Supporting Information

cis-Diol Functional Group Recognition by Reactive Desorption Electrospray Ionization (DESI)

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Figure 1S shows the CID MS^2 spectra of the product ions **3** and **4** (m/z 283) generated in heterogenous reactions of $PhB(OH)_3^-$ anions with (a) D-fructose and (b) D-glucose, respectively. In the Figure 1Sa, the fragment ion of m/z 239 is likely to arise from the cleavage of C_2H_4O from the anion **3** as marked. The fragment ion of m/z 180 was shown by MS^2 experiments to be due to a background component at m/z 283.

Figure 2Sa is the blank negative ion reactive DESI spectrum recorded by spraying an aqueous phenylboronic acid solution adjusted using NaOH to be slightly basic (pH=9~10). The reactant ion $PhB(OH)_3^-$ (m/z 139) is the base peak in the spectrum. By contrast, in the reactive DESI spectrum (Figure 2Sb) recorded with solid D-glucose on a paper surface the heterogeneous reaction of the $PhB(OH)_3^-$ anion yields the cyclic boronate product ion (m/z 283). The deprotonated glucose was also observed at m/z 179.

Figure 3S displays the CID MS^2 spectrum of the authentic cyclic boronate product ion (m/z 283) generated by electrospray ionization of a basic aqueous solution containing both glucose and phenylboronic acid. The dissociation to give fragment ions, m/z 179, 205, 229, 247 and 265, is in agreement with the corresponding data for the reactive DESI product (Figure 1Sb in the text), confirming the structure of the reaction product.

Figures 4Sa and 4Sc show the recorded reactive DESI mass spectra for the model aromatic diols catechol and 3-fluorocatechol. The product ions (m/z 213 for catechol and m/z 231 for 3-fluorocatechol) lose benzene and Ph-B=O during the CID process, as shown in Figures 4Sb and 4Sd. The occurrence of heterogeneous reactions between $PhB(OH)_3^-$ and the biomolecules quercetin and (-)-epinephrine on surfaces has been successfully observed and the product ions appear at m/z 405 (Figure 5Sa) and 286 (Figure 5Sb), respectively. Analogous to the products ion generated from the parent catechols, the product ion of m/z 405 (Figure 5Sc) yields fragment ions of m/z 327 and 301 by loss of benzene and Ph-B=O as well as m/z 387 by loss of water upon CID. The product ion of m/z 286 (Figure 5Sd) undergoes similar fragmentation channels, losing benzene and Ph-B=O to form the ions at m/z 208 and 182, respectively. The other fragment ion, with m/z 164, arises from the further loss of water from m/z 182.

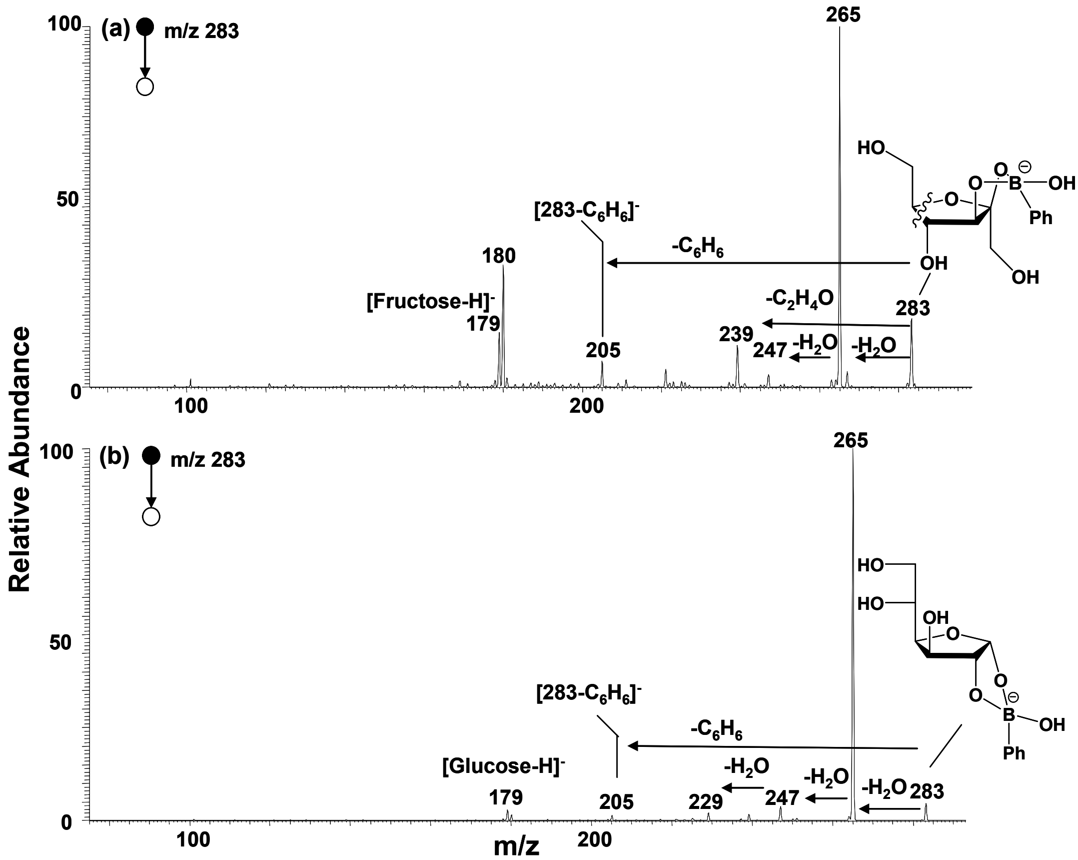

Figure 1S CID MS^2 spectra of the product ions of m/z 283 generated in heterogenous reactions of $PhB(OH)_3^-$ anions with (a) D-fructose and (b) D-glucose

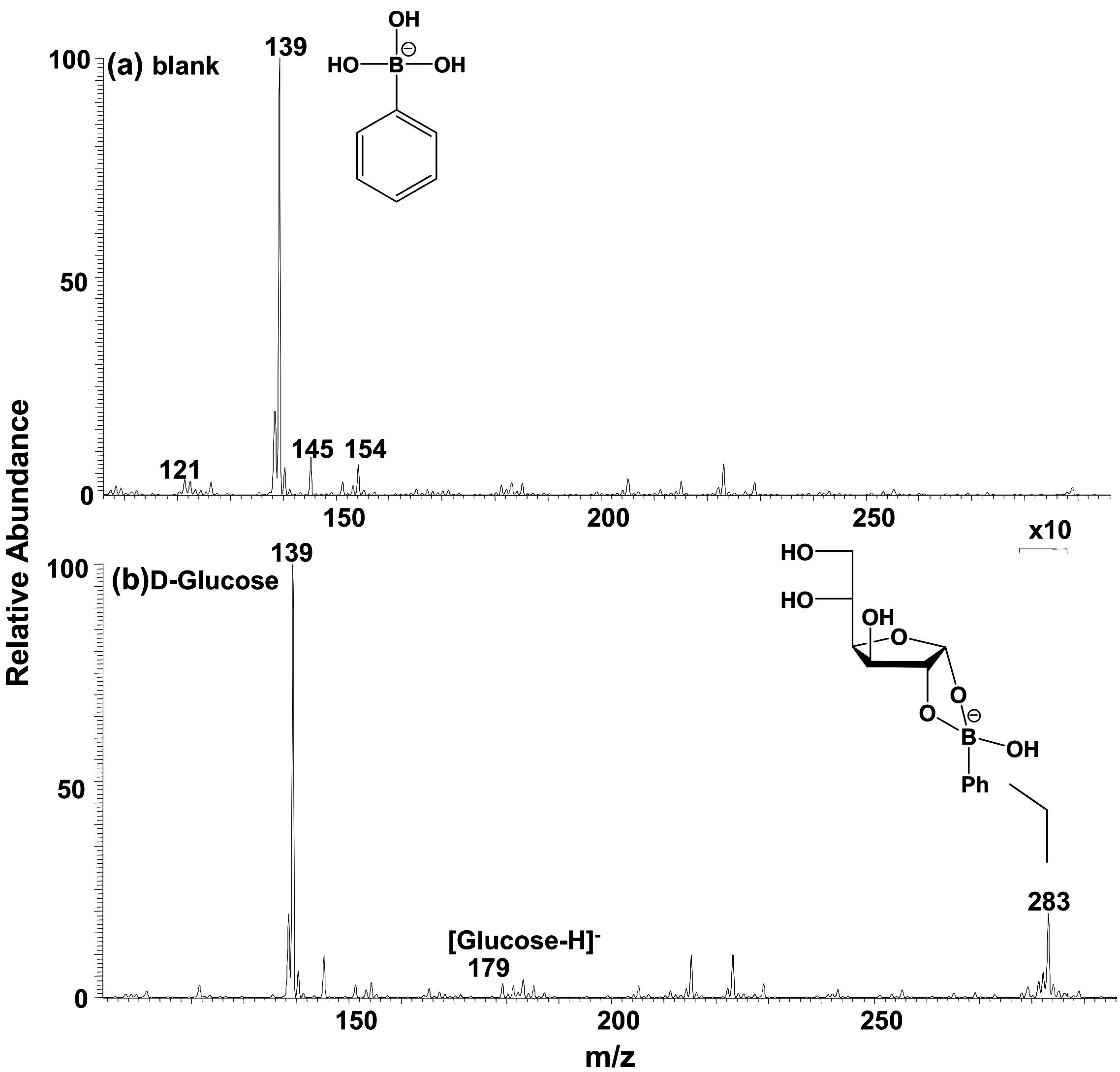

Figure 2S Reactive DESI mass spectra showing the ionic species generated from the $PhB(OH)_3^-$ anions upon interaction with (a) a blank surface and (b) D-glucose on the surface

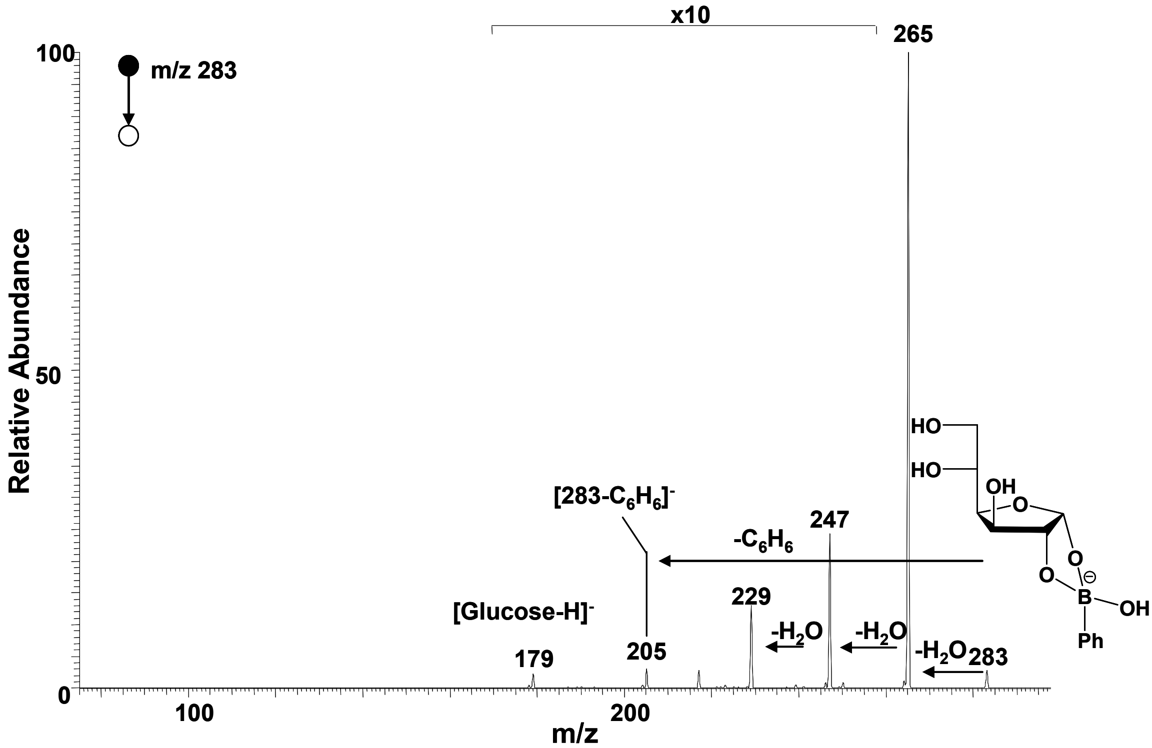

Figure 3S MS^2 spectrum of the observed authentic product ion (m/z 283) generated by electrospray ionization of a basic aqueous solution containing D-glucose and phenylboronic acid

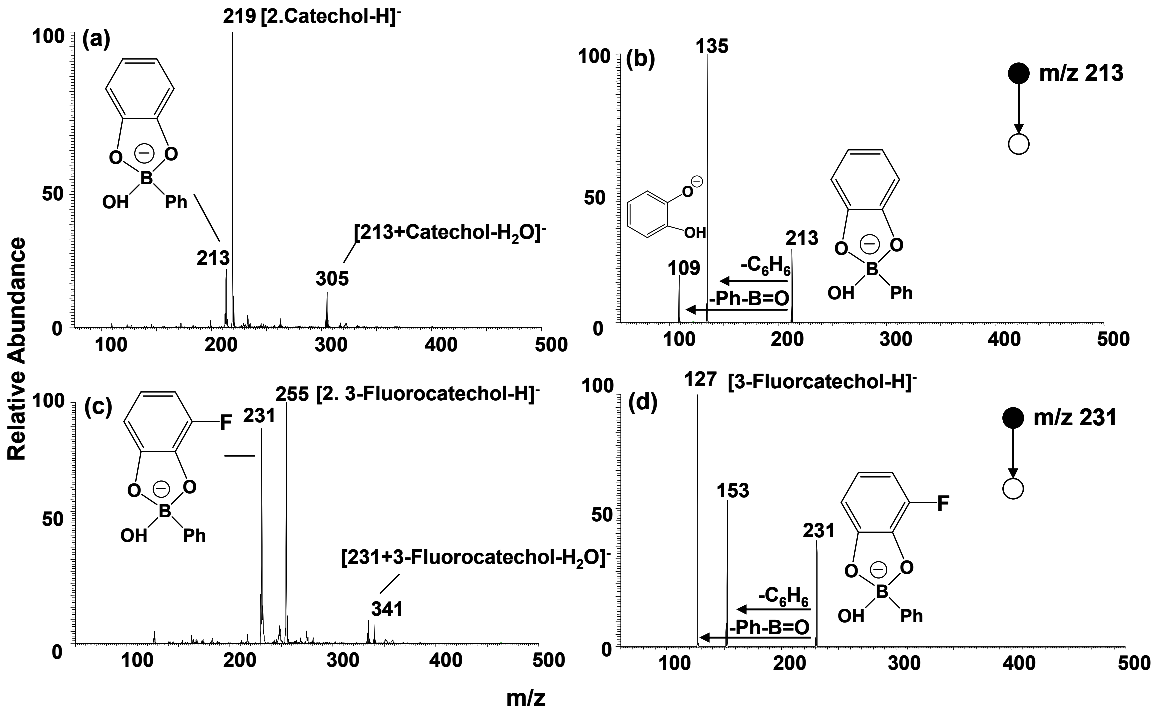

Figure 4S Reactive DESI spectra showing the heterogeneous reactions of $PhB(OH)_3^-$ anions with (a) catechol and (c) 3-fluorocatechol both present as solids on surfaces; MS^2 spectra of the reaction product ions from (b) catechol (m/z 213) and (d) 3-fluorocatechol (m/z 231)

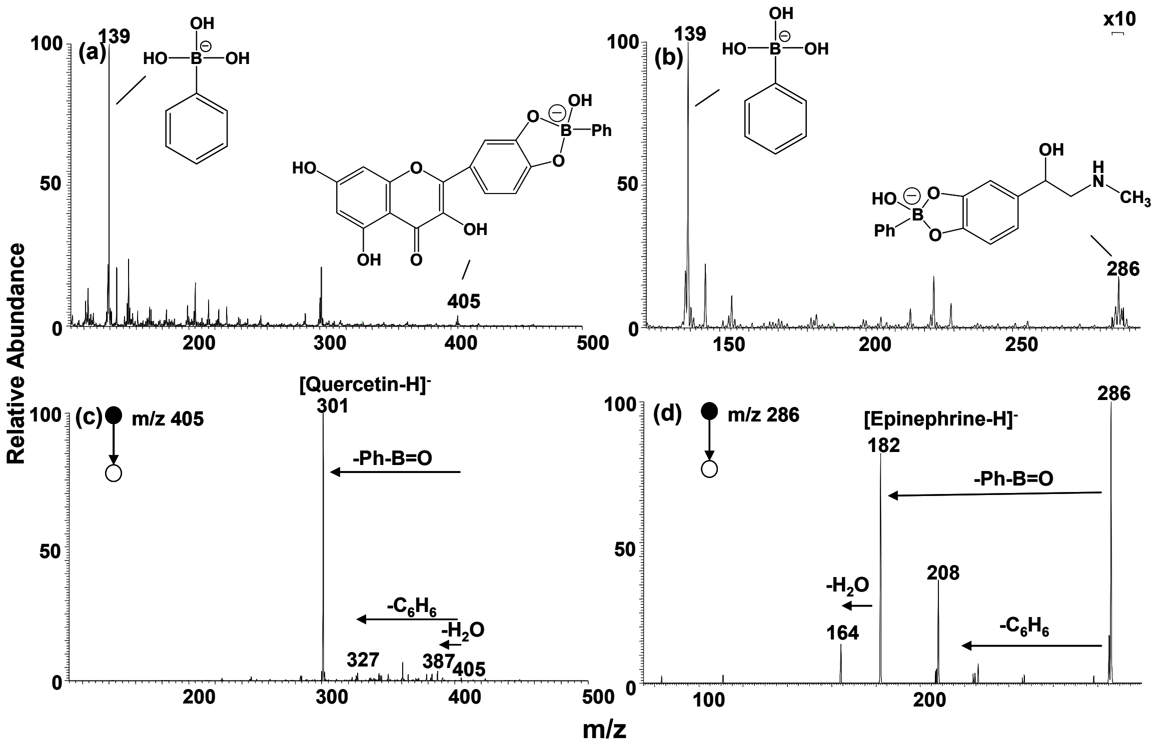

Figure 5S Reactive DESI spectra showing the heterogeneous reactions of $PhB(OH)_3^-$ anions with (a) quercetin and (b) (-)-epinephrine on surfaces; MS^2 spectra of the reaction product ions of (c) m/z 405 and (d) m/z 286