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# 1,8,10-Trisubstituted anthracenyl hydrocarbons: Towards versatile scaffolds for multiple-H-bonded recognition arrays

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## article info

Dedicated to Professor Nuno Maulide on the occasion of his receipt of the Tetrahedron Young Investigator Award.

### Keywords:

Anthracene  
Polycyclic aromatic hydrocarbons  
Boronic acids  
Hydrogen-bonds

## abstract

In this work, we describe the synthesis of 1,8,10-trisubstituted anthracenyl scaffolds that, bearing boronic acid functionalities, can act as multiple H-bonding donor systems. The trisubstituted anthracenyl derivatives are synthesized following two main synthetic pathways. Whereas in the first approach trisubstituted anthracenyl derivatives are prepared through the regioselective addition of the relevant organomagnesium nucleophile to 1,8-dichloroanthraquinone, in the second avenue a triflate-bearing anthracene is prepared by reduction of the anthraquinone into the anthrone precursor and functionalized through metal-catalysed cross-coupling reactions. Complementary studies of the Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>-mediated reduction of 1,8-dichloroanthraquinone allowed to shed further light on the possible mechanism of formation of the anthrone precursor, suggesting the presence of a cis-diol intermediate undergoing antiperiplanar elimination. Solid-state X-ray diffraction investigations of the bisboronic acids show that the molecules self-assemble into dimers through the formation of four H-bonds established between the anti-syn conformers of the boronic acid moieties. <sup>1</sup>H-NMR titrations between bisboronic acids and tetra H-bond acceptor, diisoquinolino-naphthyridine, showed a significant shift of the -B(OH)<sub>2</sub> proton resonances, suggesting the presence of H-bonding interactions between both molecules.

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## 1. Introduction

Organoboronic acids are one of the most important functional groups used in organic chemistry [1]. They are commonly used as organometallic species in Pd-catalysed Suzuki cross-coupling reactions [2e5], in sensing [6e9], and in dynamic covalent chemistry to form boronate esters [10e13]. In the recent years, organoboronic acids have also been proposed as versatile H-bonding donors [14e19]. Depending on the type of conformation adopted by the boronic acid functionality, i.e. syn-syn, syn-anti and anti-anti, they can form different non-covalent H-bonded arrays both in solution and in the solid state [20]. For instance, in the solid state phenyl-boronic acid undergoes formation of doubly-H-bonded dimers (DA-AD-type), in which the boronic acid moieties adopt a syn-anti conformation. The dimers are organised in tapes through the

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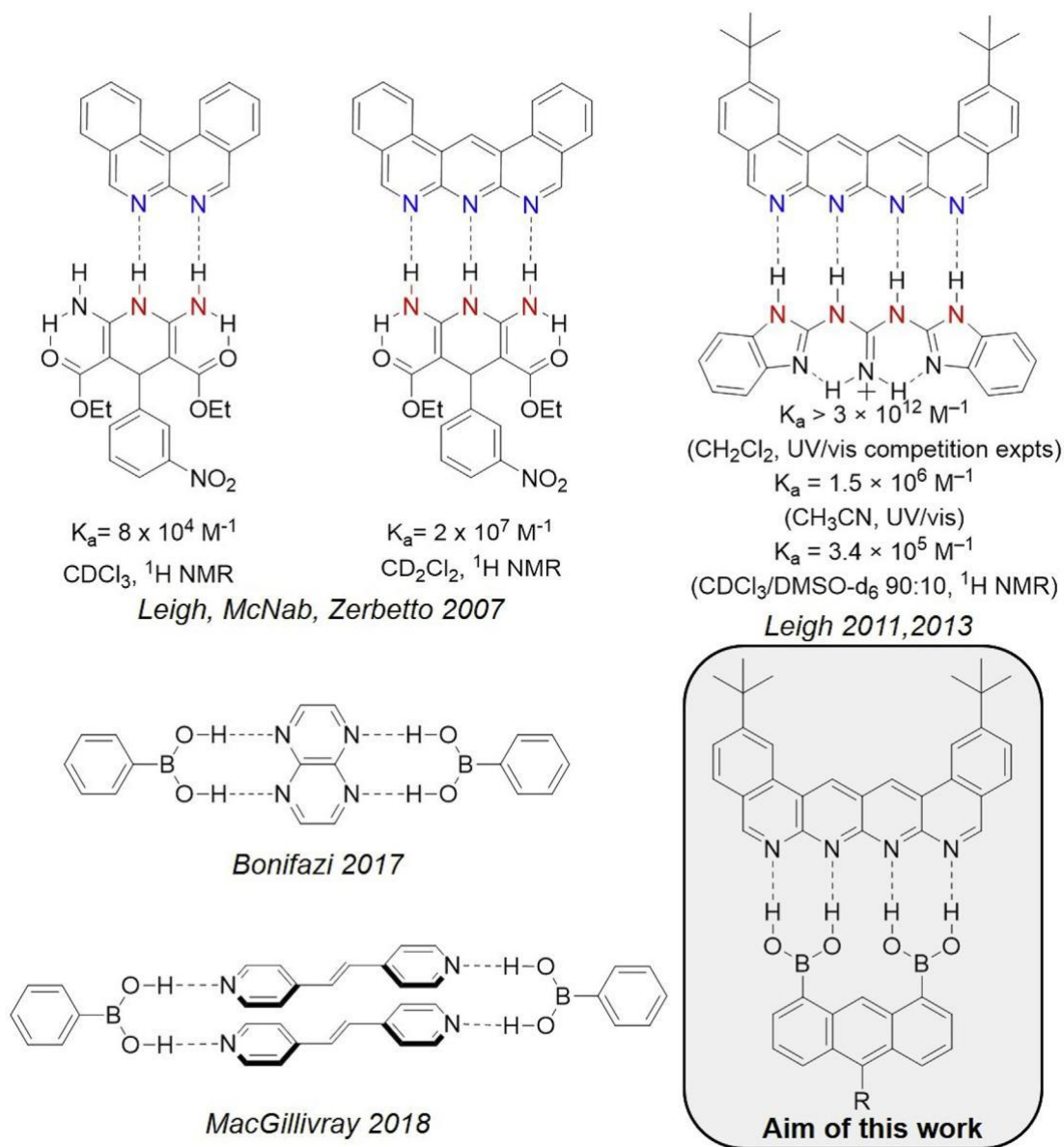


Fig. 1. Common multiple H-bonded complexes [30e34] with (below) and without (above) boronic acids.

with 5,6,11,12-tetraazaphthalene [31]. However, to the best of our knowledge no examples of multiple H-bonded arrays involving boronic acids have been reported so far both in solution and in the solid state.

Due to their high directionality, selectivity, and reversibility, multiple H-bonding arrays are one of the most exploited non-covalent interactions for the preparation of self-assembled functional organic architectures. In particular, linear H-bonded arrays have been extensively used to self-assemble and self-organise functional molecules into well-defined supramolecular architectures [35e40]. Through the demonstration with key examples in the field [32e34], it has been shown that increasing the number of H-bonds in D-type arrays, the strength of association is dramatically enhanced (Fig. 1) [32e34]. It is with this idea in mind that in this paper we describe our efforts to prepare suitable molecular structures that, bearing two boronic acid functionalities, could act as versatile scaffolds for preparing multiple H-bonded complexes. In particular, we have envisioned the preparation of peri-

substituted anthracenyl derivatives that, bearing two frontal boronic acids at positions 1 and 8, could undergo formation of quadruple H-bonding interactions in the presence of a suitable acceptor (Fig. 1).

## 2. Results and discussion

### 2.1. Design of the H-bonding systems: theoretical calculations

We began our investigation with the design of the boronic acid derivatives as H-bonding donors. Capitalizing on the DFT calculation, we modelled a substituted anthracenyl structure bearing boronic acids at peri-positions 1 and 8. Geometry optimization of the anthracenyl scaffolds was performed using DFT calculations at the B3LYP/6-311G\*\* level of theory. In the optimized structure both boronic acid functionalities adopt a syn-syn conformation, arranging the acidic protons in a DDDD-type array. Notably, the non-acidic anthracenyl CH moiety in position 9 likely hampers the

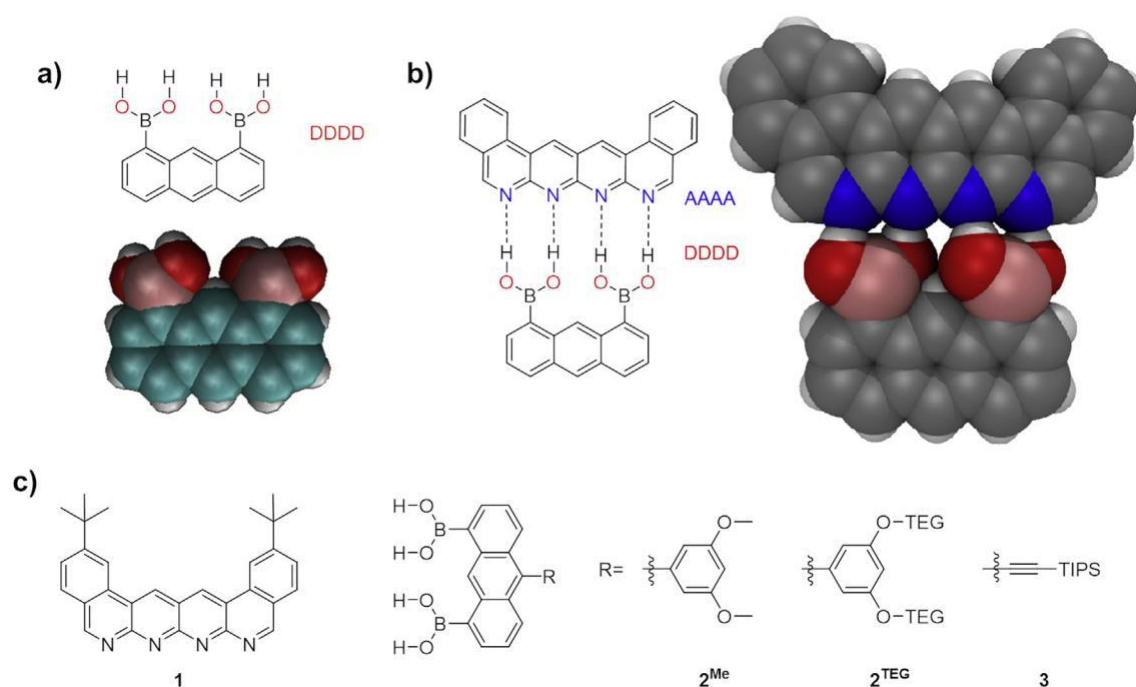


Fig. 2. a) Chemical structure and B3LYP optimized geometry of the donor backbone, b) B3LYP optimized geometry of the 4 H-bonded complex and c) structure of the target molecules.

acid functionalities to be fully co-planar with the aromatic core (Fig. 2a). When contacted to diisquinolino-naphthyridine H-bond acceptor (AAAA), single point energy calculation showed that a highly stabilized quadrupole H-bonded complex (DDDD-AAAA) is formed with a predicted DH of 32.63 kcal/mol (Fig. 2b). It is noteworthy to indicate that this value is superior to that reported for the formation of doubly H-bonded dimers of phenylboronic acid with naphthyridine of 20.41 kcal/mol [31]. Encouraged by these predictive theoretical results, we planned the synthesis of the anthracenyl derivatives shown in Fig. 2c. As we have anticipated limited solubility of bisboronic acids in common organic solvents, anthracenyl cores bearing different substituents at position 10 have been prepared. The synthesis of H-bonding acceptor compound 1

(AAAA) was accomplished following a protocol reported in the literature (see also SI) [34].

## 2.2. Synthesis of three-substituted peri-functionalized anthracenyl scaffolds bearing H-bonding boronic acids

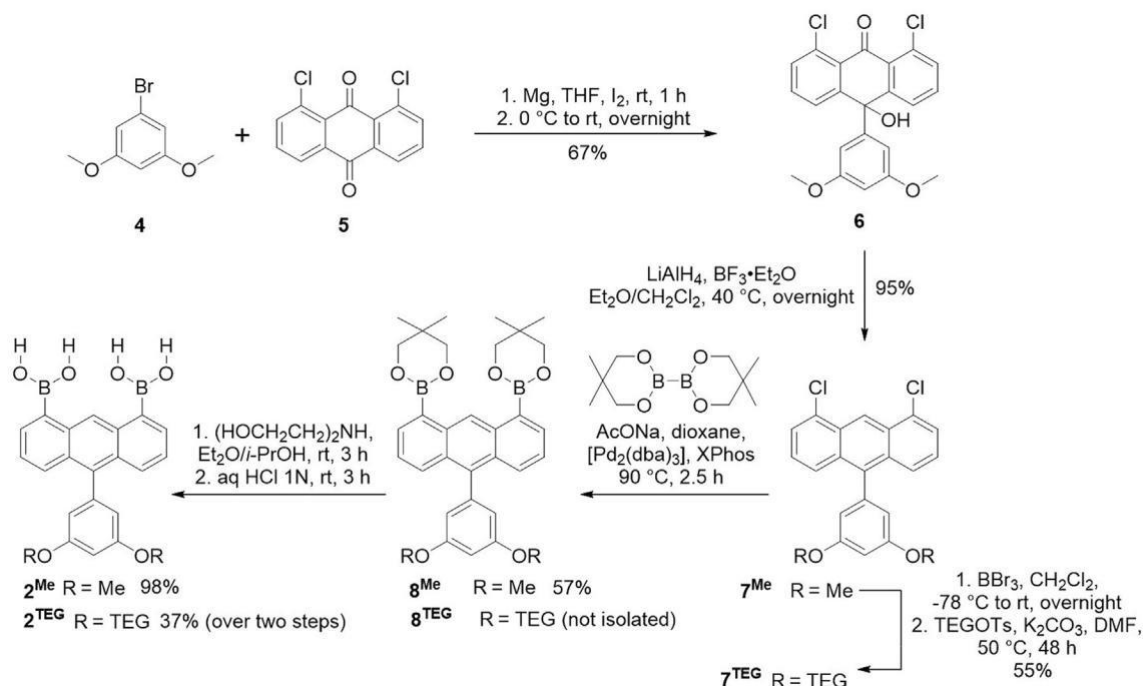
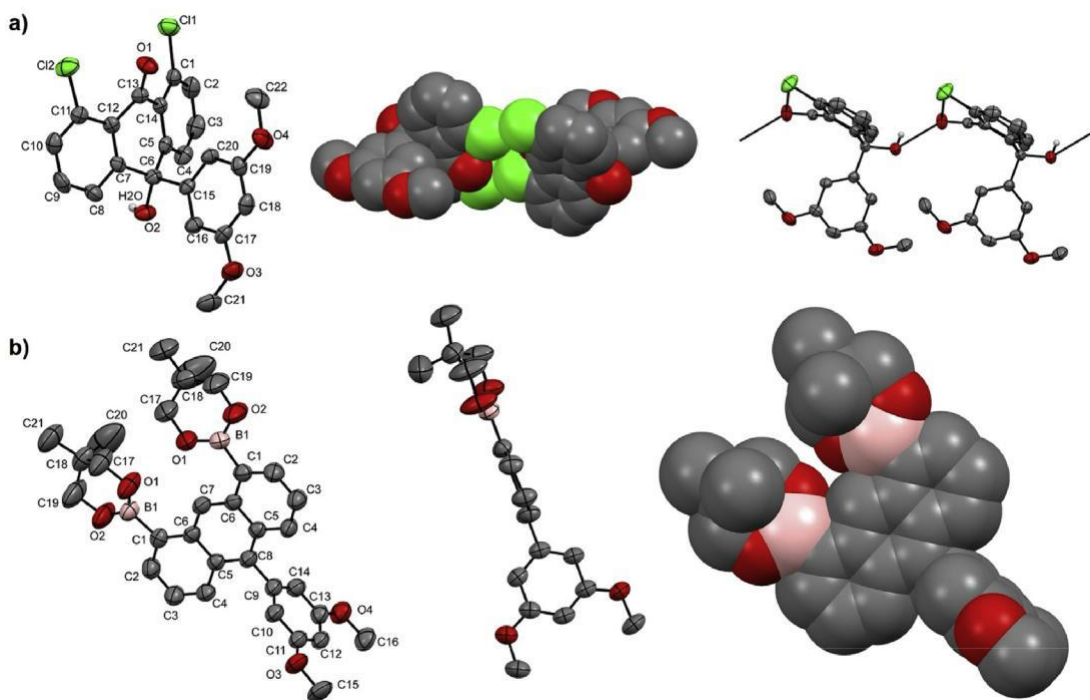
Our investigations began with the synthesis of the H-bonding donor anthracenyl derivatives 2<sup>Me</sup>, 2<sup>TEG</sup>, and 3 each featuring a different solubilising group at position 10. Starting with compound 2<sup>Me</sup> (Scheme 1), bromo-derivative 4 was first reacted with Mg in THF to form its Grignard derivative that reacting with anthraquinone 5 at position 10, yielded hydroxyl-bearing intermediate 6 in 67% yield. The structure of the addition product could be unambiguously determined by X-ray diffraction of single crystals obtained through evaporation of a solution of 6 in CHCl<sub>3</sub> (Fig. 3a). As shown by the X-ray structure, molecule 6 adopts a puckered conformation, with the hydroxyl group H-bonded to a carbonyl group (O<sub>1</sub>⋯O<sub>2</sub> ¼ 2.812(3) Å) of a neighbouring molecule in the crystal lattice. Halogen-halogen (Cl<sub>1</sub>⋯Cl<sub>2</sub> ¼ 3.424(15) Å) and halogen-oxygen (Cl<sub>1</sub>⋯O<sub>2</sub> ¼ 3.305(3) Å) short contacts were also observed. Reduction of ketone 6 with LiAlH<sub>4</sub> followed by addition of BF<sub>3</sub>·Et<sub>2</sub>O gave trisubstituted anthracenyl derivative 7<sup>Me</sup> in 95% yield.

Building on a literature protocol developed by Tanaka, Wada and co-workers [41], Miyaura borylation of anthracene 7<sup>Me</sup> using bis(neopentylglycolato)diboron in the presence of NaOAc, [Pd<sub>2</sub>(dba)<sub>3</sub>] and XPhos in 1,4-dioxane at 90 °C led to the formation of di-boronate ester 8<sup>Me</sup> in 57% yield. Transesterification with diethanolamine, followed by hydrolysis with HCl, led to diboronic acid 2<sup>Me</sup> in 98% yield. Notably, molecule 2<sup>Me</sup> proved to be soluble only in DMSO. In addition to classical <sup>1</sup>H- and <sup>13</sup>C-NMR characterizations, the structures of the boronic acid derivative was confirmed by X-ray diffraction analysis of single crystals (for molecule 2<sup>Me</sup> see section 2.5). Suitable transparent crystals of diboronate 8<sup>Me</sup> for X-ray diffraction analysis were obtained from slow evaporation of a solution of CHCl<sub>3</sub> (Fig. 3b). Pleasingly, the X-ray structure of compound 8<sup>Me</sup> shows that the two boronate ester moieties are fundamentally coplanar (dihedral angles O<sub>1</sub>eB<sub>1</sub>eC<sub>1</sub>eC<sub>6</sub> ¼ 17.6(5) and O<sub>2</sub>eB<sub>1</sub>eC<sub>1</sub>eC<sub>2</sub> ¼ 16.7(5) ) with the anthracenyl scaffold. On the other hand, the aryl substituent is perpendicular to the polycyclic aromatic core (dihedral angle C<sub>5</sub>eC<sub>8</sub>eC<sub>9</sub>eC<sub>10</sub> ¼ 88.5(4) ).

To improve the solubility of diboronic acid 2<sup>Me</sup> in organic solvents, molecular analogue 2<sup>TEG</sup> bearing two triethylene glycol tails was also prepared (Scheme 1). In this case, demethylation of intermediate 7<sup>Me</sup> in the presence of BBr<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> followed by alkylation with TEG-OTs under basic conditions led to compound 7<sup>TEG</sup> in 55% yield. Following the protocols (i.e., Miyaura borylation and transesterification reactions followed by hydrolysis) described previously for installing the boronic acid moieties in molecule 2<sup>Me</sup>, we prepared target molecule 2<sup>TEG</sup> in 37% yield over the two steps. Although the preparative route described so far led to the formation of the desired target molecules, this synthetic strategy is limited by the preparation of a suitable organometallic nucleophile. A more versatile synthetic approach would be one that allows the insertion of any substituents at position 10 through a metal-catalysed cross-coupling reaction. Indulging this line of thought, we turned our attention on anthracene derivative 9 (Scheme 2) as the key intermediate for the new route.

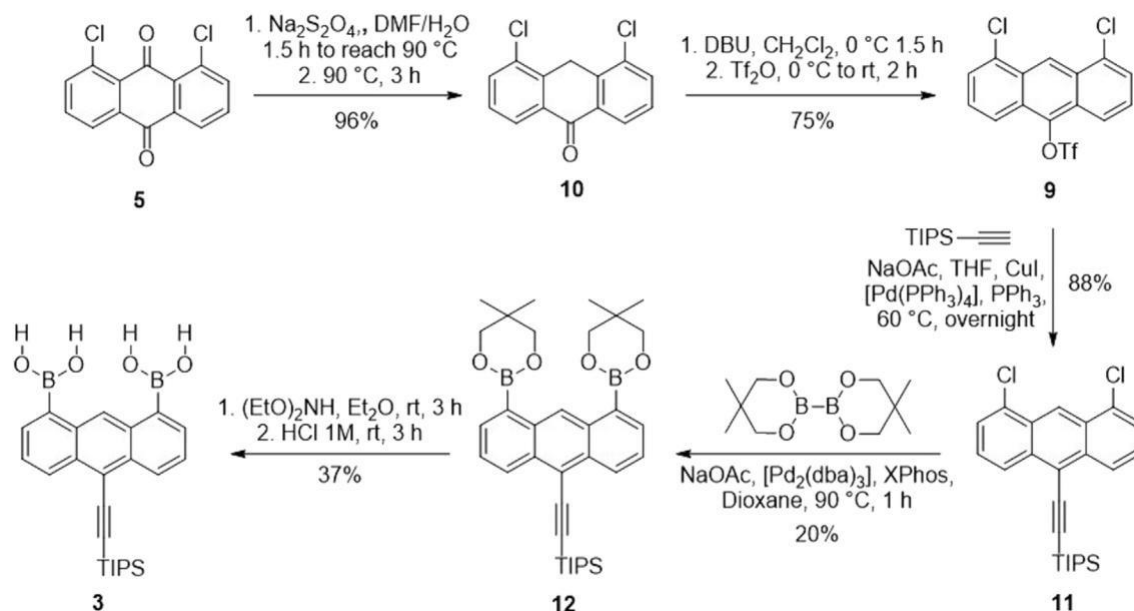
The first synthetic step of this route involves the reduction of



Scheme 1. Synthetic pathway to target anthracenyl derivatives 2<sup>R</sup>.Fig. 3. a) X-ray crystal structure of compound 6; space group: P-21/n. b) X-ray crystal structure of compound 8<sup>Me</sup>; space group: Pnma. H atoms are omitted except for OH. Atom colours: green Cl, pink B, red O, grey C, white H.

anthraquinone 5 to anthrone 10 with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (96% yield). The triflate insertion was obtained in 75% yield after deprotonation of anthrone 10 with DBU followed by the addition of Tf<sub>2</sub>O. The structure of anthracene 9 was confirmed by single crystal X-ray diffractions analysis (crystals obtained by slow evaporation of a CHCl<sub>3</sub> solution, Fig. 4). The molecular packing is governed by the presence of π-π stacking as well as halogen-halogen interactions

between chlorine and fluorine atoms. Sonogashira-type cross-coupling reaction between compound 9 and (triisopropylsilyl) acetylene (TIPSA) led to the formation of compound 11 in 88% yield. Following a similar protocol to that described previously for installing the boronic acid functionalities in molecules 2<sup>R</sup>, target molecule 3 was obtained in moderate yield.



Scheme 2. Synthetic pathway to target molecule 3.

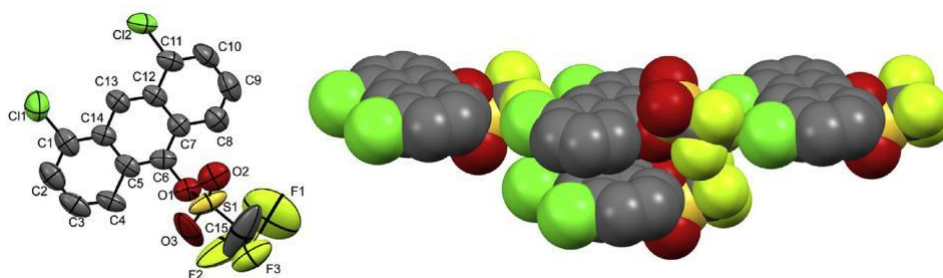


Fig. 4. X-ray crystal structure of compound 9; space group: C2/c. H atoms are omitted. Atom colours: green Cl, yellow S, pale green F, red O, grey C.

### 2.3. Study of the $\text{Na}_2\text{S}_2\text{O}_4$ reduction reaction of 1,8-dichloroanthraquinone

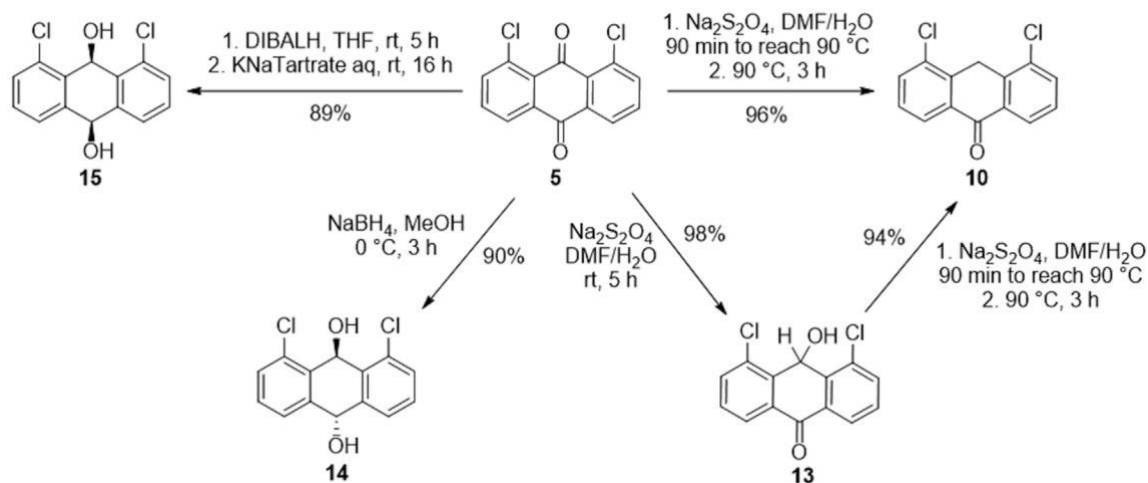
While preparing the anthracenyl intermediates, the peculiar reduction conditions of 1,8-dichloroanthraquinone 5 with  $\text{Na}_2\text{S}_2\text{O}_4$  stimulated our curiosity to shed further light on the mechanism of this reaction. In the literature, only a few studies address the challenge to unravel the mechanism of the  $\text{Na}_2\text{S}_2\text{O}_4$ -mediated reduction. In 1980 Kellogg and co-workers showed that, under basic conditions,  $\text{Na}_2\text{S}_2\text{O}_4$  is an effective reagent for the reduction of aldehydes and ketones [42]. They suggested a two-step mechanism, in which an  $\alpha$ -hydroxy sulfinate intermediate is formed followed by its reductive transformation with loss of  $\text{SO}_2$ . A similar mechanism was also proposed the year after by Saito and co-workers [43]. In 1996, Müller and co-workers reported the regioselective reduction of peri-substituted anthraquinones into the relevant anthrones [44]. They hypothesised that the reduction undergoes formation of a diol intermediate that, in the presence of an acid, eliminates to give the relevant anthrone derivative. In a previous report, Cristol reported the rate of  $\text{H}_2\text{O}$  elimination from cis- and trans-9,10-anthraquinone diols. The author showed that the syn elimination, given by trans diols, is faster than that occurring with the cis-diols, with both diols being able to yield the relevant anthrone [45]. To commence, we prepared and isolated those reactive intermediates that, we think, are possibly lying on the reaction path to the anthrone product. In a first attempt, peri-substituted

anthraquinone 5 was reacted with  $\text{Na}_2\text{S}_2\text{O}_4$  at room temperature for 5 h (Scheme 3). Interestingly, under these reaction conditions intermediate 9-hydroxy-10-anthrone 13 was quantitatively obtained (structure confirmed by X-Ray diffraction analysis of crystals obtained through vapor diffusion of cyclohexane into a  $\text{CH}_2\text{Cl}_2$  solution, Fig. 5a).

Successive reaction of 13 with  $\text{Na}_2\text{S}_2\text{O}_4$  at 90 °C led to anthrone 10 in 94% yield, the structure of which could also be confirmed by X-ray diffraction (Fig. 5b). These observations suggested that the  $\text{Na}_2\text{S}_2\text{O}_4$ -mediated reduction could occur stepwise, with the formation of 9-hydroxy-10-anthrone in the first place, and of a diol anthraquinone in the later stage. To confirm this hypothesis, both cis- and trans-diols of 1,8-dichloroanthraquinone were also synthesized (Scheme 3). trans-Diol 14 was obtained by reaction of 10 in the presence of  $\text{NaBH}_4$  in MeOH at 0 °C for 3 h, whereas cis-diol analogue 15 could be prepared in 89% yield using DIBALH in THF.

The conformational properties of both 1,8-dichloroanthraquinone diols were confirmed by single-crystal X-Ray diffraction analyses. The structures of both diols were determined from crystals obtained by slow evaporation of acetone solutions (Fig. 6a). Interestingly, molecules of trans-diol 14 arrange in a tape-like network through H-bonding interactions, connecting four neighbouring molecules ( $\text{O}_1 \cdots \text{O}_2$  2.867(4) Å and  $\text{O}_1 \cdots$

$\text{O}_2$  2.926(4) Å). In this isomer, the two hydroxyl groups are in equatorial and axial positions, respectively. On the other hand, the X-ray structure of cis-diol 15 shows the presence of the two



Scheme 3. Mechanistic study of the  $\text{Na}_2\text{S}_2\text{O}_4$ -mediated reduction of 1,8-dichloroanthraquinone to anthrone 10: synthesis of the envisaged intermediates.

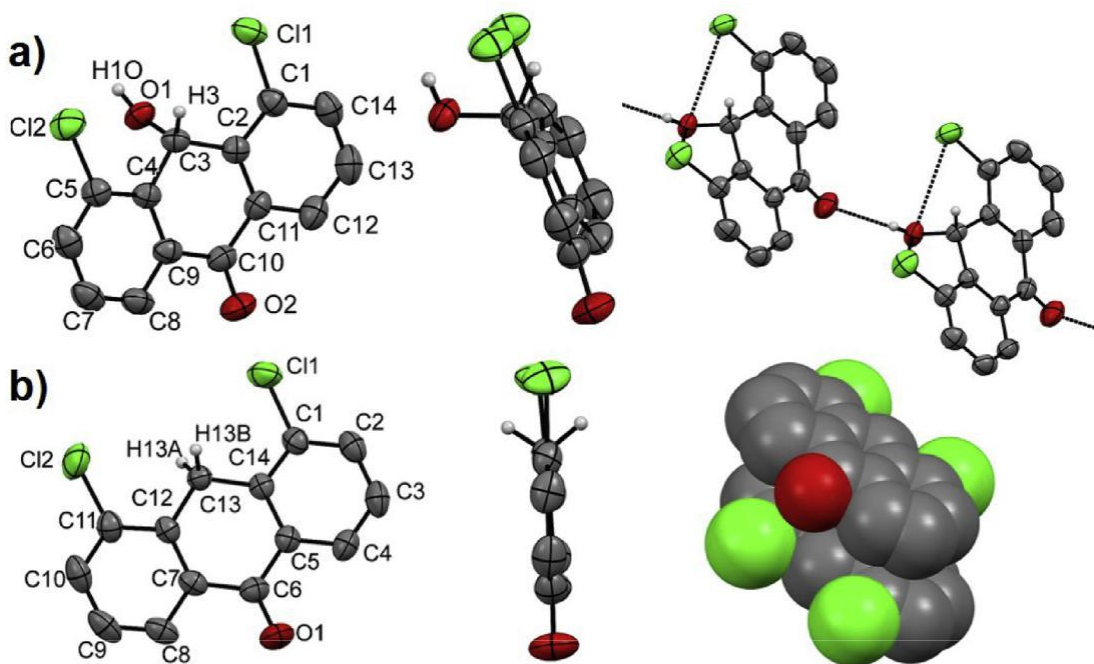


Fig. 5. a) Crystal structure of compound 13; space group:  $P2_1/c$ . b) Crystal structure of compound 10; space group:  $P-2_1$ . H atoms are omitted except for OH and  $\text{C}_{\text{sp}^2}\text{H}$ . Atom colours: green Cl, red O, grey C, white H.

hydroxyl groups in axial positions (Fig. 6b) linked through an intramolecular H-bond ( $\text{O}_1 \cdots \text{O}_2 \text{ } \frac{1}{4} 2.876(3) \text{ \AA}$ ). The molecules organize into dimers held together by two, squarely arranged H-bonds ( $\text{O}_1 \cdots \text{O}_2 \text{ } \frac{1}{4} 2.921(3) \text{ \AA}$ ). trans- and cis-Diols 14 and 15 were used to unravel the possible elimination pathways leading to anthrone 10.

As the first experiment, the thermal elimination in DMF/ $\text{H}_2\text{O}$  at  $90 \text{ }^\circ\text{C}$  for 5 h was attempted with trans- and cis-diols 14 and 15 (Table 1, entries 1&2). In both cases, no conversion was observed, which clearly suggests that heat alone is not sufficient for the re-action to occur. Therefore, we reacted independently trans- and cis-diols 14 and 15 in the presence of  $\text{Na}_2\text{S}_2\text{O}_4$  at  $90 \text{ }^\circ\text{C}$  for 5 h following the protocol conditions used to transform 1,8-dichloroanthraquinone 5 into anthrone 10. Whereas trans-diol 14 did not yield any product, the reaction with cis-diol 15 led to the

formation of anthrone 10 in 64% yield (Table 1, entries 3&4). This observation suggests that cis-diol 15 is likely the intermediate that, formed in the  $\text{Na}_2\text{S}_2\text{O}_4$ -mediated reduction, allows the trans-formation of quinone 5 into anthrone 10. When the diols are reacted independently in the presence of HCl at  $90 \text{ }^\circ\text{C}$  for 5 h, both led to desired anthrone 10 quantitatively (Table 1, entries 5&6), as previously suggested by Cristol [45].

Taken all together, these observations suggest that the  $\text{Na}_2\text{S}_2\text{O}_4$ -mediated reaction to anthrone 10 follows an antiperiplanar elimination pathway as only the cis isomer reacts under these reductive conditions (Scheme 4). Indeed, only cis-diol 15 can adopt a conformation suitable for an antiperiplanar elimination, i.e. hydrogen atom and hydroxyl group in axial positions. The elimination can occur through two different routes (Scheme 5). In route 1, a  $\text{HSO}_3^-$  anion, generated from thermal decomposition of

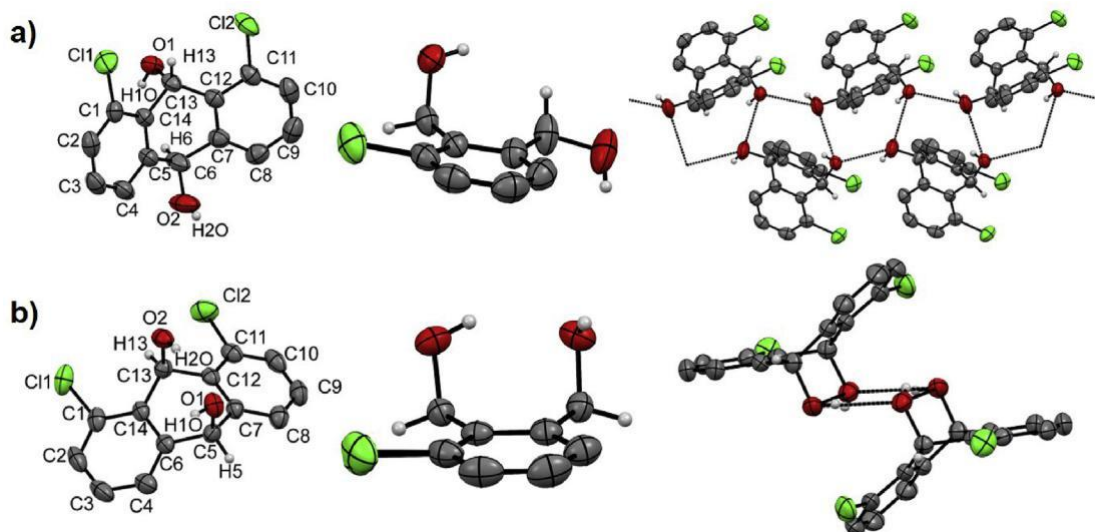
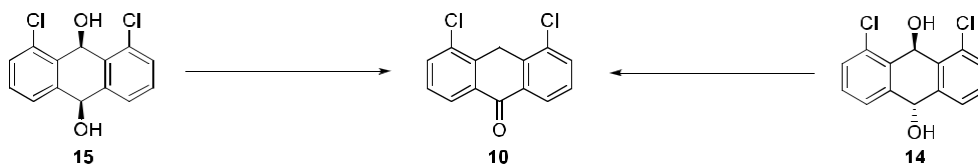


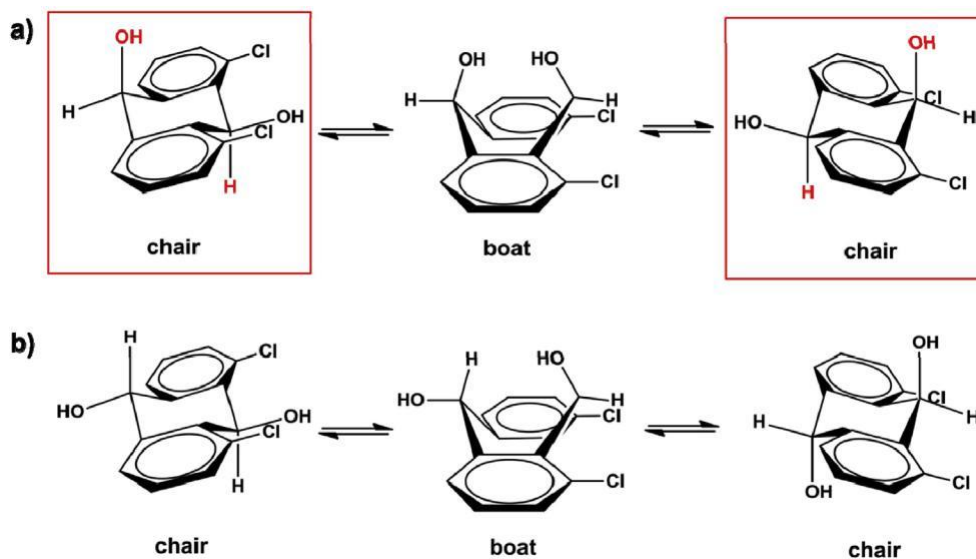
Fig. 6. a) Crystal structure of compound 14; space group: P21. b) Crystal structure of compound 15; space group: P-1. H atoms are omitted except for OH and Csp<sup>2</sup>H. Atom colours: green Cl, red O, grey C, white H.

Table 1

Mechanistic study of the Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>-mediated reduction of 1,8-dichloroanthraquinone to anthrone 10: reduction attempts of diols 14 (trans) and 15 (cis).

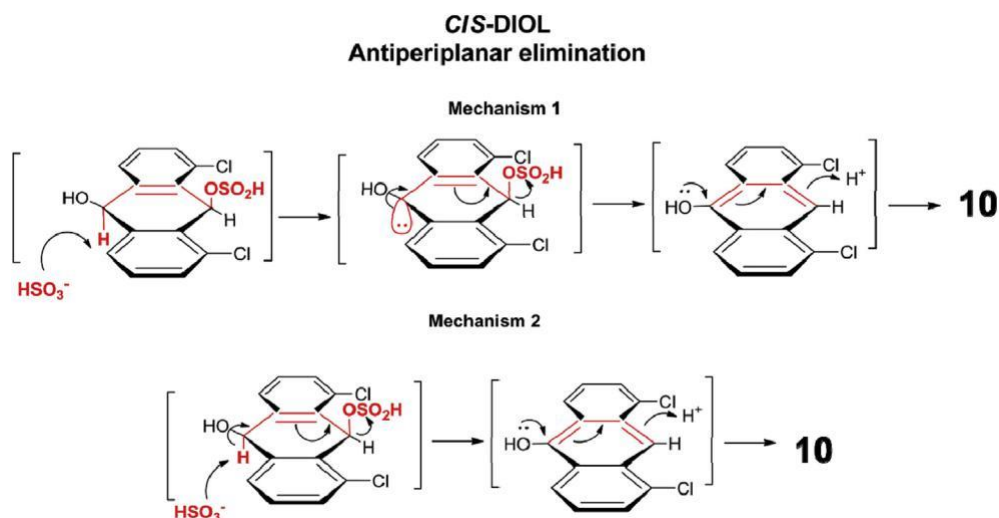


entry	Diol	Reagent	Solvent	Time	Temperature	Yield
1	14	e	DMF/H <sub>2</sub> O	5 h	90 C	0%
2	15	e	DMF/H <sub>2</sub> O	5 h	90 C	0%
3	14	Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	DMF/H <sub>2</sub> O	5 h	90 C	0%
4	15	Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	DMF/H <sub>2</sub> O	5 h	90 C	64%
5	14	HCl	DMF/H <sub>2</sub> O	5 h	90 C	96%
6	15	HCl	DMF/H <sub>2</sub> O	5 h	90 C	93%



Scheme 4. Possible conformations of a) cis-diol 15 and b) trans-diol 14. The red squares indicate the only conformation able to give antiperiplanar elimination.





Scheme 5. Possible antiperiplanar elimination routes.

$\text{Na}_2\text{S}_2\text{O}_4$ , may deprotonate the axial hydrogen triggering an  $\text{E}_{1\text{cb}}$ -type elimination reaction (top, Scheme 5). In route 2, an anti-periplanar  $\text{E}_{2\text{like}}$  elimination is proposed (down, Scheme 5). In both mechanistic propositions, a sulfinate moiety is evoked as leaving group (possibly formed in the presence of  $\text{Na}_2\text{S}_2\text{O}_4$  under refluxing conditions).

#### 2.4. Homomolecular and heteromolecular hydrogen-bonding recognition properties

##### 2.4.1. H-bonding recognition at the solid state

Suitable crystals of  $2^{\text{Me}}$  for X-ray diffraction analysis were obtained by vapor diffusion of  $\text{H}_2\text{O}$  into a DMSO solution (Fig. 7a). In the solid state, molecule  $2^{\text{Me}}$  dimerizes into H-bonded complexes ( $2^{\text{Me}} \cdot 2^{\text{Me}}$ ), in which each boronic acid moiety frontally engages into double DA-AD-type arrays ( $\text{O}_1 \cdots \text{O}_4$   $\frac{1}{4}$  2.850(3) Å and  $\text{O}_2 \cdots$

$\text{O}_3$   $\frac{1}{4}$  2.787(3) Å) as syn-anti conformers.

Notably, the syn-anti conformational preference of the hydroxyl groups forces the boronic acid moieties in the peri-positions to twist, and adopt a non-planar arrangement with the anthracene

core(dihedral angles:  $\text{O}_1\text{eB}_1\text{eC}_1\text{eC}_2$   $\frac{1}{4}$  58.9(3),  $\text{O}_2\text{eB}_1\text{eC}_1\text{eC}_{14}$   $\frac{1}{4}$  59.2(3),  $\text{O}_3\text{eB}_2\text{eC}_{11}\text{eC}_{12}$   $\frac{1}{4}$  38.1(4) and  $\text{O}_4\text{eB}_2\text{eC}_{11}\text{eC}_{10}$  36.5(5)). The arrangement of the boronic acids

observed in  $2^{\text{Me}}$  contrasts that observed for the boronate ester moieties in compound  $8^{\text{Me}}$ , in which the boron-containing functionalities and the polycyclic aromatic skeleton are co-planar. Sol-vent molecules of DMSO are also present in the crystal, each H-bonded with the hydroxyl moieties of  $2^{\text{Me}}$  ( $\text{O}_2 \cdots \text{O}_8$   $\frac{1}{4}$  2.638(16) Å and  $\text{O}_4 \cdots \text{O}_7$   $\frac{1}{4}$  2.650(3) Å). Suitable crystals of molecule 3 were obtained by vapor diffusion of EtOH into a  $\text{CHCl}_3$  solution (Fig. 7b). As for molecule  $2^{\text{Me}}$ , derivative 3 dimerizes into H-bonded complexes (3 3), in which each boronic acid moiety adopts a syn-anti conformation and frontally engages into double DA-AD-type H-bonding arrays ( $\text{O}_1 \cdots \text{O}_3$   $\frac{1}{4}$  2.781(3) Å and  $\text{O}_2 \cdots \text{O}_4$   $\frac{1}{4}$  2.787(4) Å). In contrast to the crystal packing of molecule  $2^{\text{Me}}$ , each complex 3 3 establishes lateral H-bonds with adjacent dimers ( $\text{O}_1 \cdots$

$\text{O}_3$   $\frac{1}{4}$  2.798(3) Å) forming a ladder-type network. As for  $2^{\text{Me}} \cdot 2^{\text{Me}}$ , the boronic acid moieties and the anthracenyl core adopt a non-planar conformation in dimer 3 3.

##### 2.4.2. Heteromolecular H-bonding recognition in solution

At last, we attempted to study the formation of H-bonded

heteromolecular complexes in solution using boronic acids derivatives ( $2^{\text{R}}$  and 3) as the H-bonding DDDD partners and molecule 1 as the complementary AAAA-type acceptor. Due to the poor solubility of boronic acids  $2^{\text{Me}}$  and 3 in non-competitive organic solvents, any attempts to study their H-bonding recognition properties by  $^1\text{H-NMR}$  titration failed. Thus we turned our attention to UV-vis absorption spectroscopy, and monitored any changes in the absorption profile of H-bonding acceptor 1 ( $c$   $\frac{1}{4}$   $10^6$  mol  $\text{L}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ) upon increasing amount of H-bonding donor  $2^{\text{Me}}$  (Fig. 8). As one can clearly notice in the absorption profiles shown in Fig. 8, only a decrease in the intensity of the absorption bands characteristic of acceptor 1 (420e470 nm) was observed upon increasing addition (up to 0.5 equivalents) of donor  $2^{\text{Me}}$ . No energy shifts were observed for any of the electronic transitions. Further increases of the concentration of  $2^{\text{Me}}$  (up to 3 equivalents) did not lead to any significant changes of the absorption envelope of acceptor 1. If one considers that shifts in energy are frequently observed for the strongest absorption bands when a chromophore engages in H-bonding interactions in solution, we concluded that if a non-covalent complex is formed, this crashes out of solution (some precipitate was observed in the cuvette). H-bonding donor 3 displayed a similar behaviour to that of  $2^{\text{Me}}$ , whereas no spectral changes were observed when  $2^{\text{TEG}}$  was used. Despite the numerous attempts, we could not grow suitable crystals for X-ray diffraction analysis of the H-bonded complexes ( $2^{\text{Me}}$  1 and 3 1).

Given the good solubility of H-bonding donor  $2^{\text{TEG}}$  in organic solvents, we studied the binding of  $2^{\text{TEG}}$  with 1 by means of  $^1\text{H-NMR}$  titration. As peaks fingerprinting the boronic acid protons are generally not visible in  $\text{CDCl}_3$  [31], a 1:1 mixture of  $\text{C}_6\text{D}_6$  and  $\text{THF-d}_8$  was first employed, but extensive precipitation occurred upon addition of both components to the solution. Instead, reduced precipitation was noticed with a 95:5 mixture of  $\text{C}_6\text{D}_6$  and  $\text{DMSO-d}_6$ . Titration experiments were thus performed in the latter solvent mixture using H-bonding donor  $2^{\text{TEG}}$  and acceptor 1 as host and acceptor, respectively.

Although some precipitation and peak broadening were observed during the titration experiments (Fig. 9), addition of increasing amount of 1 to a 5 mM solution of  $2^{\text{TEG}}$  led to noticeable downfield shift ( $\Delta\delta$   $\frac{1}{4}$  1.31 ppm) of the  $-\text{B}(\text{OH})_2$  proton resonances, suggesting the presence of H-bonding interactions. Together with the  $-\text{B}(\text{OH})_2$  resonances, also the peaks of the proton resonance of the aromatic peri-proton CH in position 9 revealed significant

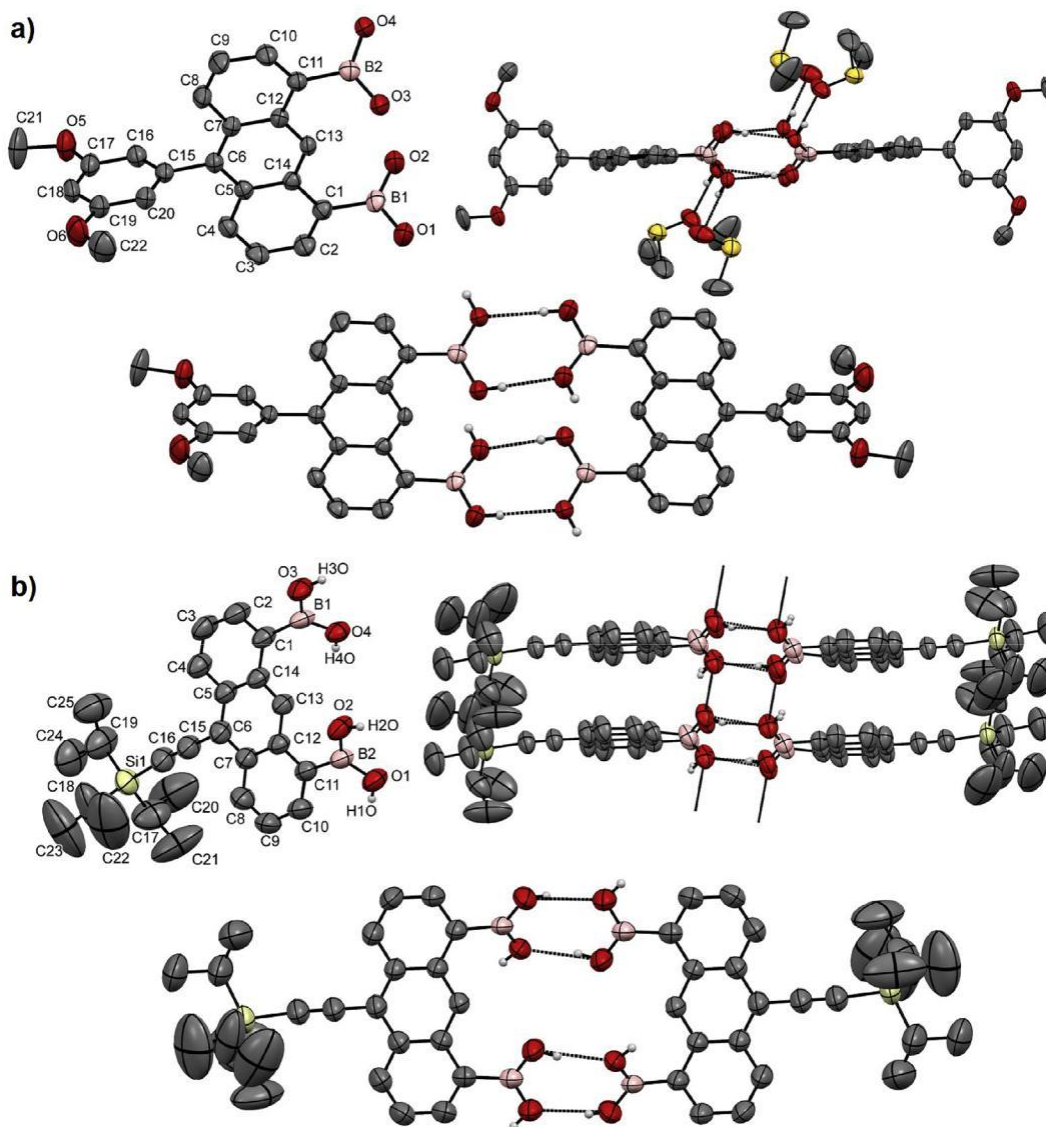


Fig. 7. a) X-ray crystal structure of compound 2<sup>Me</sup><sub>6</sub>, space group: P-21/c. b) X-ray crystal structure of compound 3; space group: C2/c. H atoms are omitted except for B(OH)<sub>2</sub>. Atom colours: pink B, red O, pale yellow Si, yellow S, grey C, white H.

downfield shifts ( $\Delta\delta \approx 0.49$  ppm) upon addition of 1, confirming the presence of interactions involving the frontal boronic acid moieties. Unfortunately, the slight precipitation observed during the titration experiments together with the significant peak broadening (Fig. 9) hampered any further attempts to produce meaningful thermo-dynamic data in solution.

### 3. Conclusion

In summary, herein we developed two synthetic pathways to prepare 1,8,10-trisubstituted anthracenes that, bearing two boronic acid functionalities, can act as multiple H-bonding donors. Whereas in the first approach the peri-substituted anthracenyl derivatives are synthesized through the addition of a Grignard nucleophile to 1,8-dichloroanthraquinone, in the second avenue a triflate-bearing 1,8,10-trisubstituted anthracene is prepared by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> reduction of the anthraquinone into the anthrone precursor and functionalized through a metal-catalysed cross-coupling reaction. Complementary studies of the Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>-mediated reduction of 1,8-

dichloroanthraquinone allowed to shed further light on the mechanism leading to the anthrone intermediate, suggesting that the reaction possibly involves the formation of a cis-diol derivative that can undergo antiperiplanar elimination. X-ray diffraction investigations of the 1,8,10-trisubstituted anthracenyl boronic acids in the solid-state show that the molecules self-assemble into dimers through the formation of frontal H-bonds established between the anti-syn conformers of the boronic acid moieties. The binding properties of the boronic acids (DDDD) were also studied in solution in the presence of a suitable multiple H-bonding acceptor (AAAA), diisoquinolino[3,4-b:4',3'-g][1,8]naphthyridine. While UV-Vis spectroscopic investigations did not lead to any conclusive observations, <sup>1</sup>H-NMR titration experiments showed a significant downfield shift of the B(OH)<sub>2</sub> proton resonances, suggesting the presence of H-bonding interactions. However, the poor solubility of the H-bonded complexes hampered precise determination of the stoichiometry of the complexes and of any thermodynamic parameters.

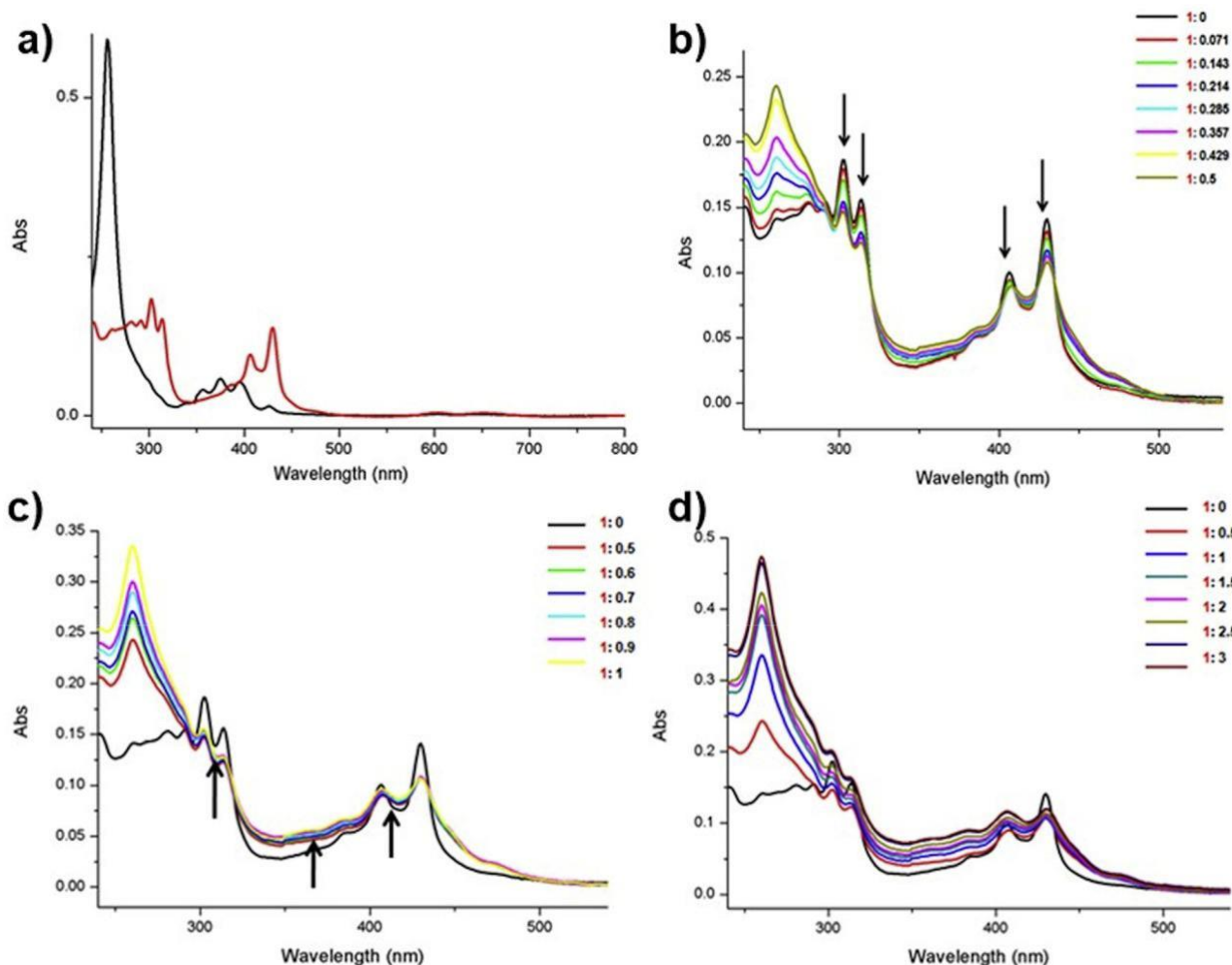


Fig. 8. a) UV-Vis absorption profiles of acceptor 1 (red) and donor 2<sup>Me</sup> (black) in CH<sub>2</sub>Cl<sub>2</sub> at 10<sup>-6</sup> M. b-d) UV-Vis titration experiments in CH<sub>2</sub>Cl<sub>2</sub> of acceptor 1 (10<sup>-6</sup> M) with donor 2<sup>Me</sup> (the 1:2<sup>Me</sup> ratio is displayed in the legend).

#### 4. Experimental part

##### 4.1. General methods

Chemicals were purchased from Sigma Aldrich, Acros Organics, Fluorochem, TCI, Carbosynth, and ABCR, and were used as received. Solvents were purchased from Sigma Aldrich and Acros Organics. Deuterated solvents were purchased from Eurisotop. General solvents were distilled in vacuo. Anhydrous solvents such as Et<sub>2</sub>O and THF were distilled from Na/benzophenone; CH<sub>2</sub>Cl<sub>2</sub> from phosphorus pentoxide. Anhydrous DMF, 1,4-dioxane and MeOH were purchased and used without further purification. Anhydrous conditions were achieved by drying Schlenk lines, 2-neck flasks or 3-neck flasks by flaming with a heat gun under vacuum and purging with argon. The inert atmosphere was maintained using argon-filled balloons equipped with a syringe and needle that was used to penetrate the silicon stoppers used to close the flasks' necks. The addition of liquid reagents was done by means of dried plastic syringes or by cannulation. Column chromatography was carried out using Grace silica gel 60 (particle size 40e63 mm). Melting points (m.p.) were measured on a Büchi Melting Point B-545. All of the melting points have been measured in open capillary tubes and have not been corrected. Nuclear magnetic resonance (NMR) <sup>1</sup>H and <sup>13</sup>C spectra were obtained on a 400 MHz NMR (Jeol JNM EX-

400). Chemical shifts were reported in ppm according to tetramethylsilane using the solvent residual signal as an internal reference (CDCl<sub>3</sub>: <sup>1</sup>H 7.26 ppm, <sup>13</sup>C 77.16 ppm, CDCl<sub>2</sub>: <sup>1</sup>H 5.32 ppm, <sup>13</sup>C 53.84 ppm, CD<sub>3</sub>OD: <sup>1</sup>H 3.30 ppm, <sup>13</sup>C 49.00 ppm, pMSO-d<sub>6</sub>: <sup>1</sup>H 2.50 ppm, <sup>13</sup>C 39.52 ppm, (CD<sub>3</sub>)<sub>2</sub>CO: <sup>1</sup>H 2.05 ppm, <sup>13</sup>C 29.84 ppm). Coupling constants (J) were given in Hz. Resonance multiplicity was described as s (singlet), d (doublet), t (triplet), q (quartet). Carbon spectra were acquired with a complete decoupling for the proton. All spectra were recorded at 25 °C. Infrared spectra (IR) were recorded on a PerkinElmer Spectrum II FT-IR System UATR, mounted with a diamond crystal. Selected absorption bands are reported in wavenumber (cm<sup>-1</sup>). Mass spectrometry was generally performed by the Federation de Recherche ICOA/CBM (FR2708) platform of Orleans in France. High-resolution ESI mass spectra (HRMS) were performed on a Bruker maXis Q-TOF in the positive ion mode. The analytes were dissolved in a suitable solvent at a concentration of 1 mg/mL and diluted 200 times in methanol (z5 ng/mL). The diluted solutions (1 mL) were delivered to the ESI source by a Dionex Ultimate 3000 RSLC chain used in FIA (Flow Injection Analysis) mode at a flow rate of 200 mL/min with a mixture of CH<sub>3</sub>CN/H<sub>2</sub>O p 0.1% of HCO<sub>2</sub>H (65/35). ESI conditions were as follows: capillary voltage was set at 4.5 kV; dry nitrogen was used as nebulizing gas at 0.6 bars and as drying gas set at 200 °C and 7.0 L/min. ESI-MS spectra were

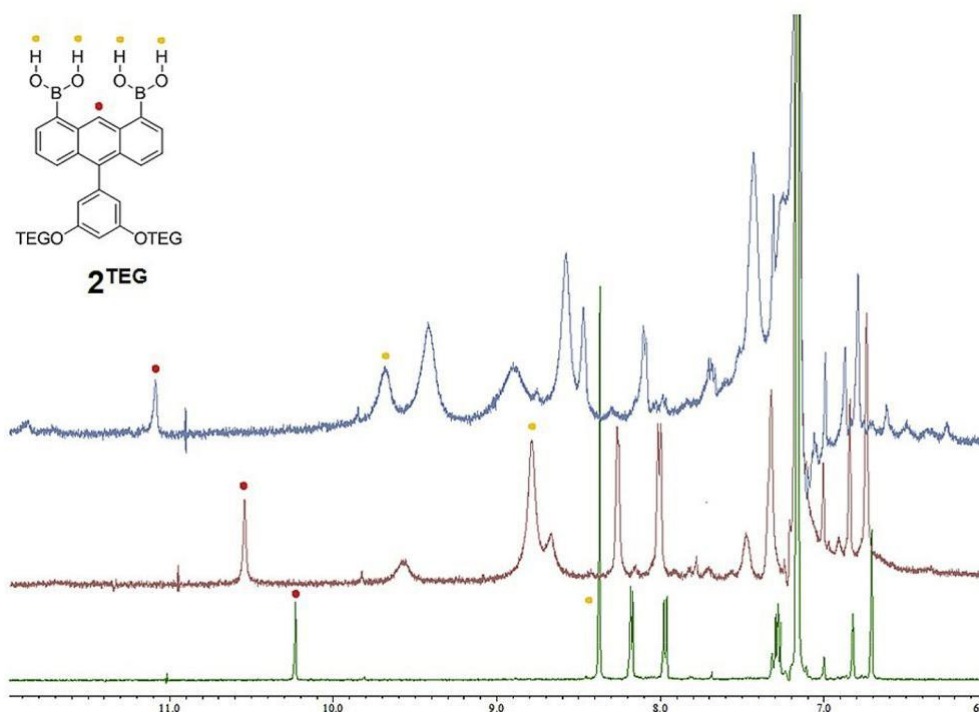


Fig. 9. Selected regions of  $^1\text{H}$  NMR titration experiments of H-bonding donor  $2^{\text{TEG}}$  (5 mM) upon addition of H-bonding acceptor **1** (500 MHz,  $\text{C}_6\text{D}_6/\text{DMSO-d}_6$  95/5, 298 K). The dots indicate the diagnostic proton resonances of H-bonding donor  $2^{\text{TEG}}$ . The molar ratios  $2^{\text{TEG}}:1$  of the different spectra are: 1:0 (bottom), 1:0.5 (middle), 1:1 (top).

recorded at 1 Hz in the range of 50e3000 m/z. Calibration was performed with ESI-TOF Tuning mix from Agilent and corrected using lock masses at m/z 299.294457 (methyl stearate) and 1221.990638 (HP-1221). Data were processed using Bruker Data-Analysis 4.1 software. MALDI-MS were performed by the Centre de spectrometrie de masse at the Universite de Mons and recorded using a Waters QToF Premier mass spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 mW delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analyses were performed in the reflectron mode at a resolution of about 10,000. The matrix solution (1 mL) was applied to a stainless-steel target and air dried. Analyte samples were dissolved in a suitable solvent to obtain 1 mg/mL solutions. 1 mL aliquots of those solutions were applied onto the target area already bearing the matrix crystals, and air dried. For the recording of the single-stage MS spectra, the quadrupole (rf-only mode) was set to pass ions from 100 to 1000 Th, and all ions were transmitted into the pusher region of the time-of-flight analyser where they were analyzed with 1 s integration time.

#### 4.2. 10-(3,5-dimethoxyphenyl)anthracene-1,8-diyl)diboronic acid $2^{\text{Me}}$

To a suspension of compound  $8^{\text{Me}}$  (100 mg, 0.186 mmol) in  $\text{Et}_2\text{O}$  (9.6 mL), a solution of diethanolamine (40 mL, 0.409 mmol) in *i*-PrOH (2 mL) was added. The mixture was stirred for 3 h at room temperature and the solution filtered. The solid was suspended in 1 M aq HCl (6.4 mL). The mixture was stirred at room temperature for 3 h, filtered and the solid washed with  $\text{H}_2\text{O}$  (3 5 mL). The solid was dried using a freeze-dryer overnight to yield compound  $2^{\text{Me}}$  (73 mg, 98%) as a bright yellow powder. M.p. 276e277 C. FTIR (ATR)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ):  $\tilde{\nu}$  3375, 1590, 1381, 1201, 1150, 1061, 1030, 992, 755, 739.  $^1\text{H}$ -NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  9.43 (s, 1H), 8.35 (s, 4H), 7.64 (d, J  $\frac{1}{4}$  6.0 Hz, 2H), 7.56 (d, J  $\frac{1}{4}$  8.7 Hz, 2H), 7.36 (t, J  $\frac{1}{4}$  7.6 Hz, 2H), 6.70

(s, 1H), 6.46 (s, 2H), 3.79 (s, 6H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  160.5, 141.0, 136.6, 136.1, 132.6, 130.8, 129.2, 128.7, 126.9, 124.9, 109.1, 99.0, 55.3.  $^{11}\text{B}$ -NMR (128 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  30.7. HRMS (ESI): m/z [M  $\pm$  H] $^{\pm}$  Calcd for  $\text{C}_{22}\text{H}_{21}\text{B}_2\text{O}_6$  403.1526; Found 403.1523.

#### 4.3. (10-(3,5-bis(2-(2-methoxyethoxy)ethoxy)phenyl)anthracene-1,8-diyl)diboronic acid $2^{\text{TEG}}$

In a dry Schlenk, compound  $7^{\text{TEG}}$  (169 mg, 0.261 mmol), bis(-neopentyl glycolato)diboron (146 mg, 0.644 mmol), XPhos (10 mg, 0.0208 mmol) and NaOAc (270 mg, 3.3 mmol) were added in 1,4-dioxane (4.5 mL). The resulting suspension was degassed through 3 freeze-pump-thaw cycles and  $[\text{Pd}_2(\text{dba})_3]$  (14 mg, 0.016 mmol) added to the mixture. The reaction was stirred at 90 C for 1.5 h. The solvent was removed in vacuo. The catalyst was precipitated upon addition of toluene, removed through filtration on celite and the filtrate concentrated. To a solution of the resulting crude mixture in  $\text{Et}_2\text{O}$  (9.6 mL), a solution of diethanolamine (40 mL, 0.409 mmol) in *i*-PrOH (2 mL) was added. The mixture was stirred for 2 h at room temperature. The solution was washed by centrifugation upon addition of  $\text{Et}_2\text{O}$  (4 8 mL) and a solid isolated. The solid was suspended in 1 M aq HCl (6.4 mL). The mixture was stirred at room temperature for 2 h. The solid was washed by centrifugation upon addition of  $\text{H}_2\text{O}$  (4 8 mL) and a solid isolated. The solid was dried using a freeze-dryer overnight, yielding compound  $2^{\text{TEG}}$  (64 mg, 37%) as a white powder. M.p. 113e115 C. FTIR (ATR)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ):  $\tilde{\nu}$  3344, 2875, 1587, 1429, 1166, 1093, 826.  $^1\text{H}$ -NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  9.42 (s, 1H), 8.37 (s, 4H), 7.64 (d, J  $\frac{1}{4}$  6.5 Hz, 2H), 7.57 (d, J  $\frac{1}{4}$  8.8 Hz, 2H), 7.36 (dd, J  $\frac{1}{4}$  8.8, 6.5 Hz, 2H), 6.73 (s, 1H), 6.44 (d, J  $\frac{1}{4}$  2.1 Hz, 2H), 4.13 (t, J  $\frac{1}{4}$  4.2 Hz, 4H), 3.73 (t, J  $\frac{1}{4}$  4.2 Hz, 4H), 3.58e3.56 (m, 4H), 3.52e3.48 (m, 8H), 3.41e3.38 (m, 4H), 3.20 (s, 6H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  170.9, 159.7, 141.0, 132.6, 130.8, 128.7, 126.9, 124.9, 109.7, 99.9, 71.3, 70.0, 69.8, 69.6, 69.0, 67.4, 58.12 (carbon missing probably due to overlap).  $^{11}\text{B}$ -NMR (128 MHz,



DMSO-d<sub>6</sub>): not detected. HRMS (ESI): m/z [M + Na]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>44</sub>B<sub>2</sub>NaO<sub>12</sub> 689.2922 Found 689.2921.

#### 4.4. (10-((triosopropylsilyl)ethynyl)anthracene-1,8-diyl)diboric acid 3

To a suspension of compound 12 (90 mg, 0.1545 mmol) in Et<sub>2</sub>O (8 mL), a solution of diethanolamine (33 mL, 0.337 mmol) in i-PrOH (1.7 mL) was added. The mixture was stirred for 3 h at room temperature. The suspension was filtered and the solid obtained suspended in 1 M aq HCl (6.4 mL). The mixture was stirred at room temperature for 3 h. The solution was filtered and the solid washed with H<sub>2</sub>O (3.5 mL). The solid was dried using a freeze-dryer overnight, yielding desired compound 3 (25 mg, 37%) as a bright yellow powder. M.p. 292e293 C. FTIR (ATR)  $\tilde{\nu}$  (cm<sup>-1</sup>):  $\tilde{\nu}$  3326, 2940, 2863, 1366, 1326, 1239, 1115, 1032, 882, 748, 662. <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  9.54 (s, 1H), 8.50 (d, J ¼ 8.5 Hz, 2H), 8.44 (s, 4H), 7.74 (d, J ¼ 6.2 Hz, 2H), 7.64 (t, J ¼ 8.5 Hz, 2H), 1.24 (s, 21H). <sup>13</sup>C-NMR (100 MHz, DMSO-d<sub>6</sub>):  $\delta$  132.5, 131.9, 131.6, 131.4, 126.6, 126.4, 115.8, 101.7, 18.7, 10.9 (2 carbon missing probably due to overlap). <sup>11</sup>B-NMR (128 MHz, DMSO-d<sub>6</sub>):  $\delta$  31.3. HRMS (ESI): m/z [M + H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>33</sub>B<sub>2</sub>O<sub>4</sub>Si 447.2338; Found 447.2336.

#### 4.5. 1,8-dichloro-10-(3,5-dimethoxyphenyl)-10-hydroxyanthracene-9(10H)-one 6

In a dry 2 neck flask, 1-bromo-3,5-dimethoxybenzene 4 (108.5 mg, 0.5 mmol) was dissolved in dry THF (2 mL). 0.5 mL of the resulting solution were added to a second dry two neck flask containing Mg (14 mg, 0.575 mmol) and a crystal of I<sub>2</sub>. The suspension was heated up (around 60 C) until reaching a point in which a transparent suspension was obtained (the iodine disjunction). As soon as no suspension was observed, the rest of the solution containing 4 was added to the solution. The mixture was stirred for 1 h at room temperature. The resulting Grignard suspension was added to a dry two neck flask containing an ice-cold solution of compound 5 (138.5 mg, 0.5 mmol) dissolved in dry THF (3 mL). The reaction was let to reach room temperature stirring overnight. The solvent was removed in vacuo and compound 6 was purified by silica gel column chromatography (Cyclohexane/EtOAc 75:25) as a white solid (139 mg, 67%). M.p. 232e233 C. FTIR (ATR)  $\tilde{\nu}$  (cm<sup>-1</sup>):  $\tilde{\nu}$  1677, 1587, 1244, 1192, 1151, 1134, 974, 788, 722. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.79e7.76 (m, 2H), 7.46e7.44 (m, 4H), 6.35 (d, J ¼ 2.2 Hz, 2H), 6.24 (t, J ¼ 2.2 Hz, 1H), 3.66 (s, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  183.4, 161.0, 148.1, 147.4, 133.0, 131.5, 130.5, 124.7, 104.3, 99.2, 74.1, 55.5 (1 peak missing, probably due to overlap).

#### 4.6. 1,8-dichloro-10-(3,5-dimethoxyphenyl)anthracene 7<sup>Me</sup>

In a dry 30 mL Schlenk containing a suspension of LiAlH<sub>4</sub> (44 mg, 1.152 mmol) in dry Et<sub>2</sub>O (4.5 mL) and cooled down at 0 C was added BF<sub>3</sub>·Et<sub>2</sub>O (0.329 mL, 2.6 mmol). A solution of 6 (133 mg, 0.48 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (4.5 mL) was added and the mixture stirred at reflux overnight. After cooling using an ice-bath, MeOH (4 mL), H<sub>2</sub>O (2 mL) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were added. The phases were separated, and the aqueous phase extracted with CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO<sub>4</sub> and filtered. The solvent was removed in vacuo and compound 7<sup>Me</sup> purified by silica gel column chromatography (Pentane/EtOAc 98:2) as a pale yellow solid (188 mg, 95%). M.p. 224e225 C. FTIR (ATR)  $\tilde{\nu}$  (cm<sup>-1</sup>):  $\tilde{\nu}$  1592, 1359, 1154, 845, 814, 123, 697. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.39 (s, 1H), 7.67 (d, J ¼ 8.9 Hz, 2H), 7.63 (d, J ¼ 7.3 Hz, 2H), 7.32e7.28 (m, 2H), 6.66e6.65 (m, 1H), 6.56e6.55 (m, 2H), 3.83 (s, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):

$\delta$  160.9, 140.4, 138.5, 132.7, 131.3, 129.2, 126.4, 126.0, 125.6, 121.1, 109.3, 100.1, 55.6. HRMS (ESI): m/z [M]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>16</sub>O<sub>2</sub>Cl<sub>2</sub> 382.0527; Found 382.0515.

#### 4.7. 10-(3,5-bis(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-1,8-dichloro anthracene 7<sup>TEG</sup>

In a dry Schlenk, compound 7<sup>Me</sup> (70 mg, 0.182 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (3 mL) and cooled down at 78 C. BBr<sub>3</sub> (0.5 mL, 0.5 mmol, 1 M in hexane) cooled at 78 C was added at this temperature. The solution was let to reach room temperature overnight, poured into ice water and extracted with EtOAc (3.5 mL). The organic layers were combined, dried over MgSO<sub>4</sub>, filtered and evaporated. The residue was precipitated in pentane. In a dry Schlenk, 50 mg of the solid obtained, TEG-OTs (107.5 mg, 0.338 mmol) and K<sub>2</sub>CO<sub>3</sub> (77.2 mg, 0.56 mmol) were added to dry DMF (1 mL). The reaction was stirred at 50 C for 48 h. The mixture was diluted with H<sub>2</sub>O (6 mL) and the aqueous suspension extracted with CH<sub>2</sub>Cl<sub>2</sub> (3.12 mL). The combined organic layers were dried over MgSO<sub>4</sub> and the solvent removed in vacuo. Compound 7<sup>TEG</sup> was purified through silica gel column chromatography (EtOAc/MeOH 99:1) as a brown viscous oil (55 mg, 61%). M.p. 53e54 C. FTIR (ATR)  $\tilde{\nu}$  (cm<sup>-1</sup>):  $\tilde{\nu}$  2872, 1592, 1434, 1350, 1169, 1100, 1064, 845, 815. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.36 (s, 1H), 7.64e7.60 (m, 4H), 7.28e7.26 (m, 2H), 6.67 (s, 1H), 6.54 (d, J ¼ 2.0 Hz, 2H), 4.13 (t, J ¼ 4.7 Hz, 4H), 3.85 (t, J ¼ 4.7 Hz, 4H), 3.74e3.71 (m, 4H), 3.68e3.65 (m, 4H),

3.64e3.60 (m, 4H), 3.53e3.50 (m, 4H), 3.34 (s, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  160.0, 140.2, 138.5, 132.6, 131.2, 129.2, 126.5, 126.0, 125.6, 121.1, 110.2, 101.3, 72.0, 71.0, 70.8, 70.7, 69.8, 67.8, 59.2. HRMS (MALDI-TOF): m/z [M]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>40</sub>O<sub>8</sub>Cl<sub>2</sub> 646.2100; Found 646.2095.

#### 4.8. 2,2'-(10-(3,5-dimethoxyphenyl)anthracene-1,8-diyl)bis(5,5-dimethyl-1,3,2-dioxaborinane) 8<sup>Me</sup>

In a dry Schlenk, compound 7<sup>Me</sup> (100 mg, 0.261 mmol), bis(-neopentyl glycolato)diboron (146 mg, 0.644 mmol), XPhos (10 mg, 0.0208 mmol) and NaOAc (270 mg, 3.3 mmol) were added in 1,4-dioxane (4.5 mL). The resulting suspension was degassed through 3 freeze-pump-thaw cycles and [Pd<sub>2</sub>(dba)<sub>3</sub>] (14 mg, 0.016 mmol) added to the mixture. The reaction was stirred at 90 C for 2.5 h. The solvent was removed in vacuo. The catalyst was precipitated by addition of toluene and removed through filtration on celite. The filtrate was concentrated and precipitation in Et<sub>2</sub>O yielded compound 8<sup>Me</sup> as a light-yellow powder (80 mg, 57%). M.p. 292e293 C. FTIR (ATR)  $\tilde{\nu}$  (cm<sup>-1</sup>):  $\tilde{\nu}$  1584, 1283, 1248, 1138, 752, 675. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.26 (s, 1H), 8.03 (d, J ¼ 6.0 Hz, 2H), 7.76 (d, J ¼ 8.7 Hz, 2H), 7.31 (dd, J ¼ 8.7, 6.6 Hz, 2H), 6.64e6.60 (m, 1H), 6.56e6.55 (m, 2H), 3.98 (s, 8H), 3.81 (s, 6H), 1.17 (s, 12H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  160.7, 142.1, 137.3, 134.3, 134.1, 129.8, 129.5, 128.3, 124.5, 109.6, 99.7, 90.2, 72.8, 55.6, 32.1, 22.3. <sup>11</sup>B-NMR (128 MHz, CDCl<sub>3</sub>): 27.0.

#### 4.9. 4,5-dichloroanthracene-9-yl trifluoromethanesulfonate 9

In a dry 50 mL flask containing a suspension of compound 10 (200 mg, 0.763 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4.2 mL), DBU (228.6 mL, 1.527 mmol) was added dropwise over a period of 90 min (26 mL every 10 min). Trifluoromethanesulfonic anhydride (0.954 mmol, 160.5 mL, 1 M in CH<sub>2</sub>Cl<sub>2</sub>) was slowly added over a period of 90 min (110 mL every 10 min). The reaction was stirred at 0 C for 10 min, after which additional trifluoromethanesulfonic anhydride (200 mL) was added and the reaction stirred for 45 min. H<sub>2</sub>O (3 mL) was added to the reaction vessel and the resulting mixture stirred overnight. The phases were separated, and the aqueous layer

extracted with  $\text{CH}_2\text{Cl}_2$  (3 20 mL). The organic layers were combined, dried over  $\text{MgSO}_4$ , filtered and evaporated. The resulting crude was purified through silica gel column chromatography ( $\text{CH}_2\text{Cl}_2/\text{Cyclohexane}$  1:1) to yield compound **9** as a crystalline yellow solid (227 mg, 75%). M.p. 123e125 C. FTIR (ATR)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ):  $\tilde{\nu}$  1398, 1323, 1207, 1126, 891, 801, 726, 727.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.39 (s, 1H), 8.16 (d,  $J$   $\frac{1}{4}$  8.9 Hz, 2H), 7.71 (d,  $J$   $\frac{1}{4}$  7.3 Hz, 2H), 7.58 (dd,  $J$   $\frac{1}{4}$  8.9, 7.3 Hz, 2H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.2, 133.1, 129.6, 128.1, 126.9, 125.9, 122.6, 120.5 (carbon bearing the fluorine atoms missing). HRMS (ESI):  $m/z$  [ $M + H$ ] $^+$  Calcd for  $\text{C}_{15}\text{H}_8\text{O}_3\text{SF}_3\text{Cl}_2$  394.9517; Found 394.9512.

#### 4.10. 4,5-dichloroanthracen-9(10H)-one 10

In a 500 mL 2 neck flask, compound **5** (2.77 g, 9.99 mmol) was suspended in DMF (100 mL) and  $\text{H}_2\text{O}$  (100 mL). The resulting mixture was heated at 30 C and  $\text{Na}_2\text{S}_2\text{O}_4$  (1.739 g, 99.9 mmol) was added under argon. Every 15 min the temperature was raised by 10 C, reaching 90 C in 1.5 h. The reaction was stirred at 90 C for 3 h. The mixture was cooled down at room temperature and  $\text{CH}_2\text{Cl}_2$  (100 mL) was added. The phases were separated and the aqueous layer extracted with  $\text{CH}_2\text{Cl}_2$  (1 200 mL; 2 150 mL). The organic layers were collected, dried over  $\text{MgSO}_4$ , filtered and evaporated. The crude material was purified through silica gel column chromatography ( $\text{CH}_2\text{Cl}_2/\text{Cyclohexane}$  1:1), to yield compound **10** as a white crystalline solid (2.533 g, 96%). M.p. 187e189 C. FTIR (ATR)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ):  $\tilde{\nu}$  1656, 1589, 1308, 1283, 1133, 818, 740.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.29 (dd,  $J$   $\frac{1}{4}$  7.8, 1.1 Hz, 2H), 7.46 (t,  $J$   $\frac{1}{4}$  7.8, 2H), 4.25 (s, 2H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.9, 137.5, 134.3, 133.9, 133.0, 128.2, 126.5, 29.6. HRMS (ESI):  $m/z$  [ $M + H$ ] $^+$  Calcd for  $\text{C}_{14}\text{H}_9\text{OCl}_2$  263.0024; Found 263.0026. Spectral characterization agrees with previously reported data [46,47].

#### 4.11. ((4,5-dichloroanthracen-9-yl)ethynyl)diisopropyl(methyl) silane 11

In a dry Schlenk containing a suspension of compound **9** (980 mg, 2.49 mmol) and  $\text{NaOAc}$  (2.577 g, 31.41 mmol) in THF (70 mL),  $\text{CuI}$  (47.5 mg, 0.249 mmol) and  $\text{PPh}_3$  (261.24 mg, 0.996 mmol) were added. 3 freeze-pump-thaw cycles were performed and  $[\text{Pd}(\text{PPh}_3)_4]$  (288 mg, 0.249 mmol) added at room temperature. After an additional freeze-pump-thaw cycle triisopropylacetylene (614.5 mL, 2.739 mmol) was added and the reaction stirred at 60 C overnight. The solvent was removed in vacuo. The crude material was purified through silica gel column chromatography (Cyclohexane) to yield **11** as a crystalline yellow solid (936 mg, 88%). M.p. 169e171 C. FTIR (ATR)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ):  $\tilde{\nu}$  2941, 2864, 1441, 1339, 1146, 994, 880, 736, 677.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.26 (s, 1H), 8.55 (d,  $J$   $\frac{1}{4}$  8.5 Hz, 2H), 7.64 (d,  $J$   $\frac{1}{4}$  7.1 Hz, 2H), 7.50 (dd,  $J$   $\frac{1}{4}$  8.5, 7.1 Hz, 2H), 1.26 (s, 21H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  134.1, 133.1, 129.7, 126.9, 126.4, 126.2, 121.9, 119.5, 104.6, 102.7, 19.0, 11.6. HRMS (ESI):  $m/z$  [ $M + H$ ] $^+$  Calcd for  $\text{C}_{25}\text{H}_{29}\text{SiCl}_2$  427.1410; Found 427.1406.

#### 4.12. ((4,5-bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)anthracen-9-yl)ethynyl) triisopropylsilane 12

In a dry Schlenk, compound **11** (556 mg, 1.300 mmol), bis(neopentyl glycolato)diboron (725 mg, 3.211 mmol), XPhos (50 mg, 0.104 mmol) and  $\text{NaOAc}$  (1.345 g, 16.400 mmol) were added in dry 1,4-dioxane (4.5 mL). The resulting suspension was degassed through 3 freeze-pump-thaw cycles and  $[\text{Pd}_2(\text{dba})_3]$  (14 mg, 0.016 mmol) added to the mixture. The reaction was stirred at 90 C for 1 h. The solvent was removed in vacuo. The catalyst was precipitated upon addition of toluene and removed through

filtration on celite. The filtrate was concentrated in vacuo. A white powder was precipitated upon addition of n-hexane and removed through filtration on celite. The solvent was removed in vacuo, yielding the desired compound **12** (151 mg, 20%) as a pale-yellow powder. M.p. 97e100 C. FTIR (ATR)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ):  $\tilde{\nu}$  2957, 2933, 1417, 1385, 1341, 1289, 1249, 1142, 663.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.25 (s, 1H), 8.73 (d,  $J$   $\frac{1}{4}$  8.5 Hz, 2H), 8.08 (d,  $J$   $\frac{1}{4}$  6.6 Hz, 2H), 7.54 (t,  $J$   $\frac{1}{4}$  8.5 Hz, 2H), 3.97 (s, 8H), 1.27e1.26 (m, 21H), 1.16 (s, 12H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  134.8, 134.1, 132.7, 131.8, 129.7, 125.9, 104.4, 88.9, 72.8, 32.1, 22.3, 19.1, 11.7 (2 peaks missing probably due to overlap).  $^{11}\text{B-NMR}$  (128 MHz,  $\text{CDCl}_3$ ):  $\delta$  27.63.

#### 4.13. 4,5-dichloro-10-hydroxyanthracen-9(10H)-one 13

In a 500 mL flask containing a suspension of compound **5** (2.77 g, 9.99 mmol) in DMF (100 mL) and  $\text{H}_2\text{O}$  (100 mL),  $\text{Na}_2\text{S}_2\text{O}_4$  (1.739 g, 99.9 mmol) was added under argon. The reaction was stirred at room temperature overnight. The solvent was removed in vacuo. The crude was dissolved in  $\text{CH}_2\text{Cl}_2$  (200 mL) and  $\text{H}_2\text{O}$  (100 mL) added. The phases were separated and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (3 150 mL). The organic layers were combined, dried over  $\text{MgSO}_4$ , filtered and evaporated. The crude material was purified through silica gel column chromatography ( $\text{CH}_2\text{Cl}_2/\text{Cyclohexane}$  1:1), to yield compound **13** as an orange powder (2.56 g, 98%). M.p. 202e205 C. FTIR (ATR)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ):  $\tilde{\nu}$  3513, 1657, 1574, 1309, 1132, 1000, 791, 753, 721.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.20 (dd,  $J$   $\frac{1}{4}$  8.0, 1.1 Hz, 2H), 7.73 (dd,  $J$   $\frac{1}{4}$  7.8, 1.1 Hz, 2H), 7.50 (dd,  $J$   $\frac{1}{4}$  8.0, 7.8 Hz, 2H), 6.39 (s, 1H) (OH signal missing).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.7, 138.4, 135.1, 135.0, 132.8, 130.2, 126.7, 61.8. HRMS (ESI):  $m/z$  [ $M + H$ ] $^+$  Calcd for  $\text{C}_{14}\text{H}_9\text{O}_2\text{Cl}_2$  278.9974; Found: 278.9970.

#### 4.14. (9r,10r)-1,8-dichloro-9,10-dihydroanthracene-9,10-diol 14

In a two necked flask under argon, a solution of compound **5** (400 mg, 1.433 mmol) in dry MeOH (7.2 mL) was cooled to 0 C and  $\text{NaBH}_4$  (217 mg, 5.732 mmol) was added in small portions in order to prevent the temperature to rise. The resulting mixture was stirred between 0 and 5 C for 3 h. The crude was poured into ice water and desired compound **14** precipitated as a white powder, filtered off and washed with  $\text{H}_2\text{O}$  (363 mg, 90%). M.p. 157e160 C. FTIR (ATR)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ):  $\tilde{\nu}$  3403, 1449, 1192, 959, 869, 786, 692.  $^1\text{H-NMR}$  (400 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  7.74 (dd,  $J$   $\frac{1}{4}$  7.2, 1.0 Hz, 2H), 7.39e7.36 (m, 4H), 6.66 (s, 1H), 5.87 (s, 1H) (OH signals missing).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  146.4, 134.8, 134.6, 130.2, 129.1, 124.5, 67.9, 64.4. HRMS (ESI):  $m/z$  [ $M + \text{Na}$ ] $^+$  Calcd for  $\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{NaO}_2$  302.9950; Found 302.9945.

#### 4.15. (9s,10s)-1,8-dichloro-9,10-dihydroanthracene-9,10-diol 15

To a solution of 1,8-dichloroanthracene-9,10-dione **5** (277 mg, 1 mmol) in dry THF (30 mL) was added dropwise DIBAH (3 mL, 3 mmol, 1 M in hexane). The reaction mixture was stirred for 5 h, followed by the addition of saturated aqueous Rochelle's salt solution (25 mL). The resulting mixture was stirred at room temperature overnight. The mixture was extracted with EtOAc (3 25 mL), the organic layers were combined, dried over  $\text{MgSO}_4$ , filtered and evaporated. Compound **15** was purified through silica gel column chromatography (Cyclohexane/EtOAc 8:2) and isolated as a white powder (252 mg, 89%). M.p. 207e210 C. FTIR (ATR)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ):  $\tilde{\nu}$  3346, 1661, 1581, 1451, 1176, 955, 810, 763.  $^1\text{H-NMR}$  (400 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  7.49e7.44 (m, 4H), 7.36 (t,  $J$   $\frac{1}{4}$  7.8 Hz, 2H), 6.37 (s, 1H), 5.51 (s, 1H) (OH signals missing).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  142.7, 137.3, 135.4, 130.8, 130.6, 129.2, 71.3, 64.3. HRMS (ESI):  $m/z$  [ $M$ ] $^+$  Calcd for  $\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{NaO}_2$  302.9950; Found 302.9950.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

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