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Catalytic Cycloaminomethylation of Aminobenzamides with 1,3-Bis[dimethylamino(methoxy)methyl]thiourea

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Abstract—Efficient methods of the synthesis of cyclophanes containing the thiourea moiety via the reaction of *o-, m-*, and *p*-aminobenzamides with 1,3-bis(dimethylaminomethyl)thiourea or 1,3-bis(methoxymethyl)thiourea using $NiCl_2 \cdot 6H_2O$ and $SmCl_3 \cdot 6H_2O$ as catalysts have been developed.

Keywords: cycloaminomethylation; aminobenzamides; bis(*N,N*-dimethylamino)methane; thiourea; cyclophanes

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Classical method for the synthesis of cyclic aminomethylated carboxamides consists in the condensation of carboxamides with formaldehyde and NH-acids [1–6]. The two-component condensation of amines with 1,3-di(methylol)urea or 1,3-di(methylol)thiourea is an efficient method of preparation of aminomethylated carboxamides [6, 7].

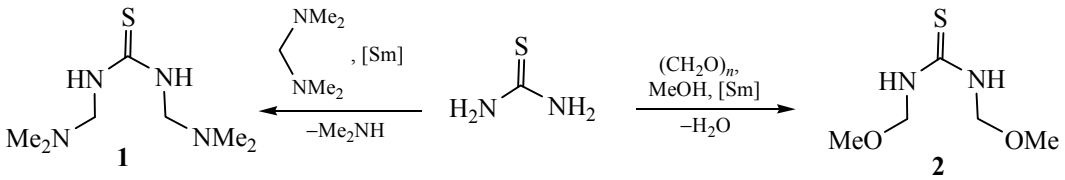
Cyclic thiocarbamides exhibit complex-forming [8] and transfection properties [9], possess antioxidant [10], antiviral, and antibacterial activity [5, 11]. Derivatives of aminobenzamides display antitumor [12–14] and antibacterial activity [15] and are promising activators of enzyme glucokinase [16, 17] and luminescence markers in biological systems [18].

Extending our studies on catalytic aminomethylation of carboxamides [19–22] and on efficient approaches to the synthesis of cyclophanes containing a thiocarbamide fragment, we studied the reaction of 1,3-bis(dimethylaminomethyl)thiourea and 1,3-bis(methoxymethyl)thiourea with *o*-, *m*-, and *p*-aminobenzamides, as well as aminomethylation of the latter with thiourea and bis(*N,N*-dimethylamino)methane or paraform catalyzed by the compounds of transition and rare-earth metals.

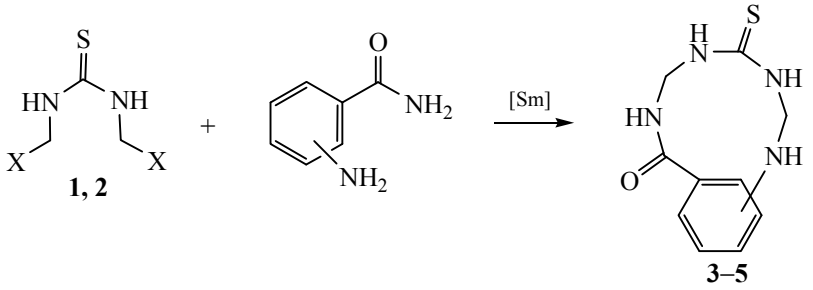
Aminomethylating reagents, 1,3-bis(dimethylaminomethyl)thiourea **1** [19] and 1,3-bis(methoxymethyl)-thiourea **2**, were obtained via the reaction of thiourea with bis(*N,N*-dimethylamino)methane in ethanol or with paraform in methanol, the reagents ratio being thiourea : bis(*N,N*-dimethylamino)methane (paraform) : $SmCl_3 \cdot 6H_2O$ = 10 : 20 : 0.5, at 80°C, for 8 h (Scheme 1).

Using the reaction of cycloaminomethylation of *o*-aminobenzamide with 1,3-bis(dimethylaminomethyl)-thiourea **1** (aminobenzamide : **1** : [cat] = 10 : 10 : 2, 70°C, EtOH, 24 h) as an example, we found that,

Scheme 1.



Scheme 2.



X = NMe_2 (**1**), OMe (**2**); *ortho*- (**3**), *meta*- (**4**), *para*- (**5**).

unlike the case of 1,3-bis(dimethylaminomethyl)urea [22], the reaction proceeded with the formation of 4-thioxo-2,3,4,5,6,7-hexahydro-1,3,5,7-benzotetraazecin-8(1*H*)-one **3** in 40 ($NiCl_2 \cdot 6H_2O$), 36 ($SmCl_3 \cdot 6H_2O$), 30 [$Sm(NO_3)_3 \cdot 6H_2O$], and 29% [$Ni(NO_3)_2 \cdot 6H_2O$] yield (Scheme 2). Cycloaminomethylation of *o*-aminobenzamide with 1,3-bis(methoxymethyl)thiourea **2** gave compound **3** in 37 ($SmCl_3 \cdot 6H_2O$), 30 [$Sm(NO_3)_3 \cdot 6H_2O$], 15 ($NiCl_2 \cdot 6H_2O$), and 12 % [$Ni(NO_3)_2 \cdot 6H_2O$] yield (Scheme 2). The reaction did not occur in the absence of a catalyst.

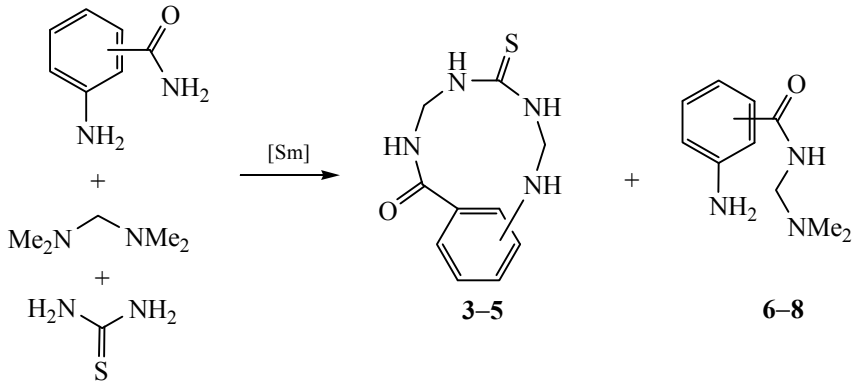
Cycloaminomethylation of *m*- and *p*-aminobenzamides with the aminomethylating reagents **1** and **2** under similar conditions [aminobenzamide : **1**(**2**) : $NiCl_2 \cdot 6H_2O$ ($SmCl_3 \cdot 6H_2O$) = 10 : 10 : 2, 70°C, EtOH, 24 h] led the formation of 5-thioxo-2,4,6,8-tetraazabicyclo[8.3.1]tetradeca-1(14),10,12-trien-9-one **4** and 5-thioxo-2,4,6,8-tetraazabicyclo[8.2.2]tetradeca-1(12),10,13-trien-9-one **5** in 40 (42%) and 39 (40%) yield, respectively (Scheme 2).

One of the methods for the synthesis of the heterocycles containing thiourea fragments is the three-component condensation of bis(*N,N*-dimethylamino) methane, (thio)urea, and NH-acids [19, 20]. In continuation of earlier studies of aminomethylation of ureas [21, 22], we studied the reaction of aminobenzamides cycloaminomethylation with bis(*N,N*-dimethylamino)methane (paraform) and thiourea in the presence of the catalysts, which had demonstrated the highest activity.

The aminomethylation of *o*-, *m*-, and *p*-aminobenzamides with bis(*N,N*-dimethylamino)methane and thiourea at the aminobenzamide : bis(*N,N*-dimethylamino)methane : thiourea : $NiCl_2 \cdot 6H_2O$ ratio of 10 : 20 : 10 : 2 (70°C, EtOH, 24 h) resulted in the formation of compounds **3–5** in 45, 50, and 40% yield, respectively (Scheme 3). Under the conditions of the reaction of aminomethylation of thiourea, as in the case of urea [22], 2-(3-,4-)-amino-*N*-[(dimethylamino)-methyl]benzamides **6–8** were formed in the yield not exceeding 15%. No aminomethylation reaction occurred in the absence of catalyst.

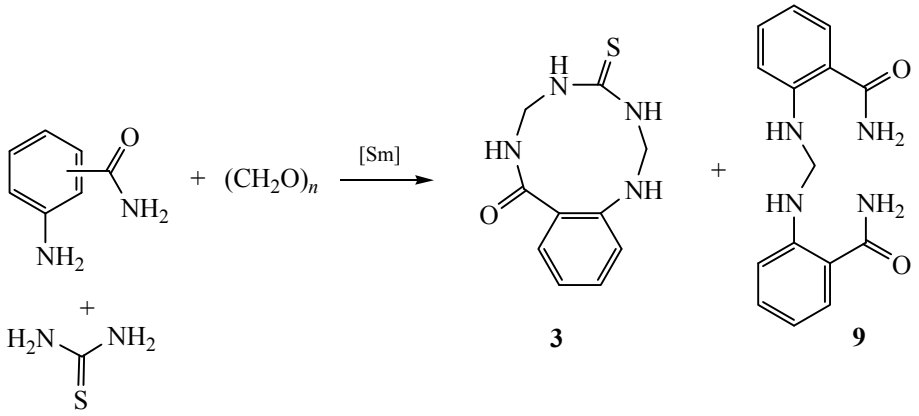
The chemoselectivity of the three-component reaction was found dependent on the order of the

Scheme 3.



ortho- (**3**, **6**), *meta*- (**4**, **7**), *para*- (**5**, **8**).

Scheme 4.



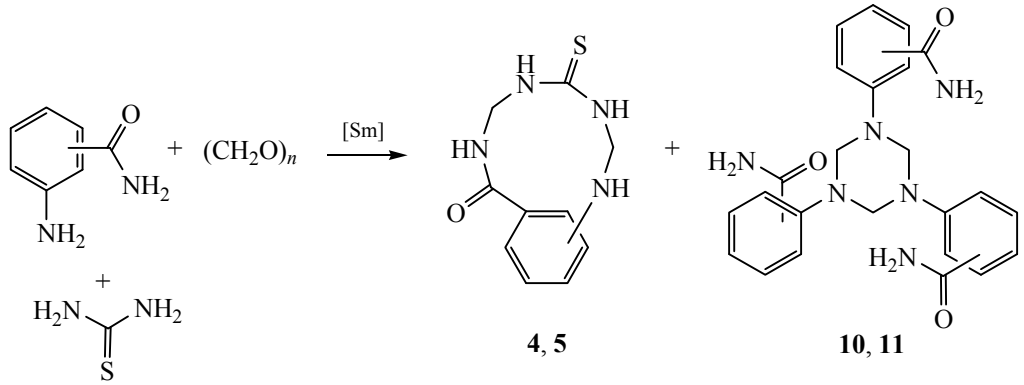
reagents mixing. For example, successive mixing of *o*-aminobenzamide with paraform and then with thiourea led to the formation of 2-({[2-(aminocarbonyl)phenyl]-amino}methylamino)benzamide **9** in ~70% yield, and the product did not further react with thiourea (Scheme 4). However, successive mixing of paraform with thiourea and then with *o*-aminobenzamide under the same conditions (paraform:thiourea : aminobenzamide : $SmCl_3 \cdot 6H_2O$ = 20 : 10 : 10 : 2, 70°C, MeOH, 24 h) yielded bicyclic compound **3** in 60% yield (Scheme 4).

Aminomethylation of *m*- and *p*-aminobenzamides with paraform and thiourea [paraform : thiourea : aminobenzamide : $SmCl_3 \cdot 6H_2O$ = 20 : 10 : 10 : 2, 70°C, MeOH, 24 h] gave cyclophanes **4** and **5** in 59 and 43% yield, respectively. Under those conditions, the formation of *sym*-1,3,5-triazinanes **10** and **11** was observed in the yields not exceeding 20% (Scheme 5).

The structure of compounds **3–5** was determined by means of NMR and IR spectroscopy as well as mass spectrometry. MALDI TOF/TOF spectra of compounds **3–5** contained the peaks of molecular ions of associates $[M + H_2O - H]^+$ 253.203 (**3**), 253.221 (**4**), and 253.260 (**5**), respectively. Positive-ion chemical ionization mass spectra at atmospheric pressure (APCI) of compounds **3–5** showed the peaks of characteristic ions $[M–C_2H_4N_2S+H]^+$ with *m/z* 149 (Scheme 6) and weaker peaks $[M - C_2H_3N_2 + H]^+$ with *m/z* 164. In the case of compounds **4**, **5**, weak peaks of molecular ions $[M + H]^+$ with *m/z* 237 and the peaks of ions of associates with the solvent $[M - C_2H_4N_2S + CH_3OH + H]^+$ with *m/z* 181 were registered, their intensity in the spectrum of compound **5** being the highest. Besides, the negative-ion APCI mass spectra of compounds **3–5** contained the peaks of molecular ions $[M - H]^-$ with *m/z* 235.

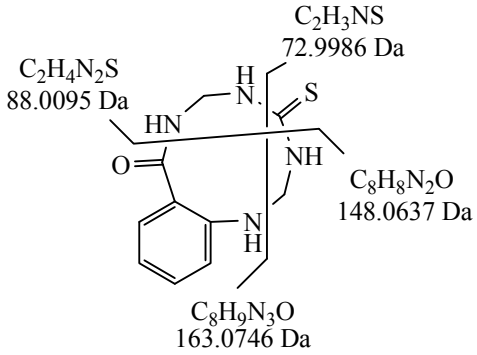
Broadened signals in the ^1H and ^{13}C NMR spectra of compounds **3–5** at δ_C ~ 66 and 52 ppm were assigned to carbon atom of the NCH_2N bond of the heterocycle. That broadening was apparently caused by slow (in the NMR timescale) conformational

Scheme 5.



meta- (**4**, **10**), *para*- (**5**, **11**).

Scheme 6.



transformations in the solution, similar to those discussed for the conformational analysis of macroheterocycle of 1,7-dithia-3,5-diazonan-4-thione with flattened N(C=S)N fragment [23].

The IR spectra of compounds **3–5** contained broadened absorption bands in the range of 1663–1648 cm^{-1}, corresponding to stretching of the (thio) carbonyl groups (Amide I band) and 1580–1505 cm^{-1} (Amide II band) from deformational vibrations of the C–N bond.

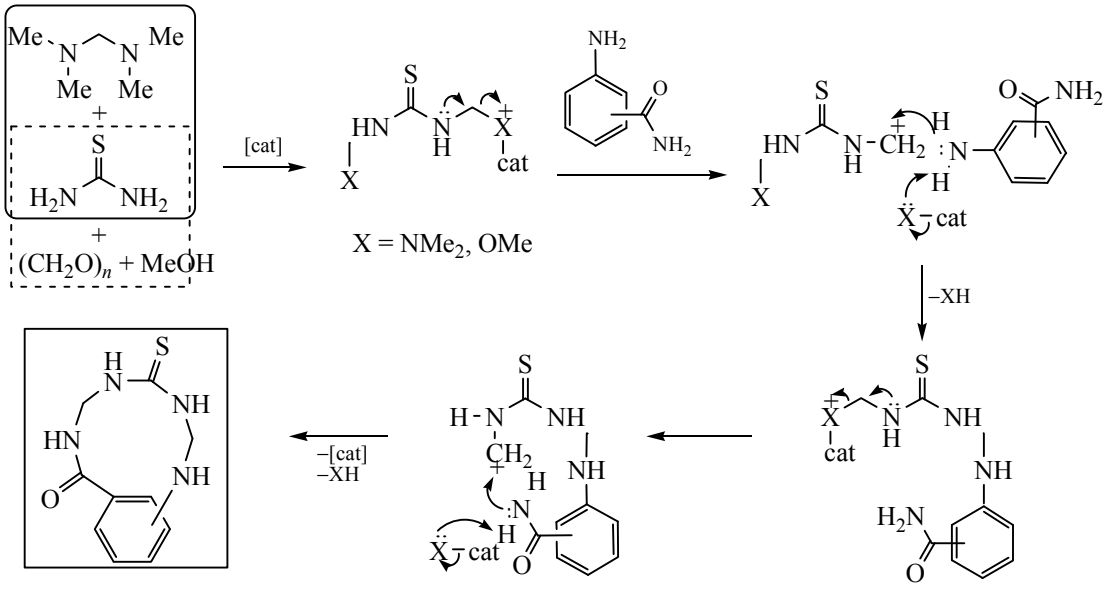
Under the conditions of the cycloaminomethylation of *o*-, *m*- or *p*-aminobenzamides with thiourea and bis-(*N,N*-dimethylamino)methane or paraform, first, apparently, 1,3-bis(dimethylaminomethyl)thiourea [19, 20] or 1,3-bis(methoxy)thiourea was formed, which was coordinated at the central atom ion of the catalyst [1, 24, 25]. Subsequent nucleophilic addition of the amino group to the formed carbocation led to the formation of new C–N bonds and assembling of the target heterocycles **3–5** according to Scheme 7.

In summary, the catalytic method for the synthesis of cyclophanes containing the thiourea motif via the reaction of cycloaminomethylation of *o*-, *m*- and *p*-aminobenzamides with 1,3-bis(dimethylaminomethyl)-thiourea and 1,3-bis(methoxymethyl)thiourea as well as with thiourea, bis(*N,N*-dimethylamino)methane, and paraform was developed.

EXPERIMENTAL

One-dimensional (^1H and ^{13}C), homo- (COSY) and heteronuclear (HSQC and HMBC) NMR experiments were performed using a Bruker Avance 400 spectrometer (100.62 and 400.13 MHz, respectively; solvent: DMSO-d_6). Mass spectra of compounds 1–11 were recorded using a MALDI TOF/TOF AUTOFLEX III Bruker instrument. The sample preparation for registration of the mass spectra was performed using the "dry drop" method. Mass spectra of compounds 1, 3, 5 were also obtained using an LCMS-2010 EV quadruple liquid chromato–mass spectrometer (Shimadzu) in the chemical ionization mode at atmospheric pressure (APCI), registering positive or negative ions with capillary potential 4.5 kV and –3.5 kV, respectively. IR spectra were recorded using a Bruker Vertex 70 v spectrometer

Scheme 7.



(suspension in Vaseline oil). Melting points were determined using a RNMK 80/2617 device. The reaction was monitored by TLC method on Sorbfil plates (PTCKh-AF-V) developed by iodine vapors. The KSK silica (100–200 μm) was used for column chromatography.

Aminomethylation (methoxymethylation) of thiourea with bis(*N*,*N*-dimethylamino)methane (paraform). 25 mmol of bis(*N*,*N*-dimethylamino)-methane (paraform) dissolved in 10 mL of ethanol (methanol) and 0.5 mmol $SmCl_3 \cdot 6H_2O$ were stirred for 5 min. Then, 10 mmol of thiourea dissolved in the mixture of solvents $CHCl_3$–EtOH (MeOH) = 1 : 1 was added, and the reaction mixture was stirred for 8 h at 40°C. Thiourea derivatives **1** and **2** were isolated from the reaction mass by column chromatography on silica.

1,3-[Bis(dimethylaminomethyl)thiourea (1) [19]. White amorphous substance, yield 99%, mp 76–80°C. MALDI TOF/TOF mass spectrum, *m/z* (I_{rel}, %): 229.374 $[M + K]^+$.

1,3-[Bis(methoxymethyl)thiourea (2). Colorless tarry substance, yield 95%, n_D^{20} 1.5000. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.18 br. s (6H, OC$\underline{H}_3$), 4.84 br. s (4H, HNC$\underline{H}_2$O), 8.34 br. s (2H, N$\underline{H}$). ^{13}C NMR spectrum, (DMSO-d_6), δ, ppm: 55.42 (O$\underline{C}$H$_3$), 75.80 (HN$\underline{C}$H$_2$O), 184.96 ($\underline{C}$=O). MALDI TOF/TOF, mass spectrum, *m/z* (I_{rel}, %): 203.112 $[M + K]^+$.

Aminomethylation of aminobenzamides. *a*. Mixture of 10 mmol of 1,3-bis(dimethylaminomethyl)-thiourea in 10 mL of EtOH, 2 mmol of $NiCl_2 \cdot 6H_2O$, and 10 mmol of aminobenzamide was stirred for 24 h at 80°C. The target products were isolated from the reaction mixture by column chromatography.

b. The reaction was performed similarly using 1,3-bis-(dimethylaminomethyl)thiourea, $SmCl_3 \cdot 6H_2O$, and MeOH.

c. Mixture of 10 mmol of thiourea, 10 mL of EtOH, and 20 mmol of bis(dimethyl-amino)methane was stirred for 1 h at 40°C, then 2 mmol of $NiCl_2 \cdot 6H_2O$ and 10 mmol of aminobenzamide dissolved in 5 mL of EtOH was added. The obtained mixture was stirred at 80°C for 12 h. The target products were isolated from the reaction mixture by column chromatography.

d. The reaction was performed similarly using thiourea, paraform, $SmCl_3 \cdot 6H_2O$, and MeOH.

4-Thioxo-2,3,4,5,6,7-hexahydro-1,3,5,7-benzo-tetraazecin-8(1*H*)-one (3). Yield 0.07 g (40%, method *a*), 0.06 g (37%, method *b*), 0.08 g (45%, method *c*), 0.10 g (60%, method *d*); cream colored amorphous powder, mp 44–48°C. IR spectrum, cm^{-1}: 3314, 2969–2850, 1648, 1610, 1580, 1492, 1380, 1259–1240, 1155, 1022, 756, 630. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.65 br. s (2H, HNC$\underline{H}_2$NH), 4.72 br. s (2H, HNC$\underline{H}_2$NH), 6.68 m (1H, $\underline{H}C_{Ar}$), 6.92 t (1H, $\underline{H}C_{Ar}$, ^3J = 7.5 Hz), 7.28 t (1H, $\underline{H}C_{Ar}$, ^3J = 7.5 Hz), 7.56 m (1H, $\underline{H}C_{Ar}$), 8.08, 8.56 and 8.90 br. s (4H, N$\underline{H}$). ^{13}C NMR spectrum, (DMSO-d_6), δ, ppm: 63.03 (HN$\underline{C}$H$_2$NH), 66.54 (HN$\underline{C}$H$_2$NH), 112.52 (Ph), 116.05 (Ph), 116.95 (Ph), 129.50 (Ph), 132.95 (Ph), 148.23 (Ph), 170.38 [$\underline{C}$(O)NH$_2$], 183.21 ($\underline{C}$=S). MALDI TOF/TOF mass spectrum, *m/z* (I_{rel}, %): 253.203 $[M + H_2O - H]^+$. Mass spectrum (APCI), *m/z* (I_{rel}, %): 149 (100) $[M - C_2H_4N_2S + H]^+$, 164 (26) $[M - C_2H_3NS + H]^+$; 147 (33) $[M - C_2H_4N_2S - H]^-$, 235 (12) $[M - H]^-$.

5-Thioxo-2,4,6,8-tetraazabicyclo[8.3.1]tetradeca-1(14),10,12-trien-9-one (4). Yield 0.07 g (40%, method *a*), 0.07 g (42%, method *b*), 0.09 g (50%, method *c*), 0.10 g (59%, method *d*); cream colored amorphous powder, mp 68–72°C. IR spectrum, cm^{-1}: 3468–3448, 2956–2871, 1663, 1618, 1550, 1458, 1384, 1195, 1142, 1076, 754, 690. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.55 br. s (2H, HNC$\underline{H}_2$NH), 4.69 br. s (2H, HNC$\underline{H}_2$NH), 6.85–6.90 m (2H, $\underline{H}C_{Ar}$), 7.05–7.17 m (2H, $\underline{H}C_{Ar}$), 6.68 and 9.00 br. s (4H, N$\underline{H}$). ^{13}C NMR spectrum, (DMSO-d_6), δ, ppm: 52.50 (HN$\underline{C}$H$_2$NH), 63.34 (HN$\underline{C}$H$_2$NH), 111.53 (Ph), 112.12 (Ph), 115.66 (Ph), 129.17 (Ph), 135.00 (Ph), 147.00 (Ph), 168.00 [$\underline{C}$(O)NH$_2$], 183.32 ($\underline{C}$=S). MALDI TOF/TOF mass spectrum, *m/z* (I_{rel}, %): 253.221 $[M + H_2O - H]^+$. Mass spectrum (APCI), *m/z* (I_{rel}, %): 149 (100) $[M - C_2H_4N_2S + H]^+$, 181 (19) $[M - C_2H_4N_2S + CH_3OH + H]^+$, 237 (9) $[M + H]^+$; 147 (97) $[M - C_2H_4N_2S - H]^-$, 235 (34) $[M - H]^-$.

5-Thioxo-2,4,6,8-tetraazabicyclo[8.2.2]tetradeca-1(12),10,13-trien-9-one (5). Yield 0.07 g (39%, method *a*), 0.07 g (40%, method *b*), 0.07 g (40%, method *c*), 0.07 g (43%, method *d*); cream colored amorphous powder, mp 65–70°C. IR spectrum, cm^{-1}: 3305, 2924–2854, 1656, 1606, 1505, 1462, 1377, 1260, 1136, 1059, 839, 768, 722. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.27 br. s (2H, HNC$\underline{H}_2$NH), 4.56 br. s (2H, HNC$\underline{H}_2$NH), 6.56 d (2H, HC_{Ar}, ^3J = 8.6 Hz), 7.62 d (2H, HC_{Ar}, ^3J = 8.6 Hz), 6.97 and 8.01 br. s (4H, N$\underline{H}$). ^{13}C NMR spectrum, (DMSO-d_6), δ, ppm: 51.92 (HN$\underline{C}$H$_2$NH), 66.76 (HN$\underline{C}$H$_2$NH), 113.02 (Ph), 122.52 (Ph), 129.15 (Ph), 151.37 (Ph), 168.67 [$\underline{C}$(O)NH$_2$], 183.28 ($\underline{C}$=S). MALDI TOF/TOF mass

spectrum *m/z* (I_{rel}, %): 253.260 $[M + H_2O - H]^+$. Mass spectrum (APCI), *m/z* (I_{rel}, %): 181 (100) $[M - C_2H_4N_2S + CH_3OH + H]^+$, 237 (5) $[M + H]^+$, 149 (22) $[M - C_2H_4N_2S + H]^+$, 164 (8) $[M - C_2H_3NS + H]^+$; 235 (17) $[M - H]^-$.

2-Amino-*N*-[(dimethylamino)methyl]benzamide (6). [22]. ^{1}H NMR spectrum, (DMSO-d_6), δ, ppm: 2.21 br. s (6H, NC$\underline{H}_3$), 4.06 br. s (2H, MeNC$\underline{H}_2$NH), 6.41 br. s (2H, N$\underline{H}_2$), 6.51 m (1H, $\underline{H}C_{Ar}$), 6.60 m (1H, $\underline{H}C_{Ar}$), 7.11 t (1H, $\underline{H}C_{Ar}$, ^3J = 8.3 Hz), 7.48 m (1H, $\underline{H}C_{Ar}$), 8.08 br. s (1H, N$\underline{H}$). ^{13}C NMR spectrum, (DMSO-d_6), δ, ppm: 41.96 (N$\underline{C}H_3$), 60.98 (HN$\underline{C}H_2$NMe), 112.52 (Ph), 115.30 (Ph), 116.45 (Ph), 129.13 (Ph), 132.60 (Ph), 150.34 (Ph), 171.92 [$\underline{C}$(O)NH$_2$]. MALDI TOF/TOF mass spectrum, *m/z* (I_{rel}, %): 193.188 $[M]^+$.

3-Amino-*N*-[(dimethylamino)methyl]benzamide (7) ([22]). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.27 br. s (6H, NC$\underline{H}_3$), 4.11 br. s (2H, MeNC$\underline{H}_2$NH), 6.89–7.30 m (4H, HC_{Ar}), 6.43 br. s (1H, N$\underline{H}$). ^{13}C NMR spectrum, (DMSO-d_6), δ, ppm: 42.22 (N$\underline{C}H_3$), 61.46 (HN$\underline{C}H_2$NMe), 113.36 (Ph), 114.97 (Ph), 115.66 (Ph), 129.26 (Ph), 135.51 (Ph), 149.12 (Ph), 168.23 [$\underline{C}$(O)NH$_2$]. MALDI TOF/TOF mass spectrum, *m/z* (I_{rel}, %): 192.941 $[M]^+$.

4-Amino-*N*-[(dimethylamino)methyl]benzamide (8) ([22]). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.21 br. s (6H, NC$\underline{H}_3$), 4.06 br. s (2H, MeNC$\underline{H}_2$NH), 6.71 d (2H, HC_{Ar}, ^3J = 8.5 Hz), 7.68 d (2H, HC_{Ar}, ^3J = 8.5 Hz), 8.43 br. s (1H, N$\underline{H}$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 42.28 (N$\underline{C}H_3$), 61.50 (HN$\underline{C}H_2$NMe), 112.17 (Ph), 121.77 (Ph), 129.29 (Ph), 150.63 (Ph), 167.46 [$\underline{C}$(O)NH$_2$]. MALDI TOF/TOF mass spectrum, *m/z* (I_{rel}, %): 232.100 $[M + K]^+$.

2-({[2-(Aminocarbonyl)phenyl]amino}methyl-amino)benzamide (9). Yield 0.07 g (70%, method *b*), white amorphous substance, mp 158–162°C. IR spectrum, cm^{-1}: 3374, 3178, 2923–2854, 1615, 1577, 1462, 1377, 1276, 1155, 1061, 743, 636. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.72 t (2H, HNC$\underline{H}_2$NH, ^3J = 4.0 Hz), 6.58 t (2H, $\underline{H}C_{Ar}$, ^3J = 8.0 Hz), 6.86 d (2H, $\underline{H}C_{Ar}$, ^3J = 8.0 Hz), 7.28 t (2H, $\underline{H}C_{Ar}$, ^3J = 8.0 Hz), 7.59 d (2H, $\underline{H}C_{Ar}$, ^3J = 8.0 Hz), 7.13 and 7.82 br. s (4H, N$\underline{H}_2$), 8.59 t (2H, $\underline{H}$N, ^3J = 6.0 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 51.63 (HN$\underline{C}H_2$NH), 112.27 (Ph), 115.06 (Ph), 115.32 (Ph), 129.53 (Ph), 132.93 (Ph), 148.94 (Ph), 171.88 [$\underline{C}$(O)NH$_2$]. MALDI TOF/TOF mass spectrum, *m/z* (I_{rel}, %): 283.260 $[M - H]^+$.

1,3,5-[3-(Aminocarbonyl)phenyl]-1,3,5-triazinane (10). Yield 0.02 g (20%, method *d*), white amorphous substance, mp 86–94°C. IR spectrum, cm^{-1}: 3375–3170, 2924–2854, 1615, 1578, 1461, 1377, 1277, 1153, 1060, 742, 633. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.01 br. s (6H, HNC$\underline{H}_2$NH), 7.07–7.16 m (6H, $\underline{H}C_{Ar}$), 7.25 m (3H, $\underline{H}C_{Ar}$), 7.31 m (3H, $\underline{H}C_{Ar}$), 6.85 br. s (6H, N$\underline{H}_2$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 67.42 (HN$\underline{C}H_2$NH), 112.07 (Ph), 116.33 (Ph), 119.76 (Ph), 129.28 (Ph), 135.43 (Ph), 148.54 (Ph), 168.53 [$\underline{C}$(O)NH$_2$]. MALDI TOF/TOF mass spectrum, *m/z* (I_{rel}, %): 467.227 $[M + Na]^+$, 483.186 $[M + K]^+$.

1,3,5-[4-(Aminocarbonyl)phenyl]-1,3,5-triazinane (11). Yield 5%, method *b*. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.60 br. s (6H, HNC$\underline{H}_2$NH), 6.72 m (6H, $\underline{H}C_{Ar}$), 7.64 m (6H, $\underline{H}C_{Ar}$), 7.08 br. s (6H, N$\underline{H}_2$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 68.25 (HN$\underline{C}H_2$NH), 112.30 (Ph), 123.75 (Ph), 129.60 (Ph), 150.34 (Ph), 169.34 [$\underline{C}$(O)NH$_2$]. MALDI TOF/TOF mass spectrum, *m/z* (I_{rel}, %): 467.437 $[M + Na]^+$.

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CONFLICT OF INTEREST

No conflict of interest was declared by authors.

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