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New tetraazafulvadienes via cascade reactions and their cyclizations to diazaborolidines

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Abstract—3,4,5,6-Tetrahydro-2-aminopyridine reacts with *bis*-imidoylchlorides derived from oxalic acid to yield new dimeric tetraazafulvadienes. Ketene aminals could be isolated and characterized as key intermediates in a cascade reaction (cyclization–prototropism–oxidation–dimerization–deprotonation). The stable tetraazafulvadienes have been transformed with boron compounds into highly fluorescent tricyclic diazaborolidines.

1. Introduction

Amidines are versatile binucleophilic building blocks that can be employed in cyclization reactions with *bis*-imidoyl chlorides derived from oxalic acid (type **1**). Depending on the nature of the substituents at the amidine carbon, different classes of compounds can be obtained. Whereas aromatic substituted amidines give an easy entry to 4*H*-imidazoles **2**,[1] formamidine reacts via carbenoid intermediates to yield 1,4,5,8-tetraazafulvalenes **3**.[2] Acetamidine forms primarily 2-methyl substituted 4*H*-imidazol **4**, which due to its tautomeric form **4′**, can be regarded as a ketene aminal. This aminal is capable to undergo cascade reactions to yield stable tetraazafulvadienes **5**.[3,4] The head–head dimerization of ketene aminals involving distonic radical cations is a good method for coupling conjugated systems. Up to now, only few examples for chemical induced radical cation formation and subsequent dimerization have been reported in the literature.[5] We have previously investigated the cyclization of 2-aminopyridine with **1** to give 2,3-dihydroimidazo[1,2-*a*]pyridines.[6] Similarly, the homologous 2-aminomethylpyridine could be reacted with **1** in a smooth reaction to obtain pyrido[1,2-*a*]pyrazines which are valuable precursor molecules for ring transformation cascades.[7] The cyclization reactions of different types of amidines with *bis*-imidoylchlorides of type **1** are depicted in Scheme 1.

In the following article, we describe the simple conversion of commercially available 3,4,5,6-tetrahydro-2-aminopyridine **6** to the bridged bicyclic systems **9** via cyclic ketene aminals of type **7**. The semicyclic amidine **6** has quite often been employed as a building block for obtaining fused heterocycles[8] which provide easy access to a wide variety of derivatives some of which are biologically active. IR-spectroscopic studies[9] on **6** and other cyclic amidines have indicated that the amino form predominates. In addition, the semicyclic amidine **6** possesses two hydrogen atoms at the β-C-atom which via prototropism allow the formation of ketene aminals, comparable to **4′**. These aminals represent electron-rich species that can undergo SET reactions to form radical cations which finally lead to tetraazapentafulvadienes.[4]

2. Results and discussion

Treatment of **6** with *bis*-imidoylchlorides **1** in acetonitrile in the presence of triethylamine furnished the ketene aminals **7** in Scheme 2. Upon short heating of the reaction mixture compounds **7** crystallize as yellow solids and are obtainable in yields of about 80%. The NMR and MS data were in agreement with the structure of derivative **7**. The best evidence for this prototropic form is its ^{1}H NMR spectrum showing a well resolved triplet at 5.17 ppm that corresponds to the methine hydrogen atom. The relevance of N,C-tautomerism of amidines in their reactions with electrophilic carbon atoms has been firmly established.[10] A final, unambiguous structural confirmation could be achieved from a single crystal X-ray analysis **7b** (Fig. 1) which

Keywords: Tetraazafulvadienes; Tetraazafulvalenes; Diazaborolidines; Cascade reaction.
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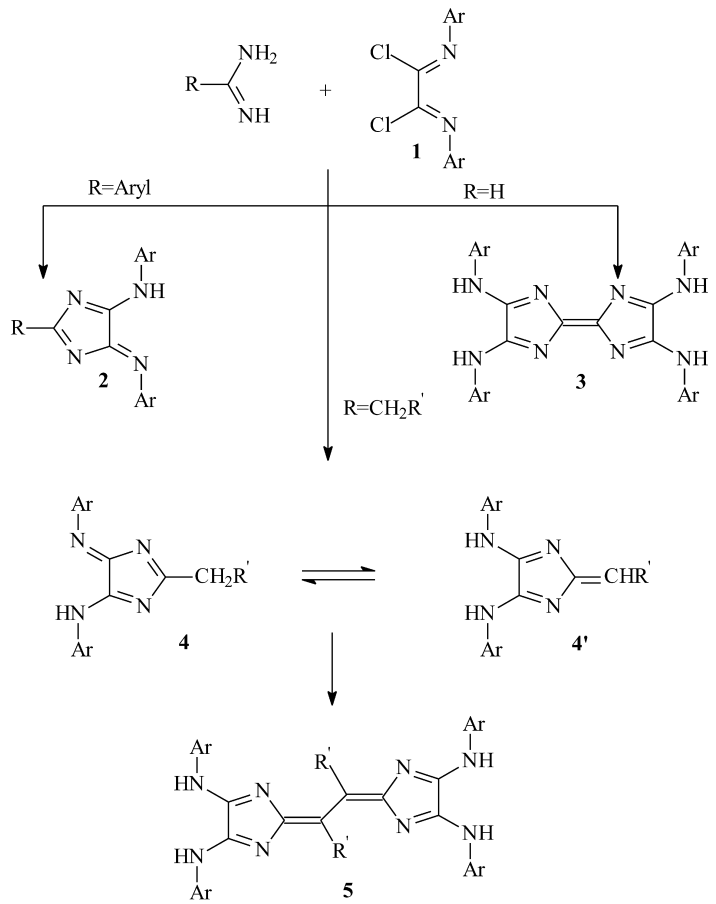
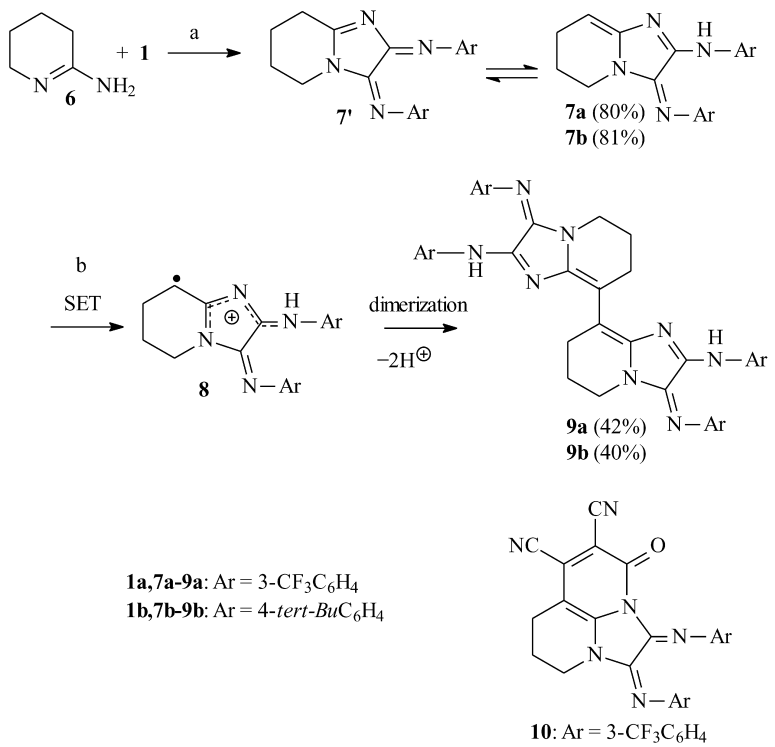


Scheme 1. The cyclization reaction of *bis*-imidoylchlorides **1** with different types of amidines.



Scheme 2. (a) Acetonitrile, triethylamine, argon atmosphere, reflux, 3 h. (b) Acetonitrile, triethylamine, atmospheric oxygen, reflux, 12 h.

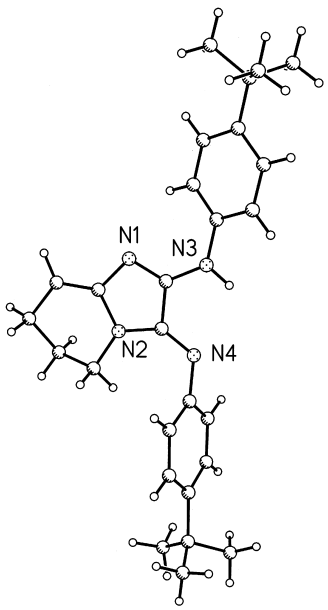


Figure 1. Motif of the molecular structure for the cyclic ketene aminal **7b**.

confirms that a methylene group has been transformed into a methine group.

Upon monitoring the formation of **7** by TLC, we observed that the product changed its color from yellow to dark red after exposing the TLC to air for a few minutes. Upon heating mixtures of **1** and **6** for some time in the presence of air, this color change also occured and the dimer **9** could be detected by TLC. Comparing these results with those of recently reported reactions,[4] we believe that a SET reaction to form a distonic radical cation of type **8** should be the key step in the dimerization cascade. Experimental findings as well as semiempirical calculations[4] suggest a high electron density at the β-carbon atom of **7**. The distonic radical cation **8** thus formed can be stabilized by dimerization and twofold proton abstraction finally leading to compounds **9**. Such dimerization processes play an important role in the industrial electropolymerization of pyrrole and thiophene. Mechanistic details of these reactions are still uncertain (radical-substrate coupling RSC or radical-radical-coupling RRC).[11] ESR spectroscopic tracking of the oxidation of ketene aminal **7a** with atmospheric oxygen yielded broad signals that did not exhibit a hyperfine structure (g=2.00309)—a characteristic of delocalized radical cations.

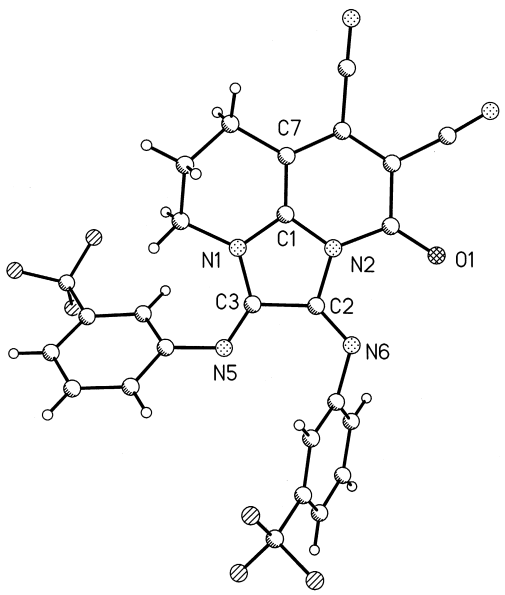
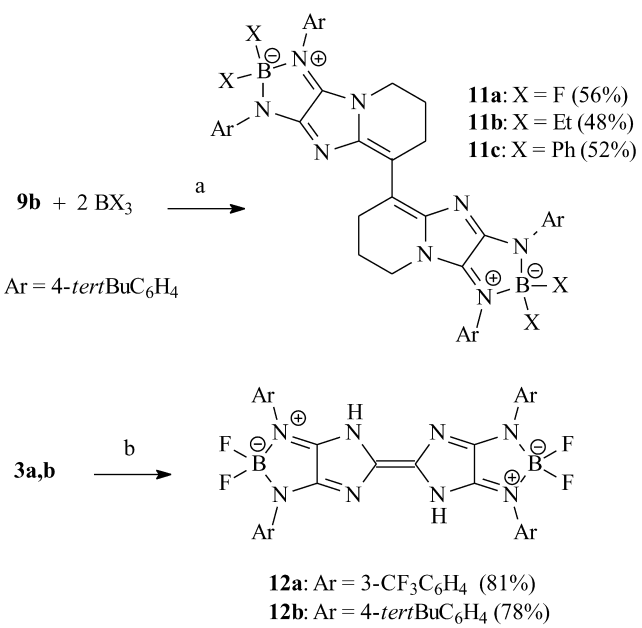


Figure 2. Molecular structure and atomic numbering for derivative **10**.

The one-electron oxidation of **7** can also be realized in the presence of tetracyanoethylene (TCE) which acts as a one-electron acceptor to form the radical cation **8**. In this case, the color change occurs faster than in air. A side reaction was observed which lead to the isolation of a small amount of red crystals in addition to **9**. An X-ray structural analysis identified this side product as the tricyclic compound **10** shown in Figure 2. The occurrence of **10** can be easily explained by a nucleophilic substitution of one cyano group[12] in TCE by aminal **7a**. A cyclization immediately follows and final hydrolysis leads to the amide subunit (Scheme 2).

The main products **9a** and **9b** were obtained, after chromatographic purification, as dark red crystals. The ^{1}H NMR spectrum of **9b** shows four doublets thus demonstrating the non-equivalence of both arylic substituents. The three methylene groups absorb as well resolved triplets at 2.9 and 3.1 ppm and a multiplet at 1.7 ppm. The successful dimerization reaction was also indicated by MS data obtained for derivative **9b**, a mol peak at m/e=826 and an M^+/2-peak with a doubled intensity at m/e=413. The UV/VIS spectra of the orange–red derivatives **9** show a broad absorption at about 498 nm.

The fulvadienes **9** react with BF_3–etherate to bridge the exocyclic nitrogen atoms thus leading to novel *bis*-1,3,2-diazaborolidines of type **11** (Scheme 3). These red colored



Scheme 3. (a) For **11a**: toluene, triethylamine, 10 min rt then 30 min reflux; for **11b**: toluene, 6 h reflux; for **11c**: toluene, 2 h reflux. (b) Boron trifluoride etherate, triethylamine, toluene, 10 min, rt then 30 min, 90 °C.

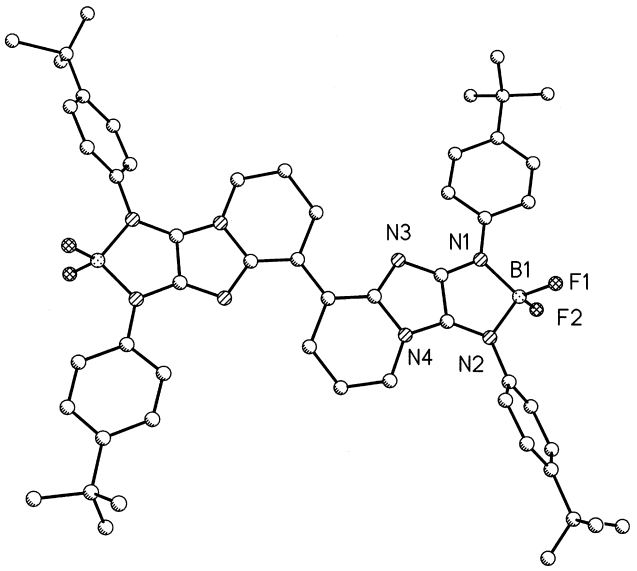


Figure 3. Motif of the molecular structure for diazaborolidine **11a**.

boracycles could be isolated in medium yields and show a strong orange fluorescence.

The ^{1}H NMR spectrum of derivative **11a** is comparable to that of uncyclized **9b**. Further information could, however, be obtained from its ^{11}B and ^{19}F NMR spectra. In the ^{11}B NMR spectrum, a triplet at 9.72 ppm shows that the boron possesses tetrahedral coordination. In the ^{19}F NMR spectrum a double doublet at −148.1 ppm shows the heteronuclear coupling of $^{19}F-^{10}B$ and $^{19}F-^{11}B$ respectively. A single crystal X-ray analysis could be performed for derivative **11a** and the motif of its molecular structure is shown in Figure 3.

For further comparison, **9b** has been converted with triethyl- and triphenylborane into derivatives **11b** and **11c**. MS and NMR data of these new boraheterocycles demonstrate a similar cyclization as in the case of *bis*-1,3,2-diazaborolidine **11a**. Encouraged by the high tendency for cyclization with boron derivatives the stability of products as well as their strong fluorescence, the 1,4,5,8-tetraazafulvalenes **3a**,**b** were also reacted with BF_3–etherate (Scheme 3). Short reaction times resulted in a dark red product which could be isolated in a good yield. A single set of signals in the ^{1}H NMR spectrum of compound **12a** shows its highly symmetric nature. A further confirmation was obtained by ^{11}B and ^{19}F NMR data (^{11}B NMR: well separated triplet at $\delta=10.18$ ppm $J=36.4$ Hz; ^{19}F NMR: singlet at $\delta=-63.5$ ppm for the aromatic CF_3 group and a double doublet at $\delta=-147.4$ ppm for the BF_2 group, $^{19}F-^{10}B$ and $^{19}F-^{11}B$). The UV/VIS spectrum recorded in DMSO shows the presence of three separated absorption bands typical for cyclized tetraazafulvalenes. The longest wavelength absorption at 508 nm (log $\varepsilon=5.0$) can be shifted bathochromically to $\lambda_{max}=551$ nm by changing the solvent to toluene. This derivative, for which we propose structure **12**, possesses a strong orange fluorescence at 577 nm in toluene. The novel boron heterocycles of types **11** and **12** show reversible redox behaviour which is still under study and will be reported soon.

3. Experimental

3.1. General

All reactions were monitored by TLC, carried out on 0,25 mm Merck silicia gel plates ($60F_{254}$) using UV light. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DRX 400 or Bruker AC 250 spectrometer. The ESR spectra were recorded with a Bruker ESP 300 E spectrometer. Melting points are measured with a Galen TM 3 apparatus and are uncorrected. UV–VIS spectra were recorded on a Perkin–Elmer Lambda 19 spectrophotometer. Fluorescence spectra were measured with an LS50B luminescence spectrometer (Perkin–Elmer). Fluorescence quantum yields were calculated relative to quinine sulfate in 0.1 N H_2SO_4 used as a standard ($\phi_f=0.55$). MS spectra were taken from measurements on a Finnigan MAT SAQ 710 mass spectrometer. Elemental analyses were carried out in-house with an automatic analyzer LECO CHNS 932.

The *bis*-imidoylchlorides (**1a**,**b**)[2] as well as the 1,4,5,8-tetraazafulvalenes (**3a**,**b**)[2] were synthesized according to literature. Other reagents were commercially available and were used without further purification. All solvents were of reagent grade and were dried and distilled before use.

3.2. Crystal structure determination

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption.[13,14]

The structures were solved by direct methods (SHELXS[15]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97[16]). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[16] The quality of the data of compounds **7b** and **11a** is too bad. We will only publish the conformation of the molecule and the crystallographic data. We will not deposit the data in the Cambridge Crystallographic Data Centre. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal data for **7b**. $C_{27}H_{34}N_4$, $Mr=414.58$ g mol^{-1}, red prism, size 0.03×0.02×0.01 mm^3, orthorhombic, space group *Pbca*, $a=13.612(3)$ Å, $b=9.703(2)$ Å, $c=34.876(5)$ Å, $V=4606.3(15)$ Å^3, $T=-153$ °C, $Z=8$, $\rho_{calcd.}=1.196$ g cm^{-3}, μ(Mo K_α)=0.47 cm^{-1}, $F(000)=1792$, 17609 reflections in $h(-15/15)$, $k(-8/10)$, $l(-38/38)$, measured in the range $1.40°\leq\Theta\leq13.73°$, completeness $\Theta_{max}=97.2\%$, 3217 independent reflections.

Crystal data for **10**.[17] $C_{26}H_{14}F_6N_6O$, $Mr=540.43$ g mol^{-1}, red prism, size 0.03×0.02×0.02 mm^3, monoclinic, space group $P2_1/c$, $a=7.5000(1)$ Å, $b=19.1998(4)$ Å, $c=16.1323(3)$ Å, $\beta=92.682(1)°$, $V=2320.48(7)$ Å^3, $T=120$ °C, $Z=4$, $\rho_{calcd}=1.547$ g cm^{-3}, μ(Mo K_α)=1.32 cm^{-1}, $F(000)=1096$, 9327 reflections in $h(-9/9)$, $k(-24/23)$, $l(-20/20)$, measured in the range $2.53°\leq\Theta\leq27.47°$, completeness $\Theta_{max}=99\%$, 5270 independent reflections, $R_{int}=0.019$, 4371 reflections with $F_o>4\sigma(F_o)$, 352

parameters, 0 restraints, $R1_{obs}$=0.059, wR^2_{obs}=0.166, $R1_{all}$=0.071, wR^2_{all}=0.177, GOOF=1.038, largest difference peak and hole: 0.996/−0.719 eÅ^{-3}.

Crystal data for **11a**. $C_{54}H_{62}B_2F_4N_8-2CH_2Cl_2$, Mr=1088.57 g mol^{-1}, red prism, size 0.03×0.03×0.02 mm^3, triclinic, space group *P-1*, a=10.3799(4) Å, b=11.1342(6) Å, c=12.9624(6) Å, α=94.187(3), β=105.305(3), γ=99.450(3)°, V=1414.65(11) Å^3, T=−90 °C, Z=1, ρ_{calcd}=1.278 g cm^{-3}, μ(Mo K$_\alpha$)=2.67 cm^{-1}, F(000)=570, 10133 reflections in h(−13/13), k(−14/14), l(−16/16), measured in the range 1.87°≤Θ≤27.54°, completeness Θ_{max}=98.9%, 6465 independent reflections.

3.3. General procedure for the syntheses of bicyclic ketene aminals (7a) and (7b)

Iminopiperidine hydrochloride **6** (2.0 g, 0.015 mol) and triethylamine (6.3 mL, 0.045 mol) were added to a solution of *N*,*N*-bis(3-trifluoromethylphenyl)oxalodiimidoyl dichloride **1a** (6.2 g, 0.015 mol) or *N*,*N*′-bis(4-*tert*-butylphenyl) oxalodiimidoyl dichloride **1b** (5.8 g, 0.015 mol) in 20 mL of acetonitrile and the resulting solution was heated under reflux for 3 h under an argon atmosphere. After evaporation of the solvent, the crude product was separated by column chromatography (SiO_2, chloroform) to yield slightly yellow crystals.

3.3.1. 3-Trifluoromethylphenyl-3-(3-trifluoromethylphenylimino)-3,5,6,7-tetrahydro-imidazo[1,2-*a*]pyridin-2-yl]-amine (7a). Yield: 5.34 g (81%); mp 103–105 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.69 (m, 2H), 2.23 (m, 2H), 3.02 (t, br., 2H), 5.33 (t, *J*=5.0 Hz, 1H), 7.02–7.43 (m, 5H), 7.72 (s, 1H), 7.89 (d, *J*=7.8 Hz, 1H), 7.95 (s, 1H); MS (DCI with water): *m*/*e*(%): 93 (90), 419 (30), 439 (M+1)$^+$ (100); UV/Vis (DMSO) λ_{max} (log ε): 343 nm (4.0). Anal. calcd for $C_{21}H_{16}F_6N_4$: C, 57.54; H, 3.68; N, 12.78. Found: C, 57.48; H, 3.65; N, 12.77.

3.3.2. 4-*tert*-Butylphenyl-[3-(4-*tert*-butylphenylimino)-3,5,6,7-tetrahydro-imidazo[1,2-*a*]pyridin-2-yl]-amine (7b). Yield: 4.98 g (80%); mp 168 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.24 (s, 9H), 1.25 (s, 9H), 1.67 (m, 2H), 2.19 (m, 2H), 3.13 (t, *J*=5.6 Hz, 2H), 5.18 (t, *J*= 4.7 Hz, 1H), 6.80 (d, *J*=8.3 Hz, 2H), 7.22 (d, *J*=8.3 Hz, 2H), 7.30 (d, *J*=8.5 Hz, 2H), 7.58 (d, *J*=8.3 Hz, 2H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 18.42, 21.81, 22.40, 31.38, 31.51, 34.29, 43.61, 97.39, 118.28, 121.14, 125.37, 125.93, 126.26, 136.03, 142.86, 145.06, 145.81, 147.78, 154.54; MS (DCI with water) *m*/*e* (%): 415 (M+1)$^+$(100); UV/Vis (DMSO) λ_{max} (log ε): 344 nm (4.5). Anal. calcd for $C_{27}H_{34}N_4$: C, 78.22; H, 8.27; N, 13.51. Found: C, 78.28; H, 8.30; N, 13.42.

3.4. General procedure for the syntheses of tetraaza-fulvadienes (9a) and (9b)

Iminopiperidine hydrochloride **6** (2.0 g, 0.015 mol) and triethylamine (6.3 mL, 0.045 mol) were added to a solution of *N*,*N*′-bis(3-trifluoromethylphenyl)oxalodiimidoyl dichloride **1a** (6.2 g, 0.015 mol) or *N*,*N*′-bis(4-*tert*-butylphenyl)oxalodiimidoyl dichloride **1b** (5.8 g, 0.015 mol) in 200 mL of acetonitrile and the resulting solution was heated under reflux for 12 h. After cooling to rt, the solvent was evaporated under reduced pressure to dryness and the crude product was purified by column chromatography (SiO_2; toluene/acetone: 100/0.8) and recrystallized from acetone.

3.4.1. *N*^{2},*N*$^{2'}$-Bis(3-trifluoromethylphenyl)-3,3′-bis(3-trifluoromethylphenylimino)-3,5,6,7,3′,5′,6′,7′-octahydro-[8,8′]bi[imidazo[1,2-*a*]pyridinyl]-2,2′-diamine (9a). Red brown crystrals; yield: 2.75 g (42%); MS (DCI with water) *m*/*e* (%): 349 (100), 416 (90), 723 (10), 875 (M+1)$^+$(10); ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.83 (m, 4H), 3.04 (m, 4H), 3.21 (t, br., 4H), 7.09 (d, *J*=8.1 Hz, 2H), 7.17 (s, 2H), 7.25 (m, 4H), 7.38 (m, 4H), 7.48 (m, br. 2H), 7.79 (m, br, 2H), 8.54 (s, 2H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 23.33, 29.29, 44.79, 100.90, 115.09 (q, *J*=4.0 Hz), 115.30 (q, *J*=4.1 Hz), 118.87 (q, *J*=4.0 Hz), 119.61 (q, *J*=4.0 Hz), 121.67, 124.67 (q, *J*=272.4 Hz), 125.60, 129.66, 129.92, 131.37 (q, *J*=32.1 Hz), 132.01 (q, *J*=32.1 Hz), 139.85, 142.52, 144.60, 149.31, 152.21 (br.); UV/Vis (DMSO) λ_{max} (log ε): 494 nm (4.2). Anal. calcd for $C_{42}H_{30}F_{12}N_8$: C, 57.67, H, 3.46, N, 12.81. Found: C, 57.75; H, 3.48; N, 12.76.

3.4.2. *N*^{2},*N*$^{2'}$-Bis(4-*tert*-butylphenyl)-3,3′-bis(4-*tert*-butylphenylimino)-3,5,6,7,3′,5′,6′,7′-octahydro-[8,8′]bi-[imidazo[1,2-*a*]pyridinyl]-2,2′-diamine (9b). Red brown crystals; yield: 2.48 g (40%); mp 253 °C; MS (DCI with water) *m*/*e* (%): 93 (60), 134 (100), 297 (38), 413 (40), 826 (M$^+$)(20); UV/Vis (DMSO) λ_{max} (log ε): 347 (4.6), 498 nm (4.6); ^{1}H NMR (250 MHz, THF-D_8) δ 1.19 (s, 18H), 1.23 (s, 18H), 1.69 (m, 4H), 2.95 (m, 4H), 3.15 (t, br. 4H), 6.77 (d, *J*=8.3 Hz, 4H), 7.20 (2d, 8H), 7.77 (d, *J*=7.4 Hz, 4H), 8.35 (s, 2H, NH); ^{13}C NMR (63 MHz, $CDCl_3$): δ 21.23, 22.37, 29.55, 31.22, 31.35, 34.29, 44.60, 102.11, 112.54, 118.33, 121.47, 125.20, 125.64, 138.32, 144.89 (br.), 145.21, 147.21. Anal. calcd for $C_{54}H_{66}N_8$: C, 78.41, H, 8.04, N, 13.55. Found: C, 78.49; H, 8.06; N, 13.45.

3.4.3. 4-Oxo-1,2-bis(3-trifluoromethylphenylimino)-1,2,8,9-tetrahydro-4*H*,7*H*-imidazo[1,2,3-*ij*][1,8]-naphthyridine-5,6-dicarbonitrile (10). Compound **7a** (0.1 g, 0.22 mmol) and tetracyanoethylene (29 mg, 0.22 mmol) were dissolved in dry THF (2 mL) and stirred at rt for 20 h. Then, the solvent was evaporated and the crude product was purified by column chromatography (Al_2O_3) at first with pure toluene to yield **9b**, than with toluene/acetone: 8/1 to yield **10** as crimson crystals. Yield: 45 mg (38%); MS (DCI with water) *m*/*e* (%): 540 (100)(M)$^+$; ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.84 (m, 2H), 2.53 (t, *J*=5.9 Hz, 2H), 3.17 (t, br., 2H), 6.72 (d, *J*=6.9 Hz, 1H), 6.79 (s, 1H), 7.07 (d, *J*=6.9 Hz, 1H), 7.22 (m, 5H); UV/Vis (toluene) λ_{max} (log ε): 534 nm (4.3). Anal. calcd for $C_{26}H_{14}F_6N_6O$: C, 57.79; H, 2.61; N, 15.55. Found: C, 57.82; H, 2.63; N, 15.49.

3.4.4. 1,3,1′,3′-Tetrakis(4-*tert*-butylphenyl)-2,2,2′,2′-tetrafluoro-2,4,5,6,2′,4′,5′,6′-octahydro-1*H*,1′*H*-2λ^4,2′λ^4-[7,7′]bi[2-bora-1,3,3b,8-tetraaza-cyclopenta[*a*]indenyl] (11a). Boron trifluoride etherate was added to a stirred solution of **9b** (0.1 g, 0.12 mmol), triethylamine (38 μL, 0.24 mmol) and dry toluene (5 mL) at rt. The color of the

solution changed from red to blue. After 10 min the reaction mixture was heated to 90 °C for 30 min and the color of the solution changed to red showing a strong orange fluorescence. After cooling the crude reaction mixture was filtered and the filtrate was chromatographed on SiO_2 with toluene to yield red crystals. Yield: 62 mg (56%); mp>300 °C; MS (DCI with water) *m/e* (%): 91 (100), 256 (20), 797 (10), 923 $(M+1)^+$ (15); ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.37 (s, 18H), 1.42 (s, 18H), 2.10 (m, 4H), 3.24 (t, J=6.1 Hz, 4H), 3.72 (t, J=6.0 Hz, 4H), 7.38 (d, J=8.5 Hz, 4H), 7.45 (d, J=8.8 Hz, 4H), 7.57 (d, J=8.6 Hz, 4H), 7.88 (d, J=8.6 Hz, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 23.33, 28.89, 31.47, 31.45, 34.66, 35.07, 44.89, 119.32, 119.59, 125.02, 126.22, 126.84, 133.36, 137.44, 146.60, 149.35, 149.67, 151.76, 155.38; ^{11}B NMR (128 MHz, CD_2Cl_2): δ 9.95 (t, J=29.97 Hz); ^{19}F NMR (188 MHz; CD_2Cl_2): δ −148.11 (m); UV/Vis (DMSO) λ_{max} (log ε): 503 nm (4.6); F_{max} 602 nm, ϕ_F=0.27. Anal. calcd for $C_{54}H_{64}B_2F_4N_8$: C 70.29; H 6.99; N 12.14. Found: C, 70.18; H, 6.85; N, 12.07.

3.4.5. 1,3,1′,3′-Tetrakis(4-*tert*-butylphenyl)-2,2,2′,2′-tetraethyl-2,4,5,6,2′,4′,5′,6′-octahydro-1*H*,1′*H*-2λ⁴,2′λ⁴-[7,7′]bi[2-bora-1,3,3b,8-tetraaza-cyclopenta[*a*]indenyl] (11b). A mixture of **9b** (0.1 g, 0.12 mmol) and triethylborane (0.04 g, 0.41 mmol) was heated under reflux in 5 mL of toluene for 6 h. The solution was concentrated in vacuo, and the residue was purified by column chromatography (SiO_2; toluene to toluene/acetone 200/1). The resulting solid was recrystallized from heptane to yield **11b** as red crystals. Yield: 55 mg (48%); mp >250 °C; MS (EI) *m/e*: 337 (40), 536 (10), 905 (60), 934 (100), 963 (10) $(M+1)^+$; ^{1}H NMR (250 MHz, CD_2Cl_2): δ 0.42 (m, 4H), 0.53 (t, J=6.7 Hz, 12H), 0.65 (m, 4H), 1.24 (s,18H), 1.28 (s, 18H), 1.86 (m, 4H), 3.00 (t, br., 4H), 3.28 (t, J=5.4, 6.2 Hz, 4H), 7.09 (d, J=8.6 Hz, 4H), 7.26 (d, J=8.8 Hz, 4H), 7.39 (d, J=8.6 Hz, 4H), 7.82 (d, J=8.6 Hz, 4H); UV/Vis (DMSO) λ_{max} (log ε): 532 nm (4.6); F_{max} 628 nm, ϕ_F=0.54. Anal. calcd for $C_{62}H_{84}B_2N_8$: C, 77.33; H, 8.79; N 11.64. Found: C, 77.38; H, 8.82; N, 11.57.

3.4.6. 1,3,1′,3′-Tetrakis(4-*tert*-butylphenyl)-2,2,2′,2′-tetraphenyl-2,4,5,6,2′,4′,5′,6′-octahydro-1*H*,1′*H*-2λ⁴,2′λ⁴-[7,7′]bi[2-bora-1,3,3b,8-tetraaza-cyclopenta[*a*]indenyl] (11c). A mixture of **9b** (0.1 g, 0.12 mmol) and triphenylborane (0.1 g, 0.42 mmol) was heated under reflux in 5 mL of toluene for 2 h. The solution was concentrated in vacuo, and the residue was purified by column chromatography (SiO_2; toluene/heptane 3/1 to toluene). The resulting solid was recrystallized from heptane/toluene to yield **11c** as red crystals. Yield: 72 mg (52%); mp 213 °C; MS (EI) *m/e*: 500 (60), 914 (25), 1078 (100), 1155 (20) $(M+1)^+$; ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.26 (s, 18H), 1.32 (s, 18H), 2.05 (m, 4H), 3.25 (t, J=5.7, 5.9 Hz, 4H), 3.41 (t, J=5.2, 6.3 Hz, 4H), 6.64 (d, J=8.6 Hz, 4H), 7.21 (d, J=8.9 Hz, 4H), 7.24 (m, 16H), 7.46 (m, 8H), 7.79 (d, J=8.9 Hz, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 22.68, 28.20, 30.94, 30.99, 34.12, 34.41, 43.49, 114.59, 120.58, 124.92, 125.28, 126.22, 126.36, 127.00, 134.12, 134.33, 138.77, 144.97, 150.07, 150.84, 157.51; UV/Vis (toluene) λ_{max} (log ε): 362 nm (4.4), 531 (4.8); F_{max} (toluene) 619 nm, ϕ_F=0.64. Anal. calcd for $C_{78}H_{84}B_2N_8$: C, 81.10; H, 7.33; N, 9.70. Found: C, 81.18; H, 7.36; N, 9.63.

3.5. General procedure for the preparation of the *bis*-diazaborolidines 12a and 12b

Boron trifluoride etherate was added to a stirred solution of 2,3,6,7-tetrakis(3-trifluoromethylphenyl)-1,4,5,8-tetraazafulvalene **3a** (107 mg, 0.14 mmol) or 2,3,6,7-tetrakis(4-*tert*-butylphenyl)-1,4,5,8-tetraazafulvalene **3b** (101 mg, 0.14 mmol), triethylamine (40 μL, 0.28 mmol) and dry toluene (5 mL) at rt. The color of solution changed from red to blue. After 10 min the reaction mixture was heated to 90 °C for 30 min and the color of solution changed then to orange with strong yellow fluorescence. After cooling the crude reaction mixture was filtered and the filtrate was chromatographed on SiO_2 with toluene/acetone: 3/2 to yield red crystals of derivatives **12**.

3.5.1. 1,3,1′,3′-Tetrakis(3-trifluoromethylphenyl)-2,2,2′,2′-tetrafluoro-2,4,2′,4′-tetrahydro-1*H*,1′*H*-2λ⁴,2′λ⁴-[5,5′]bi[2-bora-1,3,4,6-tetraaza-pentalenylidene] (12a). Yield: 98 mg (81%), (fast decomposition in the presence of impurities); mp>250 °C; MS (ESI in ethanol) *m/e*: 985.6 (100)$(M+2BF_2)^+$; ^{1}H NMR (400 MHz, acetone-d_6): δ 7.39 (d, J=7.3 Hz, 4H), 7.62 (dd, J=7.9, 7.9 Hz, 4H), 8.30 (m, 8H); ^{13}C NMR (100 MHz, acetone-d_6): δ 116.34, 119.21, 123.08, 125.78, 130.27, 130.58, 140.31; ^{11}B NMR (128 MHz, CD_2Cl_2): δ 10.18 (t, J=36.41 Hz); ^{19}F NMR (188 MHz; acetone-d_6): δ −63.53 (s), −147.43 (m); UV/Vis (DMSO): 445 nm (4.5), 474 (4.9), 508 (5.0); UV/Vis (toluene) λ_{max} (log ε): 515 (4.8), 551 (4.9); F_{max} (toluene) 577 nm, ϕ_F=0.41. Anal. calcd for $C_{34}H_{18}B_2F_{16}N_8$: C, 47.26; H, 2.10; N, 12.97. Found: C, 47.42; H, 2.13; N, 12.93.

3.5.2. 1,3,1′,3′-Tetrakis(4-*tert*-butylphenyl)-2,2,2′,2′-tetrafluoro-2,4,2′,4′-tetrahydro-1*H*,1′*H*-2λ⁴,2′λ⁴-[5,5′]bi[2-bora-1,3,4,6-tetraaza-pentalenylidene] (12b). Yield: 89 mg (78%), (fast decomposition in the presence of impurities); mp>250 °C; MS (EI) 768 (20), 816 (100) (M^+); ^{1}H NMR (250 MHz, acetone-d_6): δ 1.36 (s, 18H), 1.37 (s, 18H), 7.50 (d, J=8.7 Hz, 4H), 7.51 (d, J=8.8 Hz, 4H), 7.75 (d, J=8.7 Hz, 4H), 8.05 (d, J=8.6 Hz, 4H); ^{19}F NMR (188 MHz; acetone-d_6): −145.13 (m); UV/Vis (DMSO) λ_{max} (log ε): 512 nm (4.6), 538 (4.6); UV/Vis (toluene): 511 nm (4.6), 536 (4.6); F_{max} (toluene) 573 nm. ϕ_F=0.46. Anal. calcd for $C_{46}H_{54}B_2F_4N_8$: C 67.66, H 6.67, N 13.72. Found: C, 67.52; H, 6.60; N, 13.78.

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17. CCDC 225201 (**10**) containing the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033; or deposit@ccdc.cam.ac.uk).