

REDUCTION OF 4*H*-IMIDAZOLES – SYNTHESIS AND REACTIVITY OF 4,5-DIAMINOIMIDAZOLES BEARING A TETRA-AMINOETHENE SUBSTRUCTURE

Jens Atzrodt^a, Rainer Beckert^{*a}, and Helmar Görls^b

^aInstitut für Organische und Makromolekulare Chemie der Friedrich-Schiller-Universität, Humboldtstraße 10, D-07747 Jena, Germany

^bInstitut für Anorganische und Analytische Chemie der Friedrich-Schiller-Universität, August-Bebel-Straße 2, D-07743, Germany

Abstract – The 4*H*-imidazoles (1) can be reduced after deprotonation to the trianion (4) by two consecutive single electron transfer reactions. Subsequent quenching by simple electrophiles constitutes a convenient route to the title substances of type (5). The unexpected regioselectivity towards bielelectrophilic building blocks facilitates the synthesis of highly substituted heterospiranes (7) and the imidazo crown ethers (8). The trianion (4) reacted with two molecules of CS₂ at the exocyclic nitrogen atoms exclusively to afford after quenching the dithiocarbamates (10) and the cyclic thiuram sulfides (11). The new imidazole derivatives of type (5) showed only slight electron donor properties. An electrophilic attack led with preference to a quarternization of the unsubstituted ring nitrogen atom of 5, as shown by the synthesis of compound (13). A similar behaviour was observed by treatment of 5 with acetylenedicarboxylate, in which the red 1:2 adduct (14) was formed in yields up to 76 %.

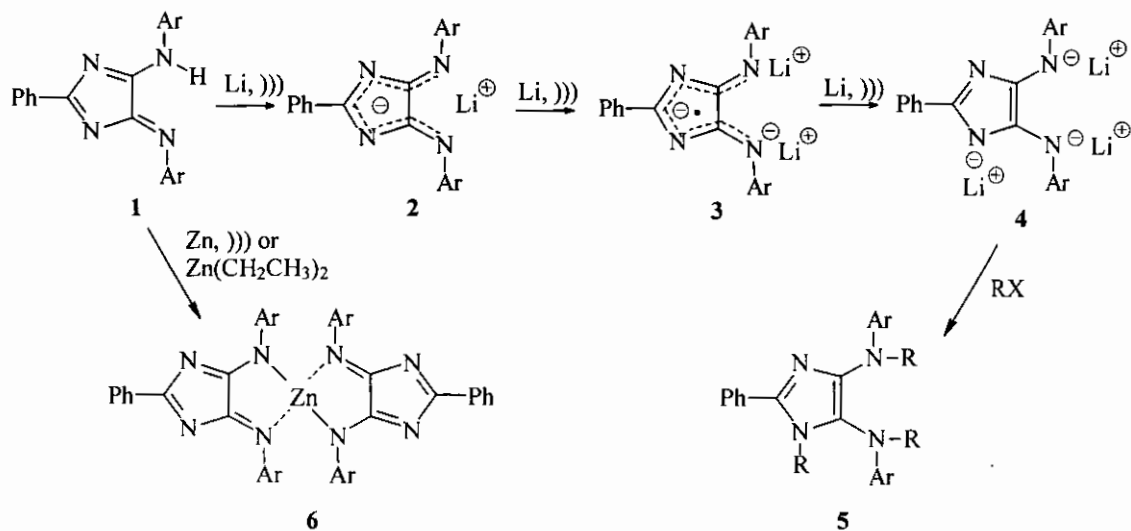
Recently, we reported a new synthetic entry to tetraaminoethenes¹ via a reduction - substitution sequence starting from oxalic amidines.² The latter may be readily reduced by alkali metals,³ because of the acceptor properties of the including 1,4-diaza-1,3-diene substructure. Subsequent reaction of the pre-formed dianion with various electrophiles constitutes a convenient route to highly substituted tetraaminoethenes.¹ Based on these experimental findings, an efficient one-pot synthesis of new macrocyclic compounds was developed.⁴

The 4*H*-imidazole derivatives (**1**),⁵ which receives particular attention concerning their special structural and light absorption properties,⁶ contain the same structural element. Therefore, they should be reduced after deprotonation to the corresponding trianion by two consecutive single electron transfer reactions. Quenching with electrophiles should, thus, furthermore facilitate the synthesis of new 4,5-diaminoimidazoles. Until now, stable derivatives of this class of new compound could be obtained only in the acylated form by reduction of 4(5)-nitro-5(4)-aminoimidazoles.⁷

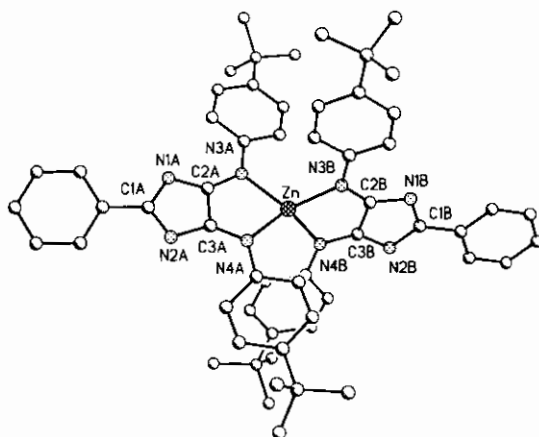
Using THF as solvent and metallic lithium as reducing agent, the formation of the unusual stable well known monoanion (**2**) is characterized by a distinct color change from orange to purple.⁸ Additional intensive stirring at room temperature lead after 48 h, *via* the ESR-spectroscopic detectable dark green radical dianion (**3**) to the brownish trianion (**4**). Carefully ventilating of the reaction vessel reversed these processes above all species gradually. Oxidation and reduction could be repeated for several times, as long as metallic lithium was available in solution. The reaction times for the formation of **4** could be reduced drastically to 8 h, by the use of ultrasonic irradiation. The electron transfer occurred quantitatively without formation of byproducts and could be monitored by ESR- and NMR-spectroscopy. The structural and aggregation behaviours of **4** in solution were of considerable interest. However, the NMR-spectrum of **4a** provided not a unified signal pattern, because of the temperature dependent equilibrium composition of different species of **4** in solution. Even at -80 °C, these dynamic behavior could not be completely suppressed, neither the spectrum of a fluctuating structure could be measured after heating the solution up to 60 °C.

However, the existence of the trianion (**4**) was proved by quenching reactions with electrophilic reagents. Treatment of **4a** with methanol as a proton source provided the air sensitive, blue fluorescent leuco compound (**5a**), which can be obtained also by reduction of **1a** with Zn/HCl or Et₃SiH/HBF₄ and subsequent addition of triethylamine. On exposure to air, the color of the solution turned from yellow to dark purple and the stable monoanion (**2a**) was formed solely.

Comparable electron transfer processes were induced by proton active compounds and were described for



	Ar	R
5a	4-CH ₃ C ₆ H ₄	H
5b	4-CH ₃ C ₆ H ₄	CH ₃
5c	4-CH ₃ OC ₆ H ₄	CH ₃
5d	4-(CH ₃) ₃ CC ₆ H ₄	CH ₃
5e	4-CH ₃ C ₆ H ₄	C ₂ H ₅
5f	4-CH ₃ C ₆ H ₄	CH ₃ CO
5g	4-CH ₃ C ₆ H ₄	C ₆ H ₅ CO



Scheme 1 and Figure 1: Perspective drawing of **6b**; the numbering corresponds to that used for the X-Ray analysis. Selected distances [Å] and angles [°]: Zn-N3A 2.019(3), Zn-N4A 2.019(3), Zn-N3B 2.011(2), Zn-N4B 2.033(3), C1A-N1A 1.371(4), C1A-N2A 1.363(4), C2A-N1A 1.349(4), C3A-N2A 1.359(4), C2A-N3A 1.325(4), C3A-N4A 1.312(4), C2A-C3A 1.511(4), N3B-Zn-N4B 86.72(10), N3B-Zn-N3A 123.33(10), N3B-Zn-N4A 124.5(11), N1A-C1A-N2A 119.3(3), C1A-N1A-C2A 102.0(3), C1A-N2A-C3A 102.2(3), C2A-N3A-Zn 108.3(2), C3A-N4A-Zn 108.3(2).

tetraaminoethenes, such as tetrakis(dimethylamino)ethylene.⁹ In the present case, the primary adduct of

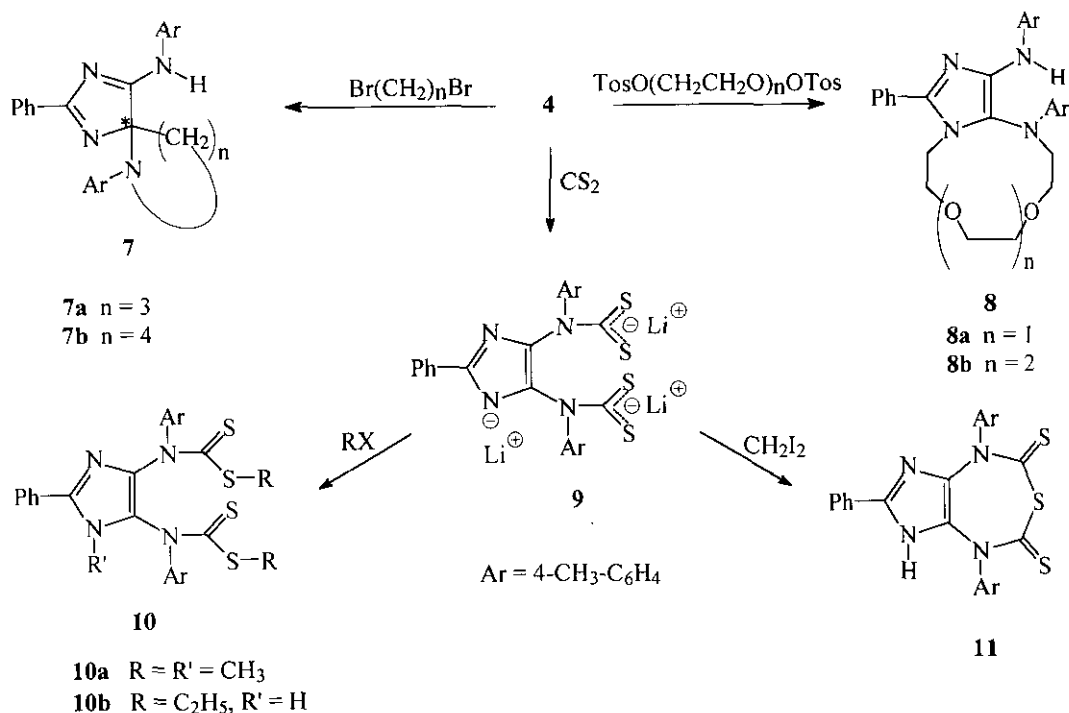
5a with oxygen probably led *via* prototropism to an elimination of hydrogen peroxide under formation of the stable monoanion (**2a**). The formation of a 1,2-dioxetane can be excluded, because in no case the characteristic C–C bond cleavage could be observed. Consequently, the substitution of the three NH-protons by alkyl residues should contribute to a stabilization of the molecule towards oxidative processes. Accordingly, the new derivatives of 2-aryl-4,5-bis(arylamino)imidazoles (**5b-g**) could be obtained, by reaction of **4** with simple alkyl and acyl halides. ¹H-, ¹³C-NMR and MS spectral data confirmed the structural assignments. In accordance to the drastic alteration of the chromophoric system of **1**, all derivatives (**5**) are colorless compounds, which show instead a strong bluish fluorescence. The different π -electron configuration was shown also in the NMR-spectra of both compound classes. Thus, compared to the ¹H-NMR spectrum of **1a**, especially the *ortho* hydrogens of the 2-phenyl residue in **5b** appeared at lower field.

The trianion (**4**) could be generated also by using other alkali metals (sodium, potassium) as reducing agents, but lithium seems to be favored. In contrast, treatment of **1** with metallic zinc under ultrasonic conditions led to a blue solution containing the slightly soluble complex (**6**). Advantageously, **6** can be obtained immediately also by reaction of **1** with zincdiethyl in nearly quantitative yield. The characteristic isotope peaks of the metal were shown in the MS spectra of **6**. Compared to the UV/Vis spectrum of **1a** ($\lambda_{\text{max}} = 481 \text{ nm}$), **6a** absorbs about 100 nm bathochromically. The X-Ray structure determination of the blue single crystals of **6b**, obtained by recrystallization from ether, could be carried out and the result is illustrated in Figure 1.

The metal is twisted tetrahedral environment between both exocyclic nitrogen atoms of the anionic imidazole systems. The molecular plans of the ligands are arranged in an orthogonal position to each other. All C–N bonds of the imidazole ring as well as the Zn–N bonds have nearly the same bondlength, respectively. Hence, the negative charge is predominately delocalized inside of the 5-ring system.

Examining the reaction of **4** with bielectrophilic reagents the regioselectivity of the cyclization was of special interest. Due to the highly charged **4**, treatment with bielectrophilic reagents also should lead to polymeric products. However, the TLC of the reaction mixtures displayed in the most cases the selective

formation of only one product.



Scheme 2

The chemical divergence of the tolyl residues was shown in the ^1H - as well as ^{13}C -NMR spectra of (7). Conspicuously furthermore, the signal of a quaternary ring carbon atom in **7b** appeared with $\delta = 94.17$ ppm at unusual high field, indicating a sp^3 hybridized bonding state. The X-Ray analysis of the colorless crystals of **7b**, obtained by recrystallization from acetone, could be carried out and the result is shown in Figure 2.

In fact, the cyclization occurred involving one ring carbon atom to afford the chiral imidazole-4-spiro-2'-piperidine derivative (**7b**). The remaining anionic nitrogen was protonated by the chromatographical work-up of the reaction mixture. The resulting NH-proton was detected as a sharp singlet at $\delta = 8.74$ ppm. In addition to the central chirality of **7**, in the crystals of **7b** a chiral axis exists, because of the suppression of ring inversion. Therefore, the common appearance of both diastereomeric pairs in the crystals of **7b** could be explained. The central chirality of the spiro carbon atom could be proved also by NMR shift experiments. After addition of small amounts of (*S*)-2,2,2-trifluoro-(9-anthranlyl)ethanol a splitting was

observed especially of the doublet of the *ortho* hydrogen atoms of the tolyl residue.

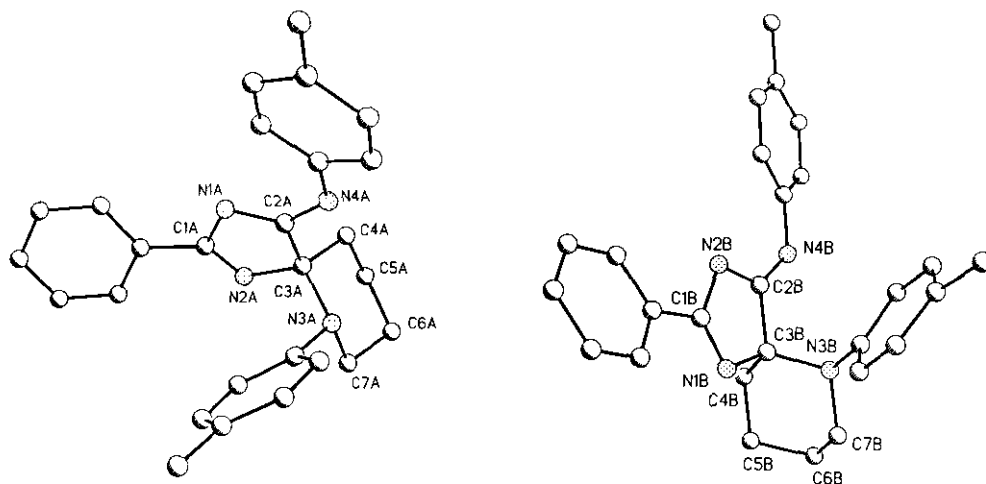


Figure 2: Representation of the molecular structure of **7b**, both diastereomeric pairs were obtained in one crystal of **7b**. Selected distances [\AA] and angles [$^\circ$]: C1A–N1A 1.414(3), C1A–N2A 1.303(3), C2A–N1A 1.312(3), C2A–N4A 1.341(3), C2A–C3A 1.527(3), C3A–N2A 1.484(3), C3A–N3A 1.487(3), C3A–C4A 1.543(3), N1A–C1A–N2A 118.0(2), N1A–C2A–N4A 126.7(2), N2A–C3A–N3A 113.6(2), C2A–C3A–C4A 111.0(2), N3A–C3A–C4A 109.3(2).

The alkylation of **4** with other α,ω -dihalogenoalkanes, such as 1,5-dibromopentane or 1,8-dibromooctane led to complex reaction mixtures. Using 1,2-dibromoethane or 1,2-dibromocyclohexane, all attempts of alkylation were in vain. Probably, the bicyclic imidazopyrazines underwent a cycloreversion process leading to unsaturated compounds and the stable monoanion (**2**). For example, using 1,2-dibromocyclohexane as an alkylating agent, besides the starting material (**1**), cyclohexene was identified by gas-chromatography. An analogous behavior was already described for hexasubstituted oxalic amidines.²

The ^{13}C -NMR spectra of the cyclization products (**8**), which were available by treatment of **4** with 1,8-bis(toluenesulfonato)-3,6-dioxaoctane and 1,11-bis(toluenesulfonato)-3,6,9-trioxaundecane revealed not the characteristic signal of the sp^3 hybridized spiro-carbon atom. Instead, for the aryl moieties in positions 4 and 5 different signal pattern was detected. In this case, the cyclization reaction occurred under inclusion of the imidazole nitrogen atom under the formation of the *N*-bridged macrocyclic derivatives of type (**8**).

Beyond that, we tested also heterocumulenes as quenching agents for **4**. The trianion (**4**) reacted with two equivalents of CS_2 at the exocyclic nitrogen atoms exclusively to afford the red colored trianion (**9**).

Subsequent treatment with alkylhalides gave the dithiocarbamates (**10**). Somewhat surprisingly, only methyl iodide led to *N*-alkylated products and therefore, by the use of ethyl iodide the NH-substituted derivative (**10b**) was isolated by chromatographical work-up. For the derivative (**10a**), crystals were obtained whose structure could be determined by single crystal X-Ray structural analysis. The result, showing the expected structure for **10a**, is illustrated in Figure 3.

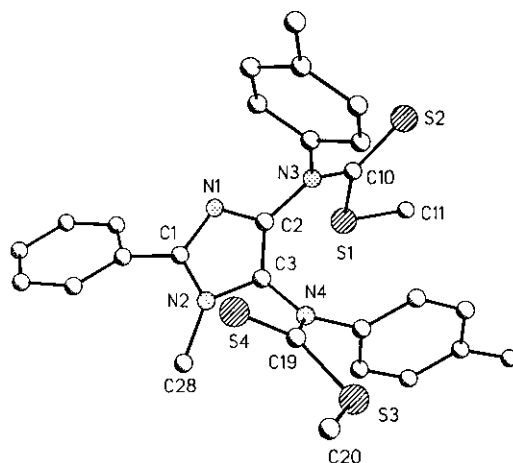


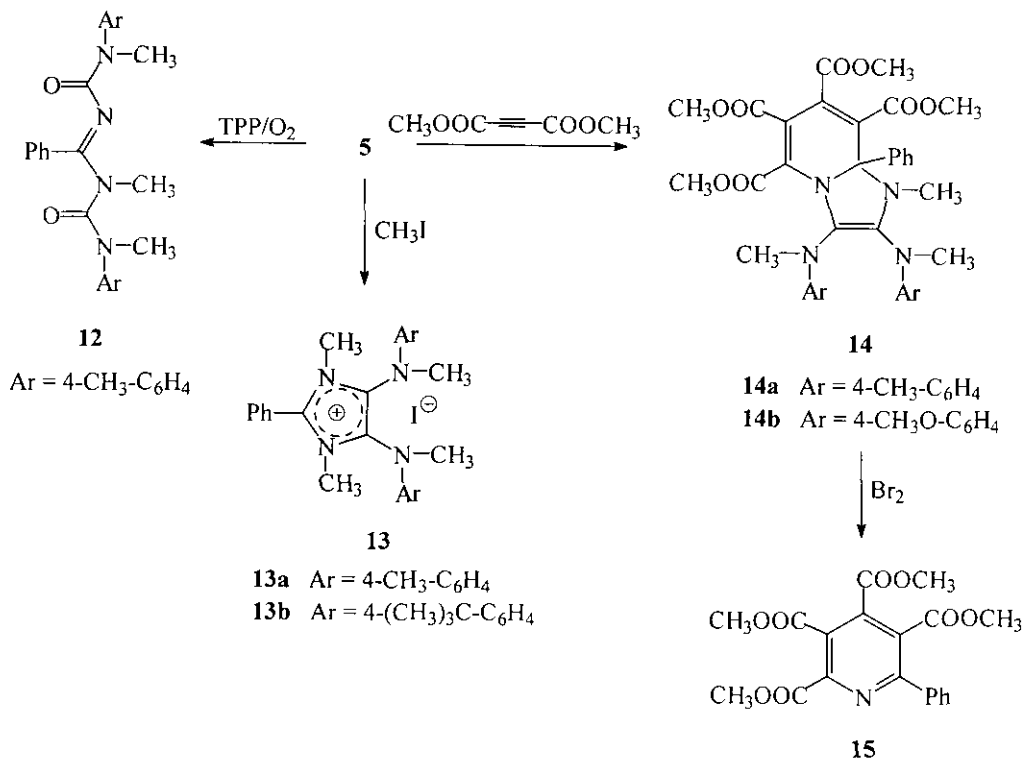
Figure 3: Molecular structure of **10a**; the numbering corresponds to that used for the X-Ray analysis; Selected distances [Å] and angles [°]: C1–N1 1.337(4), C1–N2 1.378(4), N1–C2 1.365(4), N2–C3 1.395(4), C2–C3 1.366(5), C2–N3 1.437(4), C3–N4 1.416(4), N3–C10 1.366(4), C10–S1 1.769(3), C19–S2 1.663(3), N1–C1–N2 111.6(3), N1–C2–N3 121.3(3), N2–C3–N4 122.8(3), C2–N3–C10 121.6(3), C3–N4–C19 120.7(3), S1–C10–S2 123.2(2), S3–C19–S4 124.9(2).

In an analogous manner, the imidazo[4,5-*d*]thiadiazepinedithione (**11**) was formed by cyclization of **9** with methylene iodide. MS spectral data and the absence of the methylene group in the NMR spectra of **11** indicating, that probably a ring contraction under extrusion of thioformaldehyde took place.

In comparison to typical tetraaminoethenes,¹⁰ the new imidazole derivatives of type (**5**) showed only slight electron donor properties. The distinct color change of the colorless THF solution of **5b** to green after the addition of strong acceptors, such as TCNQ or TCNE clearly indicates the formation of π -complexes but an electron transfer could not be proved by ESR-spectroscopy.

In contrast, **5b** quantitatively reacted with singlet oxygen to give the bisurea derivative (**12**) immediately. The signals in the ¹H-NMR spectrum of **12** were very broad at room temperature and no interpretation was possible. A complete separation of the signal set could be reached by heating the sample to 70 °C.

The ring cleavage had an effect especially to the *ortho* protons of the phenyl residue, which absorbed in comparison to **5b** ($\delta = 7.71$ ppm) with $\delta = 7.09$ ppm at lower field of the $^1\text{H-NMR}$ spectrum of **12**.



Scheme 3

As expected, an electrophilic attack lead with preference to a quaternization of the unsubstituted ring nitrogen atom of **5**. For example, the colorless imidazolium salts of type (**13**), which show an intensive yellow fluorescence were obtained by heating acetonitrile solutions of **5** with iodomethane.

On treatment of **5** with acetylenedicarboxylate a similar reaction was observed, in which the red 1:2 adduct (**14**) was formed. The mechanistic pathway for cyclization reactions of that type was already described for the comparable reactions of 1,2-dimethylimidazole¹¹ and similar heterocyclic systems.¹² In the course of such a multi-step reaction, the dehydropyrido[1,2-*a*]imidazole derivative (**14**) was isolated in yields up to 76%. The NMR-spectra of **14** at room temperature were very complex. The expected unified signal pattern of **14** could not be measured even by heating the samples up to 60 °C, neither at -80 °C. Probably, in solution a dynamic equilibrium of the ring opened imidazolium salt and **14** was detected.

The degree of this ring opening process in solution and its synthetic use will be the subject of further investigations. Even though the purity of the products were verified by TLC and combustion analysis.

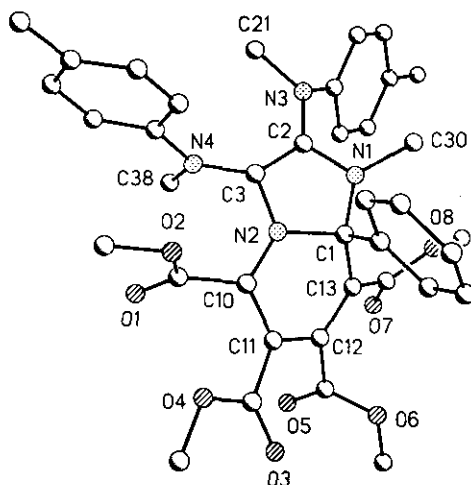


Figure 4: Perspective drawing of **14a**; the numbering corresponds to that used for the X-Ray analysis. Selected distances [Å] and angles [°]: C1–N1 1.488(5), C1–N2 1.505(5), N1–C2 1.390(5), N2–C3 1.444(5), C2–C3 1.363(5), C2–N3 1.373(5), C3–N4 1.399(5), C1–C13 1.527(5), N2–C10 1.340(5), C10–C11 1.402(5), C11–C12 1.441(6), C12–C13 1.366(5), N1–C1–N2 101.9(3), N1–C2–N3 118.8(3), N2–C3–N4 120.2(3), N2–C10–C11 118.8(3), C1–C13–C12 115.6(3).

Additional, the structure of **14a** was confirmed by X-Ray structural analysis (Figure 4). In contrast to the 1:2-adduct of 1,2-dimethylimidazole with dimethyl acetylenedicarboxylate,¹¹ **14** was stable towards glacial acetic acid. Because of the phenyl residue at the heterocycle, **14** accounted not for the loss of methylamine and the formation of diaminoindolizine derivatives. However, in the presence of bromine another ring-opening reaction forming the 6-phenylpyridinetetracarboxylate (**15**) was observed.

EXPERIMENTAL

General: All reagents were of commercial quality (Aldrich, Fluka, Merck) and were used as received. Solvents were dried and purified using standard techniques. Reactions were monitored by TLC, on plastic plates coated with neutral alumina with fluorescence indicator (Polygram ALOX N/UV₂₅₄ from Macherey-Nagel). Separations by flash chromatography were carried out on neutral alumina (Merck, aluminium oxide 90 active neutral, activity V, particle size 0.063 mm-0.2 mm, 70-230 mesh ASTM).

Melting points were measured with a Galen III (Boetius system) from Cambridge Instruments, and are uncorrected. 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 (400 MHz) and Bruker AC 250 (250 MHz) spectrometers (^1H -NMR shifts: relative to ^1H signals of the solvent). 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.

Crystal Structure Determination :

Data collection: The intensity data for the compounds were collected on an Nonius KappaCCD diffractometer, using graphite-monochromated Mo- K_α radiation and the φ - scan technique (180 frames, 30s per frame, $\Delta\varphi = 1^\circ$) at -90°C . Data were corrected for Lorentz and polarization effects, but not for absorption.¹⁴

Structure Solution and Refinement: The structure was solved by direct methods (SHELXS¹⁵) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97¹⁶).

The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. XP (SIEMENS Analytical X-Ray Instruments, Inc.) was used for structure representations.

*Crystal Data for 6b*¹⁷: $\text{C}_{58}\text{H}_{62}\text{N}_8\text{Zn} \cdot \frac{1}{2}\text{C}_4\text{H}_{10}\text{O}$, Mr = 973.59 g mol^{-1} , pinc prism, size 0.34 x 0.32 x 0.28 mm^3 , monoclinic, space group $\text{P}2_1/\text{n}$, a = 15.7967(5), b = 18.6123(4), c = 19.6979(6) Å, $\beta = 94.303(1)^\circ$, V = 5775.1(3) Å³, Z = 4, $\rho_{\text{calcd.}} = 1.120 \text{ g cm}^{-3}$, $\mu (\text{Mo-}K_\alpha) = 4.69 \text{ cm}^{-1}$, F(000) = 2068, 15176 reflections in h(0/17), k(-20/20), l(-21/21), measured in the range $2.07^\circ \leq \Theta \leq 23.22^\circ$, 8181 independent reflections, $R_{\text{int}} = 0.086$, 6366 reflections with $F_o > 4\sigma(F_o)$, 649 parameters, $R_{1\text{obs}} = 0.048$, $wR_{2\text{obs}}^2 = 0.132$, GOOF = 1.037, completeness $\Theta_{\text{max}} = 98\%$, $R_{1\text{all}} = 0.073$, $wR_{2\text{all}}^2 = 0.176$, largest difference peak and hole: 0.518 / -0.331 e \AA^{-3} .

*Crystal Data for 7b*¹⁷: $\text{C}_{27}\text{H}_{30}\text{N}_4\text{O}$, Mr = 426.55 g mol^{-1} , colorless prism, size 0.35 x 0.34 x 0.32 mm^3 ,

triclinic, space group P-1, $a = 13.3141(4)$, $b = 13.8739(5)$, $c = 13.9606(5)$ Å, $\alpha = 82.552(2)$, $\beta = 72.628(2)$, $\gamma = 76.112(2)$ °, $V = 2384.5(1)$ Å³, $T = -90$ °C, $Z = 4$, $\rho_{\text{calcd.}} = 1.188$ gcm⁻³, μ (Mo-K α) = .74 cm⁻¹, $F(000) = 912$, 12715 reflections in $h(0/14)$, $k(-14/15)$, $l(-14/15)$, measured in the range $2.22^\circ \leq \Theta \leq 23.30^\circ$, 6498 independent reflections, $R_{\text{int}} = 0.044$, 6003 reflections with $F_o > 4\sigma(F_o)$, 602 parameters, $R1_{\text{obs}} = 0.054$, $wR^2_{\text{obs}} = 0.149$, GOOF = 1.041, completeness $\Theta_{\text{max}} = 97$ %, $R1_{\text{all}} = 0.0797$, $wR^2_{\text{all}} = 0.186$, largest difference peak and hole: 0.281 / -0.282 e Å⁻³.

*Crystal Data for 10a*¹⁷: C₂₈H₂₈N₄S₄, $M_r = 548.78$ gmol⁻¹, colorless prism, size 0.40 x 0.35 x 0.32 mm³, triclinic, space group P-1, $a = 9.2016(7)$, $b = 11.8920(8)$, $c = 13.4032(10)$ Å, $\alpha = 90.894(4)$, $\beta = 100.670(4)$, $\gamma = 103.561(4)$ °, $V = 1398.4(2)$ Å³, $T = -90$ °C, $Z = 2$, $\rho_{\text{calcd.}} = 1.303$ gcm⁻³, μ (Mo-K α) = 3.64 cm⁻¹, $F(000) = 576$, 7478 reflections in $h(0/10)$, $k(-13/12)$, $l(-14/14)$, measured in the range $2.28^\circ \leq \Theta \leq 23.29^\circ$, 3805 independent reflections, $R_{\text{int}} = 0.043$, 3307 reflections with $F_o > 4\sigma(F_o)$, 325 parameters, $R1_{\text{obs}} = 0.055$, $wR^2_{\text{obs}} = 0.158$, GOOF = 1.190, completeness $\Theta_{\text{max}} = 96$ %, $R1_{\text{all}} = 0.069$, $wR^2_{\text{all}} = 0.197$, largest difference peak and hole: 0.410 / -0.422 e Å⁻³.

*Crystal Data for 14a*¹⁷: C₃₈H₄₀N₄O₈, $M_r = 680.74$ gmol⁻¹, red prism, size 0.32 x 0.30 x 0.28 mm³, triclinic, space group P2₁/n, $a = 13.8495(6)$, $b = 15.3751(4)$, $c = 16.1310(7)$ Å, $\beta = 94.035(2)$ °, $V = 3426.4(2)$ Å³, $Z = 4$, $\rho_{\text{calcd.}} = 1.320$ gcm⁻³, μ (Mo-K α) = 0.93 cm⁻¹, $F(000) = 1440$, 9127 reflections in $h(-15/0)$, $k(-16/16)$, $l(-17/17)$, measured in the range $2.30^\circ \leq \Theta \leq 23.28^\circ$, 4916 independent reflections, $R_{\text{int}} = 0.053$, 3330 reflections with $F_o > 4\sigma(F_o)$, 452 parameters, $R1_{\text{obs}} = 0.063$, $wR^2_{\text{obs}} = 0.169$, GOOF = 0.987, completeness $\Theta_{\text{max}} = 97$ %, $R1_{\text{all}} = 0.112$, $wR^2_{\text{all}} = 0.228$, largest difference peak and hole: 0.469 / -0.423 e Å⁻³.

General Procedure for the Synthesis of Trilithium Complex (4): In a 250 mL Schlenk vessel 0.35 g (1.0 mmol) of **1** was dissolved in ca. 30 mL of THF under argon and 0.3 g (4.3 mmol) of lithium was added. The mixture was brought to reaction in an ultrasonic bath. After 8 h, a clear brownish solution was

obtained from which excess lithium was removed by filtration.

General Procedure for the Synthesis of 4,5-Diamino-1H-imidazoles (5, 7, 8, 9 and 10): To a solution of 1.0 mmol of **4** in *ca.* 30 mL of THF, 3.0 mmol of a monofunctional [synthesis of compound (**5**)] or 1.0 mmol of a bifunctional electrophile [synthesis of compounds (**7**) and (**8**)] or 3.0 mmol of CS₂ [synthesis of compounds (**9**) and (**10**)] was added under stirring at -78 °C. In the case of compounds (**9**) and (**10**), the appropriate electrophile was added after 30 min. After completion of the addition, the mixture was allowed to warm to room temperature and stirring was continued for 30 min. After filtration the solvent was removed in *vacuo* and the residue was purified by column chromatography, ethyl acetate/heptane (1:5) or recrystallization from acetone/heptane.

2-Phenyl-4,5-bis(4-tolylamino)-1H-imidazole (5a): To a solution of 1.0 mmol of **4a** in *ca.* 30 mL of THF, 0.1 g (3.0 mmol) of methanol was added with stirring at -78 °C. After completion of the addition, the reaction mixture was allowed to warm to rt. The solvent was evaporated and the residue was extracted with *n*-heptane under inert conditions (argon stream). Yield 0.27 g (76 %), highly air-sensitive colorless oil - ¹H-NMR; (250 MHz, THF-d₈): δ = 11.25 (br s, 1H, NH), 7.90 (d, J = 7.46 Hz, 2H), 7.33 (t, J = 7.78 Hz, 2H), 7.16 (t, J = 7.61 Hz, 1H), 6.87 (br m, 8H), 6.43 (br s, 2H, NH), 2.18 (s, 6H). - MS *m/z* (%): 354 [M+H⁺] (100), 337 (17), 249 (16), 118 (45), 106 (67).

1-Methyl-2-phenyl-4,5-bis(methyl-4-tolylamino)-1H-imidazole (5b): Yield 0.28 g (72 %), colorless oil - ¹H-NMR (400 MHz, CDCl₃): δ = 7.73 (d, J = 7.23 Hz, 2H, *o*-Ph), 7.47 (t, J = 7.16 Hz, 2H, *m*-Ph), 7.39 (t, J = 7.27 Hz, 1H, *p*-Ph), 7.05 (d, J = 8.34 Hz, 2H, Tol), 6.95 (d, J = 8.34 Hz, 2H, Tol), 6.72 (d, J = 8.47 Hz, 2H, Tol), 6.56 (d, J = 8.46 Hz, 2H, Tol), 3.46 (s, 3H, ring-CH₃), 3.11 (s, 3H, amino-CH₃), 3.08 (s, 3H, amino-CH₃), 2.29 (s, 3H CH₃-Tol), 2.24 (s, 3H CH₃-Tol). - ¹³C-NMR (100 MHz, CDCl₃): δ = 141.13, 140.36, 136.71, 133.86, 126.86, 126.77, 125.14, 124.58, 124.49, 124.45, 124.14, 123.78, 123.11, 36.24, 35.91, 28.69, 17.66, 17.59. - MS *m/z* (%): 397 [M+H⁺] (100), 381 [M⁺-CH₃] (6), 308 (8), 118 (10). -

Anal. Calcd for $C_{26}H_{28}N_4$: C 78.80, H 7.12, N 14.14. Found: C 78.31, H 7.63, N 13.86.

1-Methyl-2-phenyl-4,5-bis(methyl-4-methoxyphenylamino)-1H-imidazole (5c): Yield 0.31 g (71 %), colorless oil - 1H -NMR (250 MHz, $CDCl_3$): δ = 7.70 (d, J = 8.44 Hz, 2H), 7.40 (m, 3H), 6.73 (m, 6H), 6.52 (d, J = 8.52 Hz, 2H), 3.74 (s, 3H), 3.69 (s, 3H), 3.42 (s, 3H), 3.09 (s, 3H), 2.99 (s, 3H). - ^{13}C -NMR (62 MHz, $CDCl_3$): δ = 152.65, 152.54, 142.88, 142.01, 141.27, 139.04, 131.00, 128.42, 127.82, 127.06, 116.82, 114.64, 114.03, 114.03, 113.85, 55.63, 39.06, 38.87, 31.38. - MS m/z (%): 429 $[M+H^+]$ (100), 413 (4), 118 (6). - Anal. Calcd for $C_{26}H_{28}N_4O_2$: C 72.87, H 6.59, N 13.07. Found: C 72.69, H 6.73, N 12.73.

1-Methyl-2-phenyl-4,5-bis(methyl-4-tert-butylphenylamino)-1H-imidazole (5d): Yield 0.37 g (78 %), colorless oil - 1H -NMR (250 MHz, $CDCl_3$): δ = 7.70 (d, J = 8.24 Hz, 2H), 7.40 (m, 3H), 7.21 (d, J = 8.85 Hz, 2H), 7.09 (d, J = 8.75 Hz, 2H), 6.72 (d, J = 8.76 Hz, 2H), 6.54 (d, J = 8.81 Hz, 2H), 3.44 (s, 3H), 3.12 (s, 3H), 3.07 (s, 3H), 1.28 (s, 9H), 1.23 (s, 9H). - ^{13}C -NMR (62 MHz, $CDCl_3$): δ = 146.00, 145.25, 141.54, 141.06, 140.55, 138.56, 131.04, 128.43, 128.37, 128.31, 127.51, 125.91, 125.22, 114.55, 112.53, 39.02, 38.57, 33.84, 33.76, 31.49. - MS m/z (%): 481 $[M^+]$ (100), 350 (5), 225 (7), 220 (16), 164 (11), 118 (9). - Anal. Calcd for $C_{32}H_{40}N_4$: C 79.96, H 8.39, N 11.66. Found: C 79.78, H 8.62, N 11.34.

1-Ethyl-2-phenyl-4,5-bis(ethyl-4-tolylamino)-1H-imidazole (5e): Yield 0.28 g (65 %), colorless oil - 1H -NMR (250 MHz, $CDCl_3$): δ = 7.66 (d, J = 7.71 Hz, 2H), 7.50 (m, 1H), 7.39 (m, 2H), 7.00 (d, J = 8.28 Hz, 2H), 6.90 (d, J = 8.34 Hz, 2H), 6.62 (d, J = 8.59 Hz, 2H), 6.52 (d, J = 8.62 Hz, 2H), 3.80 (br m, 2H, CH_2CH_3), 3.50 (m, 4H, CH_2CH_3), 2.25 (s, 3H, CH_3 -Tol), 2.19 (s, 3H, CH_3 -Tol), 1.13-1.10 (m, 9H, CH_2CH_3). - ^{13}C -NMR (62 MHz, $CDCl_3$): δ = 145.71, 145.05, 141.90, 138.17, 130.85, 129.69, 129.16, 128.78, 128.47, 128.32, 126.46, 119.69, 114.71, 113.35, 68.15, 46.12, 45.59, 20.36, 20.30, 15.92, 14.05, 13.33. - MS m/z (%): 439 $[M^+]$ (83), 409 $[M^+-C_2H_5]$ (12), 391 (68), 279 (16), 192 (100), 167 (12), 149 (21). - Anal. Calcd for $C_{29}H_{34}N_4$: C 79.41, H 7.81, N 12.77. Found: C 79.23, H 8.03, N 12.65.

l-Acetyl-2-phenyl-4,5-bis(acetyl-4-tolylamino)-1H-imidazole (**5f**): Yield 0.26 g (54 %), colorless solid, mp 195-197 °C - ¹H-NMR (400 MHz, DMSO-d₆, 343 K): δ = 7.87 (d, J = 7.79 Hz, 2H), 7.37 (br m, 3H), 7.09 (d, J = 8.28 Hz, 2H), 7.00 (br d, J = 7.95 Hz, 2H), 6.99 (d, J = 8.01 Hz, 2H), 6.56 (d, J = 8.16 Hz, 2H), 2.98 (s, 3H), 2.46 (s, 3H), 2.21 (s, 3H), 2.16 (s, 3H), 1.96 (s, 3H). - ¹³C-NMR (100 MHz, DMSO-d₆, 343 K): δ = 171.38, 170.71, 144.26, 143.29, 140.30, 140.11, 133.18, 130.99, 129.66, 129.48, 129.12, 128.94, 128.26, 127.32, 126.55, 125.04, 115.46, 114.55, 23.12, 22.98, 20.77, 20.47, 20.39. - MS *m/z* (%): 481 [M⁺] (13), 439 [M⁺-CH₃CO] (9), 397 [M⁺-2CH₃CO] (100), 150 (17), 93 (30). - Anal. Calcd for C₂₉H₂₈N₄O₃: C 72.48, H 5.87, N 11.66. Found: C 72.66, H 5.57, N 11.46.

l-Benzoyl-2-phenyl-4,5-bis(benzoyl-4-tolylamino)-1H-imidazole (**5g**): Yield 0.31 g (46 %), colorless solid, mp >116 °C (decomp) - ¹H-NMR (250 MHz, CDCl₃): δ = 7.52 (m, 4H), 7.36-7.03 (m, 18H), 6.91 (d, J = 8.56 Hz, 4H), 6.79 (d, J = 8.22 Hz, 2H), 2.20 (s, 3H), 2.15 (s, 3H). - ¹³C-NMR (62 MHz, CDCl₃): δ = 170.37, 169.94, 168.22, 144.50, 138.94, 138.84, 136.80, 135.92, 135.87, 135.25, 134.51, 133.94, 132.08, 131.29, 130.39, 130.09, 129.86, 129.59, 129.26, 129.12, 129.05, 128.89, 128.55, 128.14, 128.06, 127.66, 127.64, 127.30, 126.40, 126.15, 21.08, 20.94. - MS *m/z* (%): 667 [M⁺] (19), 257 (20), 212 (100), 194 (11), 123 (28), 105 (65). - Anal. Calcd for C₄₄H₃₄N₄O₃: C 79.26, H 5.14, N 8.40. Found: C 79.25, H 5.32, N 8.69.

Synthesis of the Zn-complexes (6):

- In a Schlenk vessel, 0.35 g (1.0 mmol) of **1** was dissolved in 30 mL of THF under argon and 0.5 g (7.7 mmol) of zinc was added. Reaction was initiated by means of an ultrasonic bath. After 12 h, a clear blue solution was obtained, from which excess zinc was removed by filtration.
- In a Schlenk vessel, 0.35 g (1.0 mmol) of **1** was dissolved in 30 mL of THF under argon and 1 mL of a 1 M zincdiethyl solution in heptane was added. The color of the solution turned to blue immediately.

The solution was concentrated and cooled at -78 °C overnight, yielding the Zn-complexes (**6a**) and (**6b**)

as dark blue crystals.

Zn-complex (6a): Yield 0.27 g (35 %), blue solid, mp > 350 °C - ¹H-NMR (400 MHz, CDCl₃): δ = 8.71 (d, J = 7.05 Hz, 4H), 7.89 (d, J = 8.42 Hz, 8H), 7.68 (t, J = 7.42 Hz, 2H), 7.59 (t, J = 7.35 Hz, 4H), 7.09 (d, J = 8.28 Hz, 8H), 2.25 (s, 12H). - ¹³C-NMR (100 MHz, CDCl₃): δ = 171.19, 141.77, 138.11, 132.05, 131.16, 130.74, 130.64, 129.61, 125.95, 120.71, 21.95. - MS *m/z* (%): 770 [M⁺] (0.15), 769 (0.17), 768 (0.25), 767 (0.23), 766 (0.3), 751 (0.1), 268 (60), 135 (22), 107 (100), 91 (19). - UV/Vis (THF): λ_{max} (lg ε) = 338 nm (4.41), 489 (4.38), 518 (4.27), 585 (3.57) - Anal. Calcd for C₄₆H₃₈N₈Zn: C 71.92, H 4.99, N 14.59. Found: C 71.70, H 4.60, N 14.33.

Zn-complex (6b): Yield 0.36 g (39 %), blue crystals mp >350 °C - ¹H-NMR (400 MHz, THF-d₈): δ = 8.73 (d, J = 7.16 Hz, 4H), 8.07 (d, J = 8.74 Hz, 8H), 7.70 (t, J = 7.38 Hz, 2H), 7.48 (t, J = 7.64 Hz, 4H), 7.38 (d, J = 8.75 Hz, 8H), 1.13 (s, 36H). - ¹³C-NMR (100 MHz, THF-d₈): δ = 170.59, 149.71, 140.98, 134.19, 132.75, 130.44, 128.31, 126.19, 125.33, 124.67, 34.21, 30.40. - MS (FAB) *m/z* (%): 937 [M⁺] (0.2), 667 (0.3), 518 (0.5), 437 (25), 379 (9), 307 (100), 289 (55). - UV/Vis (THF): λ_{max} (lg ε) = 342 nm (4.41), 490 (4.42) 518 (4.32), 587 (3.64) - Anal. Calcd for C₅₈H₆₂N₈Zn: C 74.38, H 6.67, N 11.97. Found: C 74.06, H 6.53, N 11.67.

2-Phenyl-5-tolylamino-4H-imidazole-4-spiro-2'-(1'-tolylpyrrolidine) (7a): Yield 0.25 g (63 %), colorless crystals, mp 204 °C - ¹H-NMR (250 MHz, CDCl₃): δ = 8.32 (d, J = 7.92 Hz, 2H), 7.67 (d, J = 8.35 Hz, 2H), 7.45 (m, 3H), 7.16 (d, J = 8.24 Hz, 2H), 7.02 (s, 1H, NH), 6.86 (d, J = 8.35 Hz, 2H), 6.29 (d, J = 8.57 Hz, 2H), 3.66 (m, 2H, CH₂), 2.47 (m, 2H, CH₂), 2.32 (s, 3H), 2.24 (m, 2H, CH₂), 2.12 (s, 3H). - ¹³C-NMR (62 MHz, CDCl₃): δ = 182.62, 171.93, 143.09, 136.09, 133.71, 132.95, 130.99, 129.64, 129.58, 129.04, 128.22, 127.51, 119.32, 113.48, 96.33, 51.00, 42.71, 23.46, 20.85, 20.24. - MS *m/z* (%): 395 [M⁺] (100), 292 (11), 288 (20), 131 (12), 108 (11), 93 (18). - Anal. Calcd for C₂₆H₂₆N₄: C 79.15, H 6.64, N 14.20. Found: C 78.86, H 6.73, N 14.42.

2-Phenyl-5-tolylamino-4H-imidazole-4-spiro-2'-(1'-tolylpiperidine) (**7b**): Yield 0.27 g (65 %), colorless crystals, mp 95-97 °C - ¹H-NMR (250 MHz, CDCl₃): δ = 9.78 (s, 1H, NH), 8.26 (d, J = 7.63 Hz, 2H), 7.55 (d, J = 8.41 Hz, 2H), 7.42 (m, 3H), 7.13 (d, J = 8.29 Hz, 2H), 7.00 (d, J = 8.29 Hz, 2H), 6.82 (d, J = 8.19 Hz, 2H), 3.70 (q, J = 11.31 Hz, 1H), 3.06 (m, 1H), 2.29 (s, 3H), 2.21 (m, 1H), 2.09 (s, 3H), 1.90 (m, 4H), 1.59 (q, J = 11.10 Hz, 1H). - ¹³C-NMR (62 MHz, CDCl₃): δ = 181.70, 172.02, 146.59, 136.16, 135.24, 133.55, 133.27, 130.58, 129.35, 128.89, 128.15, 126.09, 119.12, 94.17, 52.45, 38.79, 26.55, 21.75, 20.82, 20.77. - MS *m/z* (%): 409 [M⁺] (100), 302 (9), 275 (12), 262 (6), 144 (5). - Anal. Calcd for C₂₇H₂₈N₄: C 79.38, H 6.91, N 13.71. Found: C 79.53, H 7.07, N 13.40.

11-Phenyl-N,1-di-4-tolyl-2,3,5,6,8,9-hexahydro-1H-imidazo[1,5-d][1,9,4,6]dioxadiazacycloundecene-13-amine (**8a**): Yield 0.23 g (49 %), colorless crystals, mp 115 °C - ¹H-NMR (250 MHz, dioxane-d₈): δ = 10.84 (s, 1H, NH), 7.78 (d, J = 7.30 Hz, 2H), 7.35 (t, J = 7.16 Hz, 2H), 7.24 (t, J = 7.17 Hz, 1H), 6.97 (d, J = 8.50 Hz, 2H), 6.83 (d, J = 8.87 Hz, 2H), 6.73 (m, 4H), 4.06 (m, 2H), 3.75 (m, 2H), 2.20 (s, 3H), 2.11 (s, 3H). - ¹³C-NMR (62 MHz, dioxane-d₈): δ = 145.26, 144.63, 138.72, 134.88, 130.60, 129.43, 129.11, 128.97, 127.99, 127.58, 126.44, 125.44, 124.64, 124.28, 113.50, 113.25, 71.72, 71.19, 69.32, 50.11, 49.28, 20.04, 19.88. - MS *m/z* (%): 469 [M⁺] (100), 269 (10), 234 (6), 190 (7). - Anal. Calcd for C₂₉H₃₂N₄O₂: C 74.32, H 6.89, N 11.96. Found: C 74.33, H 7.02, N 11.44

14-Phenyl-N,1-di-4-tolyl-2,3,5,6,8,9,11,12-octahydro-1H-imidazo[1,5-d][1,9,12,4,6]trioxadiazacyclotetradecene-16-amine (**8b**): Yield 0.22 g (43 %), colorless crystals, mp 93-94 °C - ¹H-NMR (400 MHz, THF-d₆): δ = 11.37 (s, 1H), 7.88 (d, J = 7.28 Hz, 2H), 7.32 (t, J = 7.44 Hz, 2H), 7.22 (t, J = 7.36 Hz, 1H), 6.91 (d, J = 8.44 Hz, 2H), 6.83 (d, J = 8.52 Hz, 2H), 6.66 (m, 4H), 4.04 (t, J = 5.3 Hz, 2H), 3.64 (t, J = 5.3 Hz, 2H), 3.51 (m, 12H), 2.19 (s, 3H), 2.04 (s, 3H). - ¹³C-NMR (100 MHz, THF-d₆): δ = 147.58, 146.03, 140.11, 136.91, 132.30, 129.89, 129.17, 128.98, 127.95, 127.31, 125.11, 123.91, 120.67, 118.23, 114.35, 71.70, 71.37, 71.22, 70.56, 69.00, 53.02, 51.32, 20.44, 20.30. - MS *m/z* (%): 513 [M⁺] (71), 269 (100), 256 (5), 190 (6), 134 (10), 107 (15). - Anal. Calcd for C₃₁H₃₆N₄O₃: C 72.61, H 7.08, N 10.94. Found: C

72.94, H 7.18, N 10.79.

1-Methyl-2-phenyl-4,5-bis(4-tolyl-methylthiocarbamato)-1H-imidazole (10a): Yield 0.35 g (63 %), colorless crystals, mp 240-241 °C - ¹H-NMR (400 MHz, CDCl₃): δ = 7.63 (d, J = 7.58 Hz, 2H), 7.41 (m, 3H), 7.30 (br m, 4H), 7.20 (d, J = 8.20 Hz, 2H), 7.11 (d, J = 8.16 Hz, 2H), 3.65 (s, 3H), 2.41 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H). - ¹³C-NMR (100 MHz, CDCl₃): δ = 205.5, 205.16, 144.19, 139.76, 138.90, 137.85, 130.14, 129.64, 129.25, 129.01, 128.48, 127.82, 127.38, 126.80, 32.45, 21.18, 21.16, 20.59, 20.46. - MS *m/z* (%): 549 [M⁺] (100), 501 [M⁺-SCH₃] (12), 352 (7), 164 (15). - Anal. Calcd for C₂₈H₂₈N₄S₄: C 61.26, H 5.15, N 10.21, S 23.38. Found: C 60.90, H 5.09, N 10.27, S 23.27.

2-Phenyl-4,5-bis(4-tolyl-ethylthiocarbamato)-1H-imidazole (10b): Yield 0.31 g (55 %), colorless crystals, mp 128-132 °C - ¹H-NMR (250 MHz, CDCl₃): δ = 10.26 (s, 1H, NH), 7.68 (d, J = 6.52 Hz, 2H), 7.29 (m, 7H), 7.04 (m, 4H), 3.08 (m, 4H), 2.35 (s, 3H), 2.28 (s, 3H), 1.19 (m, 6H). - ¹³C-NMR (100 MHz, CDCl₃): δ = 204.09, 203.8, 142.29, 139.36, 139.17, 137.74, 134.8, 130.13, 129.52, 129.21, 129.11, 128.99, 128.69, 127.94, 127.74, 125.24, 124.76, 32.41, 31.97, 21.20, 21.55, 12.99, 12.88. - MS *m/z* (%): 563 [M⁺] (65), 501 (6), 459 (3), 352 (15), 212 (7), 178 (43), 150 (100). - Anal. Calcd for C₂₉H₃₀N₄S₄: C 61.87, H 5.38, N 9.96, S 22.79. Found: C 61.41, H 5.50, N 9.89, S 21.83.

2-Phenyl-4,8-di-4-tolyl-4,8-dihydro-1H-imidazo[4,5-d][1,3,6]thiadiazepine-5,7-dithione (11): Yield 0.27 g (58 %), yellowish solid, mp >138 °C (decomp) - ¹H-NMR (400 MHz, DMSO-d₆): δ = 12.9 (br s, 1H, NH), 7.70 (d, J = 7.96 Hz, 2H), 7.48 (d, 4H), 7.34 (m, 7H), 2.37 (s, 6H). ¹³C-NMR (100 MHz, DMSO-d₆): δ = 184.97, 142.24, 139.76, 138.85, 130.14, 129.63, 129.27, 128.94, 128.58, 128.38, 126.12, 21.19. - MS *m/z* (%): 473 [M⁺] (11), 353 (17), 150 (100), 120 (5), 108 (16). - Anal. Calcd for C₂₅H₂₀N₄S₃: C 63.51, H 4.27, N 11.86, S 20.36. Found: 63.22, H 4.34, N 11.42, S 20.35.

Bisurea derivative (12): 0.2 g (0.5 mmol) of the imidazole derivative (**5b**) and 5 mg of tetraphenyl-

porphyrine were dissolved in 20 mL of methylene chloride and cooled to $-20\text{ }^{\circ}\text{C}$. A constant stream of dry oxygen was passed through the reaction mixture for 1 h, while externally irradiating with a sodium vapour lamp. After evaporation of the solvent, the residue was chromatographed with heptane/ethyl acetate (3:1), to give the product (**12**): Yield 0.20 g (94 %), colorless oil - $^1\text{H-NMR}$ (400 MHz, DMSO-d_5 , 343 K): $\delta = 7.43$ (t, $J = 7.28$ Hz, 1H), 7.37 (t, $J = 7.19$ Hz, 2H), 7.08 (m, 6H), 6.90 (d, $J = 8.16$ Hz, 2H), 6.68 (d, $J = 8.14$ Hz, 2H), 2.99 (s, 6H), 2.94 (s, 3H), 2.28 (s, 6H). - $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6 , 343 K): $\delta = 160.98, 158.54, 157.73, 141.75, 140.61, 135.71, 135.03, 133.97, 130.49, 129.66, 129.22, 128.13, 127.68, 125.97, 125.01, 38.36, 37.49, 35.28, 20.76, 20.72$. - MS m/z (%): 429 [M^+] (100), 308 (84), 148 (16), 122 (10). - Anal. Calcd for $\text{C}_{26}\text{H}_{28}\text{N}_4\text{O}_2$: C 72.86, H 6.59, N 13.08. Found: C 72.91, H 6.65, N 13.19.

General procedure for the synthesis of imidazolium salts (13): A solution of the appropriate imidazole derivative (**5**) (1.0 mmol) and 0.20 g of iodomethane (1.5 mmol) in 30 mL of acetonitrile was heated at reflux for 5 h. The solvent was removed in *vacuo* and the residue was recrystallized from acetone/heptane to give the imidazoliumsalts (**13a**) and (**13b**).

1,3-Dimethyl-2-phenyl-bis(methyl-4-tolylamino)imidazolium iodide (13a): Yield 0.47 g (88 %), colorless crystals, mp $276\text{-}278\text{ }^{\circ}\text{C}$ - $^1\text{H-NMR}$ (250 MHz, CDCl_3): $\delta = 8.06$ (d, $J = 7.75$ Hz, 2H), 7.60 (m, 3H), 7.04 (d, $J = 8.39$ Hz, 4H), 6.75 (d, $J = 8.58$ Hz, 4H), 3.43 (s, 6H), 3.31 (s, 6H), 2.22 (s, 6H). - $^{13}\text{C-NMR}$ (62 MHz, CDCl_3): $\delta = 143.58, 140.62, 132.38, 131.52, 131.48, 130.15, 130.01, 129.55, 121.85, 114.39, 39.47, 32.93, 20.31$. - MS m/z (%): 411 [$\text{M}^+\text{-I}^-$] (8), 397 [$\text{M}^+\text{-CH}_3\text{I}$] (100), 142 (9). - Anal. Calcd for $\text{C}_{27}\text{H}_{31}\text{N}_4\text{I}$: C 60.20, H 5.81, N 10.45. Found: C 59.90, H 5.89, N 9.94.

1,3-Dimethyl-2-phenyl-bis(methyl-4-tert-butylphenylamino)imidazolium iodide (13b): Yield 0.56 g (90 %), colorless crystals, mp $272\text{ }^{\circ}\text{C}$ - $^1\text{H-NMR}$ (250 MHz, CDCl_3): $\delta = 8.05$ (d, $J = 7.71$ Hz, 2H), 7.57 (m, 3H), 7.22 (d, $J = 8.73$ Hz, 4H), 6.77 (d, $J = 8.77$ Hz, 4H), 3.42 (s, 6H), 3.31 (s, 6H), 1.21 (s, 18H). - ^{13}C -

NMR (62 MHz, CDCl_3): δ = 143.32, 143.22, 140.48, 132.27, 131.45, 131.38, 129.45, 126.30, 121.79, 113.99, 39.45, 33.88, 32.96, 31.28. - MS m/z (%): 495 [$\text{M}^+ - \text{I}$] (10) 481 [$\text{M}^+ - \text{CH}_3\text{I}$] (100), 142 (18), 127 (5). - Anal. Calcd for $\text{C}_{33}\text{H}_{43}\text{N}_4\text{I}$: C 63.66, H 6.96, N 9.00. Found: C 63.69, H 7.16, N 8.93.

General procedure of the synthesis of 14: A solution of the appropriate imidazole (5) (1.0 mmol) and 0.35 g (2.5 mmol) of dimethyl acetylenedicarboxylate in 30 mL of toluene was stirred under reflux for 8 h. The solution turned to deep-red in color. The solvent was removed *in vacuo* and the residue was purified by column chromatography with 10:1 of toluene and acetone. The solution was concentrated (*ca.* 5 mL) and cooled (-78°C) overnight, yielding dark colored crystalline solids of **14a** and **14b**.

1-Methyl-2,3-bis(methyl-4-tolylamino)-9-phenyl-1,9-dihydroimidazo[1,2-a]pyridine-5,6,7,8-tetracarboxylic acid-tetramethyl ester (14a): Yield 0.52 g (76 %), dark-red crystals, mp 191°C - $^1\text{H-NMR}$ (250 MHz, CDCl_3): δ = 7.65 (d, J = 6.33 Hz, 2H), 7.34 (m, 3H), 7.06-6.97 (m, 4H), 6.84-6.29 (m, 4H), 3.86-3.73 (m, 6H), 3.48-3.09 (m, 6H), 2.87-2.59 (m, 6H), 2.36-2.17 (m, 9H). - MS m/z (%): 681 [M^+] (18), 621 (6), 560 (7), 388 (100), 356 (8), 294 (84), 278 (6), 173 (9), 122 (8), 89 (51). - UV/Vis (THF): λ_{max} (lg ϵ) = 459 (3.72) - Anal. Calcd for $\text{C}_{38}\text{H}_{40}\text{N}_4\text{O}_8$: C 67.04, H 5.92, N 8.23. Found: C 66.96, H 6.03, N 8.20.

1-Methyl-2,3-bis(methyl-4-methoxyphenylamino)-9-phenyl-1,9-dihydroimidazo[1,2-a]pyridine-5,6,7,8-tetracarboxylic acid-tetramethyl ester (14b): Yield 0.52 g (73 %), dark-red crystals, mp $100-102^\circ\text{C}$ - $^1\text{H-NMR}$ (250 MHz, CDCl_3): δ = 7.64 (d, J = 6.84 Hz, 2H), 7.35 (m, 3H), 6.83-6.56 (m, 8H), 3.90-3.64 (m, 18H), 3.14-2.96 (m, 3H), 2.86-2.67 (m, 3H), 2.50-2.33 (m, 3H). - MS m/z (%): 713 [M^+] (5), 388 (100), 356 (8), 326 (92), 311 (6), 138 (14). - UV/Vis (THF): λ_{max} (lg ϵ) = 470 (3.71) - Anal. Calcd for $\text{C}_{38}\text{H}_{40}\text{N}_4\text{O}_{10}$: C 64.03, H 5.66, N 7.86. Found: C 63.95, H 5.78, N 7.77.

6-Phenylpyridine-2,3,4,5-tetracarboxylic acid-tetramethyl ester (15): 0.25 g (0.37 mmol) of **14a** was dissolved in 10 mL of methanol and a solution of 0.1 g (1.25 mmol) of bromine in 5 mL of methanol was

added dropwise under stirring at rt. After evaporation of the solvent, the residue was chromatographed with heptane/ethyl acetate (5:1), to give the pure product (15): Yield 95 mg (67 %), colorless crystals, spectral data confirm with Ref.¹³

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