JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b01296 • Publication Date (Web): 31 Jul 2018

ACS Publications

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Exploiting coupling of boronic acids with triols for a pH-dependent "click-declick" chemistry

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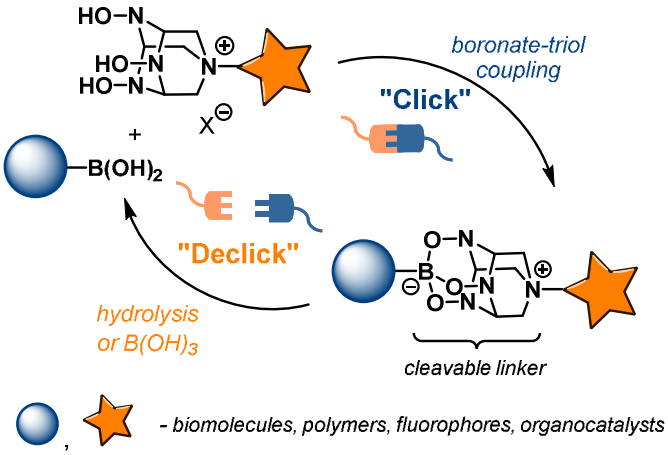


ABSTRACT

Click-like condensation of boronic acids with specifically designed triols (boronate-triol coupling) produces stable diamantane adducts in aqueous medium, which can be controllably cleaved to initial components under acidic conditions or by using boric acid as a chemical trigger. This novel "click-declick" strategy allows to create temporary covalent connections between two or more modular units that was demonstrated by the synthesis of new fluorophore-labeled natural molecules (peptides, steroids), supramolecular assemblies, modified polymers, boronic acid scavengers, solid-supported organocatalysts, biodegradable COF-like materials and dynamic combinatorial libraries.

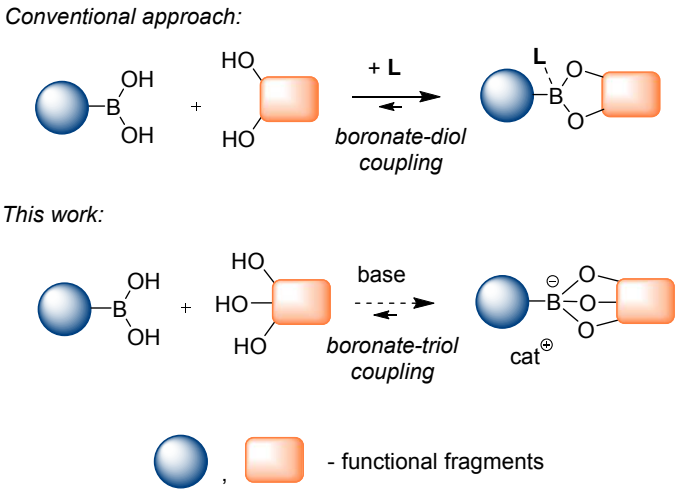
INTRODUCTION

The click chemistry concept since its introduction in 2001 has become the most eminent strategy for a covalent linkage of two or more modular units to form a single structure.[1] However, for some certain tasks related to material science and biology it is important not only to connect the functional units, but also to be able to disconnect those after the conjugate have served its role. For this purpose, reversible click chemistry is needed. In this approach, functional units are temporary connected to each other through a covalent linker, which can be cleaved ("declicked") under certain conditions (in a controllable manner) recovering the initial components. The "click/declick" strategy has a great potential for creating new drug delivery systems, dynamic combinatorial libraries, biodegradable and adaptive (smart) polymeric materials, recoverable chemical scavengers, etc.[2]

The fundamental basis behind the reversible click chemistry is the phenomenon of a so-called dynamic covalent bonding.[3] In these reactions covalent bonds are readily formed and easily broken in a reversible manner under physiological conditions. The most challenging task is to be able to control the equilibrium making covalent adducts thermodynamically preferred under one conditions and the initial reagents under another (for example, by changing pH or by adding a

chemical trigger).[2a] Thus, not any reaction, which is reversible under normal conditions, can be used for a reversible click process.

Probably, the most known dynamic covalent linkage is the boron-oxygen bond.[4] Interaction of boronic acids with alcohols occurs very easily (yet reversible) forming boronate esters $RB(OR^1)_2$ (Scheme 1).[4c] In particular, the boronate-diol condensation have recently been used for the creation of various supramolecular assemblies and nanomaterials,[5] covalent organic frameworks,[6] self-repairing polymers,[7] gels,[8] molecular imprinting systems,[9] biomolecular sensors,[10] etc.[11] However, a significant drawback of this chemistry is the low hydrolytic stability of boronate esters.[12] Typically, either anhydrous conditions or addition of a chemical trigger (ligand **L**) are needed to shift the equilibrium to the desired boronate ester (or its complex). This makes boronate-diol adducts poor candidates for a controllable click-declick chemistry in aqueous phase.



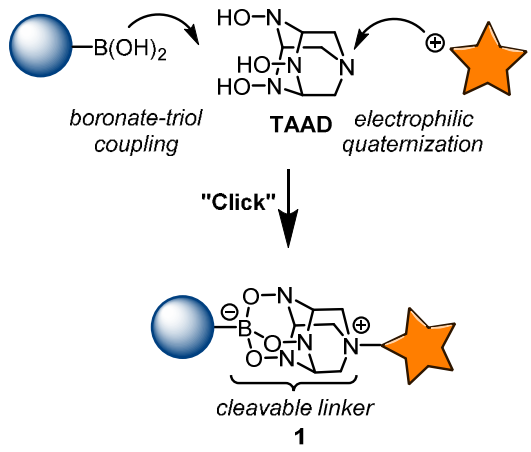
Scheme 1. Boronate-diol and boronate-triol couplings

Our approach to this problem is based on applying triols as partners for coupling with boronic acids (Scheme 1). Here, we demonstrate, that the use of specifically designed functionalized triols allows the preparation of very stable conjugates, which are resistant towards hydrolysis under basic/neutral conditions, and readily decouple under acidic conditions regenerating the initial triol and boronic acid. This new pH-controllable "click-declick" reaction was used in preparing analogs of known click-adducts, dynamic combinatorial libraries, modified polymers,

recoverable solid-supported scavengers and biodegradable materials. It should be specially noted that boronic acids are highly promising building blocks for click chemistry because of their high availability, including macromolecular boronic acids, polymer-supported boronic acids, as well as boronic acid-labeled biomolecules.

RESULTS AND DISCUSSION

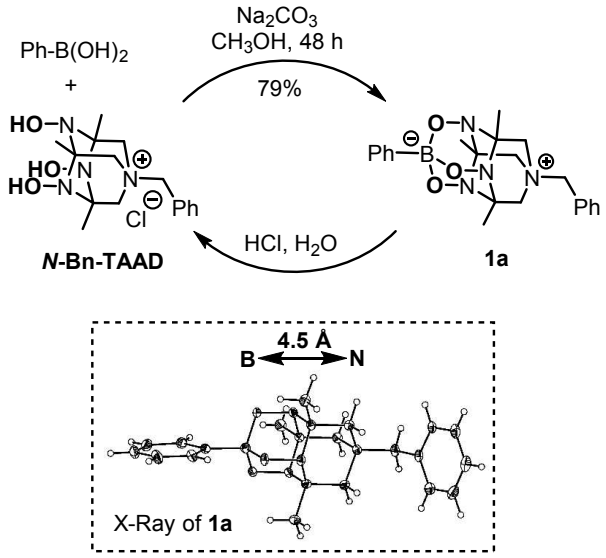
The scope of available triols is much more limited as compared to diols. Therefore, optimal partners for the condensation with boronic acids are triols, which possess an additional functional group used for prior derivatization by standard methods. *N*,*N*,*N*-Trihydroxy-1,4,6,10-tetraazaadamantanes (**TAAD**, Scheme 2), which recently became available,[13] bear three hydroxyl groups together with a nucleophilic tertiary nitrogen atom and thus can be viewed as promising bifunctional crosslinkers to couple boronic acids with appropriate electrophiles. **TAAD** adducts with boronic acids should have stable zwitterionic diamantane structures **1**, which are expected to be water soluble.[14,15]



Scheme 2. A general scheme of boronate-triol coupling with **TAAD** as crosslinker

Initially, we explored the interaction of model *N*-benzyl salt ***N*-Bn-TAAD** with phenylboronic acid (Scheme 3). In this experiment, the formation of zwitterionic adduct **1a** was detected, yet, a considerable amount of unreacted starting materials was also present. Fortunately, addition of a base (Na_2CO_3) for interception of releasing HCl completely shifted the equilibrium to the desired adduct **1a**. According to a single crystal X-Ray analysis (CCDC 1048294), this product has a

diamantane structure with nearly ideal C_{3v} symmetry. The size of diamantane measured as the distance between the quaternary nitrogen and boron atoms is ca. 4.5 Å, which corresponds to the length of rigid linker between phenyl and benzyl groups. Diamantane **1a** is exceptionally thermally stable (up to 260 °C) and is moderately soluble in water (ca. 20 mg/mL).



Scheme 3. Interaction of phenylboronic acid with model triol ***N*-Bn-TAAD**

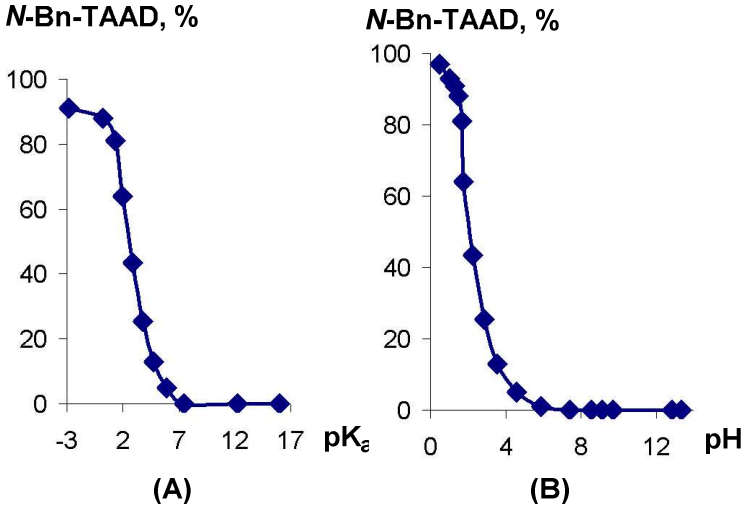


Figure 1. Hydrolysis of diamantane **1a** in water. (A) pK_a dependence, 2 equiv. of acid. (B) pH dependence, 2 equiv. of acid/base.

The need of a base in the synthesis of **1a** indicates the pH-dependent character of boronate-triol linkage formation. This is clearly demonstrated by the studies of the hydrolytic stability of diamantane **1a** summarized in Figure 1. As can be seen from these data, diamantane **1a** is stable

in a broad range of pH from alkaline to moderately acidic. A noticeable cleavage of boronate fragment to the initial components (***N*-Bn-TAAD** and $PhB(OH)_2$) was observed at pH values <3, yet complete hydrolysis required an excess of a strong acid with $pK_a<0$ (at pH<1). Importantly, change of pH from acidic to slightly alkaline (addition of $NaHCO_3$) results in the reassembly of adduct **1a** that confirms the reversible and pH-dependent character of boronate-triol condensation. Interestingly, an instantaneous change of pH from acidic to strongly alkaline by addition of NaOH does lead to recombination of components into **1a**. This is attributed to the fast transformation of phenylboronic acid to the $PhB(OH)_3^-$ anion, which does not enter coupling with triol ***N*-Bn-TAAD**.

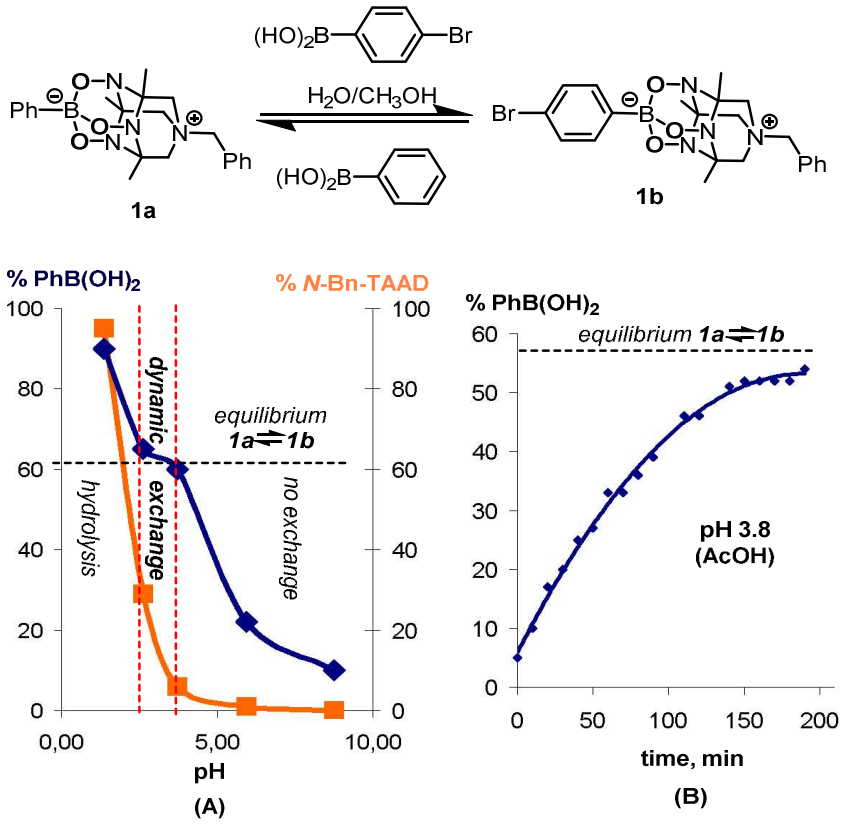


Figure 2. Boronic acid exchange in boronate adducts **1**. (A) – boronic acids exchange at different pH. (B) – kinetics of boronic acids exchange at pH 3.8.

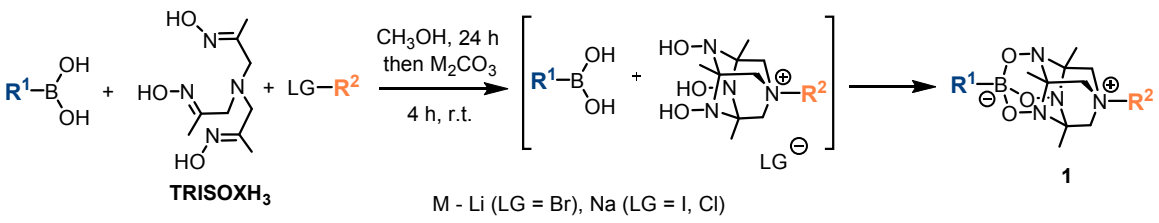
For a further study of boronate-triol equilibrium we conducted experiments on the exchange of boronic acid residues between diamantane **1a** and *p*-bromophenylboronic acid (Figure 2). Under alkaline and neutral pH these compounds co-exist ("sleeping state") indicating a large stability

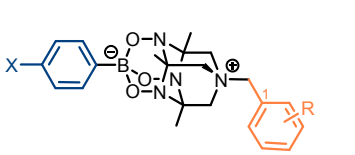
constant of complex **1a** under these conditions (Figure 2, A). In contrast, in a slightly acidic medium (AcOH in aqueous methanol) the equilibrium is established and two diamantane adducts **1a** and **1b** are detected in the reaction mixture ("dynamic exchange" area, Figure 2, A). Further increase of acidity results in a complete cleavage of both adducts affording triol ***N*-Bn-TAAD** and two boronic acids ("hydrolysis" area, Figure 2, A). Thus, in this reaction a narrow area of dynamic equilibrium exists at pH values 3.5–4.5, in which the exchange of boronate units can occur without a significant hydrolysis of adducts **1**. Kinetic measurements revealed that the equilibrium between **1a** and **1b** is achieved within ca. 3 h under these conditions. Importantly, this equilibrium can be "turned off" by raising the pH.

The reversible exchange of boronate residues in adducts **1** can be exploited to recover boronic acid from the complex with triol upon the action of $B(OH)_3$ under mild pH conditions. Thus, phenylboronic acid was almost quantitatively recovered from the aqueous solution of diamantane **1a** and an excess of $B(OH)_3$ with acetic acid additive (2 equivalents) using continuous extraction with chloroform (see Experimental section).

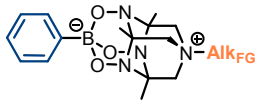
We further explored substrate scope of the developed boronate-triol condensation together with the possibility of synthesis of adducts **1** bearing various substituents and functional fragments at both ends of diamantane linker. In order to simplify the synthesis of target diamantanes **1**, we suggested a three-component procedure, in which quaternary salts ***N*-R^2-TAAD** are generated from readily available primary halides (or tosylates) **R^2-LG** and tris-oxime **$TRISOXH_3$** (Table 1). This *one-pot* process involves intramolecular cyclotrimerization of oxime groups (see Scheme 4), quaternization of tertiary nitrogen atom in **$TRISOXH_3$** and the boronate-triol coupling. The designed three-component condensation was found to be efficiently realized under ambient temperature in methanol in the presence of alkali metal carbonates. Importantly, these mild conditions are compatible with natural molecules (such as peptides) and other sensitive substrates.

Table 1. Substrate scope study of the three-component synthesis of diamantane adducts **1**

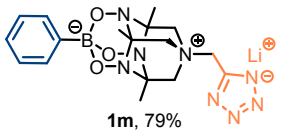




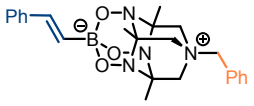
1a R, X = H, 94% (LG = Br)
1a R, X = H, 71% (LG = Cl)
1a R, X = H, 64% (LG = OTs)
1b R = H, X = Br, 90% (LG = Br)
1c R = 3-CN, X = H, 77% (LG = Br)
1d R = 4-CO_2CH_3, X = H, 84% (LG = Br)
1e R = 2-Br-4-NO_2, X = H, 99% (LG = Br)



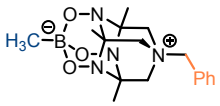
1f Alk = CH_3, 83% (LG = I)
1g Alk = $^nC_4H_9$, 90% (LG = I)
1h Alk_{FG} = CH_2CO_2Et, 98% (LG = Br)
1i Alk_{FG} = $CH_2C(O)Ph$, 97% (LG = Br)
1j Alk_{FG} = allyl, 85% (LG = Br)
1k Alk_{FG} = propargyl, 89% (LG = Br)
1l Alk_{FG} = CH_2-1-Naphtyl, 91% (LG = Br)



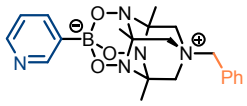
1m, 79%



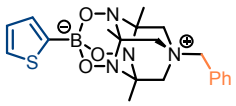
1n, 84%



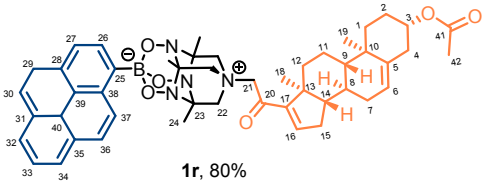
1o, 99%



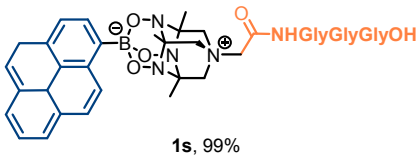
1p, 99%



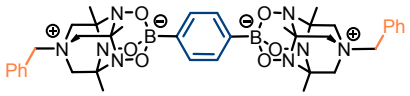
1q, 77%



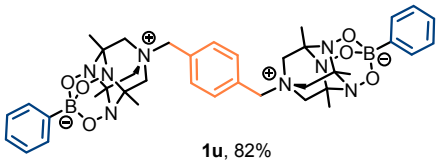
1r, 80%



1s, 99%



1t, 87%

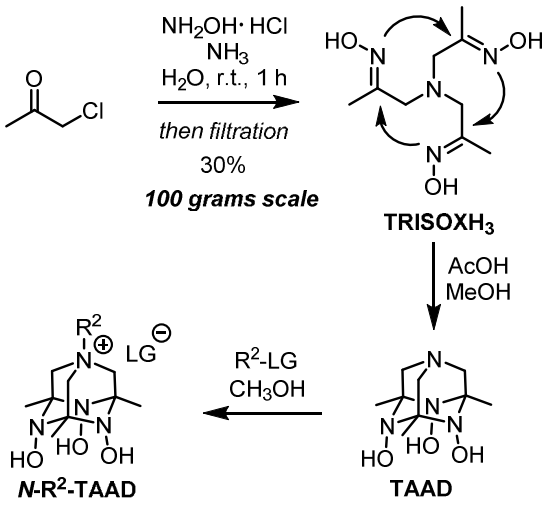


1u, 82%

This three-component procedure is applicable to a broad range of boronic acids as well as mono-/di-halo-substituted derivatives (both activated and non-activated) and tosylates. High isolated yields of corresponding adducts **1** are generally observed. Isolation of products typically requires separation from inorganic salts simply by trituration with water (for less water soluble products **1**) or acetone. Similar to **1a**, other adducts **1** are highly thermally stable and hydrolytically resistant (at pH > 7). Successful preparation of adducts **1r** and **1s** demonstrates the possibility of synthesis of fluorescent-labeled biomolecules[16] using the developed boronate-triol coupling approach.

For the synthesis of tris-oxime **$TRISOXH_3$** a simple and green *one-pot* protocol was developed employing condensation of commercially available chloroacetone with ammonia and

hydroxylamine in water (Scheme 4). Using this method, **TRISOXH$_3$** was prepared on a hundred grams scale. If needed, the latter can be transformed into corresponding **TAAD** derivatives in a single step according to our previously described procedures.[13]



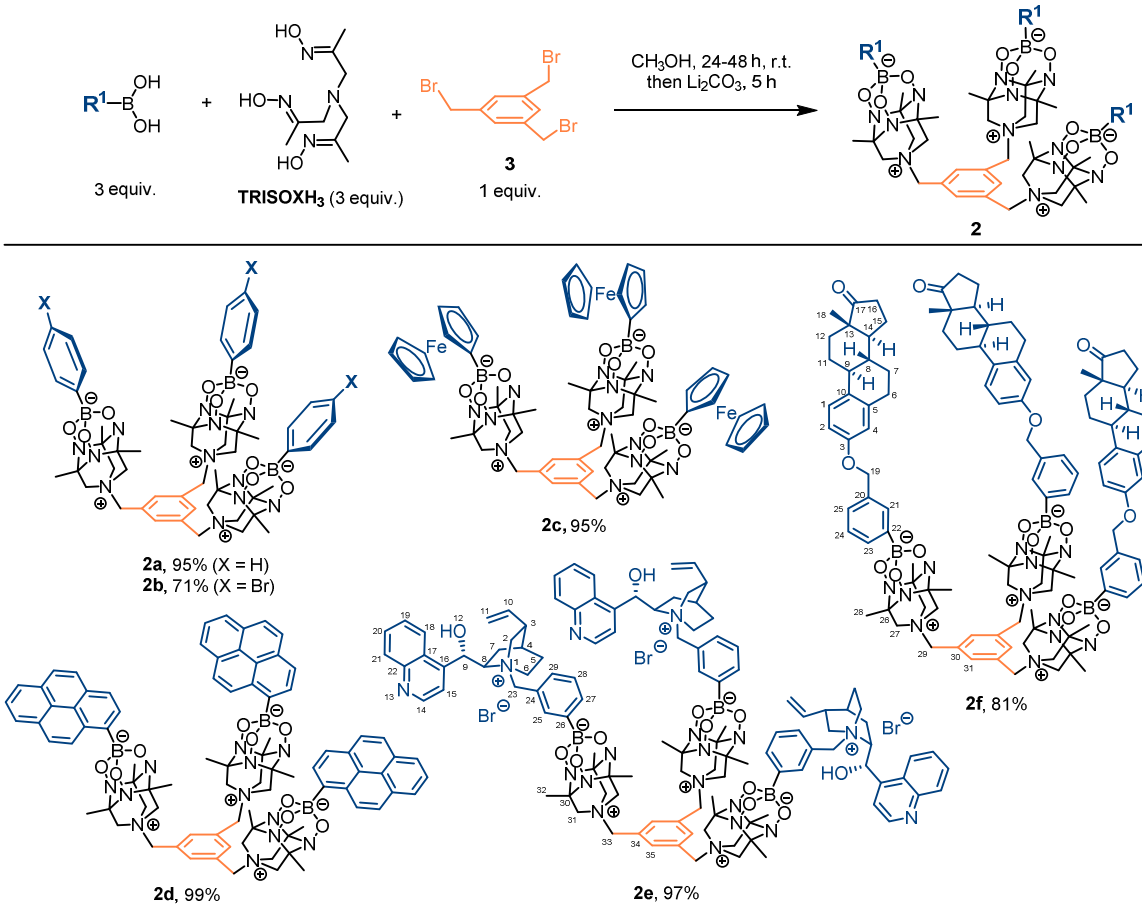
Scheme 4. Green and scalable synthesis of **TRISOXH$_3$**

Thus, high efficiency, controllable reversibility and broad scope of boronate-triol condensation make it a conceptually novel example of click-process, in which adducts are not only easily formed, but also can be cleaved ("declicked") by changing pH or by using boric acid as a chemical trigger. Here, we describe a few examples of application of this process in different subfields of organic chemistry.

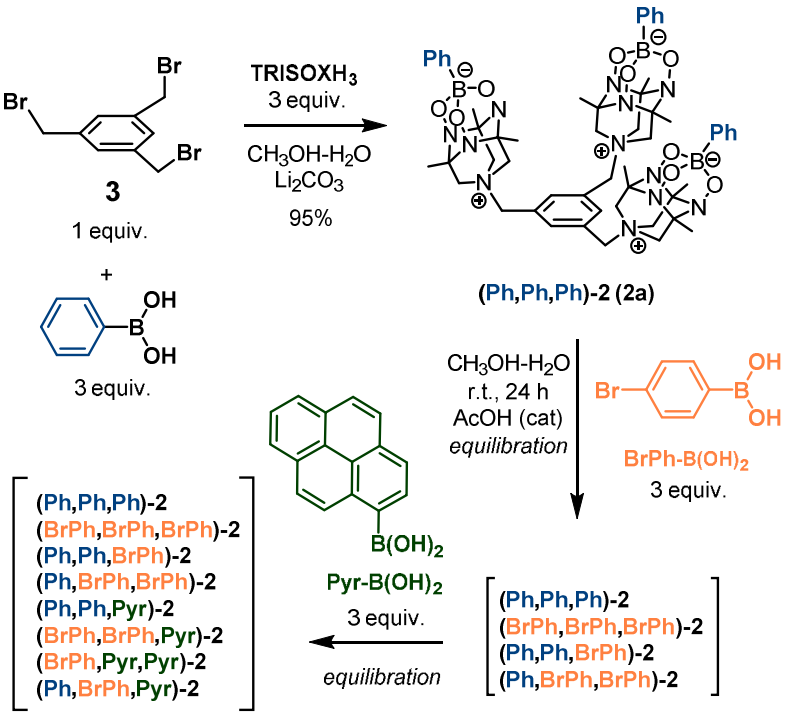
High efficiency of the three-component coupling demonstrated on model substrates suggests that it can be used to construct more complicated molecular assemblies. In particular, we explored the use of boronate-triol coupling to prepare trifunctional triad molecules. To do so, condensation of 1,3,5-tris(bromomethyl)benzene **3** (tribromomesitylene) with several functionalized boronic acids and **TRISOXH$_3$** was performed. As can be seen from Table 2, the designed multi-component condensation provides the desired triads **2** in a highly efficient manner even with complex boronic acids. Unstable boronic acids (such as ferroceneboronic acid FcB(OH)$_2$) were used in a slight excess to prevent the formation of products of mono- and bis-addition. Adducts **2** are analogs of known Van-der-Waals capsules[17] (adducts **2d** and **2f**) and

organocatalysts[18] (**2e**), which were previously prepared by conventional click-chemistry approaches (CuAAC reactions or etherification).

Table 2. Substrate scope study of the multi-component synthesis of triads **2**



The reversible character of boronate-triol linkage in adducts **1** and **2** can be exploited to generate dynamic combinatorial libraries (DCL's),[19] in which constituents are linked through a reversible chemical reaction. DCL's have a great potential utility for drug design and ultrafast *in vitro* screening.[19-21] We demonstrated the possibility of creating a dynamic covalent system comprising of eight adducts **2** from three different boronic building blocks and tribromomesitylene as shown in Scheme 5.

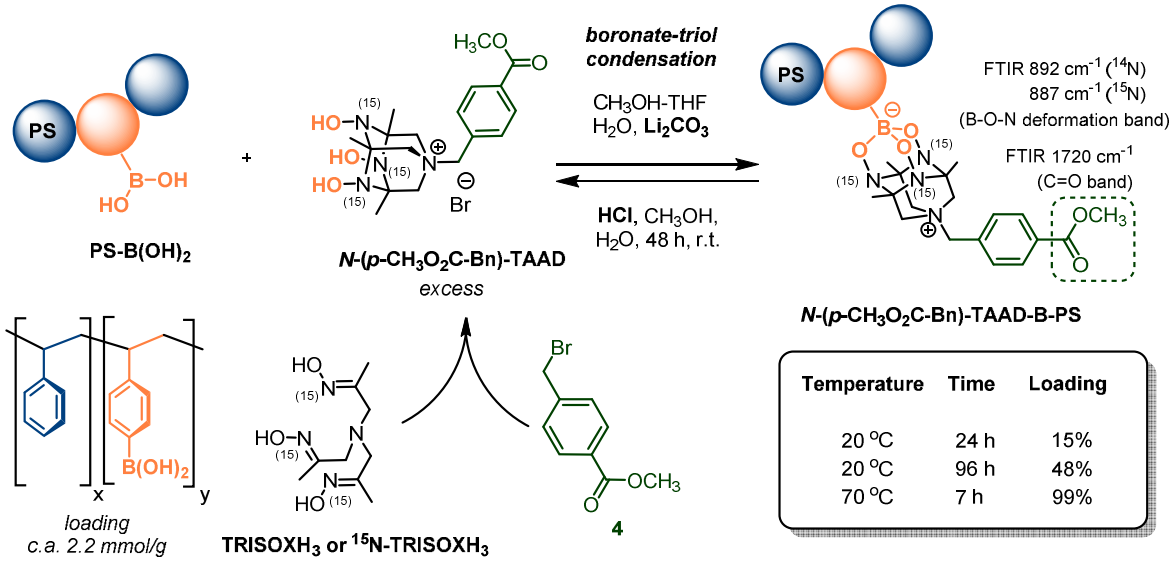


Scheme 5. Generation of dynamic combinatorial libraries employing reversible boronate-triol condensation

Thus, in the reaction of adduct **2a** with *p*-bromophenylboronic acid in the presence of AcOH redistribution of boronate fragments bounded to a tripodal matrix was observed. In the resulting mixture, four possible combinatorial adducts were detected demonstrating the dynamic covalent bond character of the boronate-triol linkage under these conditions. Addition of 1-pyreneboronic acid to this mixture leads to further redistribution of boronate fragments and formation of a dynamic combinatorial mixture of adducts **2** with almost all possible combinations of bounded boronic acids. Product **2c** (**(Pyr,Pyr,Pyr)-2**) was not observed by HRMS in this mixture indicating some selectivity in competitive binding of boronic acids under thermodynamically controlled conditions. It can be expected, that the dynamic equilibrium in combinatorial mixtures of adducts **2** can be shifted to certain products upon the external stimuli, such as complexation with metal ions[20] or biomolecules.[21] The number of species **2** generated in such a combinatorial library may be increased by using a mixture of different tris-oximes, which are also readily available.[22]

Reversible click chemistry can be efficiently exploited in materials science, in particular in the design of functionally-modified polymeric materials. In this case, a functional unit (for example, a chelator or catalyst) can be covalently immobilized on a solid polymeric matrix by means of boronate-triol linkage and after serving its role selectively removed regenerating the solid support. To test this idea, we examined two variants employing a polymeric-bound boronic acid and a polymeric-bound triol as solid supports.

In the first variant, commercially available polystyrene-bound boronic acid (**PS-B(OH)$_2$**) was used as a functionalized resin and a model quaternary salt ***N*-(*p*-MeO$_2$C-Bn)-TAAD** as a triol component (Scheme 6). In our initial experiments, the **TAAD** salt was generated *in situ* from methyl 4-(bromomethyl)benzoate **4** and **TRISOXH$_3$**. However, under these three-component conditions reaction was slow (15% and 50%-loading after 24 and 96 h, respectively). Furthermore, partial hydrolysis (and methanolysis) of bromide **4** was observed.



Scheme 6. Boronate-triol condensation for post-modification of polystyrene-bound boronic acid

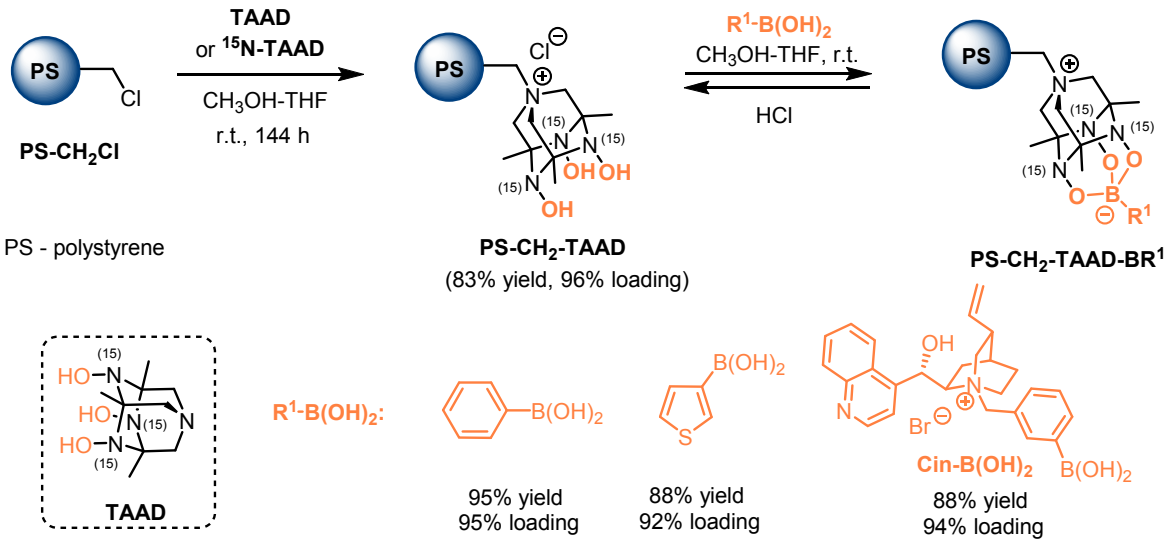
The use of a pre-synthesized quaternary salt ***N*-(*p*-MeO$_2$C-Bn)-TAAD** in reaction with **PS-B(OH)$_2$** proved to be more advantageous. After some optimization studies, we were delighted to find that at elevated temperature in a THF-CH_3OH-H_2O mixture almost maximum polymer loading was achieved within 7 h (Scheme 6). The modified polystyrene prepared in such way

was washed several times with THF, methanol and water to remove inorganic salts and the remaining **TAAD** salt, which gave the desired material in 89% yield (with respect to initial **PS-B(OH)$_2$**). Treatment of this functionalized resin with HCl resulted in almost complete regeneration of the polymer-bound boronic acid (86% recovery, 8% loading) as well as the triol salt ***N*-(*p*-MeO$_2$C-Bn)-TAAD** (Scheme 6).

The presence of boronate-triol linkage and the methoxycarbonyl group in the polymer was unambiguously proved by FT-IR spectroscopy. Characteristic B-O-N deformation band of the B,O,N-diamantane unit was identified using FT-IR study and DFT-calculations of specially synthesized ^{15}N-isotope-labeled triol ***N*-(*p*-MeO$_2$C-Bn)-TAAD**, its adduct with **PS-B(OH)$_2$** and diamantanes **1a**,**d** (see Scheme 6 and Supporting Information for details).

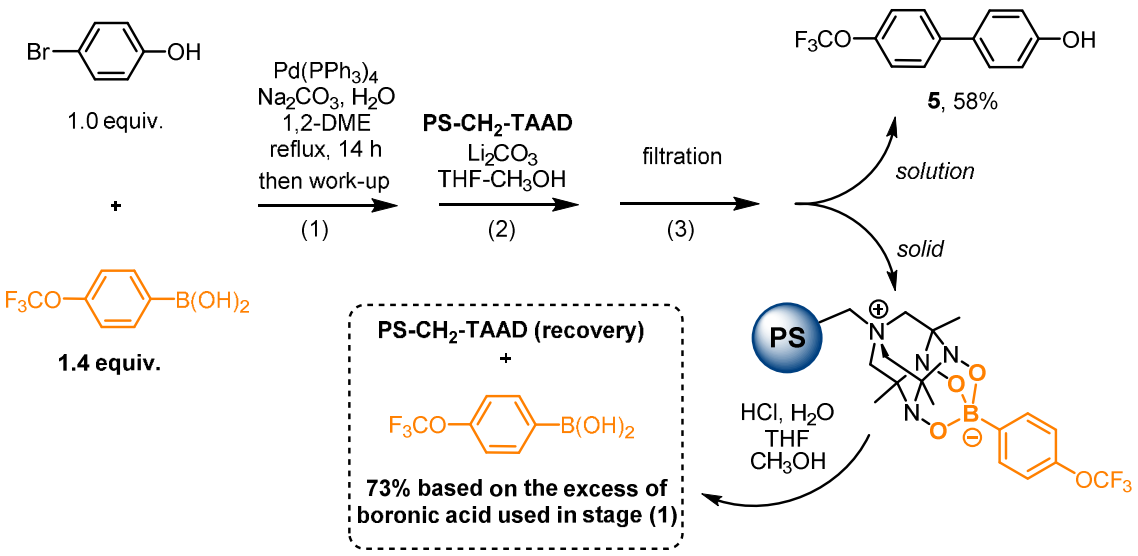
We further examined the use of a triol-modified polystyrene **PS-CH$_2$-TAAD** as a solid support for immobilization of boronic acids (Scheme 7). Polymer **PS-CH$_2$-TAAD** was prepared by reacting Merrifield resin (**PS-CH$_2$Cl**) with tetraazaadamantane **TAAD**. In the resulting polymer almost 100% of chlorine atoms were substituted for **TAAD**-groups. Application of a less nucleophilic **TRISOXH$_3$** (precursor of **TAAD**) resulted in much smaller loading of tetraazaadamantane on Merrifield resin.

When a solution of phenylboronic acid or 3-thienylboronic acid was exposed to **PS-CH$_2$-TAAD** resin in the presence of Li_2CO_3, nearly quantitative binding of both boronic acids to the solid matrix was detected (92-95% loading). FT-IR spectroscopy study again revealed the presence of the boronate-triol linkage in the obtained polymers. Using this approach, we were able to prepare a solid-supported cinchona alkaloid by immobilizing cinchonine-derived boronic acid (**Cin-B(OH)$_2$**) on **PS-CH$_2$-TAAD** resin (Scheme 7). Polymer-supported cinchona alkaloids are used as recoverable heterogeneous organocatalysts for asymmetric alkylation,[23] and aldol reactions.[24]



Scheme 7. Boronate-triol condensation for post-modification of Merrifield resin

As shown on the example of boronate-modified resin **PS-CH$_2$-TAAD-B-3-thienyl**, the initial solid support **PS-CH$_2$-TAAD** and 3-thienylboronic acid are completely regenerated upon the action of hydrochloric acid (Scheme 7). Thus, **PS-CH$_2$-TAAD** can be considered as a novel selective and regeneratable covalent scavenger of boronic acids. As demonstrated in Scheme 8, this scavenger can be used to remove the excess of boronic acid from the product in Suzuki-Miyaura coupling. A challenging synthesis of 4'-trifluoromethoxy-1,1'-biphenol **5**, which is an important building block in medicinal chemistry,[25] requires an excess of corresponding boronic acid to ensure high conversion of non-protected 4-bromophenol.[26] The residual 4-trifluoromethoxyphenylboronic acid was recovered using the above-mentioned technique by treatment of crude product with **PS-CH$_2$-TAAD** resin followed by filtration of polymer and hydrolysis. Apparently, **PS-CH$_2$-TAAD** resin can be also used to functionalize boronic acids by solid-phase synthesis.

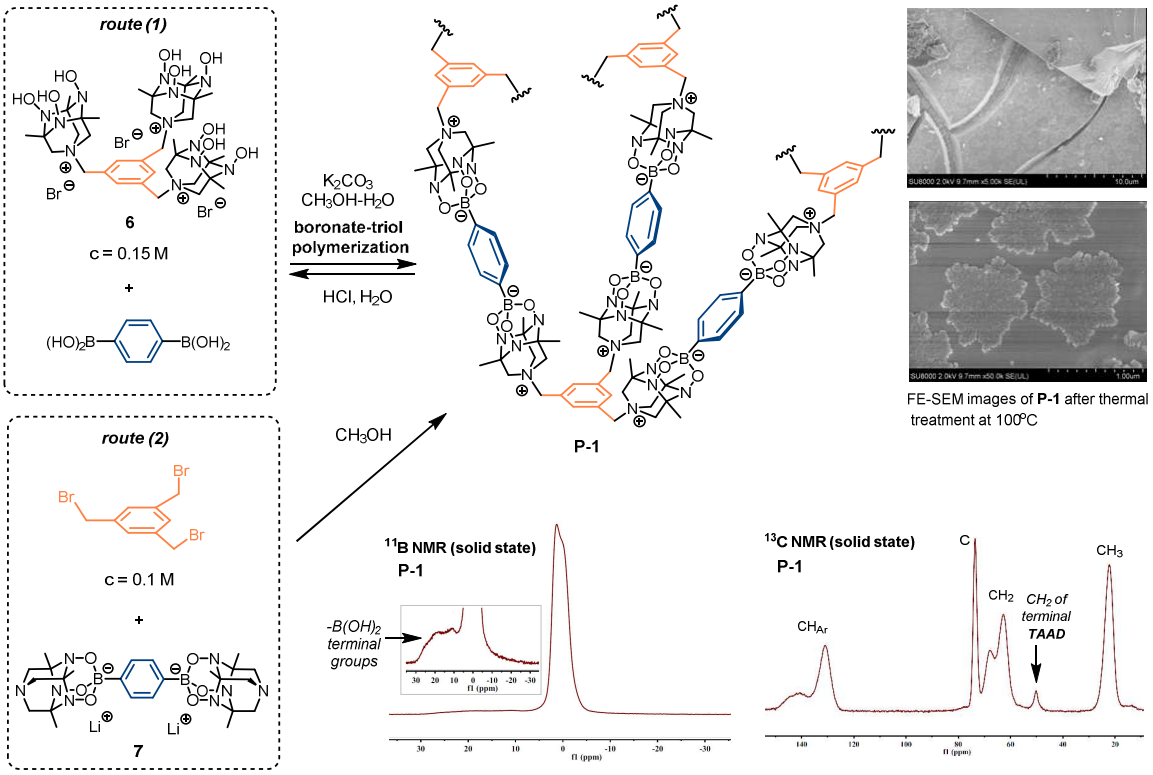


Scheme 8. PS-CH$_2$-TAAD resin as a covalent scavenger of boronic acids in Suzuki-Miyaura coupling

Finally, we tested the developed boronate-triol coupling for the preparation of biodegradable COF-like materials. Thus, condensation of tris-**TAAD** salt **6** with benzene-1,4-diboronic acid in aqueous methanol in the presence of base (K_2CO_3) produced a polymeric material **P-1** (Scheme 9, route (1)). Same material was prepared by a parallel synthesis using condensation of tribromomesitylene with dilithium salt **7** (Scheme 9, route (2)) as well as by a three-component condensation of tribromomesitylene, tris-oxime **TRISOXH$_3$**, and benzene-1,4-diboronic acid following the procedure shown in Table 2. Polymer **P-1** was characterized by solid state ^{1}H, ^{11}B, ^{13}C and ^{15}N NMR, FT-IR, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), BET, FE-SEM microscopy and elemental analysis. We were not able to determine the molar mass distribution of **P-1** due to its insolubility in water and organic solvents (yet, intensive swelling was observed in methanol).

Solid state NMR and FT-IR revealed characteristic signals related to B,O,N-diamantane linkers as well as to mesitylene and 1,4-boro-substituted phenyl rings. Furthermore, terminal triol and -B(OH)$_2$ groups were identified from these studies. According to TGA and DSC, the polymer is thermally stable up to 200^{o}C and loses absorbed water (ca. 20% mass) at around 100-140^{o}C. SEM images the thermally treated **P-1** showed a cracked surface morphology (Scheme 9). At

high magnification, the specific growth structures resembling nanostructured flowers[27] with large surface areas were seen. Even cracked area consisted of these structures.

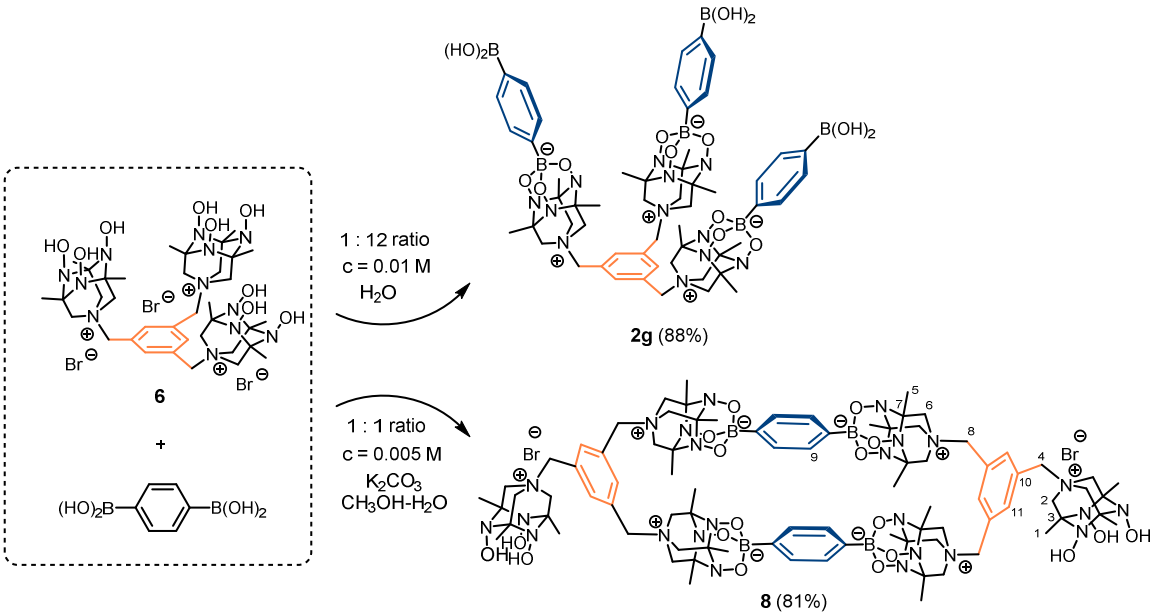


Scheme 9. Synthesis of biodegradable COF-type materials by boronate-triol condensation

Upon acidic hydrolysis, **P-1** underwent decomposition to initial **TAAD** salt **6** and benzene-1,4-diboronic acid demonstrating a biodegradable character of this material. The ratio of these monomers after hydrolysis was found to be ca. 1 : 2, respectively. Furthermore, the ratio of terminal/non-terminal benzene-1,4-diboronic residues determined as described in Supporting information was found to be ca. 1 : 2. These data indicates that the polymer has a cross-linked rather than dendrimeric structure (in a dendrimer structure the ratio terminal/non-terminal benzene-1,4-diboronic residues should be ca. 2 : 1).

Interestingly, in a 1 : 1 reaction between tris-**TAAD** salt **6** and benzene-1,4-diboronic acid in the presence of Li_2CO_3 under high-dilute conditions (0.005 M) a dimeric structure **8** was formed instead of polymer **P-1** (Scheme 10). Furthermore, the interaction of salt **6** with an excess of benzene-1,4-diboronic acid (12 equiv.) produced the tris-adduct **2g**. Both compounds **2g** and **8**

are likely to be intermediates in cross-condensations leading to the polymer **P-1** and were observed in result of partial hydrolysis of **P-1**.



Scheme 10. Oligomeric structures formed by boronate-triol condensation of tris-**TAAD** salt **6** and benzene-1,4-diboronic acid

CONCLUSIONS

In this paper we have demonstrated that boronate-triol condensation is a highly promising and efficient strategy for linkage of two or more modular units in a single stable covalent-bonded structure. Unlike traditional click approaches, the adducts formed by boronate-triol condensation can be declicked in controllable manner under the action of strong acids or a simple chemical trigger ($B(OH)_3$) allowing for creation a temporary connection between modular units. The suggested click strategy was efficiently used in the design of fluorophore-labeled natural molecules (peptides, steroids), supramolecular assemblies, modified polymers, boronic acid scavengers, solid-supported organocatalysts and biodegradable COF-like materials. Furthermore, a dynamic covalent character of B–O linkage in the boronate-triol adducts under slightly acidic conditions was successfully used to generate dynamic combinatorial libraries from available boronic acids.

EXPERIMENTAL SECTION

All reactions were carried out in oven-dried (150 °C) glassware. THF was distilled over NaOH. CH_3OH, EtOH, acetone, hexane, 1,2-dimethoxyethane and ethyl acetate were distilled without drying agents. Melting points were determined on a Kofler heating stage and were not corrected. NMR spectra of solutions were recorded at room temperature (if not stated otherwise) with residual solvent peaks as internal standards. Chemical shifts in ^{11}B are given relative to $BF_3 \cdot Et_2O$ (0 ppm). Chemical shifts in ^{14}N and ^{15}N are given relative to liquid NH_3 (0 ppm). Chemical shifts in ^{19}F are given relative to $CFCl_3$ (0 ppm). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), quint. (quintet), m (multiplet) and br. (broad). W values correspond to the full width at half-maximum of signal in Hz. Solid state NMR were recorded on a 400 MHz spectrometer with magnetic field of 9.4 T using a 4-mm CP/MAS probe. Larmor frequency for investigated nuclear ^{1}H, ^{11}B, ^{13}C and ^{15}N are 400.23, 128.41, 100.64 and 40.55 MHz respectively. Samples were loaded into a zirconium oxide 4 mm rotor which was spun at 14 kHz. TMS (0 ppm), H_3BO_3 (19.8 ppm relative to $BF_3 \cdot Et_2O$), and solid NH_4Cl at 2.5kHz spun rate (39.3 ppm relative to liquid NH_3) were used as external references for ^{1}H, ^{11}B, ^{13}C and ^{15}N respectively. Single pulse NMR spectra for ^{1}H, ^{11}B and ^{13}C respectively were acquired with 8, 8192 and 2048 scans; 3 μs, 1.5 μs and 3.2 μs pulse length; 5 s, 0.2 s and 10 s relaxation delay. $\{^{1}H\}^{13}C$ and $\{^{1}H\}^{15}N$ CP/MAS NMR spectra respectively were acquired with 8192 and 32768 scans; 0.65 ms and 10 ms contact time; 5 s and 10 s relaxation delay. HRMS experiments were performed on a mass-spectrometer with electrospray ionization and a time-of-flight (TOF) detector. Peaks in FT-IR spectra data are reported in cm^{-1} with the following relative intensities: s (strong), m (medium), w (weak), br (broad), sh (shoulder). Concentrations c in the optical rotation data are given in g/100 mL; $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. UV–Vis absorption and fluorescence spectra were measured in a 1 cm cell for 5×10^{-5} mol mL^{-1} solutions in MeOH at room temperature. Sorption/desorption isotherms of nitrogen in BET measurements were measured at -196°C (77K). Micropore volumes (V_{micro}) were determined using *t*-plot

method. The total sorbed volumes (V_{tot}), including adsorption in the micropores and mesopores and on the external surface, were calculated from the amount of nitrogen adsorbed at relative pressure p/p_0 of 0.95, before the onset of interparticle condensation.

Field-emission scanning electron microscopy (FE-SEM) experiment was performed on Hitachi SU8000. Target-oriented approach was utilized for the optimization of the analytic measurements.[28] Before measurements the samples were mounted on a 25 mm aluminum specimen stub and fixed by conductive graphite adhesive tape. Metal coating with a thin film (7 nm) of gold/palladium alloy (60/40) was performed using magnetron sputtering method as described earlier.[29] Images were acquired in secondary electron mode at 2 kV accelerating voltage and at working distance 8-10 mm. Morphology of the samples was studied taking into account possible influence of metal coating on the surface.[29] TGA and DSC were measured in flowing nitrogen with heating rate of 10 ^{o}C/min. X-ray diffraction analysis was carried out using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans) at 120 K. The structure was solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. The H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation in riding model. Quantum-chemical calculations were performed with the Gaussian 16 program. Analysis of vibrational frequencies was performed for all optimized structures. All compounds were characterized by only real vibrational frequencies.

TAAD salts **[N-Bn-TAAD]$^+$Br$^-$**,[13a] **[N-Bn-TAAD]$^+$Cl$^-$**,[13c] **[N-Me-TAAD]$^+$I$^-$**,[13b] and **6**[13c] were prepared according to previously described protocols. All reagents were commercial grade and used as received (if not stated otherwise).

Synthesis of TRISOXH$_3$. Water (3.28 mL) and NH_3 solution 25 wt. % in H_2O (3.28 mL) were added to hydroxylamine hydrochloride (^{14}N or ^{15}N) (574 mg, 8.14 mmol). Reaction mixture was stirred until dissolved with cooling in a water bath, then chloroacetone (0.65 ml, 8.14 mmol) was added. Then water bath was removed and reaction mixture was stirred for 1 hour at room

temperature. The formed precipitate was filtered off, washed with water and then with Et_2O and dried in vacuum at 0.1 Torr until constant weight to give 234 mg (yield 37%) of **TRISOXH$_3$** or **^{15}N-TRISOXH$_3$** as a white solid. ^{1}H NMR spectrum of **TRISOXH$_3$** is in agreement with literature data.[13a] *100 Grams scale synthesis:* To a solution of hydroxylamine hydrochloride (435 g, 6.3 mol) in water (5 L) was added ammonia aqueous solution (25 wt. %, 2 L, 26.7 mol) through a dropping funnel with vigorous stirring within 20 minutes. Reaction mixture was stirred until dissolved with ice-bath cooling, and then chloroacetone (500 ml, 6.3 mmol) was added through a dropping funnel within ca. 10 minutes (temperature of the reaction mixture must not exceed 45^{o}C). After addition was complete, the reaction mixture was stirred for 1 hour. The formed precipitate was filtered off and washed with 3 L of water and dried on air until constant weight to give 147 g (yield 30%) of **TRISOXH$_3$**.

Synthesis of ^{15}N-TAAD. Prepared from **^{15}N-TRISOXH$_3$** according to a previously described method used for the synthesis of **^{14}N-TAAD**.[13a] White solid. ^{1}H NMR spectrum of **^{15}N-TAAD** is in agreement with literature data for of **^{14}N-TAAD**.[13a] ^{15}N NMR: (50.68 MHz): σ = 170.0 (*N*-OH,br). FT-IR (KBr): 3382 (s,br), 3228 (s,br), 2995 (m,br), 2942 (s), 2821 (s,br), 1736 (m), 1578 (m,br), 1452(s, br), 1373 (s), 1322 (s), 1258 (w), 1234 (m), 1191 (s), 1074 (s), 1047 (w), 1011 (s), 975 (w), 960 (w), 934 (w), 891 (w), 848 (w), 818 (s), 735 (s,br), 712 (w), 658 (w), 641 (w), 611(w), 586 (w,sh), 520 (m), 511 (m), 475 (m), 456 (w), 440 (w), 409 (w). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_9H_{19}{}^{14}N^{15}N_3O_3]^+$ 234.1363; Found 234.1366; $[M+Na]^+$ Calcd for $[C_9H_{18}{}^{14}N^{15}N_3O_3Na]^+$ 256.1182; Found 256.1170.

Synthesis of (*N*-(*p*-CH$_3$O$_2$C-Bn)-TAAD. To a mixture of methyl 4-(bromomethyl)benzoate (115 mg, 0.50 mmol) and **TRISOXH$_3$** (115 mg, 0.50 mmol) was added 1 ml of methanol. The reaction mixture was stirred for 91 hours at room temperature and then 5 hours at 40^{o}C. The resulting solution was evaporated and the residue was dried in vacuum at 0.1 Torr until constant weight to give 249 mg (yield 99%) of ***N*-(*p*-CH$_3$O$_2$C-Bn)-TAAD** as a white solid. Mp = 231-235 ^{o}C (with dec.). ^{1}H NMR (300 MHz, HSQC, DMSO-d$_6$): σ = 1.23 (s, 9 H, 3 C*H*$_3$), 3.42 (s, br,

6 H, 3 CH_2), 3.87 (s, 3 H, CO_2CH_3), 4.77 (s, 2 H, $CH_2C_6H_4$), 7.77 (d, J = 8.1 Hz, 2 H, 2 CH_{Ar}), 8.05 (d, J = 8.0 Hz, 2 H, 2 CH_{Ar}), 8.30-8.90 (br, 3 H, 3 O*H*). ^{13}C NMR (75 MHz, JMOD, DEPT135, HSQC, DMSO-d_6): σ = 20.6 (CH_3), 52.4 (CH_3CO_2), 54-57 (CH_2, br), 66.6 ($CH_2C_6H_4$), 75.6 (*C,* br), 129.6 (2 CH_{Ar}), 130.9 (C_{Ar}), 131.4 (C_{Ar}), 133.7 (2 CH_{Ar}), 165.7 (CO_2Me). ^{13}C NMR (75 MHz, DEPT135, HSQC, HMBC, DMSO-d_6, 363K): σ = 20.1 (CH_3), 51.8 (CH_3CO_2), 54.2 (CH_2), 66.8 ($CH_2C_6H_4$), 75.2 (*C*), 129.1 (2 CH_{Ar}), 130.4 (C_{Ar}), 131.3 (C_{Ar}), 133.1 (2 CH_{Ar}), 165.2 (CO_2Me). FT-IR (KBr): 3484 (m,br), 3278 (s,br), 3039 (w), 2996 (m), 2971 (w), 2953 (m), 2908 (w), 2828 (w), 2757 (w), 1961(w), 1838(w), 1724(s), 1679 (w), 1656(w), 1615(w), 1578 (w), 1512 (w), 1479 (m), 1446 (s), 1409 (s), 1372 (s), 1338 (w), 1320 (m), 1285 (s,sh), 1229 (w), 1194 (s), 1117 (s), 1051 (w), 1025 (s), 1003 (s,sh), 954 (m), 934 (m), 871 (m), 846 (w), 831 (w), 811 (w), 794 (w), 770 (m), 749 (w), 709 (m), 670(w), 607 (m,br), 585 (m), 528(m), 466 (m,br), 430 (w), 413 (w). ESI-HRMS m/z: $[M-Br]^+$ Calcd for $[C_{18}H_{27}N_4O_5]^+$ 379.1976; Found 379.1975. Anal. Calcd for $C_{18}H_{27}BrN_4O_5$•MeOH: C, 46.44; H, 6.36; N, 11.40. Found: C, 46.06; H, 6.20; N, 11.42.

^{15}*N*-(*p*-CH_3O_2C-Bn)-TAAD was prepared according to the procedure described above from 39 mg (0.1717 mmol) of methyl 4-(bromomethyl)benzoate, 115 mg (0.5 mmol) of **^{15}N TRISOXH_3** in MeOH (0.4 ml). 78 mg (Yield 99%). FT-IR (KBr): 3279 (s,br), 2996 (m,sh), 2952 (s,sh), 1725 (s), 1639 (w), 1616 (w), 1578 (w), 1479 (m), 1440 (s), 1408 (m), 1372 (s), 1320 (m), 1285 (s,sh), 1193 (s), 1114 (s), 1052 (s), 1025 (m), 1001 (m), 977 (m), 932 (m), 869 (m), 844 (w), 790 (w), 766 (m), 745 (w), 729 (w), 709 (m), 606 (m,sh), 583 (m), 526 (w), 490 (br,w),428 (w). ESI-HRMS m/z: $[M-Br]^+$ Calcd for $[C_{18}H_{27}{}^{14}N^{15}N_3O_5]^+$ 382.1887; Found 382.1884.

Synthesis of Est-B(OH)$_2$. To a stirred solution of estrone (135 mg, 0.5 mmol) in DMF (1.2 mL) was added K_2CO_3 (138 mg, 1.0 mmol) under argon atmosphere. After stirring for 1 hour at room temperature, 3-(bromomethyl)phenylboronic acid (160 mg, 0.75 mmol) was added, and the mixture was heated at 80 ^{o}C for 3.5 hours with stirring. Then, the reaction mixture was concentrated in vacuum, and the residue subjected to a column chromatography on silica gel.

The column was eluated with hexane-AcOEt mixtures (ratio 10 : 1 → 3 : 1) containing ca. 1% of water and AcOH to remove unreacted estrone (50 mg, 37%). Eluation with hexane-AcOEt 1 : 1 mixture provided 83 mg (41%) of target compound as white solid. Mp = 82-84 ^{o}C (AcOEt-CH_3O^tBu). R_f = 0.15 (hexane-AcOEt, 1 : 1). $[\alpha]_D$ = 83.3 (c = 0.75, AcOEt, 22 ^{o}C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.07 (s, 2H), 7.85 (s, 1H), 7.75 and 7.46 (2 d, *J* = 7.2 and 6.8 Hz, 1H and 1H), 7.36 (dd, *J* = 7.2, 6.8 Hz, 1H), 7.19 (d, *J* = 8.9 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 1H), 6.74 (s, 1H), 5.05 (s, 2H), 2.82 (m, 2H), 2.42 (dd, *J* = 18.5, 8.4 Hz, 1H), 2.35, 2.19, 2.11 and 2.01-1.91(4 m, 1H, 1H, 1H and 2H), 1.77 (m, 1H), 1.58 – 1.46 and 1.44 – 1.33 (2 m, 3H and 3H), 0.84 (s, 3H). ^{13}C NMR (75 MHz, DEPT135, DMSO-d_6) δ 219.6 (C), 156.3 (C), 137.4, 136.1 and 131.9 (C), 133.9, 133.4, 129.3, 127.4 and 126.2 (CH), 114.6 (CH), 112.3 (CH), 69.3 (CH_2), 49.6 (CH), 47.3 (CH_2), 43.4 (CH), 37.8 (CH), 35.3 (CH_2), 31.3 (CH_2), 29.1 (CH_2), 26.0 and 25.5 (CH_2), 21.1 (C), 13.5 (CH_3) (C-B not observed). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = -0.5 (br, *W* = 534 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{25}H_{30}BO_4]^+$ 405.2236; Found 405.2235.

Synthesis of Cin-B(OH)$_2$. To cinchonine (73.5 mg 0.25 mmol) and (3-(bromomethyl)phenyl)boronic acid (53.5 mg, 0.25 mmol) solvent mixture consisting of 0.5 ml of DMF, 0.4 ml of EtOH and 0.15 ml of $CHCl_3$ was added. Reaction mixture was stirred for 1 hour at room temperature, then heated in oil bath at 50 °C for 3 hours and after that kept for 12 hours at room temperature. Then, the reaction mixture was heated in oil bath at 90 °C for 1 hour (it is important to monitor temperature at this stage) and was concentrated in vacuum. The residual orange oil was and triturated with Et_2O (2×2 ml) and water (3×1 ml). The resulting beige colored solid was dried in a vacuum (0.1 Torr, 100 °C for 4 h). Yield: 88 mg (69%). Mp = 238-242^{0}C (with dec.). $[\alpha]_D$ = 50.6 (c = 1.00, MeOH, 25 ^{o}C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.02 (d, *J* = 4.4 Hz, 1H), 8.38 (d, *J* = 8.5 Hz, 1H), 8.30 (s, 2H), 8.17 – 8.09, 7.99, 7.91 – 7.69 (m, d, *J* = 6.7 Hz and m, 1H, 1H and 5H), 7.57 (t, *J* = 7.6 Hz, 1H), 6.86 (s, 1H), 6.56 (s, 1H), 6.11 – 5.97 (m, 1H), 5.40-5.15 (m, 2H), 5.14 (d, *J* = 12.1 Hz, 1H), 4.94 (d, *J* = 12.1 Hz, 1H), 4.24 (m, 1H), 3.98 – 3.88 (m, 2H), 3.51 (m, 1H), 2.96 (m, 1H), 2.69 (m, 1H), 2.30 (m, 1H), 1.98 – 1.72 (m, 3H),

1.07 (m, 1H). ^{13}C NMR (75 MHz, JMOD135, DMSO-d_6) δ 150.1 (CH), 147.6 and 145.0 (C), 139.4, 137.1, 135.6 and 135.3 (CH), 129.7, 129.3, 128.0 and 127.1 (CH), 126.9 and 124.3 (C), 123.8 and 120.0 (CH), 117.0 (CH_2), 67.0 and 64.7 (CH), 62.5 (CH_2), 56.0 and 53.7 (CH_2), 36.6 (CH), 26.4 (CH), 22.9 and 20.6 (CH_2) (C-B not observed).^{11}B NMR: (96 MHz, DMSO-d_6): σ = 2.7 (br, W = 1181 Hz). FT-IR: 3384 (s,br), 3228 (s,br), 2956 (s,br), 2375 (w), 2346 (w), 1943 (w), 1870 (w), 1846 (w), 1794 (w), 1751 (w), 1718 (m,sh), 1686 (w), 1638 (m), 1617 (m), 1591 (s), 1572 (m), 1542 (w), 1509 (s), 1438 (s,sh), 1342 (s,sh), 1262 (s), 1208 (s), 1153 (m), 1129 (s), 1090 (s), 1064 (s), 1033 (s), 1001 (s), 934 (s), 871 (s), 798 (s), 776 (s), 764 (s), 720 (s), 669 (w), 634 (m), 615 (w), 553 (s,sh), 492 (w), 459 (m), 444 (w), 423 (m). ESI-HRMS m/z: $[M\text{-}Br]^+$ Calcd for $[C_{26}H_{30}BN_2O_3]^+$ 429.2349; Found 429.2352.

Synthesis of adduct 1a from [*N*-Bn-TAAD]$^+$Cl$^-$. To a stirred solution of phenylboronic acid (61 mg, 0.5 mmol) in 3.8 mL of CH_3OH was added **[*N*-Bn-TAAD]$^+$Cl$^-$** (178 mg, 0.5 mmol). After 24 h at room temperature, Na_2CO_3 (26.5 mg, 0.25 mmol) was added and the mixture was kept for additional 24 h with occasional shaking. The reaction mixture was evaporated in vacuum and the product was separated from sodium chloride by extraction with EtOAc/EtOH (1 : 1) mixture. Combined extracts were evaporated in vacuum, the residue was triturated with AcOEt/CH_3OH (1 : 10) mixture and dried in vacuum (0.1 Torr and 100 ^{o}C) until constant weight to give 160 mg (79%) of adduct **1a** as a white solid. Mp above 260 °C. ^{1}H NMR (300 MHz, HSQC, DMSO-d_6): σ = 1.54 (s, 9 H, 3CH_3), 3.47 (s, 6 H, 3CH_2), 4.62 (s, 2 H, C$H_2C_6H_5$), 7.03 (m, 3 H, *m*- and *p*-C_6H_5), 7.31 (d, J = 6.8 Hz, 2 H, *o*- C_6H_5), 7.48–7.57 (m, 5 H, $CH_2C_6H_5$). ^{13}C NMR (75 MHz, HSQC DMSO-d_6): σ = 21.5 (CH_3), 63.4 (CH_2), 65.7 ($C_6H_5CH_2$) 71.8 (*C*), 125.4, 126.0 and 131.1 (*o*, *m*, *p*-C_6H_5), 126.2 (*i*-$C_6H_5CH_2$), 129.0, 130.4 and 132.9 (*o*, *m*, *p*-$C_6H_5CH_2$) (*C*-B not observed). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = 2.0 (br, W = 960 Hz). FT-IR (KBr): 3432 (s,br), 3067 (w,sh), 3042 (w), 2993 (w) 2946 (w), 1654 (m,sh), 1497 (w), 1483 (w), 1458 (w), 1433 (w), 1416 (w), 1369 (s), 1322 (w), 1258 (s), 1226 (s), 1202 (m), 1057 (m), 1038 (w), 1005 (s,sh), 976 (m), 940 (m), 925 (m,sh), 886 (s), 869 (w), 827 (w), 772 (s), 743 (s), 702 (s),

669 (m), 647 (m), 612 (m), 567 (s), 512 (m), 458 (w), 433 (m). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{22}H_{28}BN_4O_3]^+$ 407.2253; Found 407.2255. Anal. Calcd for $C_{22}H_{27}BN_4O_3$: C, 65.04; H, 6.70; N, 13.79. Found: C, 64.96; H, 6.61; N, 13.87. For X-Ray diffraction analysis the sample was crystallized from MeOH:H_2O (1:1) to give single crystals of **1a**•$4H_2O$ (CCDC 1048294).

Hydrolysis of adduct 1a (procedure for Figure 1). To a solution of **1a** (10 mg, 0.025 mmol) in D_2O (0.5 mL) a *reagent* (acid or base, see Supporting information, 0.05 mmol) was added and reaction mixture was stirred at room temperature for 5 hours. Then, the solution was transferred into NMR tube and ^1H NMR spectrum was recorded and concentrations of **1a** and ***N*-Bn-TAAD** were measured. For measurements of pH values same experiments were conducted in H_2O instead of D_2O (for primary data see Supporting information).

Exchange of boronic acid residues in diamantanes 1. To a solution of (4-bromophenyl)boronic acid (5 mg, 0.025 mmol) and diamantane **1a** (10 mg, 0.025 mmol) in CD_3OD-D_2O mixture (0.25 mL/0.25 mL) was added *reagent* (acid or base, see Supporting information, 0.05 mmol). The reaction mixture was stirred at room temperature for 2 hours, then transferred into NMR tube and ^1H NMR spectrum was recorded. The amount of $PhB(OH)_2$ and ***N*-Bn-TAAD** salt was measured. For measurements of pH values same experiments were conducted in CH_3OH-H_2O instead of D_2O (for primary data see Supporting information).

Kinetics of boronic acid residue exchange. A mixture of (4-bromophenyl)boronic acid (5 mg, 0.025 mmol) and diamantane **1a** (10 mg, 0.025 mmol) was dissolved in CD_3OD-D_2O (0.25 mL/0.25 mL) and kept for 96 hours at room temperature. ^1H NMR revealed that almost no exchange of boronic acid residues took place (less than 5 % of $PhB(OH)_2$). Then, AcOH solution in D_2O (25 μL, prepared by mixing 5.6 μL of AcOH in 50 μL D_2O) was added and ^1H NMR spectra were recorded with 10-20 minutes intervals (for primary data see Supporting information).

Cleavage of diamantane 1a with $B(OH)_3$. $B(OH)_3$ (2.5 mmol, 155 mg) and AcOH (29 μL, 0.5 mmol) were added to a solution of **1a** (100 mg, 0.25 mmol) in 10 ml of H_2O. Continuous liquid-

liquid extraction with hot $CHCl_3$ (30 ml) was performed for 5 hours. Then organic layer was collected and concentrated in vacuum. The residue was dried in vacuum until constant weight to give 27 mg (90%) of $PhB(OH)_2$ as a white solid.

General procedure for three-component coupling of boronic acids, alkylating agents R^2LG and TRISOXH$_3$ to give adducts 1. To boronic acid (0.5 mmol) and **TRISOXH$_3$** (115 mg, 0.5 mmol) were added methanol (1 mL) and alkylating agent R^2LG (0.5 mmol if not stated otherwise) and the mixture was stirred for 20 hours at rt. Base (0.25 mmol) was added, and stirring was continued for additional 4 hours. Then, the reaction mixture was concentrated in vacuum and triturated with acetone (if not stated otherwise) to remove inorganic salts. Crude product was dried in a vacuum at 0.1 Torr until constant weight.

Derivative 1a. Prepared according to general procedure from 61 mg (0.5 mmol) of phenylboronic acid, 115 mg (0.5 mmol) of **TRISOXH$_3$** and 58 µl (0.5 mmol) of benzyl bromide in MeOH (1 ml). Li_2CO_3 (18.5 mg, 0.25 mmol) was used as a base. 191 mg (yield 94%). Yield of **1a** prepared from benzyl chloride: 71%; from benzyl tosylate: 64%. **^{15}N-1a** was prepared according to general procedure from **^{15}N-TRISOXH$_3$** and benzyl bromide. FT-IR: 3409 (s,br), 3068 (w,sh), 2985 (w,sh) 2940 (w), 1703 (m), 1653 (m,sh), 1497 (w), 1477 (w), 1458 (w), 1434 (m), 1419 (w), 1372 (s), 1330 (w), 1264 (m,sh), 1226 (s), 1197 (m), 1056 (m), 1036 (w), 1002 (s,sh), 973 (m), 937 (m), 883 (m), 826 (w), 773 (m), 742 (s), 703 (s), 668 (m), 646 (m), 610 (m), 563 (s), 511 (w), 458 (w), 433 (m). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{22}H_{28}B^{14}N^{15}N_3O_3]^+$ 410.2165; Found 410.2170; $[M+Li]^+$ Calcd for $[C_{22}H_{27}B^{14}N^{15}N_3O_3Li]^+$ 416.2247; Found 416.2255; $[M+Na]^+$ Calcd for $[C_{22}H_{28}B^{14}N^{15}N_3O_3Na]^+$ 432.1985; Found 432.1993.

Derivative 1b. Prepared according to general procedure from 100.5 mg (0.5 mmol) of (4-bromophenyl)boronic acid, 115 mg (0.5 mmol) of **TRISOXH$_3$** and 58 µl (0.5 mmol) of benzyl bromide in MeOH (1 ml). Li_2CO_3 (18.5 mg, 0.25 mmol) was used as a base. 218 mg (yield 90%). White solid. Mp above 260 °C. ^{1}H NMR (300 MHz, DMSO-d_6): σ = 1.52 (s, 9 H), 3.45 (s, 6 H),

4.52 (s, 2 H), 7.23 (m, 4 H), 7.54 (m, 5 H). ^{13}C NMR (75 MHz, JMOD, DMSO-d_6): σ = 21.5 (*C*H_3), 63.4 (*C*H_2), 66.1 (*C*H_2) 71.9 (*C*), 119,1 (*C*), 126.1 (*C*), 128.9 and 132.9 (*C*H), 129.1, 130.5 and 133.4 (*CH*), 139.2 (*C*). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = 2.39 (br, *W* = 288 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{22}H_{27}BBrN_4O_3]^+$ 485.1358; Found 485.1349. $[M+Na]^+$ Calcd for $[C_{22}H_{26}BBrN_4O_3Na]^+$ 507.1177; Found 507.1173. $[M+K]^+$ Calcd for $[C_{22}H_{26}BBrN_4O_3K]^+$ 523.0917; Found 523.0909. Anal. Calcd for $C_{22}H_{26}BBrN_4O_3$: C, 54.46; H, 5.40; N, 11.55. Found: C, 54.42; H, 5.41; N, 11.48.

Derivative 1c. Prepared according to general procedure from 61 mg (0.5 mmol) of phenylboronic acid, 115 mg (0.5 mmol) of **TRISOXH$_3$** and 97.5 mg (0.5 mmol) of 3-(bromomethyl)benzonitrile in MeOH (1 ml). Li_2CO_3 (18.5 mg, 0.25 mmol) was used as a base. 170 mg (yield 77%). White solid. Mp above 260 °C. ^{1}H NMR (300 MHz, DMSO-d_6): σ = 1.54 (s, 9 H), 3.48 (s, 6 H), 4.55 (s, 2 H), 7.04 (m, 3 H), 7.30 (d, *J* = 6.6 Hz, 2 H), 7.72 (dd, *J* = 7.6 Hz, *J* = 7.8 Hz 1 H) 7.85 (d, *J* = 7.8 Hz, 1 H), 8.02 (s, 1H), 8.06 (d, *J* = 7.6 Hz, 1 H). ^{13}C NMR (75 MHz, DEPT 135, DMSO-d_6): σ = 21.9 (*C*H_3), 64.0 (*C*H_2), 65.2 (*C*H_2) 72.4 (*C*), 112.8(*C*), 118.8(*C*), 125.9, 126.5 and 131.6 (*C*H), 128.1 (*C*), 130.7, 134.6, 137.0 and 138,2 (*C*H), (*C*-B not observed). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = 3.69 (br, *W* = 1350 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{23}H_{27}BN_5O_3]^+$ 432.2206; Found 432.2198. Anal. Calcd for $C_{23}H_{26}BN_5O_3 \bullet H_2O$: C, 61.48; H, 6.28; N, 15.59. Found: C, 61.84; H, 6.45; N, 15.16.

Derivative 1d. Prepared according to general procedure from 61 mg (0.5 mmol) of phenylboronic acid, 115 mg (0.5 mmol) of **TRISOXH$_3$** and 114,5 mg (0.5 mmol) of methyl 4-(bromomethyl)benzoate in MeOH (1 ml). Li_2CO_3 (18.5 mg, 0.25 mmol) of was used as a base. 189 mg (yield 84%) White solid. Mp = 231-235 °C (with dec.). ^{1}H NMR (300 MHz, DMSO-d_6): σ = 1.53 (s, 9 H), 3.48 (s, 6 H), 3.89 (s, 3 H), 4.60 (s, 2 H), 7.04 (m, 3 H), 7.28 (d, *J* = 6.0 Hz, 2 H), 7.67 (d, *J* = 7.7 Hz, 2 H), 8.06 (d, *J* = 7.7 Hz, 2 H).^{13}C NMR (75 MHz, DEPT 135, DMSO-d_6): σ = 21.5 (*C*H_3), 52.4 (*C*H_3), 63.6 (*C*H_2), 65.2 (*C*H_2) 71.9 (*C*), 125.4, 126.1 and 131.2 (*C*H), 129.6, 133.4 (*C*H), 131,0 (*C*), 131,3 (*C*),148.2 (*C*), 165.7 (*C*). ^{11}B NMR: (96 MHz, DMSO-d_6): σ

= 2.03 (br, *W* = 1178 Hz). FT-IR (KBr): 3417 (m,br), 3005 (m,sh), 2941 (m), 1722 (s), 1639 (w), 1616 (w), 1578 (w), 1510 (w), 1476 (m), 1436 (s), 1421 (w), 1368 (s), 1319 (m), 1287 (s), 1256 (s), 1223 (s), 1188 (s), 1114 (s), 1058 (m), 1037 (w), 1005 (s), 994 (s), 978 (m), 944 (s), 890 (s), 871(m), 843 (w), 814 (w) , 775 (m), 762 (m), 745 (s), 728 (w), 702 (s), 665 (w), 646 (w), 581 (m), 564 (m), 529 (br,s), 486 (br,s),421 (m). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{24}H_{30}BN_4O_5]^+$ 465.2308; Found 465.2300. $[M+Na]^+$ Calcd for $[C_{24}H_{29}BN_4O_5Na]^+$ 487.2127; Found 487.2123 Anal. Calcd for $C_{24}H_{29}BN_4O_5 \bullet 2H_2O$: C, 57.61; H, 6.65; N, 11.20. Found: C, 57.35; H, 6.13; N, 10.78.

Derivative 1e. Prepared according to general procedure from 61 mg (0.5 mmol) of phenylboronic acid, 115 mg (0.5 mmol) of **TRISOXH$_3$** and 177 mg (0.6 mmol) of 2-bromo-1-(bromomethyl)-4-nitrobenzene in MeOH (1 ml). Li_2CO_3 (18.5 mg, 0.25 mmol) was used as a base. Reaction mixture was triturated with Et_2O:EtOH (10:1) to remove LiBr. 269 mg (Yield 99%). White solid. Mp = 221-223 °C (with dec.). ^{1}H NMR (300 MHz, DMSO-d_6): σ = 1.56 (s, 9 H), 3.65 (s, 6 H), 4.79 (s, 2 H), 7.05 (m, 3 H), 7.29 (d, *J* = 6.4 Hz, 2 H), 7.95 (d, *J* = 8.4 Hz, 1 H), 8.32 (d, *J* = 8.3 Hz, 1 H), 8.55 (s, 1 H). ^{13}C NMR (75 MHz, DEPT 135, DMSO-d_6): σ = 21.5 (*C*H$_3$), 64.15(*C*H$_2$), 64.32 (*C*H$_2$) 72.0 (*C*), 122.9 (*C*H), 125.4, 126.0 and 131.2 (*C*H), 127,4 (*C*), 128.5 (*C*H), 133.1 (*C*) 136.9 (*C*H), 149.1 (*C*).^{11}B NMR: (96 MHz, DMSO-d_6): σ = 2.34 (br, *W* = 709 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{22}H_{26}BBrN_5O_5]^+$ 530.1209; Found 530.1205. $[M+Na]^+$ Calcd for $[C_{22}H_{25}BBrN_5O_5Na]^+$ 552.1028; Found 552.1029. Anal. Calcd for $C_{22}H_{25}BBrN_5O_5 \bullet 0.5H_2O$: C, 49.01; H, 4.86; N, 12.99. Found: C, 49.02; H, 4.98; N, 12.95.

Derivative 1f. Prepared according to general procedure from 122 mg (1.0 mmol) of phenylboronic acid, 230 mg (1.0 mmol) of **TRISOXH$_3$** and 63 µl (1.0 mmol) of CH_3I in MeOH (2 ml). Na_2CO_3 (53 mg, 0.5 mmol) of was used as a base. 287 mg (Yield 83%). White solid. Mp = 232-240^{0}C (with dec.). ^{1}H NMR (300 MHz, DMSO-d_6): σ = 1.55 (s, 9 H), 3.00 (s, 3 H), 3.53 (s, 6 H), 7.06 (m, 3 H), 7.31 (d, *J* = 6.0 Hz, 2 H).^{13}C NMR (75 MHz, JMOD, DMSO-d6): σ = 21.4 (*C*H$_3$), 50.6 (*C*H$_3$), 65.8 (*C*H$_2$), 71.9 (*C*), 125.4, 126.0 and 131.2 (*C*H), (*C*-B not

observed).[11]B NMR: (96 MHz, DMSO-d_6): σ = 2.15 (br, *W* = 455 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{16}H_{24}BN_4O_3]^+$ 331.1939; Found 331.1940. $[M+Na]^+$ Calcd for $[C_{16}H_{23}BN_4O_3Na]^+$ 353.1758; Found 353.1761. Anal. Calcd for $C_{16}H_{23}BN_4O_3 \bullet H_2O$: C, 55.19; H, 7.24; N, 16.09. Found: C, 54.96; H, 6.86; N, 15.64.

Derivative 1g. *n*-BuI (56 µl, 1.5 mmol) was added to a mixture of 61 mg (0.5 mmol) of phenylboronic acid and 115 mg (0.5 mmol) of **TRISOXH$_3$** in MeOH (1 ml). Reaction mixture was stirred for 24 hours and then Na_2CO_3 (26.5 mg, 0.25 mmol) was added. After 48 hours additional 115 µl (1.0 mmol) of *n*-BuI were added to ensure full conversion. The mixture was stirred for additional 24 hours, concentrated in vacuum and triturated with acetone to remove LiBr. Crude product was dried in vacuum at 0.1 Torr until constant weight. 176 mg (Yield 90%). White solid. Mp above 260 °C. ^{1}H NMR (300 MHz, DMSO-d_6): σ = 0.91 (t, *J* = 7.2 Hz 3 H), 1.26-1.32 (m, 2 H), 1.58 (s, 9 H), 1.63 (m, 2 H), 3.17-3.27 (br, 2 H), 3.48 (s, 6 H), 7.05 (m, 3 H), 7.32 (d, *J* = 6.4 Hz, 2 H).[13]C NMR (75 MHz, JMOD, DMSO-d_6): σ = 13.3 (*C*H$_3$), 19.1 (*C*H$_2$) 21.4 (*C*H$_3$), 22.2 (*C*H$_2$), 62.8 (*C*H$_2$), 63.7 (*C*H$_2$), 71.9 (*C*), 125.3, 126.0 and 131.2 (*C*H), (*C*-B not observed). [11]B NMR: (96 MHz, DMSO-d_6): σ = 2.60 (br, *W* = 381 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{19}H_{30}BN_4O_3]^+$ 373.2409; Found 373.2406. $[M+Na]^+$ Calcd for $[C_{19}H_{29}BN_4O_3Na]^+$ 395.2228; Found 395.2225. Anal. Calcd for $C_{19}H_{29}BN_4O_3 \bullet H_2O$: C, 58.47; H, 8.01; N, 14.36. Found: C, 58.77; H, 7.68; N, 14.35.

Derivative 1h. Prepared according to general procedure from 61 mg (0.5 mmol) of phenylboronic acid, 115 mg (0.5 mmol) of **TRISOXH$_3$** and 56 µl (0.5 mmol) of ethyl 2-bromoacetate in EtOH (1 ml). Li_2CO_3 (18.5 mg, 0.25 mmol) was used as a base. Reaction mixture was triturated with Et_2O:MeOH (10:1) to remove LiBr. 228 mg (yield 98%). White solid. Mp = 196 °C (with dec.). ^{1}H NMR (300 MHz, DMSO-d_6): σ = 1.21 (t, *J* = 6.8 Hz, 3 H), 1.53 (s, 9 H), 3.73 (s, 6 H), 4.19 (br, 2 H), 4.54 (s, 2 H), 7.06 (m, 3 H), 7.29 (d, *J* = 6.1 Hz, 2 H). ^{13}C NMR (75 MHz, JMOD, DMSO-d_6): σ = 13.7 (*C*H$_3$), 21.5 (*C*H$_3$), 59.8 (*C*H$_2$), 62.1 (*C*H$_2$), 64.3 (*C*H$_2$) 71.9 (*C*), 125.5, 126.1 and 131.1 (*C*H), 127.2 (C), 164.1 (*C*), (*C*-B not observed). [11]B

NMR: (96 MHz, DMSO-d_6): σ = 2.2 (br, *W* = 857 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{19}H_{28}BN_4O_5]^+$ 403.2151; Found 403.2140, $[M+Na]^+$ Calcd for $[C_{19}H_{27}BN_4O_5Na]^+$ 425.1970; Found 425.1959, $[M-H]^-$ Calcd for $[C_{19}H_{26}BN_4O_5]^-$ 401.2006; Found 401.1997. Anal. Calcd for $C_{19}H_{27}BN_4O_5 \bullet 3.5H_2O$: C, 49.04; H, 7.37; N, 12.04. Found: C, 48.60; H, 6.84; N, 11.90.

Derivative 1i. Prepared according to general procedure from 61 mg (0.5 mmol) of phenylboronic acid, 115 mg (0.5 mmol) of **TRISOXH$_3$** and 99 mg (0.5 mmol) of 2-bromoacetophenone in MeOH (1 ml). Li_2CO_3 (18.5 mg, 0.25 mmol) was used as a base. 227 mg (yield 97%). White solid. Mp = 200-204 °C (with dec.) ^{1}H NMR (300 MHz, DMSO-d_6): σ = 1.58 (s, 9 H), 3.84 (s, 6 H), 5.25 (s, 2 H), 7.07 (m, 3 H), 7.31 (d, *J* = 6.6 Hz, 2 H), 7.59 (dd, *J* = 7.3 Hz, *J* = 7.7 Hz, 2 H), 7.74 (t, *J* = 7.3 Hz 1 H), 7.90 (d, *J* = 7.7 Hz, 2 H). ^{13}C NMR (75 MHz, DEPT 135, DMSO-d_6): σ = 21.6 (*C*H$_3$), 64.57 (*C*H$_2$), 64.68 (*C*H$_2$) 72.1 (*C*), 125.5, 126.2 and 131.2 (*C*H), 127.9, 129.1 and 134.9 (*C*H), 134.2 (*C*), 148.1 (*C*), 190.8 (*C*). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = 4.3 (br, *W* = 1314 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{23}H_{28}BN_4O_4]^+$ 435.2202; Found 435.2194, $[M+Na]^+$ Calcd for $[C_{23}H_{27}BN_4O_4Na]^+$ 457.2022; Found 457.2014, $[M+K]^+$ Calcd for $[C_{23}H_{27}BN_4O_4K]^+$ 473.1761; Found 473.1754, $[M-H]^-$ Calcd for $[C_{23}H_{26}BN_4O_4]^-$ 433.2057; Found 433.2048. Anal. Calcd for $C_{23}H_{27}BN_4O_4 \bullet 2H_2O$: C, 58.74; H, 6.64; N, 11.91. Found: C, 58.41; H, 6.05; N, 11.57.

Derivative 1j. Prepared according to general procedure from 61 mg (0.5 mmol) of phenylboronic acid, 115 mg (0.5 mmol) of **TRISOXH$_3$** and 43 µl (0.5 mmol) of allyl bromide in MeOH (1 ml). Li_2CO_3 (18.5 mg, 0.25 mmol) was used as a base. 158 mg (yield 85%). White solid. Mp above 260 °C. ^{1}H NMR (300 MHz, DMSO-d_6): σ = 1.56 (s, 9 H), 3.46 (s, 6 H), 3.91 (d, *J* = 7.0 Hz, 2 H), 5.58 (m, 2 H), 6.01 (m, 1 H), 7.05 (m, 3 H), 7.30 (d, *J* = 5.9 Hz, 2 H).^{13}C NMR (75 MHz, JMOD, D_2O): σ = 21.5 (*C*H$_3$), 63.7 (*C*H$_2$), 66.8 (*C*H$_2$), 72.3 (*C*), 122.2 (*C*H), 127.8, 128.0 and 131.1 (*C*H), 131.2 (*C*H$_2$), (*C*-B not observed).^{11}B NMR: (96 MHz, DMSO-d_6): σ = 3.09 (br, *W* =960 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{18}H_{26}BN_4O_3]^+$ 357.2096; Found

357.2095. $[M+Na]^+$ Calcd for $[C_{18}H_{25}BN_4O_3Na]^+$ 379.1911; Found 379.1915. Anal. Calcd for $C_{18}H_{25}BN_4O_3 \bullet H_2O$: C, 57.77; H, 7.27; N, 14.94. Found: C, 57.86; H, 6.98; N, 14.79.

Derivative 1k. Prepared according to general procedure from 61 mg (0.5 mmol) of phenylboronic acid, 115 mg (0.5 mmol) of **TRISOXH$_3$** and 55.5 µl (0.5 mmol) of propargyl bromide in MeOH (1 ml). Li_2CO_3 (18.5 mg, 0.25 mmol) was used as a base. 170 mg (yield 89%). White solid. Mp above 260 °C. ^{1}H NMR (300 MHz, HSQC, DMSO-d$_6$): σ = 1.57 (s, 9 H, 3C*H*$_3$), 3.59 (s, 6 H, 3C*H*$_2$), 4.10 (s, 1 H, C*H*≡C) 4.49 (s, 2 H, C*H*$_2$-C≡CH), 7.05 (m, 3 H, *m*- and *p*-C$_6$*H*$_5$), 7.30 (m, 2 H, *o*-C$_6$*H*$_5$).^{13}C NMR (75 MHz, HSQC, DMSO-d$_6$): σ = 21.4 (*C*H$_3$), 52.5 (*C*H$_2$-C≡CH), 63.6 (*C*H$_2$), 70.7 (*C*H≡C), 71.9 (*C*), 84.2 (CH≡*C*), 125.5, 126.1 and 131.2 (*o*, *m*, *p*-*C*$_6$H$_5$). ^{11}B NMR: (96 MHz, DMSO-d$_6$): σ = 4.06 (br, *W* = 1133 Hz). FT-IR (KBr): 3422 (s,br), 3141 (s), 2993 (w), 2959 (m), 2932 (w), 2123(s), 1624 (w,br), 1476 (s), 1441 (s), 1431 (m), 1407 (m), 1369 (s), 1346 (w), 1334(w), 1319 (w), 1258 (s), 1244 (m), 1222 (s), 1202 (m), 1191 (s), 1063 (s), 1040 (s), 1007 (s), 989 (w), 955 (m), 932 (s), 895 (s), 864 (m), 821 (w,br), 748 (s), 730 (w), 710 (m), 666 (m), 650 (m), 597 (m), 563 (m), 538 (w), 486 (w), 420 (m). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{18}H_{24}BN_4O_3]^+$ 355.1939; Found 355.1937. $[M+Na]^+$ Calcd for $[C_{18}H_{23}BN_4O_3Na]^+$ 377.1759; Found 377.1759. $[M+K]^+$ Calcd for $[C_{18}H_{23}BN_4O_3K]^+$ 393.1498; Found 393.1502. Anal. Calcd for $C_{18}H_{23}BN_4O_3 \bullet 1.5H_2O$: C, 56.71; H, 6.87; N, 14.36. Found: C, 56.87; H, 6.49; N, 14.36.

Derivative 1l. Prepared according to general procedure from 61 mg (0.5 mmol) of phenylboronic acid, 115 mg (0.5 mmol) of **TRISOXH$_3$** and 110 mg (0.5 mmol) of 2-(bromomethyl)naphthalene in MeOH (1 mL). Li_2CO_3 (18.5 mg, 0.25 mmol) was used as a base. 216 mg (yield 91%). White solid. Mp = 222-226 °C (with dec.). ^{1}H NMR (300 MHz, DMSO-d$_6$): σ = 1.54 (s, 9 H), 3.54 (s, 6 H), 4.69 (s, 2 H), 7.02 (m, 3 H), 7.30 (d, *J* = 6.3 Hz, 2 H), 7.63 (m, 3 H), 8.00-8.12 (m, 4 H). ^{13}C NMR (75 MHz, JMOD, DMSO-d$_6$): σ = 21.5 (*C*H$_3$), 63.6 (*C*H$_2$), 66.2 (*C*H$_2$) 71.9 (*C*), 123.7 (*C*), 126.8 (*C*H), 127.64 (*C*H), 127.66 (*C*H), 128.6 (*C*H), 128.7 (*C*H), 129.3 (*C*H), 132.5 (*C*), 133.3 (*C*H), 133.4 (*C*), 125.4, 126.0 and 131.2 (*C*H), (*C*-B

not observed). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = 2.69 (br, *W* = 864 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{26}H_{30}BN_4O_3]^+$ 457.2410; Found 457.2409. $[M+Na]^+$ Calcd for $[C_{26}H_{29}BN_4O_3Na]^+$ 479.2229; Found 479.2227. $[M+K]^+$ Calcd for $[C_{26}H_{29}BN_4O_3K]^+$ 495.1969; Found 495.1966.Anal. Calcd for $C_{26}H_{29}BN_4O_3 \bullet H_2O$ calcd: C, 65.83; H, 6.59; N, 11.81; Found C, 65.42; H, 6.26; N, 11.87.

Derivative 1m. To phenylboronic acid (61 mg, 0.5 mmol) and **TRISOXH$_3$** (115 mg, 0.5 mmol) was added methanol (1 mL) followed by 5-(chloromethyl)-1H-tetrazole (59 mg, 0.5 mmol) and Li_2CO_3 (37 mg, 0.5 mmol). The reaction mixture was stirred for 24 hours at rt, then concentrated in vacuum and triturated with acetone to remove LiCl. The residue was dried in vacuum at 0.1 Torr until constant weight to give 182 mg (yield 79%) of adduct **1m**. White solid. Decomposition above 245 °C. ^{1}H NMR (300 MHz, DMSO-d_6): σ = 1.51 (s, 9 H), 3.47 (s, 6 H), 4.69 (s, 2 H), 7.02 (m, 3 H), 7.28 (d, *J* = 6.2 Hz, 2 H), (N=NC*H* not observed). ^{13}C NMR (75 MHz, JMOD, DMSO-d_6): σ = 21.9 (*C*H$_3$), 58.0 (*C*H$_2$), 64.1 (*C*H$_2$), 72.2 (*C*), 125.4, 126.0 and 131.2 (*C*H), 151.4 (*C*), (C-B not observed) ^{11}B NMR: (96 MHz, DMSO-d_6): σ = 2.32 (br, *W* =1027 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{17}H_{24}BN_8O_3]^+$ 399.2062; Found 399.2062. $[M+Na]^+$ Calcd for $[C_{17}H_{23}BN_8O_3Na]^+$ 421.1873; Found 421.1881. $[M-H]^-$ Calcd for $[C_{17}H_{22}BN_8O_3]^-$ 397.1906; Found 397.1900. Anal. Calcd for $C_{17}H_{23}BN_8O_3Li \bullet 3H_2O$: C, 44.56; H, 6.16; N, 24.46. Found: C, 44.48; H, 5.73; N, 24.98.

Derivative 1n. Prepared according to general procedure from 52 mg (0.35 mmol) of *trans*-2-phenylvinylboronic acid, 80.5 mg (0.35 mmol) of **TRISOXH$_3$** and 41 µl (0.35 mmol) of benzyl bromide in MeOH (0.7 ml). Li_2CO_3 (13 mg, 0.176 mmol) was used as a base. 133 mg (yield 84%). White solid. Mp above 260 °C. ^{1}H NMR (300 MHz, DMSO-d_6): σ = 1.50 (s, 9 H), 3.42 (s, 6 H), 4.50 (s, 2 H), 5.88 (d, *J* = 18.4 Hz, 1 H), 6.40 (d, *J* = 18.3 Hz, 1 H), 7.11-7.13 (m, 1 H), 7.22-7.30 (m, 4 H), 7.54 (m, 5 H). ^{13}C NMR (75 MHz, JMOD, DMSO-d_6): σ = 21.9 (*C*H$_3$), 63.2 (*C*H$_2$), 66.3 (*C*H$_2$), 72.1 (*C*), 125.6, 126.3 and 128.5 (*C*H), 126.4 (*C*), 129.4, 130.8 and 133.2 (*C*H), 135.0 (*C*H), 140.2 (*C*), (H*C*-B not observed). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = 2.2 (br,

W = 1067 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{24}H_{30}BN_4O_3]^+$ 433.2410; Found 433.2394. $[M+Na]^+$ Calcd for $[C_{24}H_{29}BN_4O_3Na]^+$ 455.2229; Found 455.2210. $[M+K]^+$ Calcd for $[C_{24}H_{29}BN_4O_3K]^+$ 471.1969; Found 471.1956.Anal. Calcd for $C_{24}H_{29}BN_4O_3 \bullet H_2O$ calcd: C, 64.01; H, 6.94; N, 12.44; Found C, 64.07; H, 6.74; N, 12.48.

Derivative 1o. Prepared according to general procedure from 30 mg (0.5 mmol) of methylboronic acid, 115 mg (0.5 mmol) of **TRISOXH$_3$** and 58 μL (0.5 mmol) of benzyl bromide in MeOH (1 mL). Li_2CO_3 (18.5 mg, 0.25 mmol) was used as a base. 185 mg (yield 99%). White solid. Mp =222-228 °C. ^{1}H NMR (300 MHz, DMSO-d_6): σ = - 0.77 (s, 3 H), 1.43 (s, 9 H), 3.39 (s, 6 H), 4.59 (s, 2 H), 7.52–7.55 (m, 5 H). ^{13}C NMR (75 MHz, JMOD, DMSO-d_6): σ = 3.9 (*C*H$_3$), 21.6 (*C*H$_3$), 63.4 (*C*H$_2$), 65.7 (*C*H$_2$) 71.6 (*C*), 126.3 (*C*), 129.1, 130.5 and 133.0 (*C*H). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = 4.0 (br, *W* = 923 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{17}H_{26}BN_4O_3]^+$ 345.2099; Found 345.2096; $[M+H]^+$ Calcd for $[C_{17}H_{25}BN_4O_3Na]^+$ 367.1915; Found 367.1919; $[M-H]^-$ Calcd for $[C_{17}H_{24}BN_4O_3]^-$ 343.1954; Found 343.1954; Anal. Calcd for $C_{17}H_{25}BN_4O_3 \bullet 1.5H_2O$: C, 55.00; H, 7.60; N, 15.09. Found: C, 55.07; H, 7.60; N, 15.10.

Derivative 1p. To 3-pyridinylboronic acid (40 mg, 0.326 mmol) and **TRISOXH$_3$** (75 mg, 0.326 mmol) was added methanol (0.7 ml) followed by benzyl bromide (38 μL, 0.326 mmol). The reaction mixture was stirred for 20 hours and volatiles were removed in vacuum. The residue was dried in vacuum at 0.1 Torr until constant weight to give 165 mg (yield 99%) of adduct **1p** in form of hydrobromide. White solid. Mp =174-176 °C. ^{1}H NMR (300 MHz, DMSO-d_6): σ = 1.55 (s, 9 H), 3.58 (s, 6 H), 4.69 (s, 2 H), 7.51–7.58 (m, 5 H), 7.87 (dd, *J* = 5,4, 7.3 Hz, 1 H), 8.38 (d, *J* = 7.3, 1 H), 8.45, (s, 1 H), 8.71 (d, *J* = 5.4 Hz, 1 H). ^{13}C NMR (75 MHz, JMOD, DMSO-d_6): σ = 21.4 (*C*H$_3$), 63.1 (*C*H$_2$), 65.6 (*C*H$_2$) 72.2 (*C*), 126.0 (*C*H), 126.1 (*C*), 129.1, 130.5 and 133.0 (*C*H), 139.2 (*C*H), 142.1 (*C*H), 148.8 (*C*H) (*C*-B not observed). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = 2.1 (br, *W* = 634 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{21}H_{27}BN_5O_3]^+$

408.2188; Found 408.2205. Anal. Calcd for $C_{21}H_{26}BN_5O_3 \bullet HBr \bullet H_2O$: C, 49.83; H, 5.77; N, 13.84. Found: C, 50.19; H, 5.83; N, 13.78.

Derivative 1q. Prepared according to general procedure from 64 mg (0.5 mmol) of 2-thienylboronic acid, 115 mg (0.5 mmol) of **TRISOXH$_3$** and 58 μL (0.5 mmol) of benzyl bromide in MeOH (1 ml). Li_2CO_3 (18.5 mg, 0.25 mmol) was used as a base. 175 mg (yield 77%). White solid. Decomposition above 245 °C without melting. ^{1}H NMR (300 MHz, DMSO-d_6): σ = 1.54 (s, 9 H), 3.46 (s, 6 H), 4.57 (s, 2 H), 6.84 (s, 1H), 6.90 (s, 1H), 7.22 (s, 1H), 7.53–7.55 (m, 5 H). ^{13}C NMR (75 MHz, DEPT 135, DMSO-d_6): σ = 21.5 (*C*H$_3$), 63.3 (*C*H$_2$), 65.8 (*C*H$_2$) 71.9 (*C*), 124.6, 126.2 and 127.3 (*C*H), 126.1 (*C*), 129.1, 130.5 and 132.9 (*C*), 148.9 (br, *C*). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = 2.4 (br, *W* = 332 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{20}H_{26}BN_4O_3S]^+$ 413.1817; Found 413.1813; $[M+Na]^+$ Calcd for $[C_{20}H_{25}BN_4O_3SNa]^+$ 435.1636; Found 435.1632; $[M+K]^+$ Calcd for $[C_{20}H_{25}BN_4O_3SK]^+$ 451.1376; Found 451.1372; Anal. Calcd for $C_{20}H_{25}BN_4O_3S \bullet 2.5H_2O$: C, 52.52; H, 6.61; N, 12.25. Found: C, 52.88; H, 6.28; N, 12.20.

Derivative 1r. Prepared according to general procedure from 26 mg (0.104 mmol) of pyrene-1-boronic acid, 24 mg (0.104 mmol) of **TRISOXH$_3$** and 45 mg (0.104 mmol) of (3β)-21-bromo-20-oxopregna-5,16-dien-3-yl acetate[13c] in MeOH (1 ml). Li_2CO_3 (5 mg, 0.068 mmol) was used as a base. Reaction mixture was evaporated in a vacuum and triturated with H_2O (5ml): THF (50μl) and then with EtOAc (2 ml). Crude product was dried in a vacuum at 0.1 Torr until constant weight. 66 mg (yield 80%). White solid. Mp = 194-196 ºC. ^{1}H NMR (400 MHz, HSQC, DMSO-d_6) δ 9.25 (d, *J* = 9.4 Hz, 1H, HC-26), 8.29 (d, *J* = 7.7 Hz, 1H), 8.17 – 8.12 (m, 2H), 8.10 – 8.01 (m, 3H) and 8.00 – 7.92 (m, 2H) (HC-27, HC-29, HC-30, HC-31, HC-33, HC-34, HC-36 and HC-37), 7.02 (s, 1H, HC-16), 5.37 (d, *J* = 3.9 Hz, 1H, HC-6), 4.90 (d, *J* = 17.4 Hz, 1H, HC-21), 4.75 (d, *J* = 17.4 Hz, 1H, HC-21), 4.54 – 4.39 (br m, 1H, HC-3), 3.85 (s, 6H, 3 H_2C-22), 2.40 – 2.19 (m, 4H, H_2C-4, HC-7 and HC-15), 2.12 (dd, *J* = 16.8, 11.5 Hz, 1H, HC-15), 2.00 (s and m, 4H, H_3C-42 and HC-2), 1.84 (m, 1H, HC-1), 1.79 (m, 1H, HC-12), 1.75 (s, 9H, 3 H_3C-

24), 1.68 – 1.46 (m, 5H, HC-2, HC-8, H_2C-11 and HC-12), 1.41 – 1.22 (m, 2H, HC-7 and HC-14), 1.08 (m, 1H, HC-1), 1.02 (s and m, 4H, H_3C-18 and HC-9), 0.89 (s, 3H, H_3C-19). ^{13}C NMR (101 MHz, HSQC, DMSO-d_6) δ 188.8 (C-20), 169.7 (C-41), 151.7 (C-17), 148.9 (C-16), 139.9 (C-5), 133.6, 130.8, 129.2, 124.9, 124.5 and 123.5 (C-28, C-31, C-35, C-38, C-39 and C-40), 131.0, 127.6, 125.7, 125.0, 124.1 and 123.6 (C-27, C-29, C-30, C-32, C-33, C-34, C-36 and C-37), 130.6 (C-26), 121.6 (C-6), 73.1 (C-3), 72.3 (3 C-23), 64.5 (3 C-22), 63.5 (C-21), 55.3 (C-14), 49.7 (C-9), 46.2 (C-13), 37.7 (C-4), 36.3 (C-1), 36.2 (C-10), 34.0 (C-7), 32.4 (C-15), 30.7 (C-2), 29.5 (C-8), 27.3 (C-12), 22.0 (3 C-24), 21.0 (C-42), 20.1 (C-11), 18.8 (C-19), 15.7 (C-18) (C-B not observed). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = 3.3 (br, W = 1613 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{48}H_{56}BN_4O_6]^+$ 795.4296; Found 795.4280; $[M+Na]^+$ Calcd for $[C_{48}H_{55}BN_4O_6Na]^+$ 817.4115; Found 817.4104.

Derivative 1s. Pyrene-1-boronic acid (36 mg, 0.147 mmol), **TRISOXH$_3$** (34 mg, 0.147 mmol) and LiI (20 mg 0.147 mmol) were added to a solution of 2-{2-[2-(2-chloroacetamido)acetamido]acetamido}acetic acid[30] (39 mg, 0.147 mmol) in MeOH (0.4 ml), and reaction mixture was stirred for 12 h at room temperature. Then, Li_2CO_3 (11 mg, 0.147 mmol) was added and the mixture was stirred for additional 168 h. Volatiles were removed under reduced pressure and the residue was triturated with acetone. Crude product was dried in vacuum at 0.1 Torr until constant weight to give 99 mg (yield 99%) of adduct **1s**. White solid. Mp = 262-266 ºC (with dec.). ^{1}H NMR (300 MHz, HSQC, DMSO-d_6): σ = 1.71 (s, 9 H, 3 CH_3), 3.72 (d, J = 5.3 Hz, 2 H, CH_2), 3.78 (d, J = 5.7 Hz, 2 H, CH_2), 3.87 (br m, 9 H, 3 CH_2-N$^+$, CH_2 and O*H*), 4.33 (s, 2 H, C(O)-H_2C-N$^+$), 7.92-8.15 (br, 8 H, $C_{16}H_9$B and *H*N), 8.27 (d, J = 7.7 Hz, 1 H, $C_{16}H_9$B), 8.47 (br m, 1 H, *H*N), 9.22 (d, J = 9.3 Hz, 1 H, $C_{16}H_9$B), 9.28 (br m, 1 H, *H*N).^{13}C NMR (75 MHz, HSQC, DMSO-d_6): σ = 21.9 (3 CH$_3$), 41.3, 41.9 and 42.1 (3 CH$_2$), 61.8 (C(O)-H$_2$$C$-N$^+$), 64.7 (3 C$H_2$-N$^+$), 72.3 (3 *C*), 123.52, 123.64, 124.15, 124.53, 125.11, 125.39, 125.78, 126.07, 126.13, 127.63, 129.21, 130.63, 130.85, 131.04 and 133.70 (C_{16}H$_9$), 145.1 (*C*-B), 162.9, 168.3 and 168.9 (3 N-*C*=O), 171.3 (*C*OOH). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = -3.5 (br, W =

1964 Hz). UV-Vis spectrum (MeOH, c = 5×10^{-5} M) peaks λ nm: 218 (w), 255 (m), 290 (s), 333 (w). Fluorescence spectrum (MeOH, c = 5×10^{-5} M) peaks λ nm: 376 (m), 393 (s), 576 (w). ESI-HRMS m/z: $[M-H]^-$ Calcd for $[C_{33}H_{35}BN_7O_8]^-$ 668.2651; Found 668.2665.

Derivative 1t. To a mixture of benzene-1,4-diboronic acid (83 mg, 0.5 mmol) and **TRISOXH$_3$** (230 mg, 1.0 mmol) were added methanol (2 mL) and 120 μL (1.0 mmol) of benzyl bromide. Reaction mixture was stirred for 20 hours and Li_2CO_3 (37 mg, 0.5 mmol) was added and the mixture was continued stirring for another 4 hours. Then, volatiles were removed under reduced pressure and the residue was triturated with MeOH : H_2O (1:1) mixture. The residue was dried in vacuum at 0.1 Torr until constant weight to give 346 mg (yield 87%) of adduct **1t**. White solid. Mp = 250-254 °C. ^{1}H NMR (300 MHz, D_2O): σ = 1.73 (s, 18 H), 3.70 (s, 12 H), 4.60 (s, 4 H), 7.39 (s, 4 H), 7.58-7.63 (br, m, 10 H). ^{13}C NMR (75 MHz, JMOD, D_2O): σ = 20.0 (*C*H$_3$), 62.9 (*C*H$_2$), 68.1 (*C*H$_2$) 72.4 (*C*), 124.3 (*C*), 129.0, 129.6 and 132.4 (*C*H), 130.9 (*C*H), (*C*-B not observed). ^{11}B NMR: (96 MHz, D_2O): σ = -3.5 (br, *W* = 1987 Hz). FT-IR (KBr): 3423 (s,br), 3006 (m,br), 2985 (m), 2942 (m), 1686 (w), 1654 (m), 1638 (s), 1561 (w), 1543 (w), 1523 (w), 1509 (w), 1498 (w), 1477 (s), 1458 (m,br), 1412 (m), 1373 (s), 1322 (m), 1263 (s), 1234 (s), 1201 (s), 1058 (s), 1034 (m), 995 (m), 978 (s), 933 (s), 918 (s), 863 (m), 821 (s), 762 (s), 713 (m), 699 (m), 669 (m), 615 (m), 564 (s), 519 (m), 420 (m). ESI-HRMS m/z: $[M+2H]^{2+}$ Calcd for $[C_{38}H_{50}B_2N_8O_6]^{2+}$ 368.2021; Found 368.2035; Anal. Calcd for $C_{38}H_{48}B_2N_8O_6\bullet3.5H_2O$: C, 57.23; H, 6.95; N, 14.05. Found: C, 57.06; H, 6.53; N, 14.35.

Derivative 1u. To phenylboronic acid (110 mg, 0.9 mmol) and **TRISOXH$_3$** (207 mg, 0.9 mmol) was added a solution of 1,4-bis(bromomethyl)benzene (88 mg, 0.3 mmol) in methanol (4 ml) and the resulting mixture was stirred for 48 hours at room temperature. Then, Li_2CO_3 (34 mg, 0.46 mmol) was added and the reaction mixture was continued stirring for another 24 h. Volatiles were removed under reduced pressure and the residue was triturated with water. The residue was dried in vacuum at 0.1 Torr until constant weight to give 194 mg (yield 82%) of adduct **1u**. White solid. Mp above 260 °C. ^{1}H NMR (300 MHz, D_2O): σ = 1.76 (s, 18 H), 3.76 (s, 12 H),

4.70 (br, 4 H), 7.35 (m, 6 H), 7.48 (m, 4 H), 7.76 (m, 4 H). ^{13}C NMR (75 MHz, JMOD, D_2O): σ = 19.9 (*C*H_3), 62.9 (*C*H_2), 67.0 (*C*H_2) 72.4 (*C*), 127.2, 127.4 and 133.5 (*C*H), 127.5 (*C*), 130.4 (*C*H) (*C*-B not observed). ^{11}B NMR: (96 MHz, D_2O): σ = -7.7 (br, *W* = 1872 Hz). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{38}H_{49}B_2N_8O_6]^+$ 735.3968; Found 735.3969; $[M+Na]^+$ Calcd for $[C_{38}H_{48}B_2N_8O_6Na]^+$ 757.3788; Found 757.3782, $[M+K]^+$ Calcd for $[C_{38}H_{48}B_2N_8O_6K]^+$ 773.3527; Found 773.3540. Anal. Calcd for $C_{38}H_{48}B_2N_8O_6 \bullet 3H_2O$: C, 57.88; H, 6.90; N, 14.21. Found: C, 58.00; H, 6.68; N, 14.07.

Derivative 2a. To a mixture of phenylboronic acid (55mg, 0.45 mmol) and **TRISOXH$_3$** (104 mg, 0.45 mmol) were added methanol (3 ml) and 1,3,5-tris(bromomethyl)benzene (54 mg, 0.15 mmol). The resulting mixture was stirred for 44 hours at room temperature. Then, Li_2CO_3 (17 mg, 0.23 mmol) was added and stirring was continued for another 4 hours. Then, volatiles were removed under reduced pressure, and the residue was triturated with acetone and then with acetone containing a few drops of water. The resulting solid was dried in vacuum at 0.1 Torr until constant weight to give 152 mg (yield 95%) of adduct **2a**. White solid. Mp = 252-256 °C (with dec.). ^{1}H NMR (300 MHz, DMSO-d_6): σ = 1.58 (s, 27 H), 3.57 (s, 18 H), 4.64 (s, 6 H), 7.05 (m, 9 H), 7.29 (d, *J* = 7.0 Hz, 6 H), 7.79 (s, 3 H). ^{13}C NMR (75 MHz, JMOD, DMSO-d_6): σ = 21.9 (*C*H_3), 63.8 (*C*H_2), 65.3 (*C*H_2) 72.3 (*C*), 125.8, 126.4 and 131.5 (*C*H), 128.4 (*C*), 139.5 (*C*H), (*C*-B not observed). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = 0.2 (br, *W* = 1661 Hz). ESI-HRMS m/z: $[M+Li]^+$ Calcd for $[C_{54}H_{69}B_3N_{12}O_9Li]^+$ 1069.5769; Found 1069.5770.

Derivative 2b. To a mixture of (4-bromophenyl)boronic acid (100.5 mg, 0.5 mmol) and **TRISOXH$_3$** (115 mg, 0.5 mmol) were added 1,3,5-tris(bromomethyl)benzene (60 mg, 0.17 mmol) and methanol (3.3 ml). The resulting mixture was stirred for 48 hours at room temperature. Then, Li_2CO_3 (19 mg, 0.26 mmol) was added and stirring was continued for another 5 hours. Then, reaction mixture was concentrated under reduced pressure, and the residue was triturated with acetone and then with acetone containing a few drops of water. Crude product was dried in vacuum at 0.1 Torr until constant weight to give 155 mg (yield 71%) of

adduct **2b**. White solid. Mp = 233-237 °C (with dec.) ^{1}H NMR (300 MHz, DMSO-d_6): σ = 1.55 (s, 27 H), 3.59 (s, 18 H), 4.71 (s, 6 H), 7.24 (m, 12 H), 7.87 (s, 3 H). ^{13}C NMR (75 MHz, JMOD, DMSO-d_6): σ = 21.6 (*C*H$_3$), 63.4 (*C*H$_2$), 64.8 (*C*H$_2$) 72.0 (*C*), 119,2 (*C*), 129.0 and 133.6 (*C*H), 128.1 (*C*), 139.3 (*C*H), (*C*-B not observed). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = -0.3 (br, *W* = 1417 Hz). ESI-HRMS m/z: $[M+Na]^+$ Calcd for $[C_{54}H_{66}B_3Br_3N_{12}O_9Na]^+$ 1319.2799; Found 1319.2806.

Derivative 2c. To a mixture of ferroceneboronic acid (115 mg, 0.5 mmol), **TRISOXH$_3$** (58 mg, 0.25 mmol) and 1,3,5-tris(bromomethyl)benzene (27 mg, 0.075 mmol) was added methanol (3 ml). The reaction mixture was stirred for 36 hours at room temperature. Then, Li_2CO_3 (8.5 mg, 0.115 mmol) was added and stirring was continued for another 8 hours. Volatiles were removed under reduced pressure, and the residue was triturated with EtOAc and then with EtOAc:EtOH (10:1). The resulting solid was dried in vacuum at 0.1 Torr until constant weight to give 100 mg (yield 95%) of adduct **2c**. White solid. Decomposition without melting above 215 °C. ^{1}H NMR (300 MHz, DMSO-d_6): σ = 1.56 (s, 27 H), 3.54 (s, 18 H,), 3.90-4.09 (br, 27 H), 4.67 (s, 6 H), 7.83 (s, 3 H). ^{13}C NMR (75 MHz, JMOD, DMSO-d_6): σ = 21.6 (*C*H$_3$), 63.5 (*C*H$_2$), 65.0 (*C*H$_2$), 68.1, 71.0 and 73.4 (*C*H), 71.8 (*C*), 128.2 (*C*), 139.2 (*C*H), (*C*-B not observed). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = -1.9 (br, *W* = 1571 Hz). ESI-HRMS m/z: $[M]^+$ Calcd for $[C_{66}H_{81}B_3Fe_3N_{12}O_9]^+$ 1386.4604; Found 1386.4631. $[M+H]^+$ Calcd for $[C_{66}H_{82}B_3Fe_3N_{12}O_9]^+$ 1387.4682; Found 1387.4633.

Derivative 2d. To a mixture of pyrene-1-boronic acid (123mg, 0.5 mmol), **TRISOXH$_3$** (58 mg, 0.25 mmol) and 1,3,5-tris(bromomethyl)benzene (27 mg, 0.075 mmol) was added methanol (3 ml). The reaction mixture was stirred for 44 hours at room temperature. Then, Li_2CO_3 (8.4 mg, 0.113 mmol) was added and stirring was continued for another 7 hours. Volatiles were removed under reduced pressure, and the residue was triturated with acetone and then with EtOAc. The resulting solid was dried in vacuum at 0.1 Torr until constant weight to give 108 mg (yield 99%) of adduct **2d**. Beige solid. Mp = 258-262 °C (with dec.). ^{1}H NMR (300 MHz, DMSO-d_6): σ =

1.78 (s, 27 H), 3.74 (s, 18 H), 4.80 (s, 6 H), 7.94-8.13 (br, 21 H and 3 H), 8.29 (d, J = 7.5 Hz, 3 H), 9.24 (d, J = 9.2 Hz, 3 H). ^{13}C NMR (75 MHz, JMOD, DMSO-d_6): σ = 22.0 (CH_3), 63.5 (CH_2), 65.0 (CH_2), 72.2 (*C*), 123.45 (*C*H), 123.58 (*C*H), 123.60 (*C*), 124.14 (*C*H), 124.48 (*C*H), 124.89 (*C*H), 125.04 (*C*H), 125.73 (*C*H), 127.58 (*C*H), 128.19 (*C*), 129.16 (*C*), 130.58 (*CH*), 130.63 (C), 130.80 (*C*), 131.00 (*C*H), 133.66 (*C*), 139.3 (*C*H), (*C*-B not observed). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = 2.50 (br, W = 794 Hz). ESI-HRMS m/z: $[M+Na]^+$ Calcd for $[C_{84}H_{81}B_3N_{12}O_9Na]^+$ 1457.6454; Found 1457.6436. $[M+2Na]^{2+}$ Calcd for $[C_{84}H_{81}B_3N_{12}O_9Na_2]^{2+}$ 740.3173; Found 740.3180.

Derivative 2e. To a stirred solution of 1,3,5-tris(bromomethyl)benzene (12 mg, 0.033 mmol) in 0.6 ml of methanol was added **TRISOXH$_3$** (23 mg, 0.11 mmol) and **Cin-B(OH)$_2$** (56 mg, 0.11 mmol). The reaction mixture was stirred for 26 hours at room temperature. Then, K_2CO_3 (7.6 mg, 0.055 mmol) was added and stirring was continued for another 5 hours. Volatiles were removed under reduced pressure, and the residue was triturated with water (2×2ml). The resulting solid was dried in a vacuum at 0.1 Torr until constant weight to give 72 mg (yield 97%) of adduct **2e**. White solid. Decomposition above 210 °C (without melting). $[\alpha]_D$ = 110.8 (c = 1.00, MeOH, 25 ^{o}C). ^{1}H NMR (300 MHz, COSY, TOCSY, HSQC, DMSO-d_6) δ 9.00 (d, J = 4.5 Hz, 3H, 3 HC-14), 8.35 (d, J = 8.1 Hz, 3H, 3 HC-21), 8.12 (d, J = 8.1 Hz, 3H, 3 HC-18), 7.96 (s, 3H, 3 HC-35), 7.84 (m, 6H, 3 HC-15 and 3 HC-19), 7.78 (dd, J = 7.9, 7.5 Hz, 3H, 3 HC-20), 7.60 (s, 3H, 3 HC-25), 7.50 and 7.41 (2 d, J = 6.6 Hz and J = 7.1 Hz, 3H and 3H, 3 HC-27 and 3 HC-29), 7.33 (dd, J = 7.5, 7.1 Hz, 3H, 3 HC-28), 6.85 (s, 3H, 3 HO-12), 6.54 (s, 3H, 3 HC-9), 6.02 (m, 3H, 3 HC-10), 5.28 – 5.16 (m, 6H, 3 H_2C-11), 5.00 and 4.87 – 4.73 (d, J = 12.2 Hz and m, 3H and 9H, 3 H_2C-23 and 3 H_2C-33), 4.18 (m, 3H, 3 HC-2), 3.93 (m, 6H, 3 HC-6 and 3 HC-8), 3.66 (s, 18H, 9 H_2C-31), 3.49 (m, 3H, 3 HC-2), 2.91 (m, 3H, 3 HC-6), 2.67 (m, 3H, 3 HC-3), 2.29 (m, 3H, 3 HC-7), 1.85 (m, 3H, 3 HC-4), 1.82 – 1.71 (m, 6H, 3 H_2C-5), 1.63 (s, 27H, 9 H_3C-32), 1.03 (m, 3H, 3 HC-7).^{13}C NMR (75 MHz, HSQC, JMOD, DMSO-d_6) δ 150.2 (3 C-14), 147.6 (3 C-22), 145.1 (3 C-16), 139.4 (3 C-35), 137.1 (3 C-10), 136.4 (3 C-25), 133.2 and 131.2

(3 C-27 and 3 C-29), 129.8 (3 C-18), 129.4 (3 C-19), 128.2 and 125.3 (3 C-24 and 3 C-34), 127.2 (3 C-20), 127.0 (3 C-28), 124.3 (3 C-17), 124.0 (3 C-21), 120.1 (3 C-15), 117.0 (3 C-11), 72.1 (9 C-30), 66.7 (3 C-8), 64.7 (3 C-9), 63.4 and 63.1 (3 C-23, 9 C-31 and 3 C-33), 55.8 (3 C-6), 53.3 (3 C-2), 36.6 (3 C-3), 26.4 (3 C-4), 22.9 (3 C-5), 21.7 (9 C-32), 20.6 (3 C-7) (3 C-B (C-26) not observed). ^{11}B NMR (96 MHz, DMSO) δ -0.09 (br, *W* = 1000 Hz).^{14}N NMR (22 MHz, DMSO-d_6) δ 15.1 (3 N-1) (br, *W* = 850 Hz). ESI-HRMS m/z: $[M-2Br]^{2+}$ Calcd for $[C_{114}H_{138}B_3BrN_{18}O_{12}]^{2+}$ 1031.5100; Found 1031.5117; $[M-3Br]^{3+}$ Calcd for $[C_{114}H_{138}B_3N_{18}O_{12}]^{3+}$ 661.3672; Found 661.3692.

Derivative 2f. To a stirred solution of 1,3,5-tris(bromomethyl)benzene (18 mg, 0.052 mmol) in 1 ml of methanol was added **TRISOXH$_3$** (40 mg, 0.173 mmol) and **Est-B(OH)$_2$** (70 mg, 0.173 mmol). The reaction mixture was stirred for 20 hours at room temperature. Then, Li_2CO_3 (6.5 mg, 0.087 mmol) was added and stirring was continued for another 6 hours. Volatiles were removed under reduced pressure, and the residue was triturated with water (2×2ml). Crude product was dried in a vacuum at 0.1 Torr until constant weight to give 80 mg (yield 81%) of adduct **2f**. White solid. Mp =256-258 °C (with dec.). For analytical purposes product was recrystallized from MeOH:Et_2O. $[\alpha]_D$ = 50.6 (c = 1.00, MeOH, 25 ^oC). ^{1}H NMR (300 MHz, COSY, HSQC, DMSO-d_6) δ 7.80 (s, 3H, 3 HC-31), 7.38 (s, 3H, 3 HC-21), 7.27 (m, 3H, 3 HC-24), 7.17 (d, J = 8.5 Hz, 3H, 3 HC-1), 7.13 – 7.08 (m, 6H, 3 HC-23 and 3 HC-25), 6.76 (d, J = 8.1 Hz, 3H, 3 HC-2), 6.72 (s, 3H, 3 HC-4), 4.94 (s, 6H, 3 H_2C-19), 4.64 (s, 6H, 3 H_2C-29), 3.59 (br s, 18H, 9 H_2C-27), 2.81 (m, 6H, 3 H_2C-6), 2.43 (dd, J = 18.4, 6.8 Hz, 3H, 3 HC-16), 2.33 (m, 3H, 3 HC-11), 2.15 (m, 3H, HC-9), 2.05 (m, 3H, 3 HC-16), 2.00 – 1.85 (2 m, 3H and 3H, 3 HC-7 and 3 HC-15), 1.76 (m, 3H, 3 HC-12), 1.60 (s, 27H, 9 H_3C-28), 1.55 – 1.45 (m, 9H, 3 HC-8, 3 HC-14 and 3 HC-15), 1.44 – 1.30 (m, 9H, 3 HC-7, 3 HC-11 and 3 HC-12), 0.84 (s, 9H, 3 H_3C-18).^{13}C NMR (75 MHz, JMOD, HSQC, DMSO-d_6) δ 219.8 (3 C-17), 156.6 (3 C-3), 139.4 (3 C-31), 137.4 (3 C-5), 134.5, 131.7 and 128.2 (3 C-10, 3 C-20 and 3 C-30), 131.0 and 130.9 (3 C-21 and 3 C-24), 129.9, 126.2 and 125.2 (3 C-1, 3 C-23 and 3 C-25), 114.6 (3 C-4), 112.4 (3 C-2),

72.1 (9 C-26), 70.2 (3 C-19), 64.7 (3 C-29), 63.5 (9 C-27), 49.6 (3 C-14), 47.4 (3 C-13), 43.5 (3 C-9), 37.9 (3 C-8), 35.4 (3 C-16), 31.4 (3 C-12), 29.2 (3 C-6), 26.1 (3 C-7), 25.5 (3 C-11), 21.6 (9 C-28), 21.2 (3 C-15), 13.6 (3 C-18) (C-B (3 C-22) not observed).^{11}B NMR: (96 MHz, DMSO-d_6): σ = 3.7 (br, W = 1651 Hz). ESI-HRMS m/z: $[M+2H]^{2+}$ Calcd for $[C_{111}H_{137}B_3N_{12}O_{15}]^{2+}$ 955.5303; Found 955.5276; $[M+2Na]^{2+}$ Calcd for $[C_{111}H_{135}B_3N_{12}O_{15}Na_2]^{2+}$ 977.5122; Found 977.5119.

Derivative 2g. A solution of benzene-1,4-diboronic acid (95 mg, 0.57 mmol) in 5 ml of MeOH was added to a solution of tribromide salt **6** (50 mg, 0.048 mmol) and Li_2CO_3 (5.4 mg, 0.073 mmol) in water (5 ml). The reaction mixture was stirred for 38 hours at room temperature. Then, volatiles were removed under reduced pressure. The residue was dried in vacuum at 0.1 Torr until constant weight (to remove water), then triturated with 8 ml of THF, 8 ml of Et_2O and 8 ml of acetone, and dried again under reduced pressure to give 66 mg of white solid. According to NMR analysis, the latter consisted of 88% mass (58 mg) of **2g** and 12% mass (8 mg) of benzene-1,4-diboronic acid. For analytical purposes, a sample of this mixture was dissolved in water-MeOH mixture (1:1). Upon isothermic evaporation of this solution, crystalline benzene-1,4-diboronic acid precipitated. Mother liquor containing almost pure **2g** was removed from crystals, evaporated and dried in vacuum to give **2g** as white amorphous solid. ^{1}H NMR (300 MHz, D_2O): σ = 1.79 (s, 27 H), 3.84 (18 H), 7.51 (d, *J* = 7.5 Hz, 6H), 7.68 (d, *J* = 7.5 Hz, 6H), 8.03 (s, 3 H). ^{13}C NMR (75 MHz, JMOD, D_2O): σ = 20.1 (*C*H_3), 63.3 (*C*H_2), 66.3 (*C*H_2) 72.5 (*C*), 127.8 (*C),* 130.0 (CH), 132.2 (CH), 139.5 (*C*H), (*C*-B not observed). ^{11}B NMR: (96 MHz, D_2O): σ = 2.7 (br), 17.8 (benzene-1,4-diboronic acid). FT-IR (KBr): 3422 (s,br), 2990 (m,br), 1638 (s,br), 1561 (w), 1542 (w), 1509 (m), 1478 (s), 1373 (s,br), 1343 (s), 1269 (s), 1256 (s), 1231 (s), 1195 (s), 1114 (m), 1065 (s), 1032 (s), 1001 (s,br), 979 (m), 929 (m,sh), 872 (m), 825 (m), 767 (s), 745 (s), 653 (m), 564 (s), 444 (w), 421 (m). ESI-HRMS m/z: $[M+Na]^+$ Calcd for $[C_{54}H_{72}B_6N_{12}O_{15}Na]^+$ 1217.5702; Found 1217.5691; $[M+K]^+$ Calcd for $[C_{54}H_{72}B_6N_{12}O_{15}K]^+$ 1233.5441; Found 1233.5459; $[M-H]^-$ Calcd for $[C_{54}H_{71}B_6N_{12}O_{15}]^-$ 1193.5737; Found 1193.5774.

Generation of 4-component DCL of adducts 2. 4-Bromophenylboronic acid (60 mg, 0.3 mmol) was added to adduct **2a** (106 mg, 0.1 mmol) followed by methanol (1 mL) and water (1 mL). Then, acetic acid (12 mg, 0.2 mmol) was added and the reaction mixture was stirred for 24 hours at room temperature to give a 4-component DCL. A sample of reaction mixture was taken, gently evaporated at room temperature in vacuum at 0.1 Torr and NMR and HRMS spectra of residue were recorded. HRMS revealed the presence of symmetrical adducts (Ph,Ph,Ph)-**2** (**2a**) and (BrPh,BrPh,BrPh)-**2** (**2b**), as well as non-symmetrical combinatorial adducts (Ph,Ph,BrPh)-**2** and (Ph,BrPh,BrPh)-**2**. Ratio of coordinated PhB-/BrPhB- residues ca. 1 : 1 (^{1}H NMR data).

Generation of 8-component DCL of adducts 2. To the 4-component DCL solution (500 μL) from the previous experiment 1-pyreneboronic acid (18.5 mg, 0.075 mmol) and THF (250 μL) were added. The resulting solution was stirred for 24 hours at room temperature to establish the equilibrium. Then, a sample from reaction was taken, gently evaporated at room temperature in a vacuum at 0.1 Torr and NMR and HRMS spectra were recorded. HRMS revealed the presence of symmetrical adducts (Ph,Ph,Ph)-**2** (**2a**) and (BrPh,BrPh,BrPh)-**2** (**2b**), as well as non-symmetrical combinatorial adducts (Ph,Ph,BrPh)-**2**, (Ph,BrPh,BrPh)-**2**, (Ph,Ph,Pyr)-**2**, (BrPh,BrPh,Pyr)-**2**, (BrPh,Pyr,Pyr)-**2**, (Ph,BrPh,Pyr)-**2**. Ratio of coordinated PhB-/PyrB-/p-BrPhB- residues ca. 1 : 1.1 : 1.2 (^{1}H NMR data).

Characterization of DCL's. Characterization of dynamic mixtures was accomplished by careful analysis of NMR spectra/HRMS data and comparison with authentic samples of **2a**, **2b**, **2d**, $PhB(OH)_2$, *p*-bromophenylboronic and 1-pyreneboronic acid (for details see Supporting information). Characteristic signals of coordinated PhB-residues – ^{1}H NMR: 7.05 (m, 3H), 7.29 (m, 2H). ^{13}C NMR: 126.1, 126.2 and 131.2 (*C*H). Characteristic signals of coordinated BrPhB-residues – ^{1}H NMR: 7.25 (m, 4H). ^{13}C NMR: 119.2 (*C*), 129.0 and 133.5 (*C*H). Characteristic signals of coordinated PyrB-residues – ^{1}H NMR: 9.23 (d, J = 8.8 Hz, 1H). ^{13}C NMR selected characteristic signals: 130.81 (*C*); 133.67 (*C*). ESI-HRMS m/z: Cation $[\mathbf{2a}+Na]^+$ Calcd for $[C_{54}H_{69}B_3N_{12}O_9Na]^+$ 1085.5506; Found 1085.5492. Cation $[\mathbf{2b}+Li]^+$ Calcd for

$[C_{54}H_{66}B_3Br_3N_{12}O_9Li]^+$ 1303.3091; Found 1303.3206. Cation [(Ph,Ph,BrPh)-**2**+H]$^+$ $[C_{54}H_{69}B_3BrN_{12}O_9]^+$ 1141.4795; Found 1141.4764; Anion [(Ph,Ph,BrPh)-**2**+Br]$^-$ $[C_{54}H_{68}B_3Br_2N_{12}O_9]^-$ 1219.3878; Found 1219.3852. Cation [(Ph,BrPh,BrPh)-**2**+H]$^+$ $[C_{54}H_{68}B_3Br_2N_{12}O_9]^+$ 1219.3876; Found 1219.3928; Anion [(Ph,BrPh,BrPh)+Br]$^-$ $[C_{54}H_{67}B_3Br_3N_{12}O_9]^-$ 1297.2983; Found 1297.2975. Anion [(Ph,Ph,Pyr)-**2**+Br]$^-$ $[C_{64}H_{73}B_3BrN_{12}O_9]^-$ 1265.5112; Found 1265.5010. Anion [(BrPh,BrPh,Pyr)-**2**+Br]$^-$ $[C_{64}H_{71}B_3{}^{79}Br_2{}^{81}BrN_{12}O_9]^-$ 1423.3315; Found 1423.3378. Anion [(BrPh,Pyr,Pyr)-**2**+Br]$^-$ $[C_{74}H_{76}B_3Br_2N_{12}O_9]^-$ 1467.4513; Found 1467.4685. Anion [(Ph,BrPh,Pyr)-**2**+Br]$^-$ $[C_{64}H_{72}B_3Br_2N_{12}O_9]^-$1343.4200; Found 1343.4109.

Synthesis and characterization of *N*-(*p*-CH_3O_2C-Bn)-TAAD-B-PS resin. Salt ***N*-(p-CH_3O_2C-Bn)-TAAD** (98 mg, 0.21 mmol) and Li_2CO_3 (8 mg, 0.11 mmol) were added to the polystyrene-bound boronic acid **PS-B(OH)$_2$** (200-400 mesh, extent of labeling: 1.4-2.2 mmol/g loading, 1 % cross-linked with divinylbenzene) (50 mg, 0.11 mmol). Then, 0.5 mL of methanol, 0.3 mL of H_2O and 0.5 mL of THF were added and reaction mixture was heated for 7 hours at 70 ^oC. The polymeric material was filtered off using sorbent-free PrepSep® column, washed with 40 mL of THF, 20 mL of MeOH and 10 mL of H_2O, and then dried in a vacuum at 0.1 Torr and 75 ^oC until constant weight. 78 mg (yield 89%). FT-IR (KBr): 3424 (s,br), 3060 (w,sh), 3024 (w), 2908 (m,br) 1946 (w), 1804 (w), 1720 (s), 1603 (s,br), 1561 (m), 1512 (m), 1493 (w), 1477 (w), 1438 (s), 1408 (w), 1369 (s), 1317 (w), 1283 (s), 1255 (s), 1183 (s), 1110 (s), 1057 (m), 996 (s), 928 (w), 892 (w), 866 (w), 818 (m), 760 (s), 738 (m), 723 (m), 697 (s), 662 (m), 560 (s), 512 (m), 458 (m), 433 (s). Anal. Calcd for 100% loading; N, 7.03. Found N, 7.14. (99% loading of **TAAD** salt).

^{15}N-Labeled polymer ***N*-(*p*-CH_3O_2C-Bn)-TAAD-B-PS** was prepared according to the procedure described above from ^{15}N-labeled ***N*-(*p*-CH_3O_2C-Bn)-TAAD** (20 mg), Li_2CO_3 (1.6 mg) and polystyrene-bound boronic acid (20 mg). 24 mg (yield 69%). FT-IR (KBr): 3423 (s,br), 3059 (w,sh), 3023 (w), 2928 (m,br), 2856 (w), 1944 (w), 1803 (w), 1720 (s,sh), 1638 (s,sh), 1606

(s,br), 1561 (w), 1513 (m), 1493 (m), 1477 (m), 1438 (s), 1408 (m), 1368 (s), 1283 (s,br), 1227 (s), 1185 (s), 1111 (s), 1053 (m), 992 (s), 924 (w), 887 (w), 870 (w), 817 (m), 753 (m), 736 (m), 723 (m), 697 (s), 634 (w), 561 (s), 479 (m), 413 (s). Anal. Calcd for 100% loading; N, 7.03. Found N, 5.79 (82% loading of **TAAD** salt).

Cleavage of *N*-(*p*-CH_3O_2C-Bn)-TAAD-B-PS and reverse reaction. To a suspension of ***N*-(*p*-CH_3O_2C-Bn)-TAAD-B-PS** (100 mg, 0.125 mmol of **TAAD**) in 2 ml of methanol and 0.5 ml of H_2O was added 36 wt. % aqueous HCl (189 μL, 2.2 mmol). The mixture was stirred for 48 hours at room temperature. The polymeric material was filtered off using sorbent-free PrepSep® column, washed with 20 mL of MeOH, 10 mL of H_2O, and then dried in vacuum at 0.1 Torr and 75°C until constant weight. 49 mg (yield 86%). FT-IR spectrum is in agreement with authentic sample of **PS-B(OH)$_2$**. Anal. Calcd for 0% loading; N, 0.00. Anal. Calcd for 100% loading; N, 7.03. Found N, 0.54 (8% loading of **TAAD** salt). To the recovered **PS-B(OH)$_2$** (46 mg, ca. 0.1 mmol) were added **TRISOXH$_3$** (50 mg, 0. 217 mmol), Li_2CO_3 (8 mg, 0.11 mmol), MeOH (1 mL) and water (0.3 mL). The reaction mixture was heated for 6 hours at 60 °C. After cooling to room temperature, methyl 4-(bromomethyl)benzoate (50 mg, 0.217 mmol) was added and the mixture was stirred for 24 hours at room temperature. The polymeric material was filtered off using sorbent-free PrepSep® column and washed with 10 mL of THF, 20 mL of MeOH, and then dried in vacuum at 0.1 Torr and 75°C until constant weight to give 74 mg (yield 93%) of ***N*-(*p*-CH_3O_2C-Bn)-TAAD-B-PS**. FT-IR spectrum is in agreement with authentic sample of ***N*-(*p*-CH_3O_2C-Bn)-TAAD-B-PS**. Anal. Calcd for 100% loading; N, 7.03. Found N, 6.19 (88% loading of **TAAD** salt).

Synthesis of *N*-PS-CH_2-TAAD resin. To a mixture of **TAAD** (30 mg, 0.13 mmol) and Merrifield Resin (50 mg, 0.06 mmol, 200-400 mesh, 1.0-1.3 mmol/g loading, 1 % cross-linked) were added methanol (1 mL) and THF (1 mL). The mixture was stirred for 144 hours at room temperature. The polymeric material was filtered off using sorbent-free PrepSep® column, washed with 10 mL of THF and 30 mL of methanol, and then dried in vacuum at 0.1 Torr and 70

°C until constant weight. 52 mg (yield 83%). FT-IR (KBr): 3423 (s,br), 3082 (w), 3059 (w), 3024 (m), 2920 (s), 2851 (m), 1945 (m), 1871 (m), 1803 (m), 1774 (w), 1742 (m), 1719 (w), 1629 (s), 1601 (s), 1583 (m), 1561 (w), 1544 (w), 1511 (m), 1492 (s,sh), 1451 (s), 1408 (m), 1371 (s), 1317 (m), 1262 (m), 1217 (w), 1194 (s,br), 1155 (m), 1113 (m), 1067 (m), 999 (s), 979 (s), 933 (m), 908 (m), 850 (w), 834 (m,br), 755 (s), 697 (s), 620 (m), 538 (m), 450 (w), 431 (w), 414(w). Anal. Calcd for 100% loading; N, 5.09. Found N, 4.90 (96% loading of **TAAD**).

^{15}N-Labeled polymer **PS-CH$_2$-TAAD** was prepared according to procedure described above from 30 mg (0.13 mmol) of **^{15}N-TAAD**. 60.5 mg (yield 95%). FT-IR (KBr): 3424 (s,br), 3082 (w), 3059 (w), 3025 (w), 2928 (m), 2842 (w), 1944 (m), 1870 (m), 1803 (m), 1774 (w), 1751 (w), 1719 (w), 1602 (s,br), 1583 (m), 1560 (w), 1542 (w), 1508 (m), 1492 (s,sh), 1451 (s), 1371(s,sh), 1314 (m), 1259 (m), 1192 (s,br), 1155 (m), 1117 (w), 1028 (m), 992 (m), 973(m), 929 (m), 909 (m), 849 (m), 833 (m), 756 (s), 696 (s), 537 (m), 486 (w), 425 (m). Anal.Calcd for 100% loading; N, 5.35. Found N, 4.82 (90% loading of **TAAD**).

Synthesis of *N*-PS-CH$_2$-TAAD-B-Ph. To a mixture of ***N*-PS-CH$_2$-TAAD** (76 mg, approx. 0.07 mmol, 99% loading), Li_2CO_3 (9.5 mg, 0.128 mmol) and phenylboronic acid (62 mg, 0.508 mmol) were added methanol (3.2 mL) and THF (3.2 mL). The mixture was stirred for 96 hours at room temperature. Then, the polymer was filtered off using sorbent-free PrepSep® column, washed with 40 mL of THF, 60 mL of methanol and 40 mL of water, and then dried in vacuum at 0.1 Torr and 70°C until constant weight to give 76 mg (yield 95%) of ***N*-PS-CH$_2$-TAAD-B-Ph**. FT-IR (KBr): 3423 (s,br), 3082 (m), 3023 (s), 3003 (w), 2909 (s,br), 2849 (s), 1944 (m,br), 1871 (m,br), 1803 (m,br), 1774 (w), 1752 (w), 1719 (w), 1701 (w), 1671 (m), 1638 (m), 1601 (s,br), 1561 (w), 1543 (w), 1509 (m), 1492 (s), 1450 (s,br) 1409 (m), 1365 (s), 1317 (m), 1254 (s), 1222 (s), 1200 (s), 1186 (s), 1155 (w), 1112 (w), 1056 (s), 1029 (m), 1003 (s), 991 (s), 973 (m),938 (m), 886 (m), 861 (m), 826 (m), 739 (s), 694 (s,br), 646 (m), 594 (m), 559 (m), 530 (s,br), 448 (w), 414 (s). Anal. Calcd for 100% loading; N, 4.87; B, 0.96. Found N, 4.65; B, 0.90 (95% loading of $PhB(OH)_2$).

^{15}N-Labeled polymer ***N*-PS-CH$_2$-TAAD-B-Ph** was prepared according to the same procedure from 38 mg (0.035 mmol, 90% loading of **TAAD**) of ^{15}N-labeled ***N*-PS-CH$_2$-TAAD**. 38 mg (yield 95%). FT-IR (KBr): 3420 (s,br), 3082 (w), 3059 (m), 3025 (s), 3003 (w), 2923 (s,br), 2850 (s), 1944 (w), 1871 (w), 1803 (w), 1774 (w), 1752 (w), 1719 (w), 1701 (w), 1638 (w), 1601 (s), 1560 (w), 1542 (w), 1509 (m), 1493 (s), 1452 (s,br), 1367 (s), 1319 (m), 1255 (m), 1224 (s), 1198 (m), 1185 (m), 1155 (w), 1054 (m), 1029 (w), 1001 (s), 990 (s), 971 (m), 940 (m), 908 (w), 884 (m), 826 (m), 755 (s), 740 (s), 699 (s,br), 666 (m), 647 (m), 561 (s), 540 (s,br), 494 (m,br), 418 (s). Anal. Calcd for 100% loading; N, 5.12; B, 0.95. Found N, 4.24; B, 0.79 (83% loading of PhB(OH)$_2$).

Synthesis of *N*-PS-CH$_2$-TAAD-B-Cin resin. To a mixture of ***N*-PS-CH$_2$-TAAD** resin (17 mg, approx. 0.0157 mmol, 96% loading of **TAAD**), Li_2CO_3 (1.5 mg, 0.02 mmol) and **Cin-B(OH)$_2$** (8 mg, 0.0157 mmol) were added methanol (0.5 mL) and THF (0.5 mL). The reaction mixture was stirred for 67 hours at room temperature. Then, the polymer was filtered off using sorbent-free PrepSep® column, washed with 10 ml of THF, 15 ml of methanol and 5 ml of water, and dried in vacuum at 0.1 Torr and 70 °C until constant weight. 21 mg (yield 88%). FT-IR (KBr): 3411 (s,br), 3082 (m), 3059 (s), 3025 (s), 3001 (m), 2923 (s), 2850 (m), 1943 (w), 1869 (w), 1801 (w), 1773 (w), 1734 (w), 1637 (s,br), 1601 (s), 1560 (w), 1541 (w), 1509 (m), 1493 (s), 1475 (m), 1452 (s), 1369 (s), 1321 (m,sh), 1265 (s), 1184 (s), 1056 (m), 1029 (s), 1004 (s), 978 (s), 939 (s), 889 (m), 841 (m), 761 (s), 699 (s), 669 (m), 559 (m, sh), 420 (m). Anal. Calcd for 100% loading: N, 5.46 B, 0.72. Found N 4.82; B, 0.72 (94% loading of **Cin-B(OH)$_2$**).

Synthesis of *N*-PS-CH$_2$-TAAD-B-3-Thienyl. To a mixture of *N*-**PS-CH$_2$-TAAD** resin (42 mg, approx. 0.04 mmol, 96% loading), Li_2CO_3 (3 mg, 0.041 mmol) and thiophen-3-ylboronic acid (10 mg, 0.08 mmol) were added methanol (1 mL) and THF (1 mL). The mixture was stirred for 96 hours at room temperature. Then, the polymer was filtered off using sorbent-free PrepSep® column, washed with 20 ml of THF, 30 ml of methanol and 20 ml of water, and dried in vacuum at 0.1 Torr and 70 °C until constant weight. 39 mg (yield 88%). FT-IR (KBr): 3409 (s,br), 3082

(m), 3058 (m), 3024 (m), 3000 (w), 2979 (w), 2921 (s), 2851 (s), 2632 (w), 1944 (w,br), 1871 (w,br), 1803 (w,br), 1774 (w,br), 1736 (w), 1719 (w), 1685 (m), 1637 (s,br), 1601 (s), 1583 (s), 1561 (w), 1542 (w), 1508 (s), 1492 (s), 1474 (s), 1451 (s), 1407 (m,br), 1366 (s), 1255 (s), 1216 (s), 1201 (s), 1185 (s), 1163 (s), 1056 (s), 1021 (s), 1003 (s), 976 (s), 938 (s), 938 (s), 900 (s), 855 (s), 837 (s), 757 (s,br), 697 (s), 619 (m), 595 (m), 556 (m), 533 (m), 441 (w), 417 (s,sh). Anal. Calcd for 100% loading; N, 5.04; S, 2.88. Found N, 4.48; S, 2.72 (92% loading).

Cleavage of *N*-PS-CH_2-TAAD-B-3-Thienyl resin. To a suspension of polymer ***N*-PS-CH_2-TAAD-B-3-Thienyl** (25 mg, approx. 0.015 mmol, 65% loading) in THF (1 mL) were added water (20 μL, 1.1 mmol) and 4 M solution of HCl in 1,4-dioxane (212 μL, 0.85 mmol). The mixture was stirred for 6 hours at 60 ^oC, then kept without stirring for 12 hours at room temperature and then heated for another 6 hours at 60 ^oC. The polymer was filtered off using sorbent-free PrepSep® column, washed with 30 mL of THF and 30 mL of water, and dried in vacuum at 0.1 Torr and 70^oC until constant weight. 16 mg (yield 99%). FT-IR spectrum is in agreement with authentic sample of ***N*-PS-CH_2-TAAD**. Anal. Calcd for 65% loading of **TAAD** in ***N*-PS-CH_2-TAAD**: N, 3.32. Found: N, 3.10 (60% loading of **TAAD** in ***N*-PS-CH_2-TAAD**). Anal. Calcd for 65% loading of thiophen-3-ylboronic acid in ***N*-PS-CH_2-TAAD-B-3-Thienyl**: S, 1.87. Found S, 0.25 (<10% loading of thiophen-3-ylboronic acid in ***N*-PS-CH_2-TAAD-B-3-Thienyl**).

Suzuki-Miyaura coupling with regeneration of excess boronic acid. *Stage 1*. To a stirred solution of 4-bromophenol (129 mg, 0.75 mmol) and 4-trifluoromethoxyphenylboronic acid (214 mg, 1.04 mmol) in 1,2-dimethoxyethane (3.4 mL) was added $Pd(PPh_3)_4$ (47 mg, 0.04 mmol) followed by a 1 M solution of Na_2CO_3 (1.18 mL). The mixture was refluxed with intensive stirring for 14 h under argon atmosphere. The resulting solution was poured into a mixture of 1 M solution NH_4Cl (25 mL) and AcOEt (25 mL). After separation of organic layer, the aqueous phase was additionally washed with AcOEt (25 mL). Combined organic layers were washed with brine (25 mL), dried under anhydrous Na_2SO_4 and concentrated in vacuum. *Stage 2*. The

residue was dissolved in a mixture of THF (1.1 mL) and methanol (1.1 mL). Polymer **PS-CH_2TAAD** (164 mg approx 0.16 mmol, 92% loading of **TAAD**) and Et_3N (144 μL, 1.04 mmol) were added and the mixture was stirred for 96 h. Then, the precipitate was centrifuged off, washed consequently with THF (ca. 20 mL), methanol (ca. 20 mL) and water (ca. 20 mL), and dried in vacuum to give 168 mg of loaded polymer (first portion). Combined organic mother solutions were concentrated in vacuum. The residue was dissolved in a mixture of THF-methanol mixture (1.1 mL/1.1 mL) and treated with the second portion of **PS-CH_2TAAD** (164 mg 0.16 mmol, 92% loading of **TAAD**) and Et_3N (144 μL, 1.04 mmol) following the procedure described above. This operation provided the second portion of loaded polymer (174 mg). Combined organic mother solutions were concentrated in vacuum. Column chromatography of the residue on silica gel (eluent hexane-AcOEt = 10 : 1 → 5 : 1) provided 110 mg (58% based on 4-bromophenol) of 4'-trifluoromethoxy-1,1'-biphenol **5**. Mp = 124-127 °C (lit.[26] 129-132 °C). ^{1}H NMR spectra are in accordance with literature data.[31] *Stage 3*. The first portion of loaded polymer (168 mg) was suspended in a mixture THF-MeOH-H_2O (0.6 mL : 0.6 mL : 0.3 mL) and HCl (36% wt. in H_2O) (230 μl) was added. The mixture was stirred for 96 h, then, the polymer was centrifuged off, washed successively with THF (10 mL) and methanol (10 mL) and dried in vacuum (145 mg). Combined mother solutions were concentrated in vacuum, the residual solid was treated with hot $CHCl_3$ (2×10 mL). The solution was filtered, concentrated and dried in vacuum to give 23 mg of 4-trifluoromethoxyphenylboronic acid. The second portion of loaded polymer (174 mg) was suspended in THF (7 ml), then, water (139 μL, 7.7 mmol) and 4M HCl solution in dioxane (1.5 mL, 6 mmol) were added. The mixture was stirred at 60°C for 12 h, then, the polymer was centrifuged off, washed successively with THF (10 mL) and methanol (10 mL) and dried in vacuum (151 mg). Combined mother solutions were concentrated in vacuum, the residual solid was treated with hot $CHCl_3$ (2×10 mL). The solution was filtered, concentrated and the residue was subjected to a column chromatography of the residue on silica gel (eluent hexane-AcOEt = 10 : 1 → 3 : 1 → 1 : 1 → 0 : 1), which gave 21 mg of 4-

trifluoromethoxyphenylboronic acid. Overall amount of regenerated 4-trifluoromethoxyphenylboronic acid: 44 mg (73% based on the excess used in stage 1). Mp = 88-92 °C (lit.[31] 86-92 °C). NMR spectra are in accordance with authentic sample. FT-IR spectrum of regenerated **PS-CH_2TAAD** resin is in accordance with authentic sample. Anal. Calcd for 92% loading; N, 4.70. Found N, 4.39 (86% loading of **TAAD**).

Synthesis of dilithium salt 7. To a mixture of benzene-1,4-diboronic acid (41 mg, 0.25 mmol) and **TRISOXH$_3$** (115 mg, 0.5 mmol) was added methanol (4 mL). The reaction mixture was stirred for 20 hours and 19 mg (0.26 mmol) of Li_2CO_3 were added followed by 96 hours of additional stirring. The resulting solution was evaporated, the residue was dried in vacuum at 0.1 Torr (73°C) until constant weight to give 148 mg (yield 93%) of salt **7** as a white solid. Decomposition above 240°C (without melting). ^{1}H NMR (300 MHz, DMSO-d_6): σ = 1.36 (s, 18 H), 2.68 (s, 12 H), 6.99 (s, 4 H).^{13}C NMR (75 MHz, JMOD, DMSO-d_6): σ = 21.9 (*C*H_3), 62.0 (*C*H_2),71.9 (*C*), 129.3 (*C*H), (*C*-B not observed). ^{11}B NMR: (96 MHz, DMSO-d_6): σ = 2.5 (br, *W* = 1315 Hz). ESI-HRMS m/z: $[M-Li]^-$ Calcd for $[C_{24}H_{34}B_2N_8O_6Li]^+$ 559.2947; Found 559.2950. Anal. Calcd for $C_{24}H_{34}B_2N_8O_6Li_2\bullet 4H_2O$: C, 45.17; H, 6.63; N, 17.56. Found: C, 45.57; H, 6.39; N, 17.51.

Synthesis and characterization of polymer P-1. *Method A*: A solution of benzene-1,4-diboronic acid (16.5 mg, 0.1 mmol) in 0.5 mL of MeOH was added to a solution of tris-**TAAD** salt **6** (70 mg, 0.07 mmol) and K_2CO_3 (14 mg, 0.1 mmol) in 0.5 mL of H_2O. The resulting mixture was stirred for 24 hours (soon after mixing of components, the polymer started to precipitate). The precipitate was centrifuged off, washed with 10 mL of MeOH, 10 mL of H_2O, and then dried in vacuum at 0.1 Torr, 70°C until constant weight (yield: 27 mg). *Method B*: To a mixture of dilithium salt **7** (433 mg, 0.77 mmol) and 1,3,5-tris(bromomethyl)benzene (80 mg, 0.22 mmol) was added methanol (2.7 mL). The reaction mixture was stirred for 16 hours, then, concentrated under reduced pressure and dried at 0.1 Torr, 70°C. The residue was kept overnight at room temperature and then was triturated successively with 10 mL of MeOH and 10 mL of

H_2O. The remaining non-soluble polymeric material was dried in vacuum at 0.1 Torr, 70°C until constant weight (yield: 300 mg). *Method C*: To a mixture of benzene-1,4-diboronic acid (81 mg, 0.5 mmol), **TRISOXH$_3$** (230 mg, 1 mmol) and 1,3,5-tris(bromomethyl)benzene (108 mg, 0.3 mmol) was added methanol (6 mL). The resulting mixture was stirred for 24 hours at room temperature and Li_2CO_3 (17 mg, 0.23 mmol) was added. After 4 hours of additional stirring, the reaction mixture was concentrated in a vacuum and the residue was triturated with 12 mL of water. The remaining non-soluble polymeric material was dried in vacuum at 0.1 Torr until constant weight (yield: 118 mg). White solid. Decomposition above 210°C (without melting). ^{1}H NMR (400.23 MHz, solid state): σ = 1.34 (very broad), 7.91 (very broad). ^{13}C NMR (100.64 MHz, solid state): σ = 22.1, 50.2, 62.6, 68.0, 73.6, 131.0, 140.5. ^{11}B NMR: (128.41 MHz, solid state): σ = 1.3 (br), 19.0. ^{15}N NMR: (40.55 MHz, solid state): σ = 56.2, 130.0. FT-IR (KBr): 3422 (s), 3001 (s), 2944 (s), 1637 (s,br), 1560 (w), 1542 (w), 1508 (w), 1499 (w), 1476 (s), 1448 (s,br), 1373 (s), 1341 (m,sh), 1268 (s), 1232 (s), 1194 (s), 1064 (s), 1033 (s), 999 (s), 977 (s), 927 (s,br), 867 (s), 818 (s), 763 (s,br), 669 (w,br), 564 (m), 420 (m). Elemental analysis: Found: C, 53.27; H, 6.83; N, 15.34; B, 3.29. Density: 1.3727 g/cm^3. For FE-SEM analysis the sample of **P-1** (obtained by method B) was dried in vacuum at 100 °C. For detailed characterization of polymer **P-1** obtained by different methods see Supporting information.

Hydrolysis of polymer P-1. A slurry of polymer **P-1** (20 mg) in H_2O (1 mL) was treated with 36% wt. aqueous HCl solution (43 μL, 0.5 mmol). The mixture was stirred for 24 hours at room temperature and then concentrated in vacuum and dried until constant weight. ^{1}H NMR was recorded in mixture 0.3 ml D_2O:0.4 ml DMSO-d_6. Ratio of free diboronic acid : salt **6** ca. 2 : 1.

Synthesis of dimer 8. To a solution of tris-**TAAD** salt **6** (90 mg, 0.09 mmol) and Li_2CO_3 (6.7 mg, 0.09 mmol) in 9 ml of water, a solution of benzene-1,4-diboronic acid (14.4 mg, 0.09 mmol) in of MeOH (9 ml). Reaction mixture was stirred for 24 hours at room temperature, then centrifuged, and the resulting solution was concentrated under reduced pressure. Crude product was triturated with acetone and dried in vacuum at 0.1 Torr until constant weight to give 70 mg

(yield 81%) of dimeric compound **8** as a white solid. Decomposition above 220 °C without melting. ^{1}H NMR (300 MHz, HSQC, D_2O): σ = 1.40 (s, 18 H, *H*C-1), 1.74 (s, 36 H, *H*C-5), 3.62 (s, 12 H, *H*C-2), 3.80 (s, 24 H, *H*C-6), 4.79 (br, 4 H, *H*C-4 and 8 H, *H*C-8), 7.38 (s, 8 H, *H*C-9), 8.00 (s 6 H, *H*C-11). ^{13}C NMR (75 MHz, HSQC, D_2O): σ = 19.94 (*C*-1), 20.65 (*C*-5), 55.6 (br, C-2), 63.7 (*C*-6), 66.74 (*C*-4), 68.18 (*C*-8), 72.9 (*C*-7), 76.1 (*C*-3), 128.1 (*C*-10), 130.1 (*C*-9), 139.8 (*C*-11), 140.1 (*C*-B). ^{11}B NMR: (96 MHz, D_2O): σ = -0.7 (br, *W* = 739 Hz). ^{15}N NMR: (30 MHz, HMBC, D_2O): σ = 131.5 (*N*-O). FT-IR (KBr): 3432 (s,br), 2996 (m), 2947 (w), 1718 (w), 1701 (w), 1685 (w), 1654 (s), 1637 (s), 1628 (m), 1560 (m), 1542 (m), 1523 (w), 1508 (w), 1499 (w), 1476 (s), 1458 (m), 1438 (s,br), 1374 (s), 1321 (w), 1270 (s), 1236 (s), 1196 (s), 1066 (s), 1033 (s), 999 (s), 979 (m), 928 (m,br), 871 (m), 818 (m), 764 (s), 669 (w), 568 (s), 421 (m). MW determined by DOSY experiment = ca. 2350 g/mol.

Hydrolysis of dimer 8. A solution of dimer **8** (20 mg) in H_2O (1 mL) was treated with 36% wt. aqueous HCl solution (43 μL, 0.5 mmol). The mixture was stirred for 24 hours at room temperature and then concentrated in vacuum. The residue was dried at 0.1 Torr until constant weight and analyzed by ^{1}H NMR (recorded in mixture 0.5 ml D_2O:0.2 ml DMSO-d_6). Degree of hydrolysis of dimer **8** – 95%. Ratio benzene-1,4-diboronic acid : tris-**TAAD** salt **6** = 9 : 10.

SUPPORTING INFORMATION

Primary data for all measurements, copies of NMR, FT-IR, UV-Vis, fluorescence spectra, X-ray data, Cartesian coordinates, absolute energies for all optimized geometries, calculated IR spectra data, visualization of IR vibrations. This material is available free of charge via the Internet at http://pubs.acs.org.

ACKNOWLEDGMENTS

This work was supported by Russian Science Foundation (Grant 14-50-00126). Solid state NMR studies were supported by SPSU grant 3.37.222.2015 grant (to A.S.M and S.N.B.). Authors thank Department of Structural Studies of Zelinsky Institute of Organic Chemistry for electron microscopy study, Center for Magnetic Resonance of SPSU for solid state NMR studies, Dr.

Natalya Kolotyrkina and Dr. Alexander Chizhov for HRMS measurements, Dr. Artem Semakin for performing TGA and DSC analyses, and Mrs. Irina Borisova for taking FT-IR spectra.

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