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A panel of peralkylated sulfur–guanidine type bases: Novel pro-ligands for use in biomimetic coordination chemistry

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Dedicated to Professor Hermann Josef Frohn on the occasion of his 70th birthday.

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ABSTRACT

A series of novel hybrid molecules containing sulfur and nitrogen donor functions simultaneously has been synthesized and characterized. Designed for use in biomimetic coordination chemistry, these molecules are expected to act directly or in specific precursor roles as polyfunctional Lewis bases towards metal-based Lewis acids to form complexes with biological relevance. Their principal architecture is based on aliphatic or aromatic backbones connecting guanidine moieties with sulfur-containing thioether or disulfide portions. Based on acyclic tetramethylguanidino units and their cyclic dimethylethyl-substituted counterparts, a panel of forty-six members of this class of compounds are presented here. The associated denticity extends from bidentate (N/S donor sets) and tridentate (N/N/S donor sets) via tetradentate (N/N/S/S donor sets) to pentadentate (N/N/N/S/S donor sets). Five of these novel systems were structurally characterized and subjected to geometry optimizations using density-functional theory (DFT).

1. Introduction

As the active participant in a variety of metabolic reactions catalyzed by metalloproteins or metalloenzymes, the elements copper and sulfur play a central role in biology [1–3]. The privileged position of copper can be traced back to specific redox properties originating in the unique interplay between demands of d^9 and d^{10} electronic configuration towards coordination geometries and ligand fields. In this context, the highly polarizable sulfur atom as constituent of thiolate or thioether ligand functionalities is an ideal team player to arrive at redox potentials suitable to mediate electron transfer processes between electron donors and acceptors in biology. Metalloprotein active sites based on copper/sulfur complexes have been classified as e.g. (mononuclear) type I and (binuclear) copper A (Cu_A) centers. Both of them are responsible for fast electron transfer.

In mononuclear type I centers the copper atoms are bound to one cysteine, one methionine and two histidine residues in a strongly distorted tetrahedral fashion. Variants derived thereof (e.g. in fungal laccase, ceruloplasmin) lost thioether coordination resulting in a trigonal planar ligand field [4]. Binuclear Cu_A centers as constituents of cytochrome-c oxidases and N_2O reductases contain two cysteine residues as bridging ligands resulting in a Cu_2S_2 diamond core. Each copper atom within this core binds to an exogenous histidine residue and is further connected to a ligand utilizing a weaker secondary bond [5]. Copper and sulfur have been also found as essential constituents of the active sites of peptidylglycin-α-monooxygenase (PHM) and dopamine-β-hydroxylase (DβH). Here, the mononuclear active site which is responsible for oxygen activation contains copper bound to two histidine and one methionine residues [6]. In view of this fundamental importance, it is evident that the preparative chemistry of copper complexes with polyfunctional ligands containing both N and S donor functions (in form of thiolate (S^*) and thioether (S) groups) simultaneously is among the most attractive research fields in bioinorganic chemistry.

Hydrocarbons of different constitution equipped with both N and S donor sets have widely been applied as ligands in coordination chemistry [7]. However, the reconstruction of biologically active copper sites to model their characteristic properties in the laboratory frequently failed because of difficulties in replacing the effects of the protein matrix by properly designed biomimetic ligands. There are not more than a couple of copper(I) and copper(II) complexes with N/S/S^* or N/S^* ligand systems described in the literature with partially adequate coordination geometry and electronic properties of copper- and sulfur-containing active

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centers [8]. The synthesis of copper(II)-thiolate complexes – and also the preparation of the thiolate ligands itself – with appropriate asymmetric N/S/S* or N/S* systems is hampered for several reasons. Especially the reducing potential of thiolate ligands makes the synthesis of copper(II)-thiolate complexes in many cases unpredictable or even impossible [7a,9]. For this reason, the development and synthesis of novel N/S* and N/S/S* compounds with the ability to prevent Cu(II) from being reduced to Cu(I) along with the formation of organodisulfides is highly desirable.

In this paper, we report the synthesis and the characterization of forty-six novel guanidine–sulfur compounds. Five of these were structurally characterized. The structural parameters were discussed in the context of density-functional theory (DFT) calculations.

2. Results and discussion

2.1. Ligand conception and synthesis

In search for bifunctional N-donor ligands able to stabilize unusually high metal oxidation states, we extended our interest towards guanidine-type systems. Following this approach, bis(tetramethylguanidino)propane (btmgp) was synthesized as the first member of a series of bifunctional peralkylated guanidine ligands designed for use in biomimetic coordination chemistry [10]. Modifications of the syntheses strategies enabled the successful preparation of a whole family of bidentate guanidines [11] and guanidine–pyridine or guanidine–quinoline hybrid ligands as well as their copper and zinc complexes for application in oxygen activation [12] and lactide polymerization [13]. Moreover, copper complexes with tripodal guanidines for oxygen activation have also been described [14].

Due to excellent donor capabilities and unexpected bond characteristics of guanidines and guanidine-type hybrid ligands with other N donor functionalities, a plethora of transition metal complexes utilizing these ligands have been synthesized and characterized [15]. In striking contrast, guanidine–sulfur hybrid ligands and their coordination chemistry have not been described in the literature prior to our first results reported in 2011 [16].

Based on our experience in the field of synthetic guanidine chemistry we started a modular approach to extend the series of bis-guanidine ligands towards bi- and polydentate as well as tripodal guanidine–sulfur hybrids. These novel guanidines possess – besides basic N_{Imino} donor functions as a mimic for histidine residues – either thioether or disulfide functionalities, and in this respect might be able to mimic the function of methionine residues in Cu_A or DβH and PHM (Fig. 3). Moreover, heterolytic cleavage of the thioether-carbon bond (e.g. in trityl-thioethers) with Lewis

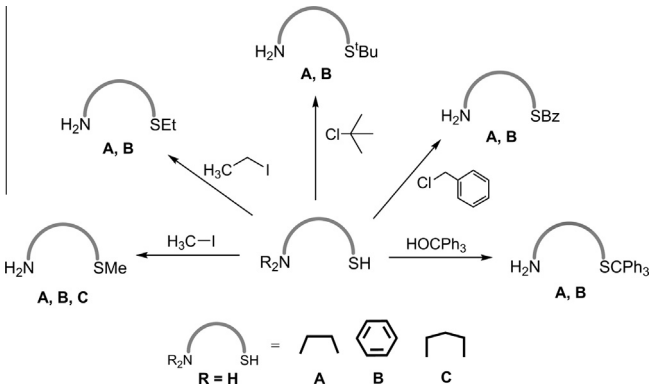

Fig. 1. Compilation of aminothiols and aminothioethers derived thereof as precursors for bidentate guanidine ligands.

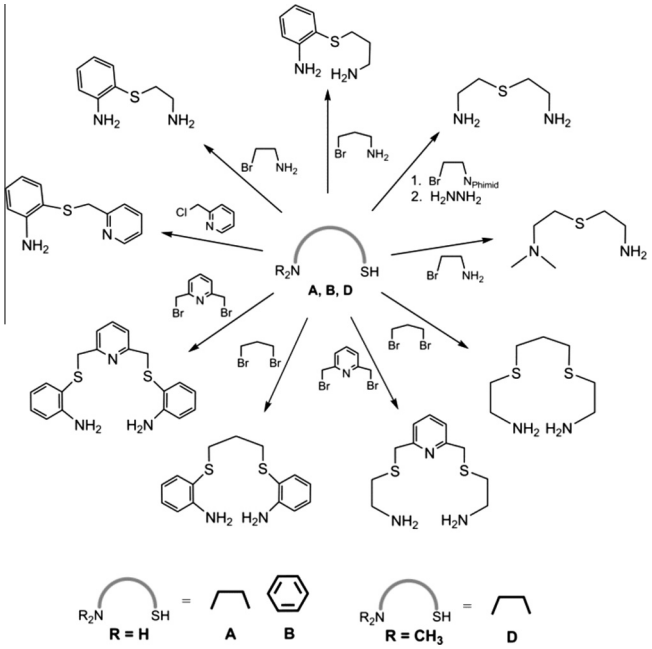

Fig. 2. Compilation of aminothiols and aminothioethers derived thereof as precursors for polydentate guanidine ligands.

acids (e.g. Cu(I) or Cu(II)) is expected to yield directly a thiolate functionality, whereas homolytic cleavage does require a suitable reductant such as Cu(I) for thiolate formation [16]. Thiolate formation can also be expected during reductive activation of organodisulfides [17]. This feature can be utilized to oxidise Cu(I) in the absence of exogenous reductants. Thus, molecules containing mixed N/S donor functions should principally be capable to mimic both histidine/methionine or histidine/cysteine coordination situations under properly defined reaction conditions. More recently, we have also shown that even tripodal guanidine-thioether hybrids can act as suitable ligands towards copper(I) and copper(II) resulting in complexes which have been investigated in view of molecular oxygen activation [18].

The synthetic protocol towards thioether-guanidines bundles up several preparative steps. In the majority of cases, 2-aminothiophenol and 2-aminoethanethiol served as educts and were converted with mono- as well as with bis-alkyl or -benzyl halides under basic conditions to the corresponding thioethers (Figs. 1 and 2). Extension of the C2-spacer separating the functionalities was achieved by reaction of 3-aminopropanethiol with alkyl halides or 1,3-dibromopropane with two equivalents of 2-aminothiophenol or 2-aminoethanethiol. Reactions of differently constituted mono- and bis- aminothioethers and disulfide amines to guanidine compounds occurred following the synthetic strategy of Kantlehner [11,19]. From reactions of the Vilsmeier salt N,N,N′,N′-tetramethylchloroformamidinium chloride and N,N,N′,N′-dimethylethylenechloroformamidinium chloride with primary amines in the presence of triethylamine, the guanidine hydrochlorides were obtained [11]. They were deprotonated with aqueous KOH solution (50%), and the free guanidines extracted with organic solvents. The resulting sulfur–guanidine compounds were isolated as liquids, oils or solids in yields ranging from 52 to 91%.

Following this path, a series of bidentate (N/S donor set), tridentate (N/N/S donor set), and multidentate (N/N/S/S resp. N/N/N/S/S donor sets) thioether–guanidines as well as molecules containing disulfide units (NSSN donor set) was successfully synthesized. The sulfur and nitrogen donor groups are linked by aliphatic C2/C3 or aromatic C2 spacers. In the case of polydentate thioether

guanidines, we obtained not only aliphatic or aromatic but also mixed aliphatic/aromatic compounds (Fig. 3). The substitution patterns of the peralkylated guanidine residues were defined by four methyl groups (tetramethyl guanidine, TMG) or two methyl groups and one ethylene spacer (dimethylethylene guanidine, DMEG), but other patterns are also easily accessible [11].

2.2. Crystal structures and DFT calculations

In order to determine the structural features of sulfur/guanidine hybrids, a set of representative compounds were crystallized by slow diffusion of diethylether into saturated solutions of the compounds or by recrystallisation processes. Accordingly, the molecular structures of the sulfur guanidines **L5-1** (Fig. 4), [20a] **L5-2**, [20b] **L10-1** (Fig. 5), [20c] **L22-1** (Fig. 6) [20d] and **L22-2** (Fig. 7) [20e] as well as of the guanidine salt **[(L10-1)H]PF$_6$** [20f] could be determined. All relevant crystallographic data and details of the data collections are deposited in the literature. Selected bond lengths and angles and the ρ value, describing the guanidine moiety, [21] are collected in Table 1.

Within the guanidyl residue, the π bond is predominantly localized within the C–N$_{imine}$ fragment which spans the distance range from 1.281(2) (within **L10-1**, Fig. 5) to 1.303(5) Å (within **L5-1**, Fig. 4). These distances are very close to the values determined by DFT: Using the semilocal PW91 functional in conjunction with a plane-wave basis, values which range from 1.297 (within **L5-2**) to 1.309 Å (within **L5-1**, Fig. 4) are calculated. (Table 1, all

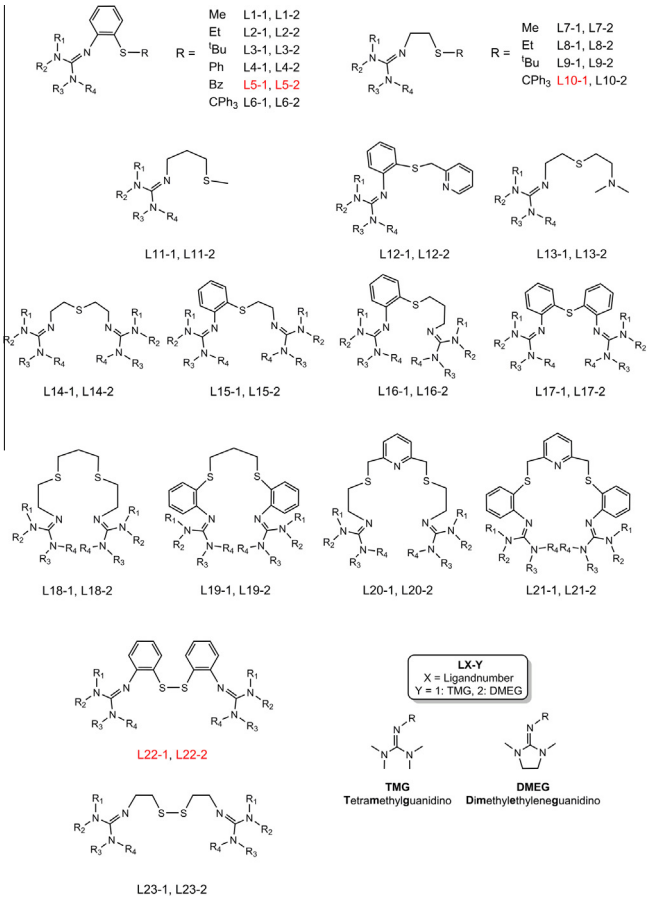

Fig. 3. Compilation of thioether and disulfide guanidines obtained in this work. Structurally characterized systems are shown in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

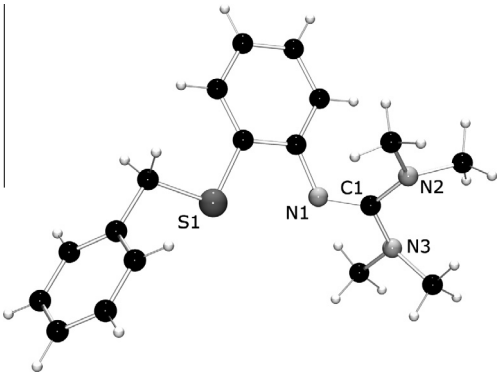

Fig. 4. Structure of **L5-1** in the crystal.

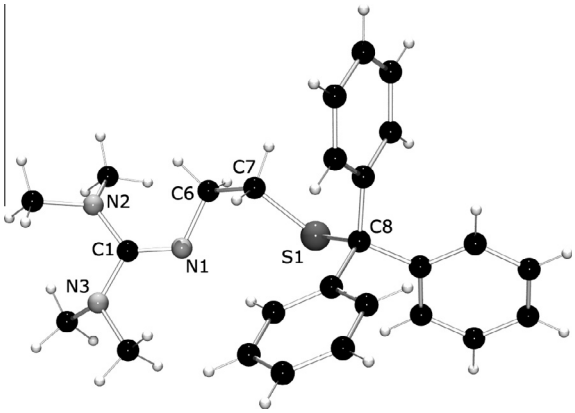

Fig. 5. Structure of **L10-1** in the crystal.

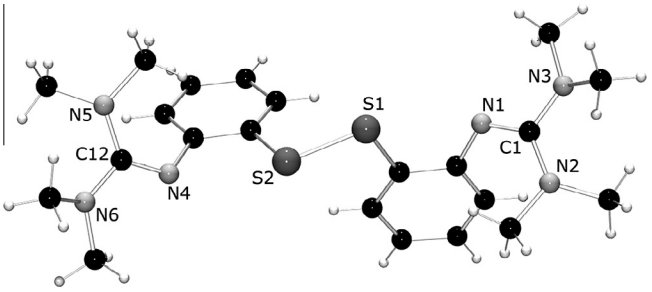

Fig. 6. Structure of **L22-1** in the crystal.

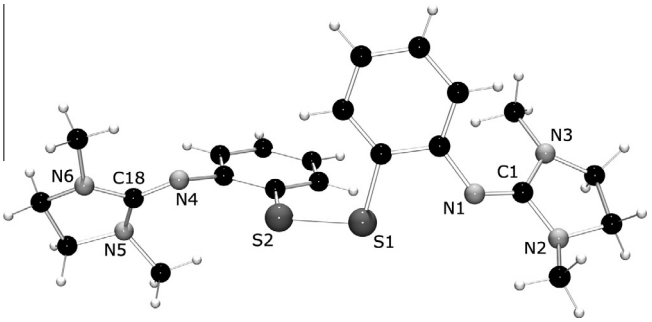

Fig. 7. Structure of **L22–2** in the crystal.

Table 1
Selected bond lengths [Å] and angles [°] of crystallized guanidines in comparison to values obtained from DFT (PW91/plane wave, averaged values without standard deviation).

	Bond lengths			Bond angles		Torsion angles	
	$C–N_{imine}$	$C–N_{amin}$	ρ	S–S	N–C–N	C–S–S–C	N–C–C–S
L5-1							
Exp.	1.303(5)	1.377	0.95		114.8(8)/118.3(3)/126.7(7)		3.8
DFT	1.309	1.390	0.94		115.0/118.7/126.3		4.1
L5-2							
Exp.	1.287(9)	1.379	0.93		108.5(2)/119.8(5)/131.6(3)		−5.0
DFT	1.297	1.395	0.93		107.8/120.9/131.3		−4.9
L10-1							
Exp.	1.281(2)	1.395	0.92		114.5(1)/120.1(1)/125.3(2)		66.0
DFT	1.299	1.401	0.93		114.6/119.2/126.1		70.8
[HL10-1]PF_6							
Exp.	1.341(3)	1.336	1.00		120.6(5) /119.0(1)/120.3(4)		21.7
DFT	1.344	1.359	0.99		119.9/121.2/118.9		21.9
L22-1							
Exp.	1.298	1.373	0.95	2.044(1)	108.5/121.5/130.0	84.7	5.8/−4.7
DFT	1.297	1.395	0.93	2.053	107.9/120.9/131.3	87.3	6.4/−4.2
L22-2							
Exp.	1.301	1.373	0.95	2.041(1)	115.7/118.7/125.4	−83.8	−7.6
DFT	1.309	1.390	0.94	2.056	115.1/118.6/126.1	−84.7	−4.8

calculated values are listed in Table S1 of the Supplementary Information).

However, one has to be cautious in the assessment of accuracy of experimentally determined distances from diffraction experiments, because the use of ellipsoids in modelling individual thermal vibrations introduces systematic errors which effect bond distances to deviate from their true values towards smaller separations. If these systematic effects are taken into account, the agreement between theory and experiment appears to be even better.

The accuracy of the calculations depends both on the XC functional as well as the basis set. In accordance with many literature results, we find the DFT GGA calculations to slightly overestimate most bond lengths in comparison to the experimental values. The calculated bond lengths are typically smaller by about 1% if hybrid DFT is performed with a plane wave basis set (cf. Table S1). In some cases, however, the calculated bond lengths are now shorter than measured ones. In case of **L22-1**, for example, B3LYP/plane wave calculations predict a $C–N_{imine}$ bond length of 1.286 Å. This is about 1% below the experimentally determined value. The calculated bond length is reduced even further, to 1.280 Å, when a localized cc-pVTZ basis is used. The PW91/plane-wave calculations, on the other hand, yield a value of 1.297 Å that is identical to the experimental result.

The comparison between the measured and calculated $C–N_{amine}$ and S–S bond lengths results in a similar picture. Here we observe that the plane-wave results are typically closer to experiment than the calculations using localized basis sets. In case of **L22-1**, for example, plane-wave calculations within PW91 and B3LYP overestimate the S–S bond length by 0.4 and 0.5%, respectively. PW91 and B3LYP calculations using cc-pVDZ (cc-pVTZ) basis result in a bond length overestimation of 2.6 (1.3) and 2.6 (1.3)%, respectively. In this case the basis set is obviously far more important than the XC functional for the molecular geometry. Given that a plane-wave basis converges in an easily controllable, smooth and monotonic manner to the target wavefunction and given the low numerical cost of semilocal XC functionals, the geometrical data calculated here suggest the combination of plane waves with the PW91 functional as an adequate method for the pro-ligands studied here. If not written otherwise, this combination is used below.

Comparing the $C–N_{amine}$ bond lengths, we do not observe strong variations between the systems under study. The mean values range from 1.373 (within **L22-1/2**, Figs. 6 and 7) to 1.395 Å (within **L10-1**, Fig. 5). The guanidyl double bonds are clearly localized, also reflected by the ρ values between 0.93 and 0.95, below the 1.0 for a symmetric guanidine. Similar double bond localization is observed in other guanidine compounds, e.g. N,N′-bis(dipiperidin-1-ylmethylene)-propane-1,3-diamine, N,N′-bis-(1,3-dimethylperhydropyrimidin-2-ylidene)propane-1,3-diamine [22] or bis(tetramethylguanidino)naphthalene [23] having a mean C=N bond length of 1.276, 1.284 and 1.282 Å, respectively. In case of **[(L10-1)H]PF_6** with a protonated imine N atom, strong delocalization is observed among the three C–N bonds, which are in the range of 1.333(1) to 1.341(3) Å, the structural parameter ρ is 1.0 stating a symmetric guanidine. This situation is typical for protonated systems, e.g. protonated stages of bis(tetramethyl-guanidino)propane (1.326(7)–1.343(3) Å) [24], bis(tetramethyl-guanidino)biphenyl (1.31(1)–1.34(1) Å) [25] or 2-cyanoguanidine (1.333(1)–1.344(1) Å).[26] The N-C-N guanidine angles span the range from 108.6(6) to 131.8(5)° with an angle sum of nearly 360°.

The molecular structures of **L22-1** and **L22-2** show nearly the same arrangement of the phenyl rings and the guanidyl groups with S–S bonds lengths of 2.041(1) and 2.044(1) Å, respectively. These values are in good agreement with values reported in the literature for disulfide compounds [27]. The same holds for and correlate very good with the C–S–S–C torsion angles of 83.8° in **L22-1** and 84.5° in **L22-2** [27a].

The S–C–C–N torsion of **L10-1** is very flexible. In fact, performing B3LYP/cc-pVTZ calculations we find a second minimum that is only 0.04 kcal/mol less favored than the global minimum. The main structural difference concerns the S–C–C–N torsion angle that amounts to 71.9° in comparison to 62.3° for the global minimum energy structure.

B3LYP calculations with double or triple zeta basis sets have been performed for investigating orbital populations using the Natural Bond Orbitals (NBO) method. [28] By summing up all sulfur d-orbitals a maximum occupation of 2% and 3%, respectively, of an electron charge is thus obtained. The same value is calculated for 2,2-diaminodiphenyl disulfide. In this case p-d-interactions of the fully occupied p_z orbital on the carbon C atom (part of the aromatic π electron cloud) with an empty d-orbital on the S atom were suggested [29]. From these calculations we conclude that the p–d interaction is in fact nearly negligible in **L22-1** and **L22-2** as well as in 2-2-diaminodiphenyl disulfide.

3. Conclusions

In summary, we report the synthesis and characterization of novel guanidine sulfur bases through reaction of different amino-

thioethers and amino-disulfides with Vilsmeier salts. Two distinct types of guanidine residues have been used to probe the effect of different electronic and steric properties: the acyclic tetramethylguanidino (TMG) and the cyclic dimethylethyl-guanidino system (DMEG). The sulfur–guanidine type bases possess flexible aliphatic and more rigid aromatic spacers in combination with bidentate (N/S), tridentate (N/N/S) and tetra- and pentadentate (N/N/S/S, N/N/N/S/S resp. N/S/S/N) donor sets.

Furthermore, the results of DFT calculations comprising six different guanidine sulfur bases of known architecture are in excellent agreement with the principal structural properties obtained by experiment. Within this class of molecules, plane wave methods appear to outperform methods bases on localized basis sets.

This straightforward entry to a broad spectrum of polydentate guanidine sulfur bases opens up unique perspectives to arrive at copper-thiolate complexes of biological relevance via both copper-induced (homolytic or heterolytic) cleavage of the thioether-carbon bond or reductive activation of the S–S bond within disulfides contrasting methods based on the direct use of thiolate precursors. In this respect, proof of principle has been successfully demonstrated by us recently for both thioether-carbon as well as sulfur–sulfur bond cleavage reactions [16,17]. Further aspects on the influence of guanidine–thioether hybrids within copper complexes on structural and redox-chemical properties are currently under investigation.

4. Experimental section

4.1. Experimental section

4.1.1. Materials and methods

All manipulations were performed under nitrogen (99.996%) dried with P_4O_{10} granulate using Schlenk techniques. Solvents were purified according to literature procedures [30] and stored under nitrogen. Triethylamine, iodomethane, iodoethane, tert-butylchloride, 1,3-bisbromopropane, 3-(methylthio)propylamine, 2-aminothiophenol, 2-aminoethanethiol, triphenylmethanol, benzylbromide, 2-(chloromethyl)pyridine hydrochloride, 2-(dimethylamino)ethanethiol hydrochloride, 3-bromopropylamine hydrobromide, 2-(phenylthio)aniline, 2,2′-diaminophenylsulfide, 2-[(2-aminophenyl)disulfanyl]phenylamine, 2-[(2-aminoethyl)-disulfanyl]ethylamine dihydrochloride were used as purchased from Fluka or Sigma–Aldrich. 2-Bromoethylamine hydrobromide was used as purchased from TCI Europe.

4.1.2. Physical measurements

Spectra were recorded with the following spectrometers: NMR: Bruker Avance 300 and Avance 500. The NMR signals were referenced to residual solvents measured relative to TMS. IR: Nicolet P510. MS (EI, 70 eV): Saturn 2. Elemental analyses: Perkin-Elmer analysator Model 2400 and Elementar MICRO Cube.

4.1.3. Computational details

Density-functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [31]. Thereby we use a plane wave basis, which is complete and orthogonal by construction and the numerical convergence of which can be reliably controlled. The energy cutoff for the plane-wave basis set is raised until the total energy is converged. We find a cutoff energy of 380 eV to be sufficient for the systems treated here. Blöchl's projector augmented wave (PAW) formalism is used to describe the electron–ion interaction [32,33]. The semi local PW91 [34] exchange–correlation (XC) functional within the general gradient approximation (GGA) or the hybrid-functional B3LYP [35–37] is used. The systems are modeled using periodic boundary conditions. Thereby the cell size is chosen such as to ensure that in every direction at least 7.5 Å vacuum separates the molecule from its periodic images. For the calculation of charged molecules, a compensating homogeneous background charge is used to avoid diverging total energies due to artificial coulomb interactions. For comparison, we also performed calculations using localized basis sets (6–31 g(d), cc-pVDZ, cc-pVTZ) again utilizing the PW91 or B3LYP functional. These calculations were performed using Gaussian09 [38]. Thereby tight convergence criteria for structural optimization and ultrafine integral grids are used.

4.2. Preparation of compounds

4.2.1. Starting materials

The following compounds were synthesized according to literature procedures: N,N,N′,N′-tetramethylchloroformamidiniumchloride (V1) and N,N,N′,N′-dimethylethylenechloroformamidinium chloride (V2) [11], 2-(methylthio)benzenamine, 2-(benzylthio)-benzeneamine, (2-(2-pyridylmethylthio)aniline [39], 2-(ethylthio)-benzenamine [40], 2-(tert-butylthio)benzenamine [41], 2-(tritylthio)benzamine [42], 2-(methylthio)ethaneamine [43], 2-(tert-butylthio)ethaneamine [44], 2-(tritylthio)ethaneamine [45], 1,9-diamino-3,7-dithiodecane, 2,2-thiodiethaneamine [46], (2-aminoethylthio)-N,N-dimethylethaneamine [47], 1,3-Bis((2-aminophenylthio)propane [48], 2,6-bis((2′-aminoethylthio)methyl) pyridine [49], 2,6-bis-((2′-aminophenylthio)methyl)pyridine [50].

4.2.1.1. 2-(Ethylthio)ethaneamine. To a solution of KOH (5.8 g, 0.1 mol) in ethanol (500 mL) was added 2-aminoethanethiol (7.72 g, 0.1 mol) and stirred at room temperature for 1 h. Iodoethane (16.1 g, 0.1 mol) was added dropwise at 0 °C to the suspension. Then the mixture was refluxed for 3 h and after cooling the ethanol was removed under reduced pressure. The oily solid was treated with 150 mL of water and extracted with dichloromethane (3 × 80 mL). The collected organic phases are dried with sodium sulfate and the solvent was removed under reduced pressure to give a yellow oil. Yield: 6.3 g (60%).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.07 (t, 3H, CH_3), 1.18 (s, 2H, NH_2), 2.35 (q, 2H, CH_2), 2.44 (t, 2H, CH_2), 2.68 (t, 2H, CH_2). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 14.8 (CH_3), 25.5 (CH_2), 35.8 (CH_2), 41.1 (CH_2). EI-MS (m/z (%)): 106.1 (6) [M^+], 105.0 (84), 76.0 (100). IR (NaCl, ν [cm^{-1}]): 850vs, 1002m, 1072w, 1228w, 1261s, 1375m, 1452s, 1591m.

4.2.1.2. (2-(2-Aminoethylthio)aniline. To a solution of sodium ethoxide prepared from sodium (1.4 g, 0.061 mol) and 500 ml of absolute EtOH was added 2-aminothiophenol (3.76 g, 0.030 mol) and the mixture was stirred at room temperature for 1 h. 3-bromoethaneamine-hydrobromid (4.7 g, 0.030 mol) was added in several portions and the mixture was refluxed for 6 h. After cooling, the ethanol was removed under reduced pressure. The oily solid was treated with 150 mL of water and extracted with diethylether (3 × 80 mL). The collected organic phases are dried with sodium sulfate and the solvent was removed under reduced pressure to give a crude product. After vacuum distillation (10 mbar, 125 °C) a yellow oil was obtained. Yield: 2.3 g (45%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.12 (bs, 2H, NH_2), 2.76 (m, 4H, CH_2CH_2), 4.08 (bs, 2H, NH_2), 6.64 (ddd, ^3J = 7.5 Hz, ^4J = 1.3 Hz, 1H, CH), 6.68 (dd, ^3J = 8.0 Hz, ^4J = 1.4 Hz, 1H, CH), 7.08 (ddd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1H, CH), 7.34 (dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 38.8 (SCH_2), 41.6 (NCH_2), 115.0 (CH), 117.0 (C_{quat}), 118.4 (CH), 129.8 (CH), 136.0 (CH), 148.5 (C_{quat}). IR (NaCl, ν [cm^{-1}]): 3431m (ν (N–H)), 3347m (ν (N–H)), 3172m, 3057w, 2928w, 2859w, 1604s, 1482s, 1444m, 1307m. EI-MS (m/z(%)): 168.1 (25) [M^+],

149.0 (18), 139.0 (44) [M^+-CH_2NH_2], 125.0 (100) [M^+-$(CH_2)_2NH_2$], 93.1 (16) [M^+-$S(CH_2)_2NH_2$], 80.0 (25), 65.0 (8), 44.0 (16), 30.0 (36).

4.2.1.3. 2-(3-Aminopropylthio)aniline. The synthesis was performed form 2-aminothiophenol and 3-bromopropylamine hydrobromide in the same manner described for (2-(2-aminoethylthio)aniline. After distillation (10 mbar, 155 °C) the final product was obtained as yellow oil. Yield: 3.8 g (70%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.21 (s, 2H, NH_2), 1.66 (m, ^3J = 6.8, 7.2 Hz, 2H, $CH_2\underline{CH_2}CH_2$), 2.75 (m, 4H, $\underline{CH_2}CH_2\underline{CH_2}$), 4.35 (s, 2H, NH_2), 6.65 (ddd, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 1H, CH), 6.68 (dd, ^3J = 8.0 Hz, ^4J = 1.4 Hz, 1H, CH), 7.07 (ddd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1H, CH), 7.34 (dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 32.1 (SCH_2), 33.4 (CH_2), 40.9 (NCH_2), 118.0 (C_{quat}), 118.4 (CH), 129.5 (CH), 135.6 (CH), 148.3 (CH), 148.8 (C_{quat}). IR (NaCl, ν [cm^{-1}]): 3438m (ν (N–H)), 3354m (ν (N–H)), 3172m, 3065m, 2928s, 2859m, 1611s, 1474s, 1444s, 1300m, 1239w, 1163w. EI-MS (m/z(%)): 182.1 (100) [M^+], 165.0 (18) [M^+-NH_2], 149.0 (10) [M^+-CH_2NH_2], 136.0 (20) [M^+-$(CH_2)_2NH_2$], 125.0 (60) [M^+-$(CH_2)_3NH_2$], 93.0 (18) [M^+-$S(CH_2)_3NH_2$], 80.0 (26), 58.0 (18), 44.0 (40).

4.2.2. General reaction of thioether or disulfide amines with chloroformamidinium chlorides V1 and V2 to guanidine–sulfur type bases

For each amine group equimolar quantities of chloroformamidinium chlorides, triethylamine and NaOH were used: a solution of the chloroformamidinium chloride in dry MeCN (60 mL) was added dropwise under vigorous stirring to an ice-cooled solution of a mono or diamine and triethylamine in dry MeCN (30 mL). After 3 h at reflux, a solution of NaOH in water (10 ml) was added. The solvent and NEt_3 were then evaporated under vacuum. In order to deprotonate the mono or bis-hydrochloride, 50 wt.% KOH (aq, 25 mL) was added and the free base was extracted (unless otherwise specified) into the MeCN phase (3 × 50 mL). The organic phase was dried with Na_2SO_4. After filtration the solvent was evaporated under reduced pressure.

The obtained guanidines were dried in vacuo and purified by recrystallization or distillation if necessary.

Modifications of the general synthesis route – if advisable – as well as details of the purification procedures are addressed in the following paragraphs.

*4.2.2.1. 1,1,3,3-Tetramethyl-2-(2-(methylthio)phenyl)guanidine (**L1-1**).* Following the general procedure, 4.96 g (0.032 mol) of 2-(methylthio)aniline was used. The final product was obtained as a white solid. Yield: 8.2 g (81%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.34 (s, 3H, SCH_3), 2.66 (s, 12H, CH_3), 6.47 (dd, ^3J = 7.8 Hz, ^4J = 1.3 Hz, 1H, CH), 6.62 (ddd, ^3J = 7.5 Hz, ^4J = 1.3 Hz, 1H, CH), 6.95 (ddd, ^3J = 7.5 Hz, ^4J = 1.3 Hz, 1H, CH), 7.02 (dd, ^3J = 7.8 Hz, ^4J = 1.3 Hz, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 14.8 (SCH_3), 39.5 (CH_3), 120.5 (CH), 120.9 (CH), 124.3 (CH), 124.8 (CH), 130.4 (C_{quat}), 149.2 (C_{quat}), 160.0 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3043w, 2978w, 2918m, 2881m, 2804w, 1593s, (ν (C=N)), 1568s, 1508m (ν (C=N)), 1464m, 1435m, 1400w, 1379s, 1282w, 1234w, 1205w, 1144m, 1122w, 1065w, 1038w, 1020m, 951w, 916w, 847w, 783m, 737m, 706w, 673w, 619w, 540w. EI-MS (m/z(%)): 235.2 (54) [M^+], 219.1 (6), 202.0 (30), 188.2 (100) [M^+-SCH_3], 186.1 (16), 153.1 (99), 138.1 (50), 120.1 (16), 109.1 (32), 94.1 (68), 77.1 (30), 69.1 (47), 57.1 (53).

*4.2.2.2. N-(1,3-Dimethylimidazolidin-2-ylidene)-2-(methylthio)aniline (**L1-2**).* Following the general procedure, 3.82 g (0.032 mol) of 2-(methylthio)aniline was used. The final product was obtained as a white solid. Yield: 5.3 g (70%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.38 (s, 3H, SCH_3), 2.62 (s, 6H, CH_3), 3.26 (s, 4H, CH_2), 6.77 (dd, ^3J = 7.7 Hz, ^4J = 1.4 Hz, 1H, CH), 6.86 (ddd, ^3J = 7.5 Hz, ^4J = 1.4, 1.5 Hz, 1H, CH), 6.96 (ddd, ^3J = 7.5 Hz, ^4J = 1.5, 1.6 Hz, 1H, CH), 7.01 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 14.6 (SCH_3), 34.8 (CH_3), 48.5 (CH_2), 121 (CH), 121.8 (CH), 123.8 (CH), 124.5 (CH), 133.7 (C_{quat}), 147.2 (C_{quat}), 155.3 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3043w, 2911m, 2848m, 1618s (ν (C=N)), 1568s (ν (C=N)), 1500m (ν (C=N)), 1437m, 1388m, 1313w, 1284m, 1257w, 1234w, 1201w, 1122w, 1068w, 1034m, 970m, 949w, 864w, 847w, 771m, 739m, 702m, 650w, 588w, 540w, 480w, 447w. EI-MS (m/z(%)): 235.2 (54) [M^+], 219.1 (6), 202.0 (30), 188.2 (100) [M^+-SCH_3], 186.1 (16), 153.1 (99), 138.1 (50), 120.1 (16), 109.1 (32), 94.1 (68), 77.1 (30), 69.1 (47), 57.1 (53).

*4.2.2.3. 2-(2-(Ethylthio)phenyl)-1,1,3,3-tetramethylguanidine (**L2-1**).* Following the general procedure, 6.12 g (0.040 mol) of 2-(ethylthio)aniline was used. The final product was obtained as colorless oil. Yield: 8.5 g (84%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.25 (t, ^3J = 7.3 Hz, 3H, $^{et}CH_3$), 2.62 (s, 12H, CH_3), 2.81 (q, ^3J = 7.3 Hz, 2H, $^{et}CH_2$), 6.47 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, CH), 6.74 (ddd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H, CH), 6.96 (ddd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H, CH), 7.06 (dd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 14.0 ($^{et}CH_3$), 25.9 ($^{et}CH_2$), 39.4 (CH_3), 120.3 (CH), 121.6 (CH), 125.1 (CH), 126.4 (CH), 128.7 (C_{quat}), 150.2 (C_{quat}), 159.8 (C_{gua}). IR (NaCl, ν [cm^{-1}]): 3049w, 2925m, 2870w, 1597s (ν (C=N)), 1570s (ν (C=N)), 1502m (ν (C=N)), 1458m, 1379m, 1281w, 1205w, 1142m, 1068w, 1018m, 968m, 920w, 850w, 777w, 739m, 712w, 540w. EI-MS (m/z (%)): 251.1 (18) [M^+], 236.1 (4) [M^+-CH_3], 216.1 (4), 190.1 (9) [M^+-SCH_2CH_3], 181.1 (26), 153.0 (94), 136.0 (25), 124.0 (100), 93.0 (26), 80.0 (66), 65.1 (19).

*4.2.2.4. N-(1,3-Dimethylimidazolidin-2-ylidene)-2-(ethylthio)aniline (**L2-2**).* Following the general procedure, 6.12 g (0.040 mol) of 2-(ethylthio)aniline was used. The final product was obtained as yellow oil. Yield: 8.9 g (89%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.28 (t, ^3J = 7.3 Hz, 3H, $^{et}CH_3$), 2.57 (s, 6H, CH_3), 2.81 (q, ^3J = 7.3 Hz, 2H, $^{et}CH_2$), 3.20 (s, 4H, CH_2), 6.73 (dd, ^3J = 7.7 Hz, ^4J = 1.4 Hz, 1H, CH), 6.77 (ddd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H, CH), 6.92 (ddd, ^3J = 7.5 Hz, ^4J = 1.6 Hz, 1H, CH), 7.05 (dd, ^3J = 7.7 Hz, ^4J = 1.4 Hz, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 14.1 ($^{et}CH_3$), 25.4 ($^{et}CH_2$), 34.8 (CH_3), 48.4 (CH_2), 117.6 (CH), 120.7 (CH), 122.1 (CH), 125.0 (CH), 126.0 (C_{quat}), 148.4 (C_{quat}), 155.1 (C_{gua}). IR (NaCl, ν [cm^{-1}]): 3049w, 2925m, 2854m, 1649vs (ν (C=N)), 1574m (ν (C=N)), 1437m, 1394w, 1281m, 1122w, 1070w, 1032m, 968w, 868w, 769w, 710w, 646w. EI-MS (m/z (%)): 249.1 (7) [M^+], 216.1 (7), 188.1 (6) [M^+-SCH_2CH_3], 153.0 (91), 138.0 (6), 124.0 (100), 98.1 (18), 93.0 (21), 80.0 (70), 65.0 (17).

*4.2.2.5. 2-(2-(tert-Butylthio)phenyl)-1,1,3,3-tetramethylguanidine (**L3-1**).* Following the general procedure, 7.24 g (0.040 mol) of 2-(tert-butylthio)aniline was used. The final product was obtained as yellow oil. Yield: 7.3 g (65%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.19 (s, 9H, $^{tBu}CH_3$), 2.58 (s, 12H, CH_3), 6.67 (m, 2H, CH), 7.06 (ddd, 1H, CH), 7.36 (dd, ^3J = 7.5 Hz, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 31.3 ($^{tBu}CH_3$), 39.3 (CH_3), 46.7 ($^{tBu}C_{quat}$) 119.3 (CH), 123.4 (CH), 124.0 (C_{quat}), 129.2 (CH), 138.3 (CH), 156.1 (C_{quat}), 160.1 (C_{gua}). IR (NaCl, ν [cm^{-1}]): 3047w, 2956m, 2856m, 1658s, 1577s (ν (C=N)), 1522w (ν (C=N)), 1487m, 1454m, 1413w, 1392m, 1361w,

1281m, 1242m, 1151w, 1030w. EI-MS (m/z(%)): 279.3 (36) [M^+], 222.2 (16) [M^+-tBu], 190.1 (14) [M^+-StBu], 179.1 (100) [M^+-C(N(CH_3)$_2$)$_2$], 136.1 (19), 100.1 (10) [C[N(CH_3)$_2$]$_2^+$].

*4.2.2.6. N-(2-(tert-butylthio)phenyl)-1,3-dimethylimidazolidin-2-imine (**L3-2**).* Following the general procedure, 7.24 g (0.040 mol) of 2-(tert-butylthio)aniline was used. The final product was obtained as yellow oil. Yield: 6.1 g (55%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.23 (s, 9H, $^{tBu}CH_3$), 2.50 (s, 6H, CH_3), 3.18 (s, 4H, CH_2), 6.69 (dd, ^3J = 7.1 Hz, 1H, CH), 7.82 (ddd, 1H, CH), 7.05 (ddd, 1H, CH), 7.35 (dd, ^3J = 7.5 Hz, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 31.4 ($^{tBu}CH_3$), 34.7 (CH_3), 45.0 ($^{tBu}C_{quat}$), 48.3 (CH_2), 119.7 (CH), 123.2 (CH), 124.5 (C_{quat}), 129.1 (CH), 138.6 (CH), 150.4 (C_{quat}), 154.7 (C_{gua}). IR (NaCl, ν [cm^{-1}]): 3047w, 2920m, 2804w, 1603s (ν (C=N)), 1574s (ν (C=N)), 1504m (ν (C=N)), 1454s, 1427m, 1377s, 1279w, 1234w, 1203w, 1140s, 1016w. EI-MS (m/z(%)): 277.2 (57) [M^+], 220.1 (18) [M^+-tBu], 188.2 (22.1) [M^+-StBu], 178.1 (20), 125.1 (100), 98.1 (26), 57.1 (12) [tBu^+].

*4.2.2.7. 1,1,3,3-Tetramethyl-2-(2-(phenylthio)phenyl)guanidine (**L4-1**).* Following the general procedure, 7.0 g (0.035 mol) of 2-(phenylthio)aniline was used. The final product was obtained as yellow oil. Yield: 8.8 g (84%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.59 (s, 12H, CH_3), 6.73 (m, 2H, CH), 7.01 (dd, ^3J = 8.1 Hz, ^4J = 1.5, 1.6 Hz, 1H, CH), 7.09 (ddd, ^3J = 7.6 Hz, ^4J = 1.5 Hz, 1H, CH), 7.17 (m, 1H, CH), 7.25 (m, 2H, CH), 7.31 (m, 2H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 39.4 (CH_3), 120.5 (CH), 122.5 (CH), 126.4 (CH), 126.9 (C_{quat}), 127.6 (CH), 128.9 (CH), 129.6 (CH), 131.1 (CH), 134.5 (CH), 136.3 (C_{quat}), 151.6 (C_{quat}), 159.8 (C_{gua}). IR (NaCl, ν [cm^{-1}]): 3053m, 3001m, 2926s, 2885m, 2792w, 1599s (ν (C=N)), 1568vs (ν (C=N)), 1504m (ν (C=N)), 1475m, 1455m, 1439w, 1381s, 1282w, 1238w, 1205w, 1142m, 1059w, 1018w. EI-MS (m/z (%)): 299.1 (22) [M^+], 267.1 (1), 255.1 (11) [M^+-C_2H_6N], 228.1 (13), 212.0 (10), 201.1 (65) [M^+-C(N(CH_3)$_2$)$_2$], 179.1 (17), 167.1 (14), 149.0 (6), 116.1 (34), 100.1 (8) [C(N(CH_3)$_2$)$_2^{2+}$], 72.0 (100), 44.1 (27).

*4.2.2.8. N-(1,3-Dimethylimidazolidin-2-ylidene-2-(phenylthio)aniline (**L4-2**).* Following the general procedure, 7.0 g (0.035 mol) of 2-(phenylthio)aniline was used. The final product was obtained as yellow oil. Yield: 7.5 g (72%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.54 (s, 6H, CH_3), 3.15 (s, 4H, CH_2), 6.74 (ddd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H, CH), 6.87 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz,1H, CH), 7.00 (dd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1H, CH), 7.03 (ddd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H, CH), 7.22 (m, 1H, CH), 7.27 (m, 2H, CH), 7.40 (m, 2H, CH) ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 34.7 (CH_3), 48.4 (CH_2), 120.7 (CH), 122.8 (CH), 126.5 (CH), 127.0 (CH), 128.4 (C_{quat}), 129.0 (CH), 129.9 (CH), 131.2 (CH), 132.1 (CH), 137.3 (C_{quat}), 149.3 (C_{quat}), 155.0 (C_{gua}). IR (NaCl, ν [cm^{-1}]): 3049w, 2964w, 2925m, 2854m, 1649s (ν (C=N)), 1574m (ν (C=N)), 1483m, 1437m, 1414w, 1394w, 1281m, 1252w, 1198vw, 1157vw, 1122w, 1070w, 1032m, 991vw, 968m, 868w, 769w, 737m, 710w, 646w, 586vw, 540vw. EI-MS (m/z(%)): 297.1 (5) [M^+], 264.1 (1), 201.1 (100) [M^+-C(N(CH_3)$_2$)$_2$], 186.0 (14), 167.1 (18), 139.1 (3), 114.1 (13), 96.0 (5), 80.1 (14), 65.0 (9).

*4.2.2.9. 2-(2-(Benzylthio)phenyl)-1,1,3,3-tetramethylguanidine (**L5-1**).* Following the general procedure, 6.45 g (0.03 mol) of 2-(benzylthio)aniline was used. The final product was obtained as yellow solid. Yield: 6.5 g (69%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.68 (s, 12H, CH_3), 4.10 (s, 2H, $^{bz}CH_2$), 6.59 (dd, ^3J = 7.5 Hz, 1H, CH), 6.80 (ddd, ^3J = 7.6 Hz, ^4J = 1.3 Hz, 1H, CH), 7.03 (ddd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H, CH), 7.15 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, CH), 7.21 (m, 1H, CH), 7.28 (m, 2H, CH), 7.36 (m, 2H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 37.3 ($^{bz}CH_2$), 39.5 (CH_3), 120.5 (CH), 121.7 (CH), 126.1 (CH), 126.9 (CH), 127.2 (CH), 127.6 (CH), 128.4 (CH), 128.7 (C_{quat}), 129.1 (CH), 136.6 (C_{quat}), 137.8 (C_{quat}), 160.0 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3053w, 3030w, 3003w, 2918m, 2848m, 2790w, 1589m (ν (C=N)), 1558s (ν (C=N)), 1500m (ν (C=N)), 1460m, 1425m, 1377s, 1279w, 1232w, 1207w, 1144m, 1066m, 1038m, 1020s, 914w, 850w, 806vw, 777m, 715s, 696m, 682w, 621w, 571w, 545w, 498vw, 484w, 461w, 445w. EI-MS (m/z(%)): 313.0 (100) [M^+], 280.0 (31), 269.1 (8) [M^+-N(CH_3)$_2$], 242.0 (5), 237.0 (10) [M^+-Ph], 222.0 (14) [M^+-CH_2Ph], 215.0 (20), 190.0 (12) [M^+-SCH_2Ph], 179.0 (76), 148.9 (28), 135.9 (20), 124.0 (9) [SCH_2Ph^+],91.0 (76), 72.0 (20).

*4.2.2.10. 2-(Benzylthio)-N-(1,3-dimethylimidazolidine-2-yliden)aniline (**L5-2**).* Following the general procedure, 6.45 g (0.030 mol) of 2-(benzylthio)aniline was used. The final product was obtained as white solid. Yield: 5.6 g (60%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.63 (s, 6H, CH_3), 3.25 (s, 4H, CH_2), 4.11 (s, 2H, $^{bz}CH_2$), 6.80 (m, 2H, CH), 7.01 (ddd, ^3J = 7.6 Hz, ^4J = 1.5 Hz, 1H, CH), 7.14 (dd, ^3J = 7.7 Hz, ^4J = 1.4 Hz, 1H, CH), 7.21 (m, 1H, CH), 7.28 (m, 2H, CH), 7.38 (m, 2H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 34.8 (CH_3), 36.6 ($^{bz}CH_2$), 48.5 (CH_2), 120.8 (CH), 122.3 (CH), 125.7 (CH), 126.8 (CH), 127.2 (CH), 128.3 (CH), 129.1 (CH), 129.3 (C_{quat}), 137.9 (C_{quat}), 148.6 (C_{quat}), 155.2 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3053w, 3030w, 3003vw, 2933m, 2920m, 2868m, 2839m, 1954vw, 1973vw, 1635vs (ν (C=N)), 1572s (ν (C=N)), 1493m, 1469m, 1437s, 1410m, 1394m, 1309w, 1281m, 1236m, 1192m, 1155vw, 1140w, 1126m,1070m, 1032s, 1003w, 991w, 970m, 920w, 858w, 845w, 816vw, 783m, 764m, 735s, 717s, 698m, 648m, 596w, 586w, 571w, 545w. EI-MS (m/z(%)): 311.2 (100) [M^+], 278.2 (89), 220.2 (62) [M^+-CH_2Ph], 202.2 (43), 187.2 (96), 177.2 (40), 165.1 (83), 150.1 (29), 136.0 (52), 126.2 (47), 109.1 (33), 91.1 (55) [CH_2Ph^+], 70.1 (28), 56.1 (95).

*4.2.2.11. 1,1,3,3-Tetramethyl-2-(2-(tritylthio)phenyl)guanidine (**L6-1**).* Following the general procedure, 8.39 g (0.022 mol) of 2-(tritylthio)aniline was used. The raw product was extracted with CH_2Cl_2. After concentration of the CH_2Cl_2 phase to 20 mL the final product crystallizes at −25 °C as a white solid. Yield: 6.2 g (83%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.69 (s, 12H, CH_3), 6.37 (ddd, ^3J = 7.5 Hz, 1H, CH), 6.54 (dd, ^3J = 7.9 Hz, 1H, CH), 6.60 (dd, ^3J = 7.8 Hz, 1H, CH), 6.91 (ddd, ^3J = 7.6 Hz, 1H, CH), 7.25 (m, 9H, Try-CH.), 7.43 (m, 6H, Try-CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 39.3 (CH_3), 70.9 (C_{quat}), 119.2 (CH), 122.1 (CH), 126.6 (CH), 127.5 (CH), 130.0 (CH), 130.5 (CH), 131.7 (CH), 137.8 (CH), 144.5 (C_{quat}), 145.0 (C_{quat}), 152.1 (C_{quat}), 160.0 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3055w, 3927w, 2872w, 1629s (ν (C=N)), 1573s (ν (C=N)), 1486m, 1440m, 1396m, 1282m, 1033w, 966m, 740m, 700s, 622w. EI-MS (m/z(%)): 465.2 (30) [M^+], 243.0 (100) [CPh_3^+], 223.0 (35) [M^+-CPh_3], 179.0 (80), 149.0 (32), 136.0 (21), 44.0 (18). *Anal.* Calc. for $C_{30}H_{31}N_3S$ (465.21): C, 77.38; H, 6.71; N, 9.02; S, 6.89. Found: C, 77.25; H, 6.69; N, 9.12; S, 6.92%.

*4.2.2.12. N-(1,3-Dimethylimidazolidin-2-ylidene)-2-(tritylthio)aniline (**L6-2**).* Following the general procedure, 6.1 g (0.016 mol) of 2-(tritylthio)aniline was used. The raw product was extracted with CH_2Cl_2. After concentration of the CH_2Cl_2 phase to 20 mL the final product crystallizes at −25 °C as a white solid. Yield: 6.3 g (85%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.56 (s, 6H, CH_3), 3.27 (s, 4H, CH_2), 6.33 (ddd, ^3J = 7.2 Hz, 1H, CH), 6.45 (dd, ^3J = 7.9 Hz, 1H, CH), 6.73 (dd, ^3J = 7.8, 1H, CH), 6.84 (ddd, ^3J = 7.6 Hz, 1H, CH), 7.20 (m, 9H, Try-CH.), 7.46 (m, 6H, Try-CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 34.8 (CH_3), 58.5 (CH_2), 69.7 (C_{quat}), 119.7 (CH), 122.2 (CH), 126.5 (CH), 127.5 (CH),

127.29 (CH), 130.0 (CH), 130.5 (CH), 131.2 (CH), 137.8 (CH), 144.4 (C_{quat}), 144.8 (C_{quat}), 149.6 (C_{quat}), 155.7 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3054w, 3933w, 2854w, 1635vs (ν (C=N)), 1573s (ν (C=N)), 1488s, 1440s, 1392m, 1278m, 1031w, 968m, 740w, 698s, 624w. EI-MS (m/z(%)): 463.3 (10) [M^+], 243.2 (30) [CPh_3^+], 220.1 (100) [M^+-CPh_3], 191.1 (27), 165.0 (80), 136.0 (21), 109.0 (10), 56.0 (9).

*4.2.2.13. 1,1,3,3-Tetramethyl-2-(2-(methylthio)ethyl)guanidine (**L7-1**).* Following the general procedure, 3.47 g (0.038 mol) of 2-(methylthio)ethaneamine was used. The final product was obtained as bright green liquid. Yield: 4.7 g (65%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.81 (s, 3H, SCH_3), 2.37 (m, 8H, $^{gua}CH_3$, $NCH_2\underline{CH_2}S$), 2.47 (s, 6H, $^{gua}CH_3$), 3.05 (m, 2H, $N\underline{CH_2}CH_2S$). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 15.6 (SCH_3), 37.1 ($S\underline{C}H_2CH_2$), 38.6 ($^{gua}CH_3$), 39.4 ($^{gua}CH_3$), 49.4 ($N\underline{C}H_2CH_2$), 160.4 (C_{gua}). IR (KBr, ν [cm^{-1}]): 2993m, 2912s, 2871s, 2800m, 1616s (ν (C=N)), 1496m, 1450m, 1404vw, 1367s, 1313w, 1284w, 1234m, 1132s, 1109w, 1063w. EI-MS (m/z(%)): 189.1 (14) [M^+], 142.1 (15) [M^+-SCH_3], 128.1 (37) [M^+-CH_2SCH_3], 97.1 (8), 85.1 (100), 75.1 (26) [$CH_2CH_2SCH_3^+$], 69.0 (19), 61.0 (9) [$CH_2SCH_3^+$].

*4.2.2.14. N-(1,3-Dimethylimidazolidine-2-ylidene)-2-(methylthio) ethaneamine (**L7-2**).* Following the general procedure, 3.47 g (0.038 mol) of 2-(methylthio)ethaneamine was used. The final product was obtained as yellow oil. Yield: 5.3 g (75%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.02 (s, 3H, SCH_3), 2.52 (m, 2H, $N\underline{CH_2}CH_2S$), 2.64 (s, 6H, $^{gua}CH_3$), 3.02 (s, 4H, $^{gua}CH_2$), 3.45 (m, 2H, $N\underline{CH_2}CH_2S$). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 16.0 (SCH_3), 36.1 ($^{gua}CH_3$), 37.4 ($N\underline{C}H_2CH_2S$), 48.0 ($N\underline{C}H_2CH_2S$), 49.4 ($^{gua}CH_2$), 157.4 (C_{gua}). IR (KBr, ν [cm^{-1}]): 2914m, 2833s, 1662s (ν (C=N)), 1481m, 1437m, 1412w, 1383m, 1350w, 1265m, 1219w, 1198vw. EI-MS (m/z(%)): 187.1 (13) [M^+], 140.1 (10) [M^+-CH_3S], 126.1 (100) [M^+-CH_2SCH_3], 114.1 (23), 98.1 (5), 85.1 (17), 69.0 (16), 56.1 (32).

*4.2.2.15. 2-(2-(Ethylthio)ethyl)-1,1,3,3-tetramethylguanidine (**L8-1**).* Following the general procedure, 2.42 g (0.023 mol) of 2-(ethylthio)ethaneamine was used. The final product was obtained as yellow oil. Yield: 4 g (85%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.04 (t, ^3J = 7.4 Hz, $^{et}CH_3$), 2.36 (q, ^3J = 7.4 Hz, 2H, $^{et}CH_2$), 2.45 (s, 6H, CH_3), 2.48 (t, ^3J = 7.4, 7.2 Hz, 2H, $N\underline{CH_2}CH_2S$), 2.54 (s, 6H, CH_3), 3.12 (t, ^3J = 7.4, 7.2 Hz, 2H, $N\underline{C}H_2CH_2S$). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 14.9 ($^{et}CH_3$), 26.0 ($^{et}CH_2$), 34.5 ($NCH_2\underline{C}H_2S$), 38.6 (CH_3), 39.4 (CH_3), 50.0 ($N\underline{C}H_2CH_2S$), 160.4 (C_{gua}). IR (KBr, ν [cm^{-1}]): 2916s, 2870s, 2800w, 1620s (ν (C=N)), 1496s, 1452s, 1404w, 1367s, 1313w, 1236m, 1132s, 1063m, 1001m, 980w, 912m, 785w, 746m, 706w, 656w, 580m, 538w. EI-MS (m/z(%)): 203.1 (5) [M^+], 174.1 (2) [M^+-CH_2CH_3], 143.1 (19), 128.1 (23) [M^+-$CH_2SCH_2CH_3$], 115.0 (2), 97.0 (7), 89.1 (22) [$CH_2CH_2SCH_2CH_3^+$], 85.0 (100), 71.0 (16), 61.0 (10) [$SCH_2CH_3^+$].

*4.2.2.16. N-(1,3-Dimethylimidazolidine-2-ylidene)-2-(ethylthio) ethaneamine (**L8-2**).* Following the general procedure, 2.42 g (0.023 mol) of 2-(ethylthio)ethaneamine was used. The final product was obtained as yellow oil. Yield: 4.1 g (90%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.11 (t, ^3J = 7.4 Hz 3H, $^{et}CH_3$), 2.45 (q, ^3J = 7.4 Hz, 2H, $^{et}CH_2$), 2.54 (t, ^3J = 7.5, 7.6 Hz, 2H, $NCH_2\underline{CH_2}S$), 2.65 (s, 6H, CH_3), 3.02 (s, 4H, $^{gua}CH_2$), 3.44 (t, ^3J = 7.5, 7.6 Hz, 2H, $N\underline{CH_2}CH_2S$). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 15.0 ($^{et}CH_3$), 26.2 ($^{et}CH_2$), 34.8 ($NCH_2\underline{C}H_2S$), 36.2 (CH_3), 48.5 ($N\underline{C}H_2CH_2S$), 49.3 ($^{gua}CH_2$), 157.3 (C_{gua}). IR (KBr, ν [cm^{-1}]): 2924s, 2833s, 1662s (ν (C=N)), 1481m, 1437m, 1414m, 1383s, 1350m, 1265s, 1217m, 1198w, 1119w, 1066w, 1018w. EI-MS (m/z(%.)): 201.1 (6) [M^+], 172.1 (3) [M^+-CH_2CH_3], 149.1 (3), 141.2 (26), 126.1 (100) [$M^+CH_2SCH_2CH_3$], 112.1 (5) [M^+-$CH_2CH_2SCH_2CH_3$] 89.1 (5) [$CH_2CH_2SCH_2CH_3^+$], 85.1 (6), 69.1 (11).

*4.2.2.17. 2-(2-(Tert-butylthio)ethyl)-1,1,3,3-tetramethylguanidine (**L9-1**).* Following the general procedure, 3.99 g (0.030 mol) of 2-(tert-butylthio)ethaneamine was used. The final product was obtained as yellow oil. Yield: 5.4 g (78%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.18 (s, 9H, CH_3), 2.50 (s, 6H, CH_3), 2.54 (t, ^3J = 7.5, 7.7 Hz, 2H, $NCH_2\underline{CH_2}S$), 2.59 (s, 6H, CH_3), 3.12 (t, ^3J = 7.5, 7.7 Hz, 2H, $NCH_2\underline{CH_2}S$). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 31.0 ($^{tBu}CH_3$), 31.4 ($NCH_2\underline{C}H_2S$), 38.7 ($^{gua}CH_3$), 39.5 ($^{gua}CH_3$), 41.5 ($^{tBu}C_{quat}$), 50.2 ($N\underline{C}H_2CH_2S$), 160.3 (C_{gua}). IR (KBr, ν [cm^{-1}]): 2956m, 2924m, 2895m, 2800w, 1618m (ν (C=N)), 1496w, 1456w, 1404vw, 1363m, 1313w, 1130w. EI-MS (m/z(%)): 232.3 (100) [M^+], 187.2 (4), 174.1 (1) [M^+-tBu], 128.2 (8) [M^+-CH_2StBu], 85.1 (10), 57.1 (58) [tBu^+].

*4.2.2.18. 2-(Tert-butylthio)-N-(1,3-dimethylimidazolidine-2-ylidene)-ethaneamine (**L9-2**).* Following the general procedure, 5.33 g (0.040 mol) of 2-(ethylthio)aniline was used. The final product was obtained as yellow oil. Yield: 6 g (65%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.18 (s, 9H, CH_3), 2.52 (t, ^3J = 7.8 Hz, 2H, $NCH_2\underline{CH_2}S$), 2.69 (s, 6H, CH_3), 3.01 (s, 4H, CH_2), 3.40 (t, ^3J = 7.8 Hz, 2H, $N\underline{CH_2}CH_2S$). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 28.7 ($^{tBu}CH_3$), 30.3 ($^{gua}CH_3$), 31.1 ($^{gua}CH_3$), 31.8 ($N\underline{C}H_2CH_2S$), 41.6 ($^{tBu}C_{quat}$), 48.4 ($NCH_2\underline{C}H_2S$), 49.5 ($^{gua}CH_2$), 157.2 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3305m, 2958s, 2859s, 1662vs (ν (C=N)), 1481m, 1458m, 1439m, 1414m, 1383s, 1363m, 1348w, 1265s, 1213w, 1163m, 1140vw, 1119w, 1018w. EI-MS (m/z (%)): 230.2 (77) [M^+], 204.2 (2), 126.2 (8) [M^+-CH_2StBu], 115.3 (8), 57.1 (100) [tBu^+].

*4.2.2.19. 1,1,3,3-tetramethyl-2-(2-(tritylthio)ethyl)guanidine (**L10-1**).* Following the general procedure, 9.26 g (0.029 mol) of 2-(tritylthio)ethaneamine was used. The raw product was extracted with THF and recrystallized in MeCN. The final product was obtained as white solid. Yield: 9.0 g (74%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.36 (t, ^3J = 6.8, 6.9 Hz, 2H, $NCH_2\underline{CH_2}S$), 2.65 (s, 12H, CH_3), 3.09 (t, ^3J = 6.8, 6.9 Hz, 2H, $N\underline{CH_2}CH_2S$), 7.15 (t, 3H, Try-CH), 7.28 (t, 6H, Try-CH), 7.45 (d, 6H, Try-CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 35.3 ($NCH_2\underline{C}H_2S$), 38.9 (CH_3), 39.5 (CH_3), 48.6 ($N\underline{C}H_2CH_2S$), 66.2 ($^{Try}C_{quat}$), 126.4 (CH), 127.7 (CH), 129.7 (CH), 145.4 (C_{quat}), 160.7 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3045w, 3014w, 2993w, 2949w, 2925m, 2871m, 2829m, 2794m,1691m (ν (C=N)), 1614vs (ν (C=N)), 1492m, 1446m, 1400w, 1363s, 1311w, 1286w, 1236w, 1201w,1180w, 1132m, 1078w, 1061w, 1026m, 993w, 978w, 906w, 850w, 771m, 756m, 742s, 698s, 678w, 623m, 578w, 525w. EI-MS (m/z (%)): 418.3 (18) [M^++H], 373.2 (10) [M^+-$N(CH_3)_2$], 349.3 (73),342.3 (7), 282.2 (28), 257.3 (8), 243.1 (14) [CPh_3^+], 231.3 (16), 176.1 (44), 142.2 (69) [M^+-$SCPh_3$],116.1 (100), 72.1 (10). *Anal.* Calc. for $C_{26}H_{31}N_3S$ (417.23): C, 74.78; H, 7.48; N, 10.06. Found: C, 73.10; H, 7.56; N, 10.11%.

*4.2.2.20. N-(1,3-Dimethylimidazolidine-2-ylidene)-2-(tritylthio)ethaneamine (**L10-2**).* Following the general procedure, 16.93 g (0.053 mol) of 2-(tritylthio)ethaneamine was used. The raw product was extracted with THF and recrystallized in MeCN. The final product was obtained as white solid. Yield: 16.4 g (74%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.42 (t, ^3J = 7.2, 7.3 Hz, 2H, $NCH_2\underline{CH_2}S$), 2.71 (s, 6H, CH_3), 3.12 (s, 4H, $^{gua}CH_2$),

3.38 (t, ^3J = 7.1, 7.4 Hz, 2H, N$\underline{CH_2}CH_2S$), 7.18 (t, 3H, Try-CH), 7.27 (t, 6H, Try-CH), 7.46 (t, 6H, Try-CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 35.6 (NCH$_2\underline{C}$H$_2$S), 36.2 (CH_3), 46.6 (N$\underline{C}$H$_2$CH$_2$S), 49.5 ($^{gua}CH_2$), 66.2 ($^{Try}C_{quat}$), 126.4 (CH), 127.8 (CH), 129.7 (CH), 145.3 (C_{quat}), 157.6 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3055w, 3026w, 2964w, 2927m, 2864m, 2816m, 1653s (ν (C=N)), 1493m, 1441m, 1419w, 1387m, 1352w, 1317w, 1269m, 1200w, 1178m, 1078w, 1024m, 964m, 930w, 893w, 847w, 742m, 700s, 640w, 621m, 584w, 523w, 507w, 499m. EI-MS (m/z (%)): 416.2 (8) [M$^+$+H], 393.3 (6), 340.2 (23), 306.2 (13), 287.2 (36), 243.1 (9) [CPh$_3^+$], 227.2 (68), 174.1 (100) [M$^+$-CPh$_3$], 114.1 (61).

*4.2.2.21. 1,1,3,3-Tetramethyl-2-(3-(methylthio)propyl)guanidine (**L11-1**).* Following the general procedure, 4.94 g (0.047 mol) of 3-(methylthio)propane-1-amine was used. The raw product was extracted with THF. After fractional distillation (10 mbar, 120 °C) the final product was obtained as colorless oil. Yield: 7 g (73%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.59 (m, 2H, NCH$_2\underline{CH_2}$CH$_2$S), 1.86 (s, 3H, CH_3), 2.34 (t, ^3J = 7.2, 7.5 Hz, 2H NCH$_2$CH$_2\underline{CH_2}$S CH$_2$), 2.43 (s, 6H, CH_3), 2.53 (s, 6H, CH_3), 2.98 (t, ^3J = 6.5 Hz, 2H, N$\underline{CH_2}$CH$_2$CH$_2$S). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 15.4 (CH_3), 32.2 (SCH_2), 32.6 (CH_2), 39.4 (CH_3), 48.2 (NCH_2), 160.1 (C_{gua}). IR (KBr, ν [cm^{-1}]): 2915m, 2850m, 1741m, 1650vs (ν (C=N)), 1481w, 1442w, 1382m, 1259m, 1155m. EI-MS (m/z (%)): 203.1 (5) [M$^+$], 188.1 (57) [M$^+$-CH_3], 156.1 (19) [M$^+$-SCH_3], 142.2 (48) [M$^+$-CH_2SCH_3], 128.1 (45) [M$^+$-$(CH_2)_2SCH_3$], 104.0 (29), 89.1 (88) [M$^+$-NC(N(CH$_3$)$_2$)$_2$], 71.1 (45), 57.1 (77), 30.0 (74).

*4.2.2.22. N-(1,3-Dimethylimidazolidine-2-ylidene)-3-(methylthio)-propane-1-amine (**L11-2**).* Following the general procedure, 4.94 g (0.047 mol) of 3-(methylthio)propane-1-amine was used. The raw product was extracted with THF. After fractional distillation (10 mbar, 95 °C) the final product was obtained as colorless oil. Yield: 6.8 g (72%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.64 (m, 2H, NCH$_2\underline{CH_2}$CH$_2$S), 1.92 (s, 6H, CH_3), 2.43 (t, ^3J = 7.2, 7.2 Hz, 2H, NCH$_2$CH$_2\underline{CH_2}$S), 2.60 (s, 3H, CH_3), 2.97 (s, 4H, CH_2), 3.27 (t, ^3J = 6.7 Hz, 2H, N$\underline{CH_2}$CH$_2$CH$_2$S). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 15.5 (CH_3), 32.0 (SCH_2), 32.6 (CH_2), 39.2 (CH_3), 46.2 (NCH_2), 49.4 ($^{gua}CH_2$), 157.4 (C_{gua}). IR (KBr, ν [cm^{-1}]): 2915m, 2836m, 1660vs (ν (C=N)), 1482w, 1438w, 1378m, 1267m, 1195m. EI-MS (m/z (%)): 201.1 (6) [M$^+$], 186.1 (29) [M$^+$-CH_3], 154.1 (5) [M$^+$-SCH_3], 140.1 (12) [M$^+$-CH_2SCH_3], 126.1 (95) [M$^+$-$(CH_2)_2SCH_3$], 98.1 (5), 56.0 (9), 42.0 (5).

*4.2.2.23. 1,1,3,3-Tetramethyl-2-(2-(pyridine-2-ylmethylthio)phenyl)-guanidine (**L12-1**).* Following the general procedure, 5.84 g (0.027 mol) of 2-((pyridin-2-ylmethyl)thio)aniline was used. The final product was obtained as bright brown oil. Yield: 7.2 g (84%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.66 (s, 12H, CH_3), 4.22 (s, 2H, $^{bz}CH_2$), 6.54 (dd, ^3J = 7.8 Hz, 1H, CH), 6.73 (ddd, ^3J = 7.7, 7.4 Hz, 1H, CH), 6.99 (ddd, ^3J = 7.7, 7.4 Hz, 1H, CH), 7.08 (ddd, ^3J = 6.1, 6.2 Hz, 1H, CH), 7.13 (dd, ^3J = 7.8 Hz, 1H, CH), 7.31 (dd, ^3J = 7.8 Hz, 1H, CH), 7.52 (ddd, ^3J = 7.7, 7.6 Hz, 1H, CH), 8.50 (dd, ^3J = 4.8 Hz, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 38.9 ($^{bz}CH_2$), 39.5 (CH_3), 120.5 (CH), 121.5 (CH), 121.8 (CH), 123.1 (CH), 126.2 (CH), 127.8 (CH), 127.9 (CH), 136.4 (CH), 149.1 (C_{quat}), 150.4 (C_{quat}), 158.4 (C_{quat}), 160.0 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3045w, 3006w, 2931m, 2881m, 2796w, 1589vs (ν (C=N)), 1558vs (ν (C=N)), 1509m, 1463m, 1434m, 1376s, 1284w, 1232w, 1205w, 1139s, 1016m. EI-MS (m/z (%)): 314.1 (6) [M$^+$], 269.0 (8), 216.0 (10), 183.0 (25), 178.1 (64), 167.0 (36), 149.0 (84), 135.0 (28), 116.0 (36), 93.0 (55) [$SCH_2C_5H_4N^+$], 72.0 (100), 12.1 (5), 44.0 (35) [N(CH$_3$)$_2^+$].

*4.2.2.24. N-(1,3-Dimethylimidazolidine-2-ylidene)-3-(methylthio)-propane-1-amine (**L12-2**).* Following the general procedure, 5.84 g (0.027 mol) of 2-((pyridin-2-ylmethyl)thio)aniline was used. The final product was obtained as bright brown oil. Yield: 6.5 g (77%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.55 (s, 6H, CH_3), 3.21 (s, 4H, CH_2), 4.20 (s, 2H, $^{bz}CH_2$), 6.70 (ddd, ^3J = 7.6, 7.5 Hz, 1H, CH), 6.75 (dd, ^3J = 7.9 Hz, 1H, CH), 6.93 (ddd, ^3J = 7.6 Hz, 1H, CH), 7.04 (ddd, ^3J = 7.5 Hz, 1H, CH), 7.07 (dd, ^3J = 7.8 Hz, 1H, CH), 7.34 (dd, ^3J = 7.0 Hz, 1H, CH), 7.47 (ddd, ^3J = 7.7, 7.6 Hz, 1H, CH), 8.60 (dd, ^3J = 4.8 Hz, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 34.8 (CH_3), 38.2 ($^{bz}CH_2$), 48.4 ($^{gua}CH_2$), 120.7 (CH), 121.7 (CH), 122.2 (CH), 123.0 (CH), 125.8 (CH), 127.4 (CH), 128.4 (CH), 130.5 (C_{quat}), 148.7 (C_{quat}), 155.5 (C_{quat}), 158.7 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3049w, 2928w, 2851m, 1649vs (ν (C=N)), 1573vs (ν (C=N)), 1474m, 1428m, 1390s, 1276s, 1238w, 1033m. EI-MS (m/z (%)): 312.1 (100) [M$^+$], 279.0 (64), 220.0 (10), 202.0 (16), 188.3 (32) [M$^+$-$SCH_2C_5H_4N$], 165.0 (24), 135.0 (16), 114.0 (66), 93.0 (55) [$SCH_2C_5H_4N^+$], 65.0 (16), 56.0 (28).

*4.2.2.25. 2-(2-(2-(Dimethylamino)ethylthio)ethyl)-1,1,3,3-tetramethyl-guanidine (**L13-1**).* Following the general procedure, 2.97 g (0.020 mol) of 2-((2-aminoethyl)thio)-N,N-dimethylethaneamine was used. The final product was obtained as yellow oil. Yield: 3 g (60%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.13 (s, 6H, N(CH$_3$)$_2$), 2.39 (t, ^3J = 7.8, 7.0 Hz, 2H, SCH$_2\underline{CH_2}$N(CH$_3$)$_2$), 2.55 (s, 6H, CH_3), 2.54 (m, 2H, S$\underline{CH_2}$CH$_2$N(CH$_3$)$_2$), 2.57 (m, 2H, S$\underline{CH_2}$CH$_2$N$_{gua}$), 2.63 (s, 6H, CH_3), 3.22 (t, ^3J = 7.3 Hz, 2H, SCH$_2\underline{CH_2}$N$_{gua}$). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 30.1 (S$\underline{C}$H$_2$CH$_2$N(CH$_3$)$_2$), 35.2 (S$\underline{C}$H$_2$CH$_2$N$_{gua}$), 38.7 ($^{gua}CH_3$), 39.5 ($^{gua}CH_3$), 45.3 (N(C$\underline{H_3}$)$_2$), 50.1 (SCH$_2\underline{C}$H$_2$N$_{gua}$), 59.6 (SCH$_2\underline{C}$H$_2$N(CH$_3$)$_2$), 160.5 (C_{gua}). IR (KBr, ν [cm^{-1}]): 2935m, 2775m, 1619vs (ν (C=N)), 1497w, 1451m, 1376m, 1231w, 1125m, 1063w, 1003w, 911w, 850w. EI-MS (m/z (%)): 246.0 (3) [M$^+$], 202.1 (18) [M$^+$-N(CH$_3$)$_2$], 175.0 (84) [M$^+$-CH$_2$N(CH$_3$)$_2$], 142.2 (90) [M$^+$-CH$_2$CH$_2$N(CH$_3$)$_2$], 128.0 (70) [M$^+$-S(CH$_2$)$_2$N(CH$_3$)$_2$], 100.1 (75) [M$^+$-(CH$_2$)$_2$S(CH$_2$)$_2$-N(CH$_3$)$_2$], 85.0 (95), 70.0 (90), 58.0 (100), 44.0 (64). CI-MS (m/z (%.)): 247.2 (65) [M$^+$+H$^+$], 149.2 (25), 57.1 (100), 44.0 (32).

*4.2.2.26. 2-(2-(1,3-Dimethylimidazolidin-2-ylidenamino)ethylthio)-N,N-dimethylethaneamine (**L13-2**).* Following the general procedure, 2.97 g (0.020 mol) of 2-((2-aminoethyl)thio)-N,N-dimethylethaneamine was used. The final product was obtained as yellow oil. Yield: 4 g (82%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.09 (s, 6H, N(CH$_3$)$_2$), 2.36 (t, ^3J = 7.8, 7.0 Hz, 2H, SCH$_2\underline{CH_2}$N(CH$_3$)$_2$), 2.55 (t, ^3J = 7.8, 7.0 Hz, 2H, S$\underline{CH_2}$CH$_2$N(CH$_3$)$_2$), 2.62 (t, ^3J = 7.3, 7.5 Hz, 2H, S$\underline{CH_2}$CH$_2$N$_{gua}$), 2.75 (s, 6H, CH_3), 3.16 (s, 4H, $^{gua}CH_2$), 3.22 (t, ^3J = 7.5, 7.3 Hz, 2H, SCH$_2\underline{CH_2}$N$_{gua}$). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 30.1 (S$\underline{C}$H$_2$CH$_2$N(CH$_3$)$_2$), 35.2 (S$\underline{C}$H$_2$CH$_2$N$_{gua}$), 38.7 ($^{gua}CH_3$), 39.5 ($^{gua}CH_3$), 45.3 (N(C$\underline{H_3}$)$_2$), 50.1 (SCH$_2\underline{C}$H$_2$N$_{gua}$), 59.6 (SCH$_2\underline{C}$H$_2$N(CH$_3$)$_2$), 160.5 (C_{gua}).

^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 29.7 (S$\underline{C}$H$_2$CH$_2$N(CH$_3$)$_2$), 34.5 (S$\underline{C}$H$_2$CH$_2$N$_{gua}$), 36.1 ($^{gua}CH_3$), 45.4 (N(C$\underline{H_3}$)$_2$), 47.2 (SCH$_2\underline{C}$H$_2$N$_{gua}$), 49.3 ($^{gua}CH_2$), 59.6 (SCH$_2\underline{C}$H$_2$N(CH$_3$)$_2$), 160.5 (C_{gua}). IR (KBr, ν [cm^{-1}]): 2942m, 2829m, 2775m, 1657vs (ν (C=N)), 1451m, 1390m, 1269m, 1125w, 1041m, 949m, 850w. EI-MS (m/z (%)): 244.0 (5) [M$^+$], 200.1 (10) [M$^+$-N(CH$_3$)$_2$], 175.0 (75) [M$^+$-CH$_2$N(CH$_3$)$_2$], 140.2 (80) [M$^+$-CH$_2$CH$_2$N(CH$_3$)$_2$], 126.0 (88) [M$^+$-S(CH$_2$)$_2$N(CH$_3$)$_2$], 98.0 (55)

[M^+-$(CH_2)_2S(CH_2)_2$-$N(CH_3)_2$], 83.0 (28), 71.1 (82), 58.1 (100), 42.0 (74), 30.0 (56). CI-MS (m/z (%.)): 245.2 (65) [M^++H^+], 149.1 (55), 115.1 (32), 57.1 (100), 42.0 (32).

*4.2.2.27. 2,2-(2,2-Thiobis(ethane-2,1-diyl))bis(1,1,3,3-tetramethylguanidine) (**L14-1**).* Following the general procedure, 2.4 g (0.020 mol) of 2,2′-thiodiethaneamine was used. The final product was obtained as orange oil. Yield: 4.8 g (76%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.42 (s, 12H, CH_3), 2.46 (t, ^3J = 7.4 Hz, 4H, SCH_2), 2.51 (s, 12H, CH_3), 3.09 (t, ^3J = 7.4 Hz, 4H, NCH_2). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 34.7 (SCH_2), 38.6 (CH_3), 39.4 (CH_3), 48.8 (NCH_2), 160.3 (C_{gua}). IR (KBr, ν [cm^{-1}]): 2996m, 2882m, 2798w, 1611vs (ν (C=N)), 1497m, 1444w, 1368s, 1246w, 1132m, 1055w, 1003w, 904w. EI-MS (m/z (%)): 317.3 (3) [M^+], 272.0 (5) [M^+-$N(CH_3)_2$], 202.1 (5) [M^+-$NC((NCH_3)_2)_2$], 175.1 (80) [M^+-$(CH_2)_2NC(N(CH_3)_2)_2$], 142.2 (84) [M^+-$S(CH_2)_2$-$NC(N(CH_3)_2)_2$)], 128 (44) [M^+-$CH_2S(CH_2)_2NC(N(CH_3)_2)_2$], 97.1 (10), 85.0 (100), 71.0 (44), 44.0 (13). CI-MS (m/z (%.)): 317.3 (3) [(M + H)$^+$], 228.3 (10), 142.2 (5), 121.1 (23), 57.1 (100), 43.1 (34).

*4.2.2.28. 2,2-Thiobis(N-(1,3-dimethylimidazolidine-2-ylidene)ethaneamine) (**L14-2**).* Following the general procedure, 2.4 g (0.020 mol) of 2,2′-thiodiethaneamine was used. The final product was obtained as orange oil. Yield: 4.8 g (77%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.47 (t, ^3J = 7.4 Hz, 4H, SCH_2), 2.54 (s, 12H, CH_3), 2.91 (s, 8H, CH_2), 3.34 (t, ^3J = 7.4 Hz, 4H, NCH_2). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 35.4 (SCH_2), 35.8 (CH_3), 38.6 (NCH_2), 49.2 ($^{gua}CH_2$), 157.2 (C_{gua}). IR (KBr, ν [cm^{-1}]): 2920m, 2836m, 1665vs (ν (C=N)), 1489m, 1436w, 1383m, 1262s, 1079w, 1017w, 949w, 728w. EI-MS (m/z (%)): 313.0 (3) [M^++H^+], 200.1 (5) [M^+-$NC(NCH_3)_2)(CH_2)_2$], 173.1 (80) [M^+-$(CH_2)2NC(NCH_3)_2$)-$(CH_2)_2$], 140.1 (58) [M^+-$S(CH_2)_2NC(NCH_3)_2)(CH_2)_2$], 126.0 (11) [$M^+$-$(CH_2)_2S(CH_2)2$-$NC(NCH_3)_2)(CH_2)_2$], 124.1 (10), 113.1 (5), 69.1 (16), 56.0 (40), 42.0 (24). CI-MS (m/z (%.)): 313.3 (3) [(M + H)$^+$], 224.2 (5), 217.2 (40), 140.2 (14), 121.0 (10), 57.1 (100), 43.1 (36).

*4.2.2.29. Bis(1,1,3,3-tetramethylguanidin)-2-(2-(1,3-dimethylimidazo-lidin-2-ylidenamino)ethylthio)anilin (**L15-1**).* Following the general procedure, 2.52 g (0.015 mol) of 2-((2-aminoethyl)thio)aniline was used. The final product was obtained as brown oil. Yield: 4.8 g, (90%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.58 (s, 12H, CH_3), 2.59 (s, 12H, CH_3), 2.94 (t, 2H, SCH_2), 3.29 (t, 2H, NCH_2), 6.43 (ddd, 1H, CH), 6.69 (dd, 1H, CH), 6.86 (dd, 1H, CH), 7.09 (ddd, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 34.5 (SCH_2), 38.8 (CH_3), 39.4 (NCH_3), 48.7 ($^{gua}CH_2$), 120.2 (CH), 121.4 (CH), 125.1 (CH), 126.4 (CH), 128.8 (C_{quat}), 153.2 (C_{quat}), 160.6 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3049w, 3997w, 2922m, 2879w, 2792w, 1601s (ν (C=N)), 1563s (v (C=N)), 1506m, 1445m, 1421m, 1373s, 1284w, 1232w, 1137s. EI-MS (m/z (%)): 364.2 (2) [M^+], 320.2 (2) [M^+-$N(CH_3)_2$], 305.0 (12) [M^+-$N(CH_3)_2$,-CH_3], 249.1 (4) [M^+-$NC(N(CH_3)_2)_2$], 223.1 (40) [M^+-$(CH_2)_2NC(N(CH_3)_2)_2$], 179.1 (76), 149.0 (30), 142.0 (64), 85.0 (100), 71.0 (16), 44.0 (16).

*4.2.2.30. N-(1,3-Dimethylimidazolidine-2-ylidene)-2-(2-(1,3-dimethylimidazolidine-2-ylidene-amino)ethylthio)aniline (**L15-2**).* Following the general procedure, 2.52 g (0.015 mol) of 2-((2-aminoethyl) thio)aniline was used. The final product was obtained as brown oil. Yield: 4.9 g (91%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.55 (s, 6H, CH_3), 2.60 (s, 6H, CH_3), 3.00 (t, ^3J = 8.0, 7.8 Hz, 2H, SCH_2), 3.07 (s, 4H, $^{gua}CH_2$), 3.19 (s, 4H, $^{gua}CH_2$), 3.59 (t, ^3J = 8.0, 7.8 Hz, 2H, NCH_2), 6.69 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, CH), 6.75 (ddd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H, CH), 6.89 (ddd, ^3J = 7.4 Hz, ^4J = 1.5 Hz, 1H, CH), 7.13 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 34.4 (SCH_2), 34.7 (CH_3), 47.4 (NCH_2), 48.4 ($^{gua}CH_2$), 49.4 ($^{gua}CH_2$) 120.5 (CH), 122.0 (CH), 124.7 (CH), 125.7 (CH), 129.8 (C_{quat}), 155.2 (C_{quat}), 167.5 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3049w, 3028m, 2841m, 1648s (ν (C=N)), 1573s (ν (C=N)), 1487m, 1435m, 1416m, 1388m, 1345w, 1274s, 1227m. EI-MS (m/z (%)): 360.2 (2) [M^+], 248.0 (4) [M^+-$NC(NCH_3)_2(CH_2)_2$], 221.1 (30) [M^+-$(CH_2)_2NC(NCH_3)_2(CH_2)_2$], 188.1 (10) [$M^+$-$S(CH_2)_2NC(NCH_3)_2(CH_2)_2$], 178.1 (48), 166.0 (44), 149.0 (70), 140.1 (72), 126.1 (100), 109.0 (10), 98.0 (14), 44.0 (45).

*4.2.2.31. Bis(1,1,3,3-tetramethylguanidine)-2-(3-(1,3-dimethylimidazolidine-2-ylidenamino)propylthio)aniline (**L16-1**).* Following the general procedure, 4.56 g (0.025 mol) of 2-((3-aminopropyl) thio)aniline was used. The final product was obtained as brown oil. Yield: 7.4 g (78%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.85 (m, ^3J = 7.1, 6.8 Hz, 2H, $SCH_2\underline{CH_2}CH_2N_{gua}$), 2.57 (s, 12H, CH_3), 2.65 (s, 12H, CH_3), 2.83 (t, ^3J = 7.1, 7.3 Hz, 2H, $S\underline{CH_2}CH_2CH_2N_{gua}$), 3.15 (t, ^3J = 6.7 Hz, 2H, $SCH_2CH_2\underline{CH_2}N_{gua}$), 6.42 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, CH), 6.68 (ddd, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 1H, CH), 6.88 (ddd, ^3J = 7.4 Hz, ^4J = 1.5 Hz, 1H, CH), 7.04 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 29.6 (CH_2), 30.9 (CH_2), 39.3 (CH_3), 39.4 (CH_3), 47.2 (CH_2), 120.3 (CH), 121.4 (CH), 125.2 (CH), 126.3 (CH), 128.7 (C_{quat}), 159.9 (C_{quat}), 160.6 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3049w, 2996w, 2920m, 2874m, 2798w, 1611s (ν (C=N)), 1573s (ν (C=N)), 1505m, 1459m, 1376m, 1231w, 1132m. EI-MS (m/z (%)): 378.3 (10) [M^+], 318.0 (3), 280.0 (5), 250.0 (5), 222.1 (40) [M^+-$(CH_2)_3NC(N(CH_3)_2)_2$], 205.2 (65), 178.1 (72), 163.0 (70), 149.0 (75), 116.0 (75), 89.0 (40), 72.0 (90), 42.0 (100), 28.0 (52).

*4.2.2.32. N-(1,3-Dimethylimidazolidine-2-ylidene)-2-(3-(1,3-dimethylimidazolidine-2-ylidene-amino)propylthio)aniline (**L16-2**).* Following the general procedure, 4.56 g (0.025 mol) of 2-((3-aminopropyl)thio)aniline was used. The final product was obtained as brown oil. Yield: 7 g (75%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.85 (m, ^3J = 7.3, 6.6 Hz, 2H, $SCH_2\underline{CH_2}CH_2N_{gua}$), 2.56 (s, 6H, CH_3), 2.72 (s, 6H, CH_3), 2.94 (t, ^3J = 7.5, 7.3 Hz, 2H, $S\underline{CH_2}CH_2CH_2N_{gua}$), 3.07 (s, 4H, $^{gua}CH_2$), 3.19 (s, 4H, $^{gua}CH_2$), 3.42 (t, ^3J = 6.6 Hz, 2H, $SCH_2CH_2\underline{CH_2}N_{gua}$), 6.71 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, CH), 6.75 (ddd, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 1H, CH), 6.88 (ddd, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 1H, CH), 7.12 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 29.0 (CH_2), 32.5 (CH_2), 34.8 (CH_3), 46.6 (CH_2), 48.4 (CH_2), 49.4 (CH_2), 120.7 (CH), 122.0 (CH), 124.5 (CH), 125.4 (CH), 130.2 (C_{quat}), 155.5 (C_{quat}), 157.3 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3049w, 2928m, 2844m, 1649s (ν (C=N)), 1573s (ν (C=N)), 1489m, 1383m, 1276m. EI-MS (m/z (%)): 374.2 (10) [M^+], 278.2 (20), 262.0 (3) [M^+-$NC(NCH_3)_2(CH_2)_2$], 248.1 (10), 220.0 (68) [M^+-$(CH_2)_2NC(NCH_3)_2(CH_2)_2$], 205.2 (70), 177.1 (40), 162.0 (33), 149.1 (62), 114.1 (79), 98.1 (33), 72.0 (70), 57.1 (98), 42.0 (100), 28.0 (75).

*4.2.2.33. 2,2-(2,2-Thio-bis(2,1-phenylene))bis(1,1,3,3-tetramethylguanidine) (**L17-1**).* Following the general procedure, 4.33 g (0.020 mol) of 2,2′-thiodianiline was used. The final product was obtained as white solid. Yield: 5.2 g (63%).

^{1}H-NMR (500 MHz, CD_2Cl_2, 25 °C, δ [ppm]): 2.63 (s, 24H, CH_3), 6.70 (m, 4H, CH), 7.02 (m, 4H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 39.5 (CH_3), 120.5 (CH), 122.5 (CH), 127.0 (CH), 127.04 (C_{quat}), 131.7 (CH), 151.5 (C_{quat}), 159.5 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3042w, 2995w, 2928m, 2875m, 2791w, 1566vs (ν (C=N)), 1505s (ν (C=N)), 1452s, 1384s, 1284m, 1231m, 1201m,

1147s, 1011m, 850m. EI-MS (m/z (%)): 412.2 (100) [M^+], 368.2 (95) [M^+-N(CH_3)$_2$], 323.1 (20) [M^+-2 N(CH_3)$_2$], 314.0 (50), 298.1 (20) [M^+-NC(N(CH_3)$_2$)$_2$], 280.0 (38), 237.0 (48), 225.0 (44), 190.0 (58), 179.0 (90), 162.0 (80), 149.0 (63), 100.0 (44), 85.0 (100).

*4.2.2.34. 2,2-Thio-bis(N-(1,3-dimethylimidazolidine-2-ylidene)aniline) (**L17-2**).* Following the general procedure, 4.33 g (0.020 mol) of 2,2′-thiodianiline was used. The final product was obtained as white solid. Yield: 5.2 g (64%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.62 (s, 12H, CH_3), 3.42 (s, 8H, CH_2), 6.91 (ddd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 2H, CH), 7.10 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 2H, CH), 7.13 (ddd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 2H, CH), 7.19 (dd, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 2H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 34.6 (CH_3), 48.4 (CH_2), 123.8 (CH), 125.6 (CH), 127.7 (C_{quat}), 128.0 (CH), 131.8 (CH), 143.6 (C_{quat}), 156.0 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3050w, 2935w, 2852m, 2700m, 1642vs (ν (C=N)), 1604vs (ν (C=N)), 1467m, 1428m, 1390m, 1269m, 1025m, 980w, 767m, 736m, 698w. EI-MS (m/z (%.)): 408.2 (100) [M^+], 350.1 (8), 309.1 (19) [M^+-C(NCH_3)$_2$(CH_2)$_2$], 220.0 (16) [M^+-C_6H_4NC(NCH_3)$_2$(CH_2)$_2$], 199.0 (19), 188.1 (56) [M^+-SC_6H_4NC(NCH_3)$_2$(CH_2)$_2$], 149.1 (14), 114.1 (18), 86.1 (60), 58.0 (24).

*4.2.2.35. 2,2-(2,2-(Propane-1,3-diylbis(sulfandiyl))bis(ethane-2,1-diyl))bis(1,1,3,3-tetramethyl-guanidine) (**L18-1**).* Following the general procedure, 2.99 g (0.0154 mol) of 2,2′-(propane-1,3-diylbis(sulfanediyl))diethaneamine was used. The final product was obtained as brown oil. Yield: 3.2 g (52%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.73 (m, ^3J = 7.1 Hz, 2H, $SCH_2\underline{CH_2}CH_2S$), 2.51 (m, 8H, CH_2SCH_2), 2.53 (s, 12H, CH_3), 2.61 (s, 12H, CH_3), 3.17 (t, ^3J = 7.1, 7.4 Hz, 4H, $SCH_2CH_2\underline{CH_2}N_{Gua}$). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 29.8 (CH_2), 31.1 (CH_2), 34.9 (CH_2), 38.7 (CH_3), 39.5 (CH_3), 49.8 (CH_2), 160.7 (C_{gua}). IR (KBr, ν [cm^{-1}]): 2996w, 2912s, 2798m, 1611vs (ν (C=N)), 1489m, 1459m, 1376s, 1306w, 1238m, 1139s. EI-MS (m/z (%)): 391.2 (8) [M^+], 346.2 (8) [M^+-N(CH_3)$_2$], 249.1 (16) [M^+-(CH_2)$_2$NC(N(CH_3)$_2$)$_2$], 202.1 (6) [M^+-CH_2S(CH_2)$_2$NC(N(CH_3)$_2$)$_2$], 143.1 (95) [(CH_2)$_2$-NC(N(CH_3)$_2$)$_2^+$], 128.1 (52) [CH_2NC(N(CH_3)$_2$)$_2^+$], 100.0 (28), 85.0 (100), 72.0 (28), 58.0 (6).

*4.2.2.36. 2,2-(Propane-1,3-diyl-bis(sulfanediyl))bis(N-(1,3-dimethylimidazolidine-2-ylidene)-ethaneamine) (**L18-2**).* Following the general procedure, 2.99 g (0.0154 mol) of 2,2′-(propane-1,3-diylbis(sulfanediyl))diethaneamine was used. The final product was obtained as brown oil. Yield: 4.7 g (79%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.71 (m, 2H, $SCH_2\underline{CH_2}CH_2S$), 2.49 (m, 8H, CH_2SCH_2), 2.61 (s, 6H, CH_3), 2.64 (s, 6H, CH_3), 3.02 (s, 4H, $^{gua}CH_2$), 3.03 (s, 4H, $^{gua}CH_2$), 3.39 (t, 4H, $SCH_2CH_2\underline{CH_2}N_{Gua}$). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 29.8 (CH_2), 31.2 (CH_2), 34.9 (CH_2), 36.2 (CH_3), 38.1 (CH_2), 49.3 (CH_2), 157.7 (C_{gua}). IR (KBr, ν [cm^{-1}]): 2920m, 2844s, 1649vs (ν (C=N)), 1482m, 1444m, 1390m, 1344w, 1269s, 1216w. EI-MS (m/z (%)): 387.1 (5) [M^+], 290 (7), 247.2 (12) [M^+-(CH_2)$_2$NC(NCH_3)$_2$(CH_2)$_2$], 205.2 (18), 172.1 (27) [S(CH2)$_2$NC(NCH_3)$_2$(CH_2)$_2^+$], 141.1 (60) [(CH_2)$_2$NC(NCH_3)$_2$(CH_2)$_2^+$], 126.1 (100) [CH_2NC(NCH_3)$_2$(CH_2)$_2^+$], 113.0 (38) [NC(NCH_3)$_2$-(CH_2)$_2^+$], 88.1 (15), 56.0 (45), 44.1 (55), 30.0 (50).

*4.2.2.37. 2,2-(2,2-(Propane-1,3-diyl-bis(sulfandiyl))bis(2,1-phenylene))bis(1,1,3,3-tetramethyl-guanidine) (**L19-1**).* Following the general procedure, 4.94 g (0.017 mol) of 2,2′-(propane-1,3-diylbis (sulfanediyl))dianiline was used. The final product was obtained as brown oil. Yield: 5.7 g (69%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.91 (m, ^3J = 7.1, 7.2 Hz, 2H, $SCH_2\underline{CH_2}CH_2S$), 2.58 (s, 24H, CH_3), 2.19 (t, ^3J = 7.1, 7.2 Hz, 4H, $S\underline{CH_2}CH_2\underline{CH_2}S$), 6.44 (dd, ^3J = 7.8 Hz, ^4J = 1.3 Hz, 2H, CH), 6.67 (ddd, ^3J = 7.7, 7.4 Hz, ^4J = 1.3 Hz, 2H, CH), 6.89 (ddd, ^3J = 7.7, 7.4 Hz, ^4J = 1.3 Hz, 2H, CH), 7.02 (dd, ^3J = 7.8 Hz, ^4J = 1.3 Hz, 2H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 28.1 (CH_2), 31.1 (CH_2), 39.4 (CH_3), 120.4 (CH), 121.5 (CH), 125.6 (CH), 126.7 (CH), 128.1 (C_{quat}), 150.3 (C_{quat}), 159.8 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3049w, 3004w, 2928m, 2794w, 1596vs (ν (C=N)), 1558vs (ν (C=N)), 1498s, 1452s, 1368s, 1284w, 1239w, 1201s, 1130s, 1071m, 1018s. EI-MS (m/z (%)): 486.2 (10) [M^+], 442.1 (5) [M^+-N(CH_3)$_2$], 388.1 (7), 296.0 (3) [M^+-C_6H_4NC(N(CH_3)$_2$)$_2$], 264.1 (100), 250.1 (50), 179.0 (58), 149.0 (28), 136.0 (20), 100.0 (10), 85.0 (12), 44.0 (10).

*4.2.2.38. 2,2-(Propane-1,3-diyl-bis(sulfandiyl))bis(N-(1,3-dimethylimidazolidine-2-ylidene)aniline) (**L19-2**).* Following the general procedure, 4.94 g (0.017 mol) of 2,2′-(propane-1,3-diylbis(sulfanediyl))dianiline was used. The final product was obtained as brown oil. Yield: 7.1 g (86%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.00 (m, ^3J = 7.1, 7.2 Hz, 2H, $SCH_2\underline{CH_2}CH_2S$), 2.64 (s, 12H, CH_3), 3.05 (t, ^3J = 7.1, 7.2 Hz, 4H, $S\underline{CH_2}CH_2\underline{CH_2}S$), 3.28 (s, 8H, CH_2), 6.83 (m, 4H, CH), 7.00 (ddd, ^3J = 7.5, 7.6 Hz, ^4J = 1.5 Hz, 2H, CH), 7.13 (dd, ^3J = 7.6 Hz, ^4J = 1.3 Hz, 2H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 28.2 (CH_2), 30.8 (CH_2), 34.8 (CH_3), 48.5 (CH_2), 120.9 (CH), 122.4 (CH), 125.3 (CH), 126.7 (CH), 129.0 (C_{quat}), 148.4 (C_{quat}), 155.2 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3042w, 2921m, 2854m, 1619vs (ν (C=N)), 1566vs (ν (C=N)), 1505m, 1428m, 1452s, 1384m, 1277m, 1231w, 1117w, 1018m, 957w. EI-MS (m/z (%)): 482.2 (16) [M^+], 386.1 (16), 344.1 (10), 307.2 (18), 262.1 (90), 248.1 (95), 220.1 (36), 202.1 (20) [$CH_2C_6H_4$NC(NCH_3)$_2$(CH_2)$_2^+$], 188.1 (44) [C_6H_4NC(NCH_3)$_2$(CH_2)$_2^+$], 165.1 (50), 150.0 (48), 135.0 (42), 124.0 (84), 80.0 (36), 44.0 (28).

*4.2.2.39. 2,2-(2,2-(Pyridine-2,6-diyl-bis(methylene))bis(sulfandiyl)-bis(ethane-2,1-diyl))bis(1,1,3,3-tetramethylguanidine) (**L20-1**).* Following the general procedure, 5.01 g (0.017 mol) of 2,2′-((pyridine-2,6-diylbis(methylene))bis(sulfanediyl))diethaneamine was used. The final product was obtained as bright brown oil. Yield: 5.6 g (68%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.81 (t, 4H, CH_2), 2.88 (s, 24H, CH_3), 3.35 (t, 4H, CH_2), 3.80 (s, 4H, CH_2), 7.22 (d, 2H, CH), 7.47 (t, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 30.1 (CH_2), 35.0 (CH_3), 38.9 (CH_2), 45.6 (CH_2), 120.5 (CH), 137.1 (CH), 159.9 (C_{quat}), 162.1 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3050w, 3004w, 2921m, 2859m, 2783w, 1591vs (ν (C=N)), 1551vs (ν (C=N)), 1505m, 1460s, 1422s, 1384s, 1284w, 1239w, 1155s, 1063w, 1018s, 912w, 850w, 767m, 736s, 569w. EI-MS (m/z (%)): 453.1 (9) [M^+], 409.0 (20) [M^+-N(CH_3)$_2$], 325.1 (24) [M^+-CH_2NC(N(CH_3)$_2$)$_2$], 279.1 (43) [M^+-S(CH_2)$_2$NC(N(CH_3)$_2$)$_2$], 142.1 (77) [(CH_2)$_2$NC(N(CH_3)$_2$)$_2^+$], 128.1 (61) [CH_2-NC(N(CH_3)$_2$)$_2^+$], 101.1 (36), 84.1 (44), 44.0 (13).

*4.2.2.40. 2,2-(Pyridine-2,6-diyl-bis(methylene))bis(sulfandiyl)bis-(N-(1,3-dimethylimidazolidine-2-ylidene)ethaneamine) (**L20-2**).* Following the general procedure, 4.12 g (0.016 mol) of 2,2′-((pyridine-2,6-diylbis(methylene))bis(sulfanediyl))diethaneamine was used. The final product was obtained as bright brown oil. Yield: 4.7 g (62%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.75 (t, ^3J = 7.0, 7.4 Hz, 4H, $S\underline{CH_2}CH_2N_{gua}$), 2.88 (s, 12H, CH_3), 3.32 (s, 8H, $^{gua}CH_2$), 3.54 (t, ^3J = 7.0, 7.4 Hz, 4H, $SCH_2\underline{CH_2}N_{gua}$), 3.83 (s, 4H, $^{bz}CH_2$), 7.25 (dd, ^3J = 7.7 Hz, 2H, CH), 7.58 (ddd, ^3J = 7.7 Hz, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 31.5 (CH_2), 36.1 (CH_3), 38.1 (CH_2), 46.3 (CH_2), 49.5 (CH_2), 121.2 (CH), 137.4 (CH), 159.2 (C_{quat}), 161.9 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3069w, 2992m, 2866w,

1640vs (ν (C=N)), 1588s (ν (C=N)), 1489w, 1455m, 1413w, 1384w, 1351w, 1261m, 1223w. EI-MS (m/z (%)): 449.1 (3) [M+], 310.1 (44) [M^+-$(CH_2)_2NC(NCH_3)_2(CH_2)_2$], 277.1 (3) [$M^+$-$S(CH_2)_2NC(NCH_3)_2$-$(CH_2)_2$], 172.1 (17) [$S(CH_2)_2NC(NCH_3)_2(CH_2)_2^+$], 140.1 (70) [$(CH_2)_2NC(NCH_3)_2(CH2)_2^+$], 126.1 (100) [$CH_2NC(NCH_3)_2(CH_2)_2^+$], 113.1 (19), 56.0 (17).

*4.2.2.41. 2,2-(2,2-(Pyridine-2,6-diyl-bis(methylene))bis(sulfandiyl)-bis(2,1-phenylene))bis(1,1,3,3-tetramethylguanidine) (**L21-1**).* Following the general procedure, 4.24 g (0.012 mol) of 2,2′-((pyridine-2,6-diylbis(methylene))bis(sulfanediyl))dianiline was used. The final product was obtained as brown oil. Yield: 8.1 g (87%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.71 (s, 24H, CH_3), 4.20 (s, 4H, $^{bz}CH_2$), 6.70 (dd, ^3J = 7.7 Hz, 2H, CH), 6.79 (ddd, ^3J = 7.6 Hz, ^4J = 1.3 Hz, 2H, CH), 7.03 (ddd, ^3J = 7.6 Hz, ^4J = 1.3 Hz, 2H, CH), 7.14 (dd, ^3J = 7.7, 2H, CH), 7.18 (dd, ^3J = 7.6 Hz, 2H, CH), 7.44 (ddd, ^3J = 7.7 Hz, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 39.2 (CH_2), 39.9 (CH_3), 121.2 (CH), 121.3 (CH), 122.1 (CH), 126.4 (CH), 128.2 (CH), 128.3 (C_{quat}), 137.1 (CH), 147.5 (C_{quat}), 157.5 (C_{quat}), 160.0 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3048w, 2927w, 2850w, 1635s (ν (C=N)), 1571s (ν (C=N)), 1488w, 1452m, 1434m, 1394w, 1280m, 1228w, 1122w, 1066w, 1031m, 970w, 865w, 765w, 736m, 697w. EI-MS (m/z (%)): 549.0 (100) [M^+], 505.0 (7) [M^+-$N(CH_3)_2$], 444.0 (6), 372.0 (7), 359.0 (2) [M^+-$C_6H_4N(CH_3)_2$], 327.0 (28) [M^+-$SC_6H_4N(CH_3)_2$], 282.0 (10), 250.0 (10), 222.0 (19) [$SC_6H_4N(CH_3)_2^+$], 179.0 (100), 165.0 (18), 149.0 (54), 136.0 (24), 85.0 (12), 44.0 (28).

*4.2.2.42. 2,2-(Pyridine-2,6-diyl-bis(methylene))bis(sulfandiyl)bis-(N-(1,3-dimethylimidazolidine-2-ylidene)aniline) (**L21-2**).* Following the general procedure, 6.36 g (0.018 mol) of 2,2′-((pyridine-2,6-diylbis(methylene))bis(sulfanediyl))dianiline was used. The final product was obtained as brown oil. Yield: 6.5 g (67%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.64 (s, 12H, CH_3), 3.29 (s, 8H, $^{gua}CH_2$), 4.25 (s, 4H, $^{bz}CH_2$), 6.77 (ddd, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 2H, CH), 6.84 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 2H, CH), 7.00 (ddd, ^3J = 7.6 Hz, ^4J = 1.5 Hz, 2H, CH), 7.14 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 2H, CH), 7.25 (dd, ^3J = 7.7 Hz, 2H, CH), 7.45 (ddd, ^3J = 7.7 Hz, 1H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 34.8 (CH_3), 38.2 (CH_2), 48.5 (CH_2), 121.2 (CH), 122.4 (CH), 125.7 (CH), 125.8 (CH), 127.4 (CH), 128.9 (C_{quat}), 137.0 (CH), 148.0 (C_{quat}), 155.3 (C_{quat}), 157.5 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3048w, 2927w, 2850w, 1635s (ν (C=N)), 1571s (ν (C=N)), 1488w, 1452m, 1434m, 1394w, 1280m, 1228w, 1122w, 1066w, 1031m, 970w, 865w, 765w, 736m, 697w. EI-MS (m/z (%)): 545.1 (10) [M^+], 440.0 (8), 370.0 (90), 338.0 (55), 326.1 (8) [M^+-$SC_6H_4NC(NCH_3)_2(CH_2)_2$], 291.1 (30), 221.0 (70) [$SC_6H_4NC(NCH_3)_2(CH_2)_2^+$], 188.0 (50), [$C_6H_4NC(NCH_3)_2$-$(CH_2)_2^+$], 178.0 (83), 165.0 (95), 149.0 (100), 126.0 (81), 109.0 (35), 68.0 (48), 44.0 (100).

*4.2.2.43. 2,2-(2,2-Disulfandiylbis(2,1-phenylene))bis(1,1,3,3-tetramethylguanidine) (**L22-1**).* Following the general procedure, 4.97 g (0.020 mol) of 2,2′-disulfanediyldianiline was used. The raw product was extracted with CH_2Cl_2 and recrystallized in THF. The final product was obtained as a white solid. Yield: 6.3 g (71%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.72 (s, 24H, CH_3), 6.53 (dd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 2H, CH), 6.75 (ddd, ^3J = 7.6 Hz, ^4J = 1.3 Hz, 2H, CH), 6.99 (ddd, ^3J = 7.5 Hz, ^4J = 1.4, 1.3 Hz, 2H, CH), 7.44 (dd, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 2H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 39.5 (CH_3), 120.6 (CH), 121.2 (CH), 125.7 (CH), 126.2 (CH), 128.4 (C_{quat}), 149.4 (C_{quat}), 160.0 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3057w, 2997w, 2935m, 2883m, 2791w, 1589s (ν (C=N)), 1551vs (ν (C=N)), 1517s, 1460m, 1422m, 1384s, 1277m, 1155s, 1025s, 927w, 843w, 782m, 744s, 668w. EI-MS (m/z (%)): 442.2 (75) [M^+], 400.2 (6) [M^+-$N(CH_3)_2$], 355.1 (3) [M^+-2 $N(CH_3)_2$], 223.1 [M^+-$SC_6H_4NC(N(CH_3)_2)_2$], 191.1 (7) [$C_6H_4NC(N(CH_3)_2)_2^+$], 178.1 (100), 149.0 (78), 136.0 (58), 109.0 (28), 44.1 (62), 28.0 (30). *Anal.* Calc. for $C_{22}H_{32}N_6S_2$ (444.7): C, 59.42; H, 7.25; N, 18.90. Found: C, 59.00; H, 7.64; N, 18.61%.

*4.2.2.44. 2,2-Disulfandiyl-bis(N-(1,3-dimethylimidazolidine-2-ylidene)aniline) (**L22-2**).* Following the general procedure, 4.97 g (0.02 mol) of 2,2′-disulfanediyldianiline was used. The raw product was extracted with CH_2Cl_2 and recrystallized in THF. The final product was obtained as a white solid. Yield: 7.3 g (83%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.66 (s, 12H, CH_3), 3.29 (s, 8H, CH_2), 6.77 (m, 4H, CH), 6.97 (ddd, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 2H, CH), 7.42 (dd, ^3J = 8.1 Hz, ^4J = 1.3, 1.5 Hz, 2H, CH 2H, CH). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 34.9 (CH_3), 48.5 (CH_2), 121.2 (CH), 122.0 (CH), 125.3 (CH), 125.9 (CH), 129.0 (C_{quat}), 147.2 (C_{quat}), 155.5 (C_{gua}). IR (KBr, ν [cm^{-1}]): 3050w, 2935w, 2852w, 1635vs (ν (C=N)), 1611s (ν (C=N)), 1573vs (ν (C=N)), 1498m, 1444s, 1384m, 1277s, 1223w, 1041s, 965w, 858w, 752m. EI-MS (m/z (%)): 440.2 (35) [M^+], 344.1 (74) [M^+-$C(NCH_3)_2(CH_2)_2$], 248.0 (84), 220.0 (93) [M^+-$SC_6H_4C(NCH_3)_2(CH_2)_2$], 188.0 (65) [$C_6H_4C(NCH_3)_2(CH_2)_2^+$], 165.1 (89), 124.0 (100), 80.1 (75), 56 (78), 44.0 (80). *Anal.* Calc. for $C_{22}H_{28}N_6S_2$ (440.6): C, 59.97; H, 6.41; N, 19.07. Found: C, 60.05; H, 6.62; N, 19.00%.

*4.2.2.45. 2,2-(2,2-Disulfandiyl-bis(ethane-2,1-diyl))bis(1,1,3,3-tetramethylguanidine) (**L23-1**).* Following the general procedure, 3.05 g (0.02 mol) of 2,2′-disulfanediyldiethaneamine was used. The final product was obtained as brown oil. Yield: 5.2 g (75%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.53 (s, 12H, CH_3), 2.61 (s, 12H, CH_3), 2.71 (t, ^3J = 7.0, 6.8 Hz, 4H, CH_2S), 3.27 (t, ^3J = 7.0, 6.8 Hz 4H, CH_2N_{gua}). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 38.7 (CH_3), 39.5 (CH_3), 42.3 (CH_2S), 48.8 (CH_2N_{gua}), 165.6 (C_{gua}). IR (KBr, ν [cm^{-1}]): 2921m, 2873m, 1657vs (ν (C=N)), 1482m, 1444m, 1390m, 1345w, 1262s, 1216s. EI-MS (m/z (%)): 449.3 (4) [MH^+], 251.1 (4), 207.1 (86) [MH^+-$(CH_2)_2NC(N(CH_3)_2)_2$], 174.1 [MH^+-$S(CH_2)_2$-$NC(N(CH_3)_2)_2$], 142.1 (90) [$(CH_2)_2NC(N(CH_3)_2)_2^+$], 128.1 (98) [$CH_2NC(N(CH_3)_2)_2^+$], 108.0 (68), 98.0 (73), 85.0 (100), 71.1 (88), 44.0 (68).

*4.2.2.46. 2,2-Disulfandiyl-bis(N-(1,3-dimethylimidazolidine-2-ylidene)-ethaneamine) (**L23-2**).* Following the general procedure, 3.05 g (0.02 mol) of 2,2′-disulfanediyldiethaneamine was used. The final product was obtained as brown oil. Yield: 5.2 g (63%).

^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.53 (s, 12H, CH_3), 2.70 (t, ^3J = 7.4, 7.2 Hz, 4H, CH_2S), 2.89 (s, 8H, CH_2), 3.41 (t, ^3J = 7.4, 7.2 Hz, 4H, CH_2N_{gua}). ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C, δ [ppm]): 36.2 (CH_3), 42.3 (CH_2S), 47.2 (CH_2N_{gua}), 49.2 ($^{gua}CH_2$), 161.8 (C_{gua}). IR (KBr, ν [cm^{-1}]): 2989w, 2983s, 2799m, 1604vs (ν (C=N)), 1505s (ν (C=N)), 1444m, 1368s, 1307w, 1231m, 1139s, 1063m. EI-MS (m/z (%)): 344.2 (3) [M^+], 244.1 (3), 205.1 (86) [M^+-$(CH_2)_2NC(NCH_3)_2(CH_2)_2$], 172.1 (81) [$M^+S(CH_2)_2NC(NCH_3)_2(CH_2)_2^+$], 140.0 (88) [$(CH_2)_2NC(NCH_3)_2$-$(CH_2)_2^+$], 126.1 (100) [$CH_2NC(NCH_3)_2(CH_2)_2^+$], 106.0 (38), 85.0 (23), 69.0 (56), 56.1 (85), 44.0 (78), 28.0 (28).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2015.03.015.

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