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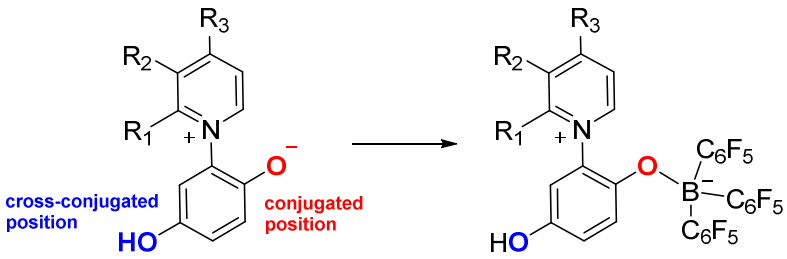

Graphical Abstract

Borane adducts of punicine and of its dehydroxy derivatives (pyridinium-1-yl)-2- and 3-phenolates

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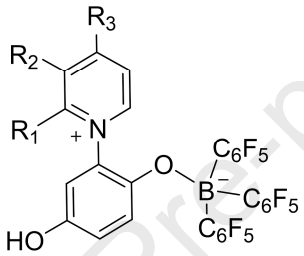

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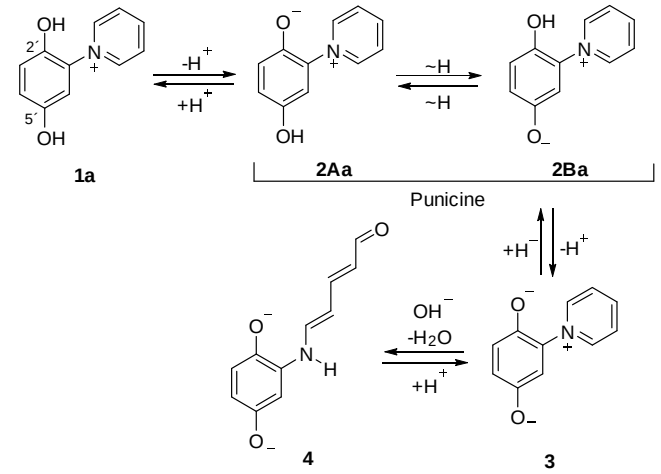
ABSTRACT

The natural product punicine (*Punica granatum*) exists in two tautomeric forms, the cross-conjugated mesomeric betaine 1-(pyridinium-1-yl)-2-hydroxy-phenyl-5-olate and the conjugated mesomeric betaine 1-(pyridinium-1-yl)-5-hydroxy-phenyl-2-olate. Punicine as well as its picoline derivatives reacted with tris(pentafluorophenyl)borane exclusively at the 2´-olate group to form zwitterionic borates. Correspondingly, the 5´-dehydroxy derivate of punicine, the conjugated heterocyclic mesomeric betaine 1-(pyridinium-1-yl)-phenyl-2-olate and its picoline derivatives also gave borates, whereas analogous reactions of the cross-conjugated isomer 2´-dehydroxypunicine [1-(pyridinium-1-yl)-phenyl-3-olate] did not result in the formation of stable adducts.

1. Introduction

Much interest is currently focused on borane adducts of N-heterocyclic carbenes,[1] of phenolate substituted N-heterocyclic carbenes,[2] and on borates of phenols. Interestingly, the latter mentioned have been formed from *p*-fluorophenyl-*tert*.-butylether and the frustrated Lewis pair consisting of *tert*.-butyl phosphane and tris(pentafluorophenyl)borane.[3] 8-Hydroxyquinoline reacted with the latter mentioned borane to yield a zwitterionic luminescent adduct,[4] whereas 1-naphthols gave stabilized keto isomers of 1-naphthol, *i.e.* benzocyclohexadienes.[5] Four-coordinated boron compounds of 2-(2-pyridyl)phenol have been developed as hole-blocking materials for phosphorescent OLEDs,[6] and other adducts serve as building blocks of 2D and 3D crystalline coordination polymer networks.[7] Interest has recently also been directed toward a thorough investigation of *Liebermann* betaines and its derivatives, which possess quinoid partial structures[8]. In view of these studies, the alkaloid punicine[9] also seemed to be an interesting target for borate formations. It has been isolated from the leaves of *Punica granatum*[10] and, as it combines a hydroquinone and a pyridinium moiety, it is an interesting redox active compound. Depending on the pH of the solution punicine can exist as salt **1a**, as mixture of mesomeric betaines **2Aa** and **2Ba**, as anion **3**, or as open-chained anionic species **4**[9] (Scheme 1). Redox reactions of punicine derivatives resulted in the formation of radical anions and radical semiquinones and the development of switchable materials.[11-14] Thus punicine proved to be a suitable model compound to study the different types of conjugation which are known to govern the chemical behaviour of mesomeric betaines considerably.[15-18] As examples, conjugated mesomeric betaines such as sydnones[19] or münchnones[20] are versatile 1,3-dipoles in cycloadditions.[18] By contrast, cross-conjugated mesomeric betaines, which possess a π-electronic charge separation, are often 1,4-dipoles[18,21] which can be used in materials chemistry.[22] Characteristic dipole increments can be dissected from the resonance forms, respectively. Conjugated as well as cross-conjugated mesomeric betaines are interesting precursors of anionic N-heterocyclic carbenes.[23] Pseudo-cross-conjugation defines the third class of mesomeric betaines. Examples are imidazolium-2-carboxylates,[24] pyrazolium-3-carboxylates[25] and indazolium-3-carboxylates[26] which decarboxylate readily under mild conditions to form the corresponding N-heterocyclic carbenes. Thus, pseudo-cross-conjugated mesomeric betaines are often *crypto*-NHCs.[27] The fourths and fifth class of mesomeric betaines, which are semi-conjugated and pseudo-semi-conjugated, respectively, still remain to be explored in more detail, as only a very limited number of representatives have been described to date.[17] In continuation of our interest in punicines,[9,11-14] conjugation in hetarenium salts,[28] mesomeric betaines[29] as well as N-heterocyclic carbenes[30] we report here that the type of conjugation also influences the borane adduct formation of mesomeric betaines. We report on the synthesis of the

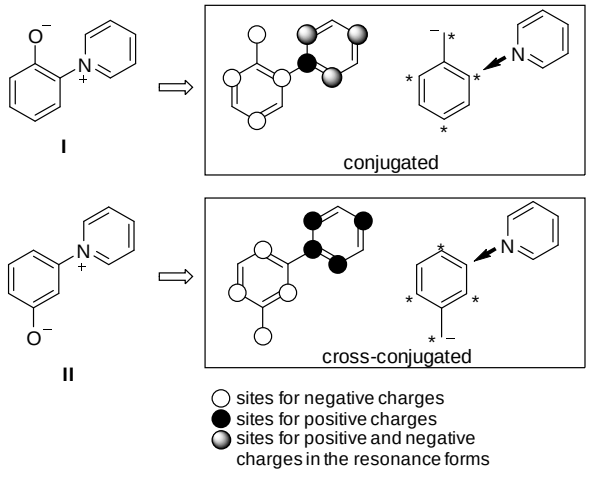
tri
derivatives. We found that the borane adduct formation strongly depends on the position of the olate group in the mesomeric betaine, *i.e.* on the type of conjugation.



Scheme 1. The alkaloid punicine **2Aa**/**2Ba**.

2. Results and Discussion

The structures **I** and **II** represent partial structures of the punicine tautomers **2Aa** and **2Ba**, respectively (Fig. 1). They display the typical characteristics of two distinct classes of mesomeric betaines. Dehydroxypunicine **I** is a member of the class of conjugated mesomeric betaines such as tautomer **2Aa** and possesses sites for positive as well as negative charges in the resonance forms as shown. By contrast, the charges in cross-conjugated partial structure **II** of tautomer **2Ba** are restricted to separated parts of the common π-electron system. In **I** the cation is joined to the anion through a starred position of the isoconjugated equivalent (the benzyl anion), whereas this position is unstarred in **II**, and these positions are active and inactive positions of the highest occupied molecular orbital (HOMO), respectively.[18] The HOMO is essentially located in the phenolate rings, whereas the lowest unoccupied molecular orbital (LUMO) is essentially located in the pyridinium rings. The inactive position in **II** causes a π-electronic charge separation in the ground state of the molecule. Thus, punicine as well as its derivatives are excellent model compounds to study borane adduct formations under variation of the type of conjugation in mesomeric betaines.



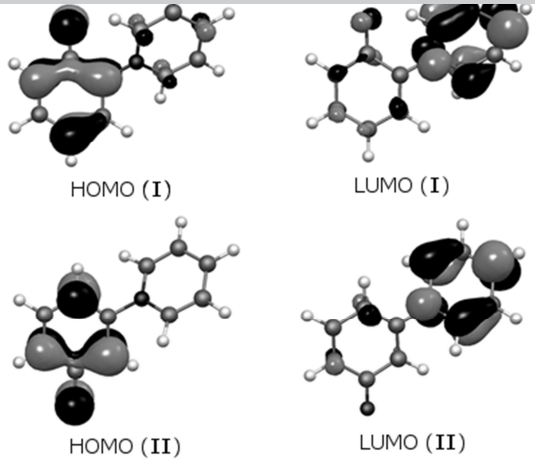
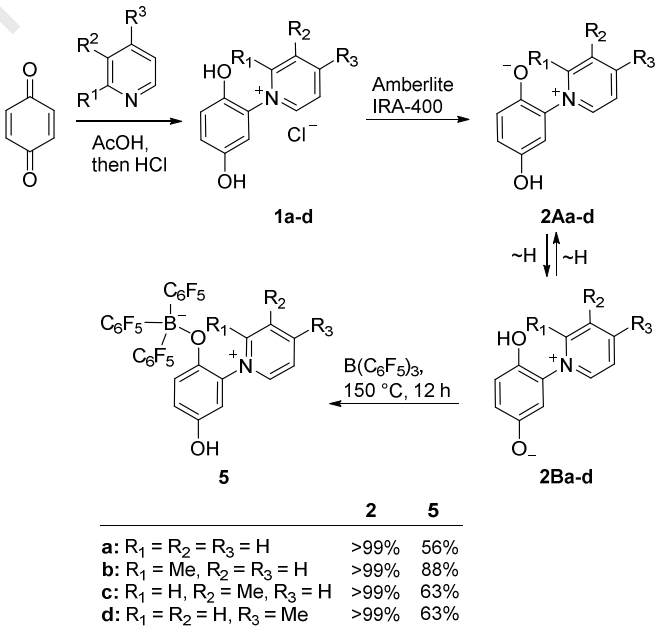


Fig. 1. Charge distribution as well as calculated frontier orbital profiles of **I** and **II**.

The 2- und 4-methylpyridinium derivatives **2b,d** of punicine **2a** have been prepared as described earlier starting from benzoquinone and the corresponding picolines,[11] whereas their 3-methyl derivative **2c** was synthesized according to modified literature procedures[31,32] (Scheme 2).



	2	5
a: $R_1 = R_2 = R_3 = H$	>99%	56%
b: $R_1 = Me$, $R_2 = R_3 = H$	>99%	88%
c: $R_1 = H$, $R_2 = Me$, $R_3 = H$	>99%	63%
d: $R_1 = R_2 = H$, $R_3 = Me$	>99%	63%

Scheme 2. Syntheses of punicine derivatives and of their borane adducts.

On titration of a DMSO-d_6 solution of **1a** with proton sponge [*i.e.* 1,8-bis(dimethylamino)naphthalene], the integral of the more deshielded resonance frequency assigned to the 5´-hydroxy group diminished twice as fast as the signal of the 2´-hydroxy group which is indicative for the predominant formation of the cross-conjugated tautomer **2Ba** in strongly polar solvents [E_T^N(DMSO) = 0.444].[9] The two tautomers, however, proved to be inseparable. In addition, no quinhydrone complex formed during the reaction, although π-stacking complexes have been observed before.[11] Single crystals of the 4-methylpyridinium punicine derivative **1d** were obtained by slow evaporation of a concentrated solution in DMSO-d_6. The molecular drawing is shown in Fig. 2. The

com… …he OH group forms a hydrogen bond to the chloride counter ion [H…Cl = 221(2) pm; O-H…Cl = 172(2)°], whereas the 2´-OH group binds one water of crystallization [H…OH2 = 180(1) pm; O-H…OH2 = 171(2)°]. The pyridinium ring is twisted by -47.30(15)° from the plane of the hydroquinone ring (C2-N1-C11-C16; crystallographic numbering).

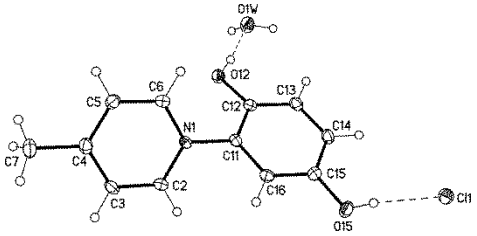


Fig. 2. Molecular drawing of punicine derivative **1d** (displacement parameters drawn at 50% probability level).

In the elemental cell the phenolate rings stack to the pyridinium rings of the molecules of the second layer (Fig. 3). The plane-to-plane distance of 3.7396(2) Å (distance between N1 and C11 of the second layer) suggests attractive π-π-interactions as it meets the distance criteria described in the literature (3.3-3.8 Å).[33,34] The parallel alignment of the stacked rings is different in comparison to crystalline benzene, the σ-π-interactions of which provoke a herringbone structure.[33] In the case of the punicines the stacking presumably is caused by intermolecular HOMO-LUMO interactions. Therefore, in accordance with the quadrupole model[35] the negative π-cloud of the hydroquinoline ring interacts with the electron-deficient pyridinium moiety and hence with an inverted quadrupole in a face-to-face rather than a face-to-edge interaction.

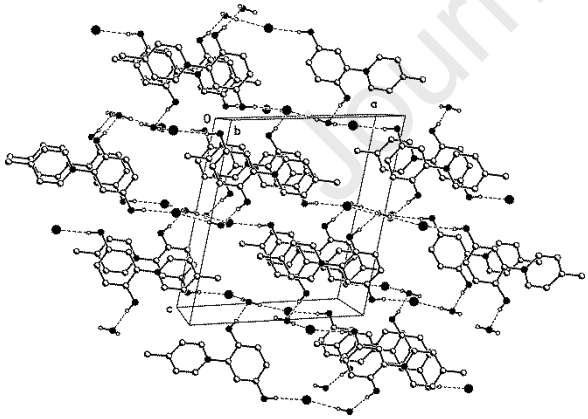


Fig. 3. Crystal packing of punicine derivative **1d** (only hydrogen atoms involved in hydrogen bonds shown).

After deprotonation by the ion exchange resin Amberlite IRA-400 punicine **2a** as well as its 2-methyl-, 3-methyl- and 4-methyl derivatives **2b-c** reacted with tris(pentafluorophenyl)borane in anhydrous dioxane to give regioselectively the zwitterionic borates **5a-d** in good yields (Scheme 2). The NMR spectra of the adducts displayed only one set of signals. Peak assignments were accomplished by 2D NMR techniques. The $^3J_{CH}$ couplings between the 5´-OH proton and the adjacent CH positions were formation of the alternative regioisomer was eliminated from consideration. In accordance with the postulated structure no NOE cross signals between the 5´-OH proton and the protons in α position of the pyridinium ring were detectable as to be expected for the regioisomer. Selected peak assignments and diagnostic NMR results are shown in Fig. 4. DFT-calculations indeed predict that the obtained structure is by 29.45 kJ/mol thermodynamically more stable *in vacuo* than its regioisomer.

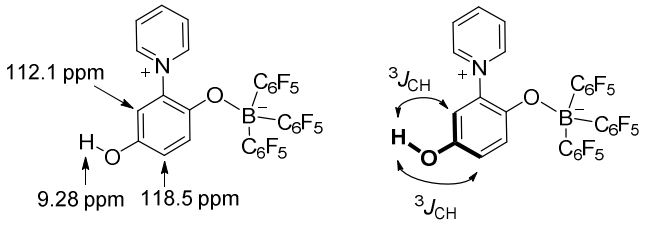


Fig. 4. Diagnostic NMR results for structure elucidation of borane adduct **5a**.

According to the calculation, the borane adduct **5a** adopts a conformation in which the pyridinium ring and the phenolate ring are twisted by 49.9°, and the borate is twisted by 8.9° out of the plane of the phenolate. The highest occupied molecular orbital (HOMO) is essentially located in the hydroquinone moiety, whereas the lowest unoccupied molecular orbital (LUMO) is located in the pyridinium ring (Fig. 5).

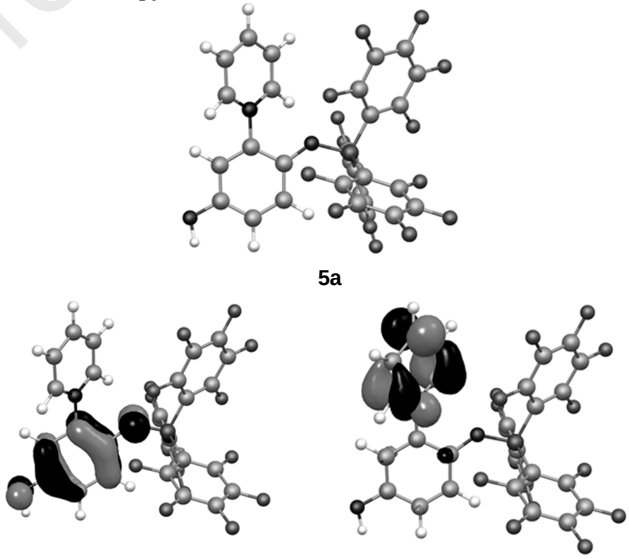


Fig. 5. Results of calculations on borane adduct **5a**. Most stable conformation (above) and frontier orbital profile (below).

A single crystal structure was obtained from the 3-methylpyridinium derivative **5c** which is in agreement with the results of the DFT calculations with respect to the geometrical properties. Thus, a torsional angle of 54.3(3)° was found between the pyridinium ring and the phenyl ring [C1-C6-N7-C12; crystallographic numbering] (Fig. 6). The borate residue is twisted by -20.5(4)° out of the plane of the phenyl ring [B1-O1-C1-C2, crystallographic numbering]. The single crystal was obtained by slow evaporation of a concentrated solution in DMSO-d_6.

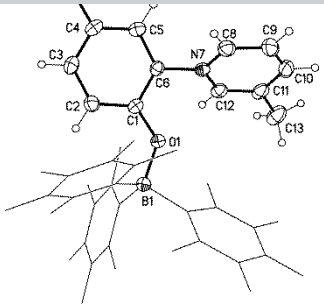
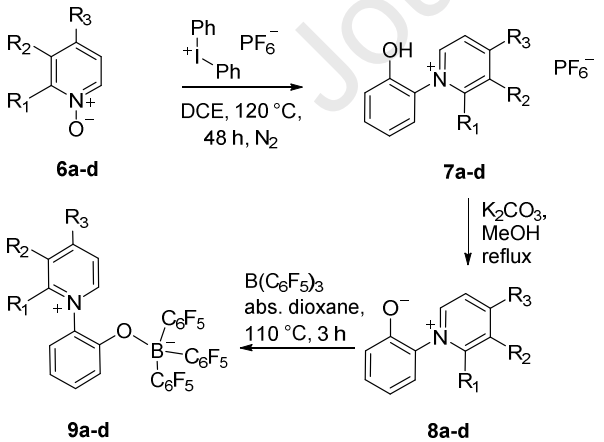


Fig. 6. Molecular drawing of borane adduct **5c (**solvent omitted for clarity, C_6F_5 moieties represented as wireframe model), displacement parameters drawn at 50% probability level.

We next focused our interest on the partial structures **I** and **II** of punicine as shown in Fig. 1. Interest has been focused on pyridinium-2-phenolates (**I**) as well as on its salts because of non-linear optical properties[36,37] and solvatochromism.[38] To the best of our knowledge pyridinium-3-phenolates (**II**) are much less examined. It has been calculated[37] and its salt[39,40] was examined mass-spectrometrically.[41] In order to prepare a series of pyridinium-2-phenolates we reacted the pyridine-N-oxides **6a-d** with diphenyliodonium hexafluorophosphate in dichloroethane under Schlenk conditions for 2 days at 120°C (Scheme 3). A slight modification of the literature procedure gave considerably increased yields of **7a** (17%[42] to 44%) and **7b** (8%[42] to 62%), and also opened the access to the isolation and characterization of **7c**,**d**. Potassium carbonate converted the salts **7a-d** into their betaines **8a-d** which were obtained as orange solids. They formed borane adducts **9a-d** on treatment with tris(pentafluorophenyl)borane in anhydrous dioxane at reflux temperature in low to very good yields. The boron atoms appear between δ = -3.45 ppm (**9a**) and -3.43 ppm (**9c**) in the ^{11}B NMR spectra. The fluorine atoms were detected at approximately -134.0 ppm, -161.6 ppm, and -166.5 ppm as doublet, triplet, and multiplet, respectively, in the ^{19}F NMR spectra.

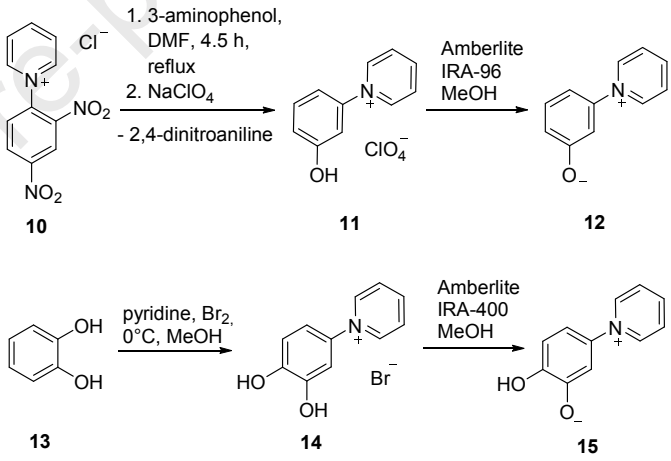


	7	8	9
a: $R_1 = R_2 = R_3 = H$	44%	56%	77%
b: $R_1 = Me, R_2 = R_3 = H$	62%	50%	10%
c: $R_1 = H, R_2 = Me, R_3 = H$	74%	47%	95%
d: $R_1 = R_2 = H, R_3 = Me$	70%	59%	50%

Scheme 3. Synthesis and borane adduct formation of 5-dehydroxypunicine.

We finally envisaged the synthesis of the 2´-dehydroxypunicine **12** to study borane adduct formations (Scheme 4). Therefore the salt **11** was prepared by a nucleophilic

…l in DMF,[39] followed by an anion exchange of the chloride to the non-hygroscopic perchlorate in order to precipitate the product with a yield of 50 %. Conversion of the salt **11** into its cross-conjugated mesomeric betaine **12**, identical to partial structure **II** shown in Scheme 2, was accomplished by the anion exchange resin Amberlite IRA-96 in its hydroxide form in quantitative yield, however, the sample decomposed rapidly on standing. No reaction with tris(pentafluorophenyl)borane occurred. Stabilization of the system by an additional hydroxyl group adjacent to the 3´-OH group of 2´-dehydroxypunicine was tested by the synthesis of betaine **15**. It was prepared starting from catechol and pyridine in the presence of bromine which resulted in the formation of the salt **14** in acceptable yields. Deprotonation was finally accomplished on treatment of the salt **14** with the anion exchange resin Amberlite IRA-400 in its hydroxide form. Indeed, betaine **15** proved to be stable. The resonance frequencies of the OH groups of the pyridinium salt **14**, detected at 9.83 ppm and 9.97 ppm, respectively, disappeared on betaine formation and all other ^{1}H NMR signals shifted to higher field. In parallel, a downfield shift of approximately 4 ppm is found in the ^{13}C NMR spectra. Reaction with the aforementioned borane, however, in analogy to the conversion of the 2´-dehydroxypunicines, were unsuccessful even under prolonged reaction times.



Scheme 4. Synthesis of 2´-dehydroxypunicine **12** and the punicine isomer **15**.

3. Conclusions

Punicine exists as a mixture of a conjugated and a cross-conjugated heterocyclic mesomeric betaine. On treatment with tris(pentafluorophenyl)borane the olate group in conjugation reacted regioselectively to give a zwitterionic borane adduct, whereas the olate group in cross-conjugated position remained unchanged. Likewise, the conjugated mesomeric betaines 1-(pyridinium-1-yl)-2-phenolates gave stable borane adducts, whereas the cross-conjugated isomer decomposed under analogous reaction conditions. These results supplement our knowledge about the chemistry of isomers which belong to different classes of heterocyclic mesomeric betaines.

Acknowledgement

I ith gratefully acknowledged for measuring a part of the HRESIMS spectra.

4. Experimental

Calculations. Density-functional theory (DFT)-calculations of **I**, **II** and both regioisomers of **5a** were carried out by using the Jaguar 9.1.013 software[43] running on Linux 2.6.18-238.el5 SMP (x86_64) on five AMD Phenom II X6 1090T processor workstations (Beowulf-cluster) parallelized with OpenMPI. MM2 optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented LACVP* (Hay-Wadt effective core potential (ECP) basis on heavy atoms, N31G6* for all other atoms) basis set and with the B3LYP density functional. All calculated structures were proven to be true minima by the absence of imaginary frequencies. Plots were obtained using Maestro 10.5.013, the graphical interface of Jaguar. Density-functional theory (DFT)-calculations of **2Aa** and **2Ba** were carried out by using the multithreaded Firefly 8.2.0 QC package,[44] which is partially based on the GAMESS (US)[45] source code, running on Windows 10 Pro (Version 10.0.17763.475) (x86_64) on a 16 core AMD 2950X processor workstation. MM2 optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented N31G6* basis set and with the B3LYP density functional. All calculated structures were proven to be true minima by the absence of imaginary frequencies.

Nuclear magnetic resonance (NMR) spectra were measured with a Bruker Avance 400 MHz and Bruker Avance III 600 MHz. ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz. ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz, with the solvent peak or tetramethylsilane used as the internal reference. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broadened. Signal orientations in DEPT experiments were described as follows, when applied: o = no signal; + = up (CH, CH_3); - = down (CH_2). Peak assignments were defined as follows. Notations such as C-3, C-3´, and C-3´´ correspond to carbon atoms of the pyridinium rings, the phenolate rings, and the pentafluorophenyl rings, respectively, and hydrogen (3-H; 3´-H) as well as fluorine atoms (3´´-F) are described analogously. The mass spectra were measured with a Varian 320 MS Triple Quad GC/MS/MS with a Varian 450-GC. The electrospray ionization mass spectra (ESIMS) were measured with an Agilent LCMSD series HP 1100 with APIES. Spectra were taken at 30V fragmentor voltage unless otherwise noted. Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi). Yields are not optimized.

General procedure for deprotonation of punicine derivatives (2a-d). A column, packed with Amberlite IRA-400 is treated with 200 mL of 10% $NaOH_{(aq)}$ and rinsed with water until reaching pH 7, subsequently. The column was than washed with 200 mL of methanol. A sample of the pyridinium salt was dissolved in a small volume of methanol and added on the ion exchange resin. The sample was eluted with methanol and the deep red eluate was collected after passing the column. Evaporation of the solvent yielded the corresponding betaines in quantitative yields. The products have been dried *in vacuo*. The spectroscopic data correspond to literature values.[11,31,32]

General procedure for the synthesis of the borates 5a-d

one equivalent of tris(pentafluorophenyl)borane and dried *in vacuo* for 30 minutes. Then 6 mL of anhydrous dioxane were added under inert atmosphere and the resulting suspension was heated to 150 °C for 18 h in a sealed pressure tube. After cooling the reaction mixture to room temperature, the solvent was evaporated and the crude product was subsequently purified by column chromatography (ethyl acetate on silica gel).

(2-(Pyridinium-1-yl)-4-hydroxy-phenoxy)tris(pentafluorophenyl)borate 5a. A sample of 73.1 mg (0,39 mmol) of 4-hydroxy-2(*N*-pyridinium)phenolate and 200 mg (0.39 mmol) of tris(pentafluorophenyl)borane was used to obtain the product **5a** as a bright yellow solid. Yield: 152 mg (56%), mp: 220 °C (decomp.). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.30 (br s. 1H, OH), 8.94 – 8.92 (m, 2H, 2-H, 6-H), 8.65 (tt, J_1 =8.0 Hz, J_2 = 1.3 Hz, 1H, 4-H), 8.14 – 8.12 (m, 2H, 3-H, 5-H), 6.98 (d, J = 2.9 Hz, 1H, 6'-H), 6.72 (dd, J_1 = 9.2 Hz, J_2 = 2.9 Hz, 1H, 4'-H), 6.40 (d, J = 9.2 Hz, 1H, 3'-H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 148.6 (o, 1C, 5'-C), 147.9 (br, o), 146.4 (br, o), 146.3 (+, 2C, 2-C, 6-C), 145.9 (+, 1C, 4-C), 144.6 (o, 1C, 2'-C), 138.9 (br, o), 137.2 (br, o), 136.6 (br, o), 135.0 (br, o), 133.1 (o, 1C, 1'-C), 126.9 (+, 2C, 3-C, 5-C), 122.2 (br, o), 118.5 (+, 1C, 5'-C), 117.7 (+, 1C, 3'-C), 112.1 (+, 1C, 6'-C) ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ = -133.94 (d, J = 19.6 Hz), -161.78 (t, J = 19.6 Hz), -166.48 – -166.58 (m) ppm. ^{11}B NMR (192.6 MHz, DMSO-d_6): δ = -3.9 ppm. IR (ATR): $\tilde{\nu}$ = 3606, 1643, 1510, 1456, 1276, 1083, 975, 955, 897, 772, 764, 692, 680, 668 cm^{-1}. HRESIMS: $C_{29}H_9BF_{15}NO_2Na^+$: required 722.0385. Found: 722.0388.

(2-(2-Methylpyridinium-1-yl)-4-hydroxy-phenoxy)tris(pentafluorophenyl)borate 5b. A sample of 79.0 mg (0,39 mmol) of 4-hydroxy-2(*N*-2-methylpyridinium)phenolate and 200 mg (0.39 mmol) of tris(pentafluorophenyl)borane was used to obtain the product **5b** as a bright yellow solid. Yield: 244 mg (88%), mp: 216 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.28 (br s. 1H, OH), 8.84 (br.s., 1H, 6-H), 8.79 (d, J =6.2 Hz, 1H, 4-H), 8.49 (d, J = 7.9 Hz, 1H, 5-H), 8.04 (dd, J_1 = 7.9 Hz, J_2 = 6.2 Hz, 1H, 3-H), 6.95 (d, J = 3.0 Hz, 1H, 6'-H), 6.72 (dd, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 1H, 4'-H), 6.44 (d, J = 9.0 Hz, 1H, 3'-H), 2.46 (s, 3H, 7-H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 148.7 (o, 1C, 5'-C), 148.0 (br, o), 146.4 (br, o), 146.1 (+, 1C, 5-C), 146.0 (+, 1C, 6-C), 144.5 (o, 1C, 2'-C), 138.9 (br, o), 137.4 (+, 1C, 2-C), 137.3 (br, o), 136.6 (br, o), 135.0 (br, o), 133.0 (o, 1C, 1'-C), 126.5 (+, 1C, 3-C), 122.1 (br, o), 118.4 (+, 1C, 4'-C), 118.0 (+, 1C, 3'-C), 112.0 (+, 1C, 6'-C), 17.4 (+, 1C, 7-C) ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ = -133.43 (d, J = 21.8 Hz), -159.54 (t, J = 21.8 Hz), -166.65 – -166.76 (m) ppm. ^{11}B NMR (192.6 MHz, DMSO-d_6): δ = -3.6 ppm. IR (ATR): $\tilde{\nu}$ = 3374, 1698, 1511, 1488, 1457, 1290, 1276, 41267, 1083, 1044, 960, 934, 819, 765, 686, 669 cm^{-1}. HRESIMS: $C_{30}H_{11}BF_{15}NO_2Na^+$: required 736.0541. Found: 736.0537.

(2-(3-Methylpyridinium-1-yl)-4-hydroxy-phenoxy)tris(pentafluorophenyl)borate 5c. A sample of 39.3 mg (0,20 mmol) of 4-hydroxy-2(*N*-3-methylpyridinium)phenolate and 100 mg (0.20 mmol) of tris(pentafluorophenyl)borane was used to obtain the product **5c** as a bright yellow solid. Yield: 88 mg (63%), mp: 189 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.30 (br s. 1H, OH), 8.85 (br.s., 1H, 6-H), 8.80 (d, J =6.0 Hz, 1H, 4-H), 8.50 (d, J = 8.0 Hz, 1H, 2-H), 8.04 (dd, J_1 = 8.0 Hz, J_2 = 6.0 Hz, 1H, 5-H), 6.96 (d, J = 3.0 Hz, 1H, 6'-H), 6.76 (dd, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 1H, 4'-H), 6.46 (d, J = 3.0 Hz, 1H, 3'-H) 2.47 (s, 3H, 7-H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 148.7 (o, 1C, 5'-C), 148.0 (br, o),

1C, 2'-C), 138.9 (br, o), 137.4 (o, 1C, 3-C), 137.3 (br, o), 136.6 (br, o), 135.0 (br, o), 133.0 (o, 1C, 1'-C), 126.5 (+, 1C, 5-C), 122.0 (br, o), 118.4 (+, 1C, 4'-C), 118.1 (+, 1C, 3'-C), 112.0 (+, 1C, 6'-C), 17.4 (+, 1C, 7-C) ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ = -133.46 (d, *J* = 21.9 Hz), -159.72 (t, *J* = 21.9 Hz), -166.77 – -166.89 (m) ppm. ^{11}B NMR (192.6 MHz, DMSO-d_6): δ = -3.7 ppm. IR (ATR): ṽ = 3136, 1644, 1490, 1405, 1274, 1082, 975, 957, 936, 765, 747, 729, 675, 668 cm^{-1}. HRESIMS: $C_{30}H_{11}BF_{15}NO_2Na^+$: required 736.0541. Found: 736.0550.

(2-(4-Methylpyridinium-1-yl)-4-hydroxyphenoxy)tris(pentafluorophenyl)borate 5d. A sample of 79.0 mg (0,39 mmol) of 4-hydroxy-2(*N*-4-methylpyridinium)phenolate and 200 mg (0.39 mmol) of tris(pentafluorophenyl)borane was used to obtain the product **5d** as a bright yellow solid. Yield: 88 mg (63%), mp: 222 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.26 (br s. 1H, OH), 8.74 (d, *J* = 6.5 Hz, 2H, 2-H, 6-H), 7.96 (d, *J* =6.5 Hz, 2H, 3-H, 5-H), 6.93 (d, *J* = 3.0 Hz, 1H, 6'-H), 6.69 (dd, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 1H, 4'-H), 6.36 (d, *J* = 9.0 Hz, 1H, 3'-H), 2.62 (s, 3H, 7-H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 159.4 (o, 1C, 4-C), 148.6 (o, 1C, 5'-C), 148.1 (br, o), 146.5 (br, o), 145.2 (+, 2C, 2-C, 6-C), 144.7 (o, 1C, 2'-C), 138.9 (br, o), 137.3 (br, o), 136.6 (br, o), 135.1 (br, o), 132.8 (o, 1C, 1'-C), 127.2 (+, 2C, 3-C, 5-C), 122.1 (br, o), 118.2 (+, 1C, 4'-C), 117.6 (+, 1C, 3'-C), 112.1 (+, 1C, 6'-C), 21.3 (+, 1C, 7-C) ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ = -133.31 (d, *J* = 21.7 Hz), -159.55 (t, *J* = 21.7 Hz), -164.76 – -164.82 (m) ppm. ^{11}B NMR (192.6 MHz, DMSO-d_6): δ = -3.6 ppm. IR (ATR): ṽ = 3606, 1642, 1511, 1456, 1275, 1083, 975, 955, 899, 824, 794, 749, 669, 636 cm^{-1}. HRESIMS: $C_{30}H_{11}BF_{15}NO_2Na^+$: required 736.0541. Found: 736.0511.

General procedure for the synthesis of the salts 7a-d.[33]

The pyridine-*N*-oxides **6a-d** and diphenyliodonium hexafluorophosphate(V) were dried *in vacuo* in a Schlenk tube over a period of 1 h. Then, 8 mL of dichloroethane were added under an inert atmosphere, and the mixture was heated at 120°C for 48 h. After cooling to rt, 5 mL of methanol were added, the mixture was poured into a round flask and treated with 1 g of silica gel. Flash column chromatography was performed with a mixture of dichloromethane, petroleum ether, and methanol (10:5:3).

1-(2-Hydroxyphenyl)-pyridinium hexafluorophosphate 7a. A sample of 0.380 g (4.00 mmol) of pyridine-N-oxide **6a** and of 1.704 g (4.00 mmol) of diphenyliodonium hexafluorophosphate(V) was used. The salt **7a** was obtained as red solid. Yield: 0.554 g (44%), mp. 62 °C. ^{1}H NMR (600 MHz, acetonitrile-d_3): δ = 8.83 (dd, J_1 = 6.8 Hz, J_2 = 1.4 Hz, 2 H, 2/6-H), 8.52 (tt, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 1 H, 4-H), 8.06 (dd, J_1 = 6.8 Hz, J_2 = 7.8 Hz, 2 H, 3/5-H), 7.33 (dd, J_1 = 7.7 Hz, J_2 = 1.7 Hz, 1 H, 6'-H), 7.30 (ddd, J_1 = 8.8 Hz, J_2 = 7.8 Hz, J_3 = 1.7 Hz, 1 H, 4'-H), 7.03 (dd, J_1 = 7.8 Hz, J_2 = 1.3 Hz, 1 H, 3'-H), 6.75 (ddd, J_1 = 8.8 Hz, J_2 = 7.7 Hz, J_3 = 1.3 Hz, 1 H, 5'-H) ppm. ^{13}C NMR (150 MHz, acetonitrile-d_3): δ = 157.2, 146.9, 146.4, 133.5, 132.2, 128.4, 126.3, 120.4, 116.5 ppm. IR (ATR): ṽ = 3129, 3067, 2926, 1469, 1455, 829, 750, 677 cm^{-1}. ESIMS (100 V, +): *m/z* (%) = 172.0 (100) $[M]^+$. HRESIMS: $C_{11}H_{10}NO$: required 172.0762. Found: 172.0764.

1-(2-Hydroxyphenyl)-2-methylpyridinium hexafluorophosphate 7b. A sample of 0.218 g (2.00 mmol) of 2-methylpyridine-N-oxide **6b** and of 0.852 g (2.00 mmol) of diphenyliodonium hexafluorophosphate(V) was used. The salt **7b** was obtained as grey solid. Yield: 0.408 g (62%), mp. 125°C. ^{1}H NMR (600 MHz, acetonitrile-d_3): δ = 8.56 (dd, J_1 = 6.2 Hz, J_2 = 1.2 Hz, 1 H, 4-H), 8.04 (dd, J_1 = 8.0 Hz, J_2 = 0.7 Hz, 1 H, 3-H), 7.95 (ddd, J_1 = 7.7 Hz, J_2 = 6.2 Hz, J_3 = 0.7 Hz, 1H, 5-H), 7.56 (ddd, J_1 = 9.0 Hz, J_2 = 7.9 Hz, J_3 = 1.6 Hz, 1 H, 4'-H), 7.41 (dd, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 1 H, 6'-H), 7.21 (dd, J_1 = 7.9 Hz, J_2 = 1.1 Hz, 1 H, 3'-H), 7.17 (ddd, J_1 = 9.0 Hz, J_2 = 7.8 Hz, J_3 = 1.1 Hz, 1 H, 5'-H), 2.52 (s, 3 H, Me) ppm. ^{13}C NMR (150 MHz, acetonitrile-d_3): δ = 158.5, 151.2, 148.0, 147.3, 134.1, 130.6, 129.4, 127.4, 126.6, 122.2, 118.1, 20.9 ppm. IR (ATR): ṽ = 3527, 3099, 1630, 1463, 1427, 820, 781, 758 cm^{-1}. ESIMS (+): *m/z* (%) = 186.0 (100) $[M]^+$. HRESIMS: $C_{12}H_{12}NO$: required 186.0913. Found: 186.0919.

1-(2-Hydroxyphenyl)-3-methylpyridinium hexafluorophosphate 7c. A sample of 0.218 g (2.00 mmol) of 3-methylpyridine-*N*-oxide **6c** and of 0.852 g (2.00 mmol) of diphenyliodonium hexafluorophosphate(V) was used. The salt **7c** was obtained as orange solid. Yield 0.490 g (74%), mp. 123°C. ^{1}H NMR (600 MHz, acetonitrile-d_3): δ = 8.66 (s, 1 H, 2-H), 8.64 (d, *J* = 6.1 Hz, 1 H, 4-H), 8.43 (d, *J* = 8.0 Hz, 1 H, 6-H), 7.99 (dd, J_1 = 8.0 Hz, J_2 = 6.1 Hz, 1 H, 5-H), 7.44 (ddd, J_1 = 8.8 Hz, J_2 = 7.8 Hz, J_3 = 1.6 Hz, 1 H, 4'-H), 7.41 (dd, J_1 = 7.7 Hz, J_2 = 1.6 Hz, 1 H, 6'-H), 7.37 (dd, J_1 = 7.8 Hz, J_2 = 1.3 Hz, 1 H, 3'-H), 7.01 (ddd, J_1 = 8.8 Hz, J_2 = 7.7 Hz, J_3 = 1.3 Hz, 1 H, 5'-H) 2.56 (s, 3 H, Me) ppm. ^{13}C NMR (150 MHz, acetonitrile-d_3): δ = 152.8, 147.8, 146.6, 144.4, 140.5, 133.6, 131.4, 128.0, 126.8, 120.2, 118.9, 18.5 ppm. IR (ATR): ṽ = 3043, 2928, 1630, 1460, 838, 756, 713 cm^{-1}. ESIMS (+): *m/z* (%) = 186.1 (100%) $[M]^+$. HRESIMS: $C_{12}H_{12}NO$: required 186.0913. Found 186.0925.

1-(2-Hydroxyphenyl)-4-methylpyridinium hexafluorophosphate 7d. A sample of 0.249 g (2.30 mmol) of 4-methylpyridine-*N*-oxide **6d** and of 0.975 g (2.30 mmol) of diphenyliodonium hexafluorophosphate(V) was used. The salt **7d** was obtained as red solid. Yield 0.529 g (70%), mp. 121°C. ^{1}H NMR (400 MHz, acetonitrile-d_3): δ = 8.62 (d, *J* = 6.6 Hz, 2 H, 2/6-H), 7.94 (d, *J* = 6.6 Hz, 2 H, 3/5-H), 7.49 (ddd, J_1 = 8.9 Hz, J_2 = 7.9 Hz, J_3 = 1.6 Hz, 1 H, 4'-H), 7.45 (dd, J_1 =7.8 Hz, J_2 = 1.6 Hz, 1 H, 6'-H), 7.17 (dd, J_1 = 7.9 Hz, J_2 = 1.2 Hz, 1 H, 3'-H), 7.09 (ddd, J_1 = 8.9 Hz, J_2 = 7.8 Hz, J_3 = 1.2 Hz, 1 H, 5'-H), 2.71 (s, 3 H, Me) ppm. ^{13}C NMR (100 MHz, acetonitrile-d_3): δ = 162.3, 151.8, 145.9, 133.8, 131.1, 129.3, 127.2, 121.2, 118.6, 22.5 ppm. IR (ATR): ṽ = 3495, 3138, 2960, 2920, 1641, 1454, 1281, 1208 cm^{-1}. ESIMS (+): *m/z* (%) = 186.0 (100%) $[M]^+$. HRESIMS: $C_{12}H_{12}NO$ required 186.0913. Found 186.0923.

General procedure for the synthesis of the betaines 8a-d.

Solutions of the salts **7a-d** in 6 mL of methanol were treated with potassium carbonate (1.5 equivalents) and stirred at reflux temperature for 2 h. After cooling to rt, the mixture was stirred for an additional hour. Then, the mixture was treated with 1 g of silica gel. A flash column chromatography was performed with a mixture of dichloromethane, petroleum ether, and methanol (5:3:1). All spectroscopic data correspond to those reported in the literature.[42]

General procedure for the synthesis of the borane adducts 9a-d.

The betaines **8a-d** and tris(pentafluorophenyl)borane were dried *in vacuo* in a Schlenk tube over a short period of time. Then, 6 mL of anhydrous dioxane were added under an inert atmosphere, and the mixture was heated at 110°C for 3 h. After cooling to rt, the mixture was poured into a round flask and treated with 1 g of silica gel. Flash column chromatography was performed with ethyl acetate.

(2-(Pyridinium-1-yl)phenoxy)tris(pentafluorophenyl)borate 9a. A sample of 0.041 g (0.24 mmol) of 2-(pyridinium-1-yl)-phenolate **8a** and of 0.102 g (0.20 mmol) of tris(pentafluorophenyl)borane was used. The borane adduct **9a** was obtained as colorless solid. Yield 0.127 g (77%), mp. 212°C. ^{1}H NMR (600 MHz, methanol-d_4): δ = 8.94 (dd, J_1 = 6.8 Hz, J_2 = 1.4 Hz, 2 H, 2/6-H), 8.64 (tt, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 1 H, 4-H), 8.11 (dd, J_1 = 7.8 Hz, J_2 = 6.8 Hz, 2 H, 3/5-H), 7.48 (dd, J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1 H, 6'-H), 7.26 (ddd, J_1 = 8.4 Hz, J_2 = 7.6 Hz, J_3 = 1.7 Hz, 1 H, 4'-H), 6.89 (ddd, J_1 = 7.9 Hz, J_2 = 7.6 Hz, J_3 = 1.2 Hz, 1 H, 5'-H), 6.70 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1 H, 3'-H) ppm. ^{13}C NMR (150 MHz, methanol-d_4): δ = 152.6, 147.8 ($^1J_{C,F}$ = 244 Hz), 146.4, 145.5, 138.8 ($^1J_{C,F}$ = 270 Hz), 136.5 ($^1J_{C,F}$ = 248 Hz), 133.9, 131.5, 126.8, 124.5, 122.0, 118.1, 117.6 ppm. ^{11}B NMR (193 MHz, methanol-d_4, $BF_3{\cdot}Et_2O$): δ = -3.45 (s, 1 B) ppm. ^{19}F NMR (376 MHz, methanol-d_4, $CFCl_3$): δ = -134.01 (d, $^1J_{C,F}$ = 19.1 Hz, 6 F, 2´´-F, 6´´-F), -161.60 (t, $^1J_{C,F}$ = 19.6 Hz, 3 F, 4´´-F), -166.39--166.50 (m, 6 F, 3´´-F, 5´´-F) ppm. IR (ATR): ṽ = 3139, 2964, 2906, 1646, 1452, 1083, 973, 937 cm^{-1}. HRESIMS: $C_{29}H_9BF_{15}NONa^+$ required 706.0435. Found 706.0433.

(2-(2-Methylpyridinium-1-yl)phenoxy)tris(pentafluorophenyl)borate 9b. A sample of 0.040 g (0.22 mmol) of 2-(2-methylpyridinium-1-yl)-phenolate **8b** and of 0.102 g (0.20 mmol) of tris(pentafluorophenyl)borane was used. The borane adduct **9b** was obtained as brownish solid. Yield: 0.016 g (10%), mp. 251°C. ^{1}H NMR (600 MHz, methanol-d_4): δ = 8.53 (dd, J_1 = 6.0 Hz, J_2 = 1.3 Hz, 1 H, 6-H), 8.49 (ddd, J_1 = 7.7 Hz, J_2 = 7.6 Hz, J_3 = 1.2 Hz, 1 H, 4-H), 8.08 (dd, J_1 = 7.7 Hz, J_2 = 0.8 Hz, 1 H, 3-H), 7.88 (ddd, J_1 = 7.6 Hz, J_2 = 6.0 Hz, J_3 = 0.8 Hz, 1 H, 5-H), 7.35 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1 H, 6'-H), 7.27 (ddd, J_1 = 8.4 Hz, J_2 = 7.5 Hz, J_3 = 1.7 Hz, 1 H, 4'-H), 6.90 (ddd, J_1 = 7.8 Hz, J_2 = 7.5 Hz, J_3 = 1.1 Hz, 1 H, 5'-H), 6.67 (dd, J_1 = 8.4 Hz, J_2 = 1.1 Hz, 1 H, 3'-H), 2.65 (s, 3 H, Me) ppm. ^{13}C NMR (150 MHz, methanol-d□): δ = 159.6, 154.5, 149.1 ($^1J_{C,F}$ = 240 Hz), 148.2, 147.1, 140.1 ($^1J_{C,F}$ = 243 Hz), 137.8 ($^1J_{C,F}$ = 249 Hz), 133.7, 132.8, 132.4, 129.9, 126.0, 125.7, 119.5, 119.0, 20.6 ppm. ^{19}F NMR (376 MHz, methanol-d□, CFCl□): δ = -134.02 (d, $^1J_{C,F}$ = 18.9 Hz, 6 F, 2´´-F, 6´´-F), -161.80 (t, $^1J_{C,F}$ = 19.4 Hz, 3 F, 4´´-F), -166.61--166.74 (m, 6 F, 3´´-F, 5´´-F) ppm. IR (ATR): ṽ = 2934, 2854, 1642, 1455, 1080, 976 cm^{-1}. HRESIMS: $C_{30}H_{11}BF_{15}NONa^+$ required 720.0592. Found 720.0579.

(2-(3-Methylpyridinium-1-yl)phenoxy)tris(pentafluorophenyl)borate 9c. A sample of 0.040 g (0.22 mmol) of 2-(3-methylpyridinium-1-yl)-phenolate **8c** and of 0.102 g (0.20 mmol) of tris(pentafluorophenyl)borane was used. The borane adduct **9c** was obtained as brownish solid. Yield: 0.145 g (95%), mp. 210 °C. ^{1}H NMR (600 MHz, methanol-d_4): δ = 8.82 (s, 1 H, 2-H), 8.73 (d, J = 6.1 Hz, 1 H, 4-H), 8.46 (d, J = 8.0 Hz, 1 H, 6-H), 7.99 (dd, J_1 = 8.0 Hz, J_2 = 6.1 Hz, 1 H, 5-H), 7.45 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1 H, 6'-H), 7.25 (ddd, J_1 = 9.0 Hz, J_2 = 7.9 Hz, J_3 = 1.7 Hz, 1 H, 4'-H), 6.89 (ddd, J_1 = 9.0 Hz, J_2 = 7.8 Hz, J_3 = 1.0 Hz, 1 H, 5'-H), 6.71 (dd, J_1 = 7.9 Hz, J_2 = 1.0 Hz, 1 H, 3'-H), 2.55 (s, 3 H, Me) ppm. ^{13}C NMR (150 MHz, methanol-d_4): δ = 153.9, 149.1 ($^1J_{C,F}$ = 240 Hz), 147.8, 147.3, 144.6, 139.7, 140.2 ($^1J_{C,F}$ = 285 Hz), 137.9 ($^1J_{C,F}$ = 247 Hz), 135.3, 132.7, 127.7, 125.9, 123.2, 119.6, 119.1, 18.2 ppm. ^{11}B-NMR (193 MHz, methanol-d_4, $BF_3{\cdot}Et_2O$): δ = -3.43 (s, 1 B) ppm. ^{19}F NMR (376 MHz, methanol-d_4, $CFCl_3$): δ = -134.03 (d, $^1J_{C,F}$ = 22.6 Hz, 6 F, 2´´-F, 6´´-F), -161.57 (t, $^1J_{C,F}$ = 18.8 Hz, 3 F, 4´´-F), -166.39--166.50 (m, 6 F, 3´´-F, 5´´-F) ppm. IR (ATR): ṽ = 2962, 2930, 1644, 1456, 1084, 975, 953 cm^{-1}. HRESIMS: $C_{30}H_{11}BF_{15}NONa^+$ required 720.0592. Found 720.0593.

(2-(4-Methylpyridinium-1-yl)phenoxy)tris(pentafluorophenyl)borate 9d. A sample of 0.044 g (0.24 mmol) of 2-(4-methylpyridinium-1-yl)-phenolate **8d** and of 0.102 g (0.20 mmol) of tris(pentafluorophenyl)borane was used. The borane adduct **9d** was obtained as reddish brown solid. Yield 50% (0.104 g), mp. 251 °C. ^{1}H NMR (400 MHz, methanol-d_4): δ = 8.71 (d, J = 6.6 Hz, 2 H, 2/6-H), 7.92 (d, J = 6.6 Hz, 2 H, 3/5-H), 7.44 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1 H, 6'-H), 7.23 (ddd, J_1 = 8.4 Hz, J_2 = 7.6 Hz, J_3 = 1.7, 1 H, 4'-H), 6.88 (ddd, J_1 = 7.8 Hz, J_2 = 7.6 Hz, J_3 = 1.1 Hz, 1 H, 5'-H), 6.65 (dd, J_1 = 8.4 Hz, J_2 = 1.1 Hz, 1 H, 3'-H), 2.71 (s, 3 H, Me) ppm. ^{13}C NMR (150 MHz, methanol-d_4): δ = 161.6, 154.1, 149.2 ($^1J_{C,F}$ = 247 Hz), 146.7, 141.0 ($^1J_{C,F}$ = 256 Hz), 137.9($^1J_{C,F}$ = 250 Hz), 135.0, 132.6, 128.6, 125.8, 123.2, 119.4, 119.0, 22.0 ppm.^{11}B-NMR (193 MHz, methanol-d_4, $BF_3{\cdot}Et_2O$): δ = -3.45 (s, 1 B) ppm. ^{19}F NMR (565 MHz, methanol-d_4, $CFCl_3$): δ = -135.65 (d, $^1J_{C,F}$ = 19.1 Hz, 6 F, 2´´-F, 6´´-F), -163.37 (t, $^1J_{C,F}$ = 19.6 Hz, 3 F, 4´´-F), -168.26--168.35 (m, 6 F, 3´´-F, 5´´-F) ppm. IR (ATR): ṽ = 1643, 1514, 1461, 1452, 1093, 1083, 975, 945, 768, 763 cm^{-1}. HRESIMS: $C_{30}H_{11}BF_{15}NONa^+$ required 720.0592. Found 720.0579.

***N*-(3-Hydroxyphenyl)pyridinium perchlorate 11.** A sample of 1.00 g (3.55 mmol) *N*-(2,4-dinitrophenyl)pyridinium chloride (**10**) and 0.775 g (7.10 mmol) of 3-aminophenol were dissolved in 7 mL of DMF and heated to 90 °C for 24 h. On cooling the reaction mixture was concentrated *in vacuo* and then dissolved in water. The aqueous phase was extracted with ethyl acetate until the organic phase stayed clear. The aqueous phase was then concentrated *in vacuo* and treated with activated carbon after addition of 0.500 g (3.55 mmol) of sodium perchlorate monohydrate. This mixture was filtered hot and after the filtrate was concentrated, some more sodium perchlorate was added. On cooling, the product **11** precipitated as brown leaves. Yield: 0.482 g (50%). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.44 (br. s., 1H, OH), 9.29 – 9.28 (m, 2H, 2-H, 6-H), 8.76 (tt, J_1 = 8.3 Hz, J_2 = 1.3 Hz, 1H, 4-H), 8.28 – 8.26 (m, 2H, 3-H, 5-H), 7.52(t, J = 8.1 Hz, 1H, 5'-H), 7.26 (ddd, J_1 = 8.1 Hz, J_2 = 2.3 Hz, J_3 = 0.8 Hz, 1H, 4'-H), 7.22 (t, J = 2.3 Hz, 1H, 2'-H), 7.12 (ddd, J_1 = 8.1 Hz, J_2 = 2.3 Hz, J_3 = 0.8 Hz, 1H, 6'-H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 158.6 (o, 1C, 1'-C), 146.6 (+, 1C, 4-C), 144.8 (+, 2C, 2-C, 6-C), 143.8 (o, 1C, 1'-C), 131.1 (+, 1C, 5'-C), 128.1 (+, 2C, 3-C, 5-C), 118.1 (+, 1C, 6'-C), 115.0 (+, 1C, 4'-C), 111.7 (+, 1C, 2'-C) ppm. ^{35}Cl NMR (58.8 MHz, DMSO-d_6): δ = 953.47 ppm. IR (ATR): ṽ = 3358, 3125, 3068, 1610, 1569, 1457, 1311, 1296, 1190, 1162, 1073, 1034, 998, 926, 892, 852, 768, 720, 683, 618, 534, 469, 429 cm^{-1}. HRESIMS: $C_{11}H_9NO^+$ required 172.0757. Found 172.0757.

3-(Pyridinium-1-yl)-phenolate 12. A sample of 100 mg (0.4 mmol) of 1-(3-hydroxyphenyl)pyridinium perchlorate was dissolved in methanol and slowly run through a column, filled with Amberlite IRA-96, using methanol as the mobile phase. The eluate was evaporated *in vacuo* and the orange residue was dried *in vacuo*. Yield: 63 mg (100%), ^{1}H NMR (600 MHz, DMSO-d_6): δ = 6.55 (d, J = 7.1 Hz, 1H, 2'-H), 6.65-6.67 (m, 2H, 4'-H, 6'-H), 7.14 (t, J = 8.2 Hz, 1H, 5'-H), 8.20 (m, 2H, 3-H, 5-H), 8.68 (m, 1H, 4-H), 9.22 (m, 2H, 2-H, 6-H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 107.2 (+, 1C, 6'-C), 112.9 (+, 1C, 2'-C), 121.1 (+, 1C, 4'-C), 128.5 (+, 2C, 3-C, 5-C), 130.6 (+, 1C, 5'-C), 144.7 (+, 2C, 2-C, 6-C), 145.2 (o, 1C, 1'-C), 146.3 (+, 1C, 4-C), 168.6 (o, 1C, 3'-C) ppm. On standing, decomposition occurred. Due to the substance's instability, no further analytical data have been recorded.

***N*-(3,4-Dihydroxyphenyl)pyridinium bromide 14.** To a solution of 2.0 mL (24.8 mmol) of freshly distilled pyridine and

(12.4 mmol) of bromine were added dropwise at 0 – 10 °C. The resulting solid was recrystallized from a 1:1 mixture of concentrated hydrobromic acid and water and precipitated as a colorless powder. Yield: 2.14 g (64 %), ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.02 (d, *J* = 8.5 Hz, 1H, H-5‘), 7.14 (dd, J_1 = 8.5 Hz, J_2 = 2.8 Hz, 1H, H-6‘), 7.22 (d, *J* = 2.8 Hz, 1H, H-2‘), 8.22-8.24 (m, 2H, H-3), 8.70 (tt, J_1 = 7.8 Hz, J_2 = 1.3 Hz, 1H, H-4), 9.22-9.23 (m, 2H, H-2), 9.83 (br.s., 1H, H-7‘/H-8‘), 9.97 (br.s., 1H, H-7‘/H-8‘) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 111.8 (+, 1C, C-2‘), 115.5 (+, 1C, C-6‘), 115.8 (+, 1C, C-5‘), 128.1 (+, 2C, C-3), 134.6 (o, 1C, C-1‘), 144.5 (+, 2C, C-2), 145.7 (+, 1C, C-4), 146.3 (o, 1C, C-3‘), 148.1 (o, 1C, C-4‘) ppm. HRESIMS: $C_{11}H_{10}NO_2^+$ required 188.0706. Found 118.0707

2-Hydroxy-4-(pyridinium-1-yl)phenolate 15. 1.14 g (4.25 mmol) of **14** was dissolved in 10 mL distilled water and heated to 60 °C. To that solution, 0.60 mL (8.0 mmol) of ammonia (25 %) were added. The product precipitated immediately as a yellow solid. After cooling to 4 °C, the mixture was filtered cold to collect **15** as a bright yellow powder after washing the residue with water and acetone. Yield: 0.674 g (85 %), ^{1}H NMR (600 MHz, DMSO-d_6): δ = 6.77 (d, *J* = 8.5 Hz, 1H, H-5‘), 6.91 (dd, J_1 = 8.5 Hz, J_2 = 2.6 Hz, 1H, H-6‘), 7.04 (d, *J* = 2.6 Hz, 1H, H-2‘), 8.15-8.18 (m, 2H, H-3), 8.61 (tt, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H, H-4), 9.17 (d, *J* = 5.7 Hz, 2H, H-2) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 109.5 (+, 1C, C-2‘), 113.2 (+, 1C, C-6‘), 114.2 (+, 1C, C-5‘), 127.9 (+, 2C, C-3), 132.4 (o, 1C, C-1‘), 143.9 (+, 2C, C-2), 144.6 (+, 1C, C-4), 150.0 (o, 1C, C-3‘), 152.8 (o, 1C, C-4‘) ppm. IR (ATR): ṽ = 3446, 3404, 3115, 3040, 3004, 1624, 1468, 1450, 1282, 1269, 1201, 1192, 1112, 1097, 1047, 1020, 919, 867, 817, 791, 766, 738, 716, 680, 616, 594, 536, 472, 455, 438 cm⁻¹. HRESIMS: $C_{11}H_{10}NO_2^+$ required 188.0706. Found 118.0706

Crystal Structure Determinations of 1d and 5c

The single-crystal X-ray diffraction studies were carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Mo-Ka radiation (**1d**, *l* = 0.71073 Å) or Cu-Ka radiation (**5c**, *l* = 1.54178 Å). Direct Methods (SHELXS-97)[46] were used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F^2).[47] Hydrogen atoms were localized by difference electron density determination and refined using a riding model (H(O) free). Semi-empirical absorption corrections were applied. For **1d** an extinction correction was applied. In **5c** there is a positional disorder of the solvent DMSO and water in the ratio 3:1 (see cif-file for details).

1d: yellow crystals, $C_{12}H_{12}NO_2Cl\cdot H_2O$, M_r = 255.69, crystal size 0.40 × 0.30 × 0.20 mm, monoclinic, space group $P2_1/n$ (no. 14), *a* = 11.9694 (7) Å, *b* = 7.3995 (4) Å, *c* = 13.9474 (7) Å, *β* = 103.151 (2)°, *V* = 1202.89(11) Å^3, *Z* = 4, *ρ* = 1.412 Mg/m^{-3}, μ(Mo-K$_\alpha$) = 0.31 mm^{-1}, *F*(000) = 536, $2\theta_{max}$ = 55.2°, 23509 reflections, of which 2777 were independent (R_{int} = 0.027), 168 parameters, 5 restraints, R_1 = 0.029 (for 2511 I > 2σ(I)), wR_2 = 0.084 (all data), *S* = 1.08, largest diff. peak / hole = 0.34 / -0.28 e Å^{-3}.

5c: yellow crystals, $C_{30}H_{11}BF_{15}NO_2\cdot 0.75(C_2H_6OS)\cdot 0.25(CH_4O)$, M_r = 779.81, crystal size 0.20 × 0.15 × 0.03 mm, triclinic, space group *P-1* (No. 2), *a* = 10.4962 (3) Å, *b* = 10.7207 (3) Å, *c* = 15.2469 (5)Å, *α* = 89.500 (2)°, *β* = 71.634 (2)°, *γ* = 74.483 (2)°, *V* = 1563.58 (8) Å^3, *Z* = 2, *ρ* = 1.656 Mg/m^{-3}, μ(Cu-K$_\alpha$) = 1.94 mm^{-1}, *F*(000) = 780, $2\theta_{max}$ = 144.2°, 27439 reflections, of which 6117 were independent (R_{int} = 0.035), 490 parameters, 86 restraints, R_1 largest diff. peak / hole = 0.96 / -0.47 e Å^{-3}.

CCDC 2005556 (**1d**), and 2005556 (**5c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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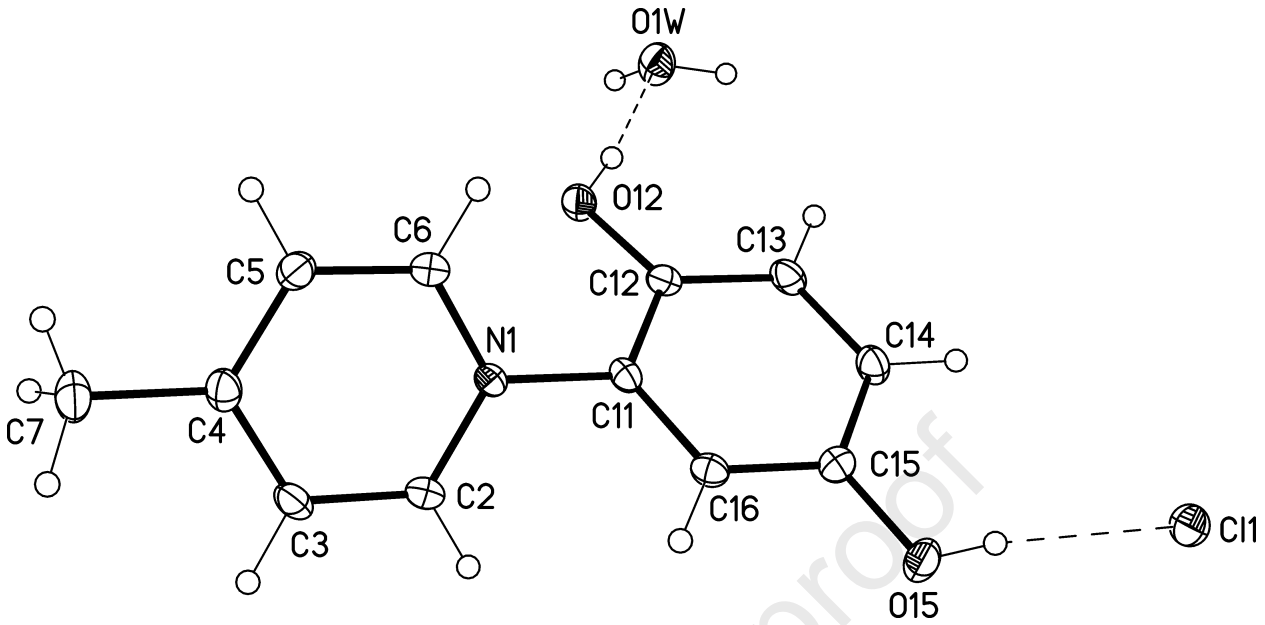

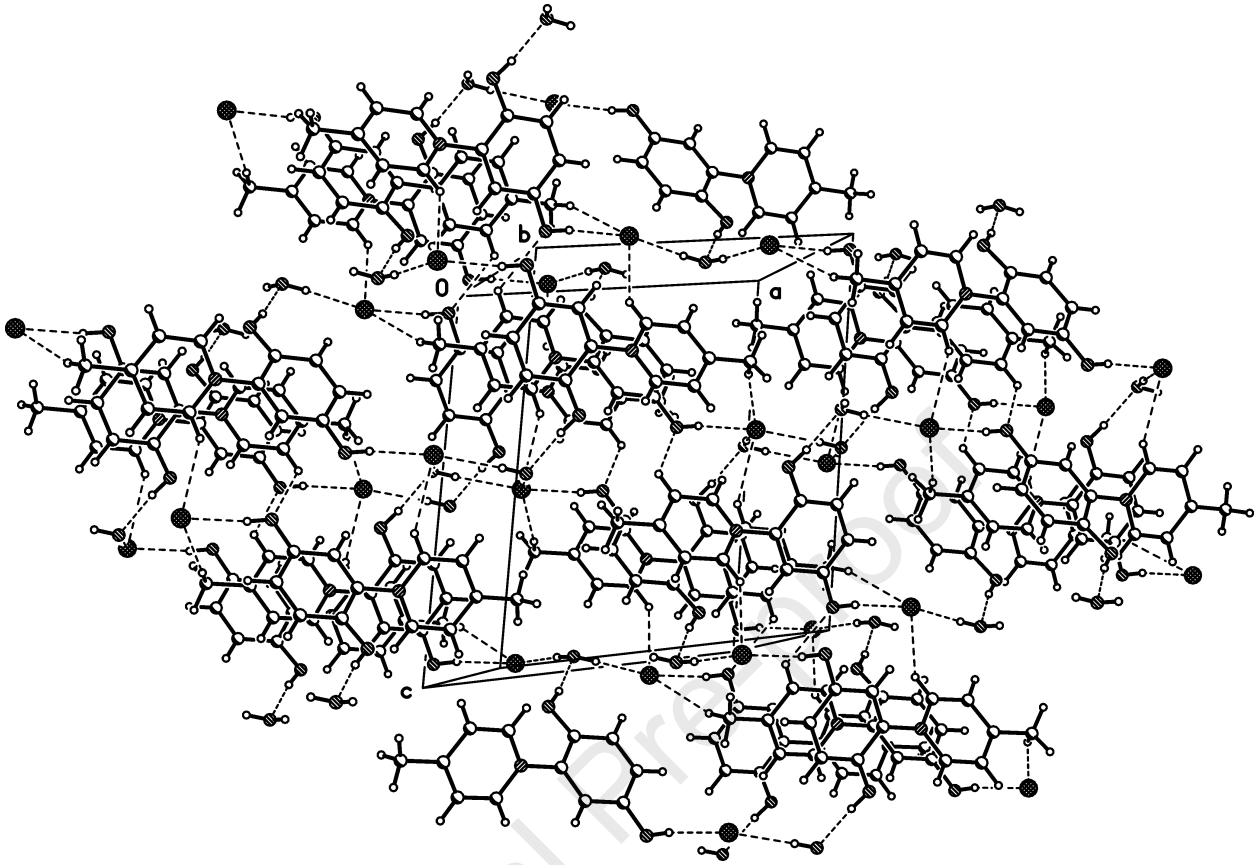

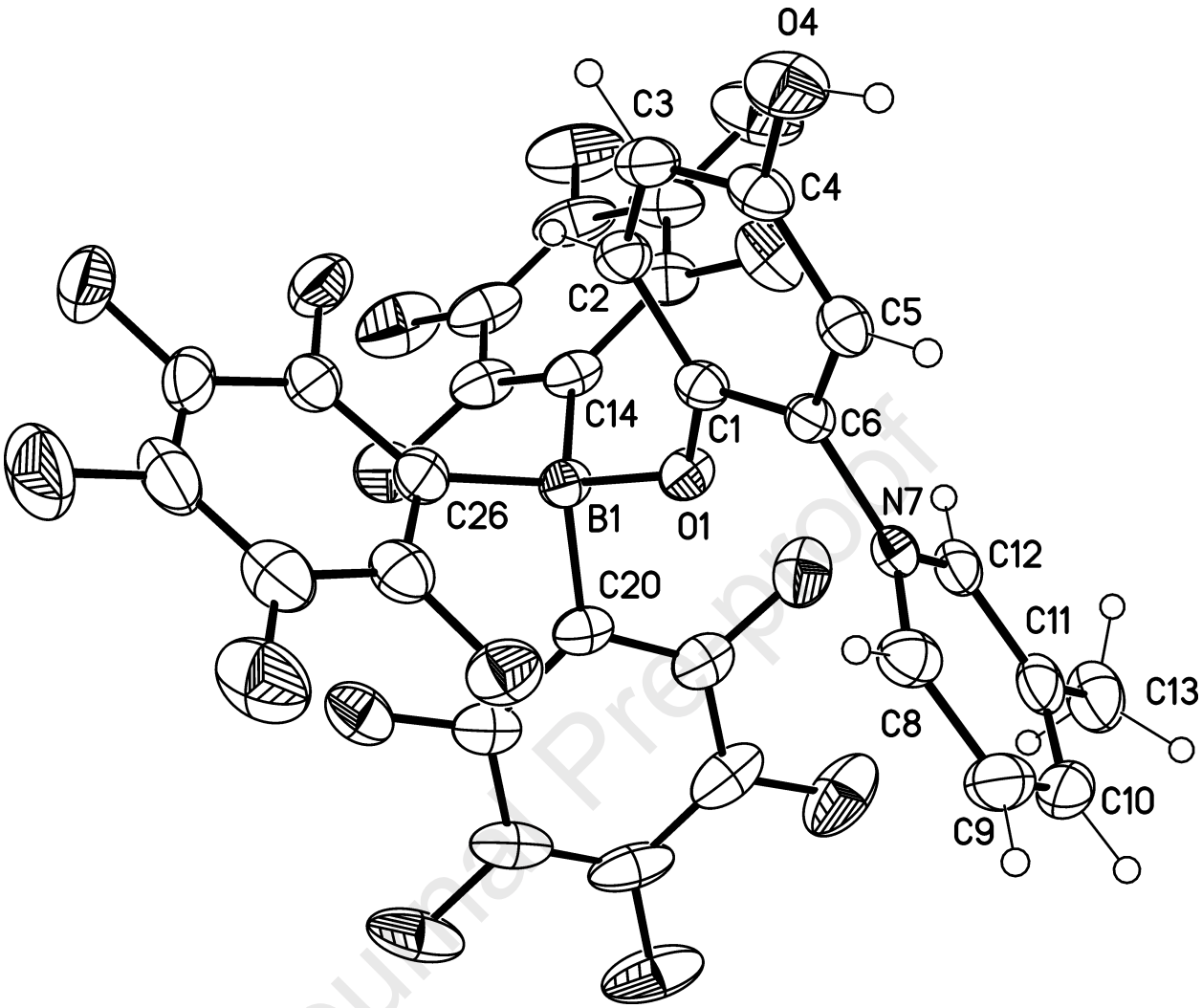

Punicine, consisting of a pyridinium attached to a 4-hydroxyphenyl-olate moiety, exists as two tautomers, a conjugated mesomeric betaine and a cross-conjugated mesomeric betaine.

Reaction with tris(pentafluorophenyl)borane occurs exclusively at the conjugated 2´-olate group to form zwitterionic borane adducts.

Conjugated as well as cross-conjugated dehydroxypunicines as model compounds behave similarly.

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: