

Syntheses and Properties of Cycloamidines Based on 4*H*-Imidazoles*

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Dedicated to Prof. Dr. Karel Waisser on the occasion of his 70th birthday

Employing three different syntheses a broad spectrum of 4*H*-imidazoles **3a**–**3s** has been synthesized. In the course of the two-fold aminolysis reaction leading to derivatives **3q**–**3s**, deeply colored byproducts could be isolated and structural characterized. These novel donor-acceptor derivatives of type **7** consist of an 1*H*- and 4*H*-imidazole which are connected by a nitrogen bridge and rearrange via rapid 1,3-/1,5-hydride shifts. Using ¹H NMR experiments the aminolysis product **3p** shows prototropic isomers which could be detected in equilibrium for the first time. Cyclovoltammetric measurements of a series of substituted 2-aryl derivatives **3d**–**3i** displayed two reversible single electron transfer steps with relatively small semiquinone formation constants between 10² and 4 × 10³. The 4*H*-imidazole **3d** was successfully converted into boratetraaza-pentalene **8a**, which showed two well separated reduction potentials. The value of semiquinone formation constant of **8a** (1.8 × 10¹⁵) is even higher than those reported for similar derivatives. 4*H*-imidazoles can also be employed for the efficient complexation of catalytically important metals as exemplified by copper complexes **11** and **12**. Derivative **3m**, which possesses an additional chelating pyridine substructure, formed a stable complex of structural composition Zn(**3m**)₂ with diethyl zinc.

Key words: Fulvenimines, 4*H*-Imidazoles, Aminolysis, Diazaborolidines, Metal Complexes, Redox Systems

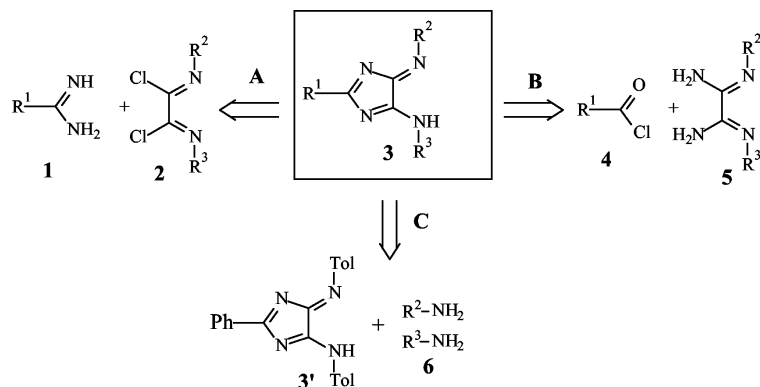
Introduction

Amidines without hydrogen in α -position, such as benzamidines of type **1**, can easily be cyclized with bis-imidoylchlorides derived from oxalic acid **2** to yield 4*H*-imidazoles **3** [1]. The rapid prototropic shift of hydrogen from cyclic to exocyclic nitrogen causes the formation of the cross-conjugated system in derivatives **3**. Starting from these diazafulvene imines a new class of chromophores/fluorophores was developed in our group [2, 3]. The protonated forms of compounds **3** can be regarded as cyclic cyanines as well as cationic 4 *π* -heteroaromatics which are stabilized by electron-donating groups. In addition, the 4*H*-imidazoles **3** possess the behavior of reversible two-electron redox systems which have been optimized to powerful

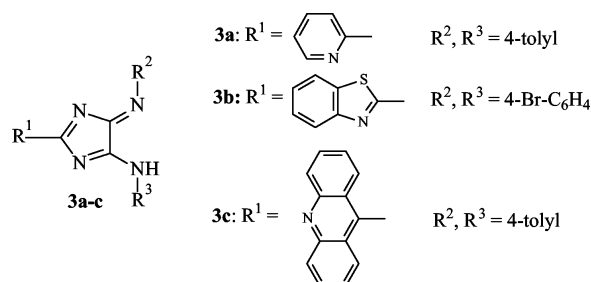
electron accepting derivatives in the form of borate-tetraazapentalenes [4]. Their radical anions are characterized by an unusual thermodynamic stability as can be seen from semiquinone formation constants K_{SEM} in the magnitude of 10¹⁴. Influenced by these results, we developed three different syntheses for the cycloamidines **3** [1, 3, 5] (Scheme 1).

Due to the fact that open-chained oxalic amidines have been successfully introduced into ligands for cross-coupling methods [6], their cyclic versions “cycloamidines” 4*H*-imidazoles, should be promising candidates as well. Furthermore, their high electron affinity is of interest for the synthesis of new electrophoric parts in light harvesting systems [7]. The aim of further investigations will be to demonstrate scope and limitations of syntheses of derivatives **3**. In addition to mono-derivatives, the synthesis should be extended to molecules which possess two 4*H*-imidazole substructures. In a series of derivatives the influence

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Scheme 1.



Scheme 2.

of the different substituents at the 2-aryl unit on the redox potentials should be studied. Finally, the possibility to install metal complexing substructures at the central heterocycle as well as at its periphery should be examined.

Results and Discussion

As a synthetic approach to cycloamidines **3** procedure **A** (Scheme 1) was chosen for those derivatives where the corresponding amidines **1** are easily accessible. Thus, the 4*H*-imidazoles **3a–c** (Scheme 2) could be synthesized by cyclization of binucleophiles **1** with bis-imidoylchlorides of type **2**. The spectroscopic data (UV/vis, NMR, MS) are in agreement with the structures of **3a–c**. Furthermore, an X-ray structural analysis could be obtained from single crystals of **3a**, the result of which is depicted in Fig. 1.

Despite high yields reported in the literature, the synthesis of some amidines required as starting materials proved to be difficult. Here, procedure **B** [5] (Scheme 1) offers an alternative synthetic entry. A large variety of structures in 2-position of heterocycle **3** can be realized employing acid chlorides **4** as educts. Because the educts are easily available, the poorer yields obtained can be tolerated. A series of

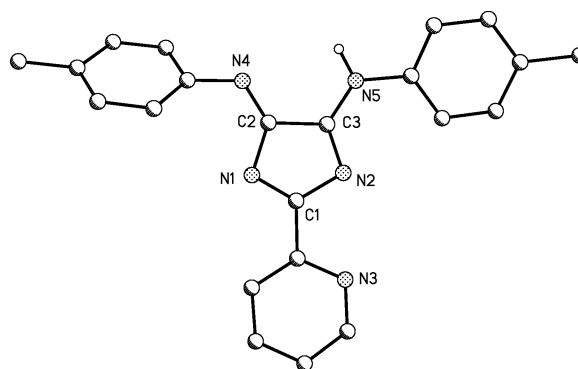
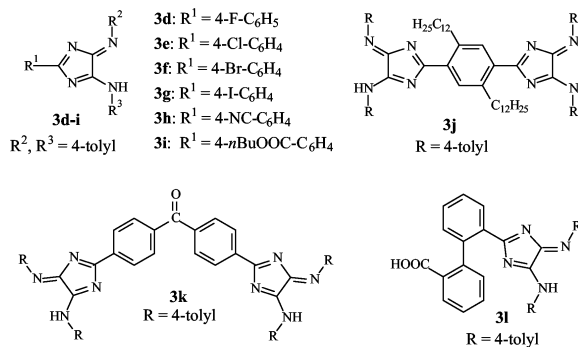


Fig. 1. Molecular structure of 4*H*-imidazole **3a** in the solid state. Selected bond lengths [Å]: C1–N2 1.403(5), C1–N1 1.311(5), C3–N2 1.314(5), C2–N1 1.407(5), C2–C3 1.506(5), C2–N4 1.276(5), C3–N5 1.337(5).



Scheme 3.

4*H*-imidazoles **3d–3i** (Scheme 3) was obtained by cycloacylation of oxalic amidine **5a** with electrophiles **4** in order to perform cyclovoltammetric measurements.

This method allowed the syntheses of bifunctional systems as exemplified by compounds **3j** and **3k** (Scheme 3). The X-ray crystal structure of derivative **3j**, which is characteristic for these symmetri-

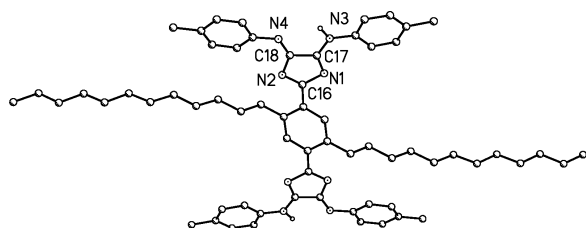
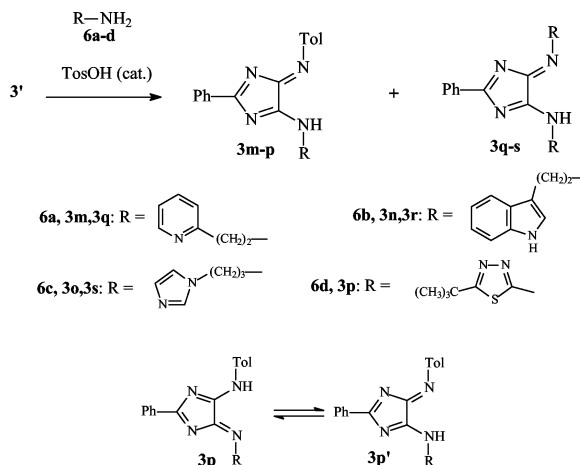


Fig. 2. Molecular structure of bis-4*H*-imidazole **3j** in the solid state. Selected bond lengths [Å]: C16–N2 1.322(2), C16–N1 1.415(2), C17–N1 1.306(2), C18–N2 1.387(2), C17–C18 1.495(3), C17–N3 1.335(3), C18–N4 1.288(3).

cally substituted 4*H*-imidazoles, is illustrated in Fig. 2. However, under analogous conditions, only the mono-product **3l** (Scheme 3) of the diphenic acid dichloride was formed. In the course of the cyclization cascade [5] the formation of one carboxylic group, which is inactive for further cyclization reactions, was observed.

Bis-imidoylchlorides with alkyl residues at the N-atoms are seldomly mentioned and in addition, often tend to thermal induced rearrangements [8]. Due to this fact, the aminolysis of easily available N³,N⁴-di(4-tolyl)-4*H*-imidazoles **3'** (Scheme 1) constitutes a versatile method in obtaining 4*H*-imidazoles which are connected with heteroaromatics through alkyl chains. The aminoalkyl heteroaromatics **6a–6c** were successfully employed as educts for aminolysis reactions. In all cases studied the mono- (**3m–3p**) as well as the bis-products **3q–3s** (Scheme 4) could be isolated and characterized. In contrast, only single transamination was observed for the less nucleophilic aminosubstituted 1,3,4-thiadiazole **6d** to yield derivative **3p**.

Due to rapid proton exchange processes, the NMR spectra of symmetrically substituted 4*H*-imidazoles **3** ($R^2 = R^3$) suggest a high molecular symmetry by single signal sets. However, for aminolysis product **3p** a double signal set could be detected in the ¹H NMR spectrum. In its ¹³C NMR spectrum broadened signals indicate the presence of a dynamic equilibrium. Using NOESY experiments with cross peak phase analysis, double signals could be identified as being exchange signals. For example, the hydrogen atoms of the *tert*-butyl groups absorb as two singlets at 1.55 and 1.50 ppm. This effect is even stronger for the ortho hydrogens of the 2-phenyl group, where a exchange signal at 8.14 ppm can be assigned to the doublet at 8.61 ppm. Single crystal X-ray analysis allowed an unambiguous structural assignment of this compound, as shown in Fig. 3. In contrast to the starting material **3'** where a statistic disorder of exo-



Scheme 4.

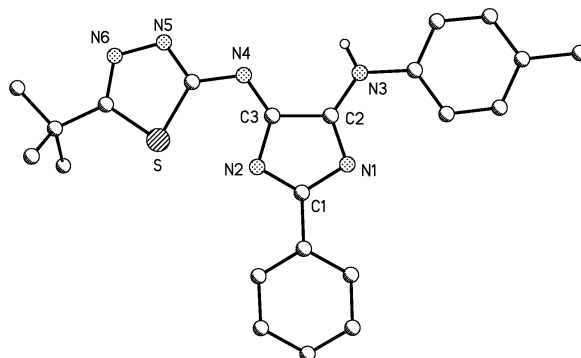
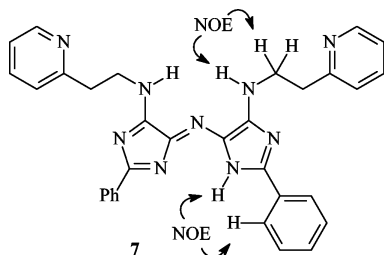


Fig. 3. Molecular structure of 4*H*-imidazole **3p** in the solid state. Selected bond lengths [Å]: C1–N1 1.386(3), C1–N2 1.332(3), C2–N1 1.322(3), C3–N2 1.372(3), C2–C3 1.512(3), C3–N4 1.290(3), C2–N3 1.330(3).

cyclic NH protons (50:50) was found [2], the proton here is definitely assigned to the tolyl-substituted N-atom. The central C–C bond (1.512 Å) is considerably longer than typical C_{sp2}–C_{sp2} bonds found in conjugated systems (1.455 Å). The CN bond lengths in the heterocyclic ring differ stronger from those in systems reported earlier [1, 2]. Furthermore, no intermolecular interactions/aggregations could be detected. With these results the prototropism between species **3p–3p'** (Scheme 4) could be evidenced for the first time. The X-ray structure obtained for **3p** can be explained by crystallization of only one prototropic species, which in solution is in equilibrium with **3p'**. Due to the high energy barrier between the transition state (26.1 kcal/mol) and both of the tautomers, predicted by quantum chemical calculations [2], an intramolecular proton shift is not favoured.



Scheme 5.

During aminolysis reactions deeply colored by-products were detectable by TLC in all cases which resulted directly from products of a twofold aminolysis of **3q**–**3s**. Upon extended heating of **3q** in toluene in the presence of catalytic amounts of TsOH, the deep blue derivative **7** (Scheme 5) could be isolated and purified by preparative TLC. Its structure was solved by two-dimensional NMR and HRMS. Remarkably, in compound **7** two imidazoles which exist in different oxidation states are connected by a nitrogen bridge. The characteristic signal for the 4*H*-imidazole at 188 ppm could be detected in the ^{13}C NMR spectrum, together with the resonances of the reduced form (1*H*-imidazole) at higher fields (161.2 ppm). Employing NOESY experiments the broad signal in the ^1H NMR spectrum at 6.64 ppm could be assigned to a superposition of imidazole-NH and an exocyclic NH proton. The remarkable bathochromic UV/vis absorption observed ($\lambda_{\text{max}} = 610 \text{ nm}$, $\lg \varepsilon = 4.0$) is due to the similarity of **7** to the push-pull chromophores found in indigoid systems. Comparable compounds, which possess aryl groups instead of alkylated heteroaromatics, were previously reported [3].

Compounds of type **7** constitute new examples of intramolecular donor-acceptor systems with fluctuating

Table 1. The first and second reduction potentials of 4*H*-imidazoles **3** ($\text{R}^1 = 4\text{-YC}_6\text{H}_4$, $\text{R}^2 = \text{R}^3 = 4\text{-tolyl}$).

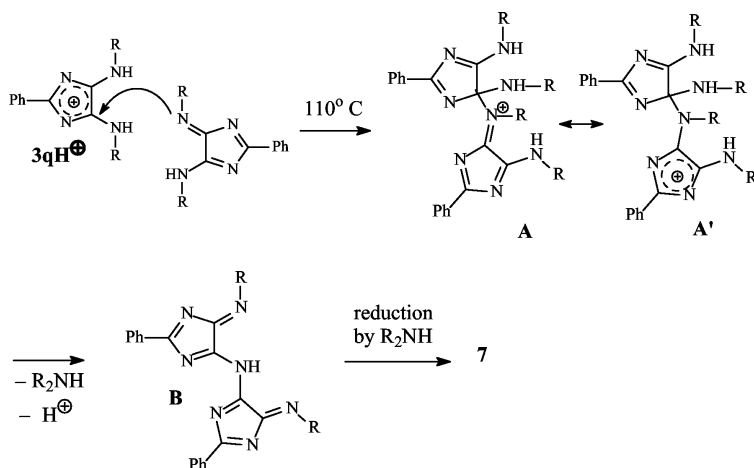
Compound	Y	Red ¹ [V]	Red ² [V]
3d	F	−1.15	−1.25
3e	Cl	−1.21	−1.31
3g	I	−1.16	−1.31
3h	CN	−0.92	−1.05
3i	<i>n</i> BuOOC	−1.13	−1.27
–	NO ₂ [1]	−0.34	−0.66
–	H [1]	−1.26	−1.39
–	CH ₃ [1]	−1.26	−1.40
–	NMe ₂ [1]	−1.26	−1.40

structures in which both ring systems show rapid inter-conversion by 1,3- and 1,5-hydride shifts. We postulate the attack of the nucleophilic imino nitrogen at protonated molecule **3qH**⁺ as first step of the mechanism leading to resonance-stabilized intermediates **A**, **A'** (Scheme 6). Then, an alkyl shift takes place followed by elimination of one molecule of R_2NH forming the bridged *bis*-4*H*-imidazole **B**. Finally, a partial reduction of one of the 4*H*-imidazoles yields 1*H*-imidazole. Most likely, the secondary amine R_2NH acts as the reducing agent in this cascade reaction.

Cyclovoltammetric Measurements

The first and second reduction potentials of selected 4*H*-imidazoles **3** ($\text{R}^1 = 4\text{-YC}_6\text{H}_4$, $\text{R}^2 = \text{R}^3 = 4\text{-tolyl}$) are given in Table 1.

These potentials show the expected behavior. Electron withdrawing groups stabilize the negative charges leading to a decrease of absolute values of potentials. Electron donating groups show an inverse effect. However, in contrast to para substituents at arylamino/imino residues [4], the differences between both types of substituents are rather small and can be explained



Scheme 6.

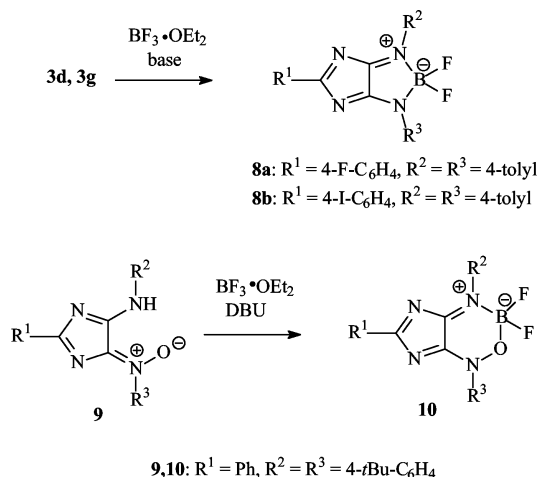
by the larger distance to the redox active center. Interestingly, electron-accepting substituents influence the position of the reduction potentials in a higher degree than donating groups, whereby the difference between both single electron transfer steps remains relatively constant ($\Delta = 0.15$ V). The semiquinone formation constants K_{SEM} , indicating the thermodynamic stability of the product of the first reduction step, lie between 100 and 4000. These values are rather small compared to those of typical acceptor parts in “organic metals” derived from tetracyanoquinodimethane (TCNQ) or *N,N'*-dicyanoquinodiiimines (DCNQI) which are in the range of $10^7 - 10^{11}$ [9, 10].

Based on experiences where the transformation of 4*H*-imidazoles into boracycles results in better separated electron transfer processes as well as in a drastic increase of values of K_{SEM} [4], boratetraazapentalenes **8a** and **8b** were synthesized (Scheme 7). Measurements in a reversible modus showed two well separated reduction potentials at $\text{Red}^1 = -0.18$ V and $\text{Red}^2 = -1.08$ V for derivative **8a**. The semiquinone formation constant with 1.8×10^{15} is even one magnitude higher than those reported recently for similar derivatives [4]. The successful cyclization method was then tested with aminonitrones of type **9** [11]. Employing boron trifluoride etherate, the six-membered boracycle **10** could be obtained in moderate yield. Due to its low stability in different solvents, reproducible cyclovoltammetric measurements were fruitless.

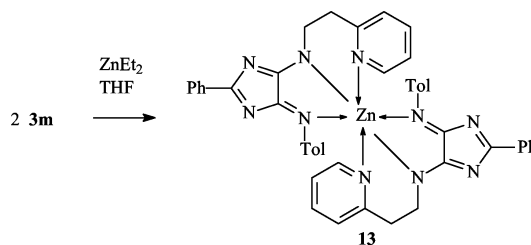
Metal complexes

Due to their chelating substructures, 4*H*-imidazoles **3** offer good requirements for the construction of metal complexes. Thus, the deprotonation of **3'** yielded a lithiated derivative which contained a stable delocalized anion. The X-ray crystal structure analysis surprisingly revealed one molecule of water in the first ligand sphere of the lithium cation [12]. With diethyl zinc a neutral complex of the type ZnL_2 was isolated and characterized [13].

The focus of further investigations was directed to the formation of complexes of catalytically active metals (Cu, Zn) with derivatives **3m–3s** which contain additional donor atoms in their ligand system. Upon treatment of ligands **3m–3s** with copper acetate in the presence of potassium *tert*-butanolate, mixtures of complexes were isolated in nearly quantitative yield whereby the species CuL_2 , Cu_2L_2 , Cu_3L_2 and others could be detected by MS. Employing $\text{Cu}(\text{OTf})_2$ struc-



Scheme 7.



Scheme 8.

turally consistent complexes were obtained. Starting from 4*H*-imidazoles **3o** and **3s**, respectively, two paramagnetic complexes **11** $[\text{Cu}(\text{3o})_2]^{++} 2\text{TfO}^-$ and **12** $[\text{Cu}(\text{3s})]^{++} 2\text{TfO}^-$ were isolated and characterized by MS and elemental analysis. However, in derivative **3s**, the stabilization of the central ion can be realized efficiently by both imidazoles. Based on these experimental findings, ligand **3m** was treated with diethyl zinc. Even at -78 °C the deprotonation of **3m** could be observed by a color change from yellow to deep red indicating the formation of the complex **13** (Scheme 8). The X-ray structural analysis of a single crystal resulted in a structural motif which confirms the structure of complex **13**.

Experimental Section

Materials and methods

All reagents were of commercial quality (Aldrich, Fluka, Merck). Solvents were dried and purified using standard techniques. Reactions were monitored by thin layer chromatography (tlc), Polygram SIL G/UV254 from Macherey-Nagel or Polygram Alox N/UV254 from Macherey-Nagel.

Flash chromatography was carried out on silica gel (Merck, Silica gel 60, particle size 0.040–0.063 mm, 230–400 mesh ASTM) or neutral alumina (Merck, aluminium oxide 90 active neutral, activity V, particle size 0.063–0.2 mm, 70–230 mesh ASTM). Melting points were measured with a Galen III (Boëtius system) from Cambridge Instruments and are not corrected. The UV-vis spectra were obtained using a Perkin Elmer Lambda 19 spectrophotometer. The ^1H and ^{13}C NMR spectra were obtained on Bruker DRX 400 and Bruker AC 250 spectrometers. Mass spectra were obtained with a Finnigan MAT SAQ 710 spectrometer. Elemental analyses were carried out using an automatic analyzer LECO CHNS 932. Cyclovoltammetry was carried out on a Metrohm VA Stand 663 mit Autolab PGSTAT20 using a mercury drop electrode in dichloromethane (anhydrous 99.8%, Aldrich) with tetrabutylammonium perchlorate vs. Ag/AgCl.

Crystallographic data

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo- $\text{K}\alpha$ ($\lambda = 0.71069 \text{ \AA}$) radiation at -90°C . Data were corrected for Lorentz and polarization effects, but not for absorption effects [14, 15]. The structures were solved by direct methods (SHELXS [16]); nearly all non-hydrogen atoms were located. Employing difference Fourier syntheses the remaining non-hydrogen atoms were determined. The structural model obtained was refined by full-matrix least squares techniques against F_o^2 (SHELXL-97 [17]). The hydrogen atoms of the amin substructures were located by difference Fourier syntheses and refined isotropically. The other hydrogen atoms were included at calculated positions with fixed thermal parameters [17]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal data for 3a [18]: $\text{C}_{22}\text{H}_{19}\text{N}_5$, $M_r = 353.42 \text{ g mol}^{-1}$, red cubes, size $0.03 \times 0.02 \times 0.01 \text{ mm}^3$, monoclinic, space group $P2_1/c$, $a = 13.3049(8)$, $b = 15.2655(9)$, $c = 9.3141(7) \text{ \AA}$, $\beta = 108.514(5)^\circ$, $V = 1793.8(2) \text{ \AA}^3$, $T = -90^\circ\text{C}$, $Z = 4$, $\rho_{\text{calcd.}} = 1.309 \text{ g cm}^{-3}$, $\mu (\text{Mo-K}\alpha) = 0.81 \text{ cm}^{-1}$, $F(000) = 744$, 7030 reflections in $h(-13/17)$, $k(-19/18)$, $l(-12/7)$ measured in the range $2.66^\circ \leq \theta \leq 27.45^\circ$, completeness to $\Theta_{\text{max}} = 91\%$, 3732 independent reflections, $R_{\text{int}} = 0.112$, 1809 reflections with $F_o > 4\sigma(F_o)$, 248 parameters, 0 restraints, $R_{1\text{obs}} = 0.083$, $wR_{2\text{obs}}^2 = 0.153$, $R_{1\text{all}} = 0.192$, $wR_{2\text{all}}^2 = 0.2037$, GOOF = 1.016, largest difference peak and hole: $0.246/-0.371 \text{ e \AA}^{-3}$.

Crystal data for 3j [18]: $\text{C}_{64}\text{H}_{82}\text{N}_8$, $M_r = 963.38 \text{ g mol}^{-1}$, red cubes, size $0.02 \times 0.02 \times 0.01 \text{ mm}^3$, triclinic, space group $P1$, $a = 6.9074(2)$, $b = 8.9307(2)$, $c = 22.8213(8) \text{ \AA}$, $\alpha = 98.119(1)$, $\beta = 97.404(1)$, $\gamma = 94.189(1)^\circ$, $V = 1376.08(7) \text{ \AA}^3$, $T = -90^\circ\text{C}$,

$Z = 1$, $\rho_{\text{calcd.}} = 1.163 \text{ g cm}^{-3}$, $\mu (\text{Mo-K}\alpha) = 0.69 \text{ cm}^{-1}$, $F(000) = 522$, 9368 reflections in $h(-8/9)$, $k(-11/11)$, $l(-26/30)$ measured in the range $1.82^\circ \leq \theta \leq 27.87^\circ$, completeness to $\Theta_{\text{max}} = 95.9\%$, 6278 independent reflections, $R_{\text{int}} = 0.042$, 4230 reflections with $F_o > 4\sigma(F_o)$, 329 parameters, 0 restraints, $R_{1\text{obs}} = 0.066$, $wR_{2\text{obs}}^2 = 0.1544$, $R_{1\text{all}} = 0.105$, $wR_{2\text{all}}^2 = 0.1776$, GOOF = 1.016, largest difference peak and hole: $0.385/-0.299 \text{ e \AA}^{-3}$.

Crystal data for 3p [18]: $\text{C}_{22}\text{H}_{22}\text{N}_6\text{S}$, $M_r = 402.52 \text{ g mol}^{-1}$, red cubes, size $0.10 \times 0.08 \times 0.07 \text{ mm}^3$, monoclinic, space group $C2/c$, $a = 22.7132(7)$, $b = 10.5157(3)$, $c = 19.9139(7) \text{ \AA}$, $\beta = 119.911(1)^\circ$, $V = 4122.8(2) \text{ \AA}^3$, $T = -90^\circ\text{C}$, $Z = 8$, $\rho_{\text{calcd.}} = 1.297 \text{ g cm}^{-3}$, $\mu (\text{Mo-K}\alpha) = 1.78 \text{ cm}^{-1}$, $F(000) = 1696$, 7863 reflections in $h(-29/29)$, $k(-13/12)$, $l(-25/25)$ measured in the range $2.20^\circ \leq \theta \leq 27.45^\circ$, completeness to $\Theta_{\text{max}} = 99.5\%$, 4690 independent reflections, $R_{\text{int}} = 0.035$, 3334 reflections with $F_o > 4\sigma(F_o)$, 338 parameters, 0 restraints, $R_{1\text{obs}} = 0.051$, $wR_{2\text{obs}}^2 = 0.111$, $R_{1\text{all}} = 0.086$, $wR_{2\text{all}}^2 = 0.1289$, GOOF = 1.007, largest difference peak and hole: $0.370/-0.322 \text{ e \AA}^{-3}$.

4*H*-Imidazoles **3a–3c** by cyclization of amidines **1** with bis-imidoylchlorides of oxalic acid **2** according to way **A**

2-(2-Pyridyl)-5-(4-tolylamino)-4-(4-tolylimino)-4*H*-imidazole (**3a**)

2-Amidinopyridinium hydrochloride (10 mmol, 1.58 g), bis-imidoylchloride **2** ($R = 4\text{-tolyl}$, 10 mmol, 3.05 g) and triethylamine (30 mmol, 3.05 g) were stirred in 10 ml of THF for 24 h at r. t. The color of the solution turned from yellow to deep-red and the progress of the reaction was monitored by TLC. Then the mixture was mixed with 50 ml of chloroform, the solution was washed three times with water, and the organic phase was dried over sodium sulfate. After removing the solvent *in vacuo* the crude product was purified by recrystallization from $\text{CHCl}_3/n\text{-hexane}$ (10 : 1). Yield: 1.55 g (44%); red crystals, m. p. 216°C . – UV-vis (CHCl_3): λ_{max} ($\lg \epsilon$) = 496 nm (4.3). – ^1H NMR (250 MHz, $[\text{D}_6]\text{-DMSO}$): $\delta = 2.34$ (s, 3 H), 2.48 (s, 3 H), 7.28 (d, $^3J = 8.7 \text{ Hz}$, 4 H), 7.63 (m, 1 H), 7.95 (d, broad, $^3J = 8.7 \text{ Hz}$, 4 H), 8.02 (m, 1 H), 8.48 (d, $^3J = 9.0 \text{ Hz}$, 1 H), 8.83 (d, $^3J = 5.8 \text{ Hz}$, 1 H). – ^{13}C NMR (62.5 MHz, CDCl_3): $\delta = 21.30$, 119.8, 121.3, 124.0, 126.5, 129.2, 136.6, 139.3, 150.7, 157.4, 163.3, 187.5. – MS (DEI): m/z (%) = 354 (40) $[\text{M}^+ + 1]$, 353 (100) $[\text{M}^+]$, 352 (95) $[\text{M}^+ - 1]$, 338 (95), 268 (25), 132 (35), 107 (45), 91 (50), 78 (25). – $\text{C}_{22}\text{H}_{19}\text{N}_5$ (353.4): calcd. C 74.77, H 5.42, N 19.82; found C 74.43, H 5.55, N 19.72.

5-(4-Bromophenylamino)-4-(4-bromophenylimino)-2-(benzothiazol-2-yl)-4*H*-imidazole (**3b**)

2-Amidinobenzothiazole hydrochloride [19] (10 mmol, 1.86 g), bis-imidoylchloride **2** ($R = 4\text{-Br-C}_6\text{H}_4$, 10 mmol,

4.35 g) and triethylamine (30 mmol, 3.05 g) were stirred in 100 ml of toluene for 3 h at 90–100 °C. The solution was washed three times with water and the organic phase was dried over sodium sulfate. After removing the solvent *in vacuo* the crude product was purified by column chromatography (silica gel, toluene/AcOEt 5 : 1).

Recrystallization from acetonitrile gave brown microcrystals. Yield: 2.05 g (38%); m. p. 223–226 °C. – UV/vis (acetonitrile): $\lambda_{\max}$ ($\lg \epsilon$) = 371 (4.2), 412 (4.2), 437 (4.2), 509 (4.2). – ^1H NMR (250 MHz, CDCl_3): δ = 6.98 (d, 3J = 8.7 Hz, 4 H), 7.35 (d, 3J = 8.7 Hz, 4 H), 7.84–8.25 (m, 4 H). – ^{13}C NMR (62.5 MHz, CDCl_3): δ = 121.2, 121.4, 121.8, 122.3, 123.1, 124.1, 125.3, 125.7, 126.6, 127.2, 127.7, 128.2, 128.6, 129.0, 132.2, 132.4, 132.5, 132.8. – MS (DEI): m/z (%) = 539 (16) [M^+], 458 (10) [$\text{M}^+ - \text{Br}$], 268 (76), 199 (77), 173 (98), 171 (100). – $\text{C}_{22}\text{H}_{13}\text{Br}_2\text{N}_5\text{S}$ (539.2): calcd. C 49.00, H 2.43, N 12.99, S 5.95; found C 48.73, H 2.39, N 12.78, S 6.07.

2-(Acridin-9-yl)-5-(4-tolylamino)-4-(4-tolylimino)-4*H*-imidazole (3c)

A mixture of *N,N,N'*-tris(trimethylsilyl)acridine-9-carbamidine (synthesized according to [20]) (2 mmol, 880 mg) and bis-imidoylchloride **2** (*R* = 4-tolyl, 2 mmol, 0.61 g) was stirred in 50 ml of THF for 2 h at reflux. The solvent was removed *in vacuo* and the residue was separated by column chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{THF}$: 50/1) to yield 194 mg (18%) of an orange solid; m. p. 265–266 °C. – UV/vis (CH_2Cl_2): $\lambda_{\max}$ ($\lg \epsilon$) = 363 (3.5), 481 (4.0). – ^1H NMR (250 MHz, CDCl_3): δ = 2.29 (s, 6 H), 7.19 (d, 4 H), 7.52 (m, 2 H), 7.77 (m, 2 H), 7.83 (d, 4 H), 8.23 (d, 2 H), 8.40 (d, 2 H). – MS (DCI, H_2O): m/z (%) = 453 (100) [M^+], 391 (40), 340 (15), 248 (35), 108 (30). – $\text{C}_{30}\text{H}_{23}\text{N}_5$ (539.2): calcd. C 79.45, H 5.11, N 15.44; found C 79.33, H 5.00, N 15.68.

General procedure for the synthesis of 4*H*-imidazoles 3d–3i by cyclization of acid chlorides **4 with oxalic amidines **5** (R^2, R^3 = 4-tolyl), according to way B**

A mixture of 2 mmol of the appropriate acid chloride **4**, 1 mmol of the oxalamidine **5** and pyridine (2 mmol, 160 mg) in 30 ml of toluene was heated at reflux for 8–24 h. The progress of the reaction was monitored by TLC. Then, the solution was washed with water, dried with sodium sulfate and the solvent was evaporated *in vacuo*. The orange-red solids were purified by column chromatography (silica gel, toluene/ethyl acetate 9 : 1).

2-(4-Fluorophenyl)-5-(4-tolylamino)-4-(4-tolylimino)-4*H*-imidazole (3d)

Yield: 200 mg (54%); red needles, m. p. 220–222 °C. – UV/vis (CHCl_3): $\lambda_{\max}$ ($\lg \epsilon$) = 487 nm (4.3). – ^1H NMR

(250 MHz, CDCl_3): δ = 2.43 (s, 6 H), 7.22 (d, 2 H), 7.29 (d, 4 H), 7.92 (d, 4 H), 8.61 (d, 2 H). – ^{13}C NMR (62.5 MHz, CDCl_3): δ = 18.9, 113.2, 113.6, 126.1, 127.5, 130.7, 134.4, 137.11(q), 161.2 (q), 162.0, 166.1 (q), 185.1 (q). – MS (DEI): m/z (%) = 370 (100) [M^+], 369 (70) [$\text{M}^+ - 1$], 355 (65) [$\text{M}^+ - \text{CH}_3$], 234 (40), 132 (50), 117 (75), 116 (70), 91 (60), 90 (45). – $\text{C}_{23}\text{H}_{19}\text{FN}_4$ (370.4): calcd. C 74.58, H 5.17, N 15.12; found: C 74.59, H 5.26, N 15.50.

2-(4-Chlorophenyl)-5-(4-tolylamino)-4-(4-tolylimino)-4*H*-imidazole (3e)

Yield: 93 mg (24%); dark red solid, m. p. 219 °C. – UV/vis (CHCl_3): $\lambda_{\max}$ ($\lg \epsilon$) = 519 nm (4.1). – ^1H NMR (250 MHz, CDCl_3): δ = 7.30 (d, 4 H), 7.52 (d, 2 H), 7.92 (d, 4 H), 8.53 (d, 2 H). – ^{13}C NMR (62.5 MHz, CDCl_3): δ = 21.7, 124.1, 129.2, 130.2, 131.6, 132.1, 137.2, 137.4, 140.2, 163.8, 187.9. – MS (DEI): m/z (%) = 386 (50) [M^+], 371 (70) [$\text{M}^+ - \text{CH}_3$], 234 (20), 132 (55), 117 (100), 91 (90). – $\text{C}_{23}\text{H}_{19}\text{ClN}_4$ (386.9): calcd. C 71.40, H 4.95, Cl 9.16, N 14.48; found C 71.69, H 5.16, Cl 9.46, N 14.28.

2-(4-Bromophenyl)-5-(4-tolylamino)-4-(4-tolylimino)-4*H*-imidazole (3f)

Yield: 155 mg (36%); red crystals, m. p. 214 °C. – UV/vis (CHCl_3): $\lambda_{\max}$ ($\lg \epsilon$) = 480 nm (4.1). – ^1H NMR (250 MHz, CDCl_3): δ = 2.32 (s, 6 H), 7.19 (d, 4 H), 7.56 (d, 2 H), 7.81 (d, 4 H), 8.34 (d, 2 H). – ^{13}C NMR (62.5 MHz, CDCl_3): δ = 21.3, 123.7, 128.8, 129.9, 131.1, 131.8, 136.9, 139.4, 163.4, 187.6. – MS (DEI): m/z (%) = 432 (45) [$\text{M}^+ - ^{81}\text{Br}$], 430 (45) [$\text{M}^+ - ^{79}\text{Br}$], 417 (50) [$\text{M} - \text{CH}_3$], 415 (50), 234 (60), 132 (50), 117 (70), 91 (100). – $\text{C}_{23}\text{H}_{19}\text{BrN}_4$ (431.3): calcd. C 64.05, H 4.44, N 12.99; found C 63.89, H 4.36, N 12.78.

2-(4-Iodophenyl)-5-(4-tolylamino)-4-(4-tolylimino)-4*H*-imidazole (3g)

Yield: 234 mg (49%); red crystals, m. p. 239–240 °C. – UV/vis (CHCl_3): $\lambda_{\max}$ ($\lg \epsilon$) = 492 nm (4.2). – ^1H NMR (250 MHz, CDCl_3): δ = 2.32 (s, 6 H), 7.17 (d, 4 H), 7.78 (d, 2 H), 7.79 (d, 4 H), 8.17 (d, 2 H). – ^{13}C NMR (62.5 MHz, CDCl_3): δ = 21.3, 103.1, 123.7, 129.9, 131.6, 136.9, 137.8, 138.4, 139.4, 163.4, 187.8. – MS (DEI): m/z (%) = 478 (35) [M^+], 463 (30) [$\text{M} - \text{CH}_3$], 234 (35), 231 (90), 132 (30), 117 (50), 76 (40). – $\text{C}_{23}\text{H}_{19}\text{IN}_4$ (478.3): calcd. C 57.75, H 4.00, N 11.71; found C 57.46, H 3.84, N 11.75.

2-(4-Cyanophenyl)-5-(4-tolylamino)-4-(4-tolylimino)-4*H*-imidazole (3h)

Yield: 72 mg (19%); dark red needles, m. p. 253–255 °C. – UV/vis (CHCl_3): $\lambda_{\max}$ ($\lg \epsilon$) = 528 nm (4.0). – ^1H NMR (250 MHz, CDCl_3): δ = 2.33 (s, 6 H), 7.20 (d, 4 H), 7.71 (d, 2 H), 7.81 (d, 4 H), 8.53 (d, 2 H). – ^{13}C NMR (62.5 MHz,

CDCl₃): δ = 21.7, 116.4, 118.9, 124.3, 130.3, 130.9, 132.5, 136.6, 137.8, 139.6, 163.6, 180.0. – MS (DEI): m/z (%) = 377 (65) [M⁺], 362 (100) [M-CH₃], 268 (39), 248 (8), 234 (20), 132 (16), 117 (20), 107 (33), 91 (23). – C₂₄H₁₉N₅ (377.4): calcd. C 76.37, H 5.07, N 18.55; found C 76.19, H 5.11, N 18.29.

2-(4-Butoxycarbonyl)-5-(4-tolylamino)-4-(4-tolylimino)-4*H*-imidazole (3i)

Yield: 145 mg (32%); red oil. – UV/vis (CHCl₃): $\lambda_{\max}$ (lg ϵ) = 525 nm (4.0). – ¹H NMR (250 MHz, CDCl₃): δ = 0.96 (t, 3 H), 1.50 (m, 2 H), 1.76 (m, 2 H), 2.34 (s, 6 H), 4.33 (t, 2 H), 7.29 (d, 4 H), 7.95 (d, 4 H), 8.14 (d, 2 H), 8.49 (d, 2 H). – C₂₂H₁₃Br₂N₅S (452.2): calcd. C 74.31, H 6.24, N 12.38; found C 74.19, H 6.19, N 12.24.

General procedure for the synthesis of bis-4*H*-imidazoles 3j–3l

A mixture of 2 mmol of the appropriate diacid dichloride, 1 mmol of the oxalamidine 5 and pyridine (2 mmol, 160 mg) in 100 ml of toluene was heated at reflux for 4–8 h. The progress of the reaction was monitored by TLC. Upon cooling to room temperature, the solution was washed with water, dried with sodium sulfate and the solvent was evaporated *in vacuo*. The red solids were purified by column chromatography (silica gel, toluene/ethyl acetate 9 : 1).

Bis-4*H*-imidazole 3j

Yield: 120 mg (25%); red crystals, m. p. 216 °C. – UV/vis (CHCl₃): $\lambda_{\max}$ (lg ϵ) = 500 nm (4.0). – ¹H NMR (250 MHz, CDCl₃): δ = 0.82 (t, 6 H), 1.16–1.70 (m, 40H), 2.34 (s, 12 H), 3.31 (t, 4 H), 7.22 (d, 8 H), 7.87 (d, 8 H), 8.43 (s, 2 H). – MS (DCI, H₂O): m/z (%) = 964 (100) [M⁺], 821 (10), 281 (20). – C₆₄H₈₂N₈ (963.4): calcd. C 79.79, H 8.58, N 11.63; found C 79.59, H 8.46, N 11.54.

Bis-4*H*-imidazole 3k

Yield: 67 mg (18%); red crystals, m. p. 283–284 °C. – UV/vis (CHCl₃): $\lambda_{\max}$ (lg ϵ) = 500 nm (4.0). – ¹H NMR (250 MHz, CDCl₃): δ = 2.33 (s, 12 H), 7.23 (d, 8 H), 7.87 (d, 8 H), 7.91 (d, 4 H), 8.62 (d, 4 H). – ¹³C NMR (62.5 MHz, CDCl₃): δ = 21.3, 119.6, 123.8, 130.1, 130.3, 135.9, 137.1, 139.3, 140.8, 163.4, 187.4, 195.7. – MS (DCI, H₂O): m/z (%) = 732 (40) [M⁺+2], 577 (10), 503 (20), 443 (15), 429 (30), 369 (20), 355 (30), 281 (10), 268 (20), 223 (20), 215 (70), 108 (100), 93 (30). – C₄₇H₄₀N₈O (730.9): calcd. C 77.24, H 5.24, N 15.33; found C 77.19, H 5.40, N 15.54.

4*H*-Imidazole 3l

Yield: 137 mg (29%); red crystals, m. p. 251 °C. – UV/vis (CHCl₃): $\lambda_{\max}$ (lg ϵ) = 488 nm (4.2). – ¹H NMR (400 MHz,

DMSO-*d*₆): δ = 2.33 (s, 6 H), 7.18 (d, 4 H), 7.27 (d, 2 H), 7.54–7.62 (m, 8 H), 7.94 (d, 1 H), 8.51 (d, 1 H), 11.53 (br. s, 1 H). – ¹³C NMR (62.5 MHz, [D₆]-DMSO): δ = 20.7, 123.8, 126.7, 127.0, 129.2, 129.5, 130.3, 130.9, 131.1, 132.0, 135.7, 143.8, 144.4, 163.3, 167.8, 187.7. – MS (DCI, H₂O): m/z (%) = 473 (11) [M⁺+1], 314 (31), 296 (28), 225 (100), 108 (49), 87 (42). – C₃₀H₂₄N₄O₂ (472.5): calcd. C 76.25, H 5.12, N 11.86; found C 76.09, H 5.00, N 11.74.

General procedure for the transamination of 4*H*-imidazole 3' with amines 6, according to way C

To a solution of 3' (2 mmol, 700 mg) in 30 ml of THF, a catalytic amount of 4-toluenesulfonic acid was added. An immediate color change was observed owing to formation of the protonated heterocycle 3'. Then an excess of the amine 6 (6 mmol) was added. The resulting mixture was heated under reflux and the progress of the reaction was monitored by TLC (typically, a mixture of mono- and bis-transamination product was detected). Reactions were generally allowed to proceed for 1–4 h. After filtration, the filtrate was concentrated *in vacuo* and the residue was purified by column chromatography (silica gel, toluene/ethyl acetate).

2-Phenyl-4-(2-(1-pyridyl)ethylamino)-5-(4-tolylimino)-4*H*-imidazole (3m)

Yield: 88 mg (12%); orange crystals, m. p. 137 °C. – UV/vis (CHCl₃): $\lambda_{\max}$ (lg ϵ) = 466 nm (3.9), 388 (3.8), 312 (4.2). – ¹H NMR (400 MHz, CDCl₃): δ = 2.31 (s, 3 H), 3.18 (t, 2 H), 4.08 (t, 2 H), 5.93 (br. 1 H, NH), 7.13–7.18 (m, 7 H), 7.71–7.76 (m, 3 H), 8.39 (d, 2 H); 8.53 (d, 1 H). – ¹³C NMR (62.5 MHz, CDCl₃): δ = 21.7, 31.3, 36.9, 122.2, 123.9, 127.1, 127.7, 128.8, 129.0, 130.6, 132.4, 133.6, 137.1, 149.8, 158.1, 167.3, 187.6. – MS (EI): m/z (%) = 367 (49) [M⁺], 275 (100), 261 (83), 106 (60), 93 (37). – C₂₃H₂₁N₅ (367.4): calcd. C 75.18, H 5.76, N 19.06; found C 75.09, H 5.68, N 19.23.

2-Phenyl-4-(2-(3-indolyl)ethylamino)-5-(4-tolylimino)-4*H*-imidazole (3n)

Yield: 130 mg (16%); orange crystals, m. p. 109 °C. – UV/vis (dioxane): $\lambda_{\max}$ (lg ϵ) = 470 nm (4.0), 290 (4.3). – ¹H NMR (250 MHz, CDCl₃): δ = 2.30 (s, 3 H), 3.16 (t, 2 H); 3.97 (t, 2 H), 7.02 (s, 1 H), 7.05–7.18 (m, 4 H), 7.31 (d, 1 H), 7.39–7.54 (m, 3 H), 7.64 (d, 1 H), 7.73 (d, 2 H), 8.05 (br. 1 H, NH), 8.43 (d, 2 H). – ¹³C NMR (62.5 MHz, CDCl₃): δ = 19.5, 23.4, 42.3, 110.4, 116.9, 117.7, 120.4, 124.8, 125.3, 126.5, 127.7, 128.4, 130.4, 131.5, 134.5, 135.9, 141.7, 158.7, 168.9, 186.7. – MS (DCI, H₂O): m/z (%) = 406 (100) [M⁺+1], 323 (47), 263 (31), 130 (49), 108 (16). – C₂₆H₂₃N₅ (405.5): calcd. C 77.01, H 5.72, N 17.27; found C 76.89, H 5.60, N 17.33.

2-Phenyl-4-(3-(1-imidazolyl)propylamino)-5-(4-tolylimino)-4*H*-imidazole (3o)

Yield: 104 mg (14%); orange crystals, m. p. 129 °C. – UV/vis (dioxane): $\lambda_{\max}$ (lg ϵ) = 470 nm (4.0), 290 (4.3). – ^1H NMR (250 MHz, CDCl_3): δ = 2.19 (m, 2 H), 2.32 (s, 3 H), 3.73 (t, 2 H), 4.05 (t, 2 H), 6.95 (br. 1 H), 7.03 (br. 1 H), 7.15 (d, 2 H); 7.41–7.53 (m, 4 H), 7.80 (d, 2 H), 8.42 (d, 2 H). – ^{13}C NMR (62.5 MHz, CDCl_3): δ = 21.7, 31.3, 42.7, 44.9, 126.1, 127.8, 128.9, 129.9, 130.3, 130.7, 132.0, 133.6, 137.5, 141.8, 161.2, 170.2, 188.7. – MS (EI): m/z (%) = 370 (21) [M^+], 302 (25), 263 (68), 144 (54), 212 (67), 106 (100), 84 (78). – $\text{C}_{29}\text{H}_{26}\text{N}_6$ (370.5): calcd. C 71.33, H 5.99, N 22.69; found C 71.25, H 5.78, N 22.47.

2-Phenyl-4-(4-tolylamino)-5-(5-tert-butyl-1,3,4-thiadiazol-2-yl)imino-4*H*-imidazole (3p)

Yield: 81 mg (10%); purple crystals, m. p. 209–210 °C. – ^1H NMR (400 MHz, CDCl_3 , mixture of two tautomers): δ = 1.50 (s, 3 H), 1.55 (s, 6 H), 2.38 (br. 4.5 H), 7.22–7.28 (m, 3 H), 7.52–7.59 (m, 3 H), 7.64–7.70 (m, 1.5 H), 7.85 (d, 1 H), 7.92 (d, 2 H), 8.13 (d, 1 H), 8.61 (d, 2 H), 12.02 (br 1 H, NH). – ^{13}C NMR (62.5 MHz, CDCl_3 , mixture of two tautomers): δ = 21.6, 31.4, 37.1, 121.5, 127.5, 128.8, 129.6, 129.8, 130.5, 131.1, 132.0, 134.9, 135.6, 137.1, 166.6, 183.5, 191.6. – MS (DCI, H_2O): m/z (%) = 403 (8) [$\text{M}^+ + 1$], 243 (100), 183 (16), 158 (13), 136 (24), 122 (17), 108 (34), 93 (18). – $\text{C}_{22}\text{H}_{22}\text{N}_6\text{S}$ (402.5): calcd. C 65.65, H 5.51, N 7.96; found C 65.55, H 5.68, N 8.12.

2-Phenyl-4-(2-(1-pyridyl)ethylamino)-5-(2-(1-pyridyl)ethylimino)-4*H*-imidazole (3q)

Yield: 306 mg (40%); yellow-greenish oil. – ^1H NMR (250 MHz, CDCl_3): δ = 3.32 (t, 4 H), 4.21 (t, 4 H), 7.14–7.26 (m, 4 H), 7.49–7.63 (m, 5 H), 8.41 (d, 2 H), 8.57 (d, 2 H). – ^{13}C NMR (62.5 MHz, CDCl_3): δ = 29.7, 38.3, 121.9, 123.8, 128.8, 130.4, 132.7, 133.5, 136.8, 149.7, 159.9, 167.5, 187.3. – MS (EI): m/z (%) = 382 (66) [M^+], 290 (36), 277 (51), 197 (27), 185 (19), 133 (25), 106 (84), 93 (100), 78 (22). – $\text{C}_{23}\text{H}_{22}\text{N}_6$ (382.5): calcd. C 72.23, H 5.80, N 21.97; found C 72.35, H 5.68, N 22.34.

2-Phenyl-4-(2-(3-indolyl)ethylamino)-5-(2-(3-indolyl)ethylimino)-4*H*-imidazole (3r)

Yield: 349 mg (38%); yellow microcrystals, m. p. 176 °C (dec.). – ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 3.10 (t, 4 H), 3.99 (br., 4 H), 7.00 (m, 2 H), 7.07 (m, 2 H), 7.21 (s, 2 H), 7.34 (d, 2 H); 7.53 (m, 2 H), 7.61–7.68 (m, 3 H), 8.31 (d, 2 H), 10.73 (s, 2 H, NH). – ^{13}C NMR (62.5 MHz, $\text{DMSO}-d_6$): δ = 21.4, 25.9, 111.7, 112.7, 118.6, 118.8, 121.3, 123.1, 125.7, 127.7, 128.6, 128.9, 129.3, 129.7, 132.6, 133.4, 136.6, 167.7, 185.7. – MS (DCI, H_2O): m/z (%) = 457 (27) [$\text{M}^+ + 1$],

323 (51), 302 (45), 249 (46), 144 (100), 130 (46), 104 (17). – $\text{C}_{29}\text{H}_{26}\text{N}_6$ (458.6): calcd. C 75.96, H 5.71, N 18.33; found C 75.85, H 5.60, N 18.45.

2-Phenyl-4-(3-(imidazolyl)propylamino)-5-(3-(imidazolyl)propylimino)-4*H*-imidazole (3s)

Yield: 544 mg (70%); yellow solid, m. p. 121 °C (dec.). – ^1H NMR (400 MHz, CDCl_3): δ = 2.08 (m, 4 H), 3.79 (t, 4 H), 4.07 (t, 4 H), 4.31–4.90 (br 1 H), 6.97 (br 2 H), 7.04 (br 2 H), 7.46–7.59 (m, 5 H), 8.41 (d, 2 H). – ^{13}C NMR (62.5 MHz, CDCl_3): δ = 31.5, 45.2, 45.4, 119.4, 128.9, 129.8, 130.5, 132.2, 133.9, 138.1, 166.2, 186.2. – MS (EI): m/z (%) = 388 (5) [M^+], 320 (22), 162 (13), 103 (22), 95 (51), 82 (54), 68 (100). – $\text{C}_{21}\text{H}_{24}\text{N}_8$ (388.5): calcd. C 64.93, H 6.23, N 28.84; found C 65.05, H 6.16, N 28.65.

2-Phenyl-4-(2-(2-pyridyl)ethylamino)-5-[2'-phenyl-4'-(2-(pyridyl)ethylamino)-imidazol-3-imino]-4*H*-imidazole (7)

Imidazole **3q** (1 mmol, 380 mg) was heated with a catalytic amount of 4-toluenesulfonic acid in 50 ml of toluene for 5 h under reflux. The solvent was removed *in vacuo* and the residue was separated by column chromatography on silica gel (ethyl acetate/acetone: 1/1) to yield 38 mg (14%) of a dark blue solid; m. p. 184 °C. – UV/vis (dioxane): $\lambda_{\max}$ = 528, 405 nm. – ^1H NMR (400 MHz, CDCl_3): δ = 3.20 (t, 4 H), 4.04 (t, 4 H), 6.64 (br 3 H, NH), 7.08 (t, 2 H), 7.17 (d, 2 H), 7.41–7.49 (m, 6 H), 7.55 (t, 2 H), 8.14 (d, 4 H), 8.49 (d, 2 H). – ^{13}C NMR (100 MHz, CDCl_3): δ = 38.3, 43.8, 121.9, 124.1, 127.5, 129.2, 130.8, 131.5, 135.7, 136.9, 149.8, 159.9, 160.4, 161.2. – HRMS (ESI, MeOH): calcd. 539.254592 for $\text{C}_{32}\text{H}_{29}\text{N}_9$, found 540.263320 for $\text{C}_{32}\text{H}_{30}\text{N}_9[\text{M}^+ + \text{H}]$.

General procedure for the synthesis of the 1,3,2-diazaborolindines 8a and 8b

To a solution of 1 mmol of the appropriate 4*H*-imidazole **3d**, **3g** in 50 ml of toluene triethylamine (5 mmol) or DBU (1.5 mmol), and BF_3 -etherate (3 mmol) was added. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC (toluene/ethyl acetate 9:1). After consumption of the educt the mixture was washed with water, dried with Na_2SO_4 and the solvent removed *in vacuo*. The residue was purified by column chromatography with toluene/ethyl acetate 19:1 as eluent.

1,3-Bis(4-tolyl)-2,2-difluoro-5-phenyl-imidazo[4,5-*d*]-1,3,2-diazaborolidine (8a)

Yield: 212 mg (51%) of deep purple crystals; m. p. 196–202 °C. – UV/vis (dioxane): $\lambda_{\max}$ (lg ϵ) = 604 (4.3), 563 (4.3), 427 (4.4), 406 nm (4.4). – Fluorescence (CHCl_3): $\lambda_{\max, \text{em}}$ = 653 nm, Φ = 0.11. – ^1H NMR (400 MHz,

CDCl₃): δ = 2.47 (s, 6 H), 7.19 (dd, 2 H), 7.22 (d, 4 H), 8.00 (d, 4 H), 8.69 (dd, 2 H). – MS: m/z (%) = 418 (100) [M⁺], 403 (80), 209 (25), 180 (60), 117 (50), 91(65). – C₂₃H₁₉BF₂N₄ (400.2): calcd. C 66.05, H 4.34, N 13.40; found C 66.22, H 4.67, N 13.63.

1,3-Bis(4-tolyl)-2,2-difluoro-5-(4-iodophenyl)imidazo[4,5-*d*]-1,3,2-diazaborolidine (8b)

Yield: 105 mg (20%) of deep purple crystals; m. p. 223–225 °C. – ¹H NMR (250 MHz, CDCl₃): δ = 2.34 (s, 6 H), 7.22 (d, 2 H), 7.36 (d, 4 H), 7.85 (d, 4 H), 7.98 (d, 2 H). – ¹³C NMR (62.5 MHz, CDCl₃): δ = 21.4, 106.2, 122.9, 125.5, 129.1, 130.3, 133.5, 138.4, 144.2, 168.2, 203.0. – C₂₃H₁₈BF₂IN₄ (526.1): calcd. C 52.51, H 3.45, N 10.65; found C 52.42, H 3.37, N 10.53.

3,6-Bis(4-tolyl)-2,2-difluoro-5-phenyl-imidazo[4,5-*d*]-[1,3,6,2]oxadiazaborinane (10)

To a solution of the nitrene **9** (0.2 mmol, 90 mg) in 50 ml of toluene, DBU (0.2 mmol, 30 mg), and BF₃-etherate (0.4 mmol, 28 mg) was added. The reaction mixture was stirred at r.t. for three days and the progress of the reaction was monitored by TLC. Then, the mixture was washed with water, dried with Na₂SO₄ and the solvent was removed *in vacuo*. The residue was purified by column chromatography (silica gel, toluene/ethyl acetate 9:1). Yield: 40 mg (39%) of deep purple crystals; m. p. 206–210 °C. – UV/vis (CHCl₃): $\lambda_{\max}$ (lg ϵ) = 533 (3.9), 509 (3.9), 378 (4.0). – Fluorescence (CHCl₃): $\lambda_{\max,em}$ = 590 nm, Φ = 0.36. – ¹H NMR (250 MHz, CDCl₃): δ = 1.37 (s, 18 H), 7.51 (d, 2 H), 7.53 (d, 2 H), 7.60 (d, 2 H), 7.67 (m, 1 H), 7.83 (m, 2 H), 8.42 (d, 2 H), 8.54 (d, 2 H). – ¹³C NMR (62.5 MHz, CDCl₃): δ = 31.2, 34.8, 35.1, 122.4, 124.2, 125.5(t), 126.3, 129.0, 131.0, 132.0, 135.6 (t), 136.4, 137.8, 152.0, 153.3, 156.6, 165.0 (t), 191.9. – MS (DEI): m/z (%) = 500 (100) [M⁺], 443 (25) [M⁺ - C₄H₉], 435 (35) [M⁺ - BF₂O]. – C₂₉H₃₁BF₂N₄O (500.4):

calcd. C 69.61, H 6.24, N 11.20; found C 69.42, H 6.30, N 11.43.

Copper complexes 11 and 12

To a solution of 0.3 mmol of imidazoles **3o** or **3s** in 20 ml of dichloromethane a suspension of Cu(O₃SCF₃)₂ (0.15 mmol, 54 mg, for complex **12**: 0.3 mmol, 108 mg), in 50 ml of dichloromethane was added under stirring during one hour. After stirring for an additional hour, the precipitate was filtered off. The precipitate was dissolved in cold methanol and an equal amount of cold diethyl ether was cautiously added so that a two phase system was generated. The pure metal complexes crystallized at the interphase after some time. Complex **11** was obtained as a brownish solid (162 mg, 98%). – MS (ESI, MeOH): m/z (%) = 803 (4) [M⁺], 433 (13), 393 (23), 371 (100), 354 (14), 251 (18). – C₄₆H₄₄F₆N₁₂O₆S₂Cu (1102.6).

Complex **12** was obtained as a pale-blue solid (176 mg, 79%), m. p. 178 °C. – MS (FAB, NBA): m/z (%) = 600 (3) [M⁺ - CF₃SO₃], 483 (14), 451 (53) [M⁺ - 2CF₃SO₃ = CuL], 389 (29), 307 (100), 289 (62), 213 (31). – C₂₃H₂₄F₆N₈O₆S₂Cu (750.2).

Zinc complex 13

Under an argon atmosphere, a 1 M solution of diethylzinc in *n*-heptane (0.075 mmol, 0.075 ml) was slowly dropped at –78 °C to a solution of **3m** (0.15 mmol, 55 mg) in 20 ml of THF. The mixture was allowed to warm up to room temperature and the precipitate was filtered off and dried *in vacuo*. Yield: 58 mg (97%) of red crystals; m. p. 164 °C. – MS (EI): m/z (%) = 796 (39) [M⁺ - 1], 716 (16), 690 (14), 431 (100). – C₄₆H₄₀N₁₀Zn (798.3).

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