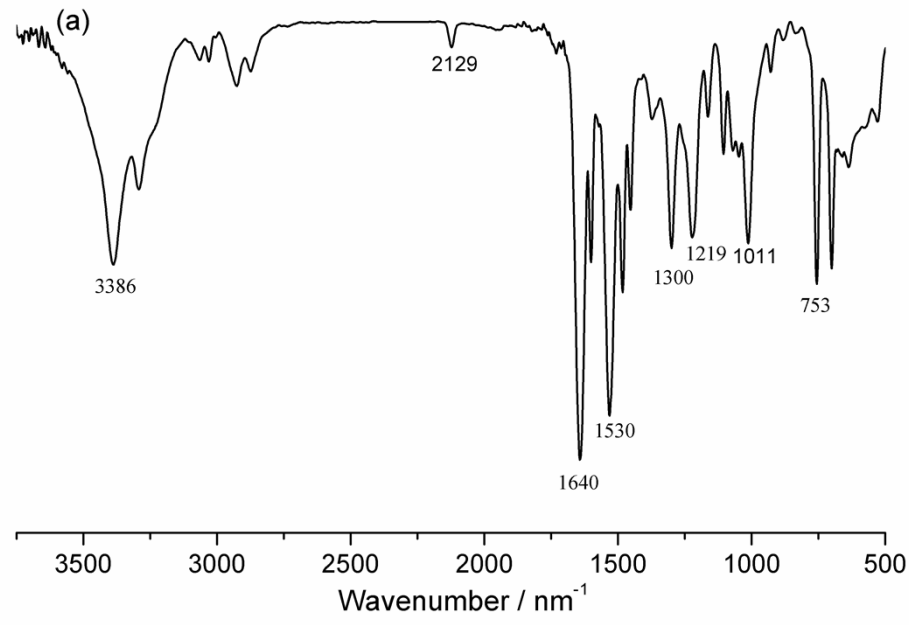
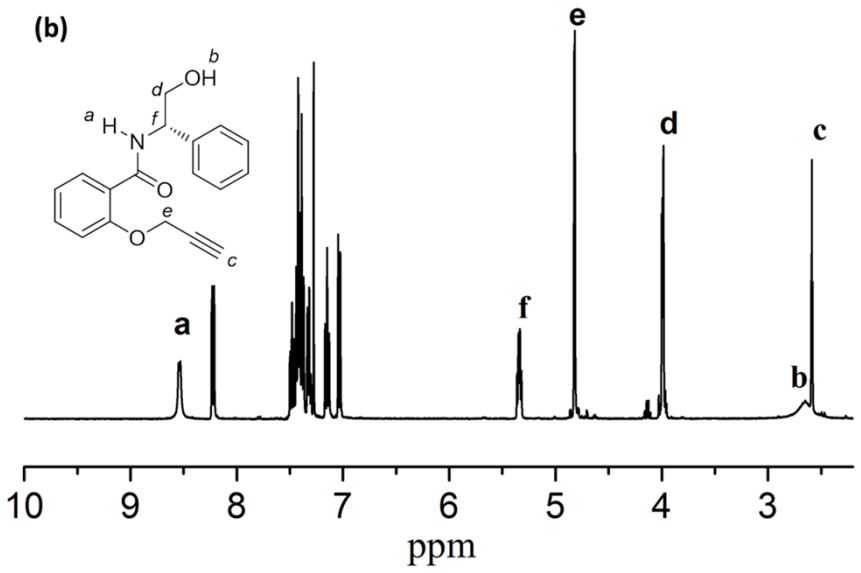
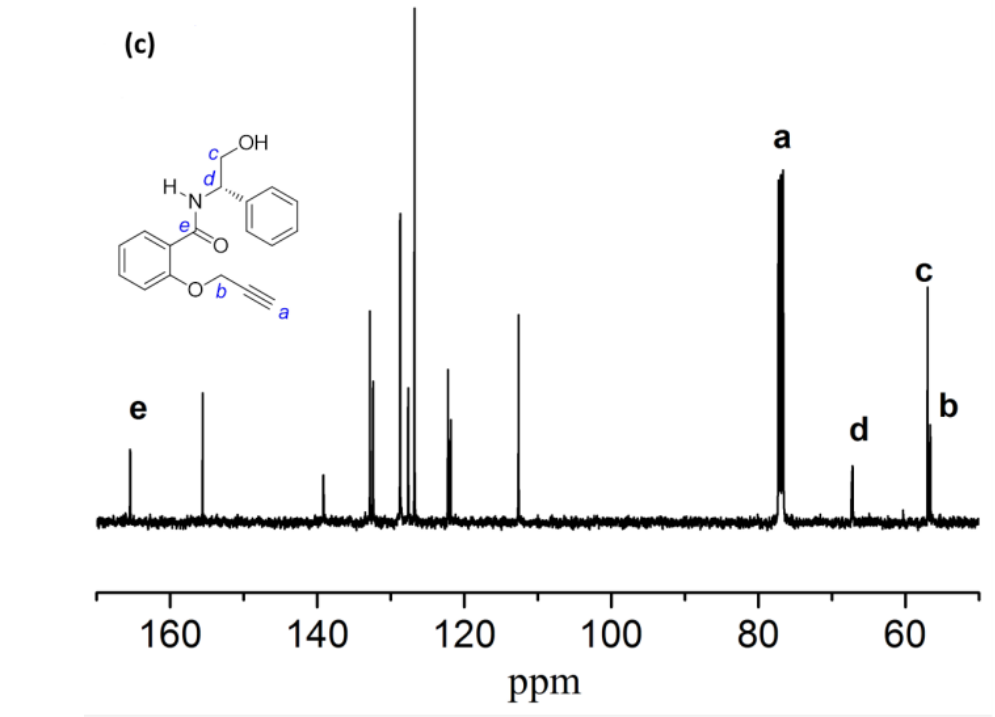


Figure S1 (a) IR, (b) ^{1}H NMR, (c) ^{13}C NMR, and (d) ESI-MS spectra of the intermediate **2**.







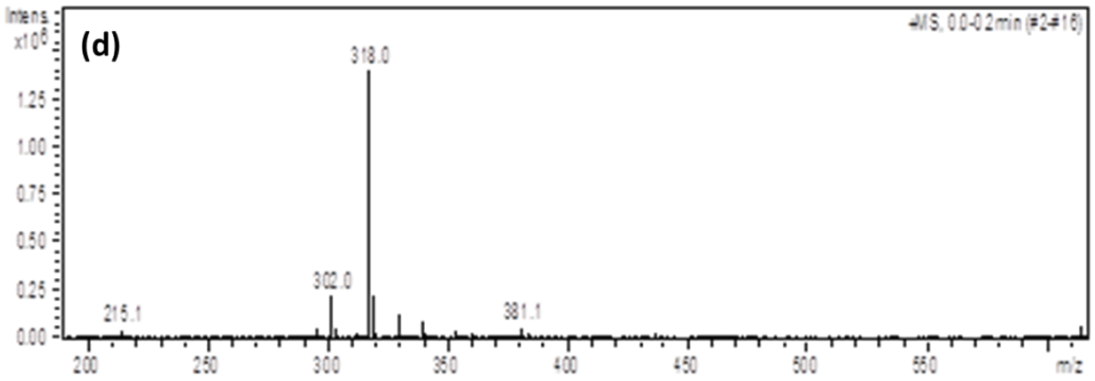


Figure S2 (a) IR, (b) ^{1}H NMR, (c) ^{13}C NMR, and (d) ESI-MS spectra of the probe **3**.

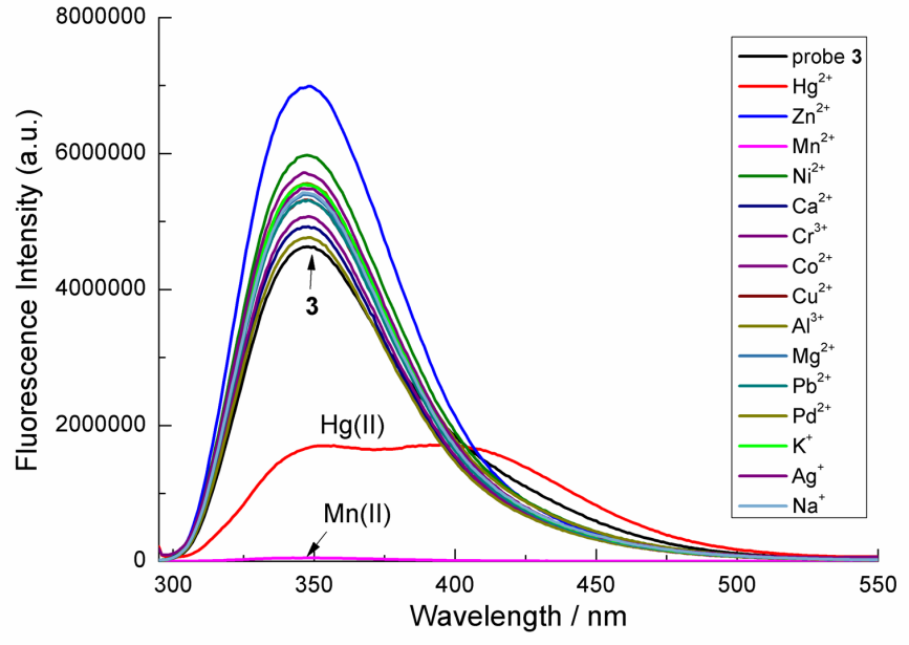


Figure S3 Fluorescence spectra of probe **3** (10^{-4} M) in HOAc-NaOAc buffer (pH 4) upon addition of different metal ions (6 equiv.) at room temperature, reaction time = 10 min, λ_{ex} = 350 nm.

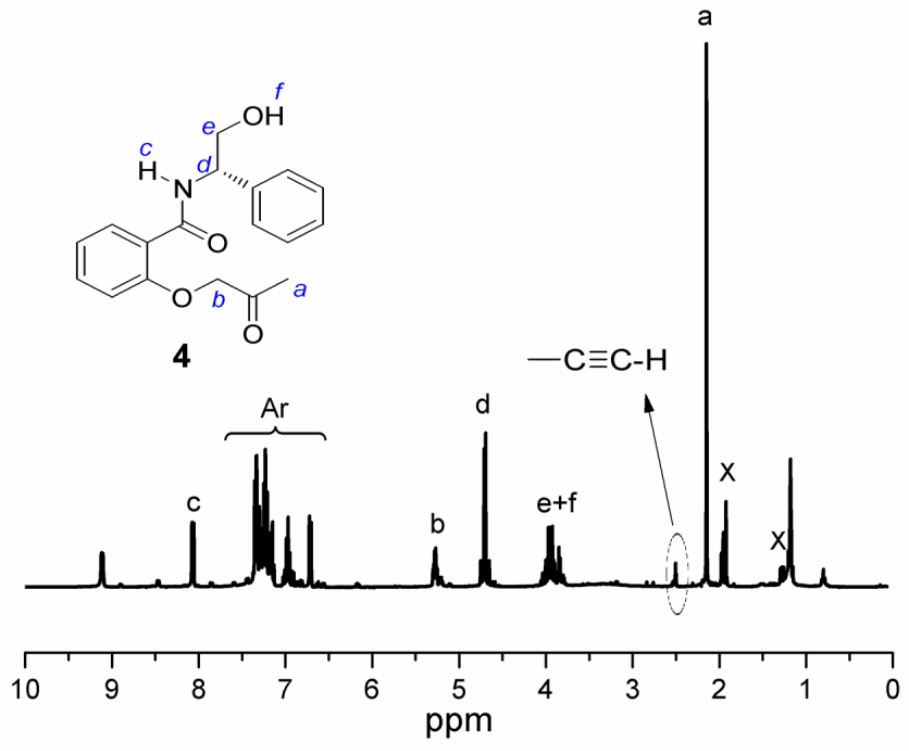


Figure S4 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the oxymercuration product (**4**) of probe **3**. Protocol: A 100 mM aqueous solution of $Hg(ClO_4)_2$ (30 μL) was added to a 0.1 mM solution of **3** in HOAc-NaOAc buffer (pH 4) containing 1% methanol (5 mL). The resulting mixture was stirred at room temperature for 10 min and then extracted with EtOAc (2 × 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The obtained residue was directly dissolved in $CDCl_3$ for ^{1}H NMR measurements. The signals marked with "x" are probably from the remaining ethyl acetate.

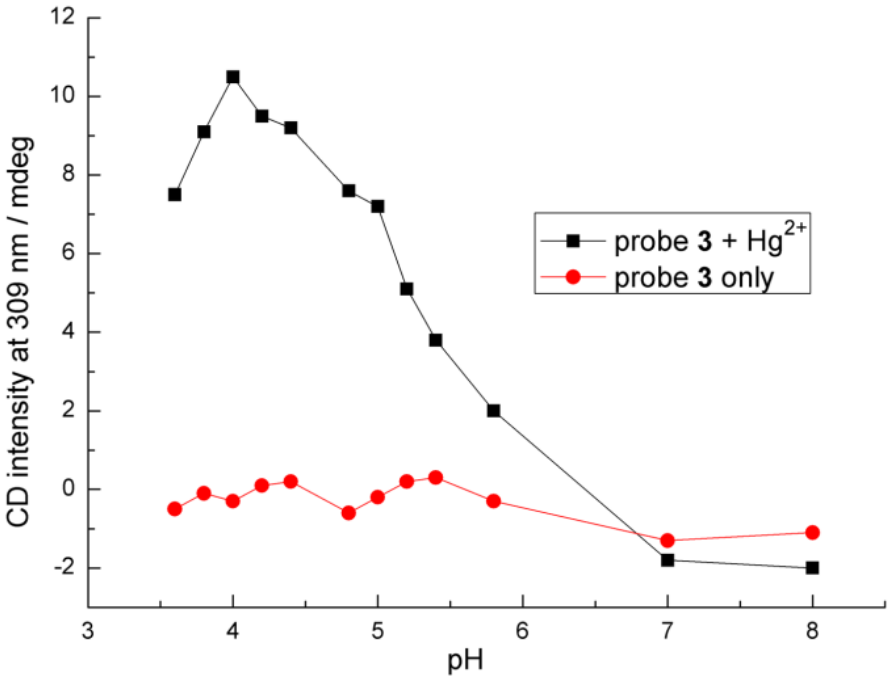


Figure S5 CD intensity of probe **3** (100 μM) with the pH value monitored at λ = 309 nm. The CD measurements were conducted in NaOAc-HOAc buffer solution (containing 1% methanol) after mixing **3** with 6 equivalents of $Hg(ClO_4)_2$ at room temperature for 10 min.