

Borinic Acids: A Neglected Class of Organoboron Compounds for Recognition of Diols in Aqueous Solution

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Accessory Publication

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General Procedures. Stainless steel syringes were used to transfer all solutions. Commercial reagents were purchased from Sigma Aldrich, with the exception of 2-fluoro-5-nitrophenylboronic acid which was purchased from Synthonix, and were used as received. Distilled water was obtained from an in-house supply. Diphenylborinic acid was prepared according to a literature procedure.¹ Optical absorption spectra were collected at room temperature on a Varian Cary 5000 UV-Vis-NIR Spectrophotometer using 2.5 mL polystyrene cuvettes and corrected for background signal with a solvent-filled polystyrene cuvette. pH measurements were performed on a EcoMet P25 pH meter with a glass electrode. All solutions were prepared in 0.1 M sodium phosphate buffer in distilled water and adjusted to pH 7.0.

I. Determination of Binding Constants

Binding constants were determined by measuring the change in absorbance of solutions containing various concentrations of analyte. In general, solutions were prepared by one of two methods depending on the rate of equilibration of the solutions. In the case of rapid equilibration, aliquots of a concentrated guest stock solution were added to a host solution in a cuvette, allowed to equilibrate (~1 minute) and the absorbance of the solution was measured. In the case of slow

¹ Lee, D.; Newman, S. G.; Taylor, M. S. *Org. Lett.* **2009**, 11(23), 5486-5489.

equilibration, a set of separate solutions were prepared in cuvettes, allowed to equilibrate (30-120 minutes) and the absorbance of the solutions was measured.

Determination of binding constants (K_{HI}) between organoboron acid host and Alizarin Red S indicator.

A solution of Alizarin Red S (guest) was prepared (solution **A**). This solution was then used as the parent solution to prepare a host (organoboron acid) solution (solution **B**). Both solutions were adjusted to pH 7.0. Titration experiments were carried out by adding aliquots of solution **B** to a fixed volume of solution **A** by syringe and measuring the absorption spectrum upon achieving equilibrium. The elapsed time between addition of sample and absorbance measurements differed depending on the host used (~1 minute for 2-fluoro-5-nitrophenylboronic acid and up to 10 minutes for diphenylborinic acid). Concentrations of host were chosen to yield data such that the occupancy ratio $\beta = [\text{complex}]/[\text{guest}]_{\text{total}}$ would fall in the range $0.2 < \beta < 0.8$ as described by Hirose.² Changes in the absorbance of the UV-vis spectra were employed in determinations of K_{HI} . Graphs of ΔA (change in absorbance at 487 nm for diphenylborinic acid (**1a**); 454 nm for 2-fluoro-5-nitrophenylboronic acid (**1c**)) against [host] were curve-fitted to a 1:1 binding isotherm (eq. 1, see section II for derivations), using Igor Pro 5.0 (WaveMetrics, Inc.).

$$A_{\text{obs}} = A_I + \Delta\epsilon \left[\frac{K_{HI} I_t [H]}{1 + K_{HI} [H]} \right] \quad (1)$$

A_{obs} is the observed absorbance, A_I is the absorbance of the unbound indicator, $\Delta\epsilon = \epsilon_{HI} - \epsilon_I$ (ϵ_{HI} and ϵ_I are the molar absorption coefficients of the host-indicator complex and the indicator, respectively), I_t is the total concentration of indicator and [H] is defined by the quadratic,

$$K_{HI}[H]^2 + (K_{HI}I_t - K_{HI}H_t + 1)[H] - H_t = 0 \quad (2)$$

where H_t is the total host concentration. Initially estimated values for the parameters A_I , $\Delta\epsilon$ and K_{HI} allowed for the determination of the value of [H] from the positive quadratic root of equation (2). Subsequent iterative nonlinear curve-fitting of the experimental ΔA vs. H_t to equation (1) at a known I_t was then applied resulting in refinement of the parameters and yielding values for A_I , $\Delta\epsilon$ and K_{HI} .

² Hirose, K. *J. Inclusion Phenom. Macrocyclic Chem.* **2001**, 39, 193-209.

Determination of binding constants (K_{HG}) between organoboron acid host and diols and related substrates via indicator-displacement assay.

A solution of Alizarin Red S and organoboron acid was prepared such that the occupancy ratio of the indicator was ~80-90% (solution **C**). This solution was then used as the parent solution to prepare a substrate solution (solution **D**). Both solutions were adjusted to pH 7.0. Titration experiments were carried out by adding aliquots of solution **D** to a fixed volume of solution **C** by syringe or by preparing separate solutions in cuvettes of varying proportions of solutions **C** and **D** and measuring the absorption spectra upon achieving equilibrium. The elapsed time between solution preparation and absorbance measurements differed depending on the host used (~1 minute for 2-fluoro-5-nitrophenylboronic acid and up to 120 minutes for diphenylborinic acid). Concentrations of substrate were chosen to yield data such that the widest range of absorbance changes was observed under reasonable concentrations of substrate. Changes in the absorbance of the UV-vis spectra were employed in determinations of K_{HG} . Graphs of ΔA (change in absorbance at 487 nm for diphenylborinic acid (**1a**); 454 nm for 2-fluoro-5-nitrophenylboronic acid (**1c**)) against [substrate] were curve-fitted to a competitive binding isotherm (eq. 1, see section II for derivations), using Igor Pro 5.0 (WaveMetrics, Inc.).

$$A_{\text{obs}} = A_I + \Delta\epsilon \left[\frac{K_{HI}I_t[H]}{1 + K_{HI}[H]} \right] \quad (1)$$

A_{obs} is the observed absorbance, A_I is the absorbance of the unbound indicator, $\Delta\epsilon = \epsilon_{HI} - \epsilon_I$ (ϵ_{HI} and ϵ_I are the molar absorption coefficients of the host-indicator complex and the indicator, respectively), I_t is the total concentration of indicator and $[H]$ is defined by the cubic,

$$K_{HI}K_{HG}[H]^3 + (K_{HI} + K_{HG} + K_{HI}K_{HG}I_t + K_{HI}K_{HG}G_t - K_{HI}K_{HG}H_t)[H]^2 + (1 + K_{HI}I_t + K_{HI}G_t - K_{HI}H_t - K_{HG}H_t)[H] - H_t = 0 \quad (3)$$

where H_t and G_t are the total host and guest concentrations, respectively. Initially estimated values for the parameters A_I , $\Delta\epsilon$ and K_{HG} , and values of K_{HI} determined from previous experiments, allowed for the determination of the value of $[H]$ from equation (3). $[H]$ was solved for using a user-defined function in Igor, employing Newton's method,

$$x_2 = x_1 - \frac{f(x_1)}{f'(x_1)} \quad (4)$$

where x_1 is a first approximation to a root of $f(x)$, $f'(x)$ is the first derivative of $f(x)$, $f(x)$ represents the function described by equation (3) and x_2 is necessarily a better estimate of the root than x_1 . This process was repeated until $|x_2 - x_1| < 10^{-14}$, thus returning an excellent approximation of the root wherein $[H] = x_2$. Subsequent iterative nonlinear curve-fitting of the experimental ΔA vs. G_t to equation (1) at known I_t and H_t was then applied resulting in refinement of the parameters and yielding values for A_I , $\Delta \epsilon$ and K_{HI} .

II. Derivations of Binding Equations

Derivation of equations describing binding (K_{HI}) between organoboron acid host and Alizarin Red S indicator.

The equilibrium between the host (organoboron acid) and indicator (Alizarin Red S) is described by equation (5),

$$K_{HI} = \frac{[HI]}{[H][I]} \quad (5)$$

where $[HI]$, $[H]$ and $[I]$ are the concentrations of host-indicator complex, unbound host and unbound indicator, respectively and K_{HI} is the host-indicator equilibrium constant.

The mass balance equations for the indicator and host are described by equations (6) and (7),

$$I_t = [I] + [HI] \quad (6)$$

$$H_t = [H] + [HI] \quad (7)$$

where I_t and H_t are the total concentrations of indicator and host, respectively.

Solving equation (6) for $[I]$ and equation (7) for $[HI]$, substituting into equation (5), expanding, rearranging and collecting like terms yields the quadratic equation (2).

$$K_{HI}[H]^2 + (K_{HI}I_t - K_{HI}H_t + 1)[H] - H_t = 0 \quad (2)$$

By applying the Beer-Lambert Law to the indicator-host system, and substituting a cell length of 1 cm, equation (8) can be obtained, which describes the observed absorbance with respect to the indicator and host-indicator concentrations.

$$A_{\text{obs}} = \epsilon_{\text{I}}[\text{I}] + \epsilon_{\text{HI}}[\text{HI}] \quad (8)$$

A_{obs} is the observed absorbance at a given wavelength and ϵ_{I} and ϵ_{HI} are the molar absorption coefficients of the indicator and indicator-host complex, respectively.

Solving equation (6) for [I], substituting into equation (8), expanding and collecting like terms yields equation (9).

$$A_{\text{obs}} = \epsilon_{\text{I}}I_{\text{t}} + (\epsilon_{\text{HI}} - \epsilon_{\text{I}})[\text{HI}] \quad (9)$$

Substituting for the absorbance of the unbound indicator, A_{I} , and defining $\Delta\epsilon = \epsilon_{\text{HI}} - \epsilon_{\text{I}}$ and substituting yields equation (10).

$$A_{\text{obs}} = A_{\text{I}} + \Delta\epsilon[\text{HI}] \quad (10)$$

Solving equation (6) for [I], substituting into equation (5), expanding and rearranging in terms of [HI] yields equation (11),

$$[\text{HI}] = \frac{K_{\text{HI}}I_{\text{t}}[\text{H}]}{1 + K_{\text{HI}}[\text{H}]} \quad (11)$$

which upon substitution into equation (10) yields equation (1).

$$A_{\text{obs}} = A_{\text{I}} + \Delta\epsilon \left[\frac{K_{\text{HI}}I_{\text{t}}[\text{H}]}{1 + K_{\text{HI}}[\text{H}]} \right] \quad (1)$$

Derivation of equations describing binding (K_{HG}) between organoboron acid host and diols and related substrates via indicator-displacement assay.

The equilibria between the host (organoboron acid) and indicator (Alizarin Red S) and host and substrate (guest) are described by equations (5) and (12),

$$K_{HI} = \frac{[HI]}{[H][I]} \quad (5)$$

$$K_{HG} = \frac{[HG]}{[H][G]} \quad (12)$$

where $[HI]$, $[HG]$, $[H]$, $[I]$ and $[G]$ are the concentrations of host-indicator complex, host-guest complex, unbound host, unbound indicator and unbound guest, respectively and K_{HI} and K_{HG} are the host-indicator and host-guest equilibrium constants, respectively.

The mass balance equations for the indicator, host and guest are described by equations (6), (13) and (14),

$$I_t = [I] + [HI] \quad (6)$$

$$H_t = [H] + [HI] + [HG] \quad (13)$$

$$G_t = [G] + [HG] \quad (14)$$

where I_t , H_t and G_t are the total concentrations of host, indicator and guest, respectively.

Solving equation (6) for $[I]$, substituting into equation (5), expanding and rearranging in terms of $[HI]$ yields equation (11),

$$[HI] = \frac{K_{HI}I_t[H]}{1 + K_{HI}[H]} \quad (11)$$

and by analogy, solving equation (14) for $[G]$, substituting into equation (12), expanding and rearranging in terms of $[HG]$ yields equation (15).

$$[\text{HG}] = \frac{K_{\text{HG}}G_{\text{t}}[\text{H}]}{1 + K_{\text{HG}}[\text{H}]} \quad (15)$$

Substituting equations (11) and (15) into equation (13), expanding, rearranging and collecting like terms yields the cubic equation (3).

$$K_{\text{HI}}K_{\text{HG}}[\text{H}]^3 + (K_{\text{HI}} + K_{\text{HG}} + K_{\text{HI}}K_{\text{HG}}I_{\text{t}} + K_{\text{HI}}K_{\text{HG}}G_{\text{t}} - K_{\text{HI}}K_{\text{HG}}H_{\text{t}})[\text{H}]^2 + (1 + K_{\text{HI}}I_{\text{t}} + K_{\text{HI}}G_{\text{t}} - K_{\text{HI}}H_{\text{t}} - K_{\text{HG}}H_{\text{t}})[\text{H}] - H_{\text{t}} = 0 \quad (3)$$

Equation (3) describes the indicator-displacement in terms of one unknown variable [H] and can be applied in the fitting to the modified Beer-Lambert equation (1), which was derived in the previous section.

III. UV-Vis Titration Data

For binding constants calculated based on UV-Vis titrations, changes in absorbance ΔA are plotted against substrate concentration (M). The curves obtained by fitting to a 1:1 or competitive binding isotherm are shown.

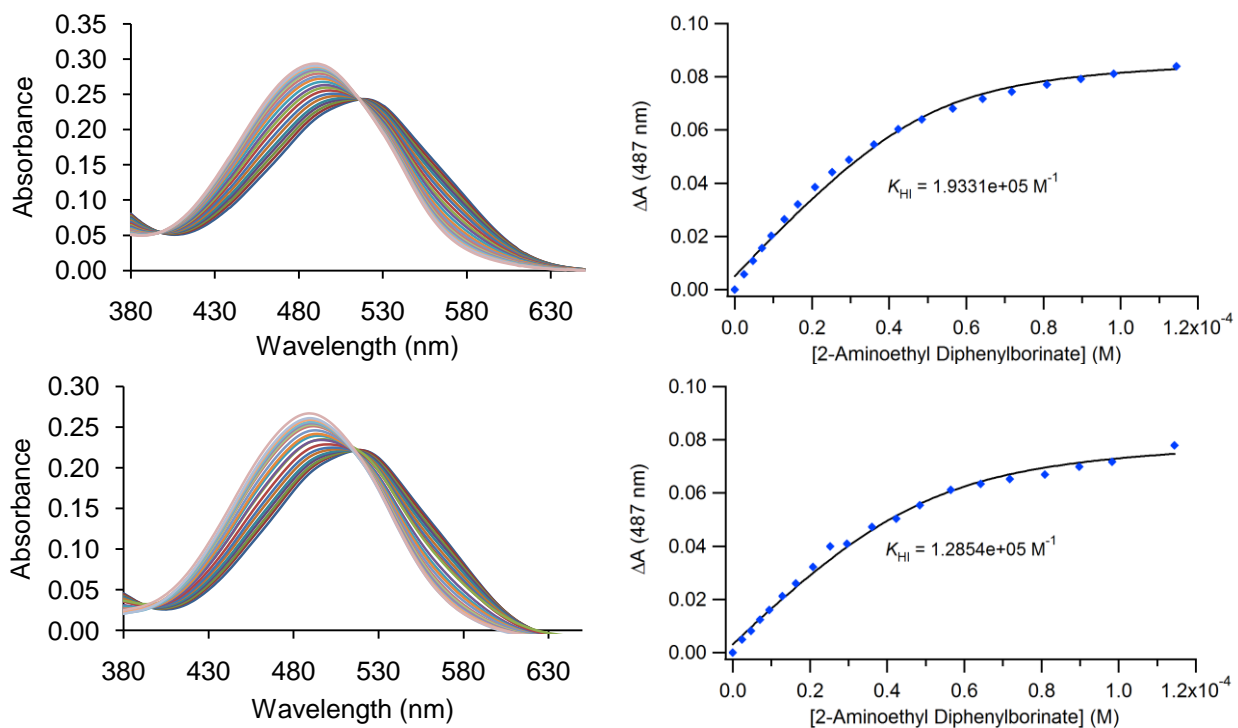


Figure S1. UV-vis titration of Alizarin Red S (ARS, 0.05 mM) with 2-aminoethyl diphenylborinate (**1d**) and the corresponding 1:1 binding isotherms (H_2O , 0.1 M sodium phosphate buffer, pH 7.0, 295 K). Two trials shown.

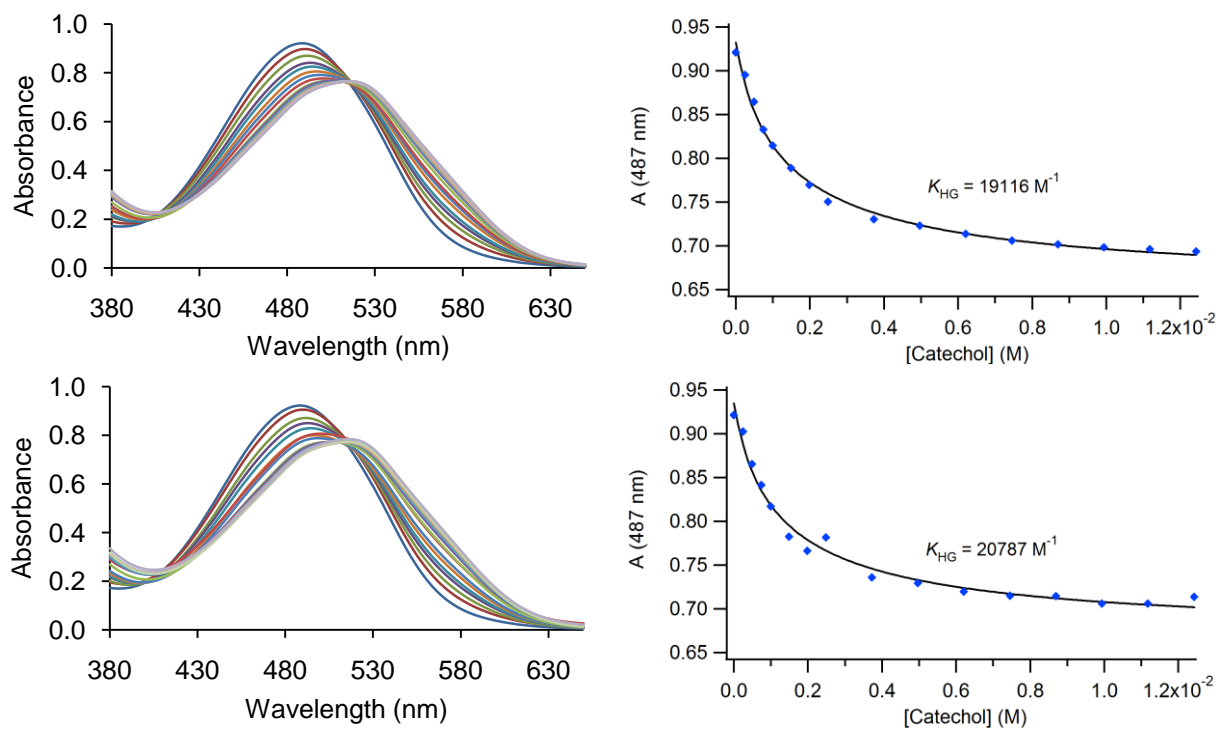


Figure S2. UV-vis spectra of the indicator displacement assay of 2-aminoethyl diphenylborinate (**1d**, 0.19 mM)-Alizarin Red S (**ARS**, 0.15 mM) with catechol and the corresponding competitive binding isotherms (H_2O , 0.1 M sodium phosphate buffer, pH 7.0, 295 K). Two trials shown.

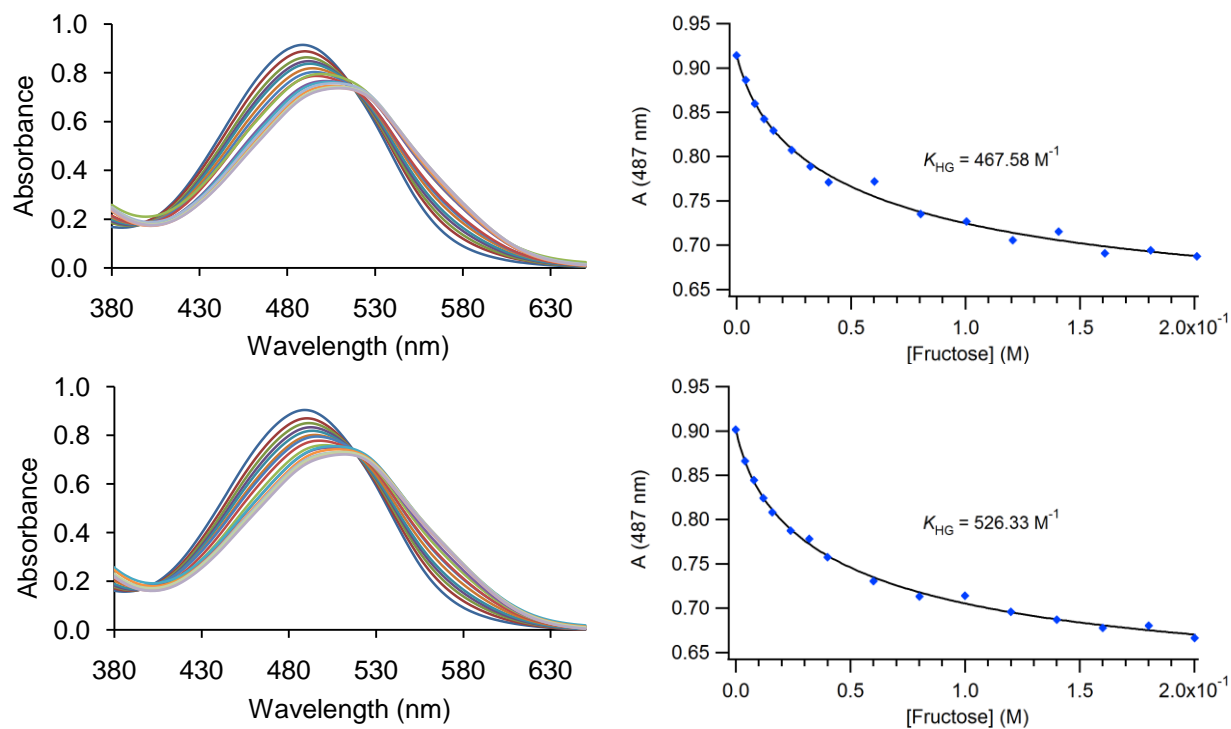


Figure S3. UV-vis spectra of the indicator displacement assay of 2-aminoethyl diphenylborinate (**1d**, 0.19 mM)-Alizarin Red S (**ARS**, 0.15 mM) with D-fructose and the corresponding competitive binding isotherms (H₂O, 0.1 M sodium phosphate buffer, pH 7.0, 295 K). Two trials shown.

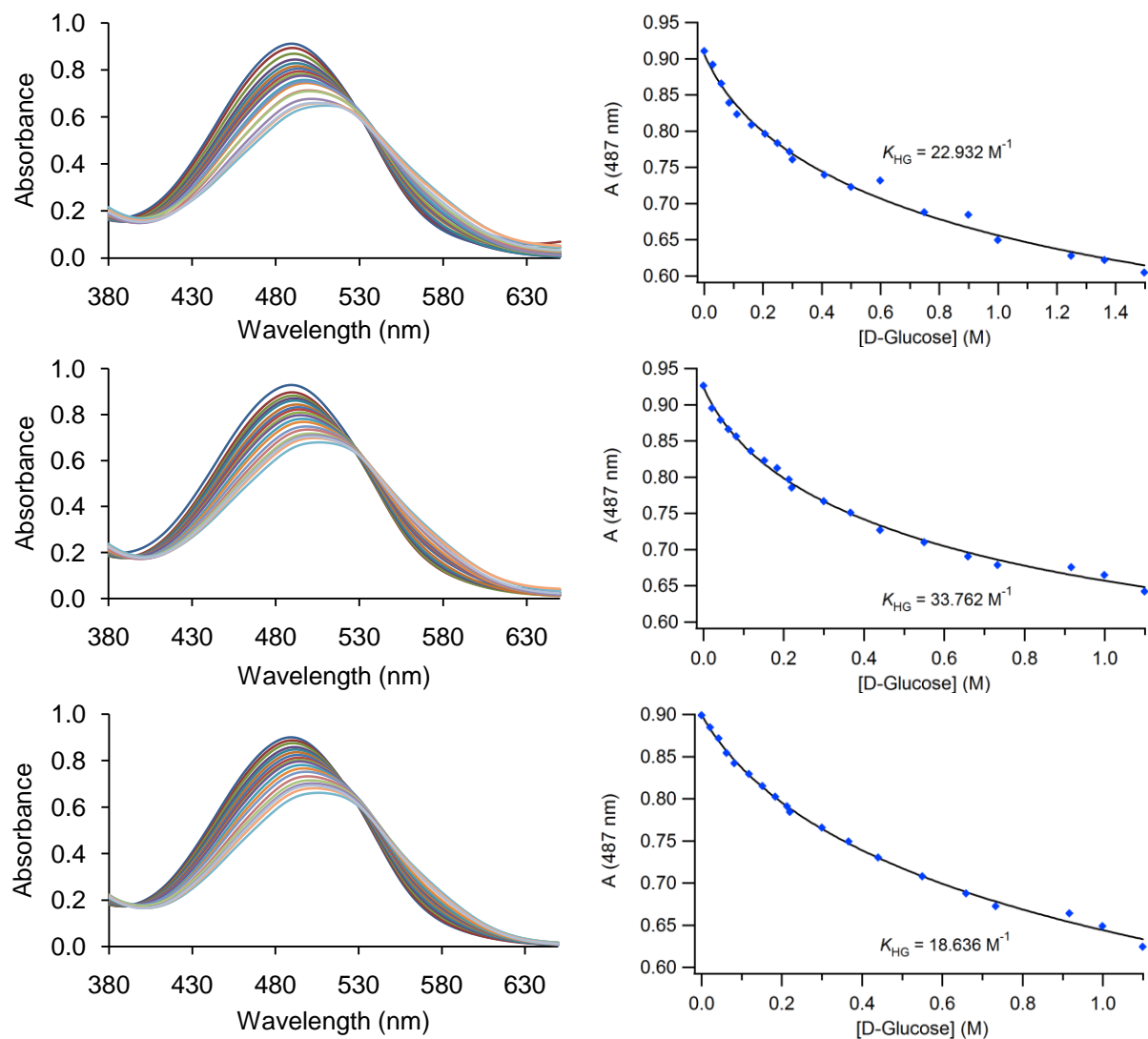


Figure S4. UV-vis spectra of the indicator displacement assay of 2-aminoethyl diphenylborinate (**1d**, 0.19 mM)-Alizarin Red S (ARS, 0.15 mM) with glucose and the corresponding competitive binding isotherms (H_2O , 0.1 M sodium phosphate buffer, pH 7.0, 295 K). Three trials shown; middle and bottom trial determined with diphenylborinic acid (**1a**) in place of 2-aminoethyl diphenylborinate.

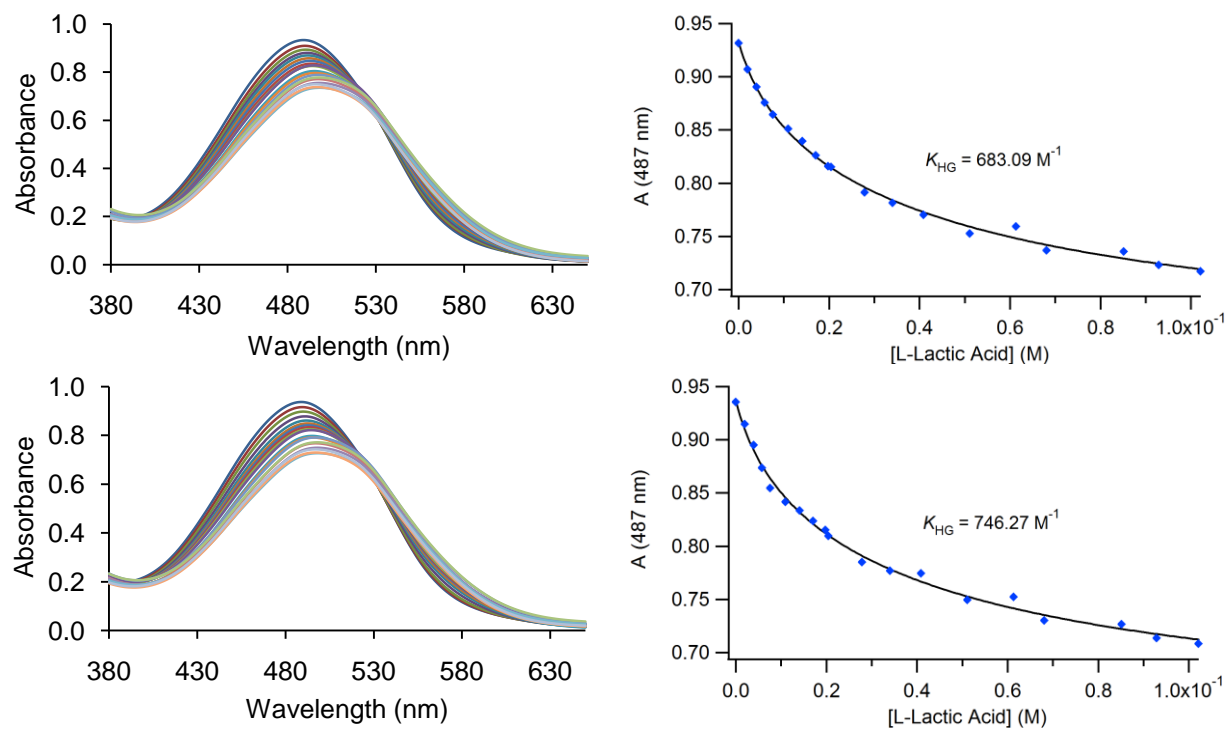


Figure S5. UV-vis spectra of the indicator displacement assay of 2-aminoethyl diphenylborinate acid (**1d**, 0.19 mM)-Alizarin Red S (**ARS**, 0.15 mM) with L-lactic acid and the corresponding competitive binding isotherms (H_2O , 0.1 M sodium phosphate buffer, pH 7.0, 295 K). Two trials shown.

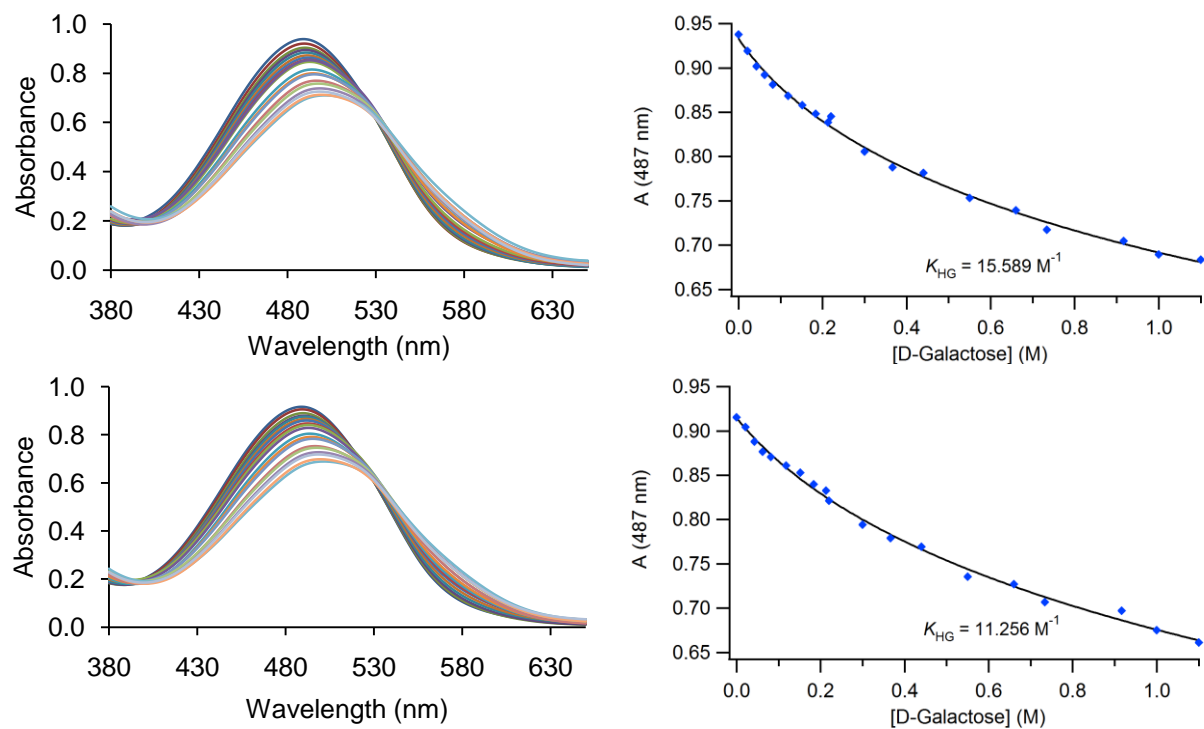


Figure S6. UV-vis spectra of the indicator displacement assay of 2-aminoethyl diphenylborinate acid (**1d**, 0.19 mM)-Alizarin Red S (**ARS**, 0.15 mM) with D-galactose and the corresponding competitive binding isotherms (H₂O, 0.1 M sodium phosphate buffer, pH 7.0, 295 K). Two trials shown.

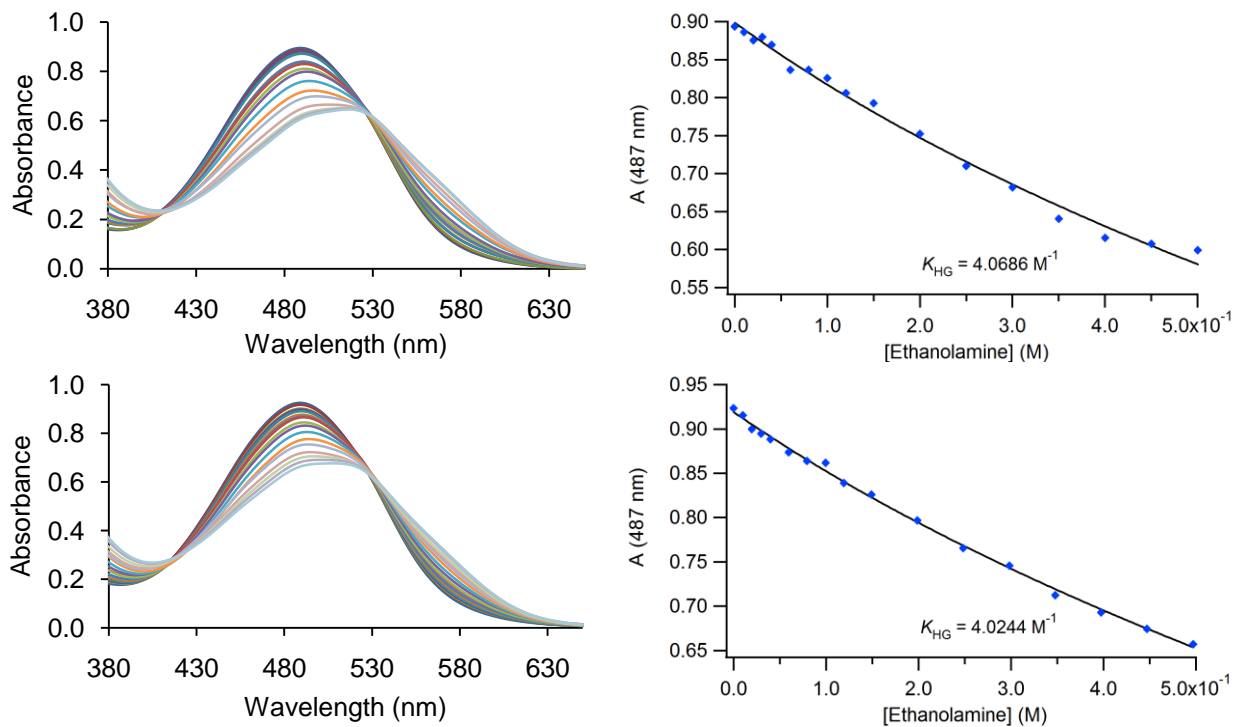


Figure S7. UV-vis spectra of the indicator displacement assay of 2-aminoethyl diphenylborinate (**1d**, 0.18 mM)-Alizarin Red S (**ARS**, 0.15 mM) with ethanolamine and the corresponding competitive binding isotherms (H₂O, 0.1 M sodium phosphate buffer, pH 7.0, 295 K). Two trials shown.

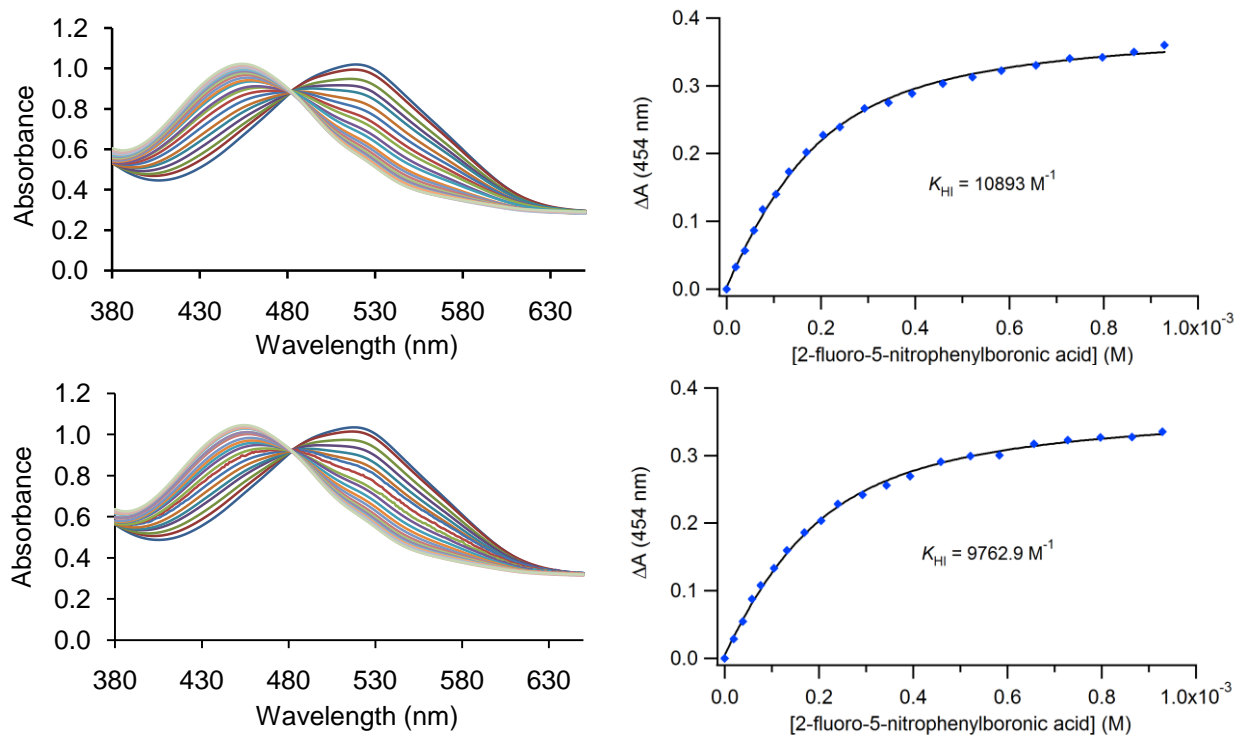


Figure S8. UV-vis titration of Alizarin Red S (**ARS**, 0.15 mM) with 2-fluoro-5-nitrophenylboronic acid (**1c**) and the corresponding 1:1 binding isotherms (H_2O , 0.1 M sodium phosphate buffer, pH 7.0, 295 K). Two trials shown.

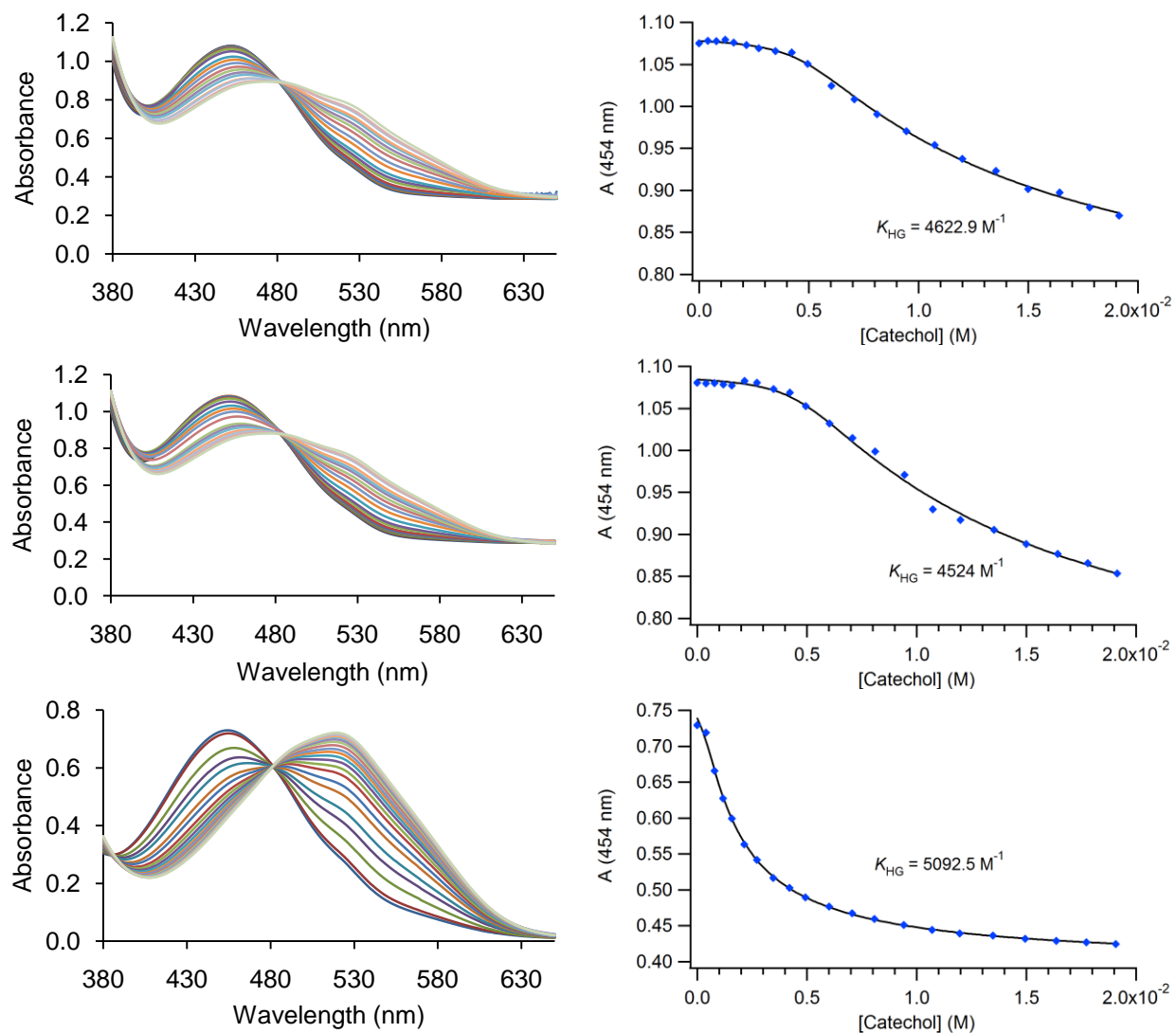


Figure S9. UV-vis spectra of the indicator displacement assay of 2-fluoro-5-nitrophenylboronic acid (**1c**, 5.1 mM for top and middle trials; 0.7 mM for bottom trial)-Alizarin Red S (ARS, 0.15 mM) with catechol and the corresponding competitive binding isotherms (H_2O , 0.1 M sodium phosphate buffer, pH 7.0, 295 K). Three trials shown.

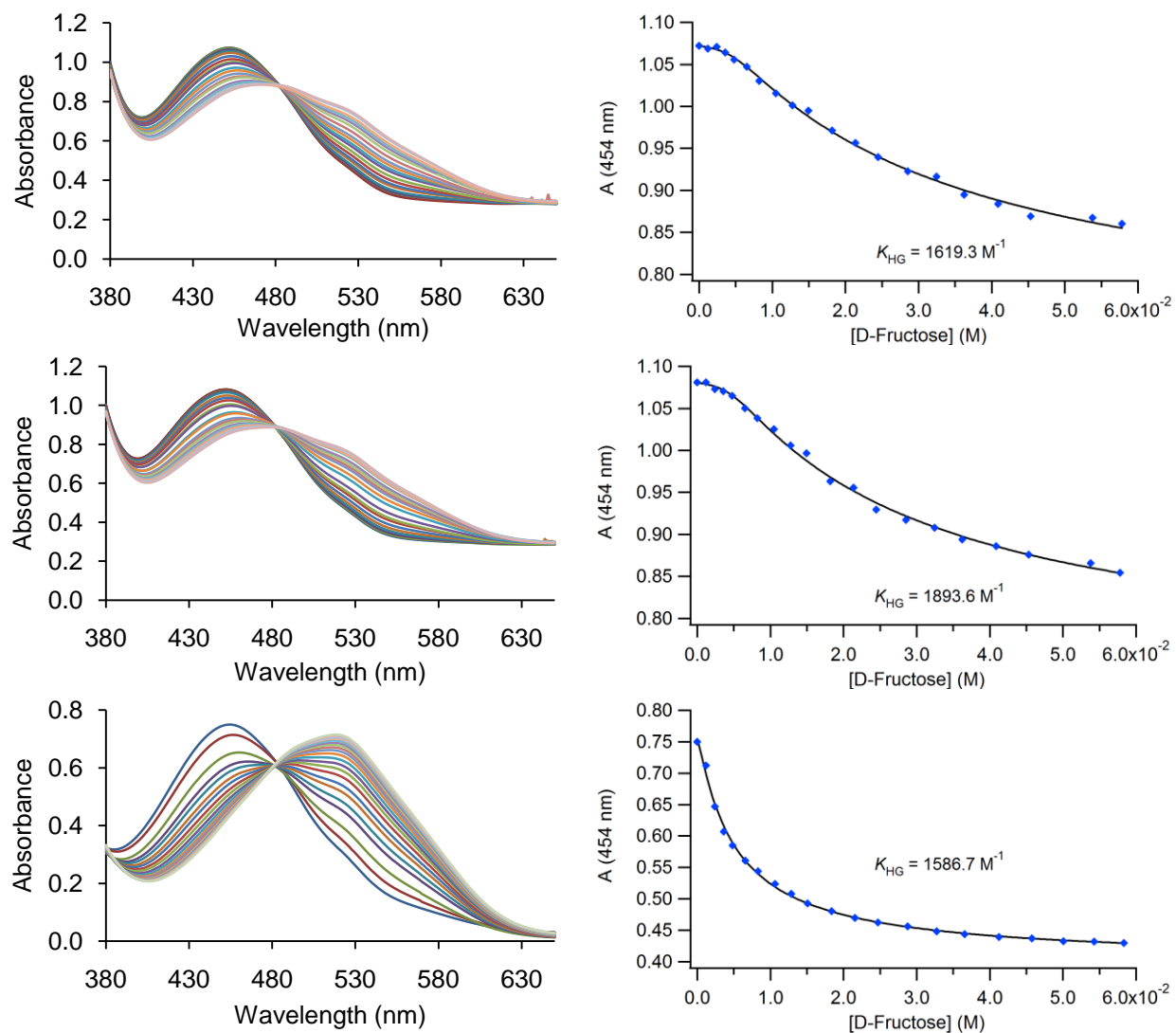


Figure S10. UV-vis spectra of the indicator displacement assay of 2-fluoro-5-nitrophenylboronic acid (**1c**, 5.1 mM for top and middle trials; 0.7 mM for bottom trial)-Alizarin Red S (ARS, 0.15 mM) with D-fructose and the corresponding competitive binding isotherms (H_2O , 0.1 M sodium phosphate buffer, pH 7.0, 295 K). Three trials shown.

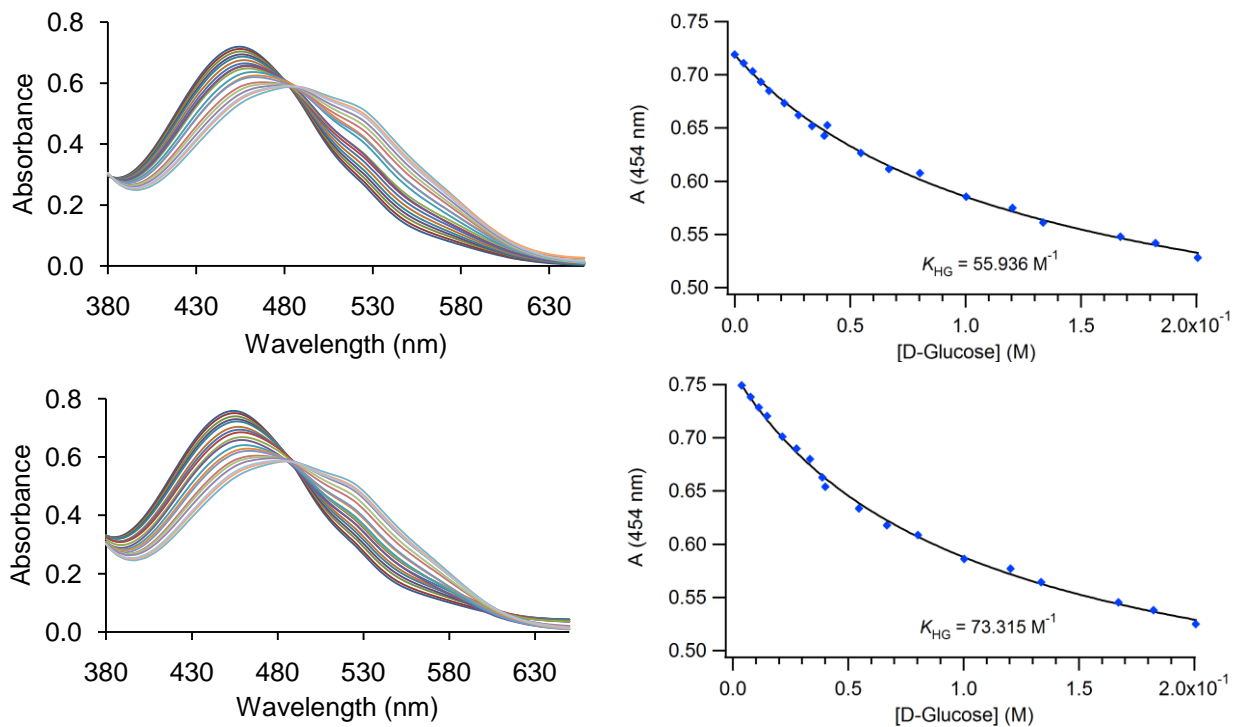


Figure S11. UV-vis spectra of the indicator displacement assay of 2-fluoro-5-nitrophenylboronic acid (**1c**, 0.7 mM)-Alizarin Red S (**ARS**, 0.15 mM) with D-glucose and the corresponding competitive binding isotherms (H₂O, 0.1 M sodium phosphate buffer, pH 7.0, 295 K). Two trials shown.

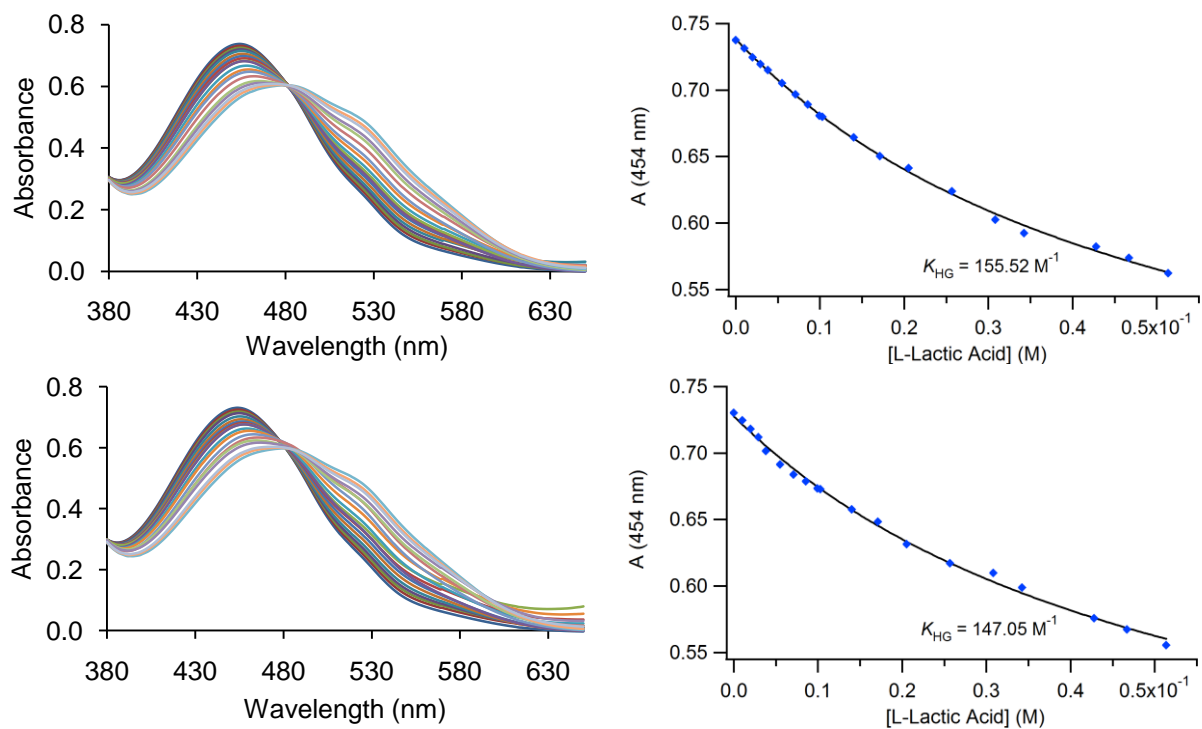


Figure S12. UV-vis spectra of the indicator displacement assay of 2-fluoro-5-nitrophenylboronic acid (**1c**, 0.8 mM)-Alizarin Red S (**ARS**, 0.15 mM) with L-lactic acid and the corresponding competitive binding isotherms (H₂O, 0.1 M sodium phosphate buffer, pH 7.0, 295 K). Two trials shown.

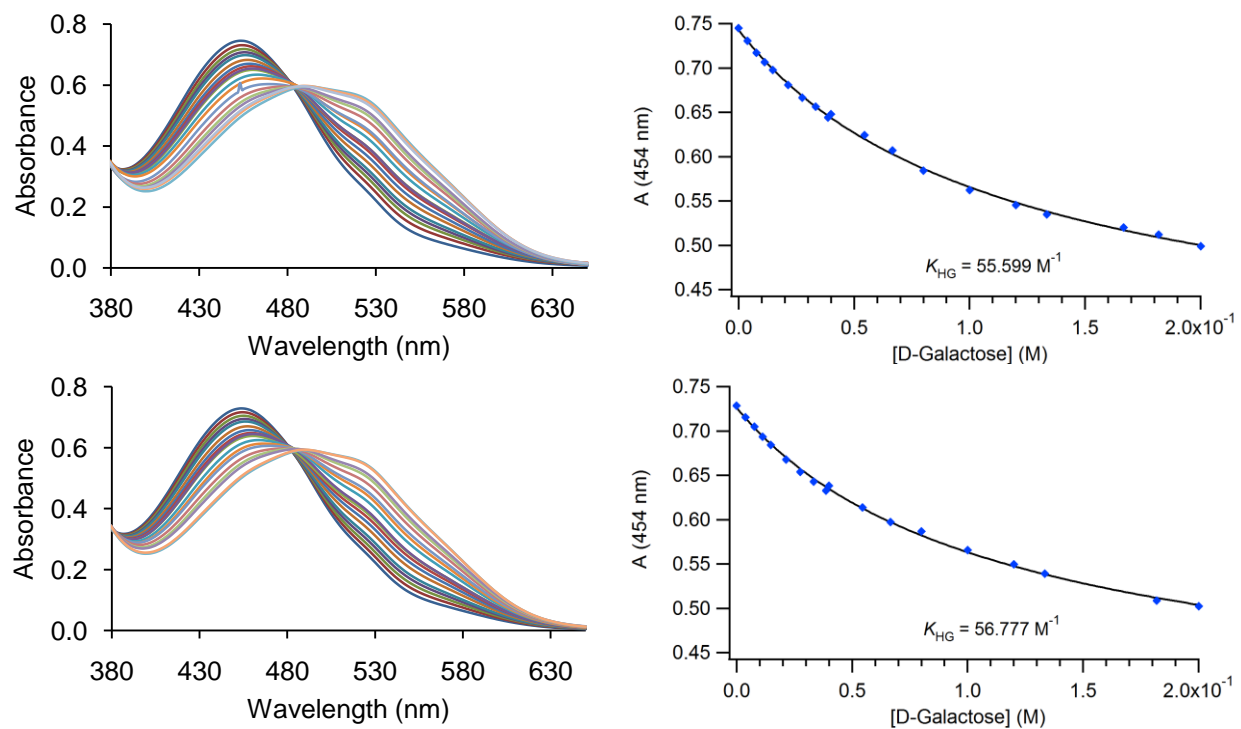


Figure S13. UV-vis spectra of the indicator displacement assay of 2-fluoro-5-nitrophenylboronic acid (**1c**, 0.6 mM)-Alizarin Red S (**ARS**, 0.15 mM) with D-galactose and the corresponding competitive binding isotherms (H₂O, 0.1 M sodium phosphate buffer, pH 7.0, 295 K). Two trials shown.

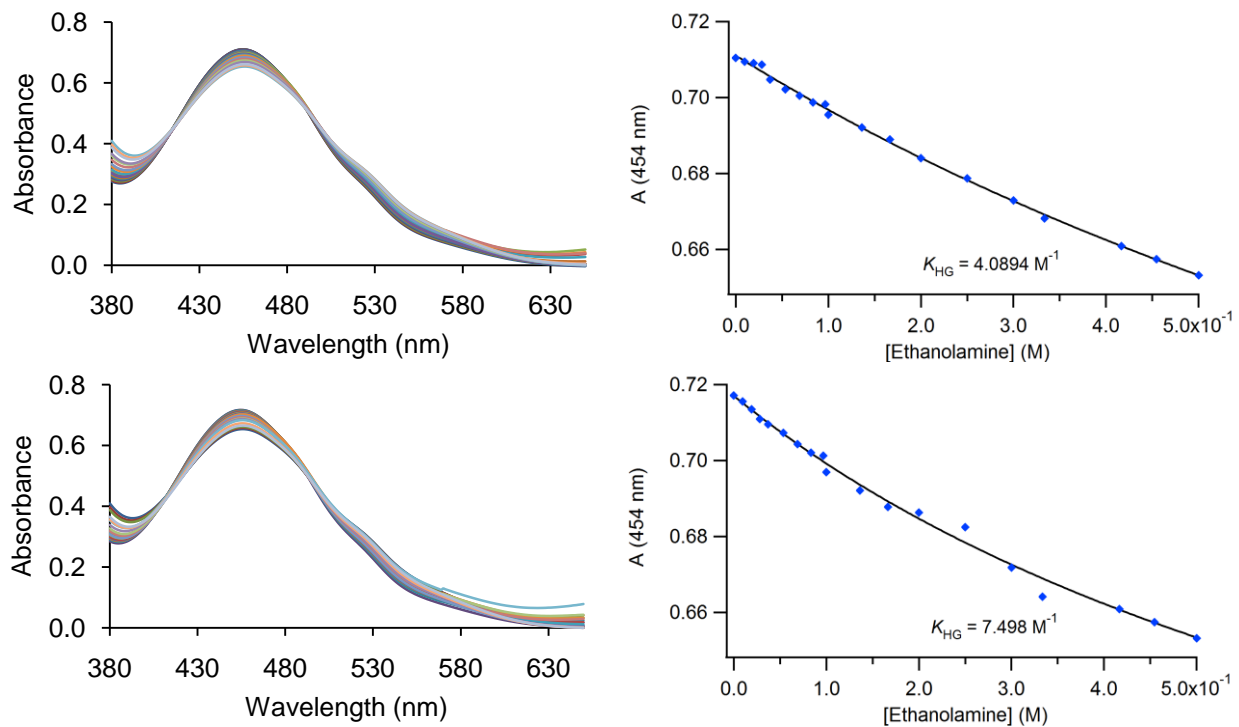


Figure S14. UV-vis spectra of the indicator displacement assay of 2-fluoro-5-nitrophenylboronic acid (**1c**, 0.7 mM)-Alizarin Red S (**ARS**, 0.15 mM) with ethanolamine and the corresponding competitive binding isotherms (H₂O, 0.1 M sodium phosphate buffer, pH 7.0, 295 K). Two trials shown.

IV. Details of Computational Studies

Calculations were carried out with the Gaussian '09 software package,³ on a Linux workstation equipped with two quad-core AMD Shanghai processors built by HardData, Inc. Edmonton, Alberta, Canada).

Geometry optimizations of the complexes were performed using density functional theory (B3LYP functional), with the 6-31+G(d,p) basis set for all atoms. Frequency calculations at the same level of theory demonstrated that the optimum structures had no imaginary vibrational frequencies. The calculated energies (Hartrees), zero-point energy corrections, and geometries (Cartesian coordinates, Å) of all complexes are provided on the pages that follow.

³ Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

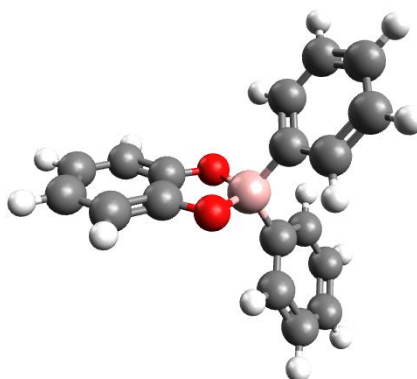
Complexes of organoboron acids with substrates

1a---Catechol

Imaginary frequencies: none

$E = -869.8615296$

ZPE correction: 0.2719726



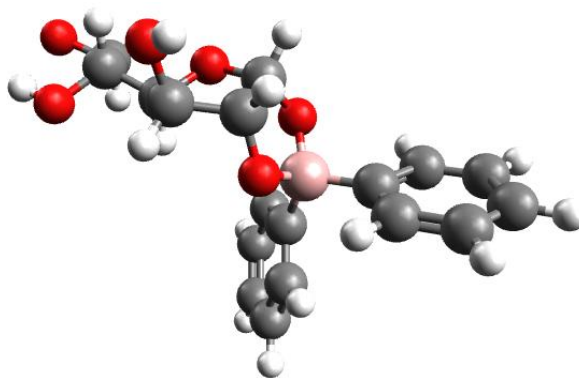
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---------------|---------------|-------------|-------------------------|-----------|-----------|
| | | | X | Y | Z |
| 1 | 6 | 0 | -4.516813 | -0.026294 | 0.697045 |
| 2 | 6 | 0 | -3.302807 | -0.052815 | 1.419259 |
| 3 | 6 | 0 | -2.109413 | -0.028436 | 0.707955 |
| 4 | 6 | 0 | -2.109421 | 0.026647 | -0.707993 |
| 5 | 6 | 0 | -3.302817 | 0.050484 | -1.419309 |
| 6 | 6 | 0 | -4.516818 | 0.023398 | -0.697108 |
| 7 | 1 | 0 | -5.459827 | -0.045779 | 1.238684 |
| 8 | 1 | 0 | -3.291093 | -0.091176 | 2.505151 |
| 9 | 1 | 0 | -3.291110 | 0.088853 | -2.505201 |
| 10 | 1 | 0 | -5.459836 | 0.042457 | -1.238755 |
| 11 | 8 | 0 | -0.855702 | 0.051238 | -1.194395 |
| 12 | 8 | 0 | -0.855694 | -0.052506 | 1.194365 |
| 13 | 6 | 0 | 1.002229 | 1.356672 | 0.057682 |
| 14 | 6 | 0 | 0.952426 | 2.331223 | -0.955259 |
| 15 | 6 | 0 | 1.868694 | 1.614410 | 1.138092 |
| 16 | 6 | 0 | 1.722852 | 3.499766 | -0.899674 |
| 17 | 1 | 0 | 0.287217 | 2.165218 | -1.799289 |
| 18 | 6 | 0 | 2.637735 | 2.779195 | 1.212201 |
| 19 | 1 | 0 | 1.940106 | 0.883813 | 1.941989 |
| 20 | 6 | 0 | 2.570271 | 3.731184 | 0.187504 |
| 21 | 1 | 0 | 1.658446 | 4.231811 | -1.703316 |
| 22 | 1 | 0 | 3.292578 | 2.945771 | 2.066008 |
| 23 | 1 | 0 | 3.169411 | 4.638173 | 0.237706 |
| 24 | 6 | 0 | 1.003607 | -1.356048 | -0.057644 |
| 25 | 6 | 0 | 1.870505 | -1.612821 | -1.137938 |
| 26 | 6 | 0 | 0.954591 | -2.330760 | 0.955178 |
| 27 | 6 | 0 | 2.640675 | -2.776862 | -1.212060 |
| 28 | 1 | 0 | 1.941369 | -0.882060 | -1.941732 |
| 29 | 6 | 0 | 1.726159 | -3.498547 | 0.899588 |
| 30 | 1 | 0 | 0.289108 | -2.165491 | 1.799138 |
| 31 | 6 | 0 | 2.573969 | -3.729031 | -0.187485 |
| 32 | 1 | 0 | 3.295810 | -2.942699 | -2.065786 |
| 33 | 1 | 0 | 1.662346 | -4.230732 | 1.703149 |
| 34 | 1 | 0 | 3.173979 | -4.635444 | -0.237694 |
| 35 | 5 | 0 | 0.097784 | -0.000153 | -0.000005 |

1a---Glucose

Imaginary frequencies: none

$E = -1174.3569429$

ZPE correction: 0.3586383



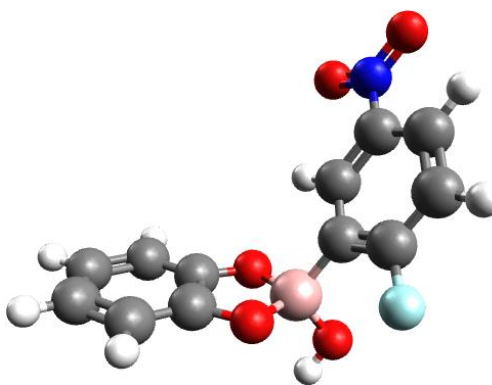
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
| | | | X | Y | Z |
| 1 | 6 | 0 | -2.458095 | -0.492060 | -0.170902 |
| 2 | 8 | 0 | -1.942043 | -0.838258 | 1.118176 |
| 3 | 6 | 0 | -0.591520 | -1.354447 | 0.966935 |
| 4 | 6 | 0 | -0.431128 | -1.667282 | -0.553440 |
| 5 | 6 | 0 | -1.849666 | -1.519054 | -1.132258 |
| 6 | 1 | 0 | -2.097721 | 0.502331 | -0.474960 |
| 7 | 1 | 0 | -0.554459 | -2.225816 | 1.633432 |
| 8 | 1 | 0 | -0.042437 | -2.690982 | -0.724269 |
| 9 | 1 | 0 | -1.824047 | -1.150498 | -2.163375 |
| 10 | 6 | 0 | -3.981398 | -0.457057 | -0.088857 |
| 11 | 1 | 0 | -4.356522 | -1.473146 | 0.090658 |
| 12 | 8 | 0 | -5.893889 | 0.495865 | 0.969413 |
| 13 | 1 | 0 | -6.209539 | 1.209567 | 1.535311 |
| 14 | 8 | 0 | -2.591172 | -2.746800 | -1.048496 |
| 15 | 1 | 0 | -2.031497 | -3.447871 | -1.405864 |
| 16 | 8 | 0 | 0.424963 | -0.687920 | -1.059226 |
| 17 | 8 | 0 | 0.381031 | -0.440217 | 1.289094 |
| 18 | 6 | 0 | 2.699230 | -0.716558 | 0.186299 |
| 19 | 6 | 0 | 3.331332 | -1.321269 | -0.916504 |
| 20 | 6 | 0 | 3.433455 | -0.685579 | 1.388537 |
| 21 | 6 | 0 | 4.621639 | -1.860819 | -0.833843 |
| 22 | 1 | 0 | 2.786750 | -1.377574 | -1.857192 |
| 23 | 6 | 0 | 4.721318 | -1.221054 | 1.489002 |
| 24 | 1 | 0 | 2.975193 | -0.237303 | 2.268125 |
| 25 | 6 | 0 | 5.326234 | -1.812313 | 0.372872 |
| 26 | 1 | 0 | 5.076330 | -2.321598 | -1.709874 |
| 27 | 1 | 0 | 5.255572 | -1.180548 | 2.437217 |
| 28 | 1 | 0 | 6.328682 | -2.229675 | 0.444732 |
| 29 | 6 | 0 | 1.252236 | 1.554895 | -0.110888 |
| 30 | 6 | 0 | 0.631638 | 2.427545 | 0.802016 |
| 31 | 6 | 0 | 1.912676 | 2.153456 | -1.201518 |
| 32 | 6 | 0 | 0.661452 | 3.818296 | 0.638473 |
| 33 | 1 | 0 | 0.112107 | 1.995214 | 1.653833 |
| 34 | 6 | 0 | 1.943359 | 3.539359 | -1.384346 |
| 35 | 1 | 0 | 2.415913 | 1.517107 | -1.927305 |
| 36 | 6 | 0 | 1.316858 | 4.383446 | -0.459710 |
| 37 | 1 | 0 | 0.170603 | 4.461730 | 1.367500 |
| 38 | 1 | 0 | 2.458383 | 3.963536 | -2.244968 |
| 39 | 1 | 0 | 1.341150 | 5.463160 | -0.593639 |
| 40 | 5 | 0 | 1.192973 | -0.068242 | 0.075838 |
| 41 | 6 | 0 | -4.449948 | 0.452347 | 1.040191 |
| 42 | 1 | 0 | -4.035190 | 1.459210 | 0.897278 |
| 43 | 1 | 0 | -4.118070 | 0.053042 | 2.003221 |
| 44 | 8 | 0 | -4.471597 | 0.030688 | -1.343048 |
| 45 | 1 | 0 | -5.412441 | 0.213369 | -1.208712 |

1c---Catechol

Imaginary frequencies: none

 $E = -1017.8326772$

ZPE correction: 0.1903144



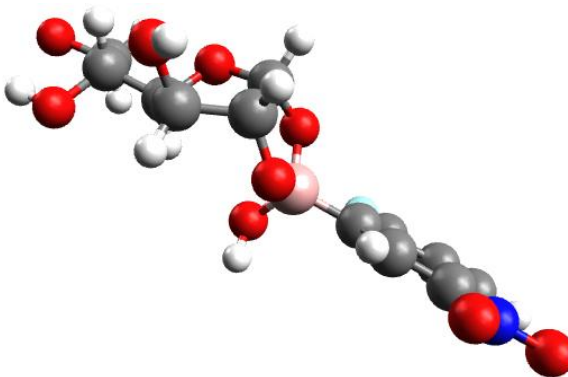
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
| | | | X | Y | Z |
| 1 | 6 | 0 | -4.193266 | -1.936736 | -0.416807 |
| 2 | 6 | 0 | -3.129370 | -1.852766 | 0.507794 |
| 3 | 6 | 0 | -2.348168 | -0.704422 | 0.508874 |
| 4 | 6 | 0 | -2.613421 | 0.358093 | -0.388109 |
| 5 | 6 | 0 | -3.662271 | 0.278397 | -1.296278 |
| 6 | 6 | 0 | -4.454648 | -0.890061 | -1.302602 |
| 7 | 1 | 0 | -4.811647 | -2.831036 | -0.437875 |
| 8 | 1 | 0 | -2.916867 | -2.661314 | 1.201675 |
| 9 | 1 | 0 | -3.858279 | 1.099712 | -1.980020 |
| 10 | 1 | 0 | -5.276684 | -0.972558 | -2.009899 |
| 11 | 8 | 0 | -1.747326 | 1.371116 | -0.203683 |
| 12 | 8 | 0 | -1.298783 | -0.411014 | 1.301314 |
| 13 | 6 | 0 | 0.748971 | 0.816910 | 0.303212 |
| 14 | 6 | 0 | 1.450070 | 1.865335 | -0.298779 |
| 15 | 6 | 0 | 1.444084 | -0.399026 | 0.363157 |
| 16 | 6 | 0 | 2.744038 | 1.767865 | -0.817964 |
| 17 | 6 | 0 | 2.743373 | -0.524406 | -0.145176 |
| 18 | 1 | 0 | 0.958869 | -1.256834 | 0.813140 |
| 19 | 6 | 0 | 3.410012 | 0.551441 | -0.741265 |
| 20 | 1 | 0 | 3.206821 | 2.639451 | -1.269466 |
| 21 | 1 | 0 | 4.413300 | 0.424706 | -1.127389 |
| 22 | 5 | 0 | -0.772894 | 0.964942 | 0.899474 |
| 23 | 8 | 0 | -0.746417 | 1.893158 | 1.995364 |
| 24 | 1 | 0 | -1.639382 | 2.015184 | 2.339470 |
| 25 | 9 | 0 | 0.860961 | 3.083385 | -0.409844 |
| 26 | 7 | 0 | 3.434939 | -1.807641 | -0.056032 |
| 27 | 8 | 0 | 2.854802 | -2.757975 | 0.479229 |
| 28 | 8 | 0 | 4.582558 | -1.890628 | -0.522542 |

1c---Glucose

Imaginary frequencies: none

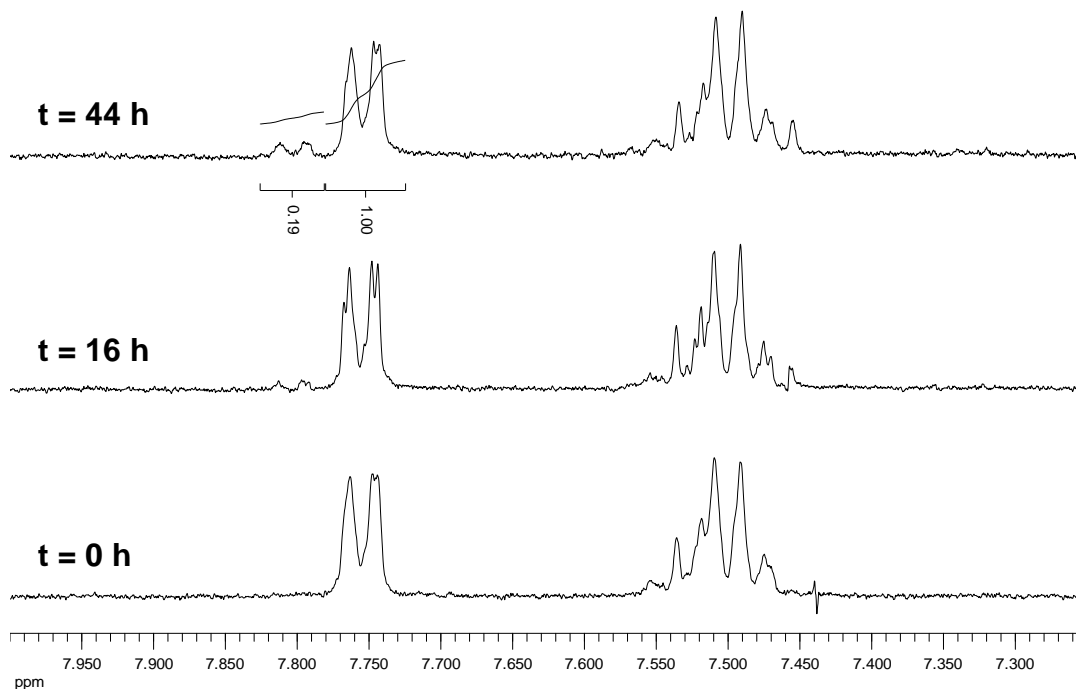
 $E = -1322.3263953$

ZPE correction: 0.2772989

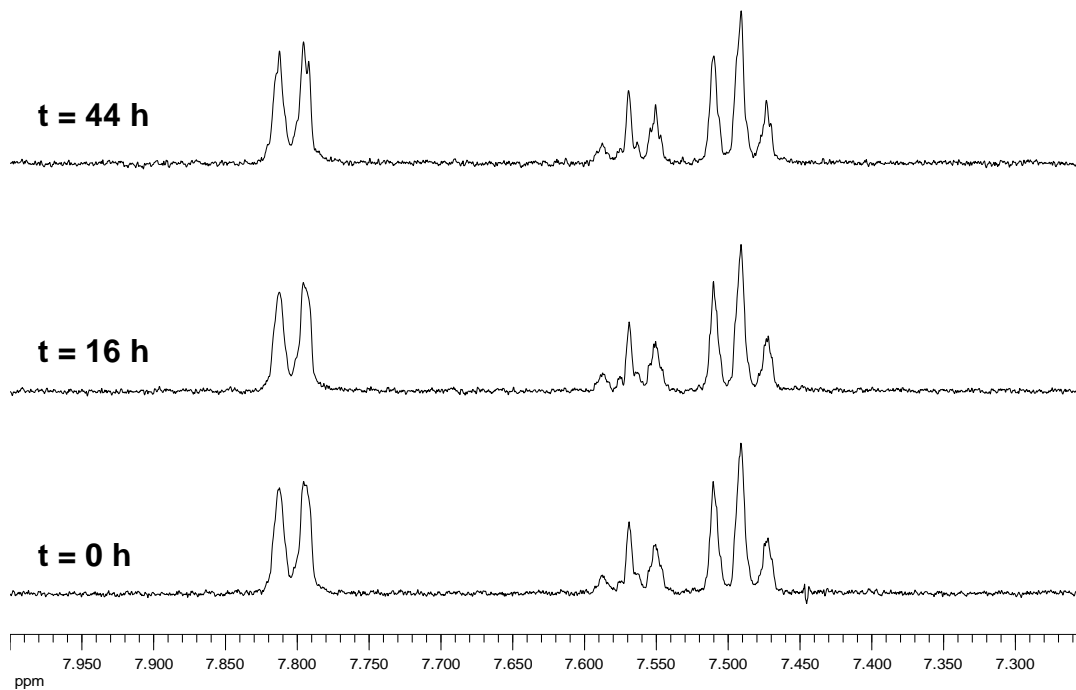


| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | | |
|---------------|---------------|-------------|-------------------------|-----------|-----------|
| | | | X | Y | Z |
| 1 | 6 | 0 | 2.981307 | -0.280684 | 0.082969 |
| 2 | 8 | 0 | 2.620350 | 0.320205 | -1.168699 |
| 3 | 6 | 0 | 1.249235 | -0.023812 | -1.456589 |
| 4 | 6 | 0 | 0.961376 | -1.333978 | -0.647676 |
| 5 | 6 | 0 | 2.302781 | -1.653928 | 0.057264 |
| 6 | 1 | 0 | 2.547490 | 0.296362 | 0.911800 |
| 7 | 1 | 0 | 1.210429 | -0.118107 | -2.547910 |
| 8 | 1 | 0 | 0.673547 | -2.176500 | -1.299631 |
| 9 | 1 | 0 | 2.132807 | -2.048860 | 1.064635 |
| 10 | 6 | 0 | 4.501187 | -0.269794 | 0.203534 |
| 11 | 1 | 0 | 4.932918 | -0.934954 | -0.555714 |
| 12 | 8 | 0 | 6.478455 | 1.063074 | 0.248478 |
| 13 | 1 | 0 | 6.823490 | 1.959311 | 0.331930 |
| 14 | 8 | 0 | 3.104162 | -2.561927 | -0.716166 |
| 15 | 1 | 0 | 2.573136 | -3.351442 | -0.879819 |
| 16 | 8 | 0 | -0.072408 | -1.026816 | 0.242771 |
| 17 | 8 | 0 | 0.329754 | 0.908240 | -1.023479 |
| 18 | 6 | 0 | -1.981557 | 0.671261 | 0.100859 |
| 19 | 6 | 0 | -2.878436 | -0.404153 | 0.183278 |
| 20 | 6 | 0 | -2.586177 | 1.922632 | -0.054960 |
| 21 | 1 | 0 | -2.478842 | -1.405072 | 0.294656 |
| 22 | 6 | 0 | -3.964625 | 2.143839 | -0.131722 |
| 23 | 6 | 0 | -4.827614 | 1.058846 | -0.041869 |
| 24 | 1 | 0 | -4.338269 | 3.154804 | -0.259532 |
| 25 | 1 | 0 | -5.902282 | 1.178181 | -0.093563 |
| 26 | 5 | 0 | -0.346276 | 0.445471 | 0.207211 |
| 27 | 6 | 0 | 5.053900 | 1.136426 | 0.006450 |
| 28 | 1 | 0 | 4.583132 | 1.820574 | 0.724700 |
| 29 | 1 | 0 | 4.848516 | 1.478869 | -1.012084 |
| 30 | 8 | 0 | 4.834381 | -0.745594 | 1.513308 |
| 31 | 1 | 0 | 5.775017 | -0.552318 | 1.634175 |
| 32 | 8 | 0 | 0.201722 | 1.134049 | 1.382685 |
| 33 | 1 | 0 | -0.091711 | 0.685410 | 2.183735 |
| 34 | 9 | 0 | -1.807262 | 3.030288 | -0.147814 |
| 35 | 6 | 0 | -4.265312 | -0.212602 | 0.117555 |
| 36 | 7 | 0 | -5.160080 | -1.361982 | 0.210959 |
| 37 | 8 | 0 | -6.384151 | -1.163060 | 0.146921 |
| 38 | 8 | 0 | -4.668322 | -2.487753 | 0.349884 |

V. ^1H NMR Study of Stability of Diphenylborinic Acid vs. Phenylboronic Acid



Partial ^1H NMR spectra of diphenylborinic acid (**1a**) in air saturated D_2O over a 44 hour period.



Partial ^1H NMR spectra of phenylboronic acid (**1b**) in air saturated D_2O over a 44 hour period.