1. NMR Experiments for Disulfide Exchange and Boronic Ester Transesterification in CDCl₃

All building block samples were 10 mM in CDCl₃ and base concentration 100 mM in CDCl₃. All Boronic ester experiments were equilibrated for 30 min before equilibrium was reached and all disulfide samples were equilibrated for 20 h.

1.1. Disulfide Exchange (Figure 5 in Manuscript)

The reversibility was investigated by starting the reaction in two different ways.

Method (a): The NMR sample was prepared by mixing the two thiols immediately 1:1 with 5 equivalent base. The NMR sample was left for 24 min before the sample was analyzed.

Method (b): The two NMR samples containing either thiol was prepared by mixing the individual thiol with 5 equivalent base. The NMR sample was left for 24 h before the sample was analyzed. Then, the two samples were combined and analyzed again after 24 h to confirm that equilibrium had been reached.

Figure S1. Schematic representation of the experiments used to establish the thermodynamic equilibrium.

1.2. Establishing Equilibrium for Boronic Ester Transesterification (Figure 6 in Manuscript)

The reversibility was investigated by starting the reaction in two different ways.

Method (i): The NMR sample contained 2 equivalent phenylboronic acid (1), 1 equivalent catechol (2), 1 equivalent methyl 3,4-dihydroxybenzoate (3) and 5 equivalent base. The NMR sample was left for 30 minutes before the sample was analyzed.

Method (ii): The NMR sample contained 2 equivalent phenylboronic acid (1), 1 equivalent catechol (2) and 5 equivalent base. The NMR sample stood for 30 min. Then, 1 equivalent methyl
3,4-dihydroxybenzoate (3) was added and the sample was left for 30 min before analysis. In method (ii), the reverse order of addition was also investigated.

**Figure S2.** Schematic representation of the experiments used to establish the thermodynamic equilibrium.

### 2. Fitting of Binding Constants (Figure 4 in Manuscript)

From the Job plots, a 1:1 stoichiometry between host and guest was found. Hence, the equilibrium constant for the host-guest complexation is given by Equation (1). In this expression, the denominator is expanded by substitution with \([H] = [H]_0 - [HG]\) and \([G] = [G]_0 - [HG]\), giving Equation (2).

\[
K = \frac{[HG]}{[H][G]} \quad (1)
\]

\[
K = \frac{[HG]}{([H]_0 - [HG]) ([G]_0 - [HG])} = \frac{[HG]}{[H]_0[G]_0 - [HG][[H]_0 + [G]_0] + [HG]^2} \quad (2)
\]

Equation (2) can be rearranged to the second order equation (Equation (3)) with \([HG]\) as the unknown, and the general solution is given in Equation (4).

\[
0 = [HG]^2 - ([G]_0 + [H]_0 + \frac{1}{K}) + [H]_0[G]_0 \quad (3)
\]

\[
[HG] = \frac{1}{2} \left( ([G]_0 + [H]_0 + \frac{1}{K}) \pm \sqrt{([G]_0 + [H]_0 + \frac{1}{K})^2 - 4[G]_0[H]_0} \right) \quad (4)
\]

Only the solution where the last term is subtracted is chemically meaningful because the solution with a plus sign results in a concentration of complex that is higher than the smallest of the numbers \([G]_0\) and \([H]_0\).

Equation (4) gives an expression where the unknowns are \([HG]\) and \(K\). The purpose is to find \(K\) and \(^1\)H-NMR was used to provide a measure of \([HG]\). Various amounts of Et₃N were titrated into a solution of the boronic ester 7 under conditions where the total concentration of host was constant and the movement of a host signal (denoted \(\delta\)) was followed.

Under the used conditions, the complexation was fast on the chemical shift time scale, and therefore the observed signal \(\delta\) is as a weighted average of the signals \(\delta_H\) (chemical shift of the proton in pure host) and \(\delta_{HG}\) (chemical shift of the proton in pure complex) with the mole fractions \(X_H\) and \(X_{HG}\) as the...
weighting factors. This is expressed in Equation (5), which, via standard manipulations, can be written as Equation (6).

\[ \delta = \delta_H X_H + \delta_{HG} X_{HG} \]

\[ = \delta_H \frac{[H]^o - [HG]}{[H]^o} + \delta_{HG} \frac{[HG]}{[H]^o} \]  

\[ = \delta_H + (\delta_{HG} - \delta_H) \frac{[HG]}{[H]^o} \]  

(5)  

(6)

For each measurement in the titration, the change from \( \delta_H \) to the observed \( \delta \) was calculated and denoted \( \Delta \delta = \delta - \delta_H \). The unknown quantity, \( \delta_{HG} - \delta_H \), indicates the maximal obtainable change in the titration and is denoted \( \Delta \delta_{\text{max}} \). With these notations, Equation (6) can be rewritten as Equation (7) and by substitution of Equation (4) into Equation (7), the final fitting equation, Equation (8), is obtained.

\[ \Delta \delta = \Delta \delta_{\text{max}} \frac{[HG]}{[H]^o} \]  

\[ = \frac{\Delta \delta_{\text{max}}}{2[H]^o} \left( (G)^o + [H]^o + \frac{1}{K} \right) - \sqrt{\left( (G)^o + [H]^o + \frac{1}{K} \right)^2 - 4[G]^o[H]^o} \]  

(7)  

(8)

In Equation (8), the quantities \( \Delta \delta_{\text{max}} \) and \( K \) are unknown but linked to the measurable quantity \( \Delta \delta \) and the known \([H]^o\) and \([G]^o\). Using the software, SciDavis, \( \Delta \delta_{\text{max}} \) and \( K \) were determined by fitting the equation data to Equation (8).

The chemical shift changes for H2, H3 and H4 were each monitored and used to determine Ddmax and K and the average taken.

<table>
<thead>
<tr>
<th>Table S1. Binding constants determined.</th>
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<tbody>
<tr>
<td>H2</td>
</tr>
<tr>
<td>( K )</td>
</tr>
<tr>
<td>590 ± 50</td>
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<tr>
<td>( \Delta \delta_{\text{max}} ) ( )</td>
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<tr>
<td>0.67 ± 0.007</td>
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<tr>
<td>H3</td>
</tr>
<tr>
<td>( K )</td>
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<td>690 ± 70</td>
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<tr>
<td>( \Delta \delta_{\text{max}} ) ( )</td>
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<td>0.46 ± 0.005</td>
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<tr>
<td>H4</td>
</tr>
<tr>
<td>( K )</td>
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<tr>
<td>850 ± 130</td>
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<tr>
<td>( \Delta \delta_{\text{max}} ) ( )</td>
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<tr>
<td>0.25 ± 0.004</td>
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