

Electronic Supporting Information (ESI)

A diboronic acid fluorescent sensor with fluorescence quenching selective recognition of D-ribose

Hao Wang,^{‡a, b, c, d} Guiqian Fang,^{‡a, b, c, d} Hongxiao Wang^{a, b, c, d} Jindi Dou^{a, b, c, d} Zhancun Bian,^{a, b, c, d}
Ying Li^{a, b, c, d} Huining Chai^{a, b, c, d} Zhongyu Wu^{*a, b, c, d} and Qingqiang Yao^{*a, b, c, d}

a. School of Medicine and Life Sciences, University of Jinan-Shandong Academy of Medical Sciences, Jinan 250200, Shandong, China

b. Institute of Materia Medica, Shandong Academy of Medical Sciences, Jinan 250062, Shandong, China

c. Key Laboratory for Biotech-Drugs Ministry of Health, Jinan 250062, Shandong, China

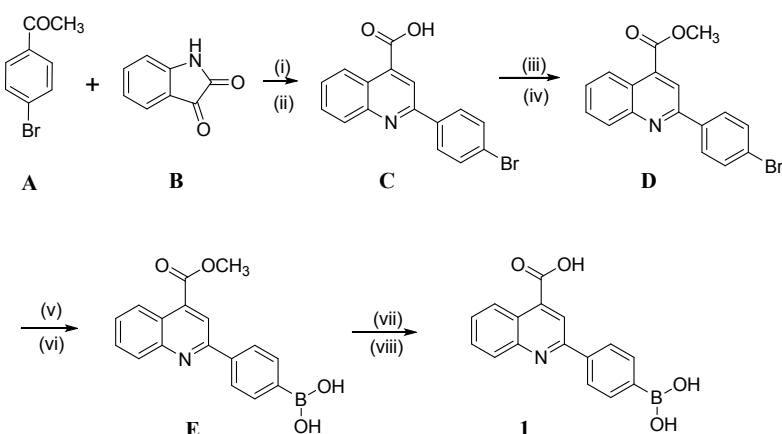
d. Key Laboratory for Rare & Uncommon Diseases of Shandong Province, Jinan 250062, Shandong, China

e. Department of Medicinal Chemistry, School of Pharmaceutical Sciences, Shandong University, Jinan, Shandong 250012, China

*Corresponding authors: E-Mail: wu_med@foxmail.com (Zhongyu Wu), yao_imm@163.com (Qingqiang Yao)

1. Synthesis of 2-(4-boronophenyl)quinoline-4-carboxylic acid (**1**)

This paper reports on the synthesis of PBAQA according to the preliminary work of our group,¹ as shown in Scheme 1. Starting from p-bromoacetophenone and eosin, PBAQA was synthesized by Pfitzinger Reaction, carboxyl esterification, palladium catalysis, hydrolysis, and so on. ¹H NMR (600 MHz, CD₃OD) δ (ppm) (Fig. S1): 8.83 (d, J = 8.5 Hz, 1H), 8.51 (s, 1H), 8.25 (d, J = 8.4 Hz, 1H), 8.12 (d, J = 7.6 Hz, 2H), 7.99 – 7.82 (m, 3H), 7.77 (t, J = 7.7 Hz, 1H). ¹³C NMR (151 MHz, CD₃OD) δ (ppm) (Fig. S2): 166.85, 156.33, 136.82, 134.17, 131.61, 128.48, 126.88, 125.99, 124.38, 120.82. ESI-MS (Fig. S3): m/z 294.0 [M+1]⁺.



Scheme 1 Synthetic route of PBAQA.¹ (i) EtOH, KOH, rt, 8 h. (ii) HCl, rt, pH 3. (iii) SOCl₂, reflux, 4 h. (iv) Methanol, TEA, 0 °C, 1 h. (v) Pd-catalyst, KOAc, Bis(pinacolato)diboron, 75 °C, 8 h. (vi) NaIO₄, HCl, rt, 12 h. (vii) NaOH, 0 °C, 1 h. (viii) HCl, rt, pH 4.

2. Figure

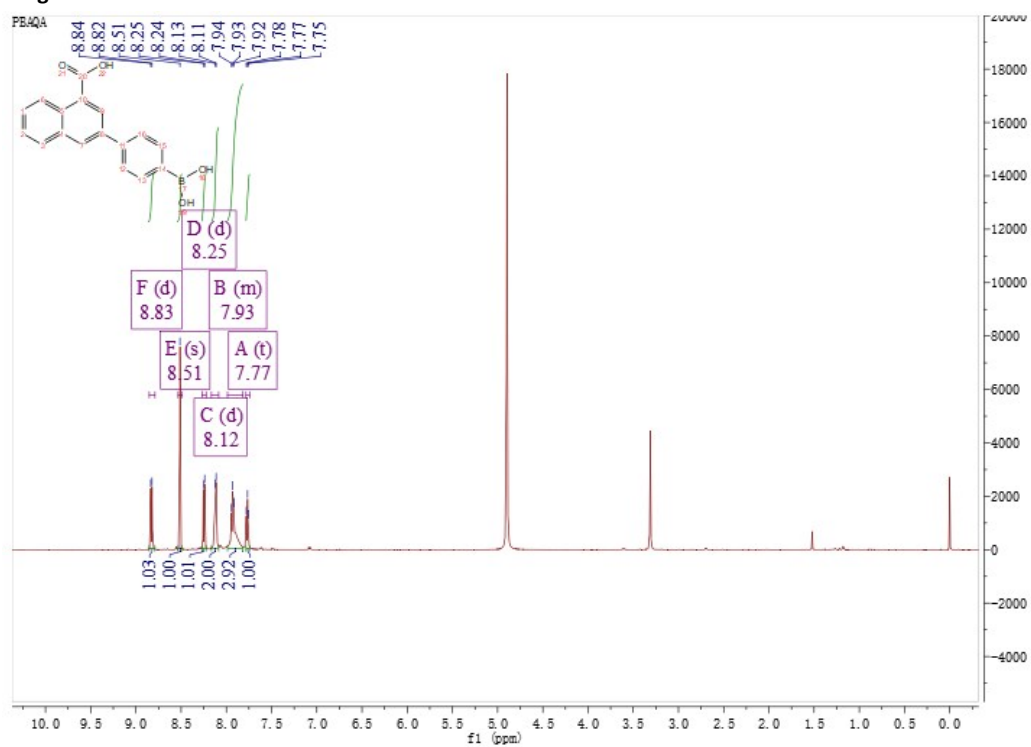


Fig. S1 ¹H NMR spectrum of 1

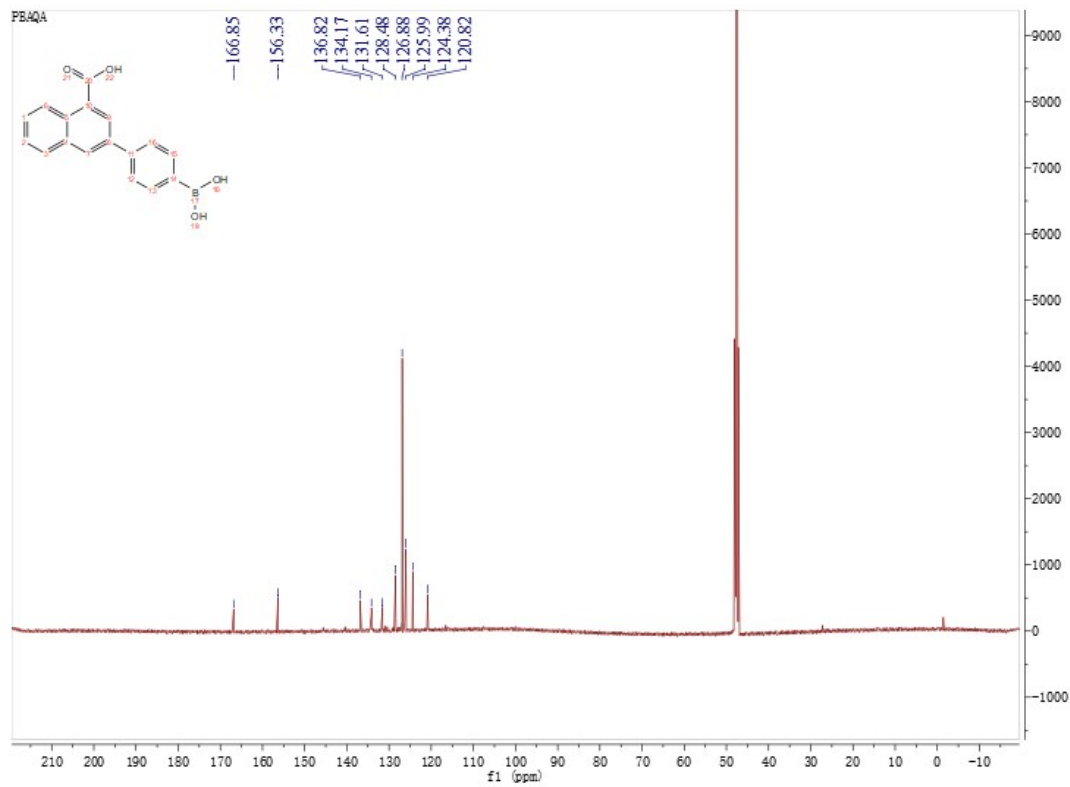


Fig. S2 ¹³C NMR spectrum of 1

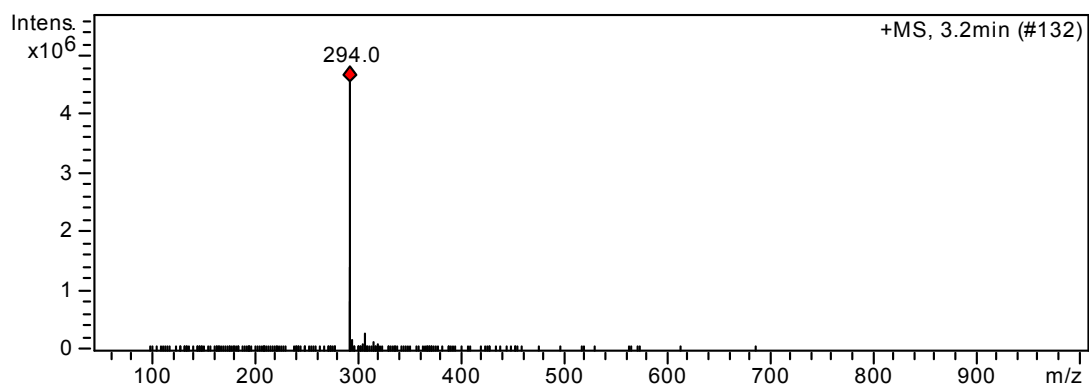


Fig. S3 ESI-MS spectrum of 1

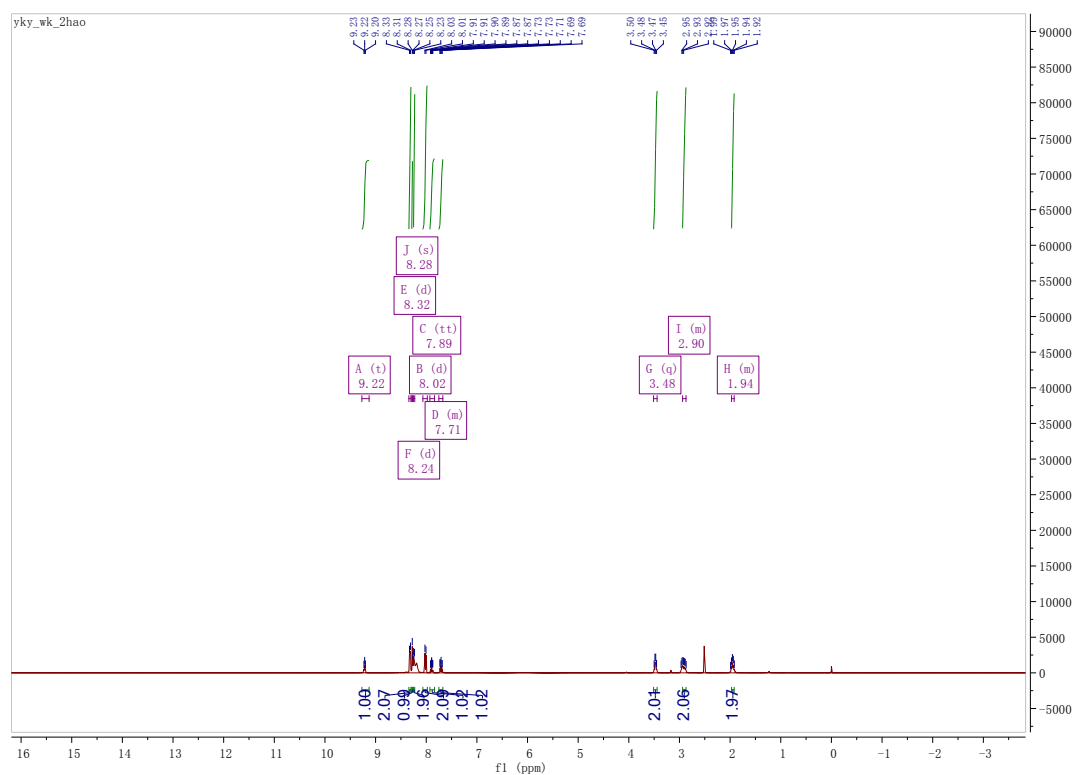


Fig. S4 ¹H NMR spectrum of compound 4

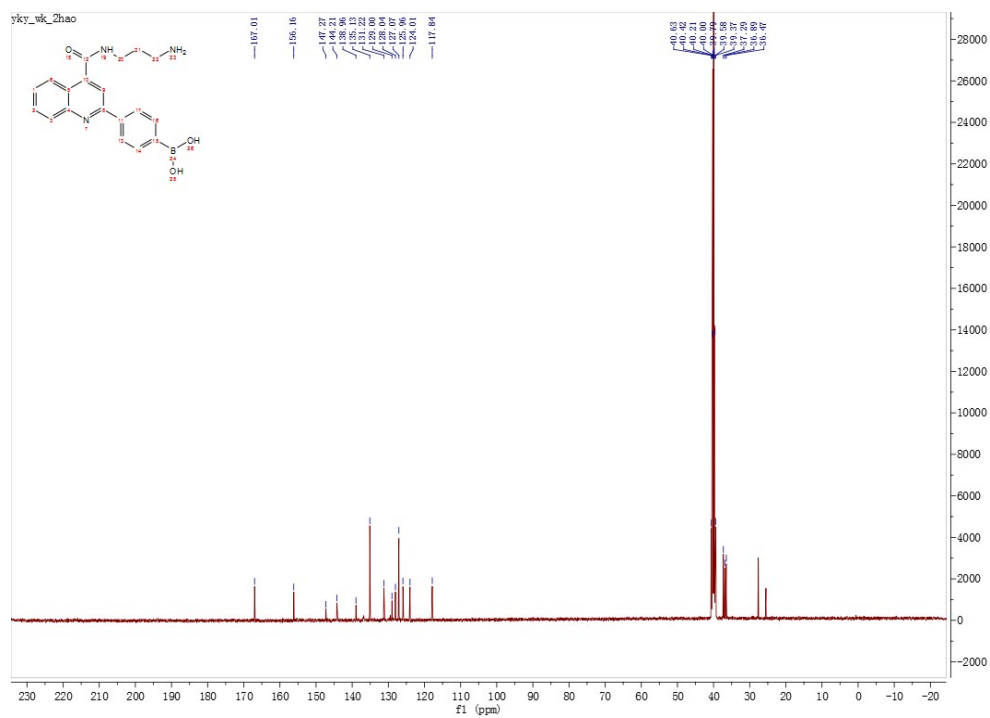


Fig. S5 ^{13}C NMR spectrum of compound 4

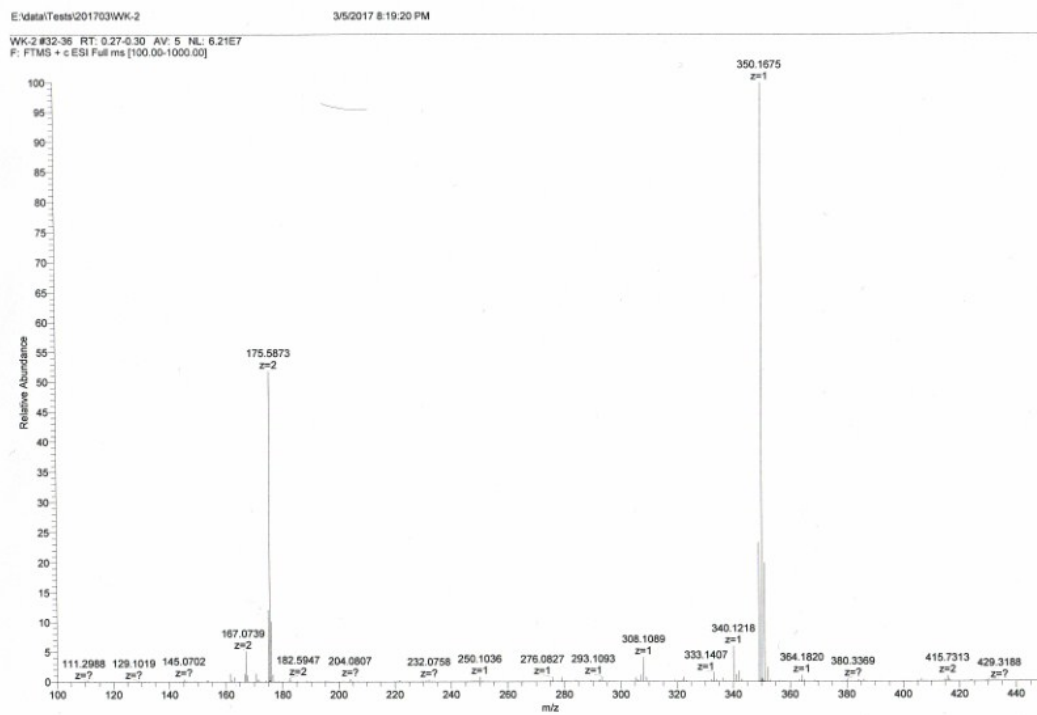


Fig. S6 HRMS spectrum of compound 4

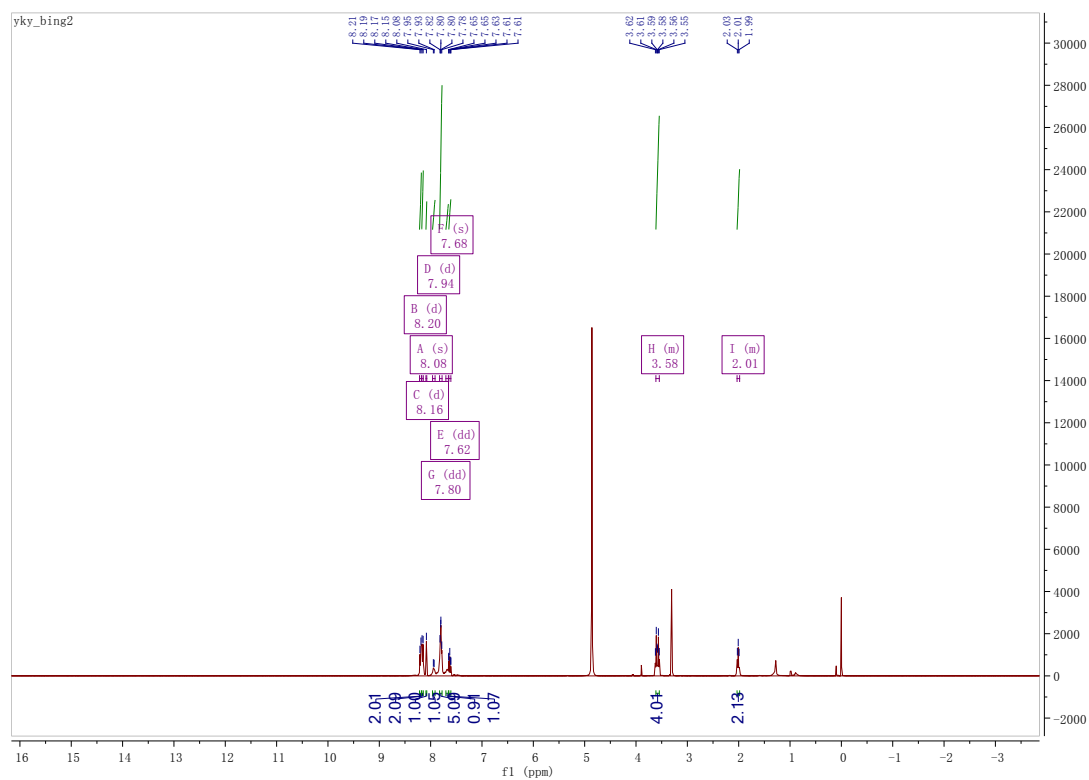


Fig. S7 ^1H NMR spectrum of sensor 6

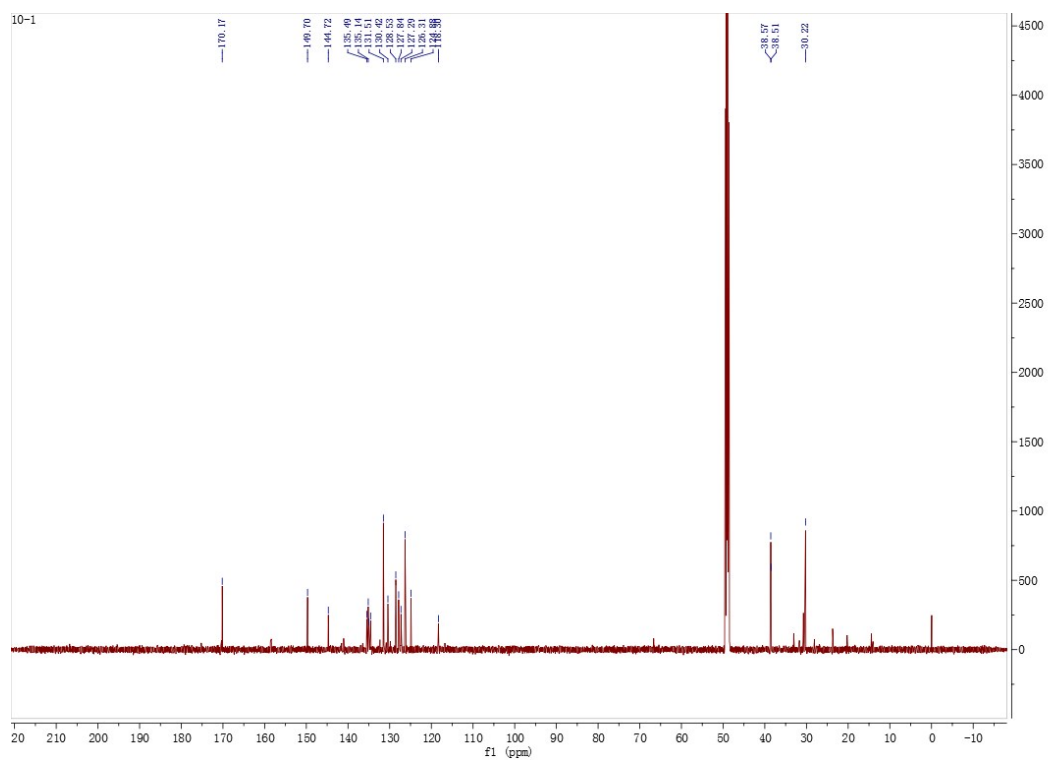


Fig. S8 ^{13}C NMR spectrum of sensor 6

AV300 11B 20190125 YQQ-WH-6



```
===== CHANNEL F1 =====
NUC1  13B
P1    1.00000000 sec
PC    1.49
===== CHANNEL F2 =====
NUC2  13B
P2    1.00000000 sec
PC    1.49
===== CHANNEL F3 =====
NUC3  13B
P3    1.00000000 sec
PC    1.49
===== CHANNEL F4 =====
NUC4  13B
P4    1.00000000 sec
PC    1.49
===== CHANNEL F5 =====
NUC5  13B
P5    1.00000000 sec
PC    1.49
===== CHANNEL F6 =====
NUC6  13B
P6    1.00000000 sec
PC    1.49
===== CHANNEL F7 =====
NUC7  13B
P7    1.00000000 sec
PC    1.49
===== CHANNEL F8 =====
NUC8  13B
P8    1.00000000 sec
PC    1.49
===== CHANNEL F9 =====
NUC9  13B
P9    1.00000000 sec
PC    1.49
===== CHANNEL F10 =====
NUC10 13B
P10   1.00000000 sec
PC    1.49
===== CHANNEL F11 =====
NUC11 13B
P11   1.00000000 sec
PC    1.49
===== CHANNEL F12 =====
NUC12 13B
P12   1.00000000 sec
PC    1.49
===== CHANNEL F13 =====
NUC13 13B
P13   1.00000000 sec
PC    1.49
===== CHANNEL F14 =====
NUC14 13B
P14   1.00000000 sec
PC    1.49
===== CHANNEL F15 =====
NUC15 13B
P15   1.00000000 sec
PC    1.49
===== CHANNEL F16 =====
NUC16 13B
P16   1.00000000 sec
PC    1.49
===== CHANNEL F17 =====
NUC17 13B
P17   1.00000000 sec
PC    1.49
===== CHANNEL F18 =====
NUC18 13B
P18   1.00000000 sec
PC    1.49
===== CHANNEL F19 =====
NUC19 13B
P19   1.00000000 sec
PC    1.49
===== CHANNEL F20 =====
NUC20 13B
P20   1.00000000 sec
PC    1.49
===== CHANNEL F21 =====
NUC21 13B
P21   1.00000000 sec
PC    1.49
===== CHANNEL F22 =====
NUC22 13B
P22   1.00000000 sec
PC    1.49
===== CHANNEL F23 =====
NUC23 13B
P23   1.00000000 sec
PC    1.49
===== CHANNEL F24 =====
NUC24 13B
P24   1.00000000 sec
PC    1.49
===== CHANNEL F25 =====
NUC25 13B
P25   1.00000000 sec
PC    1.49
===== CHANNEL F26 =====
NUC26 13B
P26   1.00000000 sec
PC    1.49
===== CHANNEL F27 =====
NUC27 13B
P27   1.00000000 sec
PC    1.49
===== CHANNEL F28 =====
NUC28 13B
P28   1.00000000 sec
PC    1.49
===== CHANNEL F29 =====
NUC29 13B
P29   1.00000000 sec
PC    1.49
===== CHANNEL F30 =====
NUC30 13B
P30   1.00000000 sec
PC    1.49
===== CHANNEL F31 =====
NUC31 13B
P31   1.00000000 sec
PC    1.49
===== CHANNEL F32 =====
NUC32 13B
P32   1.00000000 sec
PC    1.49
===== CHANNEL F33 =====
NUC33 13B
P33   1.00000000 sec
PC    1.49
===== CHANNEL F34 =====
NUC34 13B
P34   1.00000000 sec
PC    1.49
===== CHANNEL F35 =====
NUC35 13B
P35   1.00000000 sec
PC    1.49
===== CHANNEL F36 =====
NUC36 13B
P36   1.00000000 sec
PC    1.49
===== CHANNEL F37 =====
NUC37 13B
P37   1.00000000 sec
PC    1.49
===== CHANNEL F38 =====
NUC38 13B
P38   1.00000000 sec
PC    1.49
===== CHANNEL F39 =====
NUC39 13B
P39   1.00000000 sec
PC    1.49
===== CHANNEL F40 =====
NUC40 13B
P40   1.00000000 sec
PC    1.49
===== CHANNEL F41 =====
NUC41 13B
P41   1.00000000 sec
PC    1.49
===== CHANNEL F42 =====
NUC42 13B
P42   1.00000000 sec
PC    1.49
===== CHANNEL F43 =====
NUC43 13B
P43   1.00000000 sec
PC    1.49
===== CHANNEL F44 =====
NUC44 13B
P44   1.00000000 sec
PC    1.49
===== CHANNEL F45 =====
NUC45 13B
P45   1.00000000 sec
PC    1.49
===== CHANNEL F46 =====
NUC46 13B
P46   1.00000000 sec
PC    1.49
===== CHANNEL F47 =====
NUC47 13B
P47   1.00000000 sec
PC    1.49
===== CHANNEL F48 =====
NUC48 13B
P48   1.00000000 sec
PC    1.49
===== CHANNEL F49 =====
NUC49 13B
P49   1.00000000 sec
PC    1.49
===== CHANNEL F50 =====
NUC50 13B
P50   1.00000000 sec
PC    1.49
===== CHANNEL F51 =====
NUC51 13B
P51   1.00000000 sec
PC    1.49
===== CHANNEL F52 =====
NUC52 13B
P52   1.00000000 sec
PC    1.49
===== CHANNEL F53 =====
NUC53 13B
P53   1.00000000 sec
PC    1.49
===== CHANNEL F54 =====
NUC54 13B
P54   1.00000000 sec
PC    1.49
===== CHANNEL F55 =====
NUC55 13B
P55   1.00000000 sec
PC    1.49
===== CHANNEL F56 =====
NUC56 13B
P56   1.00000000 sec
PC    1.49
===== CHANNEL F57 =====
NUC57 13B
P57   1.00000000 sec
PC    1.49
===== CHANNEL F58 =====
NUC58 13B
P58   1.00000000 sec
PC    1.49
===== CHANNEL F59 =====
NUC59 13B
P59   1.00000000 sec
PC    1.49
===== CHANNEL F60 =====
NUC60 13B
P60   1.00000000 sec
PC    1.49
===== CHANNEL F61 =====
NUC61 13B
P61   1.00000000 sec
PC    1.49
===== CHANNEL F62 =====
NUC62 13B
P62   1.00000000 sec
PC    1.49
===== CHANNEL F63 =====
NUC63 13B
P63   1.00000000 sec
PC    1.49
===== CHANNEL F64 =====
NUC64 13B
P64   1.00000000 sec
PC    1.49
===== CHANNEL F65 =====
NUC65 13B
P65   1.00000000 sec
PC    1.49
===== CHANNEL F66 =====
NUC66 13B
P66   1.00000000 sec
PC    1.49
===== CHANNEL F67 =====
NUC67 13B
P67   1.00000000 sec
PC    1.49
===== CHANNEL F68 =====
NUC68 13B
P68   1.00000000 sec
PC    1.49
===== CHANNEL F69 =====
NUC69 13B
P69   1.00000000 sec
PC    1.49
===== CHANNEL F70 =====
NUC70 13B
P70   1.00000000 sec
PC    1.49
===== CHANNEL F71 =====
NUC71 13B
P71   1.00000000 sec
PC    1.49
===== CHANNEL F72 =====
NUC72 13B
P72   1.00000000 sec
PC    1.49
===== CHANNEL F73 =====
NUC73 13B
P73   1.00000000 sec
PC    1.49
===== CHANNEL F74 =====
NUC74 13B
P74   1.00000000 sec
PC    1.49
===== CHANNEL F75 =====
NUC75 13B
P75   1.00000000 sec
PC    1.49
===== CHANNEL F76 =====
NUC76 13B
P76   1.00000000 sec
PC    1.49
===== CHANNEL F77 =====
NUC77 13B
P77   1.00000000 sec
PC    1.49
===== CHANNEL F78 =====
NUC78 13B
P78   1.00000000 sec
PC    1.49
===== CHANNEL F79 =====
NUC79 13B
P79   1.00000000 sec
PC    1.49
===== CHANNEL F80 =====
NUC80 13B
P80   1.00000000 sec
PC    1.49
===== CHANNEL F81 =====
NUC81 13B
P81   1.00000000 sec
PC    1.49
===== CHANNEL F82 =====
NUC82 13B
P82   1.00000000 sec
PC    1.49
===== CHANNEL F83 =====
NUC83 13B
P83   1.00000000 sec
PC    1.49
===== CHANNEL F84 =====
NUC84 13B
P84   1.00000000 sec
PC    1.49
===== CHANNEL F85 =====
NUC85 13B
P85   1.00000000 sec
PC    1.49
===== CHANNEL F86 =====
NUC86 13B
P86   1.00000000 sec
PC    1.49
===== CHANNEL F87 =====
NUC87 13B
P87   1.00000000 sec
PC    1.49
===== CHANNEL F88 =====
NUC88 13B
P88   1.00000000 sec
PC    1.49
===== CHANNEL F89 =====
NUC89 13B
P89   1.00000000 sec
PC    1.49
===== CHANNEL F90 =====
NUC90 13B
P90   1.00000000 sec
PC    1.49
===== CHANNEL F91 =====
NUC91 13B
P91   1.00000000 sec
PC    1.49
===== CHANNEL F92 =====
NUC92 13B
P92   1.00000000 sec
PC    1.49
===== CHANNEL F93 =====
NUC93 13B
P93   1.00000000 sec
PC    1.49
===== CHANNEL F94 =====
NUC94 13B
P94   1.00000000 sec
PC    1.49
===== CHANNEL F95 =====
NUC95 13B
P95   1.00000000 sec
PC    1.49
===== CHANNEL F96 =====
NUC96 13B
P96   1.00000000 sec
PC    1.49
===== CHANNEL F97 =====
NUC97 13B
P97   1.00000000 sec
PC    1.49
===== CHANNEL F98 =====
NUC98 13B
P98   1.00000000 sec
PC    1.49
===== CHANNEL F99 =====
NUC99 13B
P99   1.00000000 sec
PC    1.49
===== CHANNEL F100 =====
NUC100 13B
P100  1.00000000 sec
PC    1.49
```

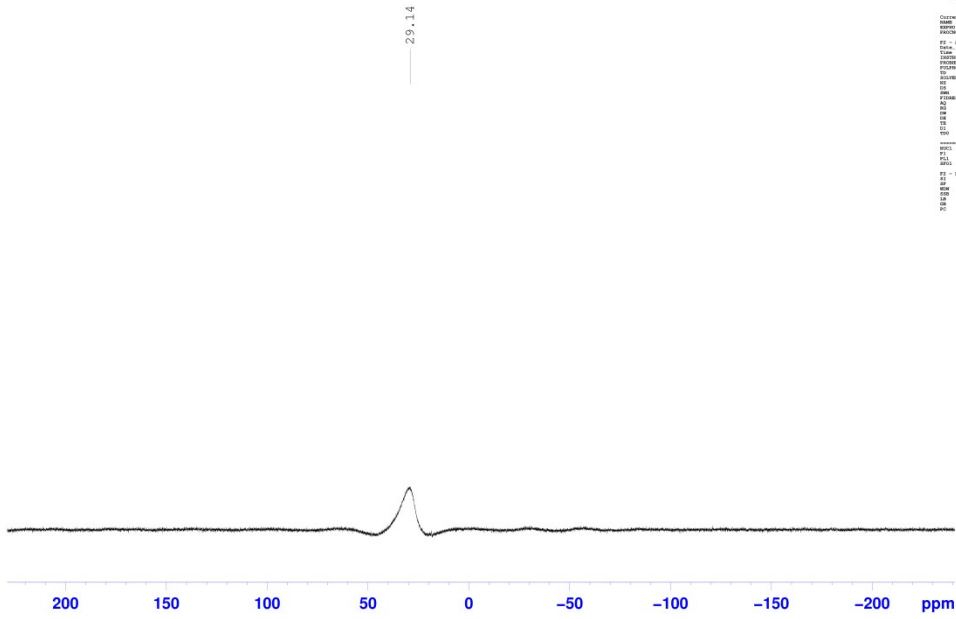


Fig. S9 ¹³B NMR spectrum of sensor 6

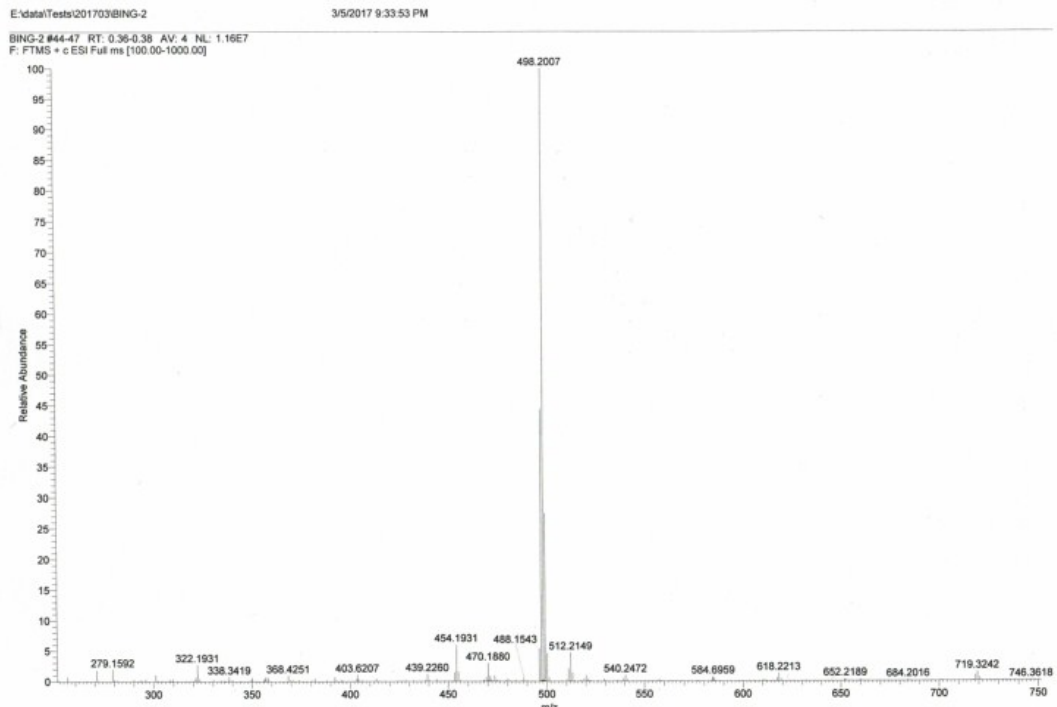


Fig. S10 HRMS spectrum of sensor 6

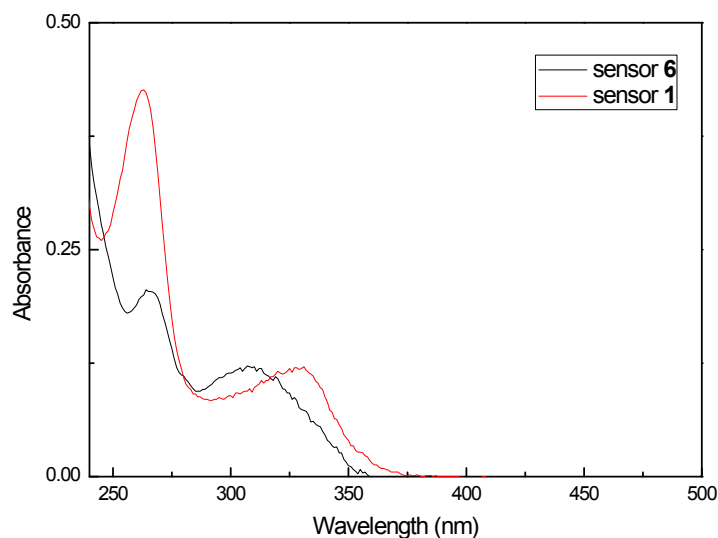


Fig. S11 UV-Vis absorption spectra of sensor **1** and **6** (10^{-5} M) in DMSO/H₂O (1:100, v/v)

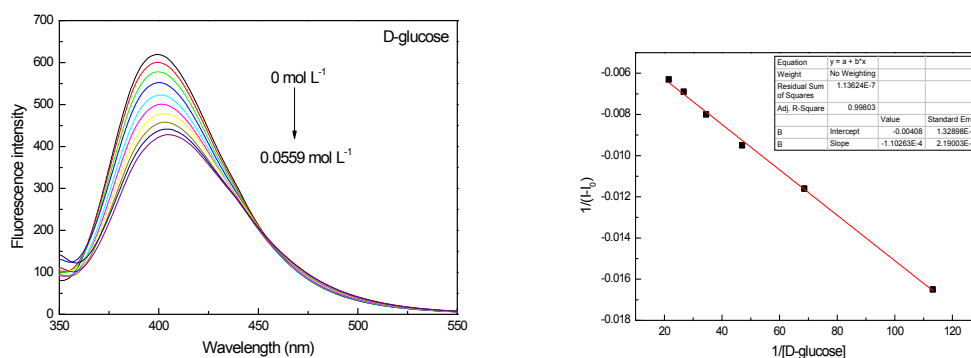


Fig. S12 Fluorescence response of sensor **6** (10^{-5} M) with increasing D-glucose concentration (0 M to 0.0559 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi–Hildebrand plot of sensor **6** $1/(I - I_0)$ versus $1/[D\text{-glucose}]$

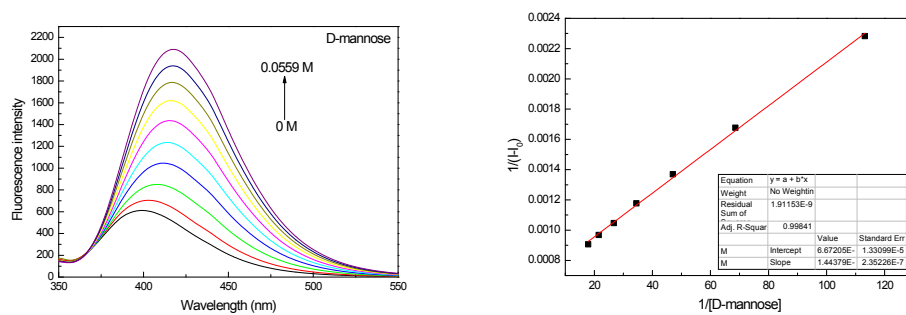


Fig. S13 Fluorescence response of sensor **6** (10^{-5} M) with increasing D-mannose concentration (0 M to 0.0559 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi–Hildebrand plot of sensor **6** $1/(I - I_0)$

versus $1/[D\text{-mannose}]$

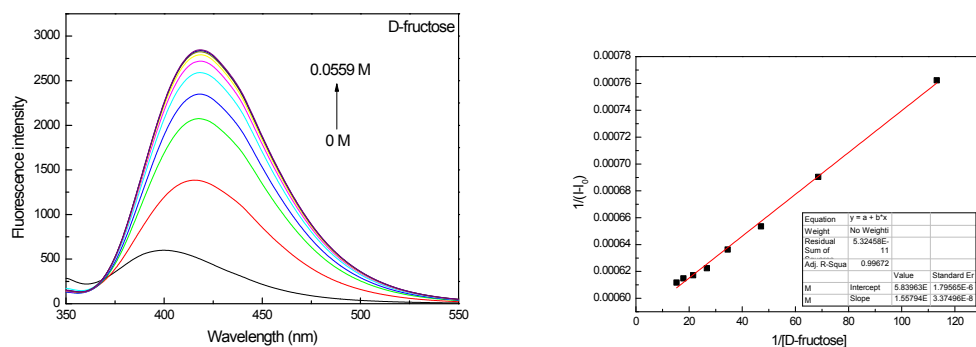


Fig. S14 Fluorescence response of sensor **6** (10^{-5} M) with increasing D-fructose concentration (0 M to 0.0559 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi-Hildebrand plot of sensor **6** $1/(I - I_0)$ versus $1/[D\text{-fructose}]$

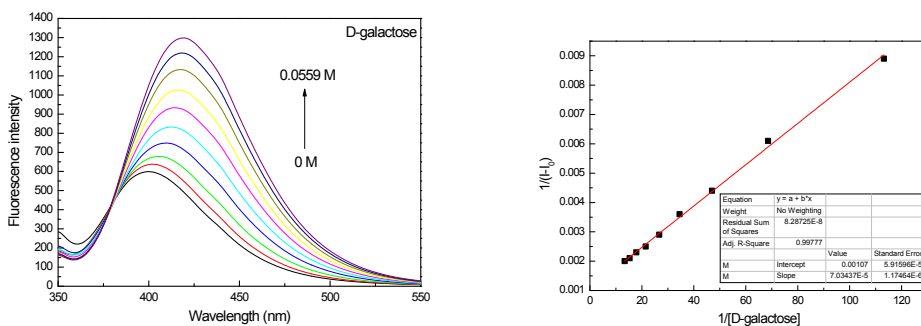


Fig. S15 Fluorescence response of sensor **6** (10^{-5} M) with increasing D-galactose concentration (0 M to 0.0559 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi-Hildebrand plot of sensor **6** $1/(I - I_0)$ versus $1/[D\text{-galactose}]$

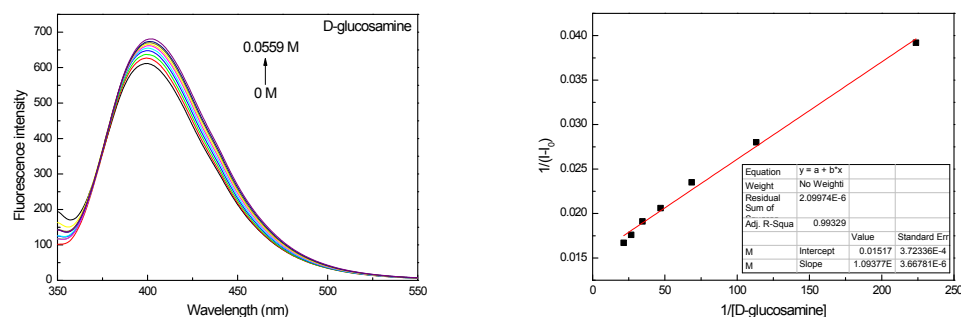


Fig. S16 Fluorescence response of sensor **6** (10^{-5} M) with increasing D-glucosamine concentration (0 M to 0.0559 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi-Hildebrand plot of sensor **6** $1/(I - I_0)$ versus $1/[D\text{-glucosamine}]$

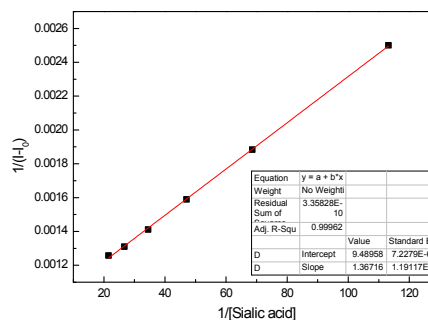
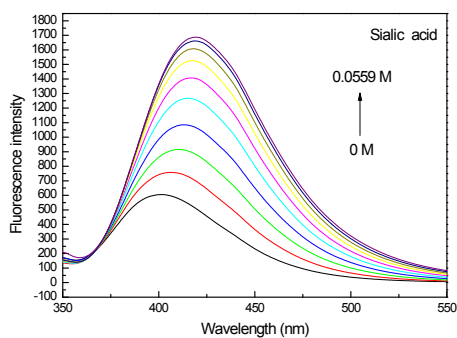


Fig. S17 Fluorescence response of sensor **6** (10^{-5} M) with increasing sialic acid concentration (0 M to 0.0559 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi–Hildebrand plot of sensor **6** $1/(I - I_0)$ versus $1/[\text{Sialic acid}]$

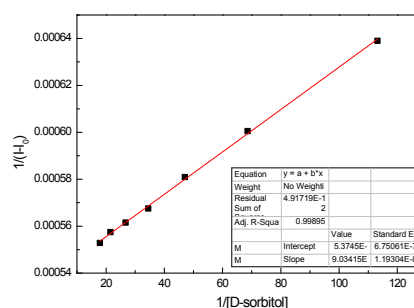
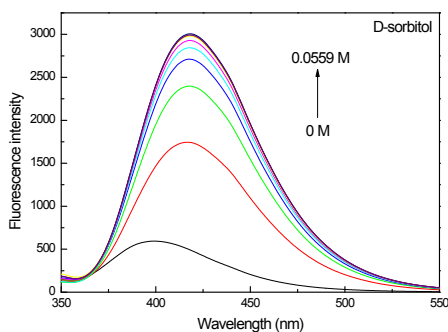


Fig. S18 Fluorescence response of sensor **6** (10^{-5} M) with increasing D-sorbitol concentration (0 M to 0.0559 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi–Hildebrand plot of sensor **6** $1/(I - I_0)$ versus $1/[\text{D-sorbitol}]$

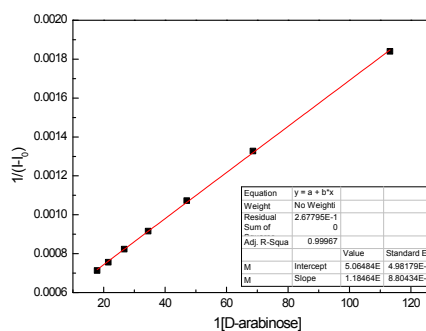
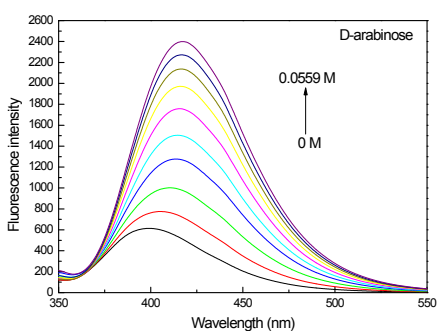


Fig. S19 Fluorescence response of sensor **6** (10^{-5} M) with increasing D-arabinose concentration (0 M to 0.0559 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi–Hildebrand plot of sensor **6** $1/(I - I_0)$ versus $1/[\text{D-arabinose}]$

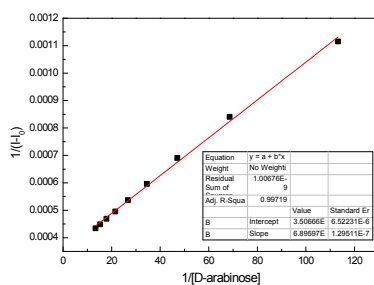
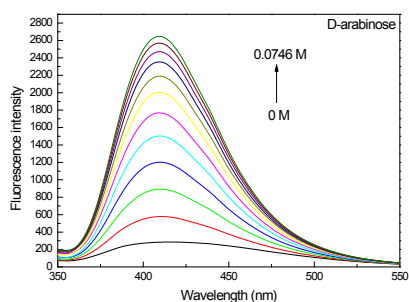


Fig. S20 Fluorescence response of sensor **1** (10^{-5} M) with increasing D-arabinose concentration (0 M to 0.0746 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi-Hildebrand plot of sensor **1** $1/(I - I_0)$ versus $1/[D\text{-arabinose}]$

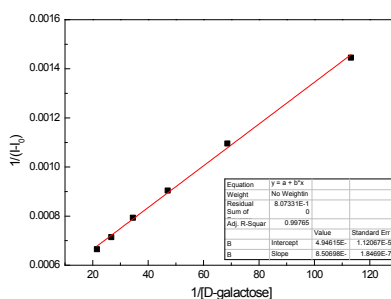
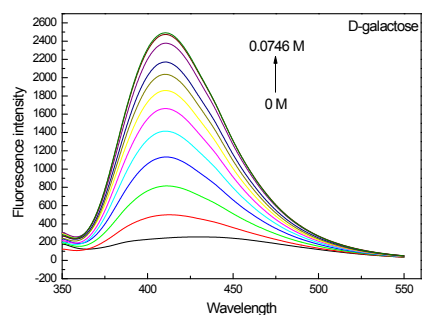


Fig. S21 Fluorescence response of sensor **1** (10^{-5} M) with increasing D-galactose concentration (0 M to 0.0746 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi-Hildebrand plot of sensor **1** $1/(I - I_0)$ versus $1/[D\text{-galactose}]$

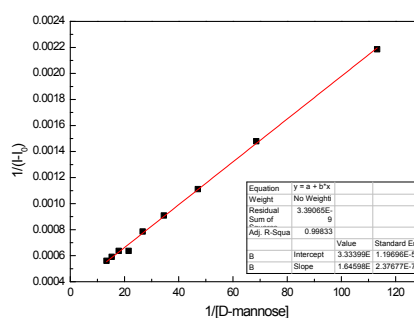
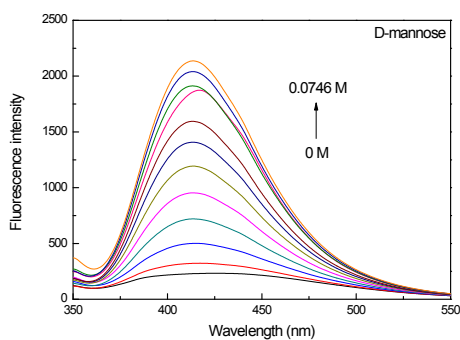


Fig.

S22 Fluorescence response of sensor **1** (10^{-5} M) with increasing D-mannose concentration (0 M to 0.0749 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi-Hildebrand plot of sensor **1** $1/(I - I_0)$ versus $1/[D\text{-mannose}]$

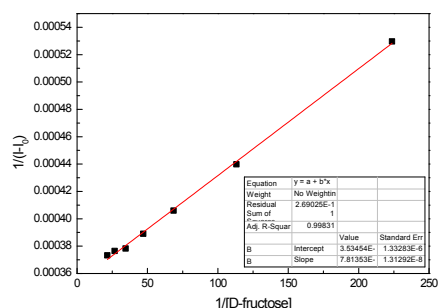
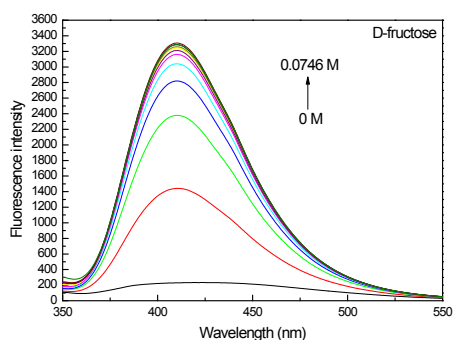


Fig. S23 Fluorescence response of sensor **1** (10^{-5} M) with increasing D-fructose concentration (0 M to 0.0746 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi-Hildebrand plot of sensor **1** $1/(I - I_0)$ versus $1/[D\text{-fructose}]$

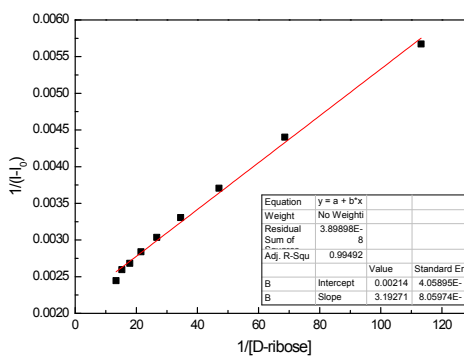
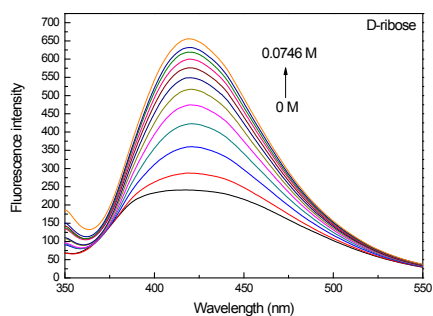


Fig. S24 Fluorescence response of sensor **1** (10^{-5} M) with increasing D-ribose concentration (0 M to 0.0746 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi-Hildebrand plot of sensor **1** $1/(I - I_0)$ versus $1/[D\text{-ribose}]$

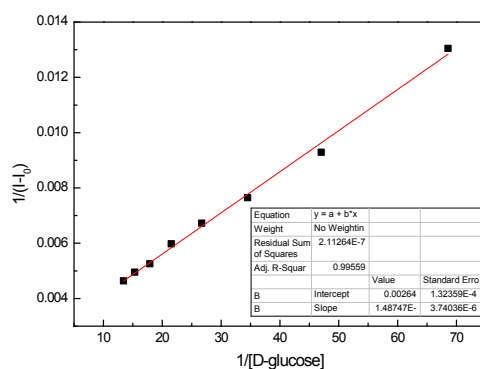
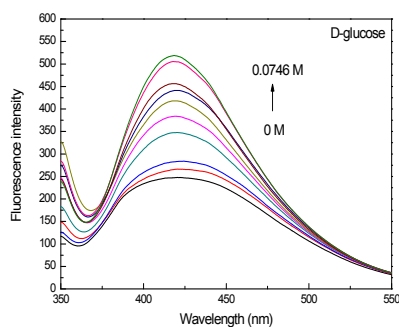


Fig. S25 Fluorescence response of sensor **1** (10^{-5} M) with increasing D-glucose concentration (0 M to 0.0746 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi-Hildebrand plot of sensor **1** $1/(I - I_0)$ versus $1/[D\text{-glucose}]$

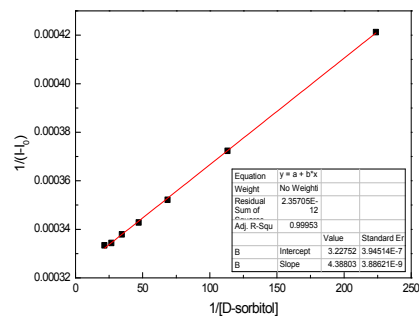
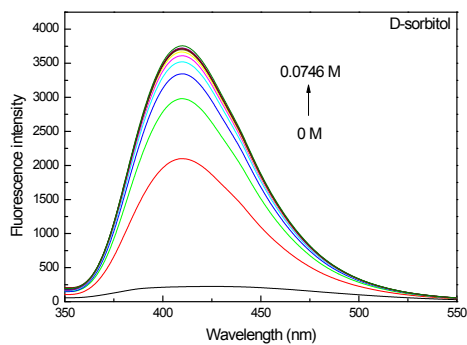


Fig.

S26 Fluorescence response of sensor **1** (10^{-5} M) with increasing D-sorbitol concentration (0 M to 0.0746 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi-Hildebrand plot of sensor **1** $1/(I - I_0)$ versus $1/[D\text{-sorbitol}]$

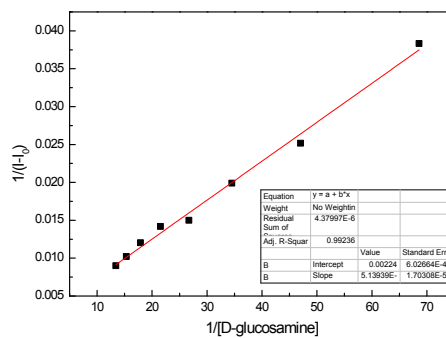
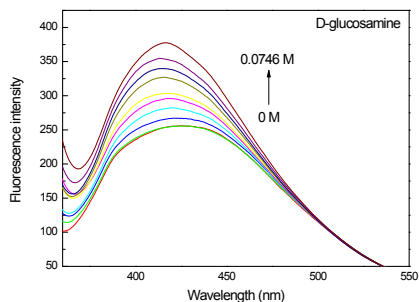


Fig. S27 Fluorescence response of sensor **1** (10^{-5} M) with increasing D-glucosamine concentration (0 M to 0.0746 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi-Hildebrand plot of sensor **1** $1/(I - I_0)$ versus $1/[D\text{-glucosamine}]$

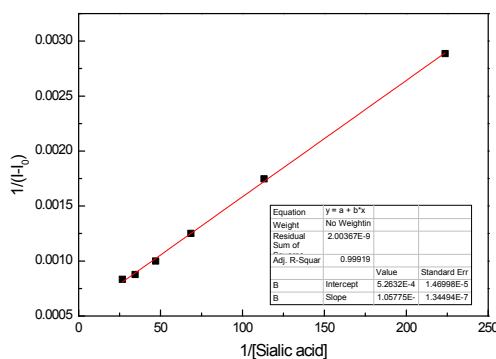
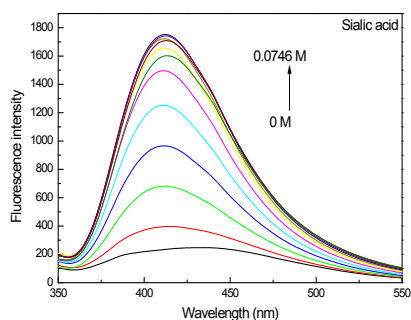


Fig. S28 Fluorescence response of sensor **1** (10^{-5} M) with increasing sialic acid concentration (0 M to 0.0746 M) in DMSO/H₂O (1:100, v/v, pH = 7.4, phosphate buffer, 0.1 M) and Benesi-Hildebrand plot of sensor **1** $1/(I - I_0)$ versus $1/[Sialic\ acid]$

1. H. Wang, G. Fang, K. Wang, Z. Wu and Q. Yao, *Analytical Letters*, 2018, 1-15.