

Supporting Information

Synthesis of BINOL-Xylose-Conjugates as "Turn-off" Fluorescent Receptors for Fe³⁺ and Secondary Recognition of Cysteine by Their Complexes

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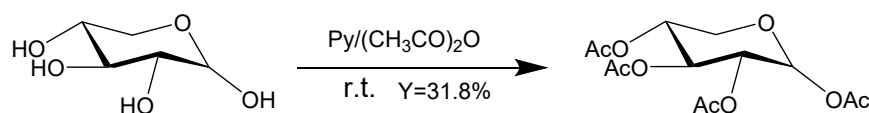
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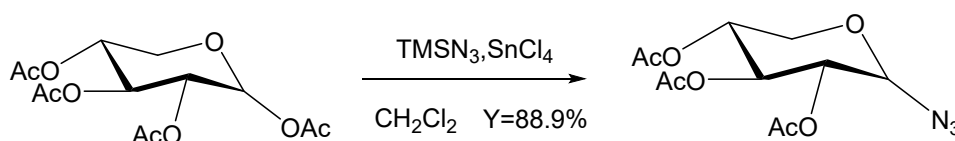
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Synthesis of 1,2,3,4-tetracetoxy- β -D-xylose



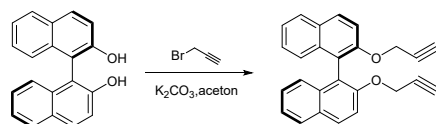
Xylose (3.18 g, 21.18 mmol) was accurately weighed in a 100 mL round-bottom flask, acetic anhydride (20.02 mL, 211.82 mmol) was added, and pyridine (5.12 mL, 63.54 mmol) was dropped after being fully stirred in an ice bath. After reaction for 15 h, TLC detection (EA: PE = 1 : 4, R_f = 0.2) showed that the reaction was complete. Then the reaction system quenched with 10 mL water, extracted with 3×30 mL CH₂Cl₂, washed with saturated salt water, and dried with anhydrous magnesium sulfate for 30 min. The liquid was filtered by vacuum pumped and removed CH₂Cl₂ with a rotary evaporator. The crude product was recrystallized with anhydrous ethanol, and white solid 2.14 g was obtained. The yield of 31.8%. ¹H NMR (400 MHz, CDCl₃) δ 5.71 (dd, J = 6.9, 1.0 Hz, 1H), 5.28 – 5.14 (m, 1H), 5.11 – 4.90 (m, 2H), 4.14 (dd, J = 12.0, 5.0 Hz, 1H), 3.52 (ddd, J = 12.0, 8.4, 1.0 Hz, 1H), 2.21 – 1.96 (m, 12H).

Synthesis of 1-azide-2,3,4-triacetoxy- β -D-xylose



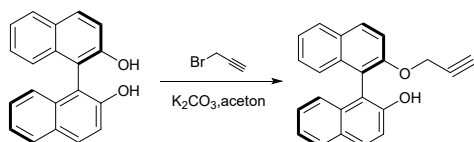
The 1,2,3,4-tetracetoxy- β -D-xylose (1.02 g, 3.20 mmol) was accurately weighed in a 100 mL round-bottom flask under the protection of argon. 10 mL Dry DCM was added at room temperature. Then TMSN₃ (1.10 mL, 8.33 mmol) and SnCl₄ (0.53 mL, 4.49 mmol) was slowly added to the solution, and stirred at room temperature for 30 min. And finally, the reaction system was diluted with 10 mL dry DCM, added with sodium bicarbonate (1.62 g, 19.23 mmol), extracted with sodium bicarbonate salt solution and water, and dried organic phase with anhydrous sodium sulfate. The crude product was separated by column chromatography to obtain colorless transparent liquid 0.87 g. The yield was 88.9%. ¹H NMR (400 MHz, CDCl₃) δ 5.19 (t, J = 8.9 Hz, 1H), 4.98 (td, J = 9.3, 5.3 Hz, 1H), 4.87 (t, J = 8.5 Hz, 1H), 4.63 (d, J = 8.0 Hz, 1H), 4.21 (dd, J = 11.7, 5.3 Hz, 1H), 3.44 (dd, J = 11.7, 9.6 Hz, 1H), 2.14 – 2.03 (m, 9H).

Synthesis of (*R*)-2,2'-bis(O-Propargyloxymethyl)-1,1'-binaphthol



At room temperature, (*R*)-BINOL (3.0 g, 10.5 mmol), potassium carbonate (4.34 g, 31.4 mmol), and acetone (20.0 mL) as solvent were added in a 100 mL three-neck flask. 3-Bromopropargyne (1.0 mL, 12.6 mmol) was slowly added to a three-necked flask and stirred for 5-10 min at room temperature. The reaction system was transferred to an oil bath at 70 °C and refluxed for 13 h. When TLC test showed that the raw material point had disappeared and new points were generated, the reaction was stopped. The system was cooled to room temperature, the reaction liquid was filtered via a circulating water pump, and the filter residue was washed with acetone for 3 times. Silica about 200-300 mesh was added to the filtrate, and the solvent was dried on a rotary evaporator to obtain a yellowish brown powder. Column chromatography was performed using petroleum ether and ethyl acetate as eluents (V (petroleum ether): V (ethyl acetate) = 20:1) to obtain 2.6 g yellowish brown solid with a yield of 76%. ¹HNMR (400 MHz, CDCl₃) δ 7.91 (d, J = 9.1 Hz, 1H), 7.88 – 7.74 (m, 3H), 7.47 (d, J = 9.1 Hz, 1H), 7.37 – 7.27 (m, 2H), 7.25 – 7.11 (m, 4H), 7.04 (d, J = 8.4 Hz, 1H), 5.11 (s, 1H), 4.52 (t, J = 2.2 Hz, 2H), 4.03 (d, J = 7.1 Hz, 1H), 2.29 (t, J = 2.1 Hz, 1H), 1.94 (s, 1H). ¹³CNMR (101 MHz, CDCl₃) δ 153.4, 134.2, 129.6, 128.1, 126.6, 125.8, 124.3, 120.9, 116.3, 79.5, 75.4, 57.5 (ppm).

Synthesis of (*R*)-2-(O-Propargyloxymethyl)-1,1'-binaphthol



The synthesis process of R-2 was similar to that of R-1, so there would be no further elaboration. At room temperature, (*R*)-BINOL, potassium carbonate, and acetone as solvent were added to a round-bottom flask at 70 °C for 13 h. When there was no raw material point monitored by TLC, the reaction was stopped and processed to obtain a yellowish-brown solid. The yield was 77%. ¹HNMR (400 MHz, CDCl₃) δ 8.05 (d, J = 9.1 Hz, 1H), 7.91 (d, J = 8.6 Hz, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 9.1 Hz, 1H), 7.40 (d, J = 7.0 Hz, 1H), 7.37 (d, J = 5.9 Hz, 1H), 7.33 (d, J = 6.1 Hz, 1H), 7.32 – 7.25 (m, 2H), 7.25 – 7.16 (m, 2H), 7.06 (d, J = 8.4 Hz, 1H), 4.97 (s, 1H), 4.65 (s, 2H). ¹³CNMR (101 MHz, CDCl₃) δ 154.0, 151.4, 134.1, 133.8, 130.8, 130.0, 129.2, 128.3, 127.4, 126.6, 125.3, 125.0, 124.8, 123.4, 117.8, 115.96 (s), 114.8, 78.9, 76.0, 60.5, 57.0 (ppm).

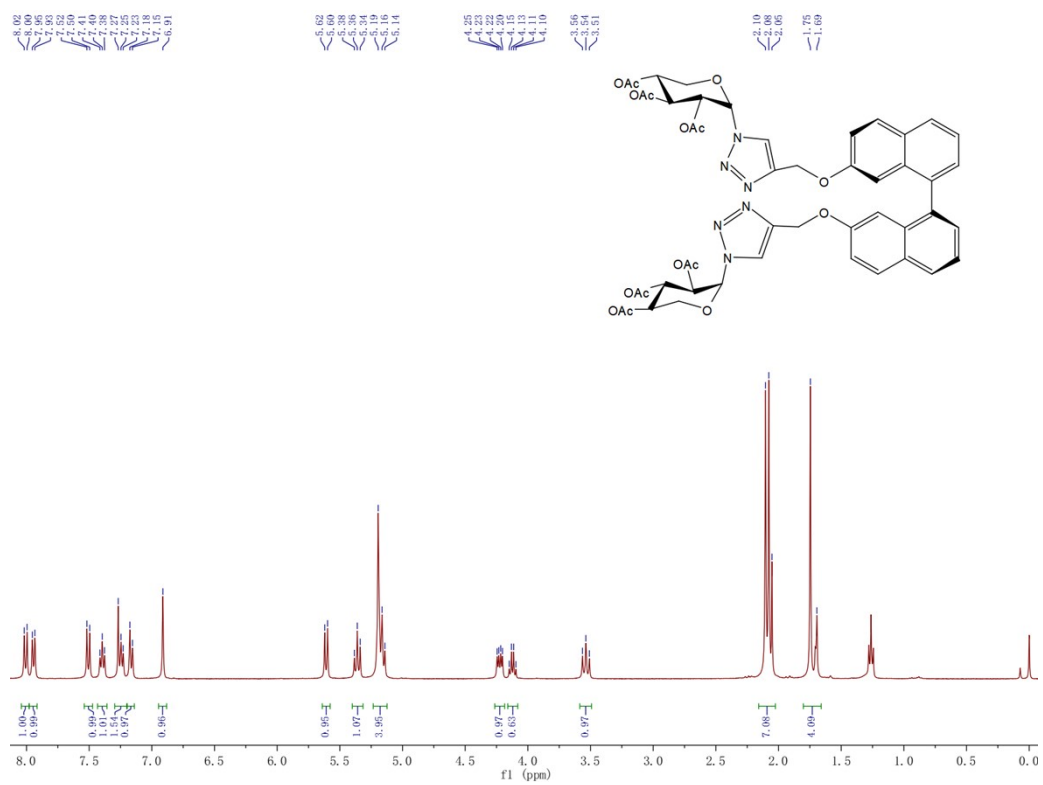


Figure S1 ¹H NMR of *R*- β -*D*-1 (CDCl₃)

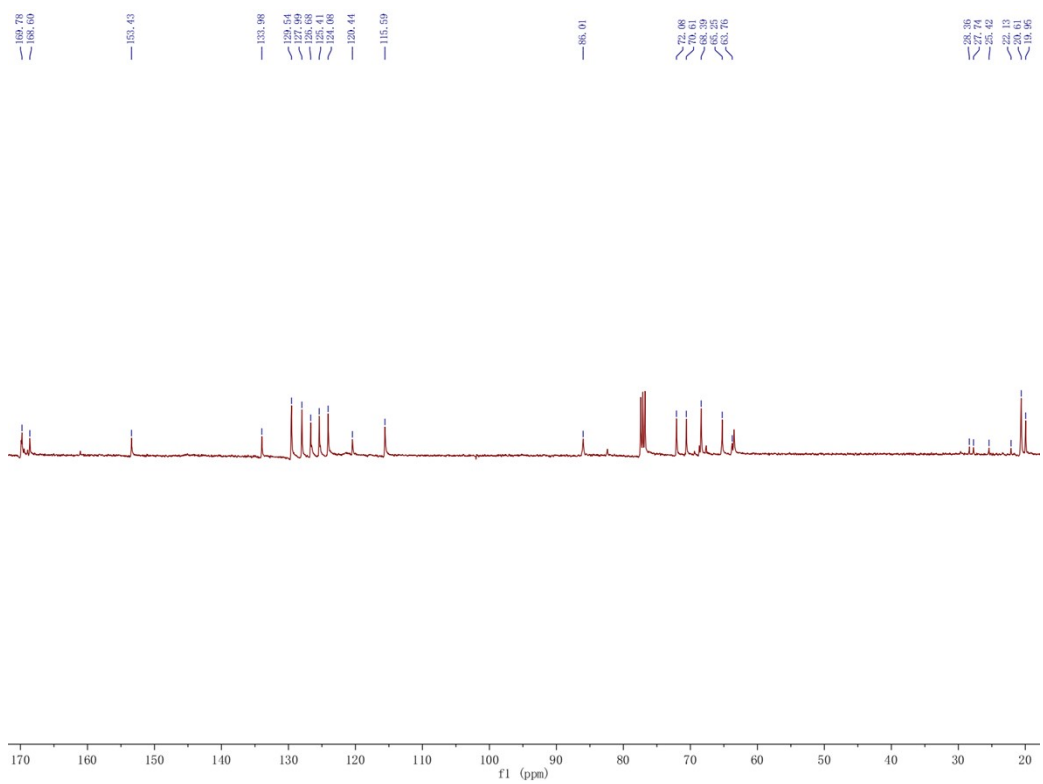


Figure S2 ¹³C NMR of *R*- β -*D*-1 (CDCl₃)

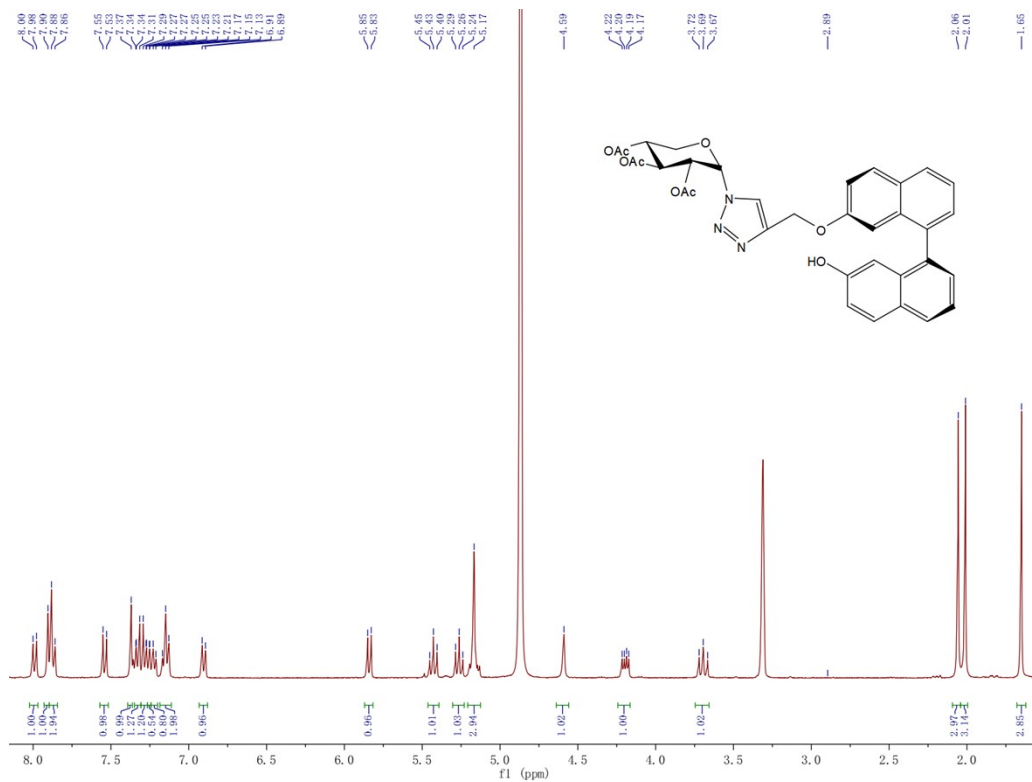


Figure S3 ¹H NMR of *R*- β -*D*-2 (CD₃OD)

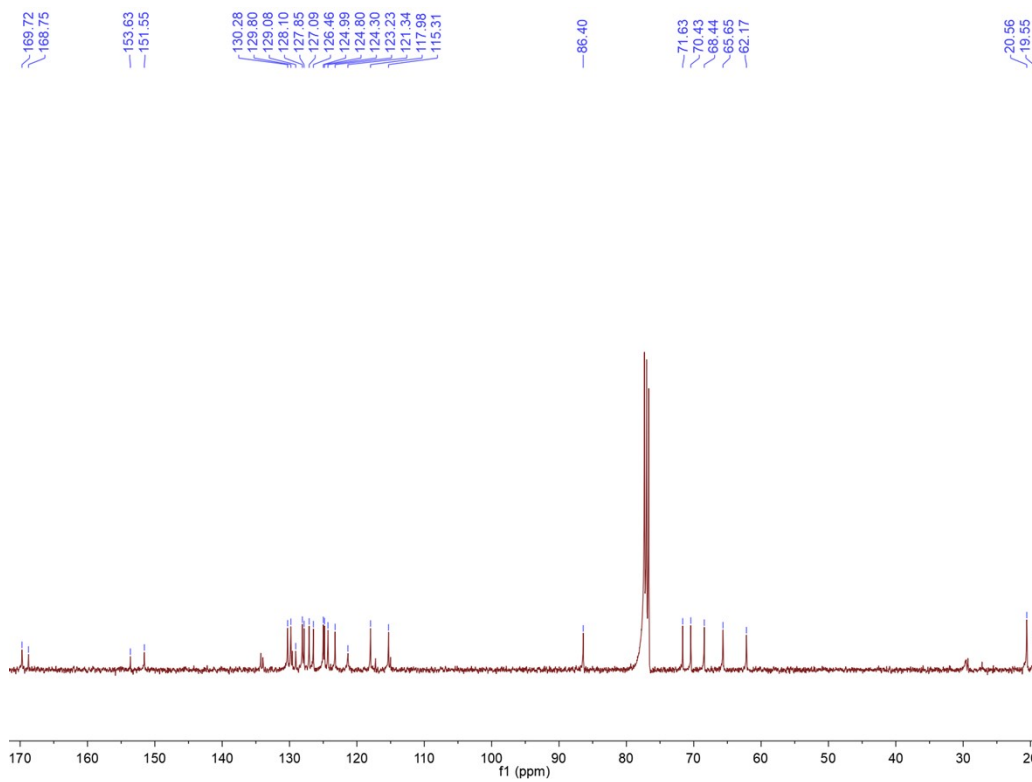


Figure S4 ¹³C NMR of *R*- β -*D*-2 (CDCl₃)

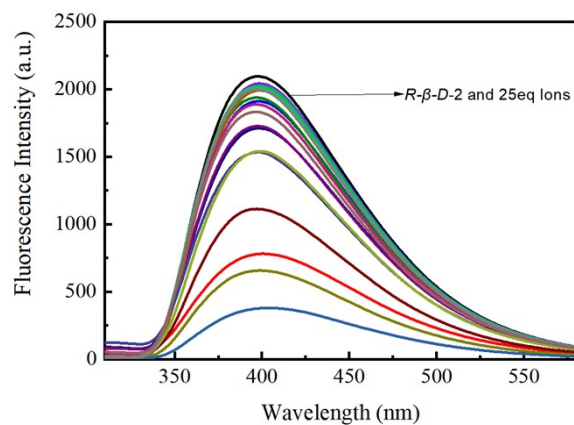


Figure S5 Fluorescence spectra of *R*- β -D-2 (2 \times 10⁻⁵ mol/L in PBS) in the presence of various ions such as K⁺, Ag⁺, Ba²⁺, Cd²⁺, Mg²⁺, Ca²⁺, Cr³⁺, Ni²⁺, Mn²⁺, Cu²⁺, Zn²⁺, Co²⁺, Hg²⁺, Al³⁺, Sn²⁺, Pb²⁺, and Sr²⁺ ions (25 equiv).

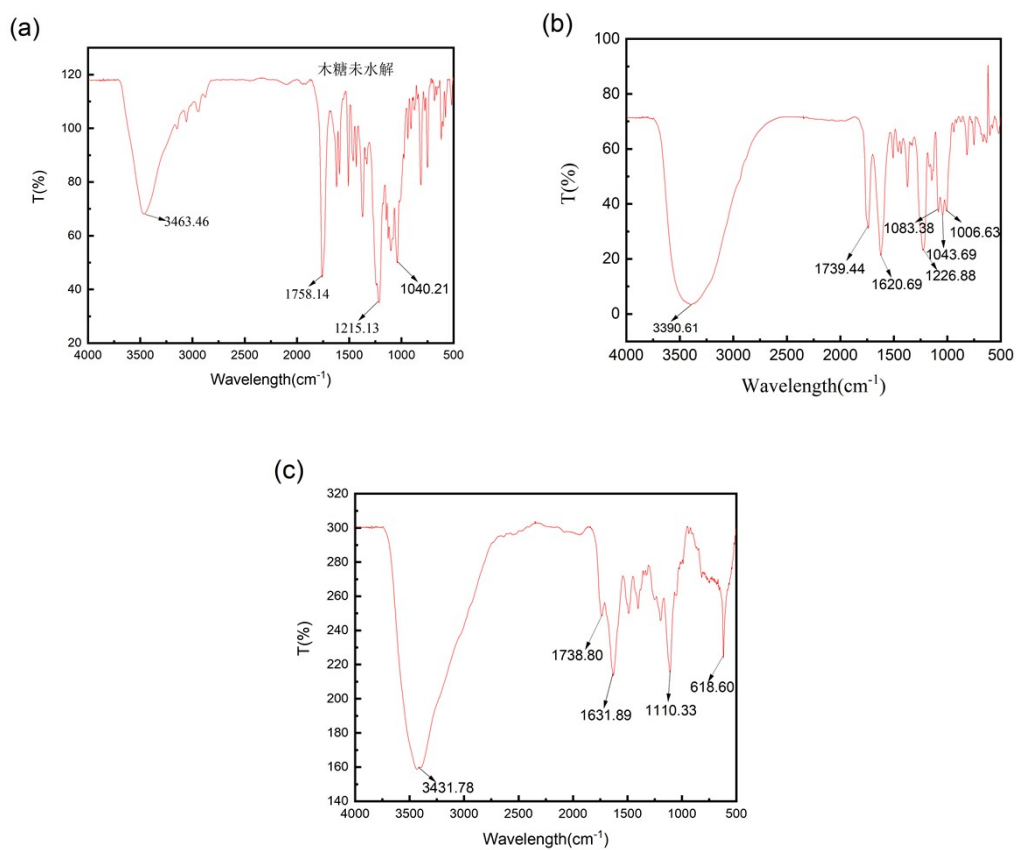


Figure S6 (a) IR spectra of *R*- β -D-2; (b) IR spectra of *R*- β -D-2-Fe³⁺; (c) IR spectra of *R*- β -D-2-Fe³⁺-Cys

Practical application of *R*- β -*D*-2 in lake water

By Hitachi F-4700 fluorescence spectrometers, we used *R*- β -*D*-2 probe to detect Fe^{3+} in the lake water, as shown in Fig. S7. With lake water added, *R*- β -*D*-2 probe found strong fluorescence quenching phenomenon. This indicated that *R*- β -*D*-2 probe could be used to detect Fe^{3+} in lake water.

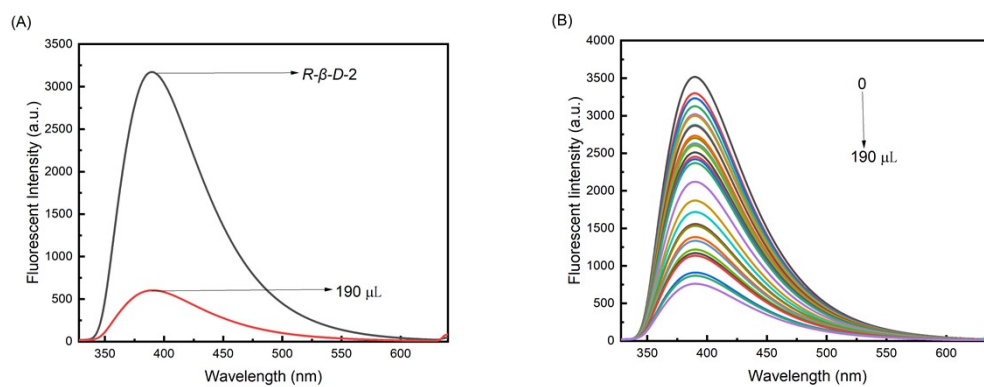


Figure S7 (A) Fluorescence spectra of *R*- β -*D*-2 (20 μM in CH_3OH) in the presence of 190 μL lake water; (B) Fluorescence responses of *R*- β -*D*-2 with increase of lake water equivalent.