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A NEW COPPER-CATALYZED PATHWAY TO BENZO AND PYRIDYL FUSED IMIDAZO-, TRIAZOLO- AND PYRIMIDO-THIAZINES

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ABSTRACT:

A simple one flask method for the selective preparation of benzo and pyridyl fused imidazo[2,1-*b*][1,3]thiazines, [1,2,4]triazolo[5,1-*b*][1,3]thiazines, and pyrimido[2,1-*b*][1,3]thiazin-6-ones from corresponding thiols and o-halobenzyl bromides or 2-bromo-3-chloromethylpyridine in the system solid KOH / CuI / TBAB / DMF has been developed.

Keywords: copper catalysis, imidazo[2,1-*b*][1,3]thiazines, [1,2,4]triazolo[5,1-*b*][1,3]thiazines, and pyrimido[2,1-*b*][1,3]thiazin-6-ones

INTRODUCTION

Imidazothiazines and pyrimidothiazines are of great interest as biologically active compounds.[1-3] Common methods for the preparation of imidazothiazine[4] and pyrimidothiazine[5] ring systems were described in reviews. Among known methods for the preparation of imidazo[1,2-*a*][3,1]benzothiazine it is necessary to mention the thermal cyclization of 2-aminobenzothiazine pyruvate salts.[6] 2-[(Pentafluorophenyl)methylthio]benzimidazole undergoes cyclization to tetrafluorobenzimidazobenzothiazine in the presence of NaH in THF.[7] 5*H*-Benzo[4,5][1,3]thiazino[2,3-*b*]quinazolin-12-one was obtained from 2-(2-hydroxymethylphenyl)-2-mercapto-3*H*-quinazolin-4-one in the presence of dry HCl / EtOH.[8]

However, there is no simple and general procedure for the synthesis of benzo and pyridyl fused imidazo[2,1-*b*][1,3]thiazines, [1,2,4]triazolo[5,1-*b*][1,3]thiazines, and pyrimido[2,1-*b*][1,3]thiazin-6-ones.[9]

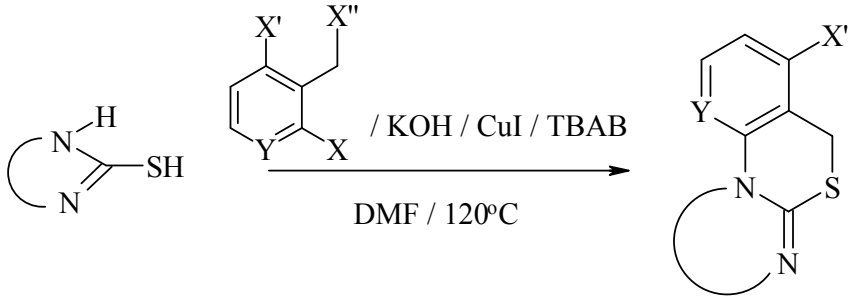
The high activity of copper(0)[10], copper (I)[11, 12] or copper (II)[13] catalysts in N-arylation of imidazole and related heterocycles were presented in literature. Beside this the combination of alkali bases with TBAB as phase transfer catalyst[14] were demonstrated in some recent articles. Recently synthesis of substituted imidazo[1,2-*a*][3,1]benzothiazines by Cu-catalyzed reaction in the presence of proline ligand was also described [15].

RESULTS AND DISCUSSION

Herein we report a novel and simple copper-catalyzed ligandless method for the preparation of imidazo[2,1-b][1,3]thiazines **1a, 2a,b,c, 3a,a'**, [1,2,4]triazolo[5,1-b][1,3]thiazines **4a** and **5a**, and pyrimido[2,1-b][1,3]thiazin-6-ones **6a-8a** from corresponding thiols o-halobenzyl bromides or 2-bromo-3-chloromethylpyridine (Scheme 1). Our previous experiments showed that in the synthesis of all above heterocycles the best base was solid KOH.
Synthesis of compounds **1c-8c, 2d,e, 3c'** was carried out using two step one flask method: the highly selective S-alkylation of thiols **1-8** in the presence of KOH, followed by Cu(I)-catalyzed cyclization of (2-halophenylsulfanyl)hetarene intermediates.

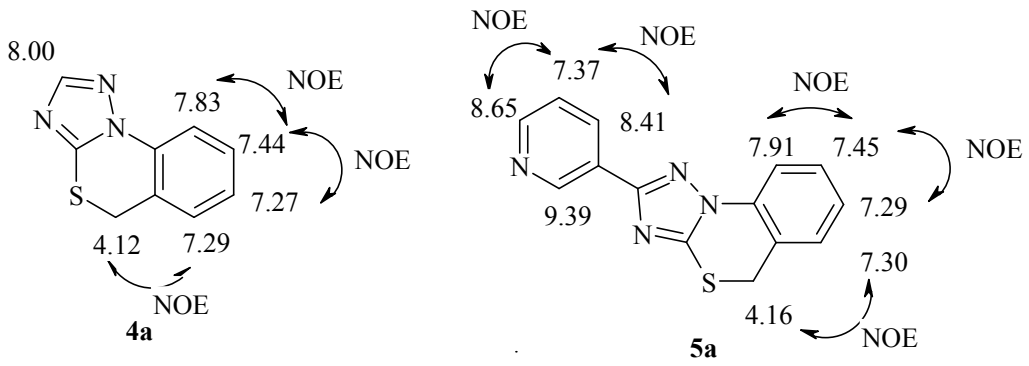
Thus, the treatment of 2-mercaptoimidazole (**1**) and 2-mercaptobenzimidazole (**2**) with 2-iodobenzyl bromide, solid KOH (1 equivalent) in DMF, and then with solid KOH (3 equivalents) and CuI (20 mol. %) afforded proposed products in 68 and 74% yields, correspondingly (Table 1, entries 1 and 2). Interestingly, that cyclization of compound **2** with 2-bromomethyl-1-chloro-3-fluorobenzene led to chlorine containing product **2b** in 29% yield (entry 3). Fluorine containing **2b'** product was detected only in trace amounts by LC-MS spectra. It means that substitution of fluorine in the Cu-catalyzed cyclization was preferable under studied conditions. Reaction of thiol **2** with 2-bromo-3-chloromethylpyridine in the system solid KOH / CuI / TBAB / DMF leads to fused thiopyrano[4,3-*b*]pyridine **2c** in 81% yield (entry 4). Treatment of 5-methyl-2-mercaptobenzimidazole **3** with 2-iodobenzyl bromide afforded 1:1 mixture of unseparatable isomeric products **3a** and **3a'** in overall yield 90% (entry 5).

The interaction of triazole thiols **4** and **5** with 2-iodobenzyl bromide leads to products **4a** and **5a** in 70 and 85% yield, correspondingly (entries 6, 7). Structure of products **4a** and **5a** were assigned by NOESY experiments to clarify the regioselectivity of the process. In the 2D NOESY spectra of both compounds cross correlation peaks were detected (Scheme 2). Beside this no correlation peaks were found between pyridine and benzene rings in compound **5a**. It clearly indicates the correct structure of products **4a** and **5a** illustrated in Scheme 2.



1-8 **1-8a, 2b, 2c**

Scheme 1



Scheme 2

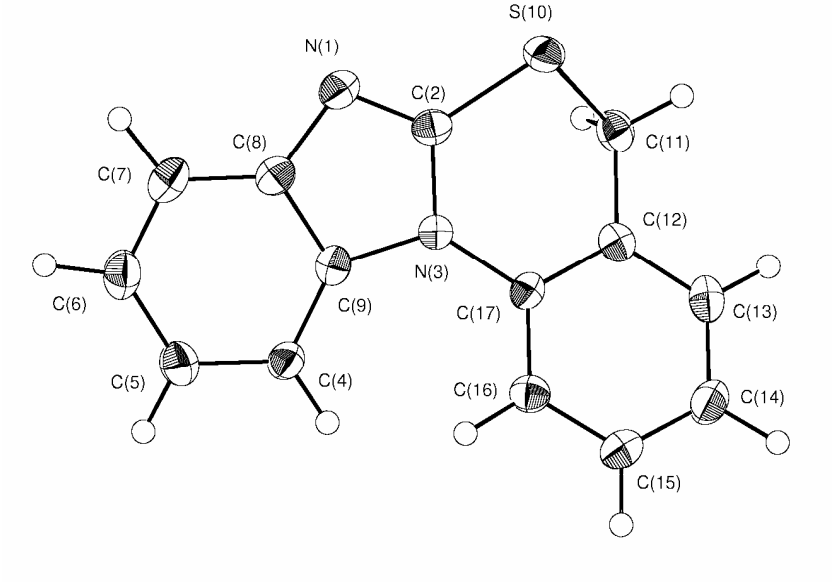


Figure 1. ORTEP molecular structure of the compound **2a**.

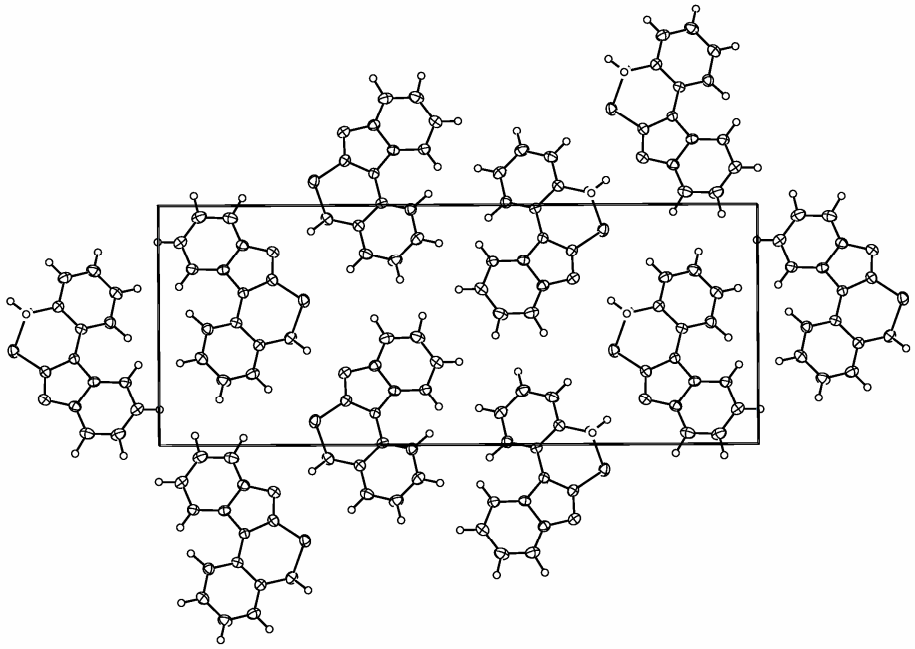


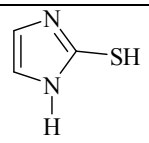
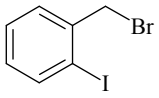
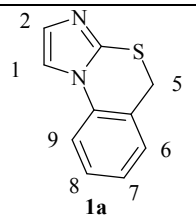
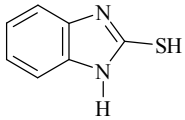
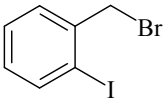
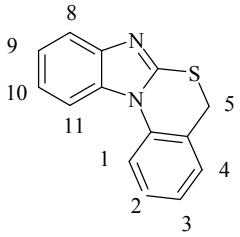
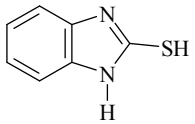
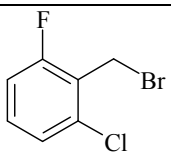
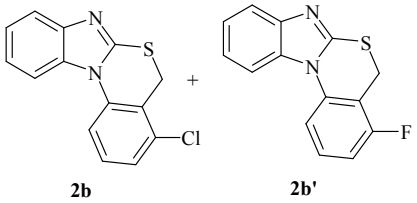
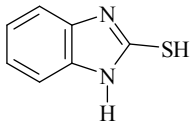
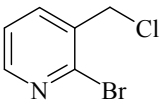
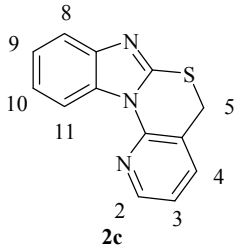
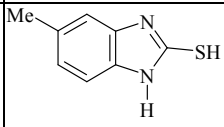
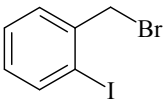
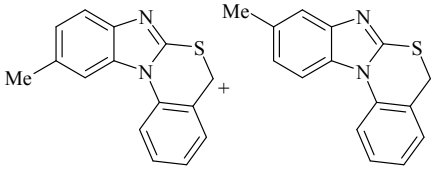
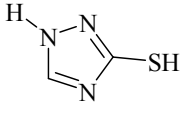
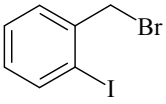
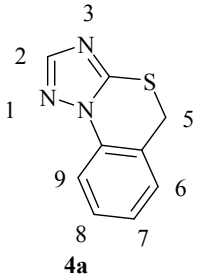
Figure 2. Molecular packing of **2c** viewed down the crystallographic axis **a**.

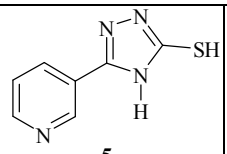
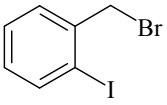
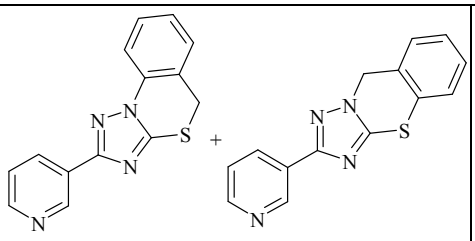
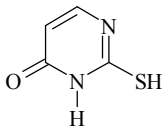
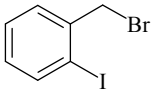
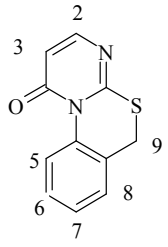
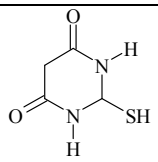
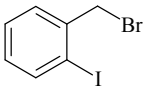
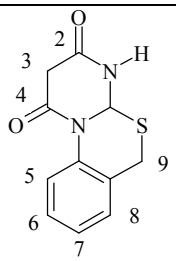
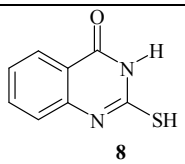
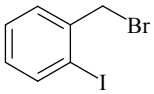
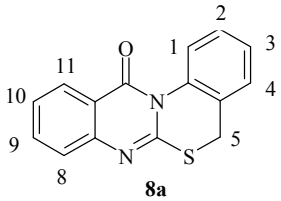
Structure of compound **2a** was confirmed by X-Ray structural data. Figure 1 illustrates a view of the molecule **2a**, showing the thermal ellipsoids and the atom-numbering scheme followed in the text. The cycle of S(10)–C(11)–C(12)–C(17)–N(3)–C(2) is characterized by twist-conformation; all the other cycles in the molecule are planar. The molecular conformation apparently cannot be planar due to repulsion of the hydrogen atoms at C(4) and C(16). Therefore, the molecule has a helical conformation: the atoms are arranged approximately on the surface of a helicoids, the parameter (step) of it is equal 0.96 Å. Thus, molecules of **2a** are chiral even though there are no asymmetric atoms. The crystal structure of **2a** has both enantiomers related to each other by centers of inversion and glide planes. Projection of the crystal structure of **2a** viewed along the small lattice parameter a is shown in Figure 2.

The above procedure was successfully used in the synthesis of substituted pyrimido[2,1-b][1,3]thiazin-6-ones **6a-8a** from corresponding thiols **6-8**. Products **6a-8a** were isolated in 32-49% yield (Table 1, entries 8-10).

In summary, unexpected high selectively of triazole containing products ([1,2,4]triazolo[5,1-b][1,3]thiazines **4a** and **5a**) was obtained using the above method.

Table 1. Cu-catalyzed synthesis of fused thiazines **1a-8a, 2b, 2c** in the system *o*-halobenzyl bromides / solid KOH / CuI / TBAB / DMF at 120°C.

Entry	Starting thiol	Halide	Products	Reaction time, h	Yield, %
1	 **1**		 **1a**	12	68
2	 **2**		 **2a**	2 0	74
3	 **2**		 **2b** **2b'**	17	29 (**2b**) traces (**2b**')
4	 **2**		 **2c**	19	81
5	 **3**		 **3a** **3a'**	19	45 (**3a**) 45 (**3a'**)
6	 **4**		 **4a**	12	70

7	 **5**		 **5a** **5a'**	24	85 **(5a)** traces **(5a')**
8	 **6**		 **6a**	12	34
9	 **7**		 **7a**	12	49
10	 **8**		 **8a**	12	32

EXPERIMENTAL SECTION

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury BB 400 MHz in $CDCl_3$ using HMDS as internal standard. LC-MS spectra were recorded on Alliance Waters 2695 instrument and Waters 3100 mass detector. HR-MS spectra were performed on Micromass *Q-TOF* Micro quadrupole-time of fight high resolution mass spectrometer. Leucine enkephalin was used as internal lock mass for accurate mass calculation. Thiols, *o*-halobenzyl bromides, Bu_4NBr and CuI (Acros and Aldrich) were used without additional purification.

Typical procedure for the synthesis of fused thiazines 1a-8a, 2b,c, 3a'. Solid KOH (0.097 g, 1.5 mmol) was added to the solution of thiols **1-8** (1.5 mmol) and *o*-halobenzyl halides (1.5 mmol) in dry DMF (10 ml) in a glass reactor (50 ml) under argon. After 1 h stirring at 100 ^{o}C solid KOH (0.29 g, 4.5 mmol), CuI (0.057g, 0.3 mmol) and TBAB (0.097 g, 0.3 mmol) were added. The reaction mixture was stirred at 120^{o}C (TLC-control, see Table 1) under argon. The solvent was removed under reduced pressure and crude residue was chromatographed on silica

using hexane : ethyl acetate (from 4:1 to 0:1) or DCM : EtOH in different mixtures as eluent. Spectroscopic data of obtained compounds were as followed.

Imidazo[1,2-*a*][3,1]benzothiazine (**1a**); Oil; LC-MS, 189 (M^++1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.01 (s, 2H, SCH_2), 7.14 and 7.49 (both d, total 2H, J = 3.0Hz, imidazole protons), 7.22 (m, 1H, H-7), 7.30 (m, 1H, H-9), 7.33 (m, 1H, H-6), 7.39 (m, 1H, H-8); ^{13}C NMR (100.58 MHz, $CDCl_3$) δ (ppm): 29.93 (SCH_2), 115.91, 117.76, 124.14, 126.03, 128.08, 128.89, 129.92, 134.90, 140.44.

Benzoimidazo[1,2-*a*][3,1]benzothiazine (2a); M.p. 125^{o}C; LC-MS, 240 (M^++2); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.05 (s, 2H, SCH_2), 7.29 (m, 1H, H-3), 7.30-7.35 (m, 2H, H-9 and H-10), 7.42 (m, 1H, H-H-4), 7.48 (m, 1H, H-2), 7.76 (m, 1H, H-8), 7.83 (m, 1H, H-11), 7.86 (m, 1H, H-1); ^{13}C NMR (100.58 MHz, $CDCl_3$) δ (ppm): 30.43 (CH_2), 111.36, 118.18, 119.51, 123.00, 123.42, 125.75, 125.83, 128.10, 128.91, 132.61, 135.45, 143.92, 150.64. Found, *m/z* (EI): 239.0650 $[M+H]^+$. $C_{14}H_{11}N_2S$. Calculated, *m/z*: 239.0643.

4-Chlorobenzoimidazo[1,2-*a*][3,1]benzothiazine (2b); M.p. 112^{o}C; LC-MS, 273 (M^++1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.25 (s, 2H, SCH_2), 7.30-7.43 and 7.7-7.8 (both m, total 7H, aromatic); ^{13}C NMR (100.58 MHz, $CDCl_3$) δ (ppm): 26.82 (CH_2), 111.35, 116.82, 119.68, 123.23, 123.77, 124.49, 126.76, 129.19, 132.64, 132.94, 136.80, 144.05, 150.61. Found, *m/z* (EI): 273.0245 $[M+H]^+$. $C_{14}H_{10}ClN_2S$. Calculated, *m/z*: 273.0253.

5H-6-Thia-1,7,11b-triazabenzo[c]fluorene (2c); M.p. 184-185^{o}C; LC-MS, 240 (M^++1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.11 (s, 2H, CH_2), 7.21 (m, 1H, H-3), 7.31 (m, 1H, H-10), 7.34 (m, 1H, H-9), 7.69 (m, 1H, H-8), 7.70 (m, 1H, H-4), 8.49 (m, 1H, H-11), 8.51 (m, 1H, H-2); ^{13}C NMR (100.58 MHz, $CDCl_3$) δ (ppm): 28.94 (CH_2), 114.93, 118.55, 118.76, 120.80, 123.58, 123.79, 132.95, 136.13, 143.51, 147.80, 148.77, 148.98. Found, *m/z* (EI): 240.0607 $[M+H]^+$. $C_{13}H_{10}N_3S$. Calculated, *m/z*: 240.0595.

10-Methylbenzoimidazo[1,2-*a*][3,1]benzothiazine and 9-methylbenzoimidazo[1,2-a][3,1]benzothiazine (3a, 3a'); LC-MS, 254 (M^++1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.49 (s, 3H, Me, **3a**), 2.53 (s, 3H, Me, **3a'**) 4.03 (s, 2H, SCH_2), 7.12-7.16, 7.25-7.30, 7.39-7.53, 7.61-7.70, 7.82-7.87 (all m, total 7H, aromatic).

[1,2,4]Triazolo[1,5-*a*][3,1]benzothiazine (**4a**); M.p. 120-121^{o}C; LC-MS, 190 (M^++1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.13 (s, 2H, SCH_2), 7.27, 7.29, 7.44 and 7.83 (all m, total 4H, aromatic H-6, H-7, H-8 and H-9), 8.00 (s, 1H, triazole proton); ^{13}C NMR (100.58 MHz, $CDCl_3$) δ (ppm): 29.24 (SCH_2), 118.01 (C-9), 121.60 (C-5a), 127.11 (C-7), 127.62 (C-6), 129.30 (C-8), 134.60 (C-9a), 149.80 (C-3a), 151.89 (C-2). Found, *m/z* (EI): 190.0437 $[M+H]^+$. $C_9H_8N_3S$. Calculated, *m/z*: 190.0439.

2-(3-Pyridyl)-[1,2,4]triazolo[1,5-*a*][3,1]benzothiazine (5a); M.p. 154-155^{o}C; LC-MS, 267 (M^++1)*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.16 (s, 2H, SCH_2), 7.29, 7.30, 7.45, 7.91 (all m, total 4H, H-7, H-6, H-8 and H-9), 7.37, 8.41, 8.65 and 9.39 (all m, total 4H, pyridyl H-5', H-4', H-6' and H-2'); ^{13}C NMR (100.58 MHz, $CDCl_3$) δ (ppm): 29.21 (SCH_2), 118.04 (C-9), 121.42 (C-9), 121.42 (C-5a), 123.42 (C-5'), 126.29 (C-3'), 127.17 (C-7), 127.67 (C-6), 129.38 (C-8), 133.76 (C-4'), 134.56 (C-9a), 148.04 (C-2'), 150.51 (C-6'), 150.83 (C-3a), 160.03 (C-2). Found, *m/z* (EI): 267.0703 $[M+H]^+$. $C_{14}H_{10}N_4S$. Calculated, *m/z*: 267.0704.

2-(3-Pyridyl)-4H-[1,2,4]triazolo[1,5-*b*][1,3]benzothiazine (**5a'**); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.42 (s, 2H, NCH_2), 7.3-7.5, 7.89 and 8.61 (all m, total 7H, aromatic and pyridine 2'-H, 4'-H and 5'-H), 9.29 (m, 1H, pyridine 6'-H).

9H-10-Thia-1,4a-diazaphenanthren-4-one (6a); M.p. 133-134°C; LC-MS, 217 (M^++1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.95 (s, 2H, SCH_2), 6.35 and 7.69 (both d, total 2H, J = 8 Hz, pyrimidine), 7.2-7.4 (m, 3H, H-6, H-7 and H-8), 7.92 (m, 1H, H-H-5); ^{13}C NMR (100.58 MHz, $CDCl_3$) δ (ppm): 29.66 (CH_2), 113.00, 124.40, 126.71, 127.89, 128.11, 129.38, 134.70, 150.82, 161.51, 162.04.

1,10a-Dihydro-9H-10-thia-1,4a-diazaphenanthren-2,4-dione (7a); M.p. 110-112°C; LC-MS, 234 (M^++1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.20 (s, 2H, SCH_2), 5.33 (s, 1H, CH_2), 7.3-7.4 and 7.75-7.8 (both m, total 4H, aromatic), 11.8 (bs, 1H, NH); ^{13}C NMR (100.58 MHz, $CDCl_3$) δ (ppm): 28.23 (SCH_2), 87.49 ($CO\underline{C}H_2CO$), 124.19, 126.71, 127.00, 129.59, 134.51, 162.24, 166.12. Found, *m/z* (EI): 217.0439 $[M+H]^+$. $C_{11}H_8N_2OS$. Calculated, *m/z*: 217.0436.

5H-6-Thia-7,12a-diazabenzo[a]anthracen-12-one (8a) [8]; M.p. 161-162°C; LC-MS, 267 (M^++1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.94 (s, 2H, SCH_2), 7.2-7.8 and 8.2-8.3 (both m, total 8H, aromatic); ^{13}C NMR (100.58 MHz, $CDCl_3$) δ (ppm): 29.95 (SCH_2), 121.15, 124.85, 126.07, 126.70, 127.37, 127.66, 127.82, 130.44, 135.02, 146.19, 153.65, 161.46, 167.71.

X-Ray crystallographic study of compound 2a. Diffraction data was collected at –80°C on a Bruker-Nonius KappaCCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystal structure of **2a** was solved by direct methods[16] and refined by full-matrix least squares[17]. All nonhydrogen atoms were refined in anisotropical approximation, all H-atoms were located from differencial Fourier map and refined by riding model. Crystal data for **2a**: monoclinic; a = 3.9810(1), b = 26.1225(6), c = 10.5381(3) Å, β = 95.609(1)°; V = 1090.65(5) Å^3, Z = 4, μ = 0.27 mm^{-1}; space group is $P\,2_1/n$. A total of 4631 reflection intensities were collected up to $2\theta_{max}$ = 57°; for structure refinement 1707 independent reflections with $I > 3\sigma(I)$ were used. The final R-factor is 0.047. For further details, see crystallographic data for **2a** deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Number CCDC 806837. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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