Supporting Information

Versatile self-adapting boronic acids for H-bond recognition: from discrete to polymeric supramolecules

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Materials and Instruments

Thin layer chromatography (TLC) was conducted on pre-coated aluminum sheets with 0.20 mm *Machevery-Nagel* Alugram SIL G/UV254 with fluorescent indicator UV254. *Column chromatography* was carried out using *Merck Gerduran* silica gel 60 (particle size 63-200 μm).

Nuclear magnetic resonance (NMR) ^{1}H, ^{13}C and ^{19}F spectra were obtained on a 400 MHz NMR (*Jeol JNM EX-400*) or 270 MHz (*Jeol JNM EX-270*) at rt otherwise stated. Chemical shifts were reported in ppm according to tetramethylsilane using the solvent residual signal as an internal reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.52 ppm). Coupling constants (*J*) were given in Hz. Resonance multiplicity was described as *s* (singlet), *d* (doublet), *t* (triplet), *dd* (doublet of doublets), *dt* (doublet of triplets), *td* (triplet of doublets), *q* (quartet), *m* (multiplet) and *broad* (broad signal). Carbon spectra were acquired with a complete decoupling for the proton.

X-ray measurements were performed on a Gemini Ultra R system (4-circle kappa platform, Ruby CCD detector) using Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (λ = 1.54178 Å) at Université de Namur in Belgium. After mounting and centering of the single crystal on the diffractometer, cell parameters were estimated from a pre-experiment run and full data sets collected at room temperature. Structures were solved by direct methods with SHELXS-86 program and then refined on F^2 using SHELXL-97 software. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms (not implicated in H-bonds) in the riding mode with isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms.

*Synthesis***.** Chemicals were purchased from *Sigma Aldrich*, *Acros Organics*, *TCI* and *ABCR* and were used as received. Solvents were purchased from *Sigma Aldrich*, while deuterated solvents from *Eurisotop*. Diethyl ether and THF were distilled from sodium-benzophenone-cetyl, toluene was refluxed over calcium hydride and dichloromethane (CH_2Cl_2) was refluxed over phosphorous pentoxide. Anhydrous DMF was purchased from *Acros Organics*. Sulfuric acid (H_2SO_4 95%) and hydrochloridic acid (HCl 32%) were purchased from *Fischer Scientific*. Pyridine was purchased from *Acros Organics*. MeOH, $CHCl_3$ and acetone were purchased as reagent-grade and used without further purification. Low temperature baths were prepared using different solvent mixtures depending on the desired temperature: -78°C with acetone/dry ice, -40 °C with CH_3CN/liquid N_2, -10 °C with ice-H_2O/NaCl, and 0 °C with ice/H_2O. Anhydrous conditions were achieved by drying Schlenk tubes or 2-neck flasks by flaming with a heat gun under vacuum and then purging with Argon. The inert atmosphere was maintained using Argon-filled balloons equipped with a syringe and needle that was used to penetrate the silicon stoppers used to close the flasks' necks. Additions of liquid reagents were performed using dried plastic or glass syringes. All reageants and solvents were purchased from commercial sources and used without additional purification unless otherwise noted. In particular, compounds **1**, **3**, **9** and **13** were purchased from Fluorochem; **2**, **12**, **16** and **Phen** from Apollo Scientific; **5** and **15** from ABCR and **4**, **8**, **10**, **11**, **4**, **17** and **18** from Sigma Aldrich. **NAP** was purchased from TCI.

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1. Computational Studies

1.1. Computational Method

In order to compute the ΔH of dimerization of the complexes studied herein, first geometry optimization at the B3LYP/6-311G** level of theory and single point energy calculation were performed on the optimized structures of each host and guest separately. Geometry optimization at the B3LYP/6-311G** level of theory of the complex formed by the host/guest already optimized structures and binding energies calculations were then performed applying the correction for the basis set superposition error (BSSE) using the Boys-Bernardi counterpoise technique.[1] The starting molecules were the crystal structures when available. Molecular properties such as electrostatic potential and dipole moment, μ were calculated on the optimized geometries at B3LYP/3-21G level of theory. Calculations were performed by the GAUSSIAN 09 program.[2]

1.2. Electronic Surface Potential (ESP)

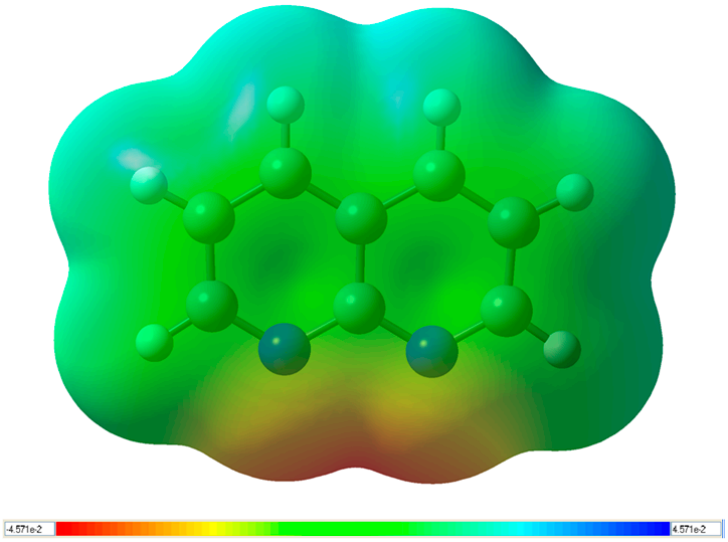


Figure S1. Electronic surface potential of 1,8-naphthyridine

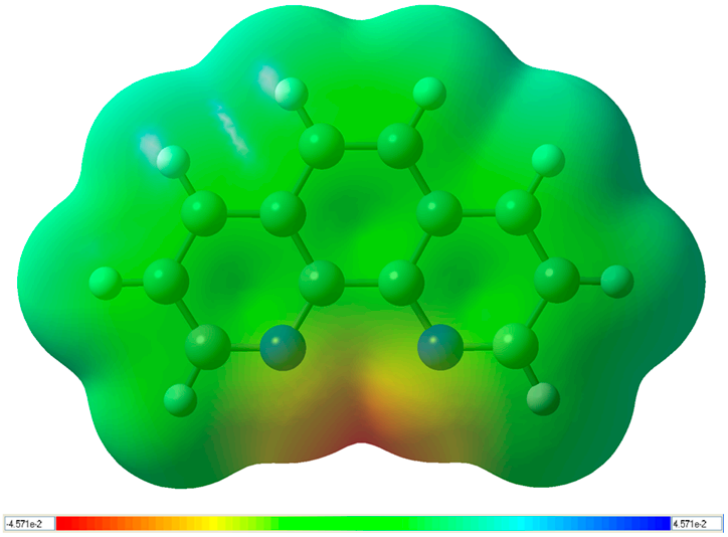


Figure S2. Electronic surface potential of 1,10-phenanthroline

2. Solution-state recognition: ^{1}H NMR Titrations – Determination of K_a

2.1. General experimental procedure for the determination of the association constant K_a

^{1}H NMR titrations were performed at 295 K in toluene-d_8 *(stored over 4 Å molecular sieves)*. A stock solution of the host system (boronic acid) of 10 mM (2 mL) concentration was initially made. From this solution 0.5 mL were placed in an NMR tube and 1 mL was used to prepare the solution of guest (1,8-naphthyridine or 1,10-phenanthroline) at 50 mM concentration. The change of chemical shift of the hydrogen atom of the $-B(OH)_2$ moiety was recorded after each 31-35 additions (blank, 18*(5 μL), 6*(10 μL), 1*(20 μL), 2*(40 μL), 3*(50 μL), 2*(100 μL) and 1*(150 μL)). From the data obtained the binding isotherms were created using the reported fitting curve parameters on Matlab.[3] The values reported are the average of two runs. In cases where the chemical shift of interest was merging with the solvent peaks the data were excluded from the binding isotherm.

2.2. ^{1}H NMR analysis and binding isotherm used for the determination of the association constant K_a

2.2.1. Between mesitylboronic acid and 1,8-naphthyridine

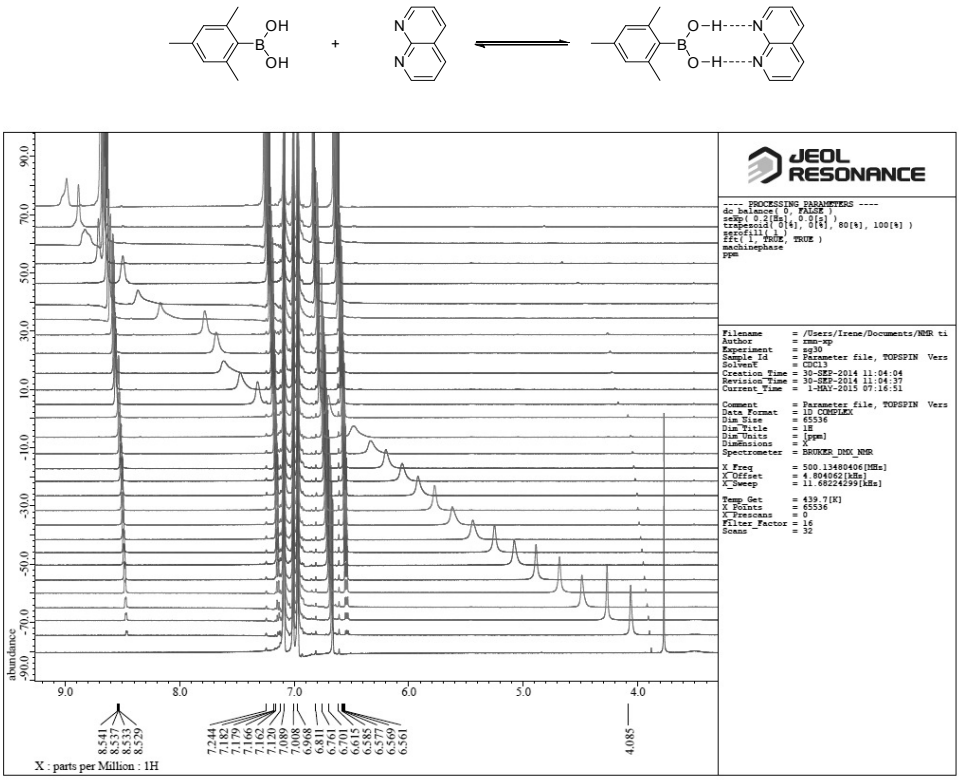


Figure S3. Selected region of a series ^{1}H NMR spectra acquired during the titration of ***mesitylboronic acid*** with ***1,8-naphthyridine*** (500 MHz, toluene-d_8, 298 K).

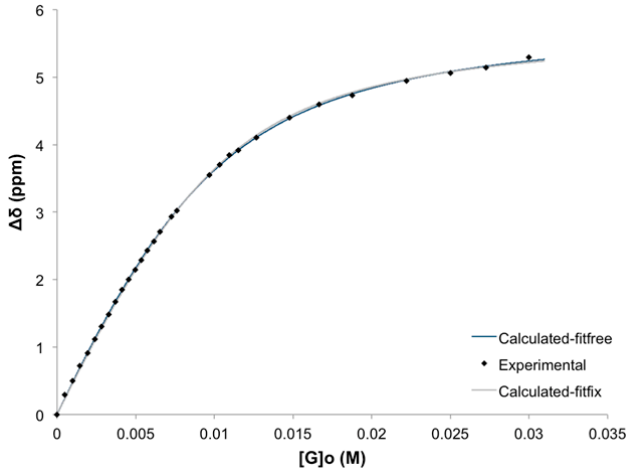
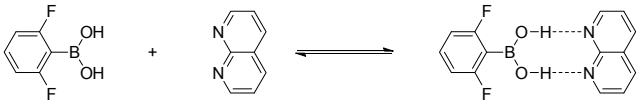


Figure S4. Binding isotherm for the formation of a 1:1 complex between ***mesitylboronic acid*** and ***1,8-naphthyridine*** (500 MHz, toluene-d_8, 298 K). Fit fix: $[H]_o$ = 10 mM, $[G]_o$ = 50 mM, $\Delta\delta_{sat}$ = 5.23, K_a (fit fix) = 449 ± 6. Fit free: K_a (fit free) = 369 ± 16, C_0' = 9.2 mM.

2.2.2. Between 2,6-diflurophenyboronic acid and 1,8-naphthyridine



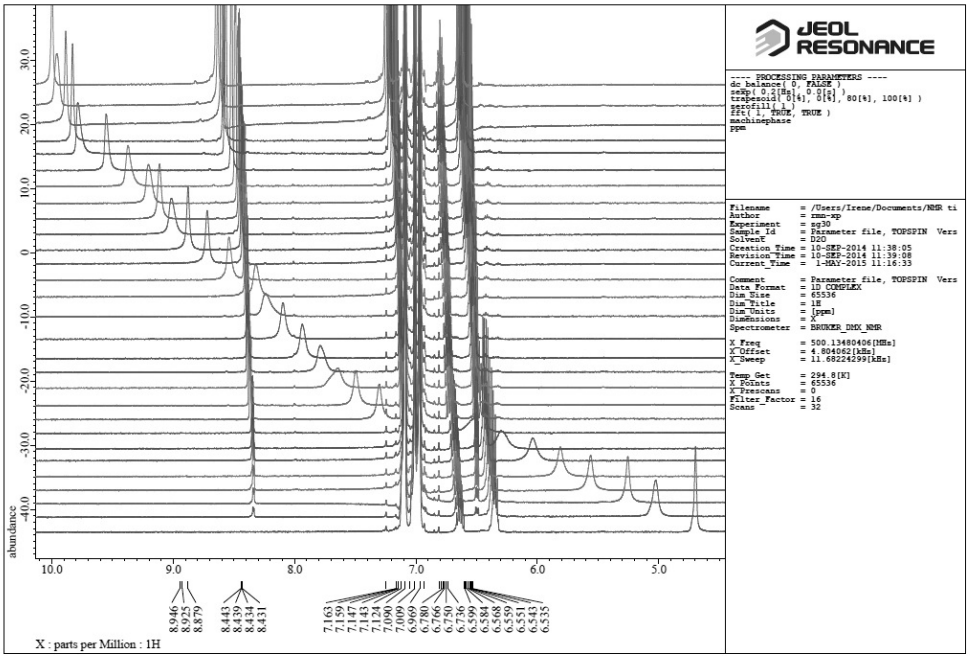


Figure S5. Selected region of a series ^{1}H NMR spectra acquired during the titration of ***2,6-difluorophenylboronic acid*** with ***1,8-naphthyridine*** (500 MHz, toluene-d_8, 298 K).

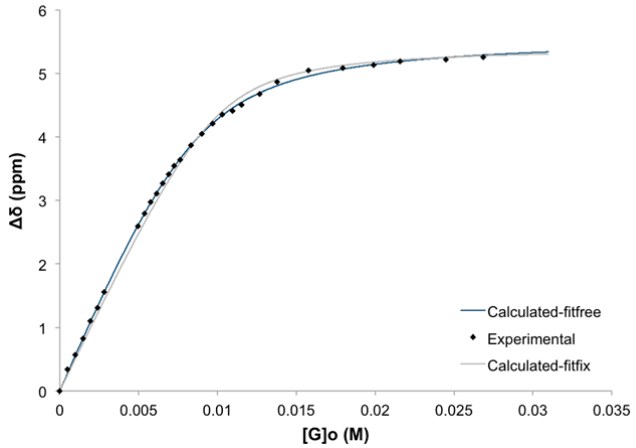


Figure S6. Binding isotherm for the formation of a 1:1 complex between ***2,6-difluorophenylboronic acid*** and ***1,8-naphthyridine*** (500 MHz, toluene-d_8, 298 K). Fit fix: $[H]_o$ = 10 mM, $[G]_o$ = 50 mM, $\Delta\delta_{sat}$ = 5.26, K_a = 1932 ± 30. Fit free: K_a (fit free) = 997 ± 62, C_0' = 8.7 mM.

2.2.3. Between 2,6-dichlorophenylboronic acid and 1,8-naphthyridine

2.2.3.1. In toluene-d_8

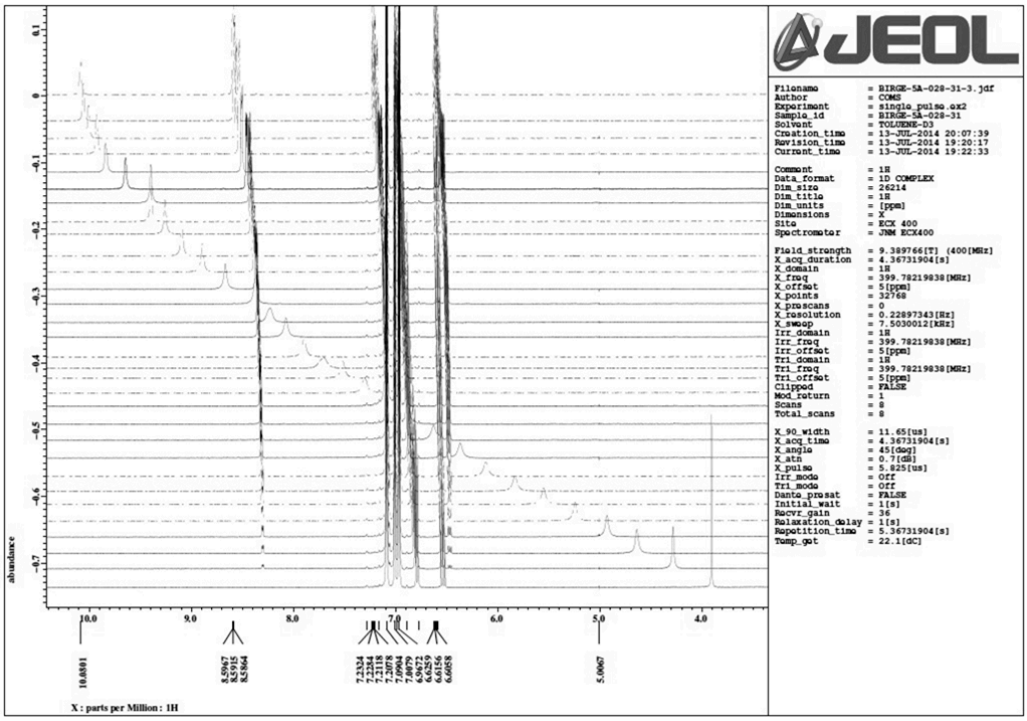


Figure S7. Selected region of a series ^{1}H NMR spectra acquired during the titration of ***2,6-dichlorophenylboronic acid*** with ***1,8-naphthyridine*** (500 MHz, toluene-d_8, 298 K).

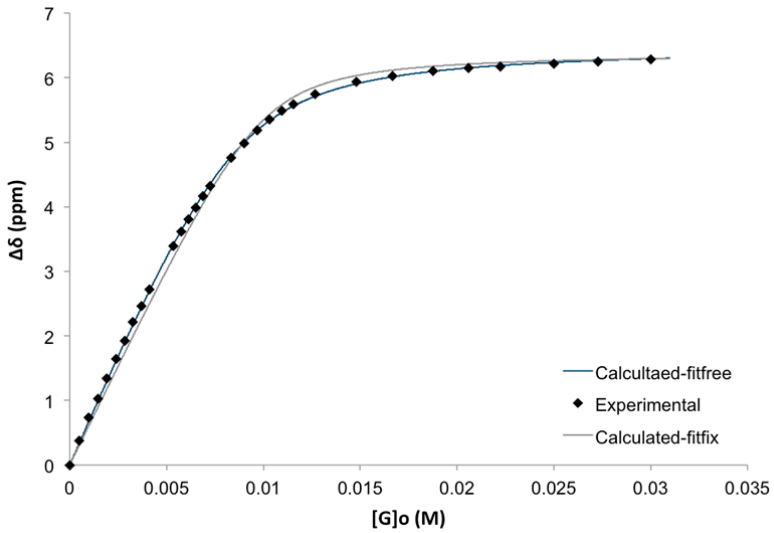


Figure S8. Binding isotherm for the formation of a 1:1 complex between ***2,6-dichlorophenylboronic acid*** and ***1,8-naphthyridine*** (500 MHz, toluene-d_8, 298 K). Fit fix: $[H]_o$ = 10 mM, $[G]_o$ = 50 mM, $\Delta\delta_{sat}$ = 6.28, K_a = 3086 ± 39. Fit free: K_a (fit free) = 1465 ± 66, C_0' = 8.7 mM.

2.2.3.2. In CD_2Cl_2

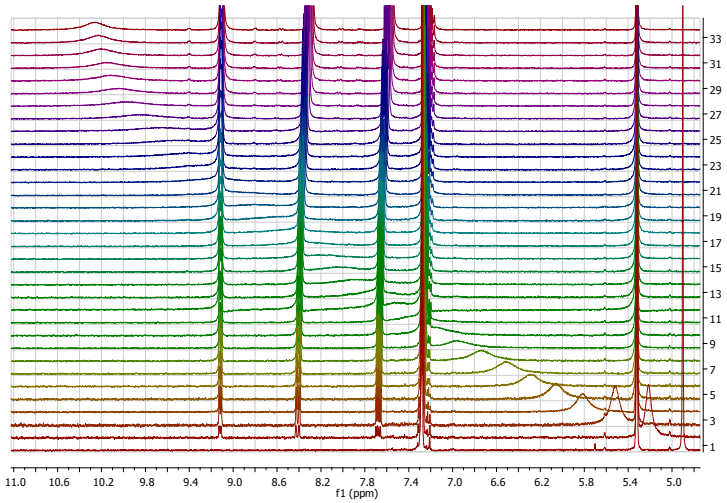


Figure S9. Selected region of a series ^{1}H NMR spectra acquired during the titration of ***2,6-dichlorophenylboronic acid*** with ***1,8-naphthyridine*** (300 MHz, CD_2Cl_2, 298 K).

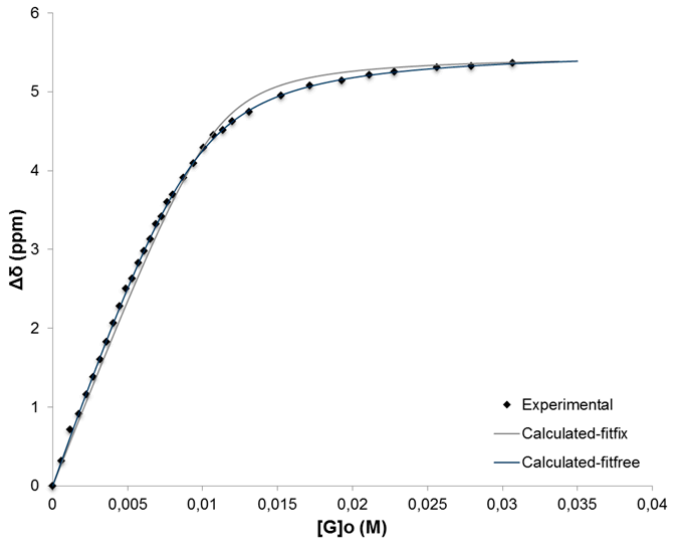


Figure S10. Binding isotherm for the formation of a 1:1 complex between ***2,6-dichlorophenylboronic acid*** and ***1,8-naphthyridine*** (300 MHz, CD_2Cl_2, 298 K). Fit fix: $[H]_o$ = 11 mM, $[G]_o$ = 51 mM, $\Delta\delta_{sat}$ = 5.48, K_a = 2580 ± 520. Fit free: K_a (fit free) = 1234 ± 54, C_0' = 9.6 mM.

2.2.3.3. In acetonitrile-d_3

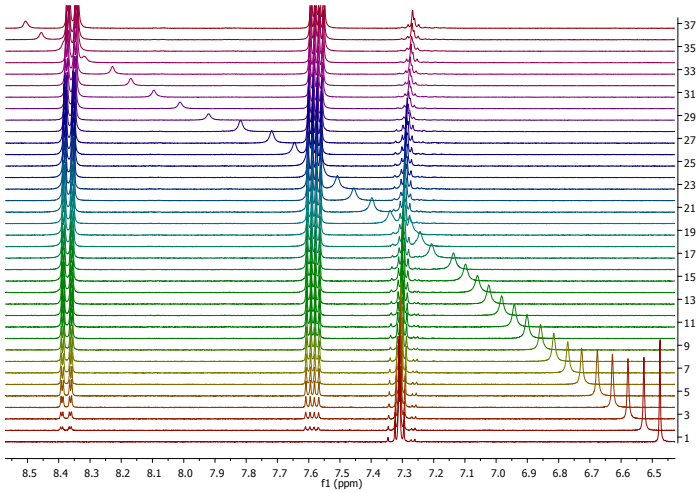


Figure S11. Selected region of a series ^{1}H NMR spectra acquired during the titration of ***2,6-dichlorophenylboronic acid*** with ***1,8-naphthyridine*** (300 MHz, MeCN-d_3, 298 K).

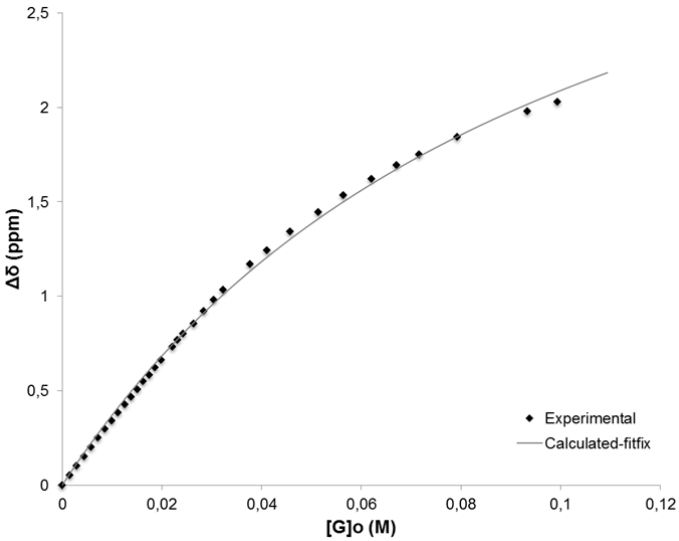
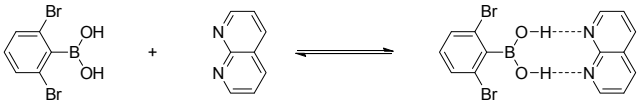


Figure S12. Binding isotherm for the formation of a 1:1 complex between ***2,6-dichlorophenylboronic acid*** and ***1,8-naphthyridine*** (300 MHz, MeCN-d_3, 298 K). Fit fix: $[H]_o$ = 10 mM, $[G]_o$ = 152 mM, $\Delta\delta_{sat}$ = 4.47, K_a = 10.94 ± 0.48.

2.2.4. Between 2,6-dibromophenylboronic acid and 1,8-naphthyridine



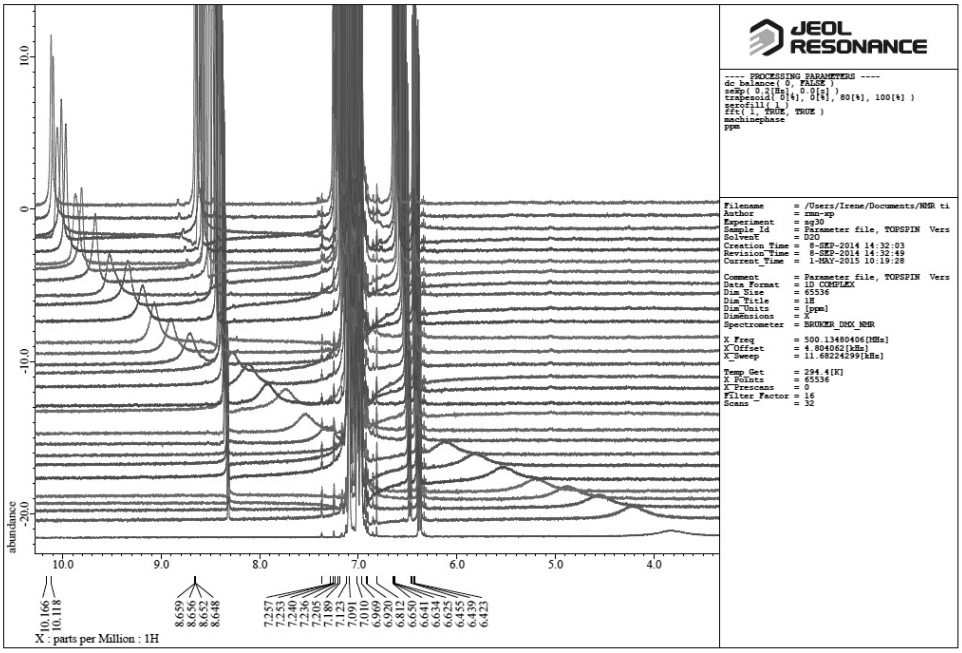


Figure S13. Selected region of a series ^{1}H NMR spectra acquired during the titration of **2,6-dibromophenylboronic acid** with **1,8-naphthyridine** (500 MHz, toluene-d_8, 298 K).

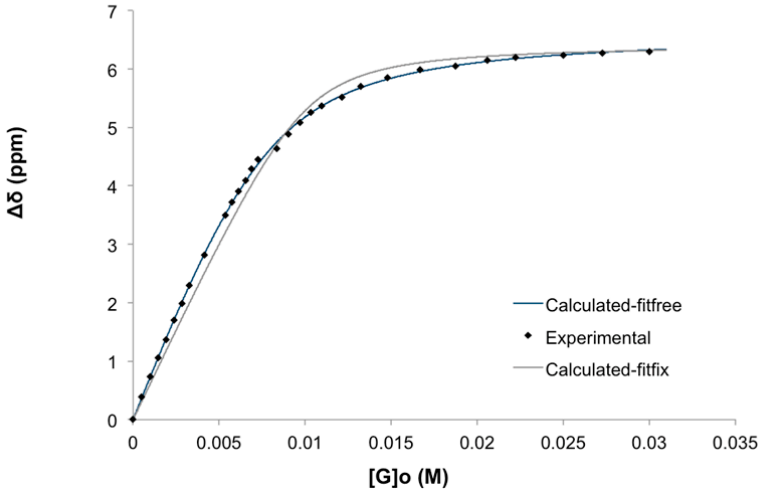


Figure S14. Binding isotherm for the formation of a 1:1 complex between ***2,6-dibromophenylboronic acid*** and ***1,8-naphthyridine*** (500 MHz, toluene-d_8, 298 K). Fit fix: $[H]_o$ = 10 mM, $[G]_o$ = 50 mM, $\Delta\delta_{sat}$ = 6.32, K_a = 2576 ± 57. Fit free: K_a (fit free) = 903 ± 41, C_0' = 7.7 mM.

2.2.5. Between 2,6-bis(trifluoromethyl)phenylboronic acid and 1,8-naphthyridine

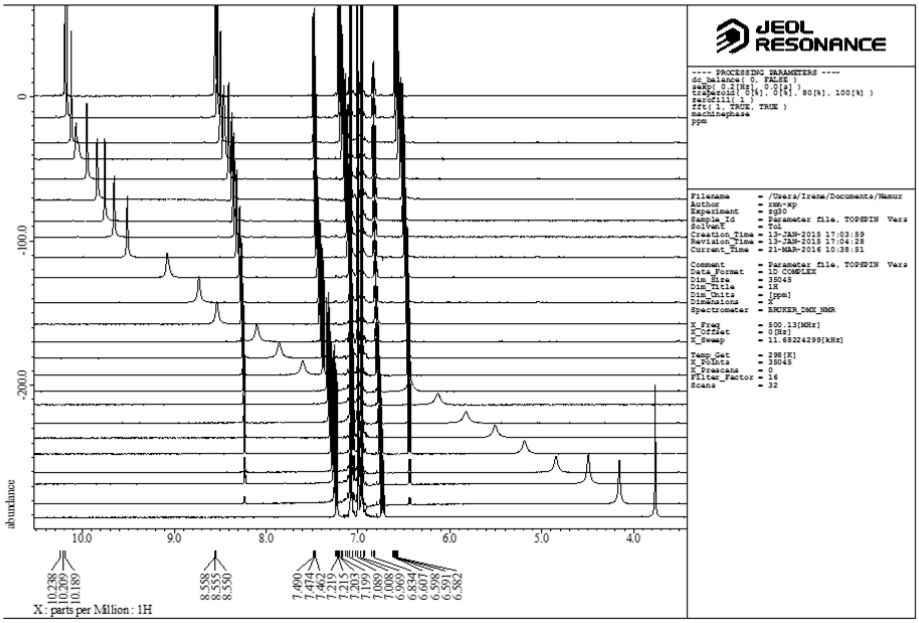


Figure S15. Selected region of a series ^{1}H NMR spectra acquired during the titration of ***2,6-bis(trifluoromethyl)phenylboronic acid*** with ***1,8-naphthyridine*** (500 MHz, toluene-d_8, 298 K).

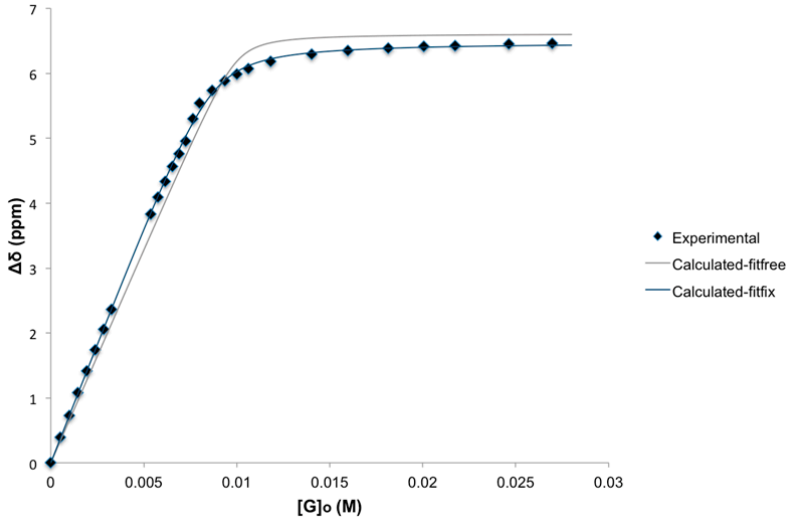


Figure S16. Binding isotherm for the formation of a 1:1 complex between ***2,6-bis(trifluoromethyl)phenylboronic acid*** and ***1,8-naphthyridine*** (500 MHz, toluene-d_8, 298 K). Fit fix:$[H]_o$ = 10 mM, $[G]_o$ = 50 mM, $\Delta\delta_{sat}$ = 6.46, K_a = 22000± 1900. Fit free: K_a (fit free) = 6900 ± 760, C_0' = 8.7 mM.

2.2.6. Between 2-methoxyphenylboronic acid and 1,8-naphthyridine

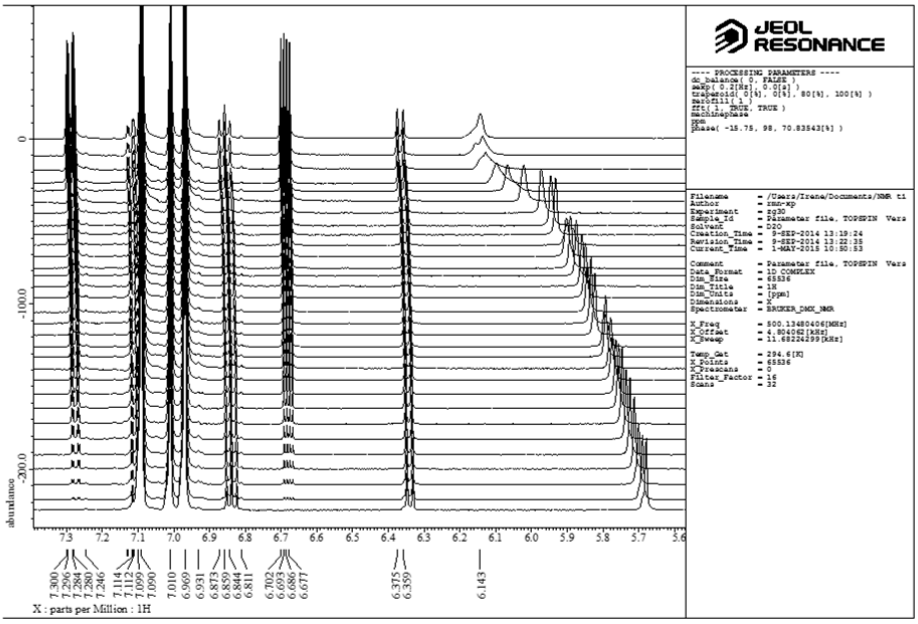
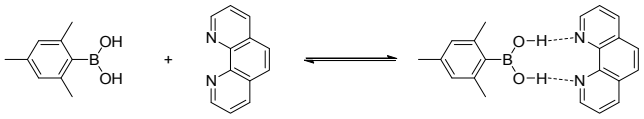


Figure S17. Selected region of a series ^{1}H NMR spectra acquired during the titration of ***2-methoxyphenylboronic acid*** with ***1,8-naphthyridine*** (500 MHz, toluene-d_8, 298 K).

2.2.7. Between mesitylboronic acid and 1,10-phenanthroline



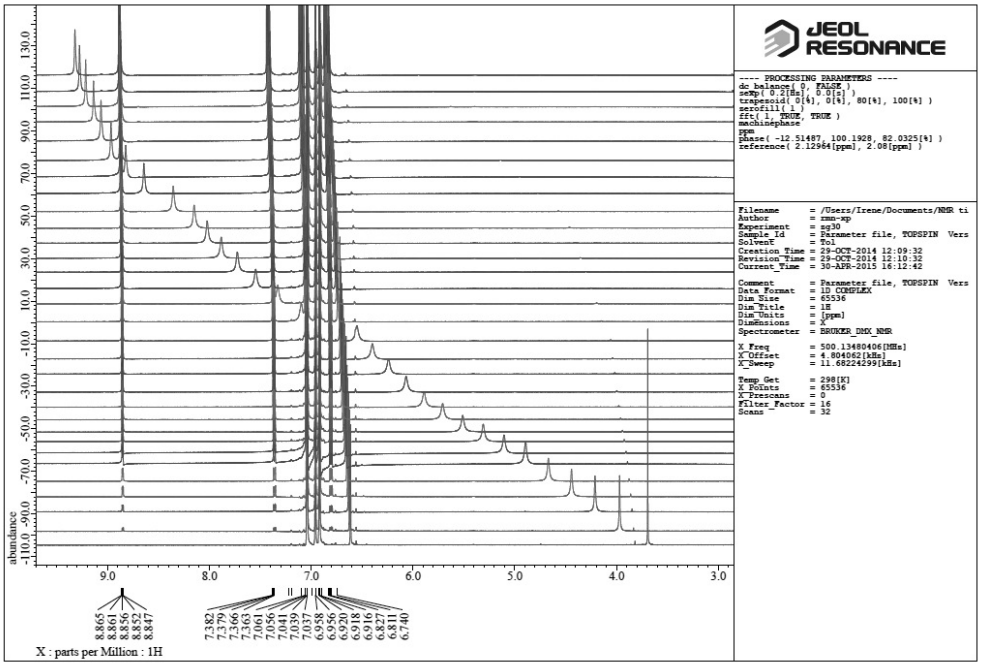


Figure S18. Selected region of a series ^{1}H NMR spectra acquired during the titration of ***mesitylboronic acid*** with ***1,10-phenanthroline*** (500 MHz, toluene-d_8, 298 K).

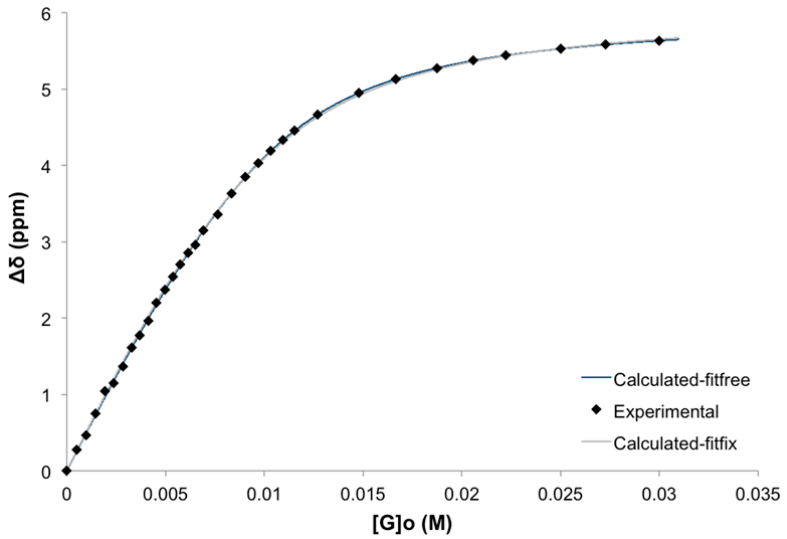


Figure S19. Binding isotherm for the formation of a 1:1 complex between ***mesitylboronic acid*** and ***1,10-phenanthroline*** (500 MHz, toluene-d_8, 298 K). Fit fix: $[H]_o$ = 10 mM, $[G]_o$ = 50 mM, $\Delta\delta_{sat}$ = 5.54, K_a = 611± 10. Fit free: K_a (fit free) = 769 ± 35, C_0' = 1.0 mM.

2.2.8. Between 2,6-dichlorophenylboronic acid and 1,10-phenanthroline

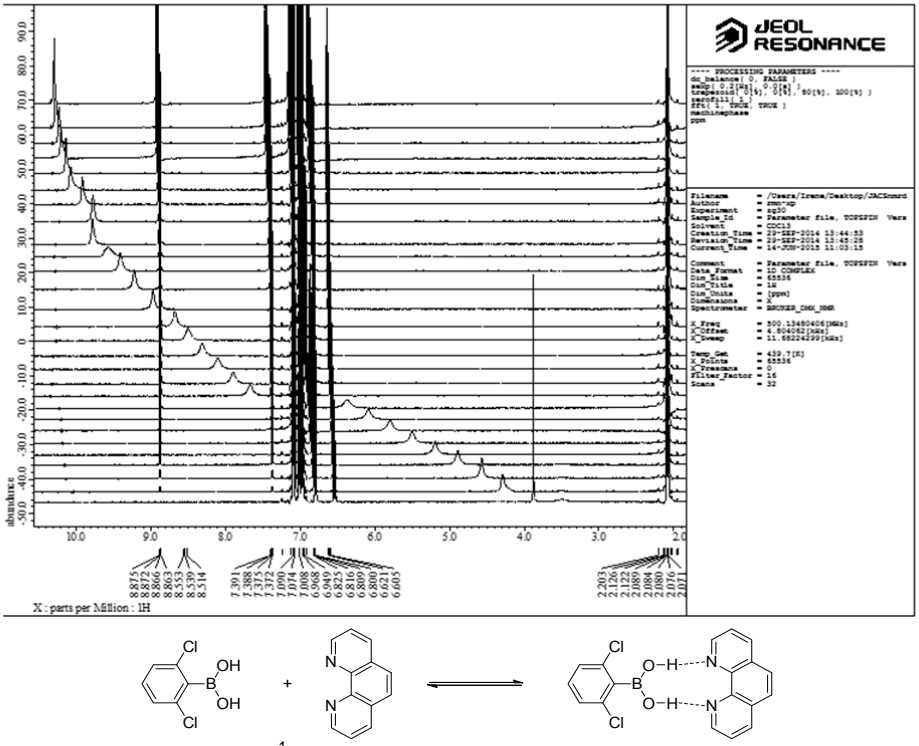


Figure S20. Selected region of a series ^{1}H NMR spectra acquired during the titration of ***2,6-dichlorophenylboronic acid*** with ***1,10-phenanthroline*** (500 MHz, toluene-d_8, 298 K).

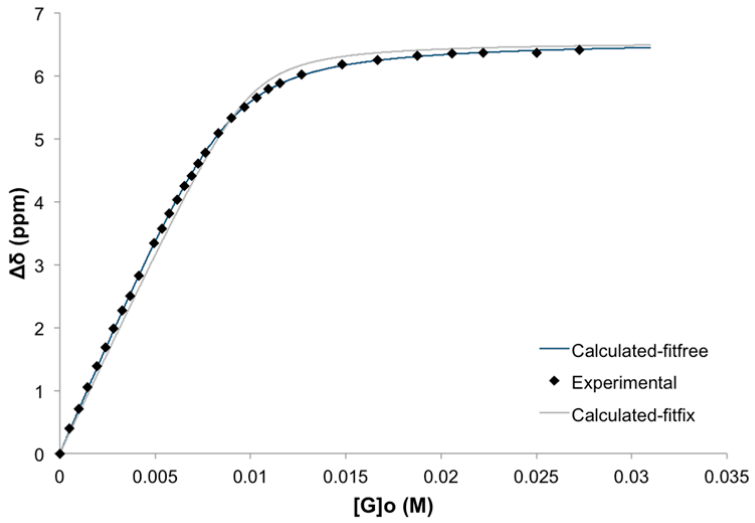
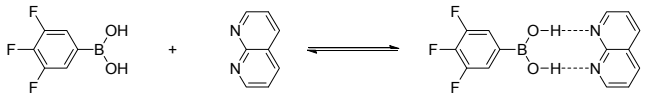


Figure S21. Binding isotherm for the formation of a 1:1 complex between ***2,6-dichlorophenylboronic acid*** and ***1,10-phenanthroline*** (500 MHz, toluene-d_8, 298 K). Fit fix: $[H]_o$ = 10 mM, $[G]_o$ = 50 mM, $\Delta\delta_{sat}$ = 6.41, K_a = 4953 ± 54. K_a (fit free) = 2306 ± 79, C_0' = 8.8 mM.

2.2.9. Between 3,4,5-trifluorophenylboronic acid and 1,8-naphthyridine



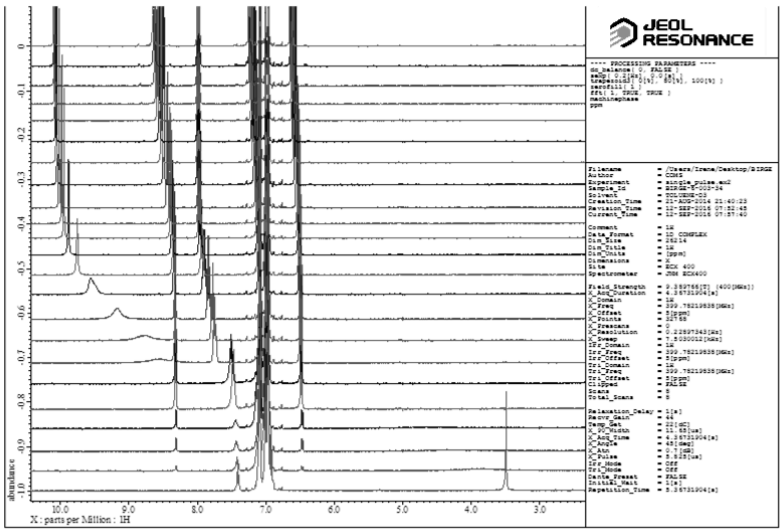


Figure S22. Selected region of a series ^{1}H NMR spectra acquired during the titration of ***3,4,5-trifluorophenylboronic acid*** with ***1,8-naphthyridine*** (500 MHz, toluene-d_8, 298 K).

2.2.10. Between 2,6-dichlorophenylboronic acid and 5,6,11,12-tetraazanaphthacene

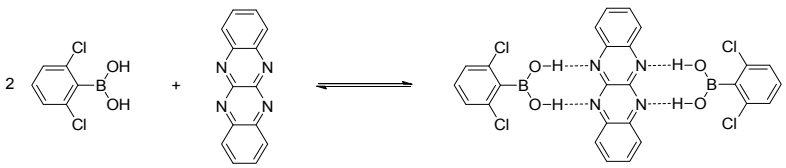


Figure S23. Selected region of a series ^{1}H NMR spectra acquired during the titration of ***2,6-dichlorophenylboronic acid*** with ***5,6,11,12-tetraazanaphthacene*** (300 MHz, CD_2Cl_2, 298 K).

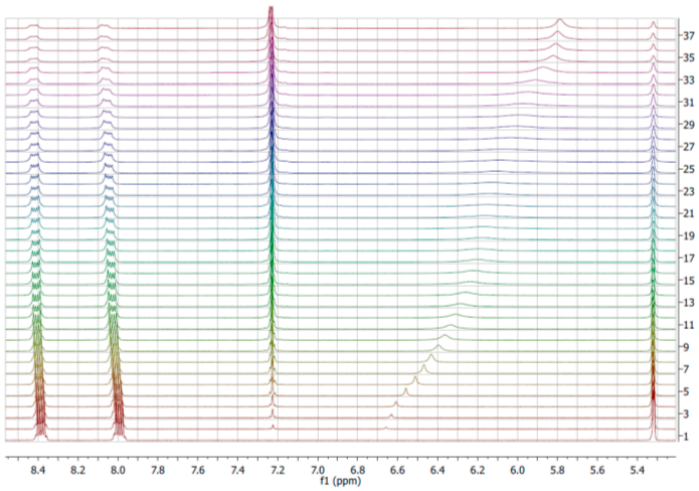


Figure S24. Selected region of a series ^{1}H NMR spectra acquired during the titration of ***2,6-dichlorophenylboronic acid*** with ***5,6,11,12-tetraazanaphthacene*** (300 MHz, CD_2Cl_2, 298 K).

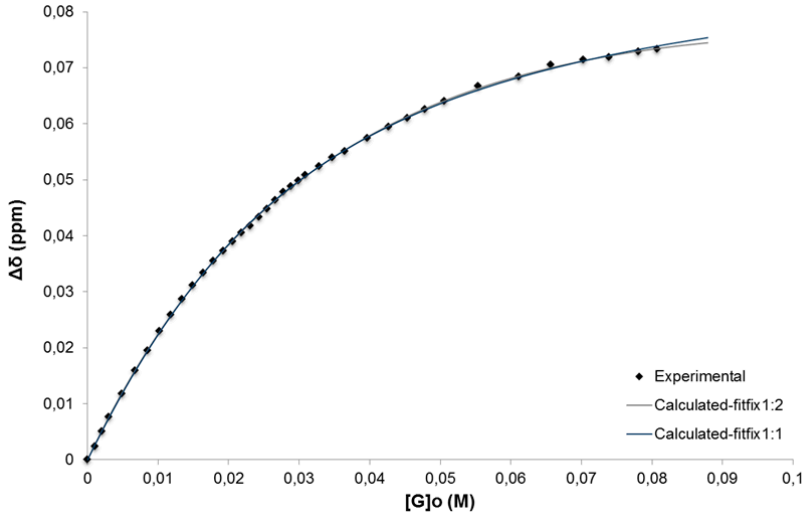


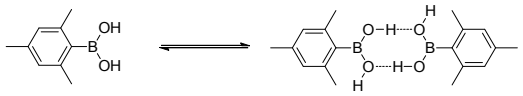
Figure S25. Binding isotherm for the formation of a 1:1 complex between ***5,6,11,12-tetraazanaphthacene*** and ***2,6-dichlorophenylboronic acid*** (300 MHz, CD_2Cl_2, 298 K). Fit fix: $[H]_o$ = 10 mM, $[G]_o$ = 102 mM, $\Delta\delta_{sat}$ = 0.06, K_{a1} = 126 ± 2 and K_{a2} = 29 ± 1.

2.3. General experimental procedure for the determination of the dimerization constant K_{dim}

^{1}H NMR dilution experiments were carried out with a solution of host (boronic acid) of 50 mM concentration which was progressively diluted with toluene-d_8. The chemical shift of the hydrogen atom of the –$B(OH)_2$ moiety was recorded after each 9 toluene-d_8 additions. From the data obtained the dilution plots were created using the equation reported and as the curve fitting software 'Scientist package' from MicroMath. The values reported are the average of two runs. In case where the chemical shift of interest was merging with the solvent peaks the data were excluded from the binding isotherm.

2.4 ^{1}H NMR analysis and curve used for the determination of the dimerization constant K_{dim}

2.4.1. Mesitylboronic acid



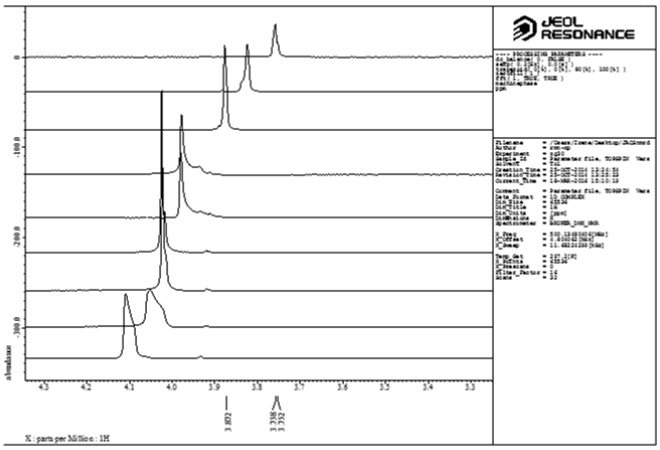


Figure S26. Selected region of a series ^{1}H NMR spectra acquired during the dilution experiment of ***mesitylboronic acid*** (500 MHz, toluene-d_8, 298 K).

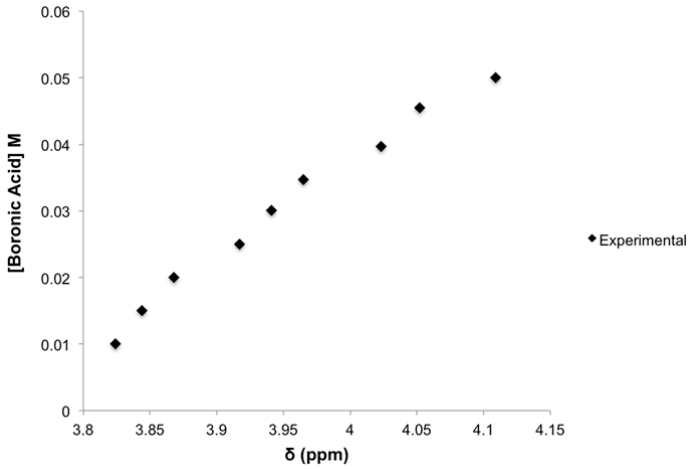


Figure S27. Dilution curve for ***mesitylboronic acid*** (500 MHz, toluene-d_8, 298 K). $[H]_o$ = 10 mM, $\Delta\delta_{sat}$ not reached, K_{dim} < 10 M^{-1}.

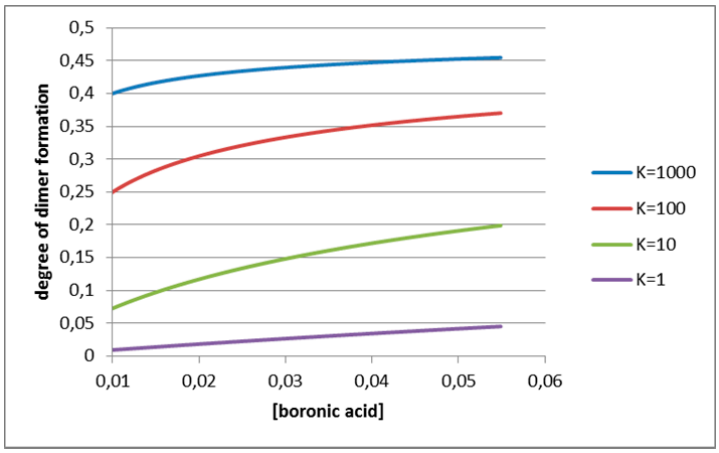
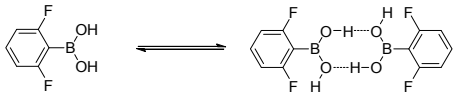


Figure S28. Calculated dilution curve for different K_{dim}. Dilution curves obtained for **mesitylboronic acid**, as well as the others, indicate a dimerization constant value between 1 and 10.

2.4.2. 2,6-Diflurophenylboronic acid



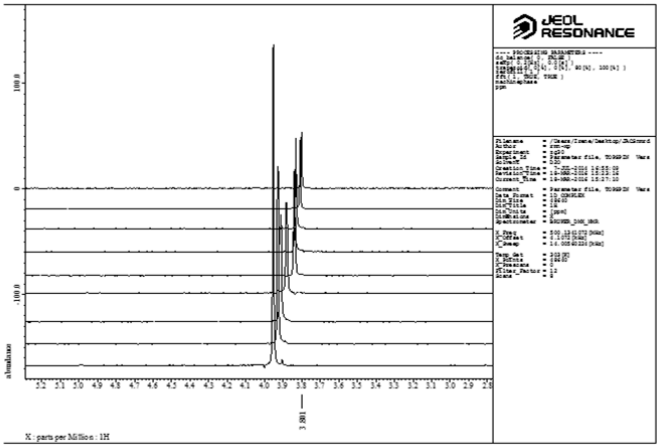


Figure S29. Selected region of a series ^{1}H NMR spectra acquired during the dilution experiment of ***2,6-difluorophenylboronic acid*** (500 MHz, toluene-d_8, 298 K).

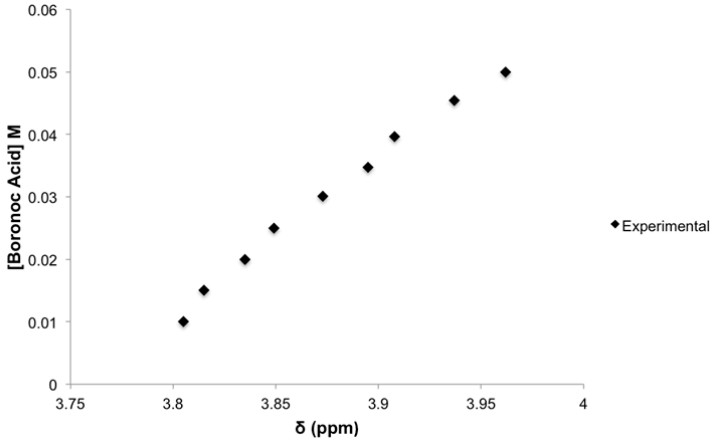
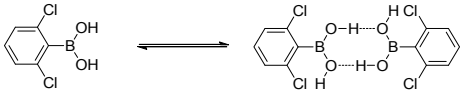


Figure S30. Dilution curve for ***2,6-difluorophenylboronic acid*** (500 MHz, toluene-d_8, 298 K). $[H]_o$ = 10 mM, $\Delta\delta_{sat}$ not reached, K_{dim} < 10 M^{-1}.

2.4.3. 2,6-Dichlorophenylboronic acid



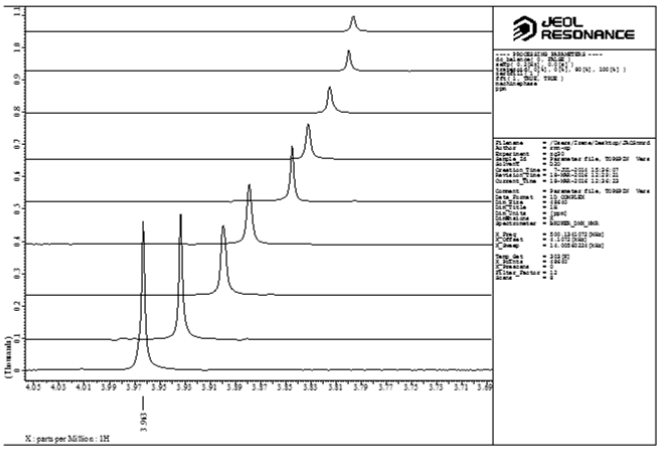


Figure S31. Selected region of a series ^{1}H NMR spectra acquired during the dilution experiment of ***2,6-dichlorophenylboronic acid*** (500 MHz, toluene-d_8, 298 K).

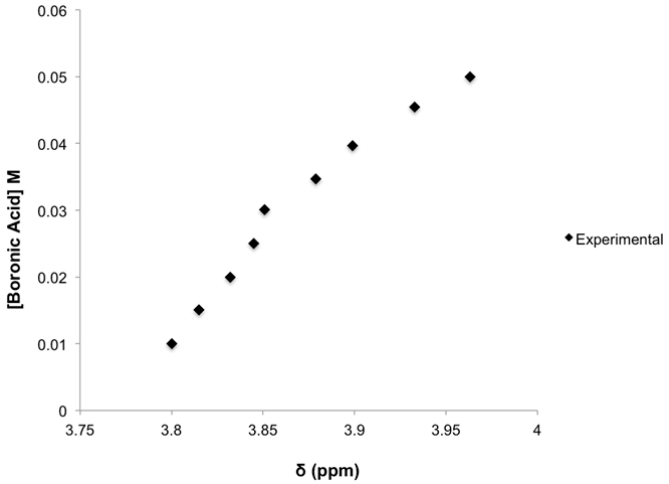
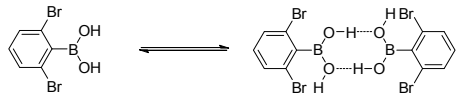


Figure S32. Dilution curve for ***2,6-dichlorophenylboronic acid*** (500 MHz, toluene-d_8, 298 K). $[H]_o$ = 10 mM, $\Delta\delta_{sat}$ = not reached, K_{dim} < 10 M^{-1}.

2.4.4. 2,6-Dibromophenylboronic acid



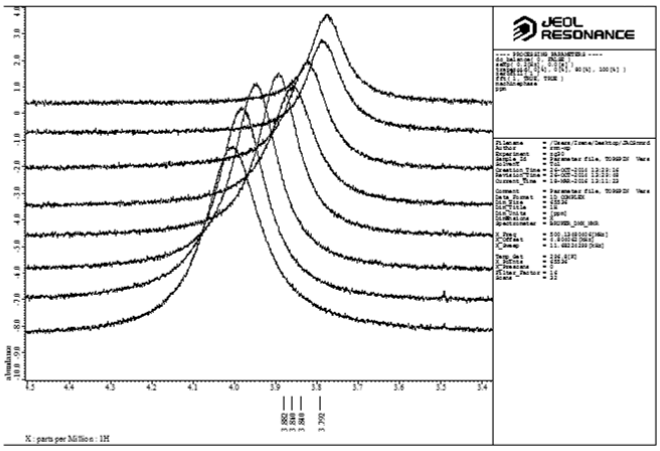


Figure S33. Selected region of a series ^{1}H NMR spectra acquired during the dilution experiment of ***2,6-dibromophenylboronic acid*** (500 MHz, toluene-d_8, 298 K).

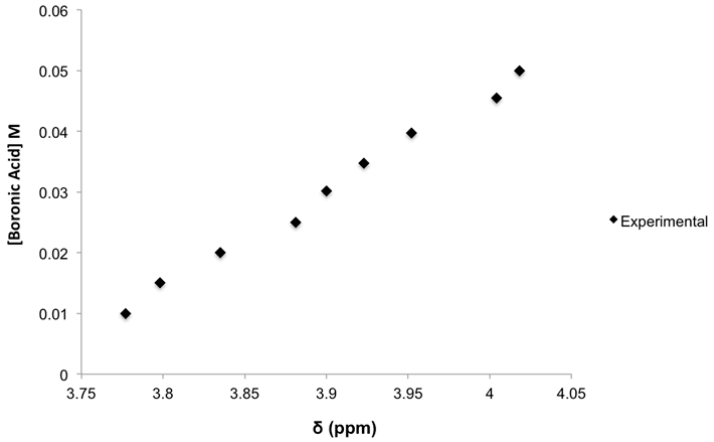
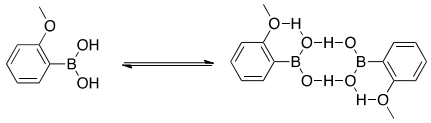


Figure S34. Dilution curve for ***2,6-dibromophenylboronic acid*** (500 MHz, toluene-d_8, 298 K). $[H]_o$ = 10 mM, $\Delta\delta_{sat}$ = not reached, K_{dim} < 10 M^{-1}.

2.4.5. 2-Methoxyphenylboronic acid



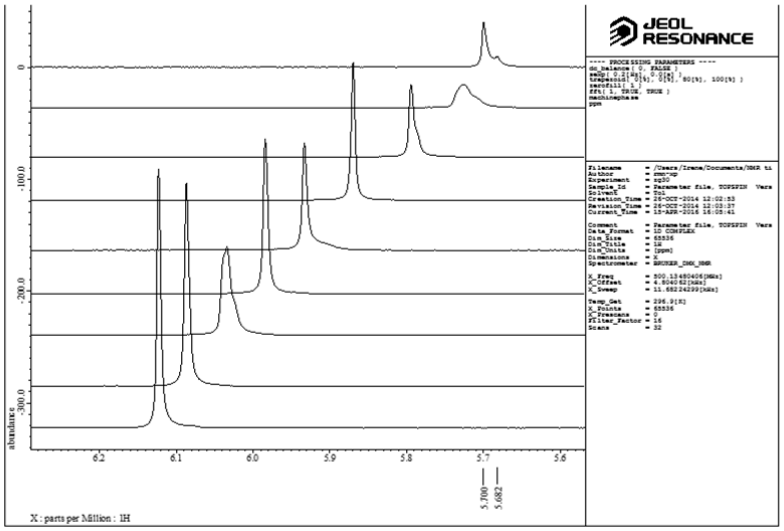


Figure S35. Selected region of a series ^{1}H NMR spectra acquired during the dilution experiment of ***2-methoxyphenylboronic acid*** (500 MHz, toluene-d_8, 298 K).

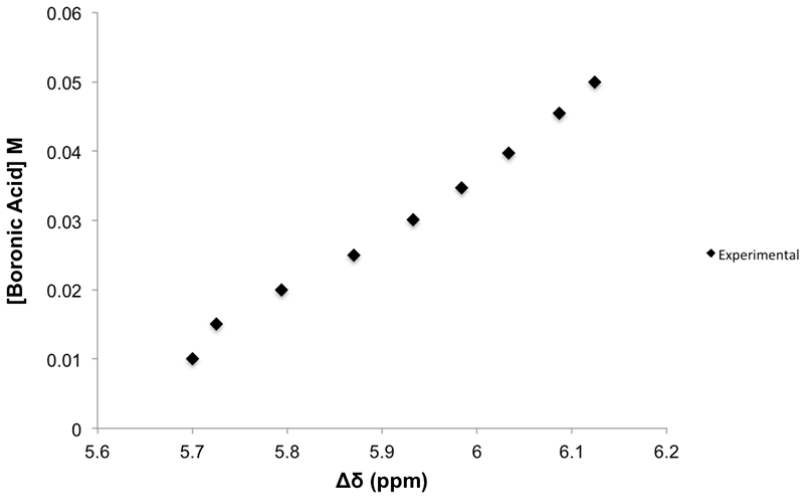


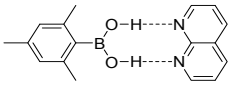
Figure S36. Dilution curve for ***2-methoxyphenylboronic acid*** (500 MHz, toluene-d_8, 298 K). $[H]_o$ = 10 mM, $\Delta\delta_{sat}$ = not reached, K_{dim} < 10 M^{-1}.

2.5. General experimental procedure for the determination of the binding stoichiometry by Job plot analysis

The 1:1 binding stoichiometry of the host-guest complexes was confirmed as follows. Two stock solutions were prepared; solution of the host (boronic acid) in 10 mM (3.5 mL) concentration in toluene-d_8 and solution of the guest (1,8-naphthyridine or 1,10-phenanthroline) in 10 mM (3.5 mL) concentration in toluene-d_8. Ten NMR tubes were filled with solutions of guest and host in the following volume ratios: 50:450, 100:400, 150:350, 200:300, 250:250, 300:200, 350:150, 400:100, 450:50 and 500:0 μL. ^{1}H NMR spectra were recorded for each mixture at 295 K and the experiment repeated twice. The concentration of the host-guest was estimated as followed: $[host{\cdot}guest]=([H]_o)(\delta_{obs}- \delta_o)/(\delta_{HG}- \delta_o)$, where $[H]_o$= the total concentration of the host receptor in solution, δ_{obs}= observed chemical shift, δ_o= chemical shift of the hydrogen atom of the $-B(OH)_2$ moiety prior to complexation and δ_{HG}= chemical shift of the hydrogen atom of the $-B(OH)_2$ moiety in the complex as observed during the ^{1}H NMR titration experiment. The molar ratio was calculated as followed: $x_H= ([H]_o)/([H]_o+[G]_o)$. The values reported are the average of two runs. In cases where the chemical shift of interest was merging with the solvent peaks the data were excluded from the Job plot.

2.6. ^{1}H NMR analysis and Job plot for the determination of the stoichiometry

2.6.1. Between mesitylboronic acid and 1,8-naphthyridine



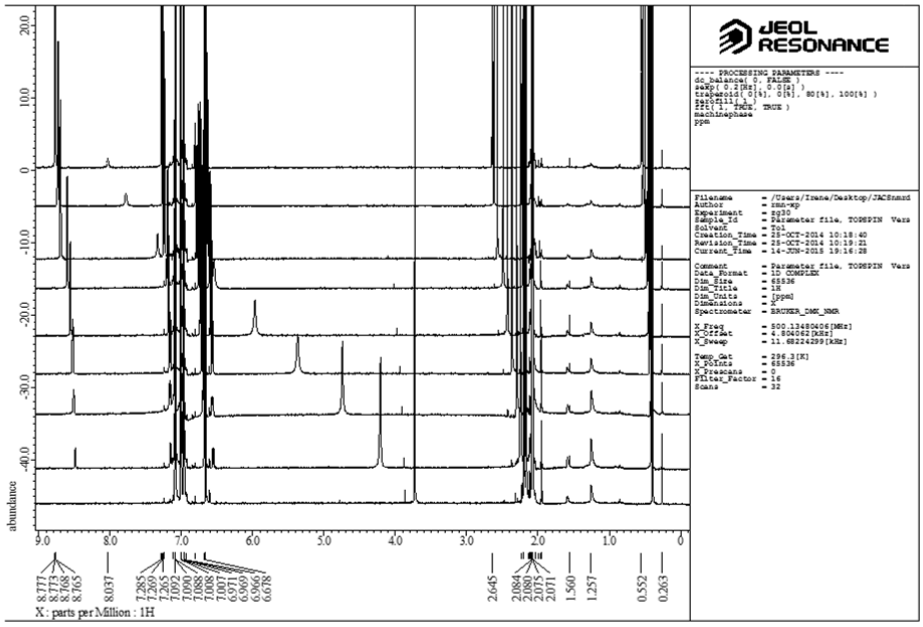


Figure S37. Selected region of a series ^{1}H NMR spectra acquired for the formation of the Job plot for the complex between ***mesitylboronic acid*** and ***1,8-naphthyridine*** (500 MHz, toluene-d_8, 298 K).

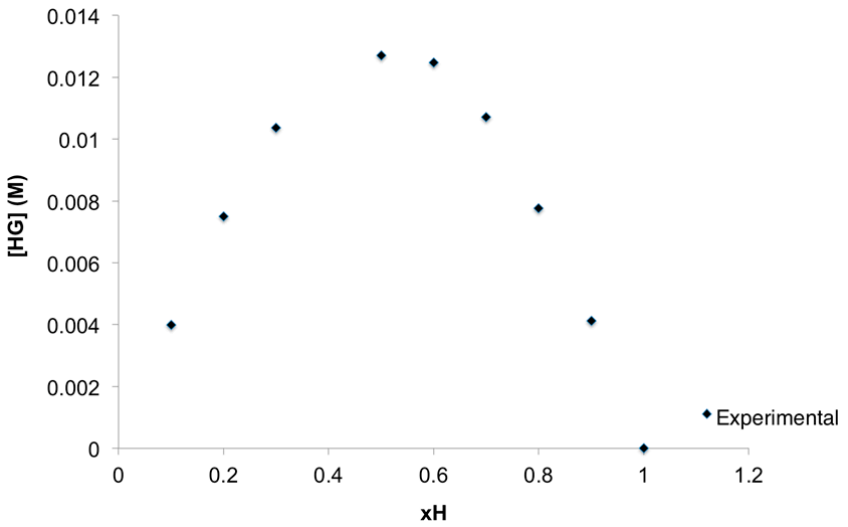
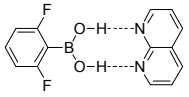


Figure S38. Job plot confirming the formation of a 1:1 complex between ***mesitylboronic acid*** and ***1,8-naphthyridine*** in toluene-d_8. $[H]_o+[G]_o$ = 10 mM. The theoretical maximum in [HG] is expected at x_H = 0.5 for a 1:1 association.

2.6.2. Between 2,6-difluorophenylboronic acid and 1,8-naphthyridine



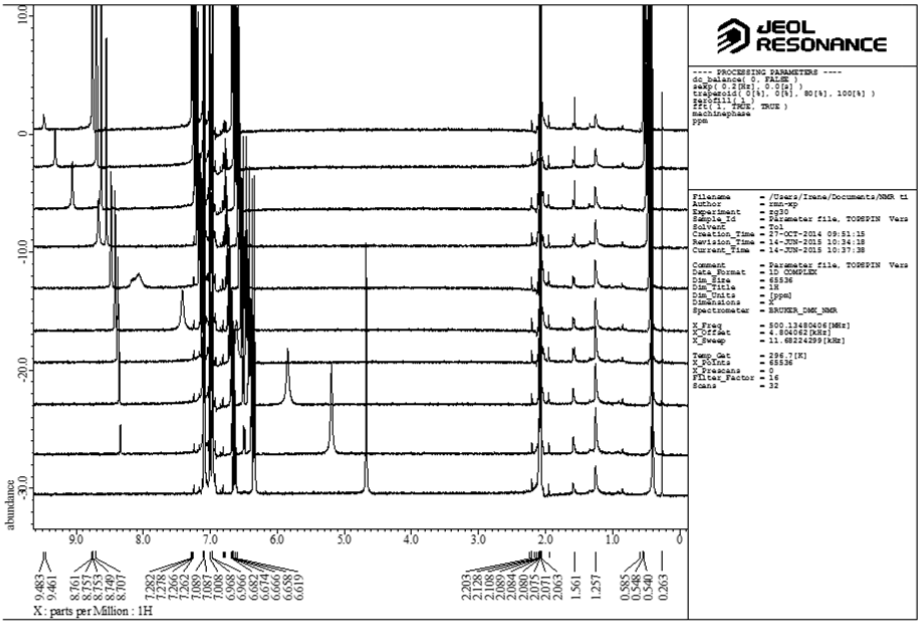


Figure S39. Selected region of a series ^{1}H NMR spectra acquired for the formation of the Job plot for the complex between ***2,6-difluorophenylboronic acid*** and ***1,8-naphthyridine*** (500 MHz, toluene-d_8, 298 K).

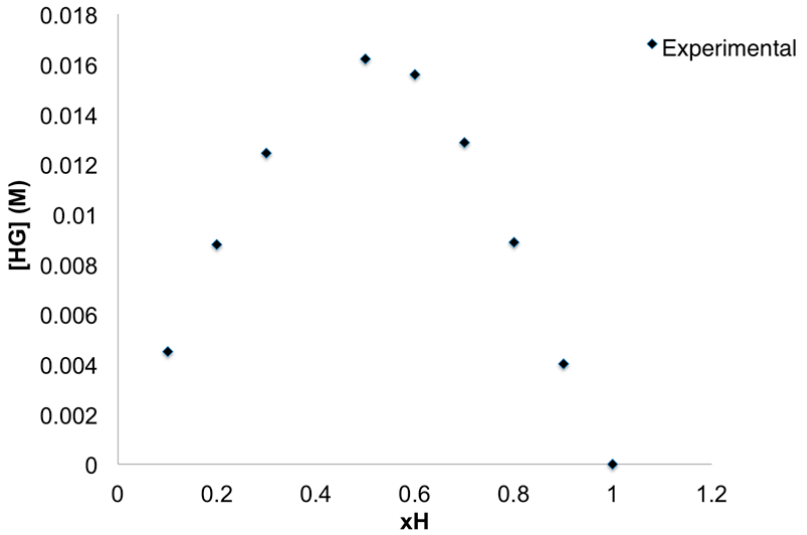
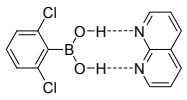


Figure S40. Job plot confirming the formation of a 1:1 complex between ***2,6-difluorophenylboronic acid*** and ***1,8-naphthyridine*** in toluene-d_8. $[H]_o+[G]_o$ = 10 mM. The theoretical maximum in [HG] is expected at x_H = 0.5 for a 1:1 association.

2.6.3. Between 2,6-dichlorophenylboronic acid and 1,8-naphthyridine



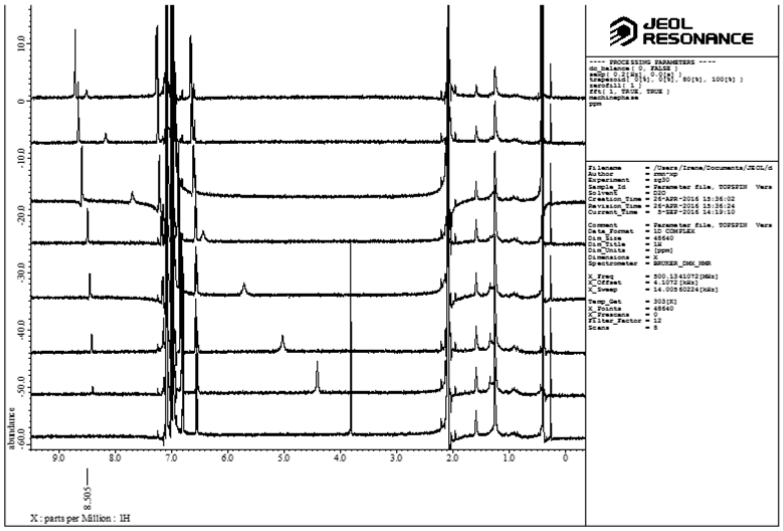


Figure S41. Selected region of a series ^{1}H NMR spectra acquired for the formation of the Job plot for the complex between ***2,6-dichlorophenylboronic acid*** and ***1,8-naphthyridine*** (500 MHz, toluene-d_8, 298 K).

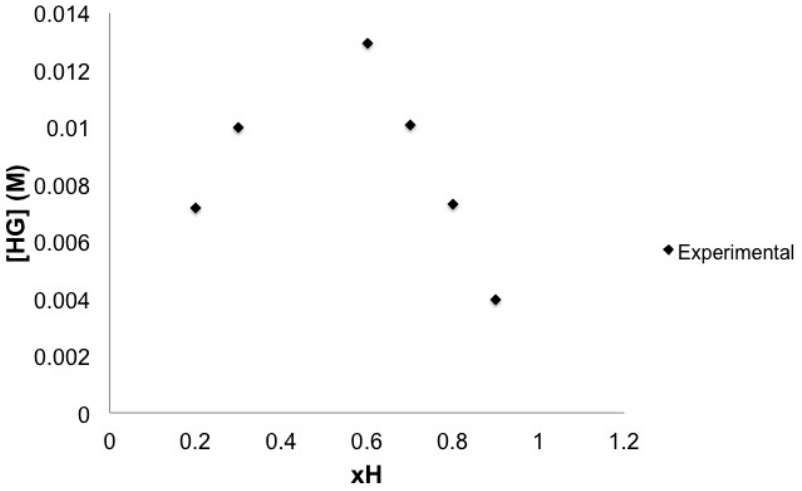
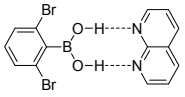


Figure S42. Job plot of the formation of complex between ***2,6-dichlorophenylboronic acid*** and ***1,8-naphthyridine*** in toluene-d_8. $[H]_o+[G]_o$ = 10 mM. The theoretical maximum in [HG] is expected at x_H = 0.5 for a 1:1 association.

2.6.4. Between 2,6-dibromophenylboronic acid and 1,8-naphthyridine



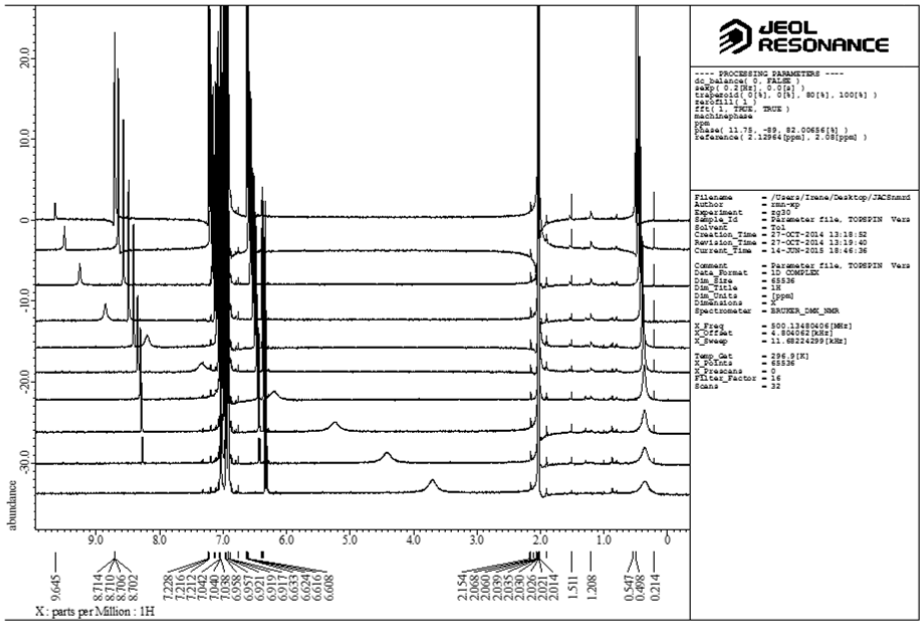


Figure S43. Selected region of a series ^{1}H NMR spectra acquired for the formation of the Job plot for the complex between ***2,6-dibromophenylboronic acid*** and ***1,8-naphthyridine*** (500 MHz, toluene-d_8, 298 K).

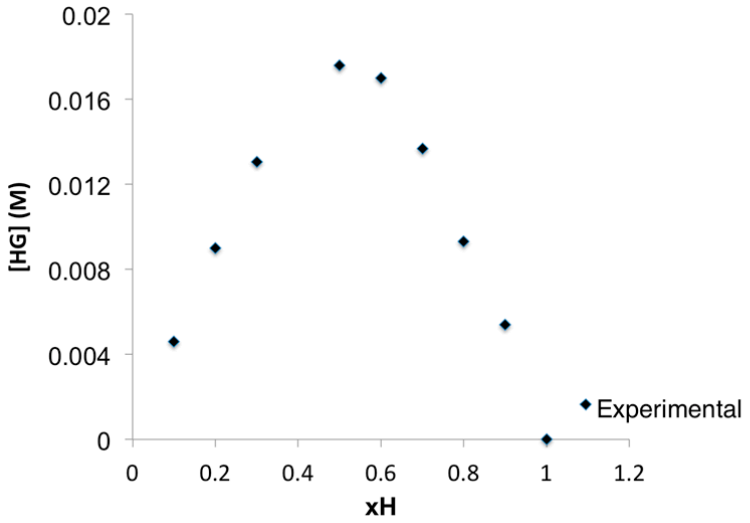
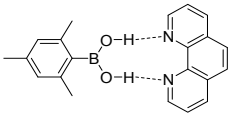


Figure S44. Job plot confirming the formation of a 1:1 complex between ***2,6-dibromophenylboronic acid*** and ***1,8-naphthyridine*** in toluene-d_8. $[H]_o+[G]_o$ = 10 mM. The theoretical maximum in [HG] is expected at x_H = 0.5 for a 1:1 association.

2.6.5. Between mesitylboronic acid and 1,10-phenanthroline



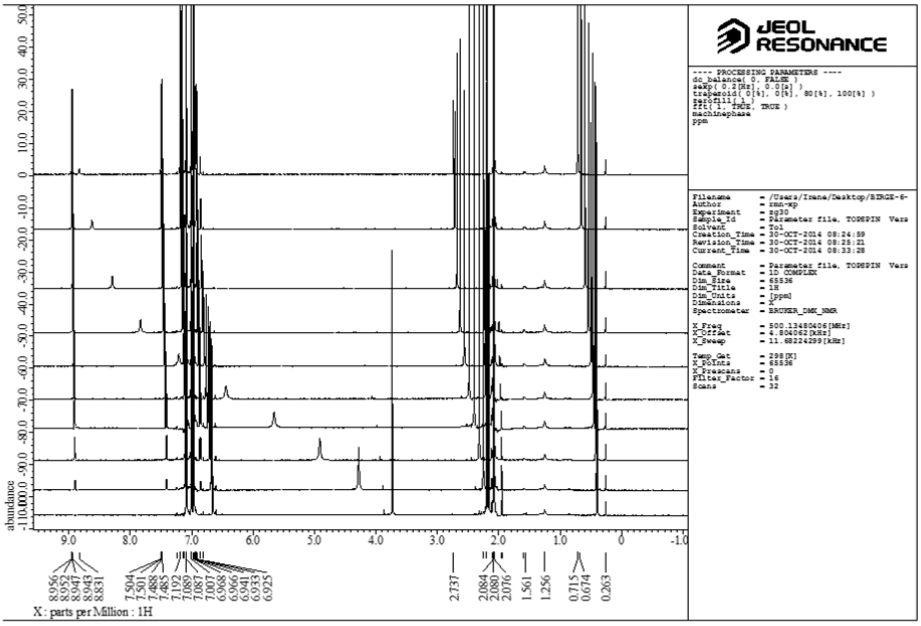


Figure S45. Selected region of a series ^{1}H NMR spectra acquired for the formation of the Job plot for the complex between ***mesitylboronic acid*** and ***1,10-phenanthroline*** (500 MHz, toluene-d_8, 298 K).

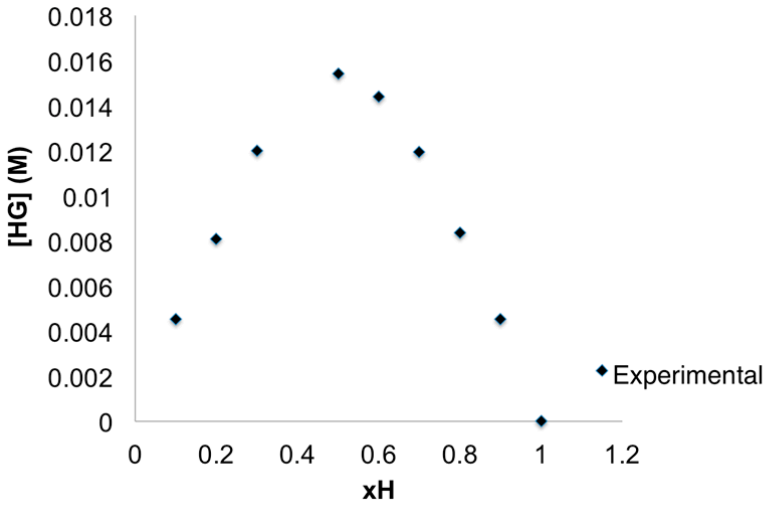
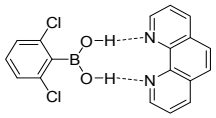


Figure S46. Job plot confirming the formation of a 1:1 complex between ***mesitylboronic acid*** and ***1,10-phenanthroline*** in toluene-d_8. $[H]_o+[G]_o$ = 10 mM. The theoretical maximum in [HG] is expected at x_H = 0.5 for a 1:1 association.

2.6.6. Between 2,6-dichlorophenylboronic acid and 1,10-phenanthroline



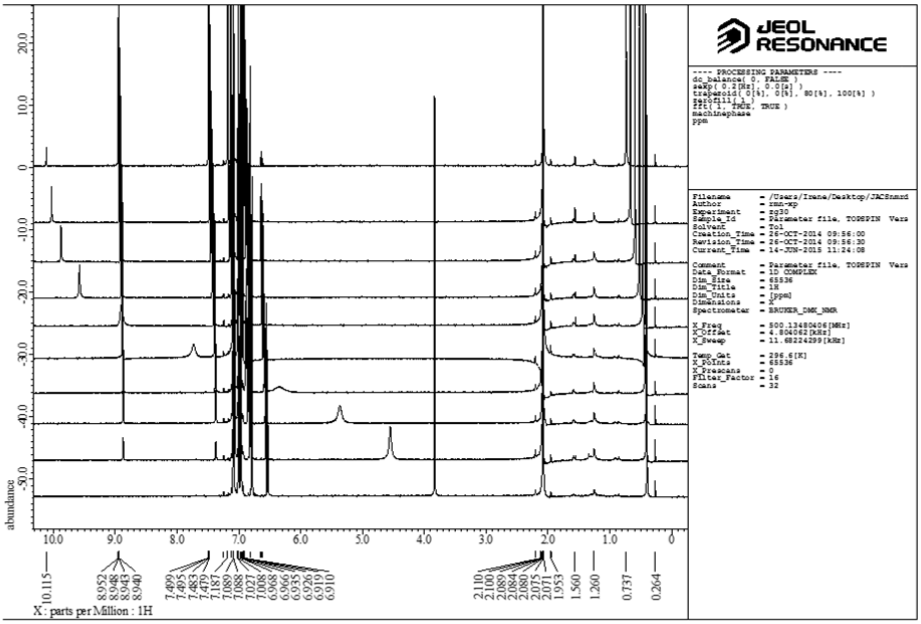


Figure S47. Selected region of a series ^{1}H NMR spectra acquired for the formation of the Job plot for the complex between ***2,6-dichlorophenylboronic acid*** and ***1,10-phenanthroline*** (500 MHz, toluene-d_8, 298 K).

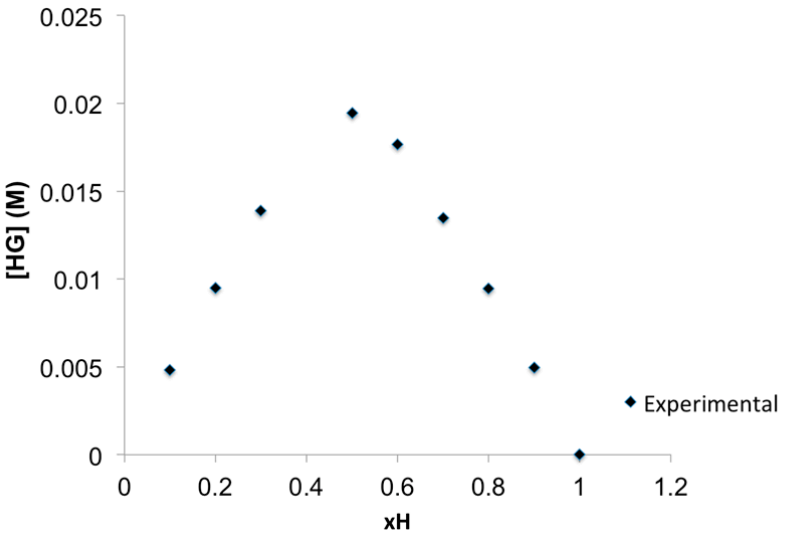


Figure S48. Job plot confirming the formation of a 1:1 complex between ***2,6-dichlorophenylboronic acid*** and ***1,10-phenanthroline*** in toluene-d_8. $[H]_o+[G]_o$ = 10 mM. The theoretical maximum in [HG] is expected at x_H = 0.5 for a 1:1 association.

2.6.7. Between 2,6-dichlorophenylboronic acid and 5,6,11,12-tetraazanaphthacene

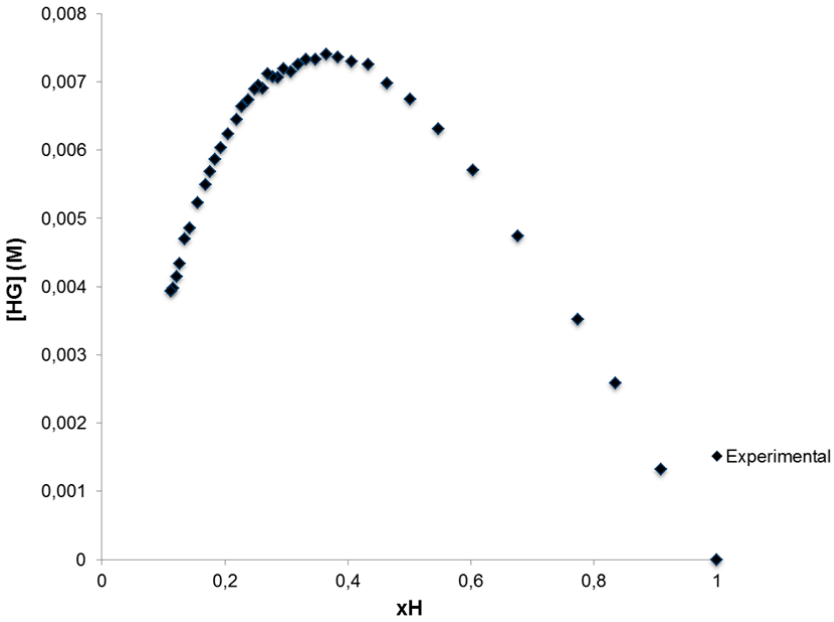


Figure S49. Job plot of the formation of complex between ***2,6-dichlorophenylboronic acid*** and ***5,6,11,12-tetraazanaphthacene*** in CD_2Cl_2. The theoretical maximum in [HG] is expected at x_H = 0.33 for a 1:2 association.

2.7. Experimental procedure for the determination of the H_2O effect

The experiment was performed at 295 K in toluene-d_8 *(stored over 4 Å molecular sieves)*. A stock solution of host (2,6-dichlorophenylboronic acid) of 10 mM (2 mL) concentration was initially made. From this solution 0.5 mL were placed in an NMR tube and 1 mL was used to prepare the solution of guest (H_2O) at 50 mM concentration. The change of chemical shift of the hydrogen atom of the $–B(OH)_2$ moiety was recorded after each 17 additions of guest to host. As shown in section 2.8 the indicative peak corresponding to the $–B(OH)_2$ moiety does not shift significantly by the addition of H_2O (3.89 ppm *vs* 3.98 ppm), and neither does the peak corresponding to H_2O (0.40ppm *vs* 0.42 ppm).

2.8. ^{1}H and ^{11}B NMR analysis for the determination of the H_2O effect

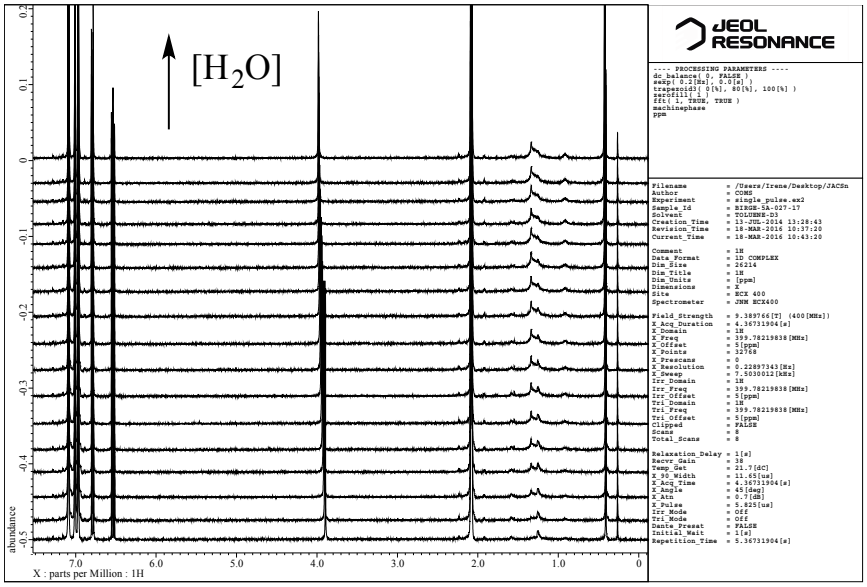


Figure S50. ^{1}H NMR spectra acquired during the titration of **2,6-dichlorophenylboronic acid** with **H_2O** (300 MHz, toluene-d_8, 298 K).

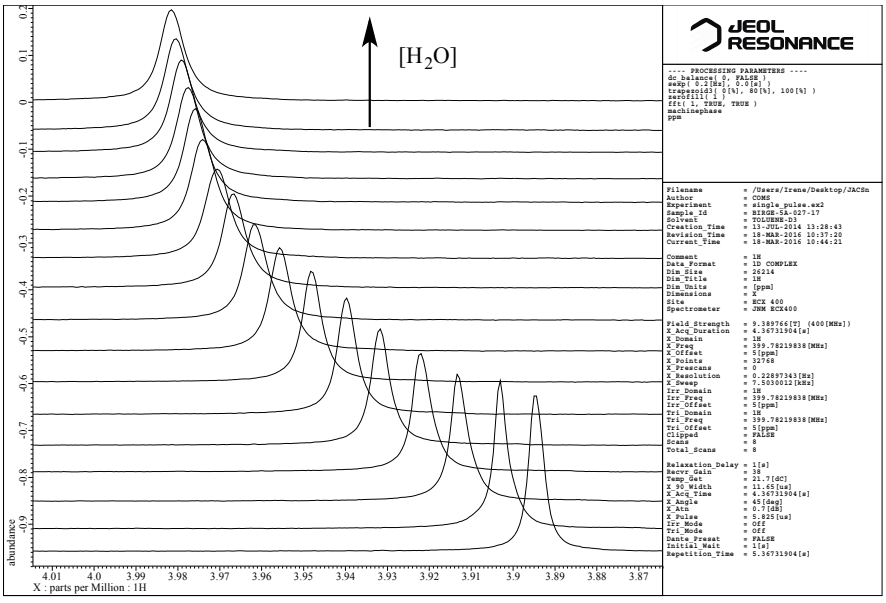


Figure S51. Selected region of the ^{1}H NMR spectra acquired during the titration of **2,6-dichlorophenylboronic acid** with **H_2O**, showing the indicative peak corresponding to the –$B(OH)_2$ moiety (300 MHz, toluene-d_8, 298 K).

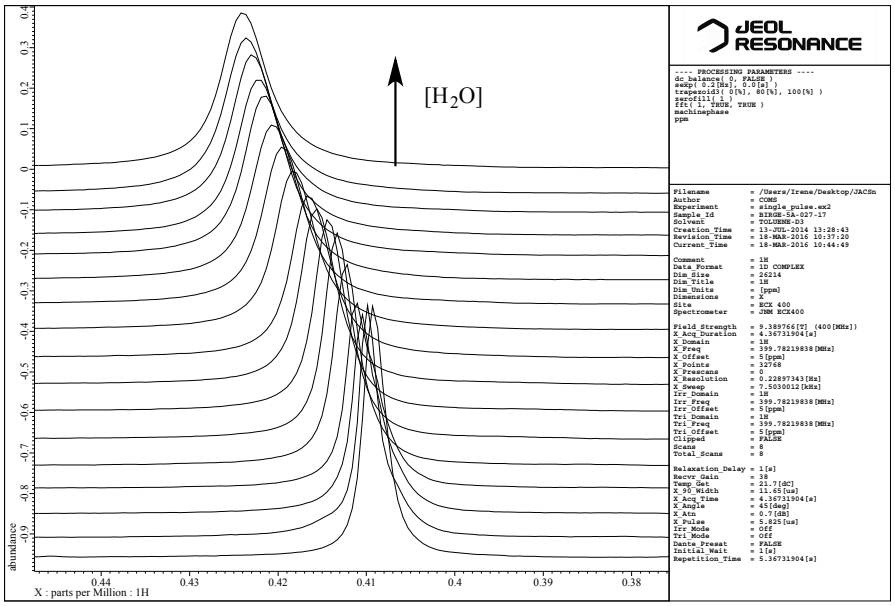


Figure S52. Selected region of the ^{1}H NMR spectra acquired during the titration of **2,6-dichlorophenylboronic acid** with **H_2O**, showing the indicative peak corresponding to H_2O (300 MHz, toluene-d_8, 298 K).

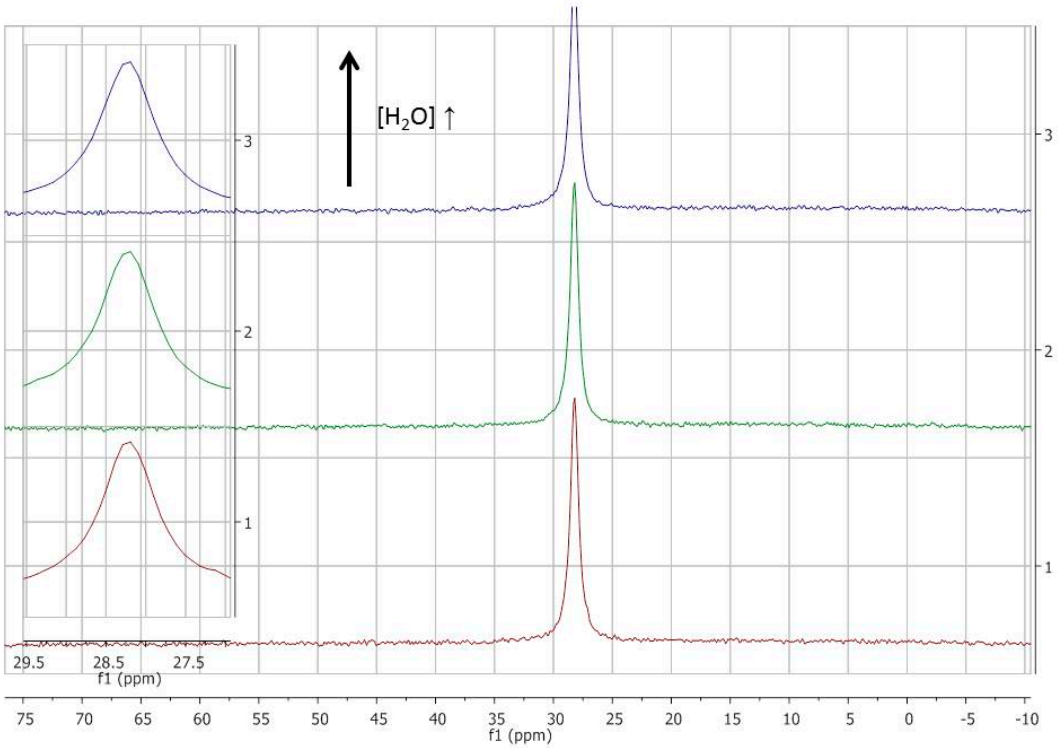


Figure S53. Selected region of the ^{11}B NMR spectra acquired during the titration of **2,6-dichlorophenylboronic acid** with **H_2O** (400 MHz, toluene-d_8, 298 K).

2.9. Experimental procedure for VT ^{1}H NMR

The experiment was performed with 5 mM solution of the boronic acid in toluene-d_8. The change of chemical shift of the hydrogen atom of the $-B(OH)_2$ moiety as well as the apparition of new peaks were recorded at different temperature: 21, 15, 0, - 10, - 20 and – 35 °C respectively. As shown in section 2.10 the indicative peak corresponding to the $-B(OH)_2$ moiety does not shift significantly by decreasing the temperature, and neither does the peak corresponding to H_2O (0.40ppm *vs* 0.42 ppm). However, a new peak appeared at low temperature and was shifted downfield as temperature decreased. Similarly, the integration of the indicative

peak of water decreased proportionally to the increasing of the extra peak indicating a correlation between the two.

2.10. ^{1}H NMR analysis for the VT experiments of boronic acid

2.10.1. Toluene

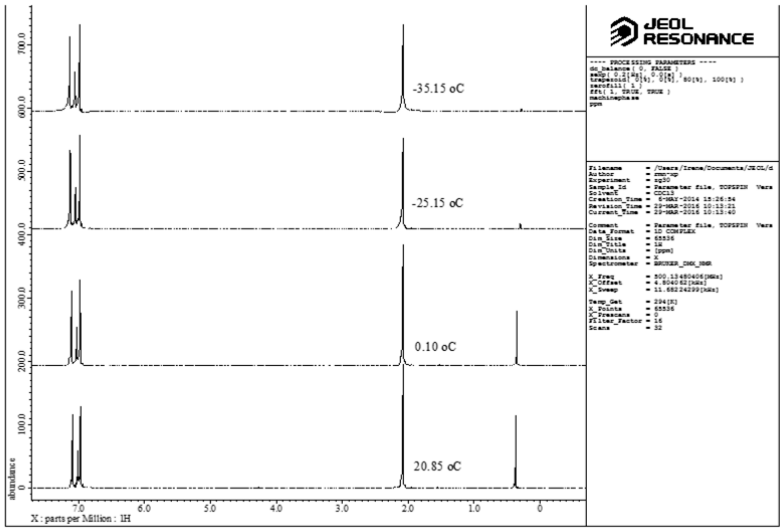


Figure S54. ^{1}H NMR spectra acquired during the VT experiments of toluene-d_8 (500 MHz).

2.10.2. 2,6-Dichlorophenylboronic acid

Table 1. ^{1}H NMR shifts and integration corresponding to H_A and H_B of the boronic acid, -OH of the boronic acid and H_2O, acquired during the VT experiment of **2,6-dichlorophenylboronic acid** (400 MHz, toluene-d_8).

T (°C)	H_A	OH	OH shift	H_2O	Extra Peak	Sum of "water" integration
21	6.58 ppm / 1H	3.90 ppm / 1.96H	-	0.44 ppm / 5.06H	-	5.06H
15	6.57 ppm / 1H	3.90 ppm / 1.80H	-	0.44 ppm / 4.00H	-	4.00H
0	6.55 ppm / 1H	3.98 ppm / 1.88H	0.08 ppm	0.44 ppm / 4.15H	5.50 ppm / 0.43H	4.48H
-10	6.53 ppm / 1H	3.98 ppm / 1.84H	0.08 ppm	0.43 ppm / 3.02H	5.62 ppm / 1.38H	3.69H
-20	6.51 ppm / 1H	3.99 ppm / 1.81H	0.09 ppm	0.43 ppm / 2.07H	5.76 ppm / 1.38H	3.45H
-35	6.48 ppm /1 H	4.09 ppm / 1.95H	0.19 ppm	0.42 ppm / 1.04H	6.00 ppm / 2.39H	3.43H

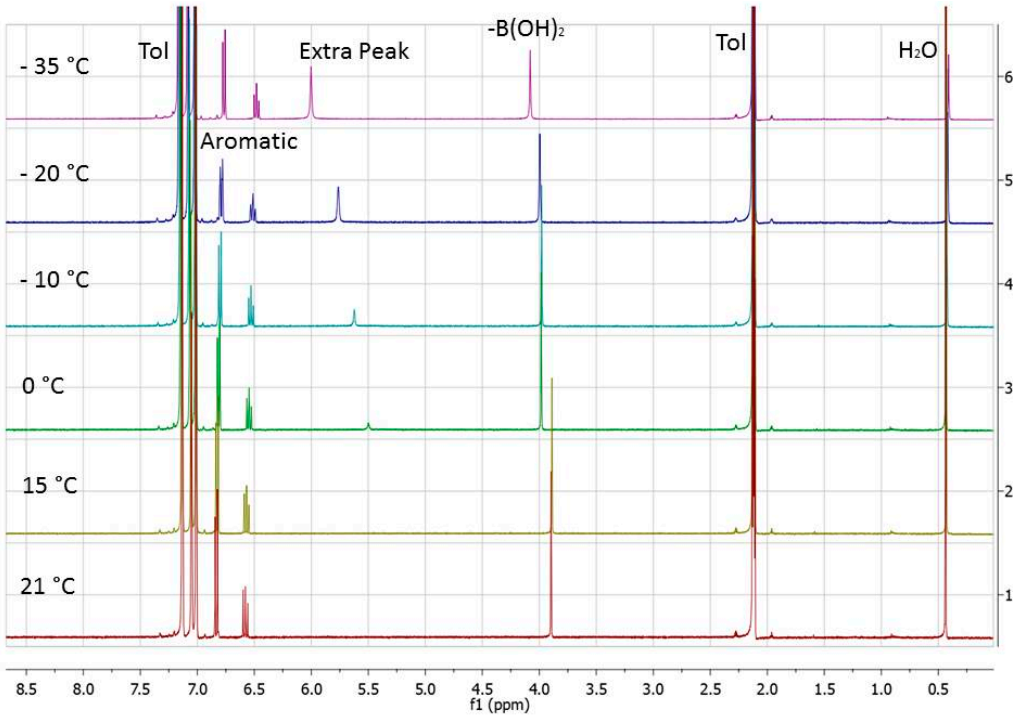


Figure S55. ^{1}H NMR spectra acquired during the VT experiments of **2,6-dichlorophenylboronic acid** (400 MHz, toluene-d_8).

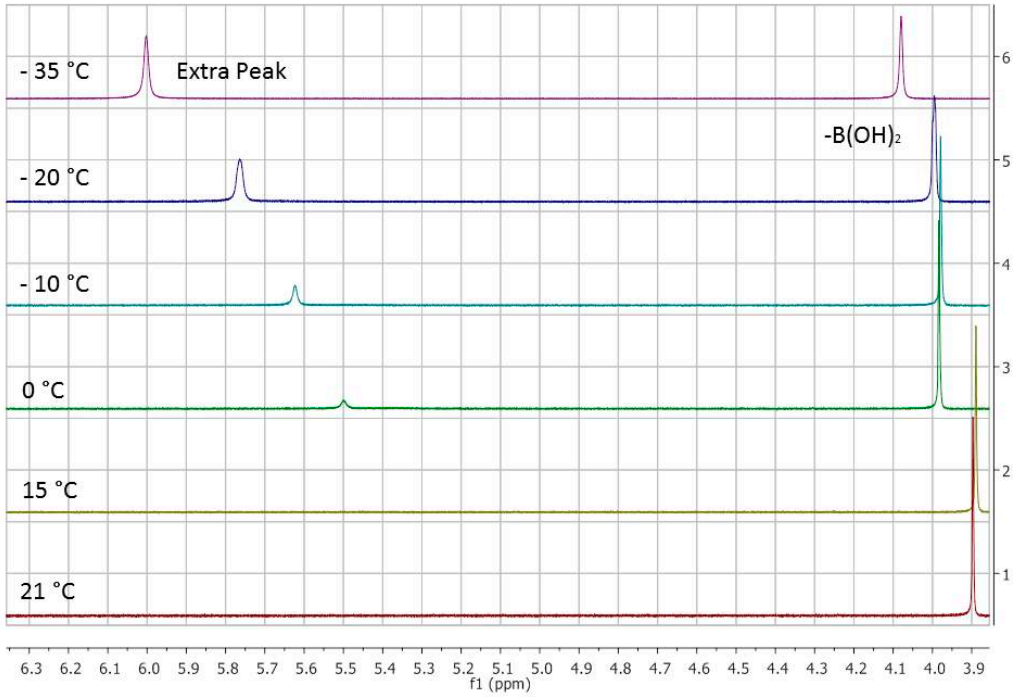


Figure S56. ^{1}H NMR spectra acquired during the VT experiments of **2,6-dichlorophenylboronic acid** (400 MHz, toluene-d_8).

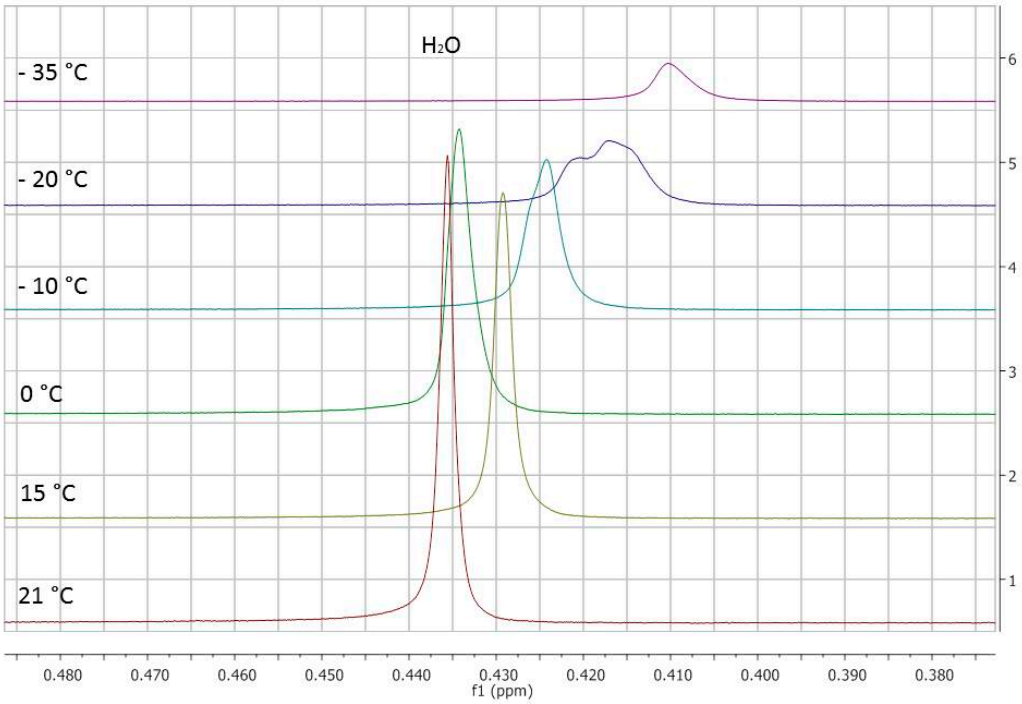


Figure S57. Selected region of the ^{1}H NMR spectra acquired during the VT experiments of **2,6-dichlorophenylboronic acid**, showing the indicative peak corresponding to H_2O (400 MHz, toluene-d_8).

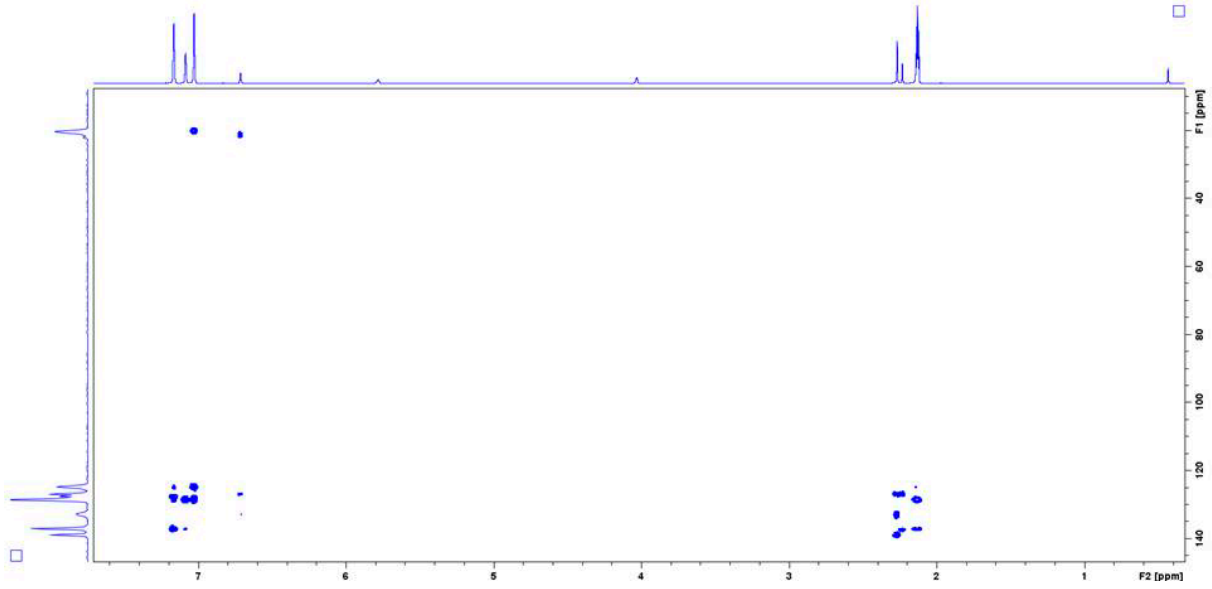


Figure S58. Selected region of the HMBC NMR spectra acquired during the VT experiments of **2,6-dichlorophenylboronic acid**, showing the indicative peak corresponding to H_2O (400 MHz, toluene-d_8).

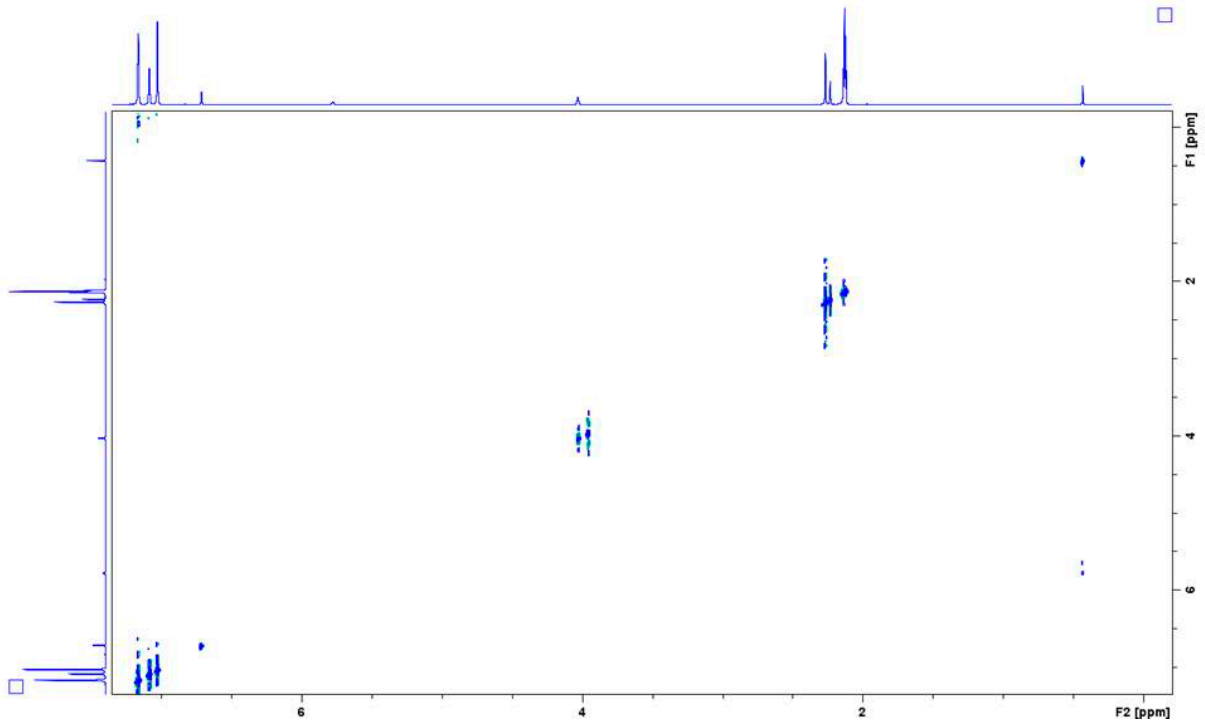


Figure S59. Selected region of the NOESY NMR spectra acquired during the VT experiments of **2,6-dichlorophenylboronic acid**, showing the indicative peak corresponding to H_2O (400 MHz, toluene-d_8).

2.10.3. 2,6-Dichlorophenylboronic and 1,8-naphthyridine in toluene

Table 2. ^{1}H NMR shifts and integration corresponding to H_A of the boronic acid, -OH of the boronic acid and H_2O, acquired during the VT experiment of **2,6-dichlorophenylboronic acid** with **1,8-naphthyridine** (500 MHz, toluene-d_8).

T (°C)	H_A	OH	OH shift	H_2O	Extra Peak	Sum of "water" integration
24	Merging with 1,8-napthyridine	-	-	0.50 ppm / very broad	-	-
15	6.60 ppm / 1H	-	-	0.46 ppm / 5.21H	-	5.21H
0	6.59 ppm / 1H	10.12 ppm / 2.44H	-	0.50 ppm / 4.80H	5.55 ppm / 0.52H	5.32H
-10	6.57 ppm / 1H	10.51 ppm / 2.04H	0.39 ppm	0.51 ppm / 3.15H	5.70 ppm / 1.48H	4.63H
-20	6.54 ppm / 1H	10.76 ppm / 1.83H	0.25 ppm	0.54 ppm / 1.55H	5.88 ppm / 2.00H	3.55H
-35	6.52 ppm /1 H	10.97 ppm / 1.80H	0.20 ppm	0.62 ppm / 0.53H	-	0.53H
-40	6.50 ppm / 1H	11.04 ppm / 1.75H		0.67 ppm / 0.44H	-	-

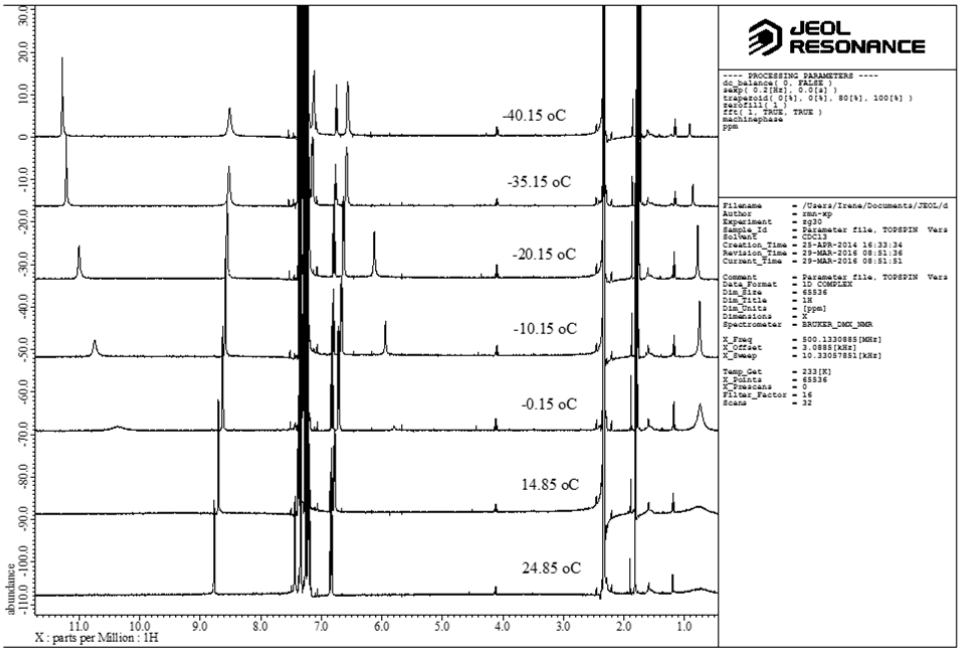


Figure S60. ^{1}H NMR spectra acquired during the VT experiments of **2,6-dichlorophenylboronic acid** with **1,8-naphthyridine** (500 MHz, toluene-d_8).

2.10.4. Mesitylboronic acid

Table 3. ^{1}H NMR shifts and integration corresponding to H_A of the boronic acid, -OH of the boronic acid and H_2O, acquired during the VT experiment of **mesitylboronic acid** (400 MHz, toluene-d_8).

T (°C)	H_A	OH	OH shift	H_2O	Extra Peak	Sum of "water" integration
21	6.71 ppm / 2H	3.76 ppm / 1.98H	-	0.43 ppm / 4.61H	-	4.61H
15	6.71 ppm / 2H	3.79 ppm / 1.98H	0.03 ppm	0.44 ppm / 4.63H	-	4.63H
0	6.71 ppm / 2H	3.88 ppm / 1.98H	0.12 ppm	0.44 ppm / 4.44H	-	4.44H
-10	6.71 ppm / 2H	3.94 ppm / 2.00H	0.17 ppm	0.43 ppm / 2.87H	5.62 ppm / 1.13H	4.56H
-20	6.71 ppm / 2H	4.03 ppm / 1.99H	0.26 ppm	0.43 ppm / 1.91H	5.77 ppm / 2.00H	4.52H
-35	6.70 ppm / 2 H	4.29 ppm / 1.92H	0.52 ppm	0.45 ppm / 0.92H	6.01 ppm / 2.25H	3.17H

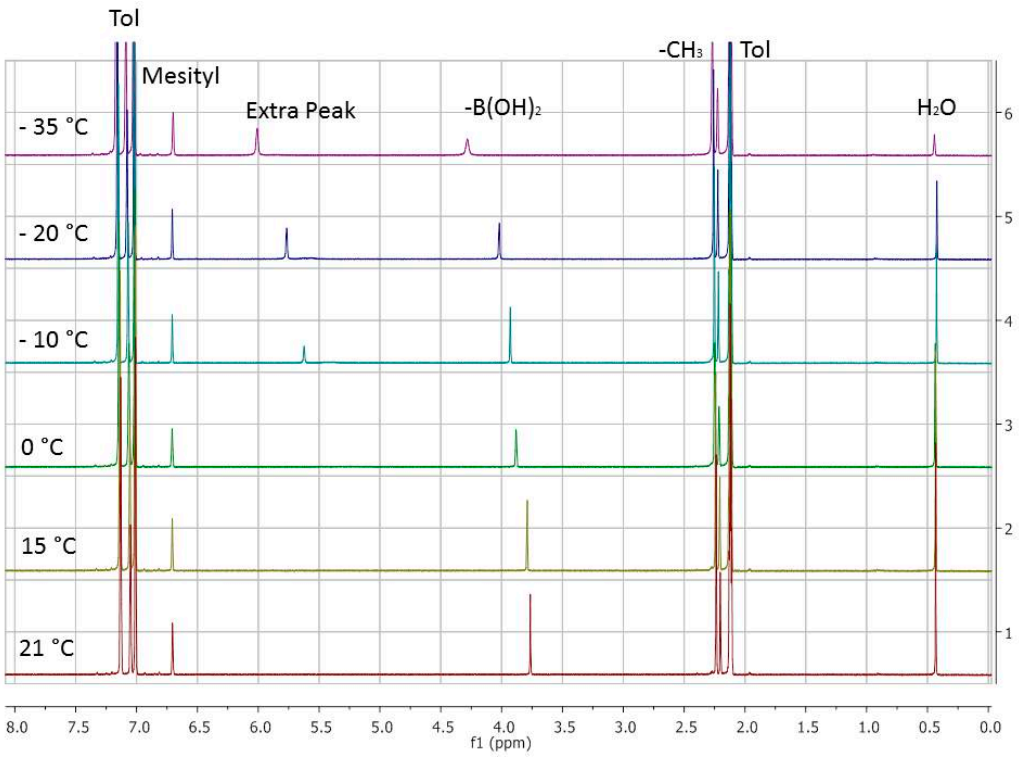


Figure S61. ^{1}H NMR spectra acquired during the VT experiments of **mesitylboronic acid** (400 MHz, toluene-d_8).

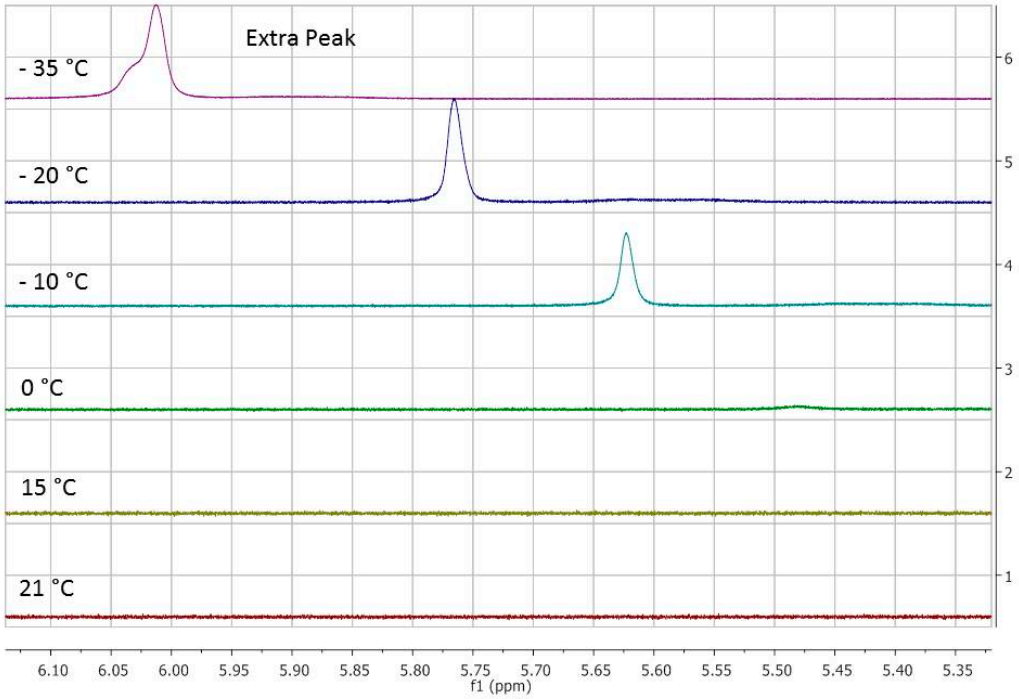


Figure S62. Selected region of the ^{1}H NMR spectra acquired during the VT experiments of **mesitylboronic acid**, showing the extra peak (400 MHz, toluene-d_8).

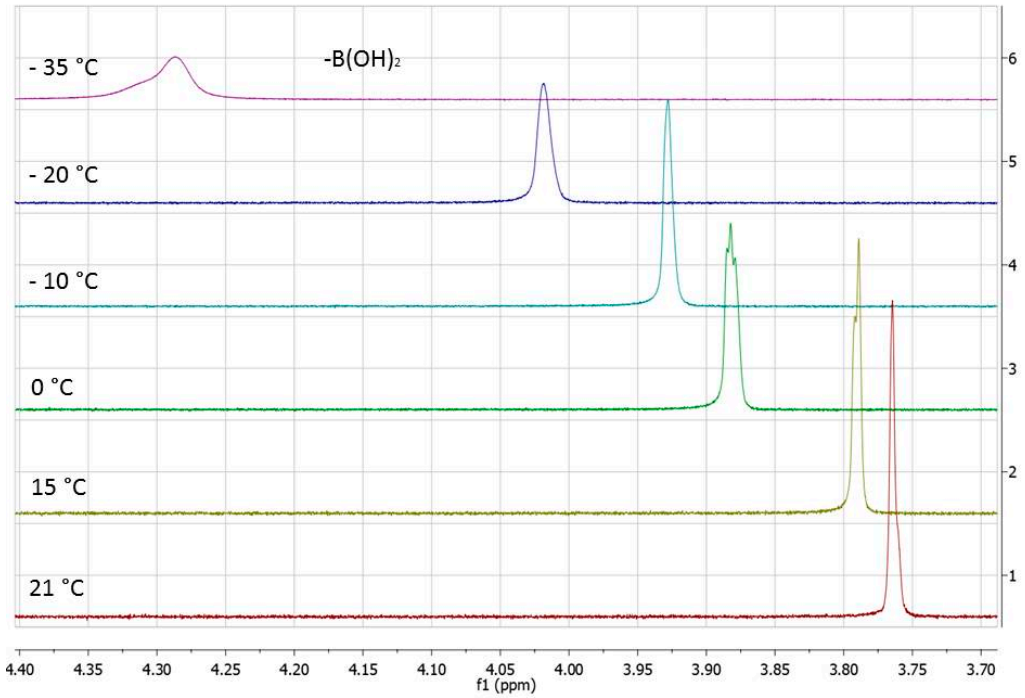


Figure S63. Selected region of the ^{1}H NMR spectra acquired during the VT experiments of **mesitylboronic acid**, showing the indicative peak corresponding to the –$B(OH)_2$ moiety (400 MHz, toluene-d_8).

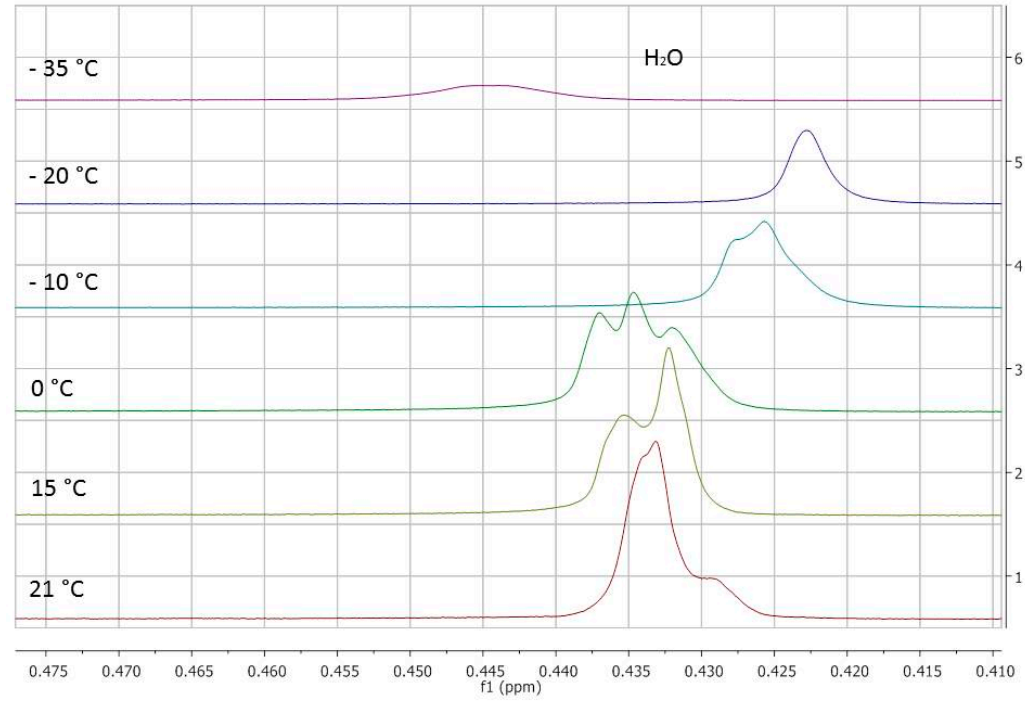


Figure S64. Selected region of the ^{1}H NMR spectra acquired during the VT experiments of **mesitylboronic acid**, showing the indicative peak corresponding to H_2O (400 MHz, toluene-d_8).

2.10.5. 2,6-Bis(trifluoromethyl)phenylboronic acid 2,6-dibromophenylboronic acid

Table 4. ^{1}H NMR shifts and integration corresponding to H_A of the boronic acid, -OH of the boronic acid and H_2O, acquired during the VT experiment of **2,6-bis(trifluoromethyl)phenylboronic acid** (400 MHz, toluene-d_8).

T (°C)	H_A	OH	OH shift	H_2O	Extra Peak	Sum of "water" integration
21	6.78 ppm / 1H	3.89 ppm / 2.00H	-	0.44 ppm / 5.36H	-	5.36H
15	6.77 ppm / 1H	3.91 ppm / 2.01H	0.02 ppm	0.44 ppm / 5.17H	-	5.17H
0	6.74 ppm / 1H	4.02 ppm / 2.06H	0.13 ppm	0.44 ppm / 5.01H	5.46 ppm / 0.35H	5.36H
-10	6.72 ppm / 1H	4.01 ppm / 2.01H	0.12 ppm	0.43 ppm / 3.40H	5.63 ppm / 1.37H	4.77H
-20	6.69 ppm / 1H	4.02 ppm / 2.02H	0.13 ppm	0.42 ppm / 2.23H	5.77 ppm / 2.57H	4.80H
-35	6.66 ppm / 1 H	3.94 ppm / 1.98H	0.05 ppm	0.38 ppm / 2.44H	6.01 ppm / 1.66H	4.10H

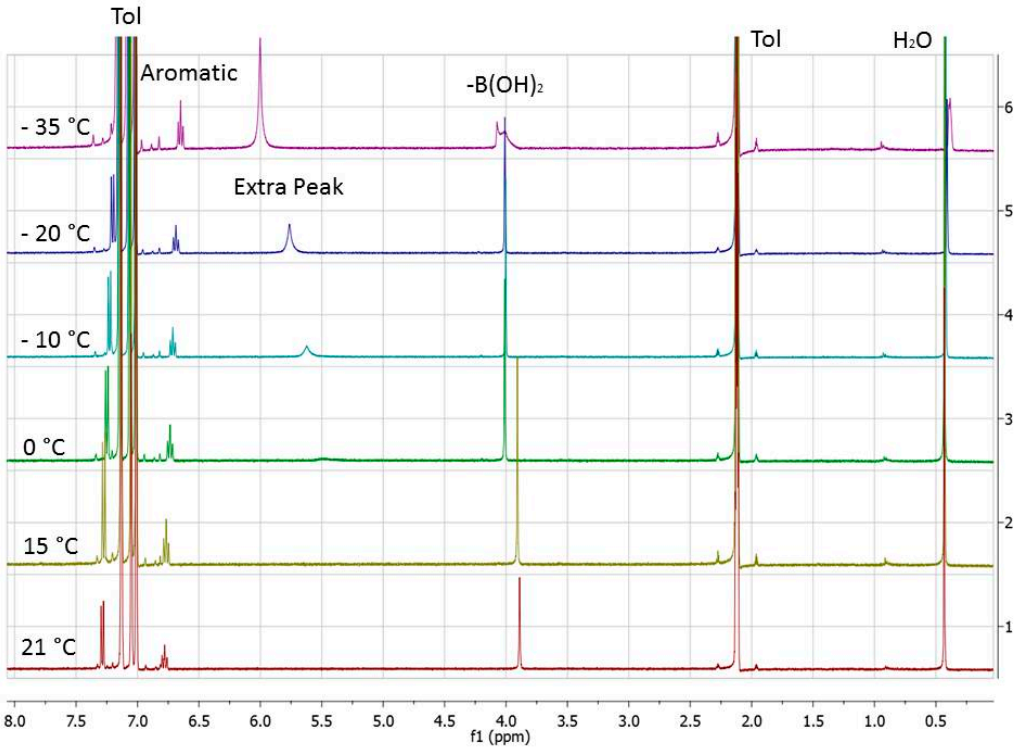


Figure S65. ^{1}H NMR spectra acquired during the VT experiments of **2,6-bis(trifluoromethyl)phenylboronic acid** (400 MHz, toluene-d_8).

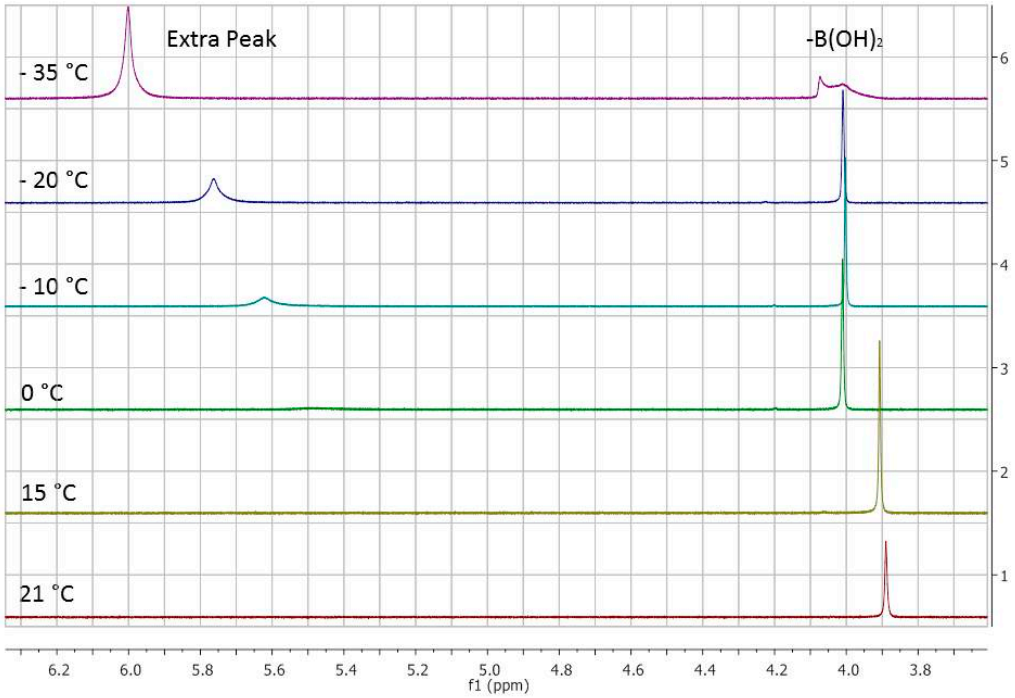


Figure S66. Selected region of the ^{1}H NMR spectra acquired during the VT experiments of **2,6-bis(trifluoromethyl)phenylboronic acid**, showing the extra peak and the indicative peak corresponding to –B(OH)$_2$ moiety (400 MHz, toluene-d_8).

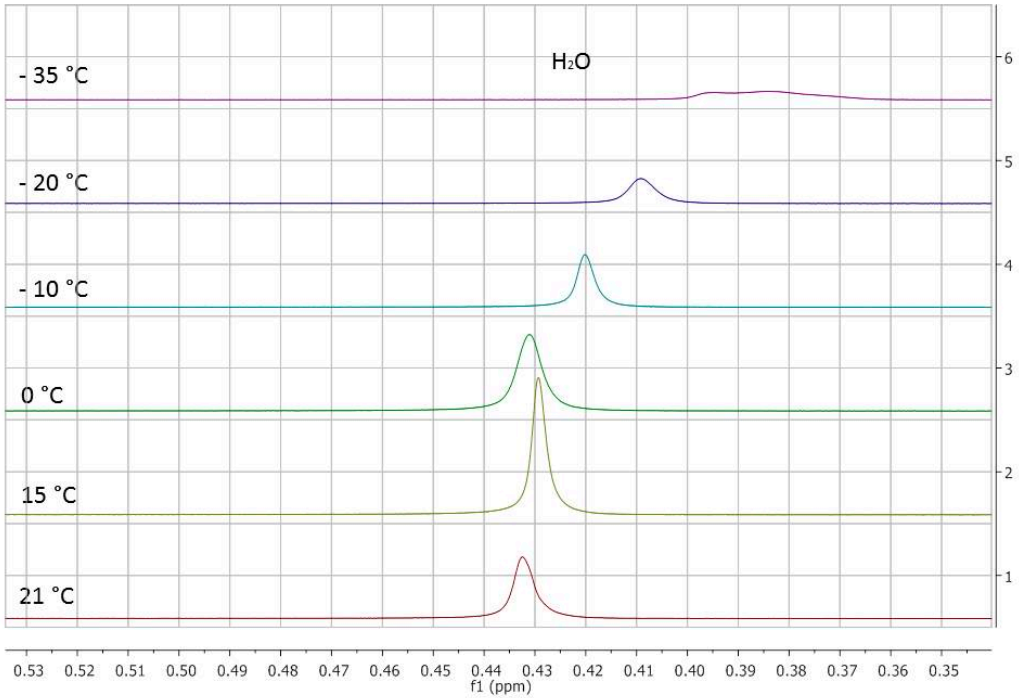


Figure S67. Selected region of the ^{1}H NMR spectra acquired during the VT experiments of **2,6-bis(trifluoromethyl)phenylboronic acid**, showing the indicative peak corresponding to H_2O (400 MHz, toluene-d_8).

2.10.6. 2,6-Dibromophenylboronic acid

Table 5. ^{1}H NMR shifts and integration corresponding to H_A of the boronic acid, -OH of the boronic acid and H_2O, acquired during the VT experiment of **2,6-dibromophenylboronic acid** (400 MHz, toluene-d_8).

T (°C)	H_A	OH	OH shift	H_2O	Extra Peak 1	Extra Peak 2	Sum of "water" integration
21	6.42 ppm / 1H	3.82 ppm / 2.00H	-	0.44 ppm / 5.39H	-	-	5.39H
15	6.41 ppm / 1H	3.83 ppm / 1.92H	0.01 ppm	0.44 ppm / 4.86H	-	-	4.86H
0	6.39 ppm / 1H	3.89 ppm / 1.99H	0.07 ppm	0.44 ppm / 4.66H	5.51 ppm / 0.23H	5.34 ppm / 0.57H	5.46H
-10	6.37 ppm / 1H	3.88 ppm / 1.96H	0.06 ppm	0.43 ppm / 3.15H	5.64 ppm / 0.76H	5.46 ppm / 0.80H	4.71H
-20	6.35 ppm / 1H	3.89 ppm / 2.00H	0.07 ppm	0.42 ppm / 2.07H	5.77 ppm / 0.89H	5.62 ppm / 2.10H	5.06H
-35	6.33 ppm / 1 H	3.96 ppm / 1.94H	0.14 ppm	0.42 ppm / 1.04H	6.01 ppm / 2.12H	5.83 ppm / 0.30H	3.44H
-35 (1 h)	6.32 ppm / 1 H	3.96 ppm / 1.98H	0.14 ppm	0.42 ppm / 0.98H	5.99 ppm / 0.23H		1.22H

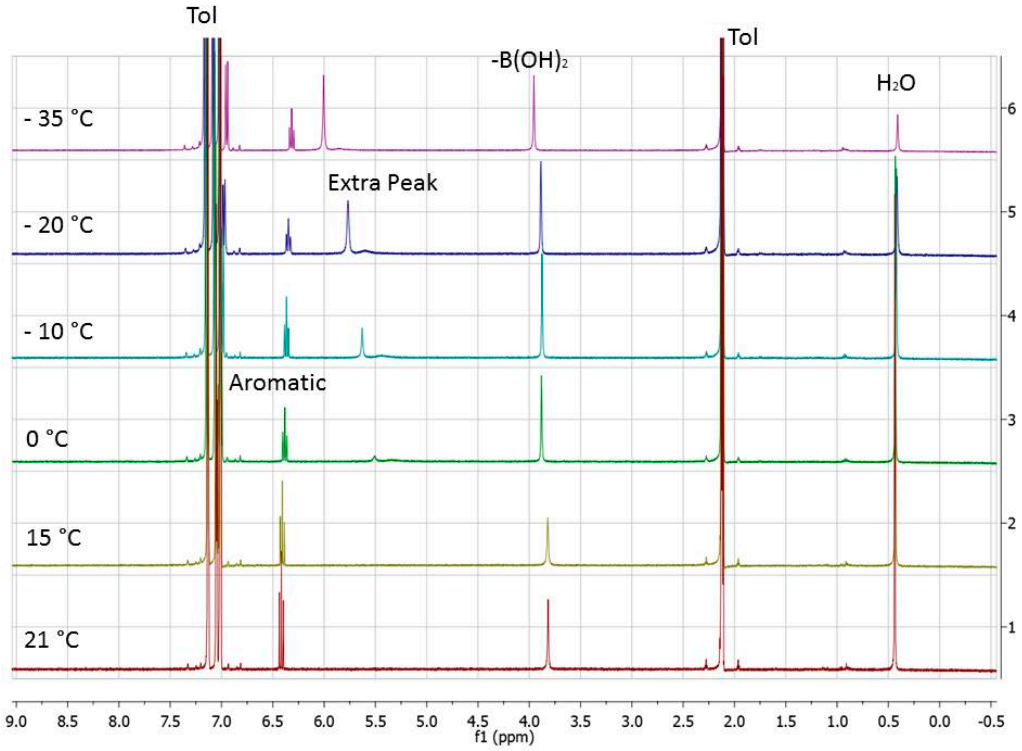


Figure S68. ^{1}H NMR spectra acquired during the VT experiments of **2,6-dibromophenylboronic acid** (400 MHz, toluene-d_8).

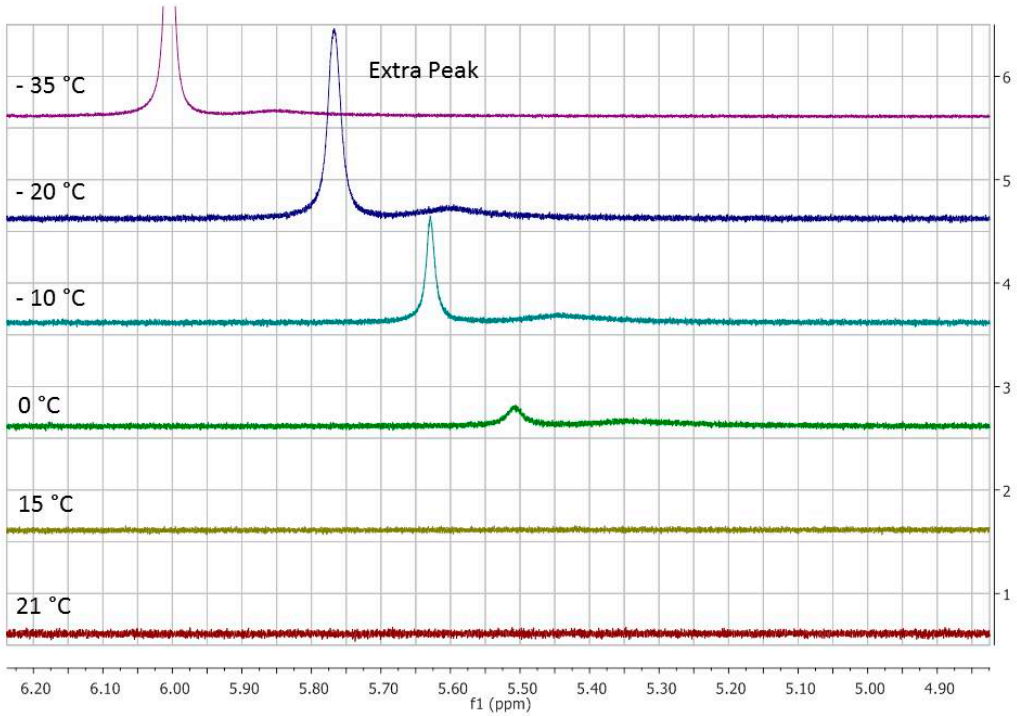


Figure S69. Selected region of the ^{1}H NMR spectra acquired during the VT experiments of **2,6-dibromophenylboronic acid**, showing the extra peak (400 MHz, toluene-d_8).

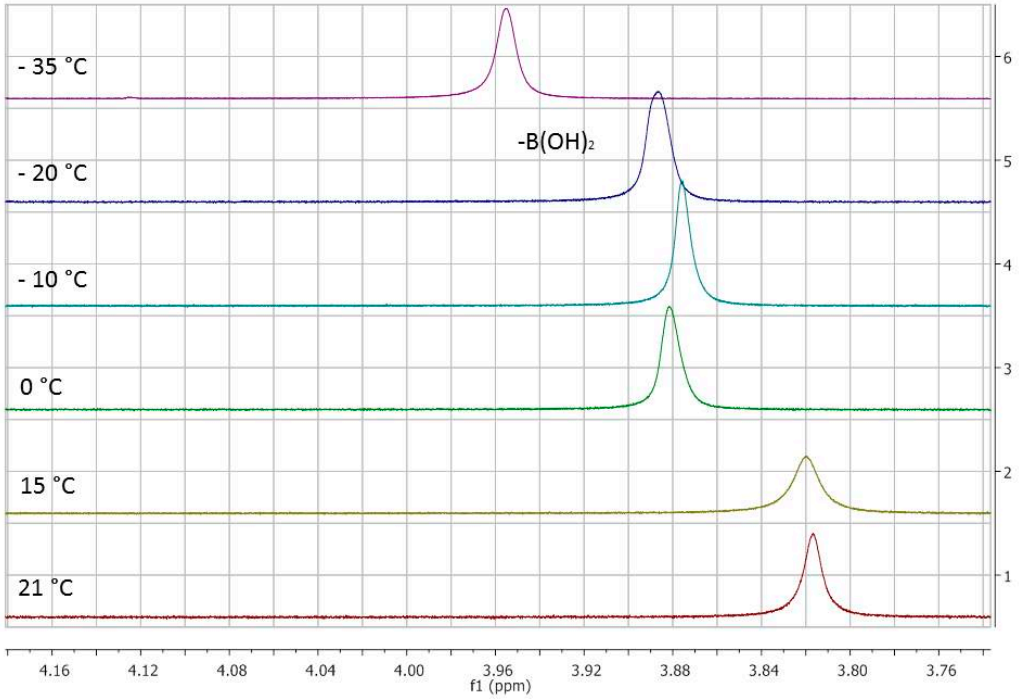


Figure S70. Selected region of the ^{1}H NMR spectra acquired during the VT experiments of **2,6-dibromophenylboronic acid**, showing the indicative peak corresponding to –B(OH)$_2$ moiety (400 MHz, toluene-d_8).

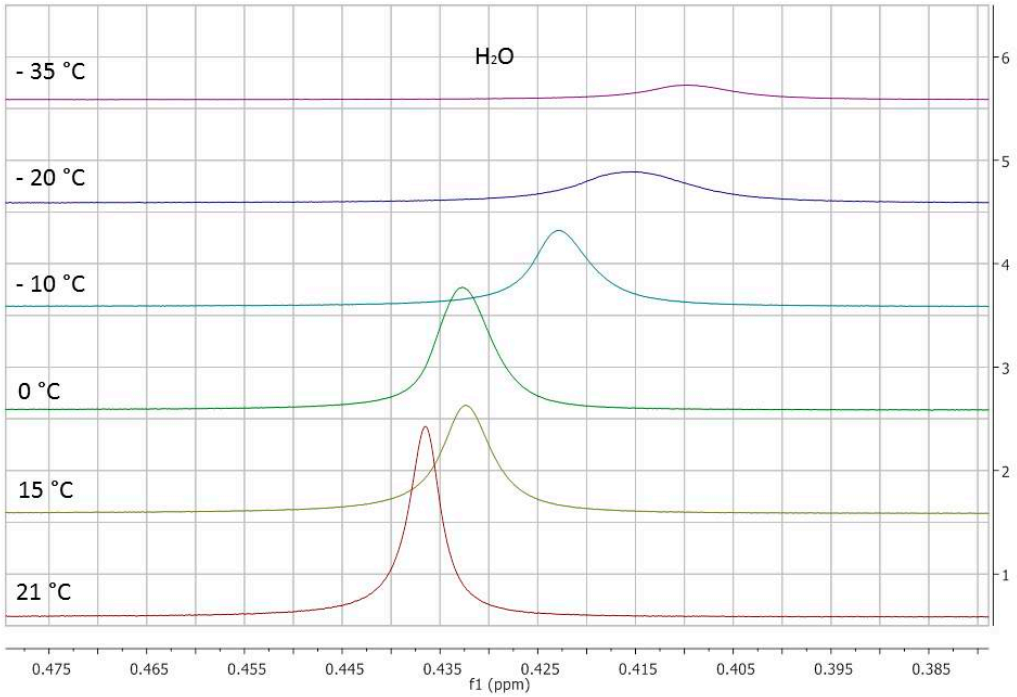


Figure S71. Selected region of the ^{1}H NMR spectra acquired during the VT experiments of **2,6-dibromophenylboronic acid**, showing the indicative peak corresponding to H_2O (400 MHz, toluene-d_8).

2.11. ^{1}H NMR analysis for the VT experiments of boroxine

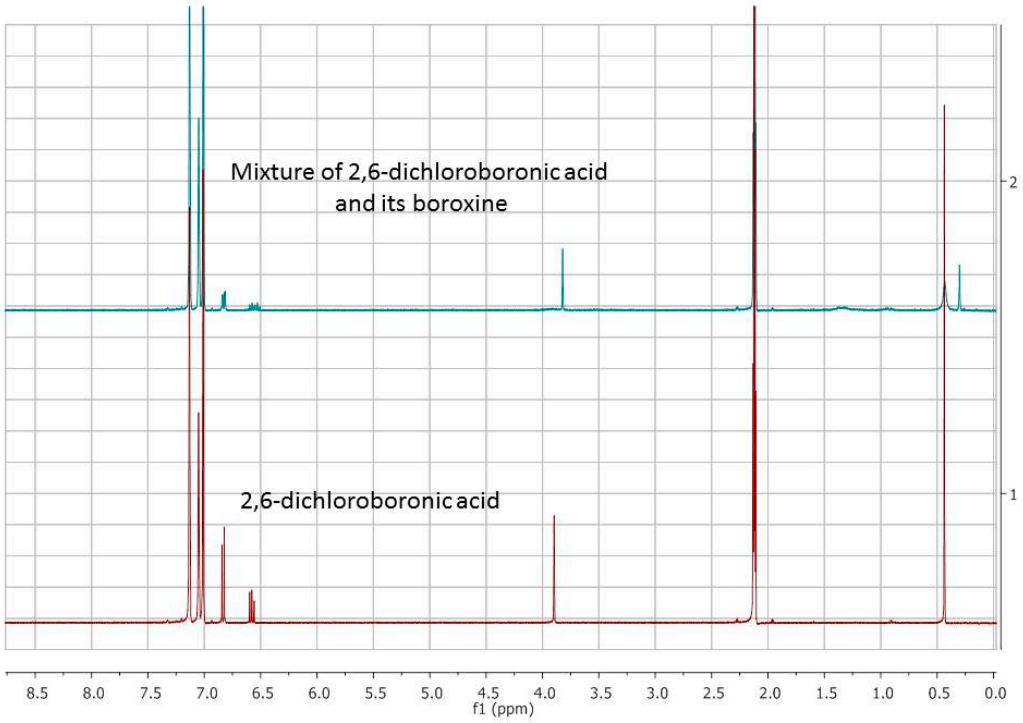


Figure S72. ^{1}H NMR spectra of **2,6-dichlorophenylboronic acid** and **a mixture with its boroxine** (400 MHz, toluene-d_8).

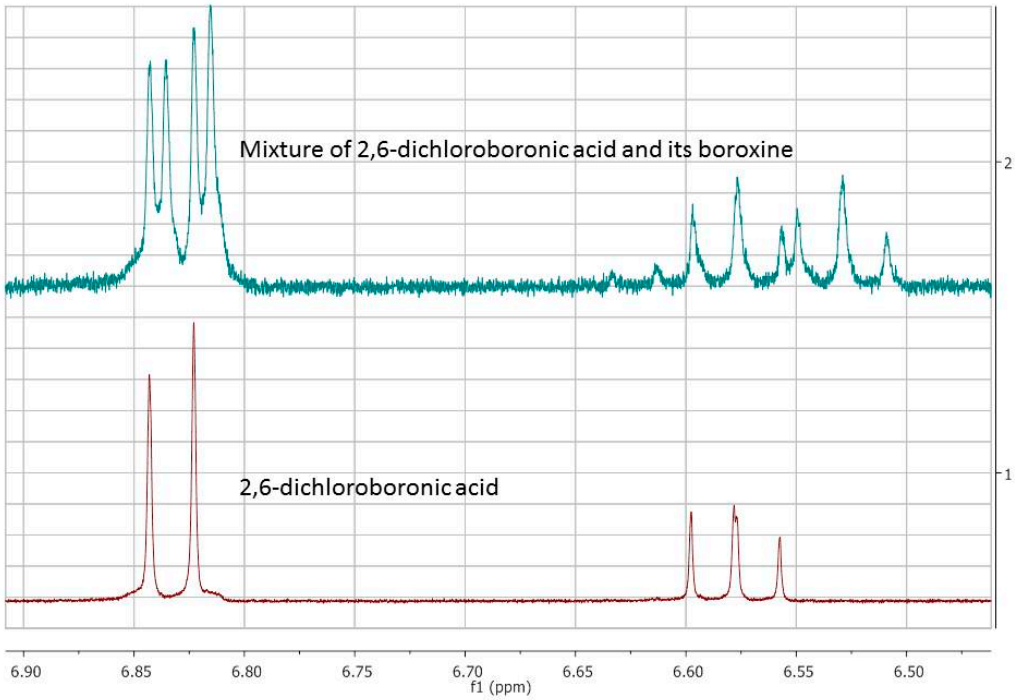


Figure S73. Selected region of the ^{1}H NMR spectra of **2,6-dichlorophenylboronic acid** and **a mixture with its boroxine** showing the indicative peak corresponding to their aromatic parts (400 MHz, toluene-d_8).

Table 6. ^{1}H NMR shifts and integration corresponding to H_A of the boronic acid, -OH of the boronic acid and H_2O, acquired during the VT experiment of a **mixture of 2,6-dichlorophenylboronic acid and its boroxine** (400 MHz, toluene-d_8).

T (°C)	H_A	OH	OH shift	H_2O	Extra Peak	Sum of "water" integration
21	6.58 ppm / 1H	3.90 ppm / 1.96H	-	0.44 ppm / 5.06H	-	5.06H
15	6.57 ppm / 1H	3.90 ppm / 1.80H	-	0.44 ppm / 4.00H	-	4.00H
0	6.55 ppm / 1H	3.98 ppm / 1.88H	0.08 ppm	0.44 ppm / 4.15H	5.50 ppm / 0.43H	4.48H
-10	6.53 ppm / 1H	3.98 ppm / 1.84H	0.08 ppm	0.43 ppm / 3.02H	5.62 ppm / 0.67H	3.69H
-20	6.51 ppm / 1H	3.99 ppm / 1.81H	0.09 ppm	0.43 ppm / 2.07H	5.76 ppm / 1.38H	3.45H
-35	6.48 ppm / 1 H	4.09 ppm / 1.95H	0.19 ppm	0.42 ppm / 1.04H	6.00 ppm / 2.39H	3.43H

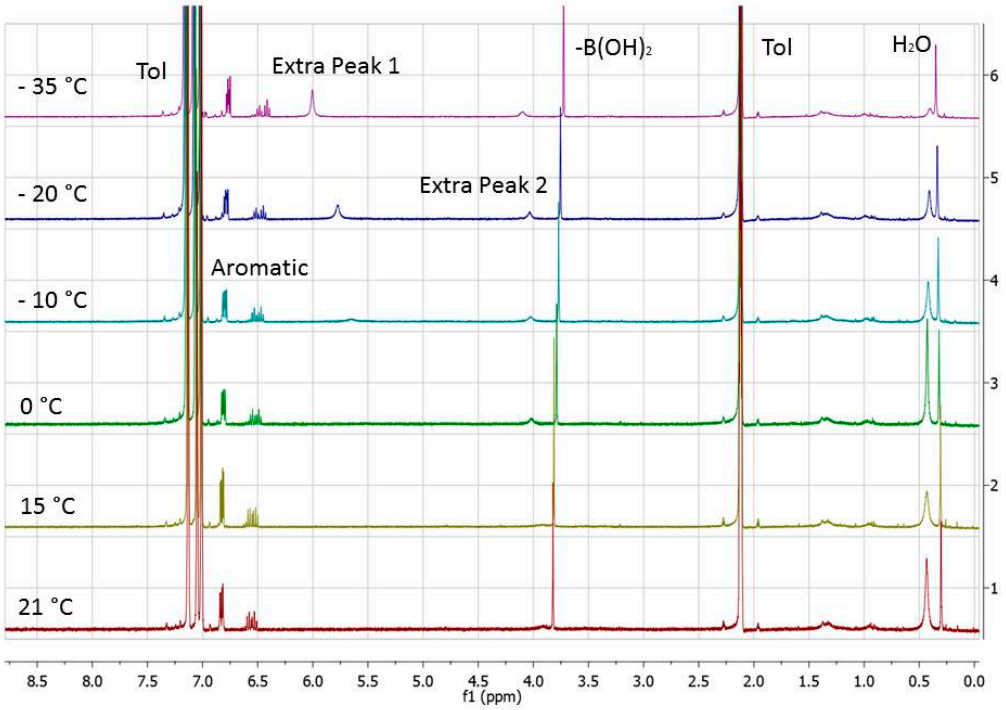


Figure S74. ^{1}H NMR spectra acquired during the VT experiments of the **mixture of 2,6-dichlorophenylboronic acid and its boroxine** (400 MHz, toluene-d_8).

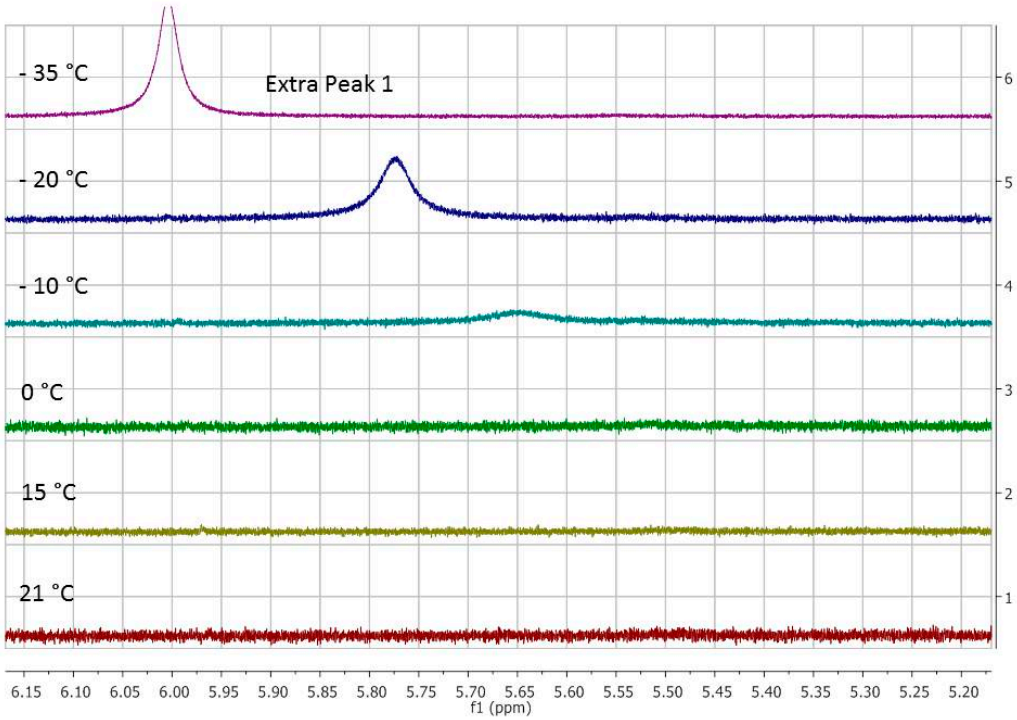


Figure S75. Selected region of the ^{1}H NMR spectra acquired during the VT experiments of the **mixture of 2,6-dichlorophenylboronic acid and its boroxine**, showing the extra peak 1 (400 MHz, toluene-d_8).

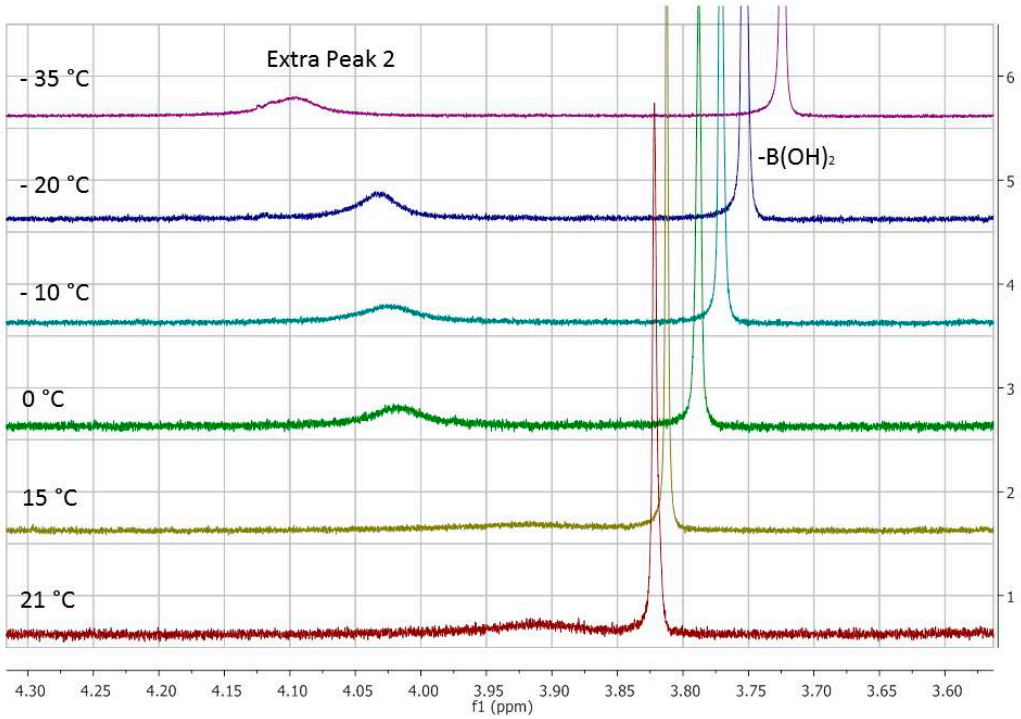


Figure S76. Selected region of the ^{1}H NMR spectra acquired during the VT experiments of the **mixture of 2,6-dichlorophenylboronic acid and its boroxine**, showing the extra peak 2 and the indicative peak corresponding to –$B(OH)_2$ moiety (400 MHz, toluene-d_8).

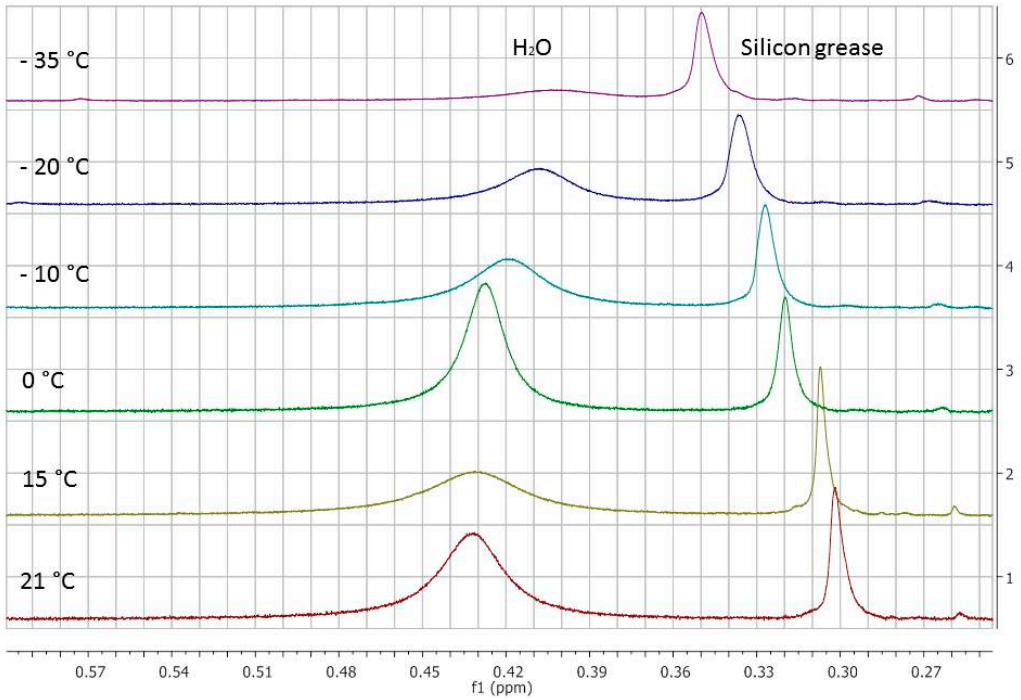


Figure S77. Selected region of the ^{1}H NMR spectra acquired during the VT experiments of the **mixture of 2,6-dichlorophenylboronic acid and its boroxine**, showing d the indicative peaks corresponding to –$B(OH)_2$ moiety and residual silicon grease (400 MHz, toluene-d_8).

3. Solution-state recognition: ITC Titrations – Determination of K_a

3.1. General experimental procedure for ITC analysis

ITC experiments were performed at 25°C on an ITC-4200 from Calorimetric Science Corporation. In a typical experiment, aliquots of 3 µL of a naphthyridine solution, at a concentration ranging from 80 to 200 mM concentration, were injected into the 1.3 mL titration cell containing the boronic acid solution at a concentration in the 1.5 to 5 mM range. Eighty injections were typically performed at intervals of 300 s to ensure the return to equilibrium. Blank experiments were performed in order to take ligand dilution heat into consideration (heat removed before analyzing the titration data). Fitting of a 1:n binding model to the experimental data was undertaken with NanoAnalyze (TA instruments) and the heat of the first injection was systematically removed for analysis.

3.2. ITC data of 1,8-naphthyridine dilution experiment

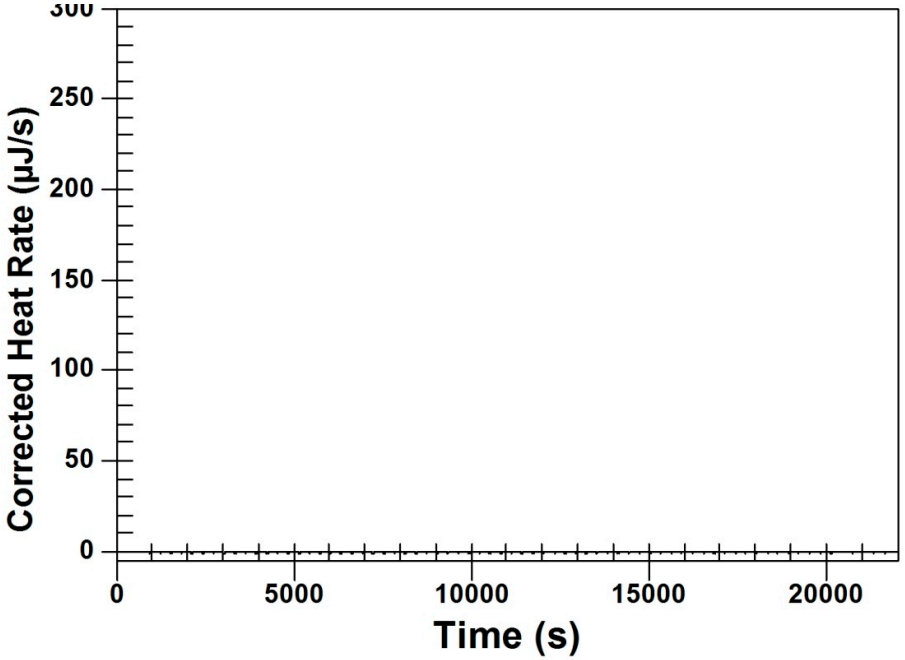


Figure S78. Representative calorimetric titration (Toluene, 298 K) of dilution for a 78 mM NAP solution.

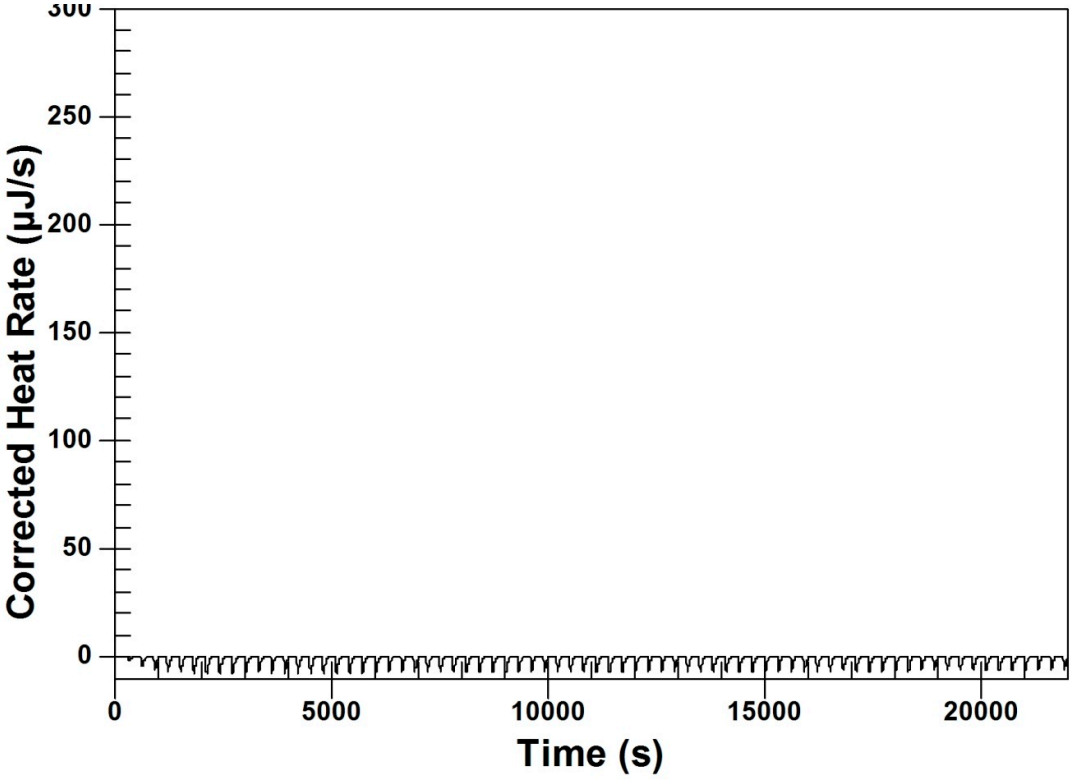


Figure S79. Representative calorimetric titration (Toluene, 298 K) of dilution for a 200 mM NAP solution.

3.3. ITC data used for the determination of the association constant K_a

3.3.1. Between mesitylboronic acid and 1,8-naphthyridine

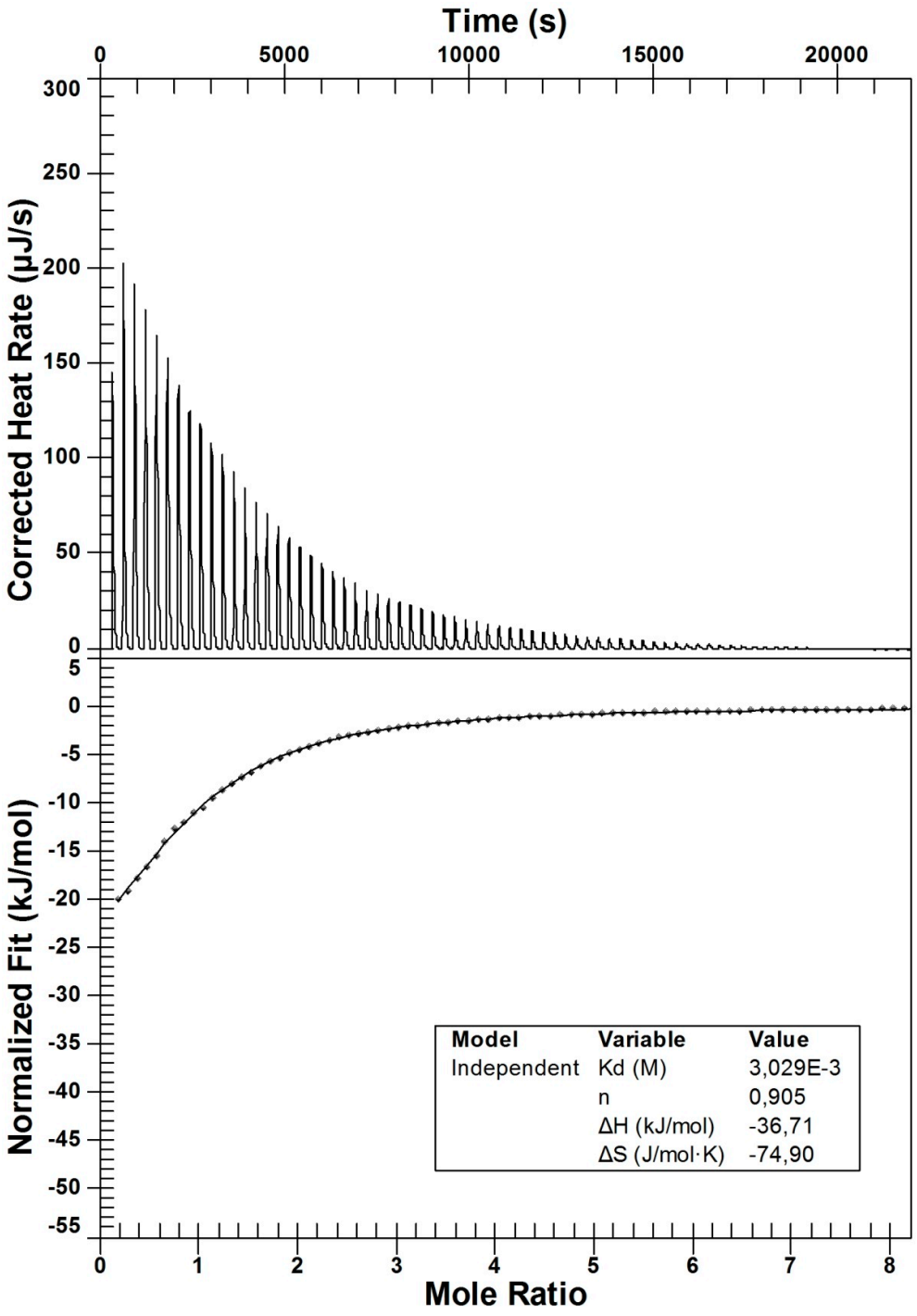


Figure S80. Representative calorimetric titration (Toluene, 298 K) of a 4.9 mM of the **mesitylboronic acid** with a 200 mM **NAP** solution. The binding curve is obtained by fitting of a 1:n binding isotherm to the integrated areas per injection corrected for the dilution heat of **NAP**.

3.3.2. Between 2,6-difluorophenylboronic acid and 1,8-naphthyridine

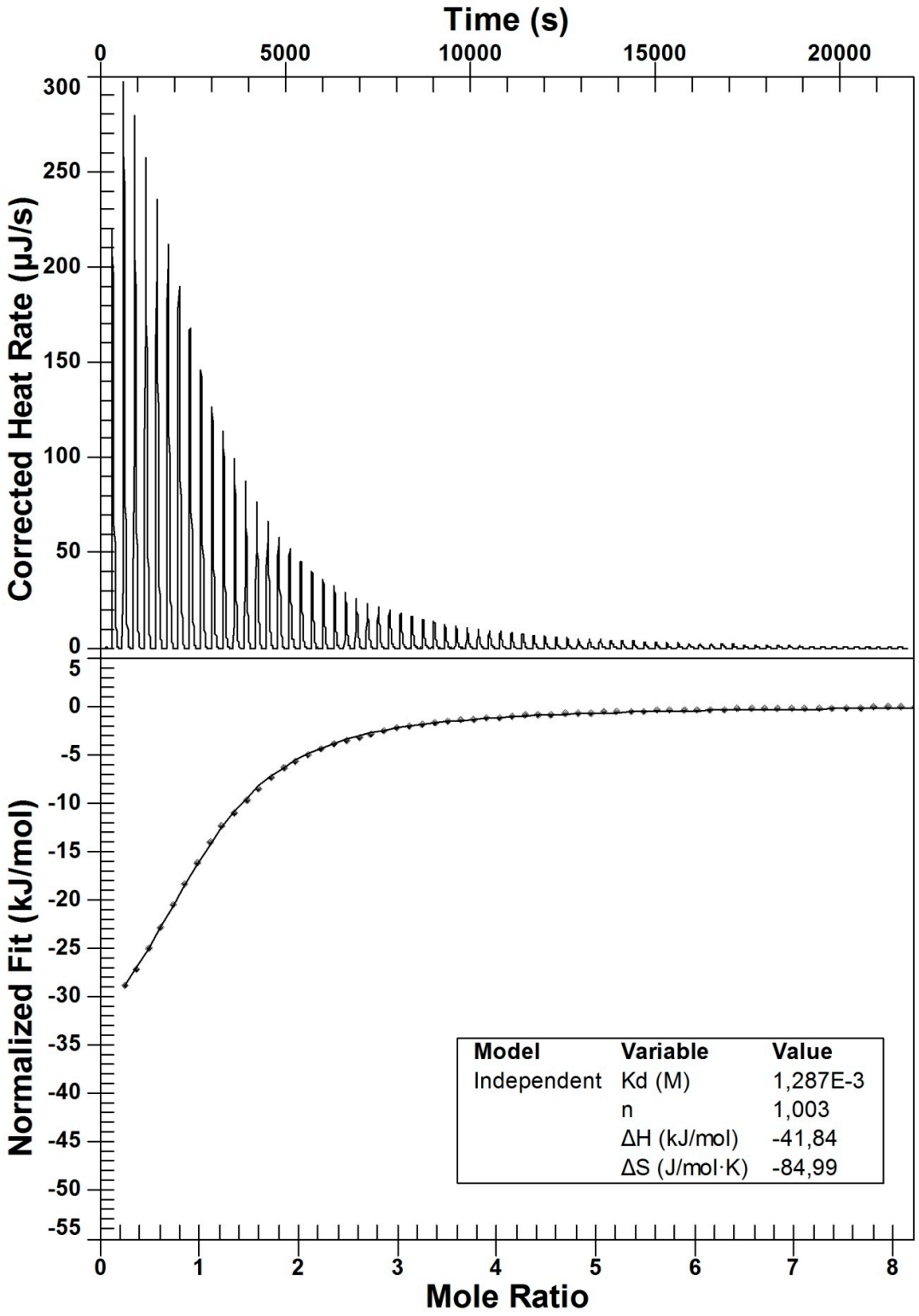


Figure S81. Representative calorimetric titration (Toluene, 298 K) of a 3.8 mM of the **2,6-difluorophenylboronic acid** with a 200 mM **NAP** solution. The binding curve is obtained by fitting of a 1:n binding isotherm to the integrated areas per injection corrected for the dilution heat of **NAP**.

3.3.3. Between 2,6-dichlorophenylboronic acid and 1,8-naphthyridine

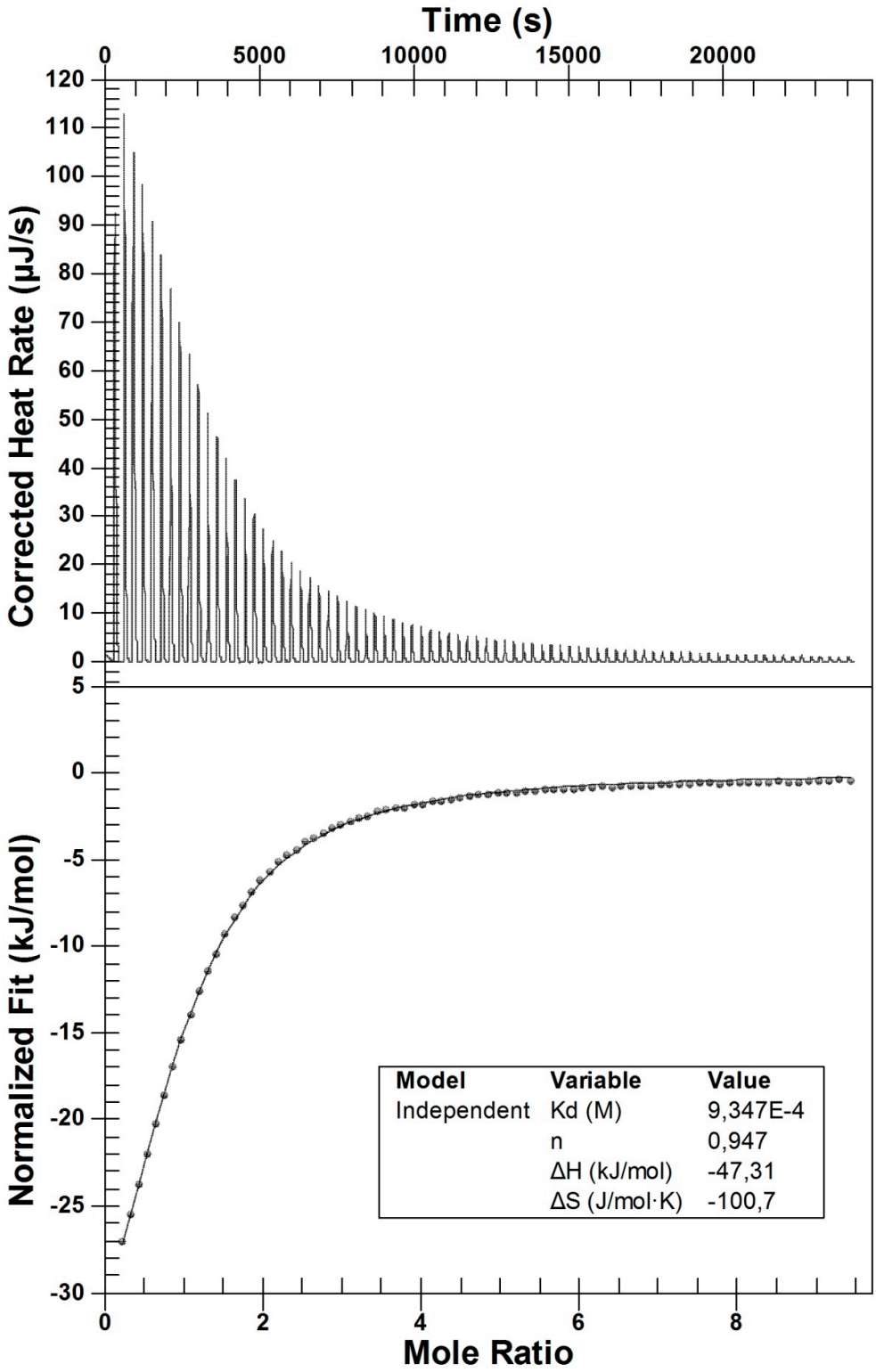


Figure S82. Representative calorimetric titration (Toluene, 298 K) of a 1.7 mM of the **2,6-dichlorophenylboronic acid** with a 78 mM **NAP** solution. The binding curve is obtained by fitting of a 1:n binding isotherm to the integrated areas per injection corrected for the dilution heat of **NAP**.

3.3.4. Between 2,6-dibromophenylboronic acid and 1,8-naphthyridine

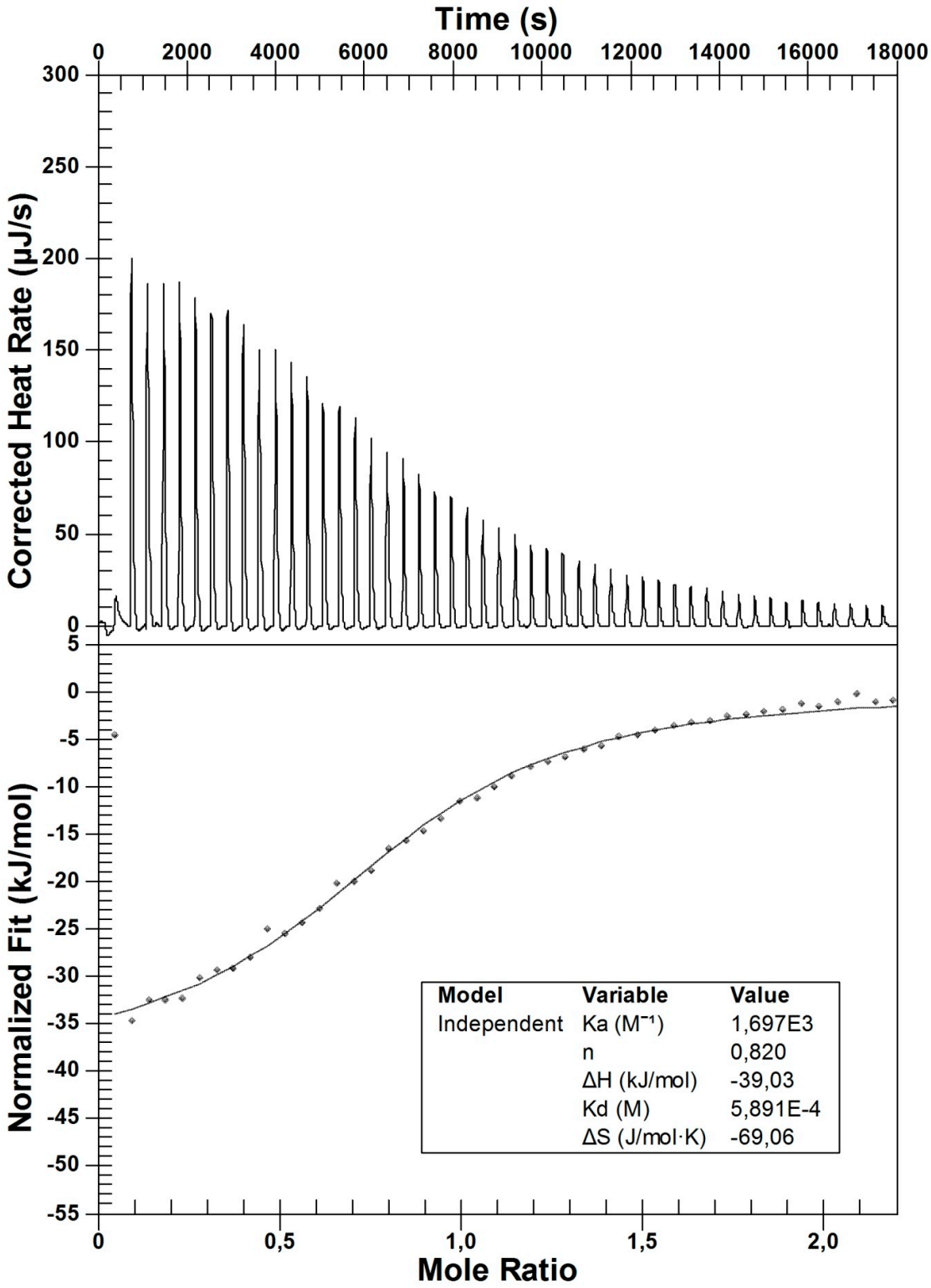


Figure S83. Representative calorimetric titration (Toluene, 298 K) of a 5 mM of the **2,6-dibromophenylboronic acid** with a 100 mM NAP solution. The binding curve is obtained by fitting of a 1:n binding isotherm to the integrated areas per injection corrected for the dilution heat of **NAP**.

3.3.5. Between 2,6-bis(trifluoromethyl)phenylboronic acid and 1,8-naphthyridine

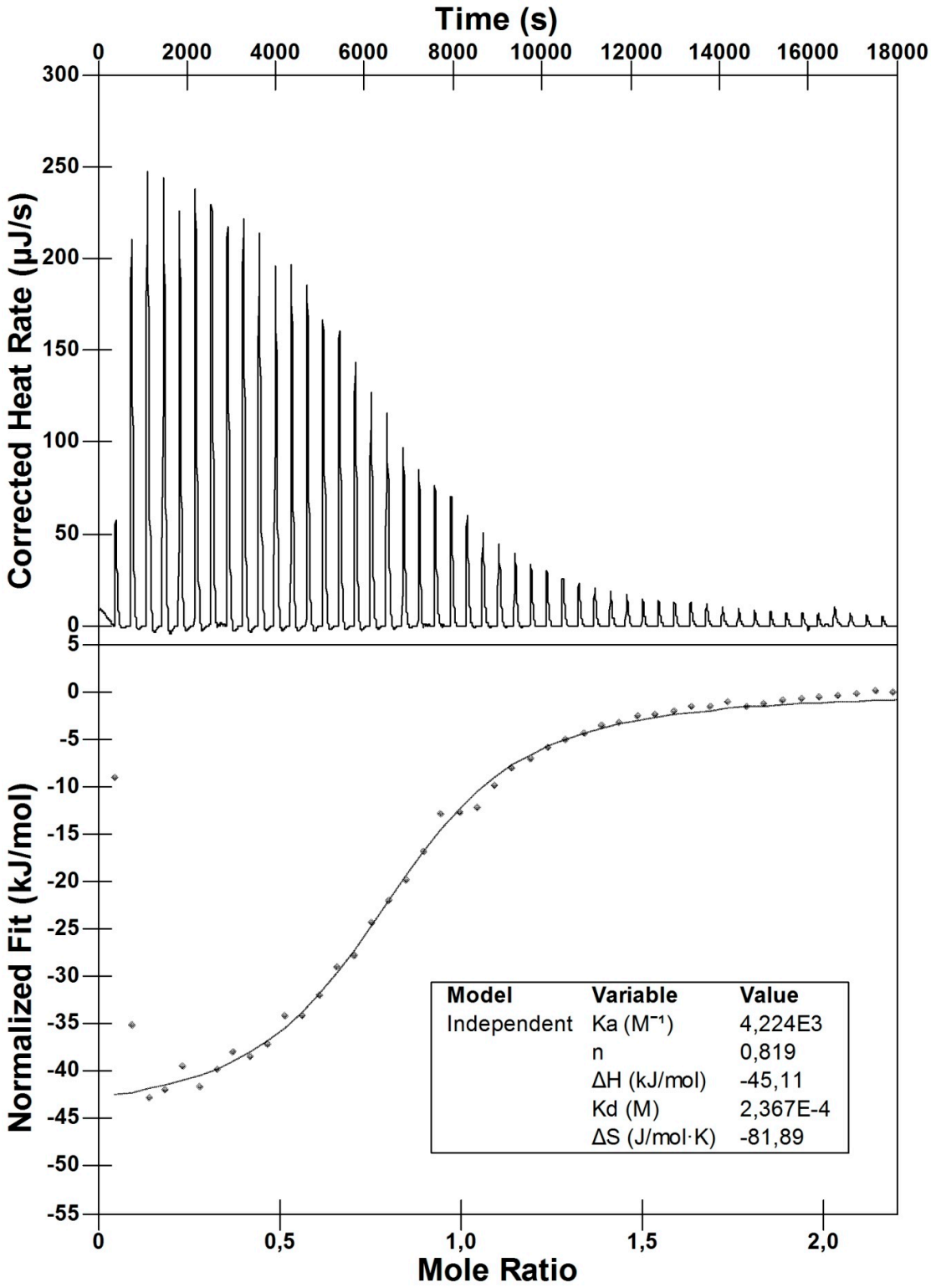


Figure S84. Representative calorimetric titration (Toluene, 298 K) of a 5 mM of **2,6-bis(trifluoromethyl)phenylboronic acid** with a 100 mM **NAP** solution. The binding curve is obtained by fitting of a 1:n binding isotherm to the integrated areas per injection corrected for the dilution heat of **NAP**.

3.3.5. Between 3,4,5-trifluorophenylboronic acid and 1,8-naphthyridine

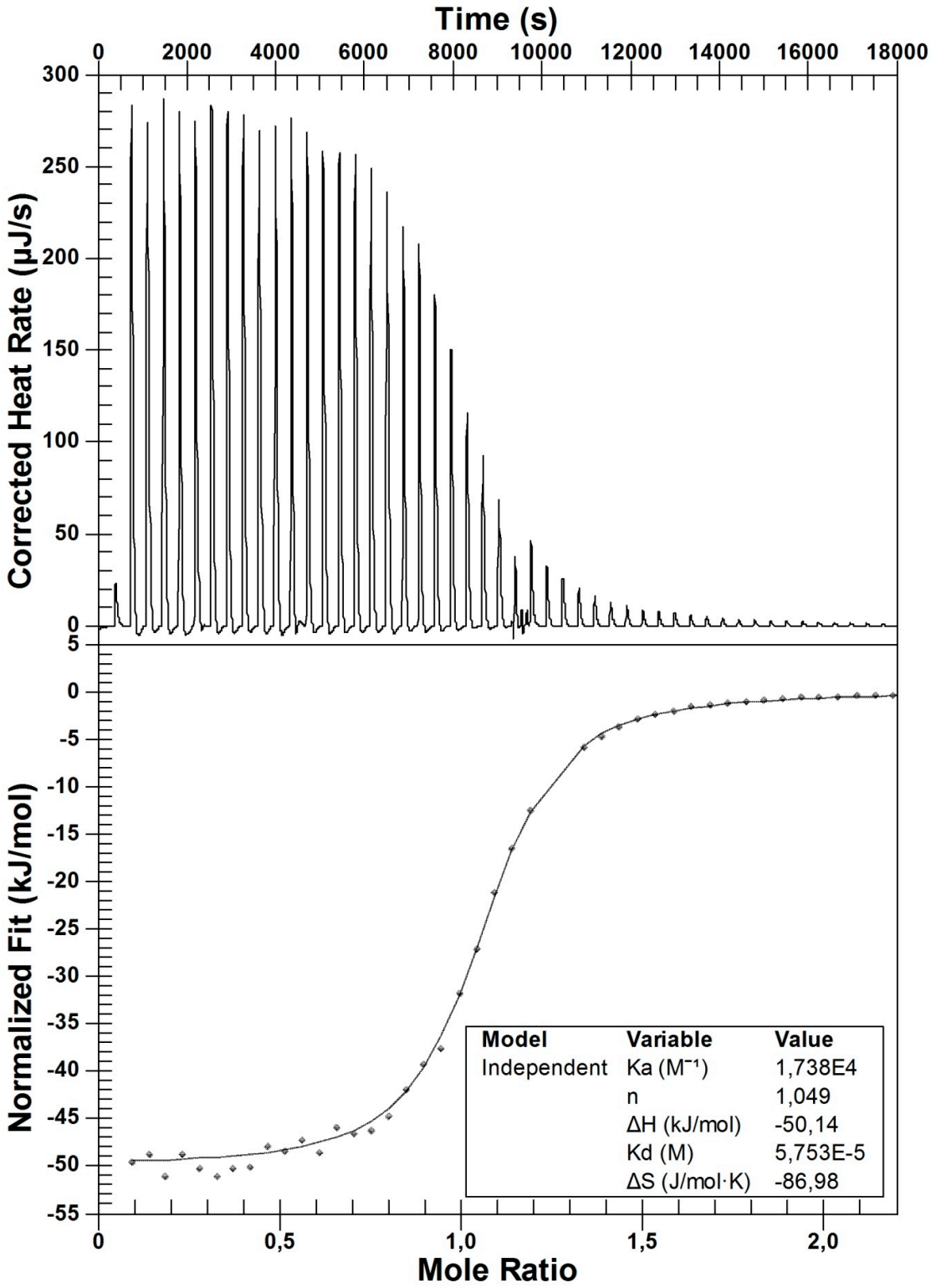


Figure S85. Representative calorimetric titration (Toluene, 298 K) of a 5 mM of the **3,4,5-trifluorophenylboronic acid** with a 100 mM **NAP** solution. The binding curve is obtained by fitting of a 1:n binding isotherm to the integrated areas per injection corrected for the dilution heat of **NAP**.

4. Solid-state recognition: Single-crystal X-ray investigations

4.1. Crystallization procedure

4.1.1. General crystallisation procedure for the formation of the dimeric and trimeric complexes

Single crystals for the dimeric and trimeric complexes were obtained by slow evaporation at 25 ^{o}C of a 1:1, 1:2 or 2 :1 molar ratio mixture, respectively of the relevant compounds in an appropriate solvent (toluene, MeOH, H_2O or $CHCl_3$).

4.1.2. Crystallization procedure for the formation of the supramolecular polymer

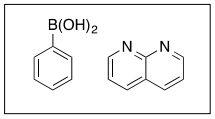
A suspension of (0.007g, 0.043 mmol) 1,4-phenyldiboronic acid and (10 mg, 0.043 mmol) 5,6,11,12-tetraazanaphthacene in (70 mL) H_2O was refluxed at 100 ^{o}C. The mixture was then subjected through hot filtration to remove any undissolved 5,6,11,12-tetraazanaphthacene residuals. The yellow solution was then placed in an oil bath at 35 ^{o}C without the presence of a stirring bar for 24 h. This resulted in the formation of orange crystals suitable for X-ray crystallography.

4.2 Single crystal X-ray diffraction methods

Single crystal X-ray diffraction was performed on a Gemini Ultra R system (4-circle kappa platform Ruby CCD detector) using Mo Ka (λ = 0.71073 Å) or Cu Ka (λ = 1.54184 Å) radiation. Selected crystals were mounted on a quartz needle using commercial glue (cyanoacrylate). Cell parameters were estimated from a pre-experiment run, and full data sets were collected at room temperature (295 K). Structures were solved by direct methods and then refined on F^2 using the SHELXL 2014 suite of programs.[5] Non-hydrogen atoms were anisotropically refined, and the hydrogen atoms (not present in H-bonds) were fixed in the riding mode with isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups). Hydrogen atoms implicated in hydrogen bonds were localized by Fourier difference maps (ΔF). X-ray crystallographic information files (CIFs) are available for all crystal structures reported from http://pubs.acs.org and they have all been deposited at the Cambridge Crystallographic Data Centre with their allocated deposition numbers present at the legend of every crystal data and structure refinement table following.

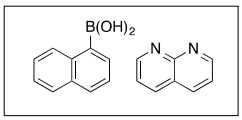
4.3. Crystal data and structure refinement

Table 7. Phenylboronic acid with 1,8-naphthyridine (CCDC 1037379)



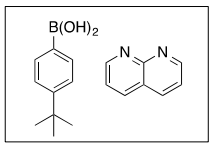
	Crystal Data	
Formula	$C_6H_7BO_2$, $C_8H_6N_2$	
Molecular Weight	252.08	
Crystal System	Monoclinic	
Space Group	$P2_1/C$	
Unit cell dimensions	a = 10.8378(6) Å	α = 90°
	b = 8.7350(5) Å	β = 103.493(5)°
	c = 14.4860(6) Å	γ = 90°
Volume	1333.51(12) $Å^3$	
Z	4	
Density (calculated)	1.256 g/cm^3	
Absorption coefficient	0.679 mm^{-1}	
F(000)	528	
Crystal size	0.02 x 0.10 x 0.23 mm	
	Data Collection	
Temperature	293 K	
Wavelenght	1.54184 Å	
Theta range for data collection	4.2 to 67.6°	
Index range	-12≤h≤13, -10≤k≤10, -17≤l≤11	
Reflections collected	6851	
Independent reflections	2394 [R(int) = 0.029]	
Observed data [*I*>2σ(*I*)]	1606	
	Refinement	
Data / parameters	2394 / 180	
R, wR2, S	0.0434, 0.1307, 1.02	
w = 1/[$\sigma^2F_0^2$)+(0.0612P)^2 +0.0198P]	where P = (F_0^2+2F_c^2)/3	
Largest diff. peak and hole	0.11 and -0.12 e.$Å^{-3}$	

Table 8. Napthalene-1-boronic acid with 1,8-naphthyridine (CCDC 1037403)



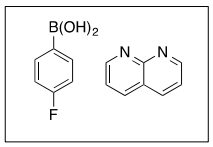
	Crystal Data	
Formula	$C_{10}H_9BO_2$, $C_8H_6N_2$	
Molecular Weight	302.14	
Crystal System	Monoclinic	
Space Group	$P2_1/n$	
Unit cell dimensions	a = 9.3053(9) Å	α = 90°
	b = 12.7855(13) Å	β = 90.721(5)°
	c = 13.0268(6) Å	γ = 90°
Volume	1549.7(3) $Å^3$	
Z	4	
Density (calculated)	1.295 g/cm^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	632	
Crystal size	0.16 x 0.20 x 0.35 mm	
	Data Collection	
Temperature	293 K	
Wavelength	0.71073 Å	
Theta range for data collection	3.1 to 25.0°	
Index range	-11≤h≤9, -15≤k≤13, -15≤l≤12	
Reflections collected	4911	
Independent reflections	2418 [R(int) = 0.028]	
Observed data [*I*>2σ(*I*)]	1844	
	Refinement	
Data / parameters	2418 / 216	
R, wR2, S	0.0658, 0.1659, 1.11	
w = 1/[$\sigma^2F_0^2$)+(0.0449P)^2 +1.2696P]	where P = (F_0^2+2F_c^2)/3	
Largest diff. peak and hole	0.17 and -0.14 e.$Å^{-3}$	

Table 9. 4-*t*-Butylphenylboronic acid with 1,8-naphthyridine (CCDC 1037399)



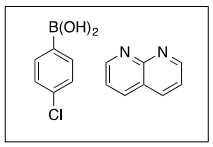
	Crystal Data	
Formula	$C_{10}H_{15}BO_2$, $C_8H_6N_2$	
Molecular Weight	308.19	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit cell dimensions	a = 11.6218(10) Å	α = 90°
	b = 11.2692(9) Å	β = 100.367(5)°
	c = 13.6669(610) Å	γ = 90°
Volume	1760.7(2) $Å^3$	
Z	4	
Density (calculated)	1.163 g/cm^3	
Absorption coefficient	0.075 mm^{-1}	
F(000)	656	
Crystal size	0.27 x 0.32 x 0.55 mm	
	Data Collection	
Temperature	293 K	
Wavelength	0.71073 Å	
Theta range for data collection	2.8 to 25.0°	
Index range	-13≤h≤12, -11≤k≤13, -16≤l≤14	
Reflections collected	8506	
Independent reflections	3110 [R(int) = 0.102]	
Observed data [*I*>2σ(*I*)]	2182	
	Refinement	
Data / parameters	3110 / 250	
R, wR2, S	0.0883, 0.2565, 1.03	
w = 1/[$\sigma^2F_0^2$)+(0.1615P)^2]	where P = (F_0^2+2F_c^2)/3	
Largest diff. peak and hole	0.34 and -0.31 e.$Å^{-3}$	

Table 10. 4-Fluorophenylboronic acid with 1,8-naphthyridine (CCDC 1037393)



	Crystal Data	
Formula	$C_6H_6FBO_2$, $C_8H_6N_2$	
Molecular Weight	270.07	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit cell dimensions	a = 12.354(2) Å	α = 90°
	b = 8.628(1) Å	β = 116.121(10)°
	c = 14.2421(19) Å	γ = 90°
Volume	1363.0(3) $Å^3$	
Z	4	
Density (calculated)	1.316 g/cm^3	
Absorption coefficient	0.097 mm^{-1}	
F(000)	560	
Crystal size	0.13 x 0.17 x 0.40 mm	
	Data Collection	
Temperature	293 K	
Wavelength	0.71073 Å	
Theta range for data collection	3.7 to 25.0°	
Index range	-14≤h≤14, -10≤k≤10, -16≤l≤16	
Reflections collected	6777	
Independent reflections	2404 [R(int) = 0.017]	
Observed data [*I*>2σ(*I*)]	1993	
	Refinement	
Data / parameters	2404 / 181	
R, wR2, S	0.0396, 0.1053, 1.04	
w = 1/[$\sigma^2F_0^2$)+(0.0483P)^2+ 0.1809P]	where P = (F_0^2+2F_c^2)/3	
Largest diff. peak and hole	0.10 and -0.17 e.$Å^{-3}$	

Table 11. 4-Chlorophenylboronic acid with 1,8-naphthyridine (CCDC 1037394)



Crystal Data

Formula	$C_6H_6ClBO_2$, $C_8H_6N_2$	
Molecular Weight	286.52	
Crystal System	Monoclinic	
Space Group	C2/m	
Unit cell dimensions	a = 12.676(2) Å	α = 90°
	b = 11.7614(19) Å	β = 97.256(15)°
	c = 9.4574(14) Å	γ = 90°
Volume	1398.7(4) $Å^3$	
Z	4	
Density (calculated)	1.361 g/cm^3	
Absorption coefficient	0.274 mm^{-1}	
F(000)	592	
Crystal size	0.12 x 0.28 x 0.48 mm	

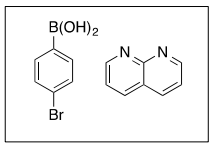
Data Collection

Temperature	293 K
Wavelength	0.71073 Å
Theta range for data collection	3.1 to 25.0°
Index range	-14≤h≤15, -14≤k≤12, -11≤l≤9
Reflections collected	3277
Independent reflections	1301 [R(int) = 0.035]
Observed data [*I*>2σ(*I*)]	1011

Refinement

Data / parameters	1301 / 104
R, wR2, S	0.0424, 0.1169, 1.06
w = 1/[$\sigma^2F_0^2$)+(0.0529P)^2+ 0.2913P]	where P = (F_0^2+2F_c^2)/3
Largest diff. peak and hole	0.19 and -0.20 e.$Å^{-3}$

Table 12. 4-Bromophenylboronic acid with 1,8-naphthyridine (CCDC 1037396)



Crystal Data

Formula	$C_6H_6BrBO_2$, $C_8H_6N_2$	
Molecular Weight	330.98	
Crystal System	Monoclinic	
Space Group	C2/m	
Unit cell dimensions	a = 12.6482(13) Å	α = 90°
	b = 11.8379(11) Å	β = 97.379(9)°
	c = 9.6038(8) Å	γ = 90°
Volume	1426.1(2) $Å^3$	
Z	4	
Density (calculated)	1.541 g/cm^3	
Absorption coefficient	2.883 mm^{-1}	
F(000)	664	
Crystal size	0.09 x 0.25 x 0.29 mm	

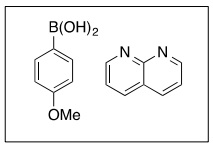
Data Collection

Temperature	293 K
Wavelength	0.71073 Å
Theta range for data collection	3.0 to 29.3°
Index range	-17≤h≤11, -11≤k≤15, -10≤l≤13
Reflections collected	3522
Independent reflections	1740 [R(int) = 0.041]
Observed data [*I*>2σ(*I*)]	1156

Refinement

Data / parameters	1740 / 104
R, wR2, S	0.0438, 0.1114, 1.02
w = 1/[$\sigma^2F_0^2$)+(0.0450P)^2+ 0.4161P]	where P = (F_0^2+2F_c^2)/3
Largest diff. peak and hole	0.31 and -0.41 e.$Å^{-3}$

Table 13. 4-Methoxyphenylboronic acid with 1,8-naphthyridine (CCDC 1037397)



Crystal Data

Formula	$C_7H_9BO_3$, $C_8H_6N_2$	
Molecular Weight	282.10	
Crystal System	Monoclinic	
Space Group	$P2_1/n$	
Unit cell dimensions	a = 10.1397(5) Å	α = 90°
	b = 12.3561(4) Å	β = 110.316(5)°
	c = 12.7615(6) Å	γ = 90°
Volume	1499.39(12) Å^3	
Z	4	
Density (calculated)	1.250 g/cm^3	
Absorption coefficient	0.087 mm^{-1}	
F(000)	592	
Crystal size	0.04 x 0.25 x 0.40 mm	

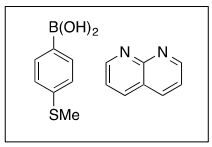
Data Collection

Temperature	293 K
Wavelength	0.71073 Å
Theta range for data collection	3.4 to 25.0°
Index range	-7≤h≤12, -14≤k≤12, -14≤l≤15
Reflections collected	5650
Independent reflections	2623 [R(int) = 0.015]
Observed data [*I*>2σ(*I*)]	2081

Refinement

Data / parameters	2623 / 199
R, wR2, S	0.0408, 0.1061, 1.01
w = 1/[$\sigma^2F_0^2$)+(0.0478P)^2+ 0.1667P]	where P = (F_0^2+2F_c^2)/3
Largest diff. peak and hole	0.11 and -0.14 e.Å^{-3}

Table 14. 4-Methylthiophenylboronic acid with 1,8-naphthyridine (CCDC 1037398)



Crystal Data

Formula	$C_7H_9SBO_2$, $C_8H_6N_2$	
Molecular Weight	298.16	
Crystal System	Monoclinic	
Space Group	Pbcn	
Unit cell dimensions	a = 24.7752(15) Å	α = 90°
	b = 13.4269(8) Å	β = 90°
	c = 27.4783(14) Å	γ = 90°
Volume	9140.8(9) $Å^3$	
Z	24	
Density (calculated)	1.300 g/cm^3	
Absorption coefficient	0.217 mm^{-1}	
F(000)	3744	
Crystal size	0.04 x 0.20 x 0.42 mm	

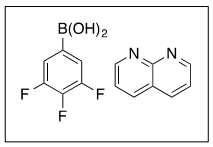
Data Collection

Temperature	293 K
Wavelength	0.71073 Å
Theta range for data collection	3.2 to 25.0°
Index range	-27≤h≤29, -15≤k≤15, -29≤l≤32
Reflections collected	29942
Independent reflections	8051 [R(int) = 0.069]
Observed data [*I*>2σ(*I*)]	4102

Refinement

Data / parameters	8051 / 568
R, wR2, S	0.0848, 0.1913, 1.04
w = 1/[$\sigma^2F_0^2$)+(0.0505P)^2+ 4.7241P]	where P = (F_0^2+2F_c^2)/3
Largest diff. peak and hole	0.39 and -0.22vc e.$Å^{-3}$

Table 15. 3,4,5-Trifluorophenylboronic acid with 1,8-naphthyridine (CCDC 1037400)



Crystal Data

Formula	$C_6H_4F_3BO_2$, $C_8H_6N_2$	
Molecular Weight	306.05	
Crystal System	Monoclinic	
Space Group	$P2_1/n$	
Unit cell dimensions	a = 3.8701(4) Å	α = 90°
	b = 12.5606(14) Å	β = 93.811(9)°
	c = 28.597(2) Å	γ = 90°
Volume	9140.8(9) $Å^3$	
Z	4	
Density (calculated)	1.465 g/cm^3	
Absorption coefficient	0.125 mm^{-1}	
F(000)	624	
Crystal size	0.05 x 0.06 x 0.40 mm	

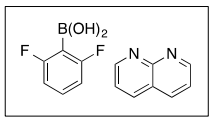
Data Collection

Temperature	293 K
Wavelength	0.71073 Å
Theta range for data collection	3.3 to 25.0°
Index range	-4≤h≤4, -14≤k≤8, -33≤l≤24
Reflections collected	5977
Independent reflections	2454 [R(int) = 0.046]
Observed data [*I*>2σ(*I*)]	1137

Refinement

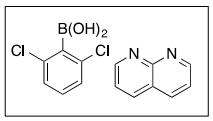
Data / parameters	2454 / 208
R, wR2, S	0.0501, 0.0987, 0.94
w = 1/[$\sigma^2F_0^2$)+(0.0147P)^2]	where P = (F_0^2+2F_c^2)/3
Largest diff. peak and hole	0.16 and -0.16vc e.$Å^{-3}$

Table 16. 2,6-Difluorophenylboronic acid with 1,8-naphthyridine (CCDC 1037381)



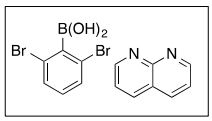
	Crystal Data	
Formula	$C_6H_5F_2BO_2$, $C_8H_6N_2$	
Molecular Weight	288.06	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit cell dimensions	a = 6.7753(3) Å	α = 90°
	b = 24.57889(11) Å	β = 117.015(4)°
	c = 9.4800(6) Å	γ = 90°
Volume	1406.44(14) $Å^3$	
Z	4	
Density (calculated)	1.360 g/cm^3	
Absorption coefficient	0.109 mm^{-1}	
F(000)	592	
Crystal size	0.08 x 0.20 x 0.20 mm	
	Data Collection	
Temperature	293 K	
Wavelength	0.71073 Å	
Theta range for data collection	3.3 to 25.0°	
Index range	-7≤h≤8, -29≤k≤25, -9≤l≤11	
Reflections collected	7142	
Independent reflections	2482 [R(int) = 0.021]	
Observed data [*I*>2σ(*I*)]	1835	
	Refinement	
Data / parameters	2482 / 198	
R, wR2, S	0.0455, 0.1221, 1.05	
w = 1/[$\sigma^2F_0^2$)+(0.0558P)^2+ 0.1438P]	where P = (F_0^2+2F_c^2)/3	
Largest diff. peak and hole	0.10 and -0.20vc e.$Å^{-3}$	

Table 17. 2,6-Dichlorophenylboronic acid with 1,8-naphthyridine (CCDC 1037384)



	Crystal Data	
Formula	$C_6H_5Cl_2BO_2$, $C_8H_6N_2$	
Molecular Weight	320.96	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit cell dimensions	a = 13.0892(6) Å	α = 90°
	b = 13.9674(4) Å	β = 1508.00(11)°
	c = 8.3002(4) Å	γ = 90°
Volume	1508.00(11) $Å^3$	
Z	4	
Density (calculated)	1.414 g/cm^3	
Absorption coefficient	0.434 mm^{-1}	
F(000)	656	
Crystal size	0.07 x 0.28 x 0.33 mm	
	Data Collection	
Temperature	293 K	
Wavelength	0.71073 Å	
Theta range for data collection	3.3 to 25.0°	
Index range	-15≤h≤10, -15≤k≤16, -9≤l≤9	
Reflections collected	6937	
Independent reflections	2659 [R(int) = 0.016]	
Observed data [*I*>2σ(*I*)]	2251	
	Refinement	
Data / restraints / parameters	2659 / 198	
R, wR2, S	0.0387, 0.0978, 1.04	
w = 1/[$\sigma^2F_0^2$)+(0.0383P)^2+ 0.4668P]	where P = (F_0^2+2F_c^2)/3	
Largest diff. peak and hole	0.25 and -0.36vc e.$Å^{-3}$	

Table 18. 2,6-Dibromophenylboronic acid with 1,8-naphthyridine (CCDC 1037387)



Crystal Data

Formula	$C_6H_5Br_2BO_2$, $C_8H_6N_2$	
Molecular Weight	409.88	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit cell dimensions	a = 13.5305(11) Å	α = 90°
	b = 14.1551(11) Å	β = 95.118(7)°
	c = 8.1397(6) Å	γ = 90°
Volume	1552.8(2) $Å^3$	
Z	4	
Density (calculated)	1.753 g/cm^3	
Absorption coefficient	5.224 mm^{-1}	
F(000)	800	
Crystal size	0.13 x 0.30 x 0.34 mm	

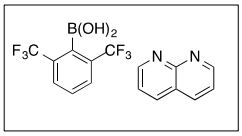
Data Collection

Temperature	293 K
Wavelength	0.71073 Å
Theta range for data collection	2.9 to 25.0°
Index range	-16≤h≤14, -15≤k≤16, -9≤l≤8
Reflections collected	7705
Independent reflections	2738 [R(int) = 0.034]
Observed data [*I*>2σ(*I*)]	1829

Refinement

Data / parameters	2738 / 198
R, wR2, S	0.0396, 0.0914, 1.04
w = 1/[$\sigma^2F_0^2$)+(0.0313P)^2+ 0.7113P]	where P = (F_0^2+2F_c^2)/3
Largest diff. peak and hole	0.36 and -0.45vc e.$Å^{-3}$

Table 19. 2,6-Bis(trifluoromethyl)phenylboronic acid with 1,8-naphthyridine (CCDC 1063177)



Crystal Data

Formula	$C_8H_5F_6BO_2$, $C_8H_6N_2$	
Molecular Weight	388.08	
Crystal System	Monoclinic	
Space Group	$P2_1/n$	
Unit cell dimensions	a = 8.3823(3) Å	α = 90°
	b = 26.3852(7) Å	β = 116.224(5)°
	c = 8.9783(3) Å	γ = 90°
Volume	1781.34(13) $Å^3$	
Z	4	
Density (calculated)	1.447 g/cm^3	
Absorption coefficient	1.219 mm^{-1}	
F(000)	784	
Crystal size	0.09 x 0.20 x 0.60 mm	

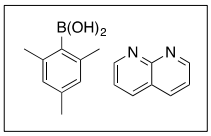
Data Collection

Temperature	293 K
Wavelength	1.54184 Å
Theta range for data collection	3.3 to 66.6°
Index range	-9≤h≤6, -31≤k≤31, -9≤l≤10
Reflections collected	9699
Independent reflections	3091 [R(int) = 0.030]
Observed data [*I*>2σ(*I*)]	2502

Refinement

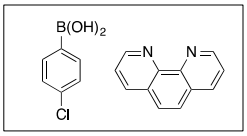
Data / parameters	3091 / 298
R, wR2, S	0.0506, 0.1526, 1.13
w = 1/[$\sigma^2F_0^2$)+(0.0683P)^2+ 0.2529P]	where P = (F_0^2+2F_c^2)/3
Largest diff. peak and hole	0.22 and -0.22vc e.$Å^{-3}$

Table 20. Mesitylboronic acid with 1,8-naphthyridine (CCDC 1037391)



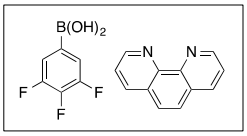
	Crystal Data	
Formula	$C_9H_{13}BO_2$, $C_8H_6N_2$	
Molecular Weight	294.15	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit cell dimensions	a = 7.6712(4) Å	α = 90°
	b = 19.9377(13) Å	β = 99.292(5)°
	c = 10.8372(6) Å	γ = 90°
Volume	1552.8(2) $Å^3$	
Z	4	
Density (calculated)	1.194 g/cm^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	624	
Crystal size	0.07 x 0.10 x 0.20 mm	
	Data Collection	
Temperature	293 K	
Wavelength	0.71073 Å	
Theta range for data collection	3.4 to 25.0°	
Index range	-9≤h≤6, -23≤k≤18, -12≤l≤12	
Reflections collected	5806	
Independent reflections	2861 [R(int) = 0.026]	
Observed data [*I*>2σ(*I*)]	1853	
	Refinement	
Data / parameters	2861 / 210	
R, wR2, S	0.0522, 0.1243, 1.04	
w = 1/[$\sigma^2F_0^2$)+(0.0452P)^2+ 0.1807P]	where P = (F_0^2+2F_c^2)/3	
Largest diff. peak and hole	0.13 and -0.11vc e.$Å^{-3}$	

Table 21. 4-Chlorophenylboronic acid with 1,10-phenanthroline (CCDC 1037395)



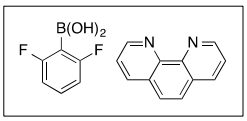
	Crystal Data	
Formula	$C_6H_6ClBO_2$, $C_{12}H_8N_2$	
Molecular Weight	336.57	
Crystal System	Monoclinic	
Space Group	P-1	
Unit cell dimensions	a = 8.0142(7) Å	α = 91.268 (6)°
	b = 9.9714(7) Å	β = 109.233(8)°
	c = 11.2985(6) Å	γ = 103.936(6)°
Volume	822.32(12) $Å^3$	
Z	2	
Density (calculated)	1.359 g/cm^3	
Absorption coefficient	0.244 mm^{-1}	
F(000)	348	
Crystal size	0.06 x 0.22 x 0.44 mm	
	Data Collection	
Temperature	293 K	
Wavelength	0.71073 Å	
Theta range for data collection	3.0 to 25.0°	
Index range	-9≤h≤8, -11≤k≤11, -12≤l≤13	
Reflections collected	6045	
Independent reflections	2907 [R(int) = 0.038]	
Observed data [*I*>2σ(*I*)]	2154	
	Refinement	
Data / parameters	2907 / 225	
R, wR2, S	0.0479, 0.1374, 1.05	
w = 1/[$\sigma^2F_0^2$)+(0.0669P)^2+ 0.0517P]	where P = (F_0^2+2F_c^2)/3	
Largest diff. peak and hole	0.20 and -0.16vc e.$Å^{-3}$	

Table 22. 3,4,5-Trifluorophenylboronic acid with 1,10-phenanthroline (CCDC 1037401)



	Crystal Data	
Formula	$C_6H_4F_3BO_2$, $C_{12}H_8N_2$	
Molecular Weight	356.11	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit cell dimensions	a = 14.6436(13) Å	α = 90°
	b = 3.9210(3) Å	β = 104.749(9)°
	c = 28.941(3) Å	γ = 90°
Volume	1607.0(3) $Å^3$	
Z	4	
Density (calculated)	1.472 g/cm^3	
Absorption coefficient	0.119 mm^{-1}	
F(000)	728	
Crystal size	0.06 x 0.19 x 0.50 mm	
	Data Collection	
Temperature	293 K	
Wavelength	0.71073 Å	
Theta range for data collection	2.9 to 25.0°	
Index range	-16≤h≤17, -4≤k≤4, -30≤l≤34	
Reflections collected	9218	
Independent reflections	2847 [R(int) = 0.058]	
Observed data [*I*>2σ(*I*)]	2143	
	Refinement	
Data / restraints / parameters	2847 / 243	
R, wR2, S	0.0877, 0.2258, 1.15	
w = 1/[$\sigma^2F_0^2$)+(0.1001P)^2+ 0.7170P]	where P = (F_0^2+2F_c^2)/3	
Largest diff. peak and hole	0.28 and -0.25vc e.$Å^{-3}$	

Table 23. 2,6-Difluorophenylboronic acid with 1,10-phenanthroline (CCDC 1037385)



Crystal Data

Formula	$C_6H_5F_2BO_2$, $C_{12}H_8N_2$	
Molecular Weight	338.11	
Crystal System	Monoclinic	
Space Group	$P2_1/n$	
Unit cell dimensions	a = 7.2690(5) Å	α = 90°
	b = 23.2180(18) Å	β = 97.038(7)°
	c = 9.8970(8) Å	γ = 90°
Volume	1657.8(2) Å^3	
Z	4	
Density (calculated)	1.355 g/cm^3	
Absorption coefficient	0.873 mm^{-1}	
F(000)	696	
Crystal size	0.04 x 0.07 x 0.20 mm	

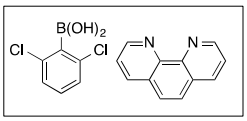
Data Collection

Temperature	293 K
Wavelength	1.54184 Å
Theta range for data collection	3.8 to 66.6°
Index range	-7≤h≤8, -27≤k≤26, -11≤l≤10
Reflections collected	9538
Independent reflections	2899 [R(int) = 0.036]
Observed data [*I*>2σ(*I*)]	1960

Refinement

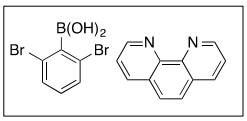
Data / parameters	2899 / 234
R, wR2, S	0.0545, 0.1514, 1.05
w = 1/[$\sigma^2F_0^2$)+(0.0642P)^2+ 0.4172P]	where P = (F_0^2+2F_c^2)/3
Largest diff. peak and hole	0.37 and -0.32vc e.Å^{-3}

Table 24. 2,6-Dichlorophenylboronic acid with 1,10-phenanthroline (CCDC 1037382)



	Crystal Data	
Formula	$C_6H_5Cl_2BO_2$, $C_{12}H_8N_2$	
Molecular Weight	371.01	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit cell dimensions	a = 10.5129(5) Å	α = 90°
	b = 12.6999(6) Å	β = 99.026(5)°
	c = 13.1644(6) Å	γ = 90°
Volume	1735.85(14) $Å^3$	
Z	4	
Density (calculated)	1.420 g/cm^3	
Absorption coefficient	0.388 mm^{-1}	
F(000)	760	
Crystal size	0.21 x 0.31 x 0.31 mm	
	Data Collection	
Temperature	293 K	
Wavelength	0.71073 Å	
Theta range for data collection	3.4 to 25.0°	
Index range	-11≤h≤12, -12≤k≤15, -15≤l≤15	
Reflections collected	8039	
Independent reflections	3063 [R(int) = 0.028]	
Observed data [*I*>2σ(*I*)]	2544	
	Refinement	
Data / parameters	3063 / 234	
R, wR2, S	0.0387, 0.1037, 1.04	
w = 1/[$\sigma^2F_0^2$)+(0.0459P)^2+ 0.4773P]	where P = (F_0^2+2F_c^2)/3	
Largest diff. peak and hole	0.17 and -0.23vc e.$Å^{-3}$	

Table 25. 2,6-Dibromophenylboronic acid with 1,10-phenanthroline (CCDC 1037388)



Crystal Data

Formula	$C_6H_5Br_2BO_2$, $C_{12}H_8N_2$	
Molecular Weight	459.93	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit cell dimensions	a = 10.4157(15) Å	α = 90°
	b = 12.9098(17) Å	β = 97.560(14)°
	c = 13.575(2) Å	γ = 90°
Volume	1809.5(4) Å^3	
Z	4	
Density (calculated)	1.688 g/cm^3	
Absorption coefficient	4.493 mm^{-1}	
F(000)	904	
Crystal size	0.32 x 0.37 x 0.60 mm	

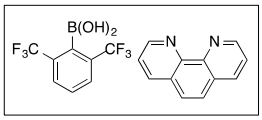
Data Collection

Temperature	293 K
Wavelength	0.71073 Å
Theta range for data collection	3.0 to 25.0°
Index range	-12≤h≤12, -15≤k≤15, -16≤l≤14
Reflections collected	8112
Independent reflections	3170 [R(int) = 0.091]
Observed data [*I*>2σ(*I*)]	1969

Refinement

Data / parameters	3170 / 231
R, wR2, S	0.0712, 0.1813, 1.03
w = 1/[$\sigma^2F_0^2$)+(0.0804P)^2]	where P = (F_0^2+2F_c^2)/3
Largest diff. peak and hole	0.51 and -0.60vc e.Å^{-3}

Table 26. 2,6-Bis(trifluoromethyl)phenylboronic acid with 1,10-phenanthroline (CCDC 1037670)



Crystal Data

Formula	$C_8H_5F_6BO_2$, $C_{12}H_8N_2$	
Molecular Weight	438.13	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit cell dimensions	a = 7.4225(15) Å	α = 90°
	b = 23.717(5) Å	β = 107.92(2)°
	c = 11.927(2) Å	γ = 90°
Volume	1997.874) $Å^3$	
Z	4	
Density (calculated)	1.457 g/cm^3	
Absorption coefficient	0.132 mm^{-1}	
F(000)	888	
Crystal size	0.06 x 0.22 x 0.40 mm	

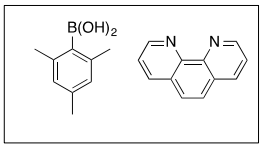
Data Collection

Temperature	293 K
Wavelength	0.71073 Å
Theta range for data collection	2.9 to 25.0°
Index range	-8≤h≤8, -24≤k≤28, -14≤l≤11
Reflections collected	7537
Independent reflections	3495 [R(int) = 0.060]
Observed data [*I*>2σ(*I*)]	1937

Refinement

Data / parameters	3495 / 288
R, wR2, S	0.0619, 0.2076, 1.04
w = 1/[$\sigma^2F_0^2$)+(0.0927P)^2+0.0744P]	where P = (F_0^2+2F_c^2)/3
Largest diff. peak and hole	0.23 and -0.22vc $e.Å^{-3}$

Table 27. Mesitylboronic acid with 1,10-phenanthroline (CCDC 1063176)



Crystal Data

Formula	$C_9H_{13}BO_2$, $C_{12}H_8N_2$	
Molecular Weight	344.21	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit cell dimensions	a = 26.2971(10) Å	α = 90°
	b = 7.0717(2) Å	β = 114.836(14)°
	c = 22.6474(2) Å	γ = 90°
Volume	3822.1(3) $Å^3$	
Z	8	
Density (calculated)	1.196 g/cm^3	
Absorption coefficient	0.606 mm^{-1}	
F(000)	1456	
Crystal size	0.06 x 0.28 x 0.60 mm	

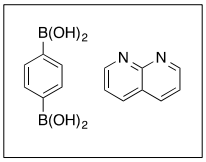
Data Collection

Temperature	293 K
Wavelength	1.54184 Å
Theta range for data collection	3.9 to 67.1°
Index range	-29≤h≤31, -4≤k≤8, -26≤l≤26
Reflections collected	15737
Independent reflections	6724 [R(int) = 0.023]
Observed data [*I*>2σ(*I*)]	5427

Refinement

Data / parameters	6724 / 489
R, wR2, S	0.0560, 0.1776, 1.10
$w = 1/[\sigma^2F_0^2)+(0.0916P)^2 + 0.7088P]$	where $P = (F_0^2+2F_c^2)/3$
Largest diff. peak and hole	0.36 and -0.44vc $e.Å^{-3}$

Table 28. 1,4-Phenyldiboronic acid with 1,8-naphthyridine (CCDC 1037668)



Crystal Data

Formula	$3(C_6H_8B_2O_2)$, $4(C_8H_6N_2)$	
Molecular Weight	1017.82	
Crystal System	Triclinic	
Space Group	P-1	
Unit cell dimensions	a = 10.1517(6) Å	α = 80.742(6)°
	b = 11.1294(8) Å	β = 86.043(5)°
	c = 11.3910(7) Å	γ = 80.122(6)°
Volume	1250.25(14) $Å^3$	
Z	1	
Density (calculated)	1.352 g/cm^3	
Absorption coefficient	0.095 mm^{-1}	
F(000)	530	
Crystal size	0.05 x 0.10 x 0.40 mm	

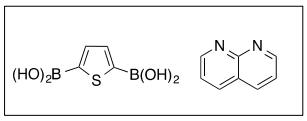
Data Collection

Temperature	293 K
Wavelength	0.71073 Å
Theta range for data collection	3.3 to 25.0°
Index range	-12≤h≤12, -13≤k≤13, -13≤l≤12
Reflections collected	10041
Independent reflections	4414 [R(int) = 0.021]
Observed data [*I*>2σ(*I*)]	3450

Refinement

Data / parameters	4414 / 375
R, wR2, S	0.0418, 0.1184, 0.96
w = 1/[$\sigma^2F_0^2$)+(0.0699P)^2 +0.0643P]	where P = (F_0^2+2F_c^2)/3
Largest diff. peak and hole	0.16 and -0.21vc e.$Å^{-3}$

Table 29. 2,5-Thiophenediboronic acid with 1,8-naphthyridine (CCDC 1037669)



Crystal Data

Formula	$C_4H_6SB_2O_4$, $2(C_8H_6N_2)$	
Molecular Weight	432.06	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit cell dimensions	a = 14.9982(6) Å	α = 90°
	b = 10.8389(3) Å	β = 93.653(3)°
	c = 13.0251(5) Å	γ = 90°
Volume	2113.11(13) $Å^3$	
Z	4	
Density (calculated)	1.358 g/cm^3	
Absorption coefficient	0.188 mm^{-1}	
F(000)	896	
Crystal size	0.09 x 0.10 x 0.21 mm	

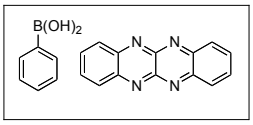
Data Collection

Temperature	293 K
Wavelength	0.71073 Å
Theta range for data collection	3.3 to 25.0°
Index range	-17≤h≤17, -10≤k≤12, -15≤l≤10
Reflections collected	1124
Independent reflections	3721 [R(int) = 0.032]
Observed data [*I*>2σ(*I*)]	2970

Refinement

Data / parameters	3721 / 296
R, wR2, S	0.0429, 0.1100, 1.06
w = $1/[\sigma^2F_0^2)+(0.0503P)^2+0.2005P]$	where P = $(F_0^2+2F_c^2)/3$
Largest diff. peak and hole	0.19 and -0.15vc $e.Å^{-3}$

Table 30. Phenylboronic acid with 5,6,11,12-tetraazanaphthacene (CCDC 1063181)



Crystal Data

Formula	$2(C_6H_7BO_2)$, $C_{14}H_8N_4$	
Molecular Weight	476.11	
Crystal System	Triclinic	
Space Group	P-1	
Unit cell dimensions	a = 7.4283(8) Å	α = 95.785(9)°
	b = 8.3837(9) Å	β = 103.104(9)°
	c = 10.8769(12) Å	γ = 114.473(11)°
Volume	585.80(13) $Å^3$	
Z	1	
Density (calculated)	1.350 g/cm^3	
Absorption coefficient	0.741 mm^{-1}	
F(000)	248	
Crystal size	0.06 x 0.10 x 0.22 mm	

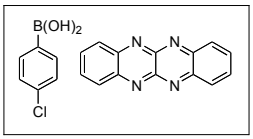
Data Collection

Temperature	293 K
Wavelength	1.54184 Å
Theta range for data collection	4.3 to 66.6°
Index range	-8≤h≤7, -9≤k≤9, -12≤l≤12
Reflections collected	4490
Independent reflections	2045 [R(int) = 0.033]
Observed data [*I*>2σ(*I*)]	1450

Refinement

Data / parameters	2045 / 171
R, wR2, S	0.0655, 0.1951, 1.36
w = 1/[$\sigma^2F_0^2$)+(0.0277P)^2+0.7454P]	where P = (F_0^2+2F_c^2)/3
Largest diff. peak and hole	0.16 and -0.17vc e.$Å^{-3}$

Table 31. 4-Chlorophenylboronic acid with 5,6,11,12-tetraazanaphthacene (CCDC 1063180)



Crystal Data

Formula	$2(C_6H_7ClBO_2)$, $C_{14}H_8N_4$	
Molecular Weight	544.98	
Crystal System	Triclinic	
Space Group	P-1	
Unit cell dimensions	a = 6.7570(3) Å	α = 112.762(4)°
	b = 9.7827(4) Å	β = 94.006(4)°
	c = 10.546(5) Å	γ = 96.904(4)°
Volume	632.96(5) $Å^3$	
Z	1	
Density (calculated)	1.430 g/cm^3	
Absorption coefficient	2.658 mm^{-1}	
F(000)	280	
Crystal size	0.24 x 0.40 x 0.50 mm	

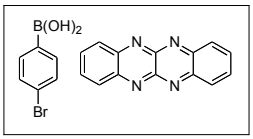
Data Collection

Temperature	293 K
Wavelength	1.54184 Å
Theta range for data collection	5.3 to 66.6°
Index range	-7≤h≤7, -11≤k≤11, -12≤l≤12
Reflections collected	10195
Independent reflections	2175 [R(int) = 0.030]
Observed data [*I*>2σ(*I*)]	2045

Refinement

Data / parameters	2175 / 180
R, wR2, S	0.0381, 0.1115, 0.85
w = 1/[$\sigma^2F_0^2$)+(0.0929P)^2+0.1244P]	where P = (F_0^2+2F_c^2)/3
Largest diff. peak and hole	0.25 and -0.31vc e.$Å^{-3}$

Table 32. 4-Bromophenylboronic acid with 5,6,11,12-tetraazanaphthacene (CCDC 1063173)



Crystal Data

Formula	$2(C_6H_7BrBO_2)$, $C_{14}H_8N_4$	
Molecular Weight	633.90	
Crystal System	Triclinic	
Space Group	P-1	
Unit cell dimensions	a = 6.8541(7) Å	α = 114.154(18)°
	b = 9.8549(19) Å	β = 93.533(11)°
	c = 10.772(2) Å	γ = 96.875(11)°
Volume	654.2(2) $Å^3$	
Z	1	
Density (calculated)	1.609 g/cm^3	
Absorption coefficient	3.139 mm^{-1}	
F(000)	316	
Crystal size	0.06 x 0.29 x 0.60 mm	

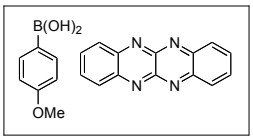
Data Collection

Temperature	293 K
Wavelength	0.71073 Å
Theta range for data collection	3.0 to 25°
Index range	-7≤h≤8, -11≤k≤10, -9≤l≤12
Reflections collected	4174
Independent reflections	2261 [R(int) = 0.040]
Observed data [*I*>2σ(*I*)]	1744

Refinement

Data / parameters	2261 / 180
R, wR2, S	0.0410, 0.1671, 1.06
w = $1/[\sigma^2F_0^2)+(0.1055P)^2+0.2338P]$	where P = $(F_0^2+2F_c^2)/3$
Largest diff. peak and hole	0.42 and -0.60vc $e.Å^{-3}$

Table 33. 4-Methoxyphenylboronic acid with 5,6,11,12-tetraazanaphthacene (CCDC 1063175)



Crystal Data

Formula	$2(C_7HBO_3)$, $C_{14}H_8N_4$	
Molecular Weight	536.15	
Crystal System	Monoclinic	
Space Group	$P2_1/n$	
Unit cell dimensions	a = 7.4105(9) Å	α = 90°
	b = 20.0298(15) Å	β = 109.863(14)°
	c = 9.3908(12) Å	γ = 90°
Volume	1311.0(3) $Å^3$	
Z	2	
Density (calculated)	1.358 g/cm^3	
Absorption coefficient	0.095 mm^{-1}	
F(000)	560	
Crystal size	0.07 x 0.14 x 0.34 mm	

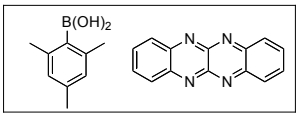
Data Collection

Temperature	293 K
Wavelength	0.71073 Å
Theta range for data collection	3.0 to 25°
Index range	-8≤h≤8, -21≤k≤23, -10≤l≤11
Reflections collected	6769
Independent reflections	2320 [R(int) = 0.039]
Observed data [*I*>2σ(*I*)]	1542

Refinement

Data / parameters	2320 / 190
R, wR2, S	0.0618, 0.1362, 1.08
w = $1/[\sigma^2F_0^2)+(0.0512P)^2+0.1129P]$	where P = $(F_0^2+2F_c^2)/3$
Largest diff. peak and hole	0.17and -0.16vc $e.Å^{-3}$

Table 34. Mesitylboronic acid with 5,6,11,12-tetraazanaphthacene (CCDC 1063179)



Crystal Data

Formula	$2(C_9H_{13}BO_2)$, $C_{14}H_8N_4$	
Molecular Weight	560.27	
Crystal System	Triclinic	
Space Group	P-1	
Unit cell dimensions	a = 7.9753(9) Å	α = 109.53(2)°
	b = 10.291(2) Å	β = 105.321(17)°
	c = 10.730(17) Å	γ = 104.113(13)°
Volume	745.1(3) $Å^3$	
Z	1	
Density (calculated)	1.249 g/cm^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	296	
Crystal size	0.08 x 0.28 x 0.38 mm	

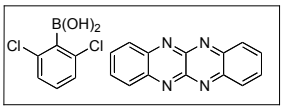
Data Collection

Temperature	293 K
Wavelength	0.71073 Å
Theta range for data collection	2.8 to 25°
Index range	-9≤h≤8, -12≤k12, -9≤l≤12
Reflections collected	5051
Independent reflections	2638 [R(int) = 0.020]
Observed data [*I*>2σ(*I*)]	2143

Refinement

Data / parameters	2638 / 205
R, wR2, S	0.0485, 0.1318, 1.05
w = $1/[\sigma^2F_0^2)+(0.0610P)^2+0.2275P]$	where P = $(F_0^2+2F_c^2)/3$
Largest diff. peak and hole	0.23 and -0.17vc $e.Å^{-3}$

Table 35. 2,6-Dichlorophenylboronic acid with 5,6,11,12-tetraazanaphthacene (CCDC 1063172)



Crystal Data

Formula	$2(C_6H_5Cl_2BO_2)$, $C_{14}H_8N_4$, $2(C_7H_8)$	
Molecular Weight	798.13	
Crystal System	Monoclinic	
Space Group	$P2_1/n$	
Unit cell dimensions	a = 7.4226(10) Å	α = 90°
	b = 25.677(4) Å	β = 109.143(16)°
	c = 10.9888(16) Å	γ = 90°
Volume	1978.6(5) $Å^3$	
Z	2	
Density (calculated)	1.340 g/cm^3	
Absorption coefficient	0.345 mm^{-1}	
F(000)	824	
Crystal size	0.15 x 0.23 x 0.29 mm	

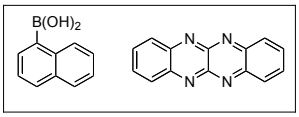
Data Collection

Temperature	293 K
Wavelength	0.71073 Å
Theta range for data collection	2.9 to 25°
Index range	-8≤h≤8, -26≤k≤30, -12≤l≤13
Reflections collected	7424
Independent reflections	3337 [R(int) = 0.072]
Observed data [*I*>2σ(*I*)]	2231

Refinement

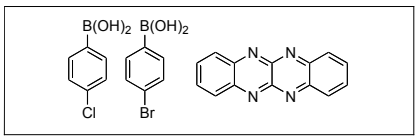
Data / parameters	3337 / 275
R, wR2, S	0.0740, 0.1997, 1.05
w = $1/[\sigma^2F_0^2)+(0.0955P)^2+0.4628P]$	where P = $(F_0^2+2F_c^2)/3$
Largest diff. peak and hole	0.36 and -0.24vc $e.Å^{-3}$

Table 36. Napthalene-1-boronic acid with 5,6,11,12-tetraazanaphthacene (CCDC 1063178)



	Crystal Data	
Formula	$2(C_{10}H_9BO_2)$, $C_{14}H_8N_4$	
Molecular Weight	576.21	
Crystal System	Monoclinic	
Space Group	P-1	
Unit cell dimensions	a = 6.8485(4) Å	α = 104.365(6)°
	b = 8.6631(6) Å	β = 92.714(5)°
	c = 14.9105(10) Å	γ = 97.449(5)°
Volume	846.82(10) $Å^3$	
Z	1	
Density (calculated)	1.130 g/cm^3	
Absorption coefficient	0.598 mm^{-1}	
F(000)	300	
Crystal size	0.02 x 0.14 x 0.17 mm	
	Data Collection	
Temperature	293 K	
Wavelength	1.54184 Å	
Theta range for data collection	5.3 to 62.4°	
Index range	-5≤h≤7, -9≤k≤9, -16≤l≤17	
Reflections collected	4327	
Independent reflections	2576 [R(int) = 0.024]	
Observed data [*I*>2σ(*I*)]	1984	
	Refinement	
Data / parameters	2576 / 199	
R, wR2, S	0.0537, 0.1932, 1.17	
w = 1/[$\sigma^2F_0^2$)+(0.1102P)^2+ 0.0551P]	where P = (F_0^2+2F_c^2)/3	
Largest diff. peak and hole	0.17 and -0.17vc e.$Å^{-3}$	

Table 37. 4-Bromophenylboronic acid and 4-chlorophenylboronic acid with 5,6,11,12-tetraazanaphthacene (CCDC 1063174)



Crystal Data

Formula	$2(C_6H_7Br_{0.4}Cl_{0.6}BO_2)$, $C_{14}H_8N_4$	
Molecular Weight	580.56	
Crystal System	Triclinic	
Space Group	P-1	
Unit cell dimensions	a = 6.7970(3) Å	α = 113.714(5)°
	b = 9.8020(5) Å	β = 93.663(4)°
	c = 10.6491(6) Å	γ = 96.856(4)°
Volume	640.03(6) $Å^3$	
Z	1	
Density (calculated)	1.506 g/cm^3	
Absorption coefficient	1.460 mm^{-1}	
F(000)	294	
Crystal size	0.16 x 0.42 x 0.60 mm	

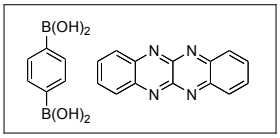
Data Collection

Temperature	293 K
Wavelength	0.71073 Å
Theta range for data collection	3.0 to 25°
Index range	-8≤h≤8, -11≤k≤11, -12≤l≤12
Reflections collected	9027
Independent reflections	2256 [R(int) = 1.10]
Observed data [*I*>2σ(*I*)]	1744

Refinement

Data / parameters	2261 / 180
R, wR2, S	0.0410, 0.1671, 1.06
w = $1/[\sigma^2F_0^2)+(0.0458P)^2+0.1151P]$	where P = $(F_0^2+2F_c^2)/3$
Largest diff. peak and hole	0.19 and -0.15vc $e.Å^{-3}$

Table 38. 1,4-Phenyldiboronic acid with 5,6,11,12-tetraazanaphthacene (CCDC 1063171)



Crystal Data

Formula	$C_6H_8B_2O_4$, $C_{14}H_8N_4$	
Molecular Weight	397.99	
Crystal System	Monoclinic	
Space Group	P2/c	
Unit cell dimensions	a = 8.9934(5) Å	α =90°
	b = 15.8317(7) Å	β = 90.808(5)°
	c = 7.2226(4) Å	γ = 90°
Volume	1028.26(9) $Å^3$	
Z	2	
Density (calculated)	1.285 g/cm^3	
Absorption coefficient	0.739 mm^{-1}	
F(000)	412	
Crystal size	0.06 x 0.08 x 0.60 mm	

Data Collection

Temperature	293 K
Wavelength	1.54184 Å
Theta range for data collection	2.8 to 66.6°
Index range	-10≤h10, -18≤k≤16, -8≤l≤5
Reflections collected	3008
Independent reflections	1624 [R(int) = 0.063]
Observed data [*I*>2σ(*I*)]	1096

Refinement

Data / parameters	1624 / 139
R, wR2, S	0.1080, 0.3144, 1.14
w = 1/[$\sigma^2F_0^2$)+(0.2000P)^2]	where P = (F_0^2+2F_c^2)/3
Largest diff. peak and hole	0.59 and -0.57vc e.$Å^{-3}$

5. SEM analysis

5.1. Heteromolecular supramolecular polymer

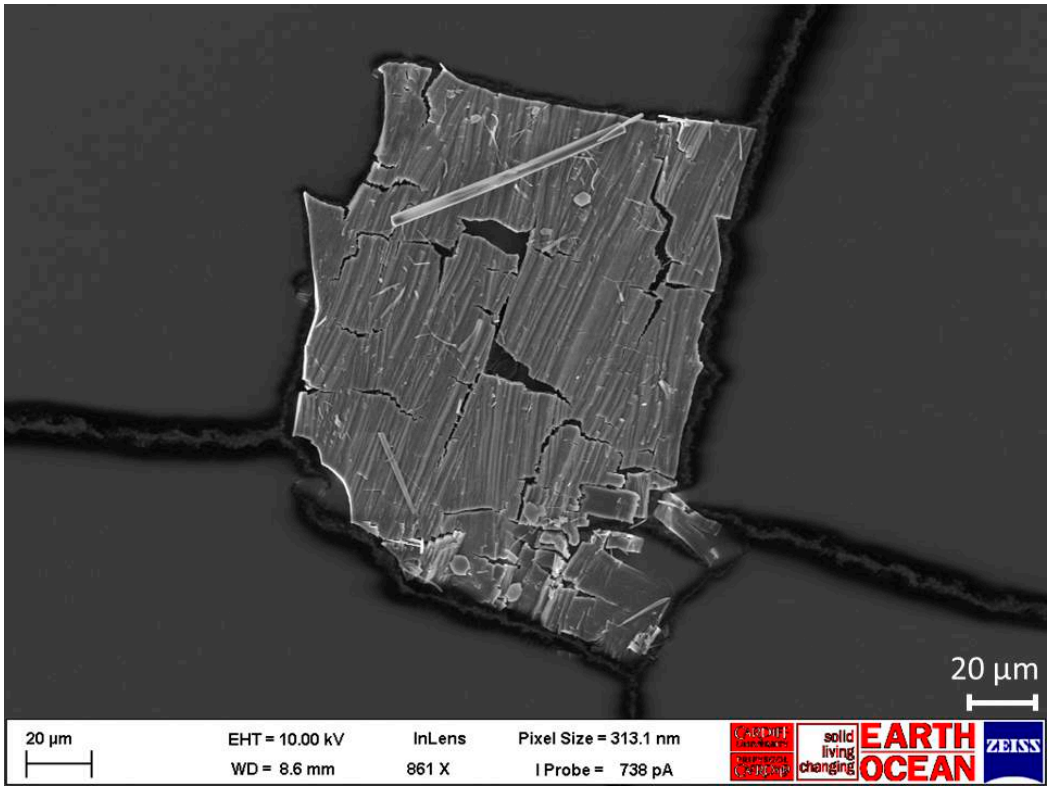


Figure S86. Selected SEM image of the heteromolecular supramolecular polymer crystal.

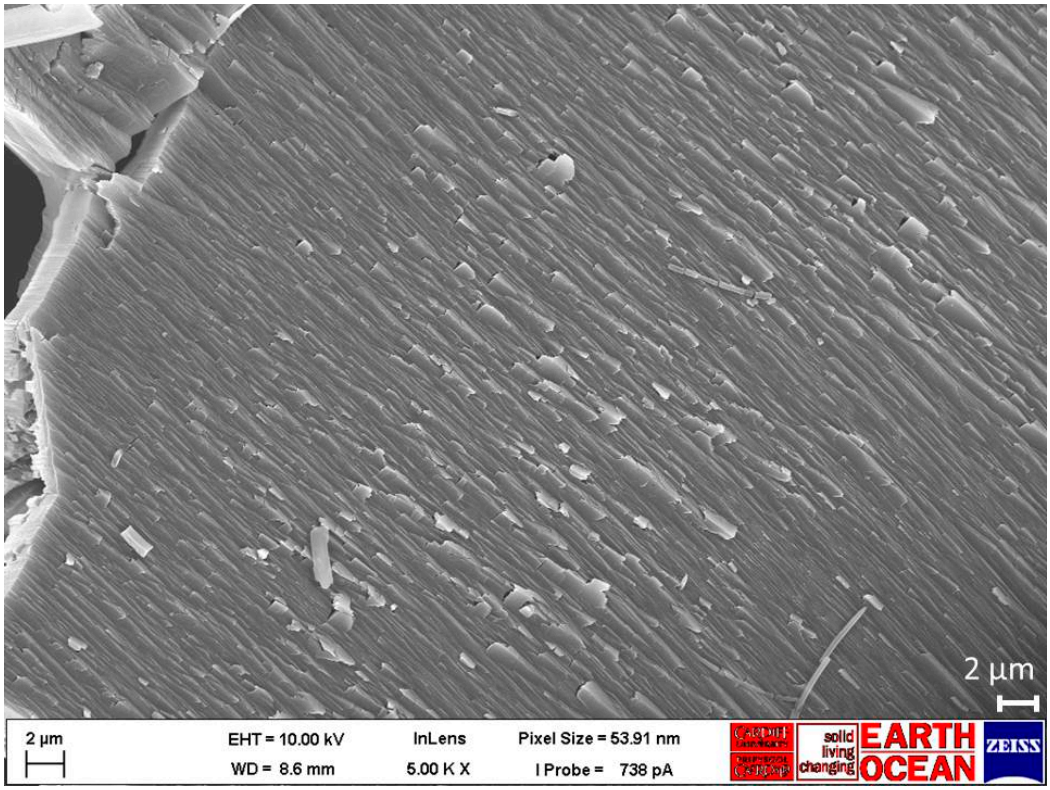


Figure S87. Selected SEM image of the heteromolecular supramolecular polymer crystal.

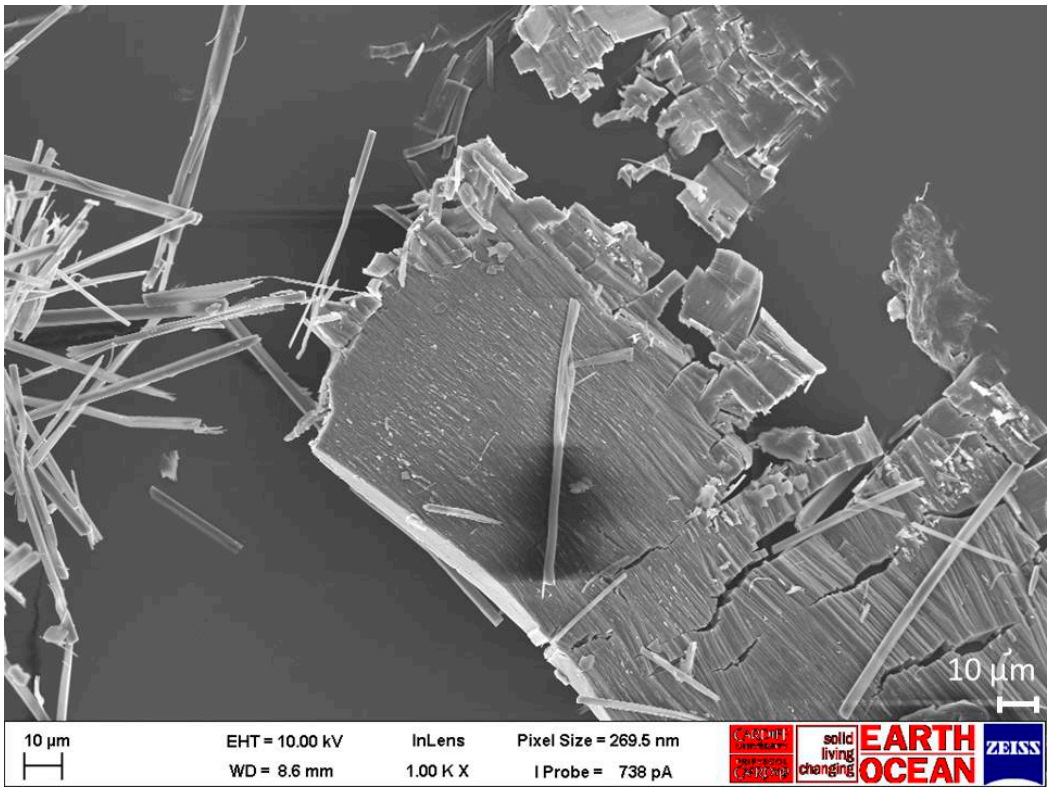


Figure S88. Selected SEM image of the heteromolecular supramolecular polymer crystal.

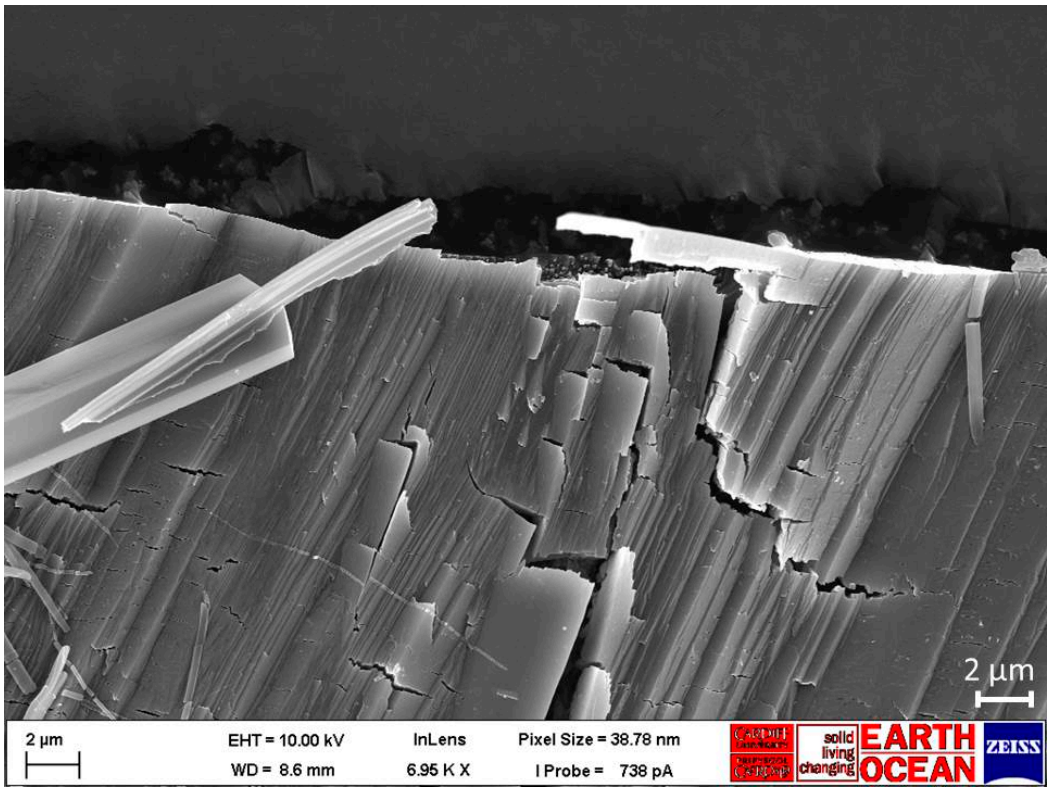


Figure S89. Selected SEM image of the heteromolecular supramolecular polymer crystal.

4.2. Tetraazanaphthacene

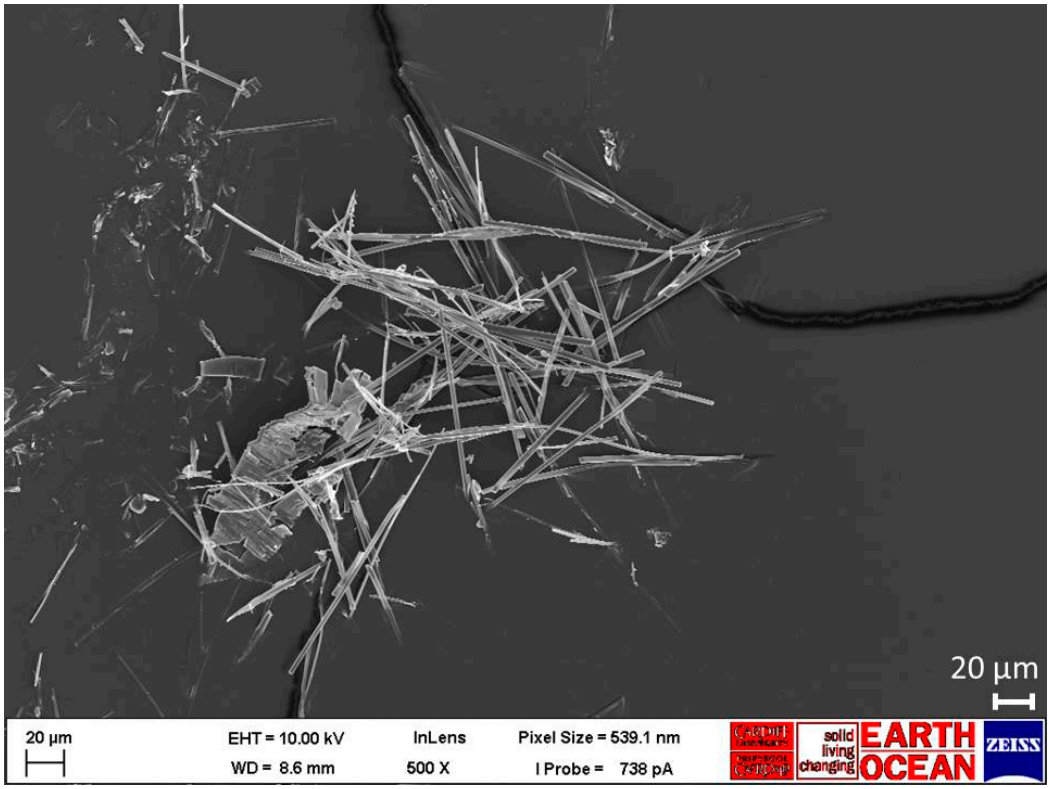


Figure S90. Selected SEM image of tetraazanaphthacene crystal.

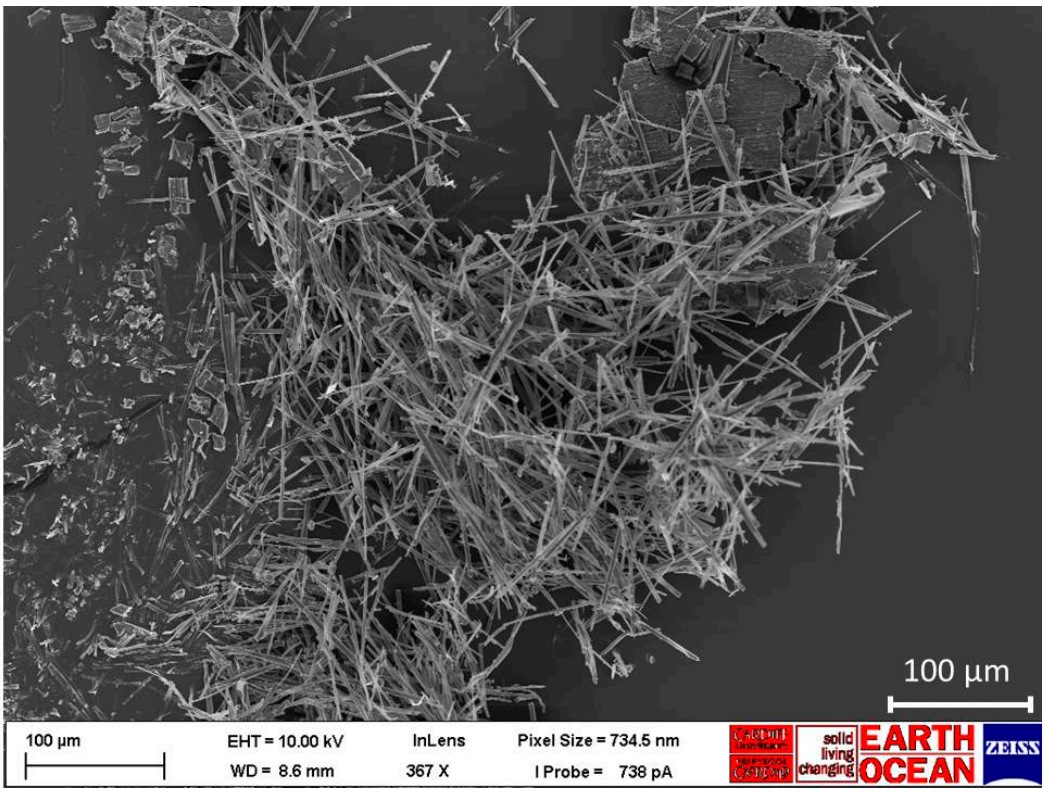


Figure S91. Selected SEM image of tetraazanaphthacene crystal.

6. References

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3. Thordarson, P. *Chem. Soc. Rev.* **2011**, *40*, 1305.
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