Konstantin Drandarov, Ioannis Tiritiris and Willi Kantlehner*

Orthoamides and iminium salts, LXXXIX. Reactions of *N*,*N*,*N*′,*N*′,*N*″,*N*″,*N*‴,*N*‴-octamethyl-acetylene-bis(carboxamidinium) tetrafluoroborate with nucleophilic reagents – new methods for the preparation of amidinium salts and ketene aminals[a]

Abstract: The acetylene-bis(carboxamidinium) salt **4** dehydrates carboxylic acids to the corresponding anhydrides, as the byproduct 2-oxo-but-2-en-amidinium salt **6b** was isolated. Aromatic hydroxy compounds and 2-furyl-methylmercaptan add to the triple bond of the salt **4** to give 2-aryloxy- and 2-alkylmercapto-but-2-ene-bis(amidinium) salts **7**–**9**. According to this reaction principle, 2-organoamino-buten-2-ene-bis(amidinium) salts **10** and **11** were prepared from **4** and primary and secondary amines, whereas 4-chlorobenzhydrazide reacted with **4** to give the imidazole-3-carboxamidinium salt **13**. The reaction of CH_2-acidic compounds as malononitrile or ethyl cyanoacetate with the bis(amidinium) salt **4** affords 2-cyanomethylene-but-3-enamidinium salts **15**. With the CH-acidic diethyl 2-bromomalonate, compound **4** undergoes a Michael-initiated ring closure cyclopropenation reaction with further ring opening by the released Br^- to the corresponding 2-diethoxycarbonylmethylene-3-bromo-but-3-enamidinium salt **18**. Unlike cyclopentadiene and furane, the reaction of *N*-methylpyrrole and bis(amidinium) salt **4** does not lead to Diels–Alder [4 + 2] cycloadduct but to the Michael-type 1:1 adduct **20**. Pyrrole- and thiophene-2-carboxamidinium salts **23**–**25** can be prepared from compound **4** and esters of glycine, *N*-methylglycine (sarcosine), and mercaptoacetic acid, respectively. The derivatives of quinoxaline-2-carboxamidinium salts **29** are accessible from aromatic 1,2-diamines and compound **4**. The reaction of the CH_2/NH-acidic cyanoacetamide with the bis(amidinium) salt **4** produced the 3-pyrroline-2-on derivatives **33**.

Keywords: acetylene; bis(amidinium) salts; CH_2- and XH-acidic compounds; ketene aminals; Michael-initiated ring closure reactions.

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Dedicated to: Professor Klaus Peseke on the occasion of his 75th birthday

1 Introduction

Only a few types of alkyne iminium salts are known (Scheme 1). The methods for the preparation of alkyne iminium salts **1**, which can formally be derived from aldehydes or ketones – or more exactly from vinylogous amides – have mainly been developed by Maas et al. [2–8]. Alkinyl-alkoxymethyleniminium salts **2** have been prepared by the alkylation of propiolamides with triethyloxonium tetrafluoroborate [9–14] or methyl fluorosulfonate [15]. The alkylation of propiolamidines seems to be of low value for the preparation of propiolamidinium salts [16]. In general, propiolamidinium salts are well accessible by the cleavage of orthoamide derivatives of alkyne carboxylic acids with benzoyl chloride [17–19], triethylsilyl trifluoromethanesulfonate and trimethylsilyl halides [18], or elemental bromine [20].

[a]Orthoamides and Iminium Salts, LXXXVIII: see ref. [1]

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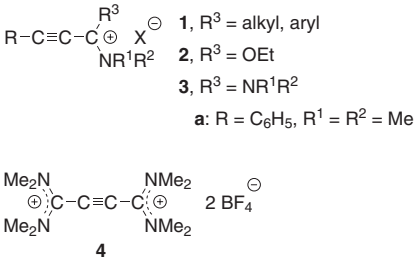


Scheme 1: Alkyne iminium salts.

A number of chemical reactions have been performed with propyne iminium salts **1** [4, 5, 8, 21–34]. In contrast, only few reactions of propiolamidinium salts **3** are known. Examples are the addition reactions of primary [19] and secondary amines [18, 19] and thiols [18].

Recently, we have described the preparation of *N*,*N*,*N*′,*N*′,*N*″,*N*″,*N*‴,*N*‴-octamethyl-acetylene-bis(carboxamidinium)-bis(tetrafluoroborate) (**4**) by the cleavage of 1,1,1,4,4,4-hexakis(dimethylamino)-2-butyne with trifluoroacetic anhydride [35]. Heterocyclic bis(amidinium) salts could be prepared from the bis(amidinium) salt **4** by cycloaddition reactions [36].

N,*N*,*N*′,*N*′-peralkylated amidinium salts are of general interest in preparative organic chemistry [37–39], because they can be used for the preparation of nearly all kinds of orthoamide derivatives [40] and ketene aminals [41, 42], which are of high synthetic importance. Thus, the precursors for very useful formylating reagents, such as *N*,*N*-dimethylformamide acetals, the Bredereck-Simchen esters, or tris(dialkylamino)methanes, are *N*,*N*,*N*′,*N*′-tetraalkyl-formamidinium salts.

From this point of view, bis(orthoamide) derivatives with close neighborhood of the orthoamide functions (e.g., 1,2 or 1,3-position) are potentially interesting building blocks, especially for cyclization reactions. The compounds of this type should be available from the corresponding bis(amidinium) salts. Unfortunately, only a few methods for the preparation of *N*-peralkylated bis(amidinium) salts of this type are known [35]. Additionally, some of the known procedures are hardly suited for preparative purposes because expensive silver salts are used as reagents in stoichiometric amounts [43]. In contrast, the above-mentioned cycloaddition reactions of the bis(amidinium)salt **4** give access to isocyclic and heterocyclic 1,2-bis(carboxamidinium) salts on a preparative scale [35, 36].

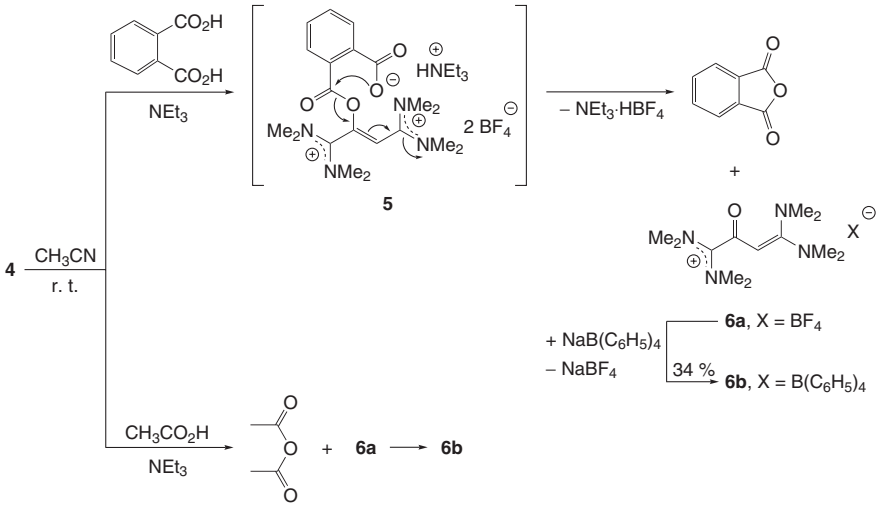
In the present paper, we report on the reactions of the salt **4** with nucleophilic reagents, furnishing various amidinium and bis(amidinium) salts and ketene aminals.

2 Results and discussion

As in propyne iminium salts **1** [21] and propiolamidinium salts **3** [18], the cation of the salt **4** can be regarded as an ambident electrophile, because nucleophilic reagents can add to the triple bond (Michael-addition analogue) or to the carbon in the center of the amidinium function. As far as investigated in nucleophilic addition reactions to propioliminium systems **1** and **3**, the Michael-type addition reactions predominate in most cases. Thus, in addition to the reactions of mercaptanes or morpholine to **3a**, the conjugated addition products were formed solely [18, 19].

In the course of our investigations on nucleophilic addition reactions to the cation of the salt **4**, we made analogous observations.

The salt **4** can act as a neutral strong dehydrating reagent. When phthalic acid was reacted with salt **4** in the presence of triethylamine in acetonitrile, phthalic acid anhydride was formed in quantitative yield [thin-layer chromatography (TLC) detection]. As a second product, the amidinium salt **6a** was formed, which was isolated easily as the well crystallizing tetraphenylborate **6b** (Scheme 2). The amidinium salt **6a** was prepared advantageously from acetic acid and salt **4** in the presence of excessive triethylamine, and **6b** was similarly precipitated by the addition of sodium tetraphenylborate to the filtered reaction mixture (Scheme 2). Possibly, the high dehydrating power of the bis(amidinium) salt **4** can be used for the formation of peptides, glycosides, or esters (in analogy to the Mitsunobu reaction [44–47]). However, at present, we do not examine this question. Colorless single crystals of **6b** were obtained by recrystallization from hot acetonitrile solution. The crystal structure of compound **6b** is shown in Fig. 1. The compound crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ (Table 1). The crystal structure analysis (Fig. 1) reveals that the planes built up from the amidine and the N···C$^+$···N unit are twisted against each other with an angle of 56.5°. The bond lengths in the N···C$^+$···N moiety are 1.321(4) and 1.326(4) Å, as expected for charge delocalization between both dimethylamino groups. The distance of 1.535(4) Å between the carbon atoms C7 and C8 is characteristic for a C–C single bond. The bond lengths of 1.409(4) Å for the C5–C6 double bond and 1.389(4) Å for the C6–C7 bond are in a similar range. Also, the C=O distance with 1.253(3) Å is typical for a carbonyl group. The C–N bond lengths in the amidine unit [*d*(C–N) = 1.348(4) and 1.356(4) Å] are slightly longer. Compared with the bisamidinium salt **4**, the four-carbon atoms chain in **6b** is not linear anymore, and the C–C–C angles with 119.2(3)° and 124.0(3)° indicate a trigonal-planar environment of the carbon atoms. The shortest



Scheme 2: Transformation of carboxylic acids to anhydrides by salt **4**.

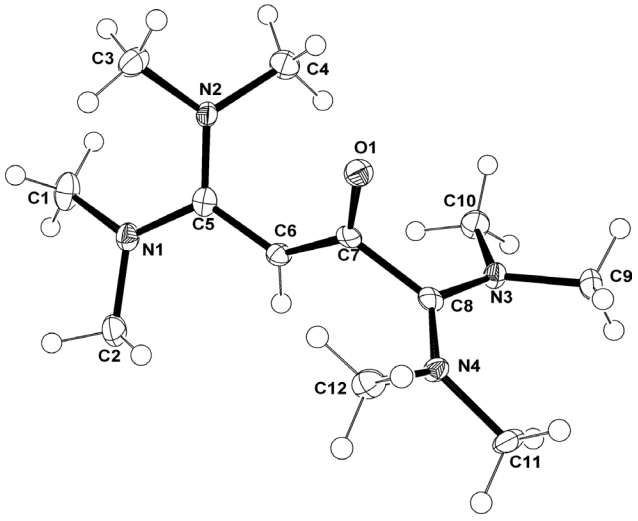


Fig. 1: ORTEP plot (50 % probability ellipsoids) of the cation in *N*,*N*,*N*′,*N*′-tetramethyl-4,4-bis(dimethylamino)-2-oxo-but-3-en-amidinium tetraphenylborate (**6b**) in the crystal.

hydrogen-bonding interactions are observable between an oxygen atom of the carbonyl and a methyl hydrogen atom of a neighboring cation [*d*(H11C···O1) = 2.46 Å]. Finally, the tetraphenylborate ion does not interact with the cation; it serves only for charge compensation.

The bis(amidinium) salts **7a**–**c** are formed by the conjugated addition of phenol or naphthols to the acetylene-bis(carboxamidinium) salt **4** in nearly quantitative yield at room temperature (r.t.) (Scheme 3). Obviously, this type of reaction is also possible with polyhydric phenols, as could be demonstrated by the formation of the six-fold charged salt **8** from compound **4** and phloroglucinol. The addition of 2-furylmethanthiol to **4** follows the same reaction pattern, delivering the bis(amidinium) salt **9a**, which was isolated as tetraphenylborate **9b** (Scheme 3).

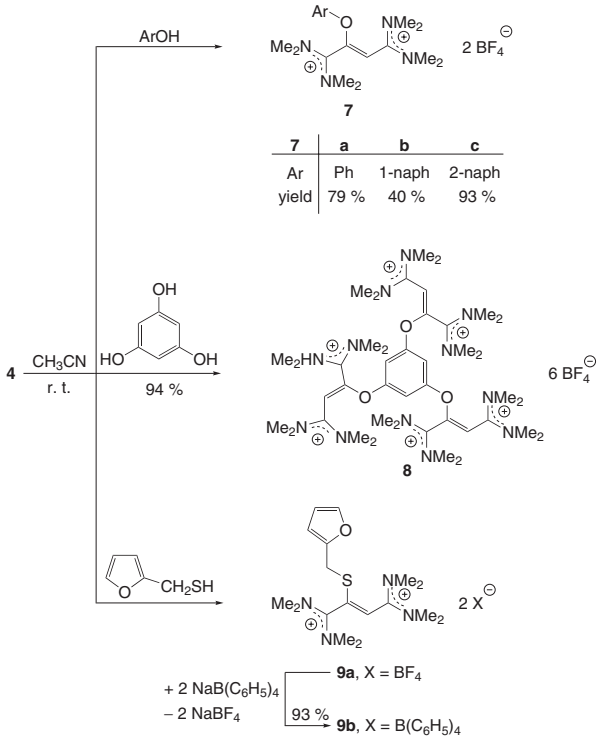
The bis(amidinium) salts **10** and **11** are accessible by the addition of aliphatic amines as dimethylamine, morpholine, and aminoacetonitrile and aromatic amines as aniline and methyl anthranilate to the salt **4** (Scheme 4). Very likely from 4-chlorobenzhydrazide and **4**, the adduct **12** is formed, which undergoes further cyclization under the applied reaction conditions to give the imidazolcarboxamidinium system of **13** (which was isolated as tetraphenylborate, Scheme 4).

Usually, CH_2-acidic compounds react with *N*,*N*,*N*′,*N*′-tetraalkyl-formamidinium salts in the presence of a base under condensation, giving rise to the formation of enamines. However, this reaction type was not observed in the reaction of the bis(amidinium) salt **4** with malononitrile or ethyl cyanoacetate in acetonitrile in the presence of sodium carbonate as a base (Scheme 5). Obviously, in the first step, the adducts **14** are formed, which correspond to compounds **5** and **7**–**11**. The adducts **14** are further deprotonated by the base yielding the amidinium tetrafluoroborates **15**, which are substituted by a "push-pull" system in the α-position. Compound **15b** was converted to the tetraphenylborate before isolation (Scheme 5).

An attempt was made for the cyclopropenation of the alkyne bis(amidinium) salt **4** with diethyl 2-bromomalonate in MeCN at r.t. in the presence of Na_2CO_3 as base (Scheme 6). The TLC analysis of the reaction mixture showed a quick appearance of a colorless intermediate, which was transformed stepwise into a bright orange final product. The product was identified as the amidinium tetrafluoroborate **18**, which analogous to compounds

Table 1: Crystallographic data for **6b**, **20**, and **29a**.

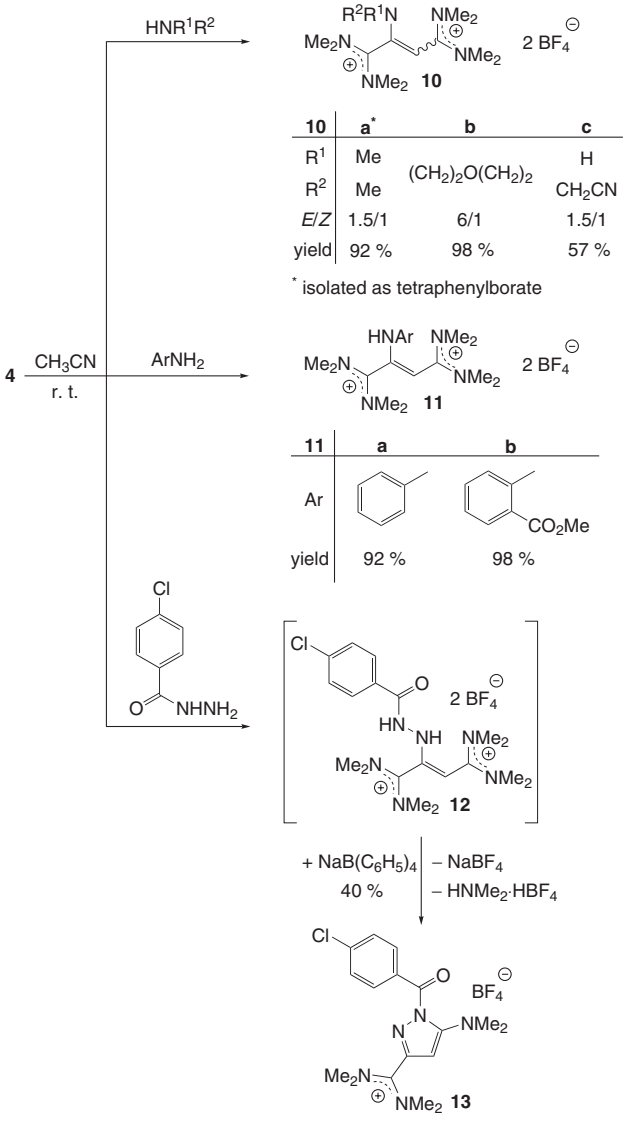
	6b	**20**	**29a**
Formula	$C_{36}H_{45}BN_4O$	$C_{65}H_{71}B_2N_5$	$C_{16}H_{25}B_2F_8N_5$
M_r	560.57	943.89	461.03
Temperature, K	100(2)	293(2)	293(2)
Crystal size, mm³	0.23 × 0.19 × 0.15	0.22 × 0.18 × 0.12	0.17 × 0.13 × 0.10
Crystal system	monoclinic	triclinic	orthorhombic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	*Pbca* (no. 61)
a, Å	10.8824(3)	11.5276(3)	13.0525(4)
b, Å	14.7536(5)	12.9323(5)	24.6540(9)
c, Å	20.0654(8)	18.5259(6)	13.8657(5)
α, °	90	100.128(3)	90
β, °	97.262(2)	97.756(2)	90
γ, °	90	91.669(2)	90
V, Å³	3195.75(19)	2689.95(16)	4461.9(3)
Z	4	2	8
$D_{calcd.}$, g cm⁻³	1.165	1.165	1.373
μ, mm⁻¹	0.1	0.1	0.1
F(000), e	1208	1012	1904
θ range, °	2.45–28.28	4.81–28.17	2.21–28.28
hkl range	±14, ±19, ±26	±15, ±17, ±24	±17, ±32, ±18
Reflections measured/unique	9486/7904	24 559/13 098	6141/5518
R_{int}/R_σ	0.0470/0.0534	0.0283/0.0419	0.0651/0.0814
Reflections with [$I \geq 2\sigma(I)$]	6499	8742	4502
Parameters refined	391	670	290
R_1/wR_2 for reflections with [$I \geq 2\sigma(I)$]	0.0419/0.0830	0.0576/0.1184	0.0516/0.0902
R_1/wR_2 (all reflections)	0.0711/0.0969	0.0986/0.1386	0.0893/0.1091
GoF (F^2)	1.112	1.059	1.058
$\Delta\rho_{fin}$ (max/min), e Å⁻³	0.17/−0.22	0.20/−0.18	0.27/−0.17



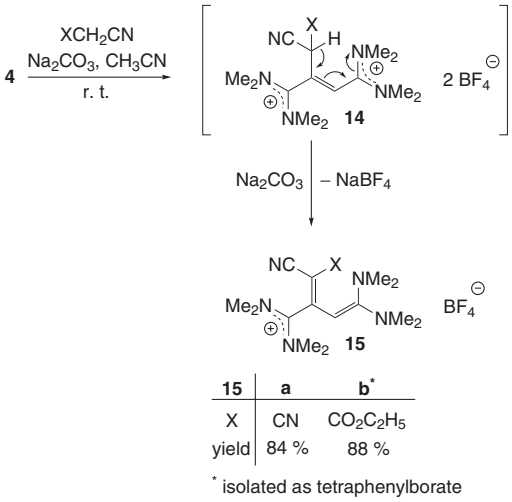
Scheme 3: Addition of hydroxy aromatic compounds and 2-furylmethylmercaptan to the salt **4**.

15 bears in the α-position a "push-pull" 1,3-butadiene system. Apparently, as an initial step, a deprotonation of the strongly CH-acidic 2-bromomalonate takes place. The formed resonance-stabilized carbanion attacks the activated triple bond of compound **4** leading to the allenic intermediate **16**. As a typical example of a Michael-initiated ring closure reaction [48, 49], the intermediate **16** undergoes an intramolecular S_n2 reaction leading to the highly substituted cyclopropene intermediate **17**. Cyclopropenes are highly strained carbocyclic compounds [50, 51]. Therefore, the released bromide anion, as a good nucleophile, further attacks the cyclopropene moiety of the intermediate **17**, causing its ring opening to compound **18** (Scheme 6). Similar Br^-- and I^--induced ring openings of cyclopropenes have been reported recently in the literature [50, 51].

As we have reported earlier, the reactions of compound **4** with cyclopentadiene and furane led to the corresponding Diels–Alder [4 + 2] cycloadducts **19a** and **19b** (Scheme 7) [35]. In contrast, the reaction with *N*-methylpyrrole led to the formation of the Michael-type 1:1 adduct **20** as a sole product. Compound **20** was isolated as the well crystallizing tetraphenylborate salt (Scheme 7). Yellow single crystals of the *N*-methyl-pyrrol-2-yl



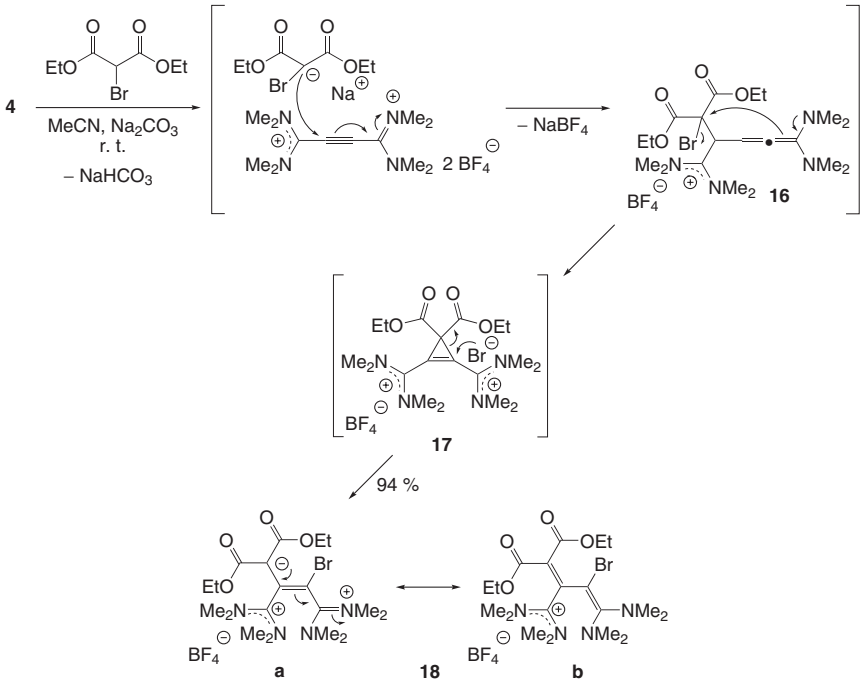
Scheme 4: Addition reactions of amines, amine derivates, and an acylhydrazine to the bis(amidinium)salt **4**.



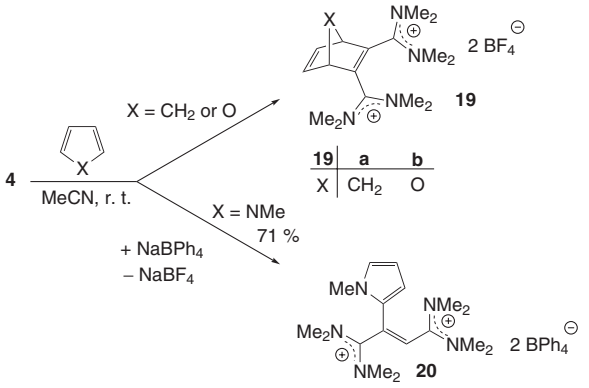
Scheme 5: Condensation of the bis(amidinium) salt **4** with malonic acid derivatives in the presence of a base.

bis(tetraphenylborate) salt **20** were obtained by recrystallization from a hot acetonitrile solution. Its X-ray structure is depicted in Fig. 2. The compound crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ (Table 1). Figure 2 shows a view of the bisamidinium ion. As expected for such type of compounds, the C–N bond lengths in both amidinium units are d(N1–C5) = 1.320(2), d(N2–C5) = 1.333(2), d(N3–C8) = 1.319(2), and d(N4–C8) = 1.320(2) Å, exhibiting also, in this case, charge delocalization between the dimethylamino groups. The distances of 1.480(2) Å between the carbon atoms C5–C6 and 1.495(2) Å between C7–C8 are typical for C–C single bonds separated by a double bond [d(C6–C7) = 1.343(2) Å]. The amidinium moieties show a *trans*-orientation with respect to the C–C double bond and are twisted against each other at an angle of 59.8°. Typically, both tetraphenylborate ions show no significant interactions with the bisamidinium ion.

It could be assumed that, from compound **4** and the methyl esters of glycine, *N*-methylglycine (sarcosine), or mercaptoacetic acid, all bearing an electron-withdrawing group in the α-position, adducts such as **21** would be formed (Scheme 8). However, in these adducts, the methylene groups in the α-position to the ester function are CH_2-acidic and carbanions, obtained from them by deprotonation, should be able to attack the amidinium function located in the γ-position to the amino or mercapto group, respectively, giving the intermediates **22**. The corresponding heterocyclic amidinium salts **23**–**25** could be formed from these "aminals" by the loss of dimethylamine. These considerations were confirmed completely by the corresponding experiments, from which the expected heterocyclic amidinium salts resulted, which were isolated as tetraphenylborates **23b**, **24b**, and **25b** (Scheme 8). Analogously, the cyanomethylamine adduct **10c** (Scheme 4) was expected to undergo a similar ring closure reaction. Unfortunately, the intermediate Michael adduct **10c** and its products showed instability after a prolonged exposure to the base (Na_2CO_3) in the reaction mixture (Scheme 8). Therefore, the expected pyrrole-5-carbonitrile derived product could not be isolated. However, the electrospray ionization-mass spectrometry (ESI-MS) spectrum of compound **10c** confirmed that the intramolecular ring closure reaction is indeed favored by showing the signal of the expected pyrrole-5-carbonitrile product as a major MS fragment (Scheme 8, highlighted, fragment **b**).



Scheme 6: Condensation of the bis(amidinium) salt **4** with diethyl-2-bromomalonate in the presence of a base.



Scheme 7: Reactions of bis(amidinium) salt **4** with cyclopentadiene, furane, and *N*-methylpyrrole.

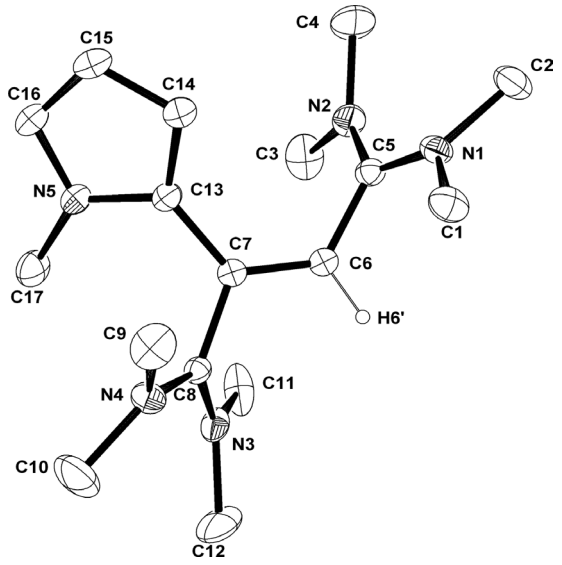
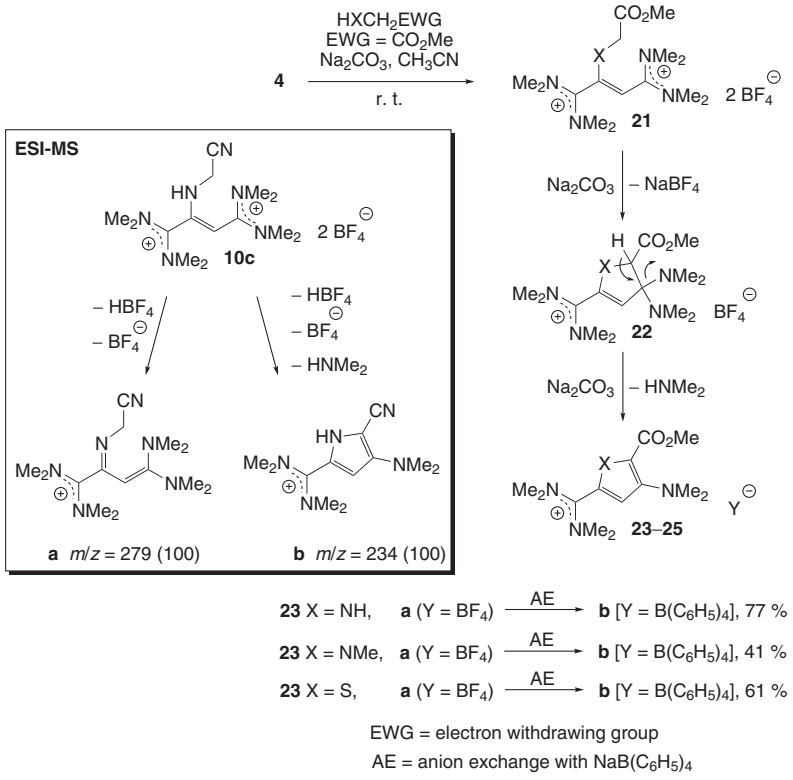


Fig. 2: ORTEP plot (30 % probability ellipsoids) of the cation showing the *trans*-orientation of the amidinium units in *N*,*N*,*N*′,*N*′,*N*″,*N*″,*N*‴,*N*‴-octamethyl-2-(*N*-methyl-pyrrol-2-yl)-2-butene-1,4-bis(amidinium) bis(tetraphenylborate) (**20**).
The hydrogen atoms (except of H6′) were omitted for clarity.

In analogy to these reactions, the addition products **26** from the bis(amidinium) salt **4** and *o*-phenylenediamine or 2,3-diaminonaphthalene, respectively, undergo further cyclization reactions (Scheme 9). However, in these cases, the amidinium function in the β-position to the added amino group reacts with the second aromatic amino group to form the condensation products **27**, which after deprotonation deliver the intensively orange-colored quinoxaline derivatives **28a** and **28b** in good yields (Scheme 9). The crude ketenaminals **28a** and **28b** were converted to the stable bis(tetrafluoroborates) **29a** and **29b**. Presumably, the cyclizations **26** → **27** are facilitated due to the proper spatial orientation of the two amino groups allowing the formation of a sterically favored six-membered transition state leading to the formation of



Scheme 8: Heterocyclic carboxamidinium salts **23**–**25** from the bis(amidinium) salt **4** and the methyl esters of glycine, *N*-methylglycine (sarcosine), and mercaptoacetic acid (EWG = COOMe). The ESI-MS fragmentation pattern of compound **10c** is highlighted in the insert.

six-membered heteroaromatic systems. Yellow single crystals of the quinoxalin-2-yl bis(tetrafluoroborate) salt **29a** were obtained by recrystallization from a hot methanol solution (Scheme 9). The crystal structure of compound **29a** is depicted in Fig. 3. The compound crystallizes in the orthorhombic space group *Pbca* with $Z = 8$ (Table 1). A view of the cation is shown in Fig. 3. The structure analysis shows an almost planar quinoxaline ring system, with the amidinium unit being twisted at an angle of 74.6° with respect to the ring plane. The bond lengths in the N···C$^+$···N moiety are 1.295(5) and 1.313(6) Å, indicating a charge delocalization between both dimethylamino groups similar to compound **29a**. The presence of C–C single bonds [*d*(C5–C6) = 1.511(6) Å, *d*(C6–C7) = 1.481(6) Å, and *d*(C7–C8) = 1.471(6) Å] is clearly indicated. The C–N double bond in the quinoxaline ring is localized between the atoms N5 and C7 [*d*(C–N) = 1.298(5) Å]. In contrast, the nitrogen atom N4 is now protonated [*d*(N4–C8) = 1.350(5) Å]. The distance of 1.319(5) Å between N3 and C8 reveals also charge delocalization within the plane defined by the atoms N3–C8–N4 (see Fig. 3). A strong N–H···F hydrogen bond is observed between the protonated nitrogen atom N4 and a fluorine atom of the tetrafluoroborate ion [*d*(H···F) = 2.19 Å]. In

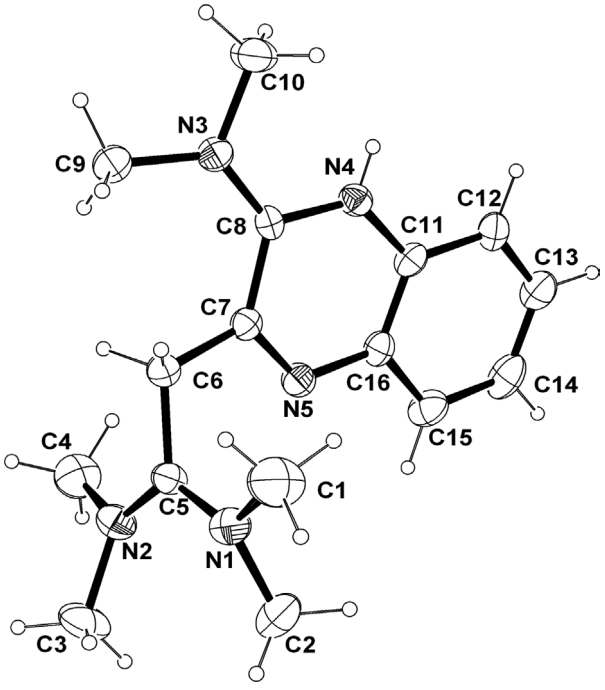
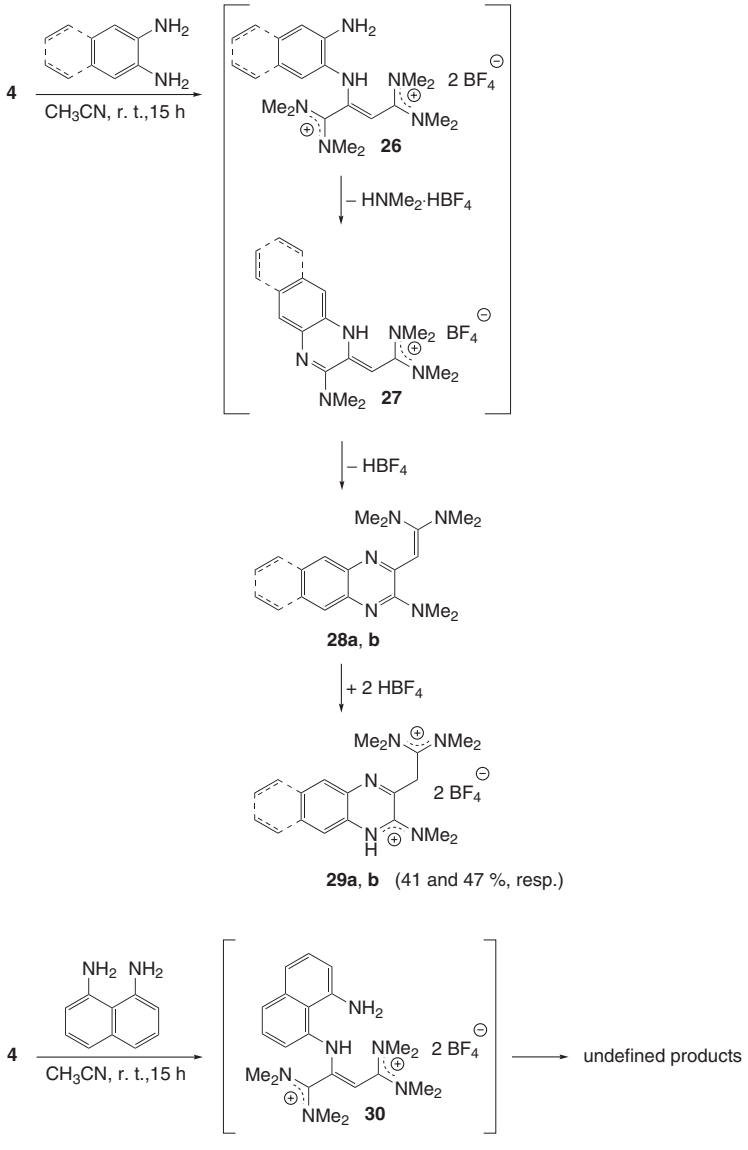


Fig. 3: ORTEP plot (30 % probability ellipsoids) of the cation in *N*,*N*,*N*′,*N*′-tetramethyl-2-(3-dimethylammonio-quinoxalin-2-yl)acetamidinium bis(tetrafluoroborate) **(29a)**.

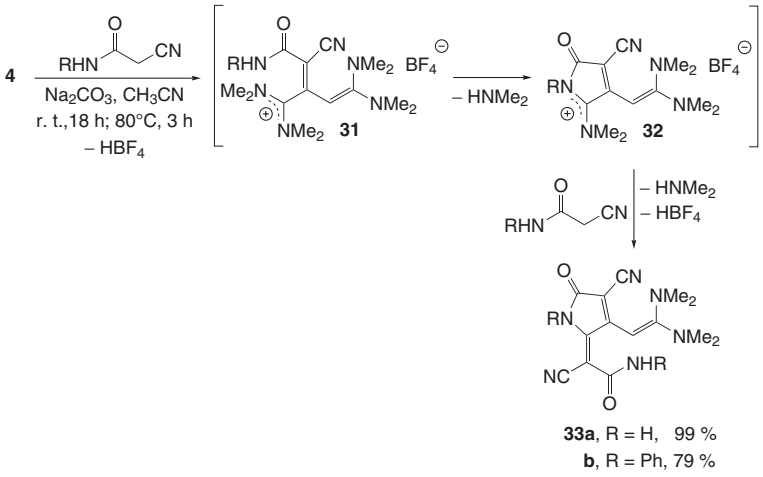
addition, much weaker C–H···F hydrogen bonds between the hydrogen atoms of methyl groups and a neighboring BF_4^- ion were detected [d(H···F) = 2.41 and 2.51 Å].

Such conditions are missing in the molecule of 1,8-diaminonapthalene, where in analogous reactions only unfavorable seven- or eight-membered rings could be formed. Thus, when the salt **4** and 1,8-diaminonapthalene were reacted in acetonitrile, a deep orange color of the reaction mixture appeared, which is typical for the formation of the first adduct **30**. After a short time, the color of the mixtures turned to brown-black. Very likely, intermolecular nucleophilic addition/substitution reactions dominate, giving rise to the formation of polymeric products (Scheme 9).

Cyanoacetamide is a 1,3-difunctional CH_2- and NH_2-acidic compound, which could be expected to react with the salt **4** under cyclization in the presence of a base. The reaction of compound **4** with cyanoacetamide led to a transient bright yellow adduct, which could be detected by TLC of the reaction mixture besides two more products. When the reaction was performed with an excess (2–3 mole equivalents) of cyanoacetamide for 18 h at r.t. and 3 h at 80 °C, only one deep purple-colored product was present, which was identified as compound **33a** (Scheme 10). Obviously, in the first step, cyanoacetamide is added to the activated triple bond of bisamidinium salt **4**, producing an adduct **31**, which undergoes further cyclization to give the transient pyrrolidone-4-carboxamidinium salt **32** (which under the condensation reacts with a second cyanoacetamide equivalent at the amidinium function to yield the final pyrrolidone-derivative **33a**).



Scheme 9: Reaction of aromatic diamines with bis(amidinium) salt **4**.



Scheme 10: Reaction of the amidinium salt **4** with cyanoacetamides.

In full analogy to this reaction, the *N*-phenylpyrrolidone derivative **33b** could be obtained from the salt **4** and *N*-phenyl-cyanoacetamide (Scheme 10).

3 Conclusion

In summary, we could show that, in the presence of a base compound, **4** dehydrates carboxylic acids to their anhydrides with the formation of compound **6a**. The latter could be regarded as a formal water adduct to the triple bond of compound **4**, which otherwise does not react directly with water. Other nucleophilic reagents, such as aromatic hydroxy compounds, mercaptans, aliphatic and aromatic amines, and an acylhydrazine, can be added to the acetylenic bis(iminium) salt **4**, yielding new, hitherto unknown, 2-butene-bis(amidinium) salts **7**–**12** and the pyrazole-carboxamidinium salt **13**. CH_2-acidic compounds such as malononitrile and cyanoacetic acid ester react similarly. However, in the presence of a base, the initially formed adducts are deprotonated to give 3-butene-amidinium salts **15**. The reaction of compound **4** with diethyl bromomalonate apparently involves a cyclopropene intermediate, which is further opened by the released bromide anion to the open-chain "push-pull" butadiene **18**. Unlike cyclopentadiene and furane, the reaction of *N*-methylpyrrole with compound **4** did not give a [4 + 2] cycloadduct but yielded merely the Michael-type 1:1 adduct **20**. From bis-nucleophilic compounds such as esters of amino acids, mercaptoacetic acid or aromatic 1,2-diamines, and the bis(amidinium) salt **4**, heterocyclic carboxamidinium salts **23**–**25** and **29** or ketene aminals **28**, respectively, can be prepared. All these reactions are started by the addition of the nucleophilic center – initially present in the reacting compounds or formed from them by the added base – at C-2 of the bis(amidinium) salt **4**. This addition step can be followed by further condensation reactions between an amidinium function of **4** and an acidic group (NH_2, CH_2) if also present in the used nucleophilic reagent.

All these reactions demonstrate that compounds of type **4** represent valuable precursors for the preparation of heterocyclic amidinium salts and ketenaminals, respectively, which at present are not accessible by other methods.

4 Experimental section

4.1 General procedures

The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX 500 instrument (operating at 500.1 MHz for ^{1}H and 125.7 MHz for ^{13}C). The spectra were calibrated using tetramethylsilane as internal standard. For the assignment of ^{1}H and ^{13}C NMR signals, distortionless enhancement by polarization transfer and two-dimensional ^{1}H,^{1}H-COSY, ^{1}H,^{13}C correlation spectra (heteronuclear single-quantum correlation and heteronuclear multiple-bond correlation spectroscopy) were recorded. The melting points were determined with a Büchi 510 apparatus (Büchi Laboratoriumstechnik AG, Flawil, Switzerland) and are uncorrected. Elemental analyses were performed by the service of the Institut für Organische Chemie, University of Stuttgart. The ESI-MS spectra were measured on a micrOTOF-Q instrument (Bruker Daltonics). Solvents and liquid reagents were purified and dried according to the established procedures.

4.2 X-ray structure determinations

X-ray single crystal diffraction data were collected on a Bruker-Nonius κ CCD diffractometer, which employs graphite-monochromated MoK_α radiation (λ = 0.71073 Å). The data collection for compounds **20** and **29a** was performed at 293 K and that for compound **6b** was performed at 100 K. Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined by employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects. The structures were solved by Direct Methods using the SHELXS-97 [52] structure solution package. All non-hydrogen atoms were located and refined anisotropically with full-matrix least squares using the program SHELXL-97 [53]. The position of hydrogen atoms belonging to the carbon atoms was geometrically optimized by applying the riding model. The crystallographic data and details of the data collection and structure refinement are listed in Table 1. The molecular graphics were drawn with the program Ortep-III [54, 55].

CCDC 796286 (**6b**), 796287 (**20**), and 796288 (**29a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

4.3 *N*,*N*,*N′*,*N′*-tetramethyl-4,4-bis(dimethylamino)-2-oxo-but-3-en-amidinium tetraphenylborate (6b)

Acetic acid (0.50 mL, 520 mg, 8.7 mmol) and triethylamine (0.15 mL, 109 mg, 1 mmol) were added to a solution of the bis(amidinium) tetrafluoroborate **4** (400 mg, 1 mmol) in acetonitrile (3 mL) and the mixture was stirred at r.t. for 19 h. The volatile compounds were removed in vacuo. The residue was dissolved in acetonitrile. A solution of sodium tetraphenylborate (0.7 g, 2 mmol) in acetonitrile (3 mL) was added. The precipitated sodium tetrafluoroborate was removed by filtration. The filtrate was evaporated in vacuo. Methanol was added to the residue. The crystalline material was collected by filtration and recrystallized from methanol to afford the amidinium salt **6b**. Yield: 195 mg (34 %), colorless crystals; m.p. 168 °C. ^{1}H NMR (500 MHz, CD_3CN): δ = 7.27 (m, 8H, ArH), 6.99 (t, J = 7.5 Hz, 8H, ArH), 6.84 (t, J = 7.2 Hz, 4H, ArH), 4.51 [s, 1H, C(3)H], 3.12 [s, 12H, 2N$(CH_3)_2$], 2.92 [s, 12H, 2N$(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 170.9 (C=O), 170.1 [C(1)], 168.5 [C(4)], 165.3, 164.9, 164.5, and 164.1 (BC_{Ph}), 136.7, 126.5, and 122.7 [o-, m-, p-Ar C, $B(Ph)_4$], 85.3 [C(3)], 43.1 [$C^+N(CH_3)_2$], 41.6 [$N(CH_3)_2$] ppm. $C_{36}H_{45}N_4BO$ (560.58): calcd. C 77.13, H 8.09, N 9.99; found C 76.68, H 8.03, N 9.90.

4.4 *N*,*N*,*N′*,*N′*,*N″*,*N″*,*N‴*,*N‴*-octamethyl-2-phenoxy-2-butene-1,4-bis(amidinium) bis-(tetrafluoroborate) (7a)

A solution of phenol (100 mg, 1 mmol) in acetonitrile (2 mL) and finely powdered anhydrous Na_2CO_3 (100 mg, 9.4 mmol) were added to a solution of the bis(amidinium) salt **4** (400 mg, 1.0 mmol) in acetonitrile (2 mL), and the mixture was stirred 18 h at r.t. The mixture was filtered. The filtrate was evaporated in vacuo, and the solid residue was recrystallized from ethanol to afford compound **7a**. Yield: 390 mg (79 %), colorless crystals; m.p. 144–146 °C. ^{1}H NMR (500 MHz, CD_3CN): δ = 7.52 (t, J = 8 Hz, 2H, m-ArH), 7.37 (t, J = 8 Hz, 1H, p-ArH), 7.13 (d, J = 8 Hz, 2H, o-ArH), 6.30 [s, 1H, C(3)H], 3.26 [br. s, 6H, $N(CH_3)_2$], 3.18 [br. s, 12H, 2 $N(CH_3)_2$], 3.01 [br. s, 6H, $N(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 162.6, 162.5 [C(1), C(4)], 153.6 (ArC), 150.3 [C(2)], 131.8, 127.7, and 118.8 (ArC), 111.9 [C(3)], 44.1, 43.5 [$N(CH_3)_2$] ppm. $C_{18}H_{30}N_4B_2F_8O$ (492.07): calcd. C 43.94, H 6.15, N 11.39; found C 43.96, H 6.07, N 11.23.

4.5 *N*,*N*,*N′*,*N′*,*N″*,*N″*,*N‴*,*N‴*-octamethyl-2-(1-naphthyloxy)-2-butene-1,4-bis(amidinium) bis-(tetrafluoroborate) (7b)

1-Naphthol (160 mg, 1.1 mmol) was added to a solution of compound **4** (400 mg, 1.0 mmol) in acetonitrile (3 mL). The yellow mixture was stirred at r.t. overnight. The volatile compounds were removed in vacuo. The solid residue was recrystallized from ethanol to give the salt **7b**. Yield: 220 mg (40 %), yellow crystals; m.p. 182–184 °C (dec.). ^{1}H NMR (500 MHz, CD_3CN): δ = 8.32–8.27 (m, 1H, ArH), 8.04–7.99 (m, 1H, ArH), 7.86 (d, J = 8.3 Hz, 1H, ArH), 7.7–7.65 (m, 2H, ArH), 7.53 (t, J = 8.2 Hz, 1H, ArH), 6.90 (d, J = 7.7 Hz, 1H, ArH), 6.51 (s, 1H, =CH-), 3.25 [br. s, 6H, $N(CH_3)_2$], 3.18 [s, 12H, 2$N(CH_3)_2$], 3.05 [br. s, 6H, $N(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 162.8, 162.7 [C(1), C(4)], 149.6 [C(2)], 149.5, 136.2, 129.2, 128.8, 128.4, 127.1, 126.8, 125.5, 122.0 (ArH), 114.3 [C(3)], 111.9 (ArH), 44.4, 43.7 [$N(CH_3)_2$] ppm. $C_{22}H_{32}N_4B_2F_8O$ (542.12): C 48.74, H 5.95, N 10.33; found C 48.53, H 5.92, N 10.33.

4.6 *N,N,N′,N′,N″,N″,N‴,N‴*-octamethyl-2-(2-naphthyloxy)-2-butene-1,4-bis(amidinium) bis-(tetrafluoroborate) (7c)

The bis(amidinium) salt **7c** was obtained from compound **4** (400 mg, 1.0 mmol) and 2-naphthol (150 mg, 1.0 mmol) in acetonitrile (3 mL) as described for **7b**. Yield: 510 mg (93 %), yellow crystals; m.p. 178–180 °C. ^{1}H NMR (500 MHz, CD_3CN): δ = 8.06 (d, J = 9 Hz, 1H, ArH), 8.0–7.96 (m, 1H, ArH), 7.65–7.55 (m, 3H, ArH), 7.32 (d, J = 9 Hz, 1H, ArH), 6.38 [s, 1H, C(3)H], 3.34 [br. s, 6H, $N(CH_3)_2$], 3.20 [s, 12H, $2N(CH_3)_2$], 2.98 [br. s, 6H, $N(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 162.8, 162.7 [C(1), C(4)], 151.5 (ArH), 150.4 [C(2)], 134.7, 132.6, 132.5, 128.9, 128.8, 128.7, 127.7, 118.5, 115.5 (ArH), 112.7 [C(3)], 44.3, 43.7 [$N(CH_3)_2$] ppm. $C_{22}H_{32}N_4B_2F_8O$ (542.12): C 48.74, H 5.95, N 10.33; found C 47.67, H 6.08, N 10.18.

4.7 2-(1,3,5-Benzenetrioxytris-)-[*N,N,N′,N′,N″,N″,N‴,N‴*-octamethyl-(but-2-en)-1,4-bis(amidinium] hexakis(tetrafluoroborate) (8)

1,3,5-Benzenetriol (phloroglucinol) (50 mg, 0.4 mmol) was added to a solution of the bis(amidinium) salt **4** (500 mg, 1.26 mmol) in acetonitrile (3 mL). The mixture was stirred at r.t. for 48 h. The volatile compounds were removed in vacuo. Methanol (10 mL) was added to the residue, and the suspension was stirred at r.t. for 24 h. The solid was collected by filtration, washed several times with methanol, and dried to afford the tetrafluoroborate **8**. Yield: 490 mg (94 %), yellowish powder; m.p. 248–250 °C (dec.). ^{1}H NMR (500 MHz, CD_3CN), mixture of rotamers: δ = 6.59–6.30 (m, 6H, ArH^+ = CH-), 3.41–3.04 [m, 72 H, $12N(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, CD_3CN), mixture of rotamers: δ = 162.6, 162.4, 162.3, 162.2, 161.8, 161.7, 161.6, 161.4, 161.2, 156.1, 155.8, 155.6, 155.2, 149.7, 149.1, 147.3, 118.0, 117.0, 114.5, 113.2, 109.6, 105.9, 103.8, 103.7, 101.3, 99.3, 44.7, 44.6, 44.5, 44.4, 44.3, 44.0, 43.9, 43.8, 43.7 ppm. High-resolution mass spectra (HRMS) [(+)-time-of-flight electrospray ionization (TOF-ESI)]: m/z = 1232.6516 {calcd. 1232.6511 for $C_{42}H_{78}N_{12}O_3 \cdot (BF_4)_5$ $[M\text{-}BF_4]^+$}.

4.8 *N,N,N′,N′,N″,N″,N‴,N‴*-octamethyl-2-(2-furyl-methylthio)-2-butene-1,4-bis(amidinium)) bis(tetraphenylborate) (9b)

2-Furyl-methanthiol (124 mg, 1.09 mmol) was added to a solution of the bis(amidinium) salt **4** (400 mg, 1.0 mmol) in acetonitrile (3 mL). The yellow mixture was stirred 2 h at r.t. A solution of sodium tetraphenylborate (0.7 g, 2 mmol) in acetonitrile (5 mL) was added. The mixture was filtered, and the filtrate was evaporated in vacuo. The crystalline residue was triturated twice with hot methanol, filtered, and washed several times with cold methanol and then dried to afford the bis(amidinium) salt **9b**. Yield: 0.91 g (93 %), yellow solid; m.p. 192 °C (dec.). ^{1}H NMR (500 MHz, CD_3CN): δ = 7.49 [s, 1H, C(3)H], 7.28 (br. s, 16H, o-ArH), 6.99 (t, J = 7.6 Hz, 16H, m-ArH), 6.84 (t, J = 7.6 Hz, 8H, p-ArH), 6.43–6.38 (m, 3H, furane H), 4.02 (s, 2H, CH_2S), 3.24 [br. s, 6H, $N(CH_3)_2$], 3.02 [s, 12H, $2N(CH_3)_2$], 3.00 [br. s, 6H, $N(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 165.3, 164.9, 164.5, 164,1 (BC_{Ph}), 163.6, 163.5 [$C^+(NCH_3)_2$], 148.6, 145.2 [C(2), C(3)], 144.9 [furane C(2)], 136.7 (ArC), 126.5 (ArC), 125.5 [furane C(5)], 122.7 (ArC), 112.3, 111.1 [furane C(3) and C(4)], 44.6, 43,9, 43.2 [$N(CH_3)_2$], 29.7 (CH_2S) ppm. $C_{65}H_{70}N_4B_2OS$ (976.96): C 79.91, H 7.22, N 5.73, S 3,28; found C 79.76, H 7.22, N 5.58, S 3.21.

4.9 (2,3-*E*/*Z*)-*N,N,N′,N′,N″,N″,N‴,N‴*-octamethyl-2-dimethylamino-2-butene-1,4-bis(amidinium) bis(tetraphenylborate) (10a)

Dimethylamine hydrochloride (170 mg, 2.1 mmol) and Na_2CO_3 (150 mg, 1.4 mmol) were added to a solution of compound **4** (400 mg, 1.0 mmol) in acetonitrile (3 mL). The mixture was stirred at r.t. for 3 h and then filtered. A solution of $NaBPh_4$ (0.7 g, 2 mmol) in acetonitrile (3 mL) was added. The precipitated $NaBF_4$ was removed by filtration. The filtrate was concentrated under reduced pressure. Methanol was added to the residue and the mixture was refluxed for few minutes. After cooling to ambient temperature, the crystalline material was collected by filtration, washed several times with methanol, and dried to afford (2,3-*E*/*Z*)-**10a** (1.5:1 ratio). Yield: 849 mg (92 %), yellow crystals; m.p. 260 °C (dec.). ^{1}H NMR (500 MHz, CD_3CN), (2,3-*E*/*Z*)-mixture: δ = 7.27 (br. s, 16H, o-ArH), 6.99 (t, J = 7.3 Hz, 16H, m-ArH), 6.84 (t, J = 7.3 Hz, 8H, p-ArH), 4.81 [s, 0.4H, (2,3-*Z*)-**10a**, C(3)H], 4.61 [s, 0.6H, (2,3-*E*)-**10a**, C(3)H], 3.24 [br. s, 2.4H, (2,3-*Z*)-10a, $C(2)N(CH_3)_2$], 3.20 [br. s, 3.6H, (2,3-*E*)-**10a**, $C(2)N(CH_3)_2$], 3.10–2.70 [m, 24H, $4N(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 166.9 + 166.8 [C(1)], 165.4, 165.0, 164.6, 164.2 (BC_{Ph}), 165.1 + 162.2 [C(4)], 150.7 + 150.3 [C(2)], 136.8 (ArC), 126.6 (ArC), 122.8 (ArC), 92.6 + 90.6 [C(3)], 44.4, 44,3, 44.1, 43.8, 43.4, 43.1, 41.5, 41.2 [$N(CH_3)_2$] ppm. $C_{62}H_{71}N_5B_2$ (907.88): C 82.02, H 7.88, N 7.71; found C 79.00, H 7.67, N 8.20.

4.10 (2,3-*E*/*Z*)-*N*,*N*,*N*′,*N*′,*N*″,*N*″,*N*‴,*N*‴-octamethyl-2-(morpholin-4-yl)-2-butene-1,4-bis(amidinium) bis(tetrafluoroborate (10b)

A mixture of morpholine (180 mg, 2.0 mmol) and acetonitrile (1.5 mL) was added to a solution of compound **4** (400 mg, 1.0 mmol) in acetonitrile (1.5 mL) and the mixture was stirred at r.t. for 19 h. The volatile compounds were removed under reduced pressure. The residual foam was washed twice with boiling tetrahydrofuran (THF) and suspended in diethylether. The pale yellow-white solid was isolated by filtration, washed several times with diethylether, and dried to afford (2,3-*E*/*Z*)-**10b** (6:1 ratio). Yield: 480 mg (98 %), pale yellow solid; m.p. 232–234 °C. ^{1}H NMR (500 MHz, CD_3CN), (2,3-*E*/*Z*)-mixture: δ = 5.29 [s, 0.14H, (2,3-*Z*)-**10b**, C(3)H], 4.90 (s, 0.86H, (2,3-*E*)-**10b**, C(3)H], 3.84–3.66 (m, 4H, CH_2OCH_2), 3.42–3.0 (m, 28H, 4N$(CH_3)_2$ and CH_2NCH_2) ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 166.6, 166.4 [C(4)], 165.2, 162.3 [C(2)], 150.5, 148.9 [C(1)], 97.6, 93.1 [C(3)], 66.7 (CH_2OCH_2), 49.7 (CH_2NCH_2), 44.8, 44.5, 44.4, 44.2, 43.6, 43.3 (NCH_3) ppm. $C_{16}H_{33}N_5B_2F_8O$ (485.07): C 39.62, H 6.86, N 14.44; found C 39.79, H 6.78, N 14.40.

4.11 (2,3-*E*/*Z*)-*N*,*N*,*N*′,*N*′,*N*″,*N*″,*N*‴,*N*‴-octamethyl-2-cyanomethylamino-2-butene-1,4-bis(amidinium) bis(tetrafluoroborate) (10c)

A mixture of compound **4** (400 mg, 1.0 mmol), aminoacetonitrile hydrochloride (110 mg, 1.2 mmol), and Na_2CO_3 (150 mg, 1.4 mmol) in acetonitrile (3 mL) was stirred at r.t. for 1 h and then filtered. The filtrate was concentrated under reduced pressure. Methanol was added to the residue. The crystalline product was isolated by filtration, washed several times with methanol, and dried to afford of (2,3-*E*/*Z*)-**10c** (3:2 ratio). Yield: 260 mg (57 %), light purple crystals; m.p. 168–170 °C. ^{1}H NMR (500 MHz, CD_3CN), (2,3-*E*/*Z*)-mixture: δ = 6.3 (br. s, 1H, NH), 5.25 [br. s, 0.4H, (2,3-*Z*)-**10c**, C(3)H], 5.11 [br. s, 0.6H, (2,3-*E*)-**10c**, C(3)H], 4.35 and 4.16 (2 br. s, 0.8H and 1.2H, CH_2CN), 3.36, 3.32, 3.19 (3 br. s, 9H, 3NCH_3), 3.14 (br. s, 15H, 5NCH_3) ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 165.9, 165.4 [C(4)], 162.6, 161.9 [C(1)], 145.9, 145.7 [C(2)], 116.7, 115.8 (CN), 94.9, 94.7 [C(3)], 44.4, 44.3, 44.2, 43.6, 43.1 [$N(CH_3)_2$], 33.9, 32.8 (CH_2CN) ppm. HRMS [(+)-TOF-ESI]: *m/z* = 279.2294 {calcd. 279.2292 for $C_{14}H_{27}N_6$, [M-HBF_4-BF_4]$^+$, (100)], 234.17 {calcd. 234.17 for $C_{12}H_{20}N_5$, [M-HBF_4-BF_4-HNMe_2]$^+$, (100)}. $C_{14}H_{28}N_6B_2F_8$ (454.02): C 37.04, H 6.22, N 18.51; found C 37.00, H 6.19, N 18.52.

4.12 *N*,*N*,*N*′,*N*′,*N*″,*N*″,*N*‴,*N*‴-octamethyl-2-phenylamino-2-butene-1,4-bis(amidinium) bis(tetrafluoroborate) (11a)

A mixture of aniline (200 mg, 2.0 mmol) and acetonitrile (1.5 mL) was added to a solution of compound **4** (400 mg, 1.0 mmol) in acetonitrile (1.5 mL) and the mixture was stirred at r.t. for 19 h. The volatile compounds were removed under reduced pressure. The residual yellow oil was triturated twice with boiling THF. After cooling to ambient temperature, the solidified residue was suspended in diethylether, isolated by filtration, washed several times with diethylether, and dried to afford compound **11a**. Yield: 470 mg (95 %), yellow solid; m.p. 218 °C. ^{1}H NMR (500 MHz, CD_3CN): δ = 7.88 (s, 1H, NH), 7.44 (t, *J* = 7.8 Hz, 2H, m-ArH), 7.26 (t, *J* = 7.6 Hz, 1H, p-ArH), 7.00 (d, *J* = 7.6 Hz, 2H, o-ArH), 5.31 [s, 1H, C(3)H], 3.35–2.70 (m, 24H, 8NCH_3) ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 165.6, 165.2 [C(1) and C(4)], 142.4 [C(2)], 138.8, 130.9, 126.8, 121.1 (ArC), 98.0 [C(3)], 44.2, 43.7, 42.8 (NCH_3) ppm. $C_{18}H_{31}N_5B_2F_8$ (491.08): C 44.02, H 6.36, N 14.26; found C 44.10, H 6.34, N 14.36.

4.13 *N*,*N*,*N*′,*N*′,*N*″,*N*″,*N*‴,*N*‴-octamethyl-2-(2-methoxycarbonylanilino)-2-butene-1,4-bis(amidinium) bis(tetrafluoroborate) (11b)

A mixture of methyl 2-aminobenzoate (methyl anthranilate) (200 mg, 1.3 mmol) and methanol (3 mL) was added to a suspension of compound **4** (400 mg, 1 mmol) in methanol (3 mL). The mixture was heated shortly to reflux until a clear yellow solution resulted, which was stirred at r.t. for 48 h. The volatile compounds were removed under reduced pressure. Ethanol (5 mL) was added to the residual yellow oil and the mixture was heated for a few minutes. The clear yellow solution was kept at 5 °C for 2 days. The yellow crystalline material formed was collected by filtration, washed twice with cold ethanol, and dried to afford compound **11b**. Yield: 500 mg (90 %), yellow crystals; m.p. 172–174 °C. ^{1}H NMR (500 MHz, CD_3CN): δ = 10.25 (s, 1H, NH), 8.10 (d, *J* = 8 Hz, 1H, ArH), 7.65 (t, *J* = 7.8, 1H, ArH), 7.27 (t, *J* = 7.7, 1H, ArH), 6.75 (d, *J* = 8 Hz, 1H, ArH), 5.55 [s, 1H, C(3)H], 3.93 (s, 3H,

$COCH_3$), 3.4–3.0 (m, 24H, $8NCH_3$) ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 169.1 (C=O), 164.7, 164.6 [C(1), C(4)], 140.4 (ArC), 140.3 [C(2)], 136.0, 133.0, 124.9, 117.9, 117.4 (ArC), 101.9 [C(3)], 53.5 ($COCH_3$), 44.3, 43.9. 43.1 (NCH_3) ppm. $C_{20}H_{33}N_5B_2F_8O_2$ (549.12): C 43.75, H 6.06, N 12.75; found C 43.06, H 6.00, N 12.60.

4.14 *N*,*N*,*N*′,*N*′-tetramethyl-1-(4-chlorbenzoyl)hydrazino]-5-dimethylamino-2H-pyrazole-3-carboxamidinium tetraphenylborate (13)

A mixture of compounds **4** (400 mg, 1.0 mmol), 4-chlorobenzohydrazide (170 mg, 1.0 mmol) and acetonitrile (3 mL) was heated at 50 °C with stirring for a few minutes until the solids were dissolved and then stirring was continued at r.t. for 19 h. The mixture was filtered. A solution of $NaBPh_4$ (0.7 g, 2 mmol) was added. The mixture was filtered and the filtrate was evaporated in vacuo. Methanol was added to the residue. The crystallized product was collected by filtration, washed several times with methanol and dried to afford compound **13**, which was recrystallized from acetonitrile. Yield: 290 mg (40 %), yellow crystals; m.p. 258–260 °C. ^1H NMR (500 MHz, CD_3CN): δ = 7.90 (d, J = 8.6 Hz, 2H, ArH), 7.55 (d, J = 8.6 Hz, 2H, ArH), 7.27 (br. s, 8H, ArH, BPh_4), 6.99 [t, J = 7.4 Hz, 8H, ArH, BPh_4], 6.83 [t, J = 7.3 Hz, 4H, ArH, BPh_4), 5.95 (s, 1H, pyrazole =CH-), 3.12 [br. s, 12H, $2N(CH_3)_2$], 2.90 [s, 6H, $N(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 167.29, 165.42, 165.05, 164.65, 164.25, 163.41, 158.65, 144.31, 140.29, 136.84, 133.62, 132.26, 129.54, 126.63, 122.81, 94.19, 44.09, 43.39 ppm. $C_{41}H_{43}N_5BClO$ (668.08): C 73.71, H 6.49, N 10.48; found C 73.73, H 6.50, N 10.65.

4.15 *N*,*N*,*N*′,*N*′-tetramethyl-2-dicyanomethylene-4,4-bis(dimethylamino)-3-butenamidinium tetrafluoroborate (15a)

A solution of malononitrile (100 mg, 1.5 mmol) in acetonitrile (1.5 mL) was added to a stirred mixture of compound **4** (400 mg, 1.0 mmol) and Na_2CO_3 (100 mg, 0.95 mmol) in acetonitrile (1.5 mL), and stirring was continued at r.t. for 20 h. The mixture was filtered and the yellow-orange filtrate was concentrated under vacuum. The residue was dissolved in hot ethanol and then filtered hot. After cooling to r.t., the crystalline material was collected by filtration, washed several times with ethanol, and dried to afford compound **15a**. Yield: 320 mg (84 %), yellow needles; m.p. 158–160 °C. ^1H NMR (500 MHz, CD_3CN): δ = 4.73 [s, 1H, C(3)H], 3.21 [br. s, 12H, $2N(CH_3)_2$], 3.11 [s, 12H, $2N(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 169.1 [C(4)], 167.6 [C(1)], 147.7 [C(2)], 119.7, 119.5, 119.1, 95.2 [C(3)], 44.4, 43.3, 42.5 (NCH_3) ppm. $C_{15}H_{25}N_6BF_4 \cdot H_2O$ (394.22): C 45.70, H 6.90, N 21.32; found C 44.21, H 6.17, N 20.61.

4.16 *N*,*N*,*N*′,*N*′-tetramethyl-2-cyan-ethoxycarbonylmethylene-4,4-bis(dimethylamino)-3-butenamidinium tetraphenylborate (15b)

A mixture of compound **4** (400 mg, 1.0 mmol), ethyl cyanoacetate (220 mg, 1.9 mmol), Na_2CO_3 (100 mg, 0.95 mmol), and acetonitrile (3 mL) was stirred at r.t. for 24 h. The mixture was diluted with acetonitrile (2 mL) and filtered. A solution of $NaBPh_4$ (360 mg, 1 mmol) in acetonitrile (4 mL) was added to the yellow-orange filtrate. The mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was dissolved in hot methanol. After cooling to ambient temperature, the crystalline material was collected by filtration, washed several times with methanol, and dried to afford compound **15b**. Yield: 580 mg (88 %), yellow needles; m.p. 184–186 °C. ^1H NMR (500 MHz, CD_3CN): δ = 7.27 (br. s, 8H, o-ArH), 6.99 (t, J = 7.4 Hz, 8H, m-ArH), 6.84 (t, J = 7.3 Hz, 4H, p-ArH), 4.55 [s, 1H, C(3)H], 4.07 (q, J = 7 Hz, 2H, OCH_2), 3.20–2.90 [m, 24H, $4N(CH_3)_2$], 1.21 (t, J = 7 Hz, 3H, CH_2CH_3) ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 173.2 [C(2)], 168.2 [C(4)], 167.6 (C=O), 165.4, 165.0, 164.6, 164.2 (BC_{Ph}), 148.3 (CCN), 136.8, 126.6, 122.8 (ArC), 121.2 (CN), 95.7 [C(3)], 60.8 (OCH_2), 44.1, 43.1, 42.3 (NCH_3), 15.0 (CH_2CH_3) ppm. $C_{41}H_{50}N_5BO_2$ (655.68): C 75.10, H 7.69, N 10.68; found C 73.86, H 7.65, N 10.63.

4.17 *N*,*N*,*N*′,*N*′-tetramethyl-2-diethoxymethylene-3-bromo-4,4-bis(dimethylamino)-3-butenamidinium tetrafluoroborate (18)

A mixture of compound **4** (200 mg, 0.5 mmol), diethyl bromomalonate (90 µL, 126 mg, 0.53 mmol), Na_2CO_3 (150 mg, 1.4 mmol), and acetonitrile (3 mL) was stirred at r.t. for 24 h. The mixture was filtered and the filtrate concentrated under reduced pressure. 2-Propanol was added to the residue and the mixture was heated shortly until a clear solution was obtained. The solution was cooled to 5 °C. The crystalline product was collected by filtration,

washed few times with 2-propanol, and dried to afford compound **18**. Yield: 260 mg (94 %), bright orange crystals; m.p. 176–178 °C. ^{1}H NMR (500 MHz, CD_3CN): δ = 4.03 (m, 4H, OCH_2), 3.17 [s, 6H, $N(CH_3)_2$], 3.07 [s, 6H, $N(CH_3)_2$], 3.06 [s, 6H, $N(CH_3)_2$], 2.97 [s, 6H, $N(CH_3)_2$], 1.20 (m, 6H, $2OCH_2CH_3$) ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 174.3, 169.6, 169.3, 168.1, 147.4, 91.9, 83.3, 60.6, 60.2, 44.4, 42.7, 42.6, 42.2, 14.9, 14.6. HRMS [(+)-TOF-ESI]: isotope distribution *m/z* = for $C_{19}H_{34}BrN_4O_4$ $[M\text{-}BF_4]^+$, rel. int. (%).

Calcd.	461.1758 (100)	462.1788 (20.5)	463.1740 (97.5)	464.1769 (20)
Found	461.1750 (100)	462.1779 (22)	463.1726 (100)	464.1742 (22)

4.18 *N,N,N′,N′,N″,N″,N‴,N‴*-octamethyl-2-(1-methyl-1H-pyrrol-2-yl)-2-butene-1,4-bis(amidinium) bis(tetraphenylborate) (20)

A mixture of compound **4** (400 mg, 1 mmol), *N*-methylpyrrole (450 mg, 5.5 mmol), and acetonitrile (3 mL) was stirred at r.t. for 7 days. A solution of $NaBPh_4$ (700 mg, 2 mmol) in acetonitrile (5 mL) was added. The mixture was filtered and the filtrate was concentrated under reduced pressure. Methanol was added to the residue, and the mixture was heated to reflux and left at r.t. The crystalline product was collected by filtration, washed several times with methanol, and dried to afford compound **20**. Yield: 670 mg (71 %), yellow-brown crystals; m.p. 254 °C (dec.). ^{1}H NMR (500 MHz, CD_3CN): δ = 7.27 (br. s, 16H, o-ArH), 7.04 (m, 1H, pyrrole CH), 6.99 (t, *J* = 7.4 Hz, 16H, m-ArH), 6.84 (t, *J* = 7.2 Hz, 8H, p-ArH), 6.35 (m, 1H, pyrrole CH), 6.29 (m, 1H, pyrrole CH), 6.25 [s, 1H, C(3)H], 3.43 (s, 3H, pyrrole NCH_3), 3.35–2.79 [m, 24H, $4N(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 167.9, 165.8, 165.4, 165.0, 164.6, 164.2, 136.8, 136.5, 132.4, 126.7, 125.0, 124.7, 122.8, 111.8, 44.9, 44.0, 42.6, 35.7 ppm. $C_{65}H_{71}N_5B_2$ (943.91): C 82.71, H 7.58, N 7.42; found C 82.47, H 7.58, N 7.52.

4.19 *N,N,N′,N′*-tetramethyl-4-dimethylamino-5-methoxycarbonyl-pyrrole-2-carboxamidinium tetraphenylborate (23b)

A mixture of methyl 2-aminoacetate hydrochloride (glycine methyl ester hydrochloride, 150 mg, 1.2 mmol), compound **4** (400 mg, 1.0 mmol), Na_2CO_3 (150 mg, 1.4 mmol), and acetonitrile (3 mL) was stirred first for 24 h at r.t. and then for 1 h at 80 °C. The mixture was diluted with acetonitrile and filtered. A solution of $NaBPh_4$ (350 mg, 1 mmol) in acetonitrile (3 mL) was added to the yellow filtrate. The mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was dissolved in hot ethanol. After cooling to r.t., the crystalline material was collected by filtration, washed several times with ethanol, and dried to afford the salt **23b**. Yield: 455 mg (77 %), yellow crystals; m.p. 196–198 °C. ^{1}H NMR (500 MHz, CD_3CN): δ = 10.9–9.0 (br. s, 1H, NH), 7.27 (br. s, 8H, o-ArH), 6.98 (t, *J* = 7.3 Hz, 8H, m-ArH), 6.83 (t, *J* = 7.3 Hz, 4H, p-ArH), 6.38 (s, 1H, pyrrole =CH-), 3.81 (s, 3H, $COOCH_3$), 3.04 [br. s, 12H, $2N(CH_3)_2$], 2.78 [s, 6H, $N(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 165.4, 165.0, 164.6, 164.2 (BC_{Ph}), 162.2 (C^+) 160.5 (C=O), 148.1 [C(4)], 136.8, 126.6, 122.8 (ArC), 120.1, 115.9 [C(2), C(5)], 108.9 [C(3)], 52.1 (OCH_3), 44.4, 43.7 (NCH_3) ppm. $C_{37}H_{43}N_4BO_2$ (586.57): C 75.76, H 7.39, N 9.55; found C 75.51, H 7.38, N 9.42.

4.20 *N,N,N′,N′*-tetramethyl-4-dimethylamino-5-methoxycarbonyl-*N*-methylpyrrole-2-carboxamidinium tetraphenylborate (24b)

A mixture of compound **4** (400 mg, 1.0 mmol), 2-(*N*-methylamino)acetate hydrochloride (*N*-methylglycine methyl ester hydrochloride, 170 mg, 1.2 mmol), Na_2CO_3 (150 mg, 1.4 mmol), and acetonitrile (3 mL) was stirred 24 h at r.t. and further 24 h at 80 °C. The mixture was diluted with acetonitrile and filtered. A solution of $NaBPh_4$ (350 mg, 1 mmol) in acetonitrile (3 mL) was added to the yellow filtrate. The mixture was filtered and the filtrate was concentrated under vacuum. The residue was dissolved in hot methanol. After cooling to 5 °C, the crystalline material was collected by filtration, washed several times with methanol, and dried to afford the salt **24b**. Yield: 250 mg (41 %), yellow plates; m.p. 174–176 °C. ^{1}H NMR (500 MHz, CD_3CN): δ = 7.27 (br. s, 8H, o-ArH), 6.98 (t, *J* = 7.5 Hz, 8H, m-ArH), 6.83 (t, *J* = 7.3 Hz, 4H, p-ArH), 6.32 (s, 1H, pyrrole =CH-), 3.84 (s, 3H, $COOCH_3$), 3.61 (s, 3H, pyrrole NCH_3), 3.19 [s, 6H, $N(CH_3)_2$], 2.85 [s, 6H, $N(CH_3)_2$], 2.69 [s, 6H, $N(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 165.4, 165.0, 164.6, 164.2 (BC_{Ph}), 161.8 (C^+), 161.7 (C=O), 148.7 [C(4)], 136.8 (ArC), 126.6 (ArC), 124.2 [C(2)], 122.8 (ArC), 118.6 [C(5)], 107.0 [C(3)], 52.0 (OCH_3), 45.0 $[N(CH_3)_2]$, 43.6, 43.4 $[N(CH_3)_2]$, 35.6 (pyrrole NCH_3) ppm. $C_{38}H_{45}N_4BO_2$ (600.60): C 75.99, H 7.55, N 9.33; found C75.97, H 7.49, N 9.33.

4.21 *N*,*N*,*N*′,*N*′-tetramethyl-3-dimethylamino-5-methoxycarbonyl-thiophene-2-carboxamidinium tetraphenylborate (25b)

A mixture of compound **4** (560 mg, 1.4 mmol), methyl thioglycolate (150 mg, 1.41 mmol), Na_2CO_3 (150 mg, 1.4 mmol), and acetonitrile (3 mL) was stirred 24 h at r.t. The mixture was diluted with acetonitrile and filtered. A solution of $NaBPh_4$ (480 mg, 1.4 mmol) in acetonitrile (3 mL) was added to the yellow filtrate. The mixture was filtered and the filtrate was evaporated in vacuo. The residue was dissolved in hot methanol. After cooling to r.t., the crystalline material was collected by filtration, washed several times with methanol, and dried to afford compound **25b**. Yield: 510 mg (61 %), yellow plates; m.p. 174–176 °C. ^{1}H NMR (500 MHz, CD_3CN): δ = 7.27 (br. s, 8H, o-ArH),7.18 (s, 1H, thiophene =CH-), 6.98 (t, J = 7.3 Hz, 8H, m-ArH), 6.83 (t, J = 7.3 Hz, 4H, p-ArH), 3.78 (s, 3H, $COOCH_3$), 3.08 [br. s, 12H, $2N(CH_3)_2$], 2.97 [s, 6H, $N(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 165.4, 165.0, 164.6, 164.3 (BC_{Ph}), 164.2 (C^+), 162.3 (C=O), 157.5 [C(4)], 136.7 (ArC) 131.7 [C(2)], 128.8 [C(3)], 126.5 (ArC), 122.7 (ArC), 111.1 [C(5)], 52,6 (OCH_3), 44.3 [$N(CH_3)_2$], 44.2 [$N(CH_3)_2$] ppm. $C_{37}H_{42}N_3BO_2S$ (603.62): C 73.62, H 7.01, N 6.96, S 5.31; found C 73.43, H 7.07, N 6.91, S 5.17.

4.22 *N*,*N*,*N*′,*N*′-tetramethyl-2-(3-dimethylammonioquinoxalin-2-yl) acetamidinium bis(tetrafluoroborate) (29a)

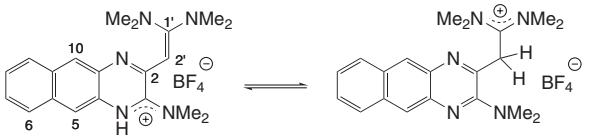
A mixture of compound **4** (480 mg, 1.2 mmol), benzene-1,2-diamine (130 mg, 1.2 mmol), and acetonitrile (3 mL) was stirred at r.t. for 15 h and then concentrated under reduced pressure. The bright yellow glass-like residual solid (**28a**) was dissolved in a minimal amount of methanol. The solution was acidified with 50 % aqueous solution of HBF_4 and concentrated under reduced pressure. The residue was dried by triple dissolving in absolute ethanol and vacuum evaporation. The resulting light yellow glass-like solid was dissolved in the minimal amount of methanol, heated for a few minutes until a clear solution was obtained, and left overnight at 5 °C. The crystalline product was collected by filtration, washed several times with chilled methanol, and dried to afford the hydrotetrafluoroborate-tetrafluoroborate salt **29a**. Yield: 230 mg (41 %), yellow crystals; m.p. 260–264 °C. ^{1}H NMR (500 MHz, CD_3CN): δ = 11.12 (br. s, 1H, NH^+), 7.94 and 7.93 [2d, J = 8.3 Hz, 2H, C(5)H and C(8)H], 7.85 and 7.68 (2t, J = 8.1 Hz, 2H, C(6)H and C(7)H], 4.55 (s, 2H, CH_2), 3.55 [s, 6H, $N(CH_3)_2$], 3.18 [s, 12H, $2N(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 170.7, 148.4, 146.0, 135.0, 134.7, 130.3, 129.3, 128.8, 43.9, 43.6, 40.8 ppm. $C_{16}H_{25}N_5B_2F_8 \cdot H_2O$ (479.03): C 40.12, H 5.68, N 14.62; found C 40.59, H 5.55, N 14.70.

4.23 *N*,*N*,*N*′,*N*′-tetramethyl-2-(3-dimethylammonio-benzo[*g*]quinoxalin-2-yl)acetamidinium bis(tetrafluoroborate) (29b)

A mixture of compound **4** (240 mg, 0.6 mmol), naphthalene-2,3-diamine (80 mg, 0.5 mmol), triethylamine (0.5 mL, 360 mg, 3.6 mmol), and acetonitrile (7 mL) was stirred at r.t. for 18 h. The solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and the solution was washed consecutively with an aqueous solution of K_2CO_3 and water, dried over Na_2SO_4, and concentrated under vacuum. The residual bright orange glass-like solid (**28b**, 110 mg) was dissolved in 4 mL acetonitrile. The solution was acidified with 50 % aqueous HBF_4, and the solvent was evaporated to dryness. The residue was dried by thrice dissolving in acetonitrile and vacuum evaporation. Methanol was added to the residue. The mixture was refluxed for a few minutes and left at r.t. The crystalline product formed was collected by filtration, washed several times with methanol, and dried to afford the hydrotetrafluoroborate-tetrafluoroborate salt **29b**. Yield: 80 mg (47 %), orange crystals; m.p. 248–252 °C. ^{1}H NMR (500 MHz, CD_3CN) [an equilibrium mixture of differently protonated species (~1:1) in CD_3CN solution]: δ = 8.56 (br. s, 0.5H, NH^+), 8.54 [s, 0.5H, C(10)H], 8.33 [s, 0.5H, C(5)H], 8.14 [d, J = 8.4 Hz, 0.5H, C(6)H], 8.10 [d, J = 8.4 Hz, 0.5H, C(9)], 7.96 [s, 0.5H, C(10)H], 7.87 [d, J = 8.2 Hz, 0.5H, C(6)], 7.82 [d, J = 8.2 Hz, 0.5H, C(9)], 7.73 [t, J = 8 Hz, 0.5H, C(7)H], 7.68 [s, 0.5H, C(5)], 7.65 [t, J = 7.7 Hz, 0.5H, C(8)H], 7.51 [t, J = 7.6 Hz, 0.5H, C(7)H], 7.46 [t, J = 7.8 Hz, 0.5H, C(8)H], 5.56 (s, 0.5H, =CH-), 4.59 (s, 1H, $-CH_2-$), 3.61 (s, 3H, NCH_3), 3.50 (s, 3H, NCH_3), 3.22 [s, 6H, $N(CH_3)_2$], 3.21[s, 6H, $N(CH_3)_2$] ppm. $C_{20}H_{27}N_5B_2F_8 \cdot H_2O$ (529.09): C 45.40, H 5.52, N 13.24; found C 45.70 H 5.51, N 13.31.

4.24 2-{3-[2,2-Bis(dimethylamino)vinyl]-4-cyano-5-oxo-2,5-dihydro-pyrrol-2-ylidene}-cyanoacetamide (33a)

A mixture of compound **4** (400 mg, 1.0 mmol), cyanoacetamide (330 mg, 3.9 mmol), triethylamine (0.5 mL), and



28b·HBF_4 **28b**·HBF_4*

	C(5)H	C(6)H	C(7)H	C(8)H	C(9)H	C(10)H	C(2′) H/H_2	NH^+	C(3) NMe_2	C(1′) $N(Me)_2$
28b·HBF_4	8.33 (s)	8.14 (d), *J* = 8.4 Hz	7.73 (t), *J* = 8 Hz	7.65 (t), *J* = 7.7 Hz	8.10 (d), *J* = 8.4 Hz	8.54 (s)	5.56 (s)	8.56 (br. s)	3.61 (s)	3.22 (s)
28b·HBF_4*	7.68 (s)	7.87 (d), *J* = 8.2 Hz	7.51 (t), *J* = 7.6 Hz	7.46 (t), *J* = 7.8 Hz	7.82 (d), *J* = 8.2 Hz	7.96 (s)	4.59 (s)	–	3.50 (s)	3.21 (s)

acetonitrile (4 mL) was stirred at r.t. for 18 h and then at 80 °C for 3 h. The volatile compounds were removed under vacuum. The residue was dissolved in $CHCl_3$ and purified by flash chromatography on silica gel (eluted consecutively with $CHCl_3$, $CHCl_3$/acetone 1:1). The eluate was evaporated in vacuo to afford compound **33a**, which was recrystallized from methanol. Yield: 300 mg (99 %), deep purple solid; m.p. 202–204 °C. ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 10.76 [s, 1H, N(1)H], 7.74 and 7.50 (2s, 2H, $CONH_2$), 6.07 (s, 1H, =CH-), 3.10 [s, 12H, $2N(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 168.4 (NCN), 166.8 and 166.5 (2C=O), 157.5 [C(2)], 148.5 [C(3)], 118.4 and 118,2 (2CN), 90.9 (=CH-), 74.6 (NH_2COC), 65.7 [C(4)], 41.5 [$N(CH_3)_2$] ppm. HRMS [(+)-TOF-ESI]: *m/z* = 323.1215 (calcd. 323.1227 for $C_{14}H_{16}N_6O_2Na$, $[M+Na]^+$). $C_{14}H_{16}N_6O_2$ (300.32): C 55.99, H 5.37, N 27.98; found C 55.67, H 5.37, N 27.33.

4.25 *N*-phenyl-2-{3-[2,2-bis(dimethylamino) vinyl]-4-cyano-5-oxo-2,5-dihydropyrrol-2-ylidene}-cyanoacetanilide (33b)

A mixture of compound **4** (400 mg, 1.0 mmol), *N*-phenylcyanoacetamide (500 mg, 3.1 mmol), Na_2CO_3 (200 mg, 1.9 mmol), and acetonitrile (6 mL) was stirred at 60 °C for 1.5 h. After cooling to ambient temperature, the mixture was filtered. The collected purple solid was washed several times with acetonitrile, methanol, and water and dried to afford **33b**. Yield: 360 mg (79 %), deep purple solid, which was recrystallized from acetonitrile; m.p. 180–182 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$) (mixture of rotamers): δ = 7.83 (s, 1H, NH), 7.61–6.93 (m, 10H, ArH), 6.16 and 5.33 (2s, 1H, -CH=C), 3.14 and 2.98 (2s, 12H, $2NMe_2$) ppm. HRMS [(+)-TOF-ESI]: *m/z* = 475.1845 (calcd. 475.1853 for $C_{26}H_{24}N_6O_2Na$, $[M+Na]^+$). $C_{26}H_{24}N_6O_2 \cdot CH_3CN$ (452.51): C 68.14, H 5.51, N 19.87; found C 67.32, H 5.62, N 19.72.

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