Synthesis and photolysis of 3-*tert*-butyl-4-oxy(mercapto)-1,4-dihydropyrazolo[5,1-*c*][1,2,4]triazines

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Reactions of 3-*tert*-butyl- or 3,4-di-*tert*-butyl-substituted 8-methylpyrazolo[5,1-*c*][1,2,4]-triazines with trifluoroacetic anhydride afforded 1-(2,2,2-trifluoroacetyl)-1,4-dihydropyrazolo-[5,1-*c*][1,2,4]triazin-4-yl 2,2,2-trifluoroacetates. The treatment with H_2X and RXH (X = O or S; R = Me or Et) of covalent trifluoroacetate that does not contain the Bu^t group at the C(4) atom allowed us to synthesize 1-(3-*tert*-butyl-4-R-pyrazolo[5,1-*c*][1,2,4]triazin-1(4*H*)-yl)-2,2,2-trifluoroethan-1-ones. The structure of 4-ethylthio derivative was fully established by the single-crystal X-ray diffraction analysis. The UV irradiation of obtained 2,2,2-trifluoroethan-1-ones leads to the aromatization of triazine ring. The UV photolysis of 1-trifluoroacetyl-4-hydroxy derivative has been proposed as a novel method for the photogeneration of acidity. Antimicrobial and antifungal activities of the synthesized compounds were evaluated.

Key words: pyrazolo[5,1-*c*][1,2,4]triazine, 1,2,4-triazine, acylation, photolysis, photogeneration of acidity.

Among a variety of six-membered heterocycles, 1,2,4-triazines excel in their diverse practical applications.[1—3] This is certainly related to specific chemical properties exhibited by the compounds of this type.[4—6] Recently, an application of triazines as the framework in novel sensory systems has been intensively investigated. Thus, highly structured mesoporous carbon nitride, which is a sensor for vapors of acids and bases, has been prepared *via* a polymerization of 3-amino-1,2,4-triazine.[7] A fluorescent indicator based on the complex of iridium(III) with the anion of 3-(2-pyridyl)-5,6-bis(4-sulfophenyl)-1,2,4-triazine was successfully applied for the both qualitative and quantitative determinations of albumin in human serum.[8] The use of 6-azauridine and its analogues as pH-dependent bioorthogonal fluorescent labels for DNA[9] and proteins[10] was also reported. Aryl- and hetaryl-substituted triazines have been proposed as chromogenic reagents for the forensic examination of traces formed by metal objects on tissue and skin.[11]

We have previously explored aromatic 8-alkylpyrazolo[5,1-*c*][1,2,4]triazines containing one[12] or few[13] *tert*-butyl substituents at the triazine core. Diastereomerically pure 3,4-dihydropyrazolo[5.1-*c*][1,2,4]triazine-3,4-diyl diacetates were obtained *via* a bromination in the presence of carboxylic acids.[14] Treatment with *N*-halogenosuccinimides of compounds possessing a vacant position at the C(8) atom leads to products of the electrophilic heteroaromatic substitution.[15] A deprotonation of the C(4)H moiety in some 1,4-dihydro derivatives bearing the trifluoroacetamide group allowed obtaining pyrazolo[1,5-*a*]-[1,3,5]triazines.[16] In the present work, we have for the first time synthesized 1-trifluoroacetyl-1,4-dihydropyrazolo[5,1-*c*][1,2,4]triazin-4-yl trifluoroacetates, studied their reactions, and considered the structure and UV photolysis of oxygen and sulfur-containing products of their solvolysis, as well as their biological activity.

We have found that the reaction of 8-methyl-3-*tert*-butyl(3,4-di-*tert*-butyl)pyrazolo[5,1-*c*][1,2,4]triazines **1a,b** with trifluoroacetic anhydride in aprotic solvents within 1—3 min at room temperature leads to the formation of covalent trifluoroacetates **2a,b** (Scheme 1). The

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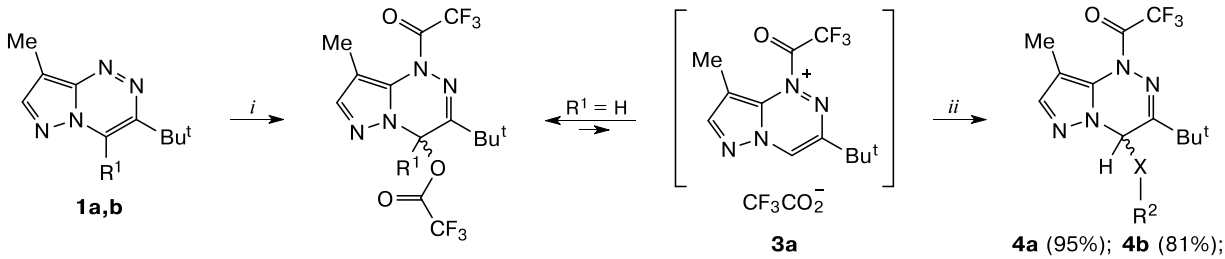
Scheme 1



1, 2: R^1 = H (**a**), Bu^t (**b**)

Compound **4**	X	R^2	Compound **4**	X	R^2
a	O	H	**c**	S	H
b	O	Me	**d**	S	Et

Reagents and conditions: *i*. $(CF_3CO)_2O$, 15 min, 20 °C; *ii*. 1) R_2XH, THF, 5 min—3 h, −35—0 °C; 2) $KHCO_3$, H_2O, 5 min, 0 °C.

subsequent treatment with an aqueous $KHCO_3$ solution results in a fast solvolysis of compound **2a** to give 1-[3-(*tert*-butyl)-4-hydroxy-8-methylpyrazolo[5,1-*c*][1,2,4]triazin-1(4*H*)-yl]-2,2,2-trifluoroethan-1-one (**4a**). Structure of the latter was confirmed by IR and NMR spectroscopy and high resolution mass spectrometry data. Thus, the IR spectrum of this compound contains characteristic bands of the OH and C=O groups at 3101 and 1743 cm^{-1}, respectively. Its ^{19}F NMR spectrum consists of a single signal at δ = −68.90 (Fig. 1). A presence of the C(4)H—OH group was confirmed by the two doublets appeared at δ = 6.32 and 7.65 with J = 8.5 Hz in the ^1H NMR spectrum and by the signal of C(4) atom at δ = 70.1 in the ^{13}C NMR spectrum.

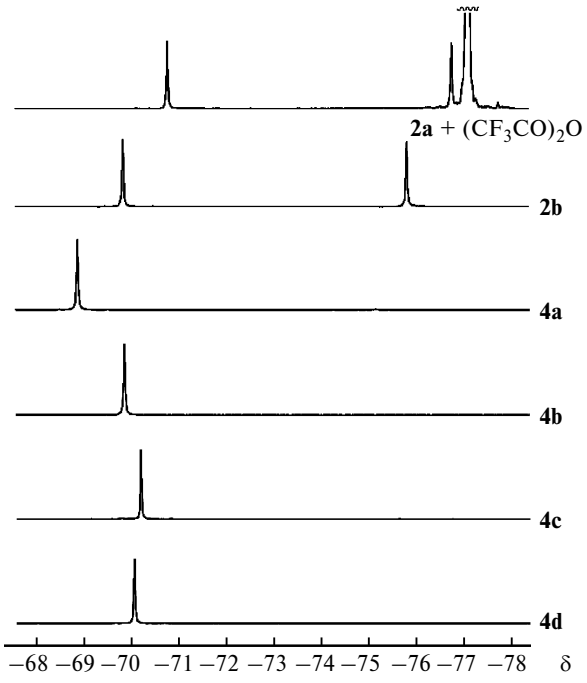


Fig. 1. ^{19}F NMR spectra of compounds **2a,b** and **4a—d**.

3,4-Di-*tert*-butyl-8-methyl-1-(2,2,2-trifluoroacetyl)-1,4-dihydropyrazolo[5,1-*c*][1,2,4]triazin-4-yl 2,2,2-trifluoroacetate (**2b**) turned out to be stable upon a short-time treatment with diluted solutions of the acids and bases. It was isolated using flash chromatography (SiO_2), but its defragmentation occurred during the recording of mass spectra, showing a fragmentation ion with its mass corresponding to starting triazine **1b**. Compound **2b** was isolated as a solid crystalline substance with low melting point, which was decomposed with resinification during its storage for several days at room temperature. The quantitative composition of trifluoroacetate **2b** was determined by the elemental analysis performed for a freshly prepared sample. The formation of unstable compound **2a** upon the dissolution of triazine **1a** in a mixture of $(CF_3CO)_2O$ (13—14 equiv.) and $CDCl_3$ has been confirmed by ^1H and ^{19}F NMR spectroscopy of the reaction mixture. In particular, signals from all the protons were shifted upfield by 0.3—0.5 ppm relative to the corresponding signals of compound **1a** in pure $CDCl_3$, as well as discoloration of the solution was observed, which may indicate a broken aromaticity of the heterocycle. In the ^{19}F NMR spectrum (see Fig. 1), there were two new singlets at δ = −76.79 and −70.80 with the same integral intensities, assigned to the $CF_3CO_2C(4)$ and $CF_3CON(1)$ groups, in addition to an intense peak of trifluoroacetic anhydride that was the cosolvent. In the case of trifluoroacetate **2b**, its IR and ^{13}C NMR spectra were also recorded. Characteristic vibrations of the C=O and CF_3 bonds appeared as the narrow intense bands at 1802 (CF_3C=O), 1737 (CF_3C=ON), and 1171 (CF_3) cm^{-1}, while quadruplets of the two C atoms of CF_3 groups were located at δ = 110.6—119.4 (J = 286—287 Hz). Signals at δ = 151.4—156.2 (J = 39—44 Hz) in the ^{13}C NMR spectrum were assigned to the carbonyl group.

The solvolysis of compound **2a** was carried out not only with H_2O, but also with a large molar excess (32—238 equiv.) of MeOH, EtSH, or H_2S in a THF me-

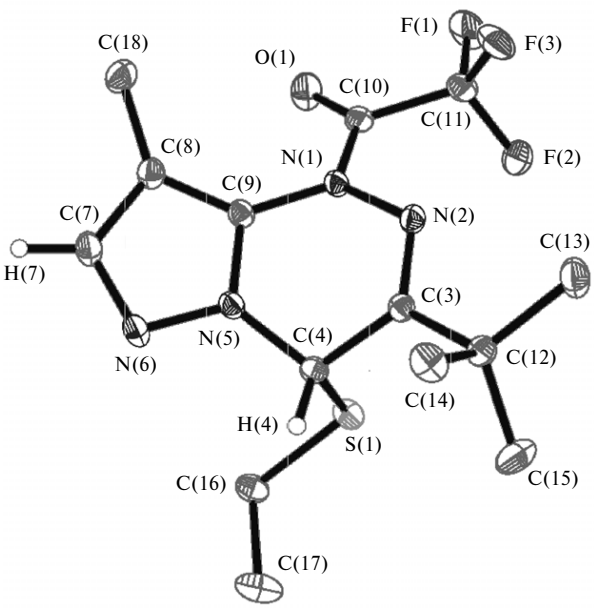


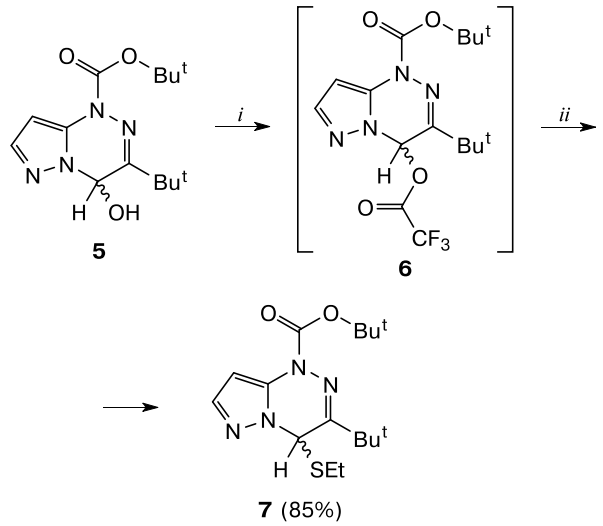
Fig. 2. Molecular structure of compound **4d** in its crystal, represented by ellipsoids of the thermal vibrations (p = 50%).

dia at the temperature ranging from −35 to 0 °C, and resulted in the formation of expected products **4b—d** (see Scheme 1). The structure 1-(3-*tert*-butyl-4-ethylthio-8-methylpyrazolo[5,1-*c*][1,2,4]triazin-1(4*H*)-yl)-2,2,2-trifluoroethane-1-one (**4d**) was proved by the single crystal X-ray diffraction analysis (Fig. 2) and also confirmed by IR and NMR spectroscopy and high resolution mass spectrometry.

It has been found that compound **2a** does not practically react either with 2-propanol or *n*-butanol. An S_N2-like mechanism has been previously proposed[17] for the nucleophilic substitution reactions of 3-nitro-4-trifluoroacetoxyazolo[5,1-*c*][1,2,4]triazines. It was assumed that covalent 3-*tert*-butyl trifluoroacetate **2a** dissociates in a protic medium under the certain conditions (see Scheme 1) due to the formation of hydrogen bonds between the solvent and trifluoroacetate residue, proceeding with the consequent solvolysis of intermediate pyrazolo[5,1-*c*]-[1,2,4]triazin-1(5)-ium cations according to the S_N1-like mechanism (see Scheme 1). In the case of either bulky molecules of a solvent or di-*tert*-butyl-substituted substrate **2b**, the efficient formation of hydrogen bonds is hindered, which leads to the slowed down dissociation step and to the impossibility of nucleophilic substitution. In the reactions of trifluoroacetates **2a,b** with such strong nucleophiles as MeO^- or EtO^-, AlkMgBr or AlkLi, small amounts of initial triazines **1a,b** were formed in addition to the resinification, which might be a result of the attack at the carbonyl groups of side chain. Compounds **2a,b** were inert towards their treatment with NaN_3 or NaCN in anhydrous hexamethylphosphoramide at room temperature for few days. An addition of water or methanol led only to the formation of solvolysis products **4a,b**.

It should be noted that aromatic triazines **1a,b** did not interact with either acetic anhydride or di-*tert*-butyl dicarbonate even at the boiling point of reagent (> 140 °C, only the starting compound was isolated). However, 1-Boc-protected 4-hydroxypyrazolo[5,1-*c*][1,2,4]triazine **5** was successfully converted into the corresponding 4-ethylthioderivative **7** *via* its sequential treatment with trifluoroacetic anhydride and ethyl mercaptan at a decreased temperature (Scheme 2).*

Scheme 2



Reagents and conditions: *i*. $(CF_3CO)_2O$, THF, 10 min, −50 °C; *ii*. 1) EtSH, THF, 15 min, −(50—20) °C; 2) $KHCO_3$, H_2O, 30 min, 0 °C.

It has been experimentally found that compound **5** is not protonated by trifluoroacetic acid at −20 °C. Thus, the ^1H NMR spectrum of heterocycle **5** recorded in a $CDCl_3$—CF_3CO_2H mixture was not significantly different from those recorded in either $CDCl_3$ or DMSO-d_6 media (see Experimental). Apparently, the acylation of alcohol group in aminal **5** with trifluoroacetic anhydride leads to the formation of highly reactive trifluoroacetate **6**, which consequently undergoes the solvolysis in EtSH medium.

It is known that *N*-acyl-substituted derivatives of partially hydrogenated hetarenes possess an increased photochemical sensitivity and are capable of aromatization upon UV irradiation. Thus, the photolysis of [3,7-bis-(diethylamino)-10*H*-phenoxazin-10-yl]methanones is accompanied by the removal of acyl protection and by the intense fluorescence of generated dye.[18] Acyl derivatives of dihydro form of Coumarin 6 upon an irradiation undergo

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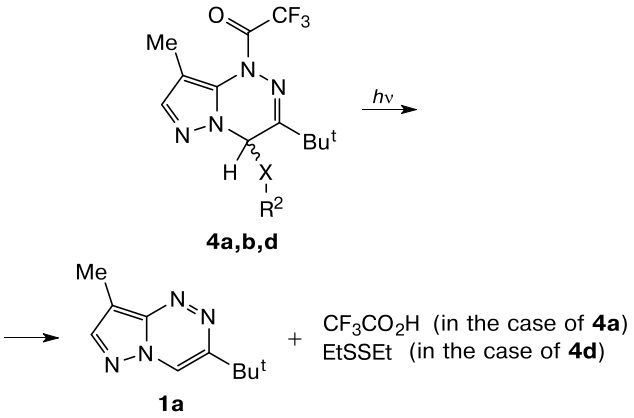
photoaromatization with the formation of laser dye that has been applied in a design of the new medium for the optical recording of information.[19,20]

We have found that the UV irradiation of compounds **4a,b,d** is also leading to their aromatization to give bright yellow triazine **1a** (Scheme 3). The irradiation of diluted solution of compound **4d** with UV light (λ = 240—400 nm) results in the decreased absorption maxima at 246 and 284 nm and in the appearance of intense absorption band at 236 nm and wide band in the range of 320—450 nm (its maximum at 368 nm) (Fig. 3). Similar changes in the spectra were observed during the photolysis of compound **4b** (Fig. 4).

Scheme 3



Compound **4a** can also be readily photolysed upon the UV irradiation, resulting in the gradual decrease in the absorption maxima at 252 and 278 nm and in the shift of long-wavelength maximum to 300 nm. Upon its UV irradiation for 40 s, the optical density increases at 236 nm and also in the range of 300—450 nm (Fig. 5), thus indicating the formation of compound **1a**.

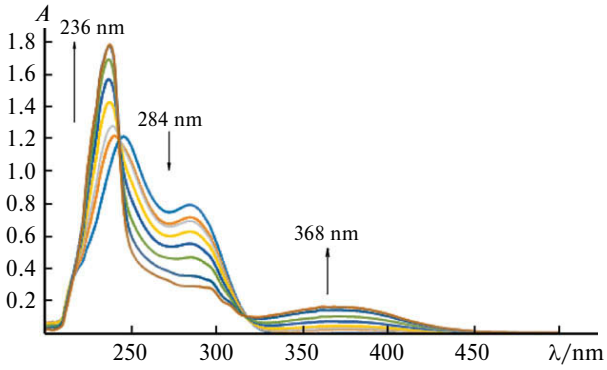


Fig. 3. Changes in the absorption spectra of compound **4d** dissolved in THF ($C = 1.38 \cdot 10^{-4}$ mol L^{-1}) upon UV irradiation (A03 filter, maximum exposure time of 120 s).
Note. Figures 3—5 are available in full color on the web page of the journal (https://link.springer.com/journal/volumesAndIssues/11172).

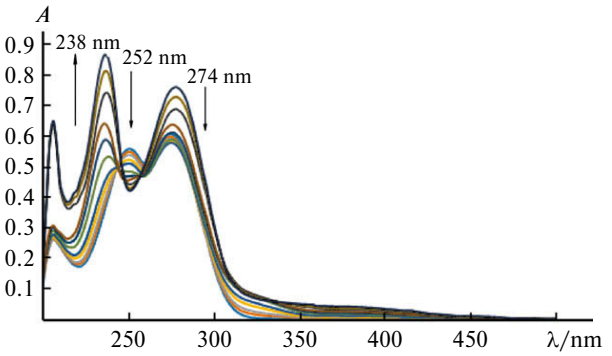


Fig. 4. Absorption spectra of compound **4b** dissolved in CH_3CN ($C = 5.24 \cdot 10^{-5}$ mol L^{-1}) upon UV irradiation (A03 filter, maximum exposure time of 300 s).

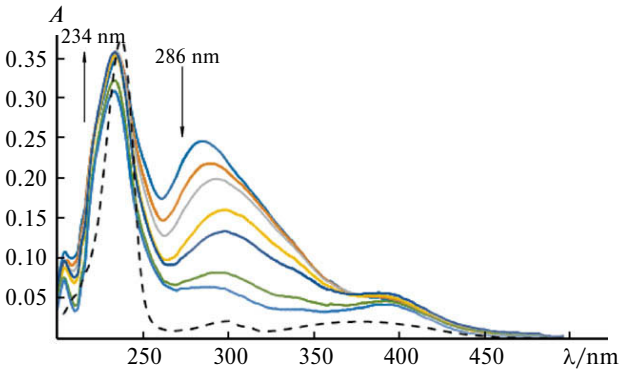


Fig. 5. Absorption spectra of compound **4a** dissolved in CH_3CN ($C = 5.48 \cdot 10^{-5}$ mol L^{-1}) upon UV irradiation (A03 filter, maximum exposure time of 40 s, the dashed line corresponds to the absorption spectrum of compound **1a**).

According to the Scheme 3, the photoaromatization of compound **4a** should be concerted with the formation of trifluoroacetic acid. This fact was confirmed by pH measurements for the aqueous acetonitrile solution of compound **4a** (Fig. 6, curve *2*). The pH value of this solution decreases upon UV irradiation much faster than that in a control experiment without any irradiation (see Fig. 6, curve *1*). Thus, increases in the acidity were estimated as $2 \cdot 10^{-3}$ pH s^{-1} upon the UV irradiation and as $7 \cdot 10^{-4}$ pH s^{-1} without any irradiation.

The generation of acidity during the photolysis of compound **4a** is of undoubted interest. An irradiation of the acidity photogenerators in a non-polar solvent (*e.g.*, toluene) or in a polymethylmethacrylate film in the presence of lactone Rhodamine B is accompanied by the appearance of intense fluorescence from the open form of dye, which is applied in systems for the optical recording of information. Moreover, data on the application of acidity photogenerators to control biochemical reactions have been reported in recent years.[21,22]

Table 1. GC/MS data for the reaction mixture obtained *via* the photolysis of compound **4b** (THF, λ = 240—400 nm, 50 min)

t_{ret} (I_{rel} (%))	MS (EI, 70 eV), *m/z* (I_{rel} (%))
11.59 (0.5, **1a**)	190 $[M]^+$ (61), 175 [M – NH] (100), 148 [M – NH – HCN] (87), 67 (13), 41 $[C_2H_3N]^+$ (14)
11.53 (100, **4b**)	318 $[M]^+$ (55), 287 $[M - OCH_3]^+$ (74), 191 (45), 178 (66), 166 (100), 148 (22), 138 (26), 69 $[CF_3]^+$ (35), 57 $[Bu^t]^+$ (58)

Table 2. GC/MS data for the reaction mixture obtained *via* the photolysis of compound **4d** (THF, λ = 240—400 nm, 50 min)

t_{ret} (I_{rel} (%))	MS (EI, 70 eV), *m/z* (I_{rel} (%))
13.00 (100%, **4d**)	348 $[M]^+$ (1), 287 $[M - EtS]^+$ (100), 189 $[M - CF_3CO - EtSH]^+$ (5), 175 $[M - CF_3CO - EtS - NH]^+$ (14), 148 $[M - CF_3CO - EtS - NH - HCN]$ (19), 69 $[CF_3]^+$ (5), 57 $[Bu^t]^+$ (3)
11.57 (65%, **1a**)	190 $[M]^+$ (59), 175 [M – NH] (100), 148 [M – NH – HCN] (88), 67 (13), 41 $[C_2H_3N]^+$ (12)
4.73 (34%, EtSSEt)	122 $[M]^+$ (100), 94 (47), 86 (79), 66 (45), 56 (36), 42 (100), 28 (43)

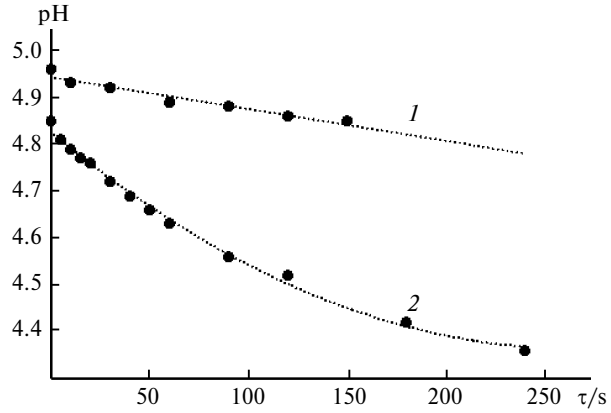


Fig. 6. Changes in the pH value of compound **4a** dissolved in CH_3CN (the solvent was a CH_3CN : H_2O mixture (1 : 5), $C = 5.48 \cdot 10^{-5}$ mol L^{-1}) without any exposure to UV radiation (*1*) and UV-irradiated through an A03 light filter (*2*).

Beyond our expectations, GC/MS monitoring of the reaction mixture upon UV irradiation of substrates dissolved in methanol, aqueous (95%) ethanol, absolute THF, or diglyme has not confirmed the formation of any appreciable amounts of methyl and ethyl thiotrifluoroacetates from compounds **4b** and **4d**, respectively (Tables 1 and 2).

In the case of ethylthio derivative **4d**, subequimolar amounts of diethyl disulfide were formed in addition to aromatic triazine **1a** (see Table 2). In addition, we have observed trace amounts of products of the free radical degradation of solvent, as well as of unidentified compounds bearing a CF_3 moiety according to the mass spectra.

Pyrazolo[5,1-*c*][1,2,4]triazines **4a—c** were screened for their possible antimicrobial and antifungal activity using five bacterial and two fungal cell lines (Table 3). These compounds have demonstrated the weak (the inhibition of 15—30%) antimicrobial and antifungal activities at the concentration of 32 μg mL^{-1}.

Therefore, we have investigated the reactions of aromatic pyrazolo[5,1-*c*][1,2,4]triazines with trifluoroacetic anhydride, resulting in the formation of covalent 1-(2,2,2-trifluoroacetyl)-1,4-dihydropyrazolo[5,1-*c*][1,2,4]-triazin-4-yl 2,2,2-trifluoroacetates. Their treatment with water, methanol, ethyl mercaptan, or hydrogen sulfide allowed us to synthesize a series of previously unknown 4-substituted 1-(3-*tert*-butyl-pyrazolo[5,1-*c*][1,2,4]triazin-1(4*H*)-yl)-2,2,2-trifluoroethan-1-ones. The photolysis of the latter upon UV irradiation leads to their aromatization and can be proposed as a novel method for the photogeneration of acidity. The isolated compounds exhibited weak both antimicrobial and antifungal activities.

Table 3. Antimicrobial and antifungal activities of compounds **4a—d**

Compound	Growth inhibition (%)						
	Bacteria					Fungi	
	S. aureus — MRSA	*E. coli*	*K. pneumoniae — MDR*	*P. aeruginosa*	*A. baumannii*	*C. albicans*	*C. neoformans*
4a	12.26	2.74	21.58	19.41	12.69	4.76	3.51
4b	18.39	4.32	14.39	20.44	16.81	1.37	11.62
4c	29.78	17.69	24.31	18.89	19.48	3.05	12.29
4d	19.26	0.15	18.84	14.32	15.09	2.38	18.18

Experimental

UV spectra were recorded on an SF-104 spectrophotometer. IR spectra were recorded neat or in KBr pellets using an Agilent Cary 660 FTIR spectrometer. ^{1}H, ^{13}C (APT, attached proton test), and ^{19}F NMR spectra were recorded on Bruker AM–300, Bruker DRX–500 and Bruker AV–600 instruments operating at the frequencies of 300 MHz for ^{1}H, 75, 126, or 151 MHz for ^{13}C, and 282 MHz for ^{19}F, respectively. Internal standards were DMSO-d_5 and $CHCl_3$ (^{1}H), DMSO-d_6 and $CDCl_3$ (^{13}C), and CF_3CO_2H (^{19}F). GC/MS was performed on a TRACE GC ULTRA chromatograph equipped with a TR-5MS capillary column (length of 30 m, diameter of 0.25 mm, and phase thickness of 0.25 μm) and with a DSQ II quadrupole mass spectrometer as the detector (electron impact, ionization energy of 70 eV), and operating in the following temperature mode: 70 °C (2 min) → → 280 °C (15 deg min^{-1}) → 280 °C (10 min). High resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF II instrument using electrospray ionization. The measurements were carried out in the mode of positive ions (the voltage on the capillary was 4500 V), and the solvent was methanol. Single crystal X-ray diffraction analysis was performed on a Bruker APEX II CCD diffractometer (λ(MoKa) = 0.71072 Å). Melting points were determined using a Melting point SMP30 instrument (STUART). The pH values of solutions were measured using a PHS-3D instrument (Sancin). Merck Silica (60—200 mesh) silica gel was used for the chromatography. Compounds **1a,b** and **5** were prepared according to the known procedures.[12,13] Dry H_2S was obtained *via* careful heating[23] of a mixture of finely dispersed S_8 (10 g, 312 mmol), paraffin $[CH2]_n$ (10 g, 713 mmol), and asbestos (20 g) at 300 °C.

Photolysis of compounds 4a,b,d (general procedure). A portion of the corresponding compound **4a,b,d** (50 mg) was dissolved in the solvent (50 mL, either MeOH, CH_3CN, or THF). The resulting solution was diluted to the desired concentration. The photolysis was carried out under an air atmosphere in a quartz flask under stirring and irradiation with a Hamamatsu LC-4 source of UV radiation equipped with an L8253 xenon lamp (power of 150 W) and an A03 filter (transmission range of 240—400 nm). The reaction progress was monitored by changes in the absorption spectra, as well as using GC/MS (see Tables 1 and 2).

Biological experiments were carried out according to the methods reported previously.[14] The inhibition percentage was estimated *via* measuring the difference in the fluorescence intensity of culture solutions in water without addition and in the presence of studied compounds (C = 32 μg mL^{-1}) after incubation for 18 h at 37 °C for bacteria (density of colony forming units of $5 \cdot 10^5$ mL^{-1}) and for 24 h at 35 °C for fungi (density of colony forming units of $2.5 \cdot 10^3$ mL^{-1}). 7-Hydroxy-3*H*-phenoxazin-3-one-10-oxide was selected as the indicator of viability of microorganisms.

3-*tert*-Butyl-8-methyl-1-(2,2,2-trifluoroacetyl)-1,4-dihydropyrazolo[5,1-*c*][1,2,4]triazin-4-yl 2,2,2-trifluoroacetate (2a). Compound **1a** (20 mg, 0.11 mmol) was dissolved in $CDCl_3$ (0.5 mL) under an argon atmosphere. The ^{1}H NMR spectrum of obtained bright yellow solution was recorded. A portion of $(CF_3CO_2)O$ (0.20 mL, 1.44 mmol) was then added to the solution at ~20 °C. The discoloration was observed. The resulting solution was mixed well, and ^{1}H and ^{19}F NMR spectra were recorded.

A bright yellow solution of compound **1a**. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.33 (s, 1 H, C(7)H); 7.97 (s, 1 H, C(4)H); 2.59 (s, 3 H, C(8)CH_3); 1.52 (s, 9 H, Bu^t). UV (THF), λ_{max}/nm (logε): 236 (4.116), 368 (3.162), 384 (2.869). UV (CH_3CN), λ_{max}/nm (logε): 234 (2.905), 298 (1.626), 375 (1.802).

A colorless solution of compound **2a**. ^{1}H NMR (300 MHz, $CDCl_3$ (0.5 mL)—$(CF_3CO_2)O$ (0.2 mL)), δ: 7.71 (s, 1 H, C(7)H); 7.55 (s, 1 H, C(4)H); 2.25 (s, 3 H, C(8)CH_3); 1.35 (s, 9 H, Bu^t). ^{19}F NMR (282 MHz, $CDCl_3$ (0.5 mL)—$(CF_3CO_2)O$ (0.2 mL)), δ: −70.80 (s, 3 F, CF_3CON(1)); −76.79 (s, 3 F, CF_3CO_2C(4)); −77.13 (s, ~50 F, cosolvent (CF_3CO_2)O). UV (THF), λ_{max}/nm (logε): 296 (2.945), 384 (2.204).

3,4-Di-*tert*-butyl-8-methyl-1-(2,2,2-trifluoroacetyl)-1,4-dihydropyrazolo[5,1-*c*][1,2,4]triazin-4-yl 2,2,2-trifluoroacetate (2b). Under an argon atmosphere, $(CF_3CO_2)O$ (0.50 mL, 3.60 mmol) was added in one portion at ~20 °C to a bright yellow solution of compound **1b** (0.25 g, 1.01 mmol) in THF (15 mL). The resulting solution was almost colorless. It was stirred for 15 min and then added dropwise within 2 min to a cooled (0 °C), vigorously stirred two-phase mixture of CH_2Cl_2 (30 mL) and an aqueous (100 mL) solution of $KHCO_3$ (10 g, 0.1 mol). It was vigorously stirred for additional 10 min at the same temperature. The organic phase was separated, washed with water (50 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was also filtered through a thin layer of SiO_2 and evaporated *in vacuo* at 40 °C. Compound **2b** was obtained as white crystals, m.p. 82—84.5 °C (decomp.), the yield of 0.41 g (89%). IR (KBr), ν/cm^{-1}: 2985, 2938, 2884 (CH), 1802 (CF_3C=OO), 1737 (CF_3C=ON), 1592, 1495, 1400, 1359, 1233, 1203, 1171 (CF_3), 1129, 1100, 1073, 1034, 1007, 967, 939, 892, 851, 789, 754, 726, 648, 567, 526. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.11 (s, 9 H, C(4)Bu^t); 1.43 (s, 9 H, C(3)Bu^t); 2.15 (s, 3 H, C(8)CH_3); 7.41 (s, 1 H, C(7)H). ^{19}F NMR (282 MHz, $CDCl_3$), δ: −75.84 (s, 3 F, CF_3CO_2C(4)); −69.86 (s, 3 F, CF_3CON(1)). ^{13}C NMR (APT, 126 MHz, $CDCl_3$), δ: 10.41 (C(8)CH_3); 25.40 (C(4)C$(CH_3)_3$); 31.21 (C(3)C$(CH_3)_3$); 40.76 (C(4)CMe_3); 44.16 (C(3)CMe_3); 93.72 (C(8)); 105.18 (C(4)); 110.62, 112.59, 115.17, 117.44 (q, CF_3CON(1), J = 286.2 Hz); 112.89, 114.87, 117.15, 119.43 (q, CF_3CO_2C(4), J = 287.1 Hz); 128.63 (C(8a)); 142.14 (C(7)H); 151.37, 151.68, 151.99, 152.29 (q, CON(1), J = 38.7 Hz); 155.14, 155.49, 155.84, 156.19 (q, CO_2C(4), J = 44.1 Hz); 160.94 (C(3)). MS (EI, 70 eV), m/z (I_{rel} (%)): 246 [**1b**]$^+$ (100), 231 [**1b** − NH]$^+$ (52), 189 [**1b** − Bu^t]$^+$ (67), 175 [**1b** − NH − Bu^t]$^+$ (17), 162 [**1b** − N_2 − Bu^t + H]$^+$ (31), 148 (13), 109 (13), 82 [4-methylpyrazole]$^+$ (18), 57 [Bu^t]$^+$ (9), 41 $[C_2H_3N]^+$ (12), 29 $[N_2H]^+$ (4). HRMS: found m/z (I_{rel} (%)) 247.1908 (40), 376.2322 (100); $C_{18}H_{22}F_6N_4O_3$; calculated for **2b** + H = 457.1669, **1b** + H = = 247.1917. Elemental analysis. Found (%): C, 47.29; H, 5.03; N, 12.23. $C_{18}H_{22}F_6N_4O_3$. Calculated (%): C, 47.37; H, 4.86; N, 12.28.

Solvolysis of trifluoroacetate 2a (general step in the synthesis of compounds 4a—d). Under an argon atmosphere, $(CF_3CO_2)O$ (0.50 mL, 3.60 mmol) was added in one portion at ~20 °C to a solution of compound **1a** (0.25 g, 1.31 mmol) in THF (20 mL). The resulting solution of compound **2a** was almost colorless. It was stirred for 15 min and then cooled down to −20 °C (for the synthesis of compounds **4a,b,d**) or to −35 °C (in the case of **4c**, external cooling with a heptane—liquid N_2 mixture). Water (5 mL, 0.28 mol), MeOH (2.5 mL, 61.8 mmol), or EtSH (3.0 mL, 41.6 mmol) precooled to 0 °C were added dropwise within 1—3 min in order to obtain compounds **4a**, **4b**, or **4d**, respectively. Compound **4c** was synthesized *via* flushing the solution of compound **2a** with a stream of dry gaseous H_2S (312 mmol, cooled

to a temperature below 0 °C) for 30 min. The reaction mixture was stirred at 0 °C for 5 min (**4a**), 30 min (**4b**), or 2—3 h (**4c,d**). Crystalline $KHCO_3$ (5 g, 49.9 mmol, in small portions), EtOAc (30 mL, to isolate compounds **4b—d**), and cooled water (0 °C, 50 mL) were subsequently added under vigorous stirring. The reaction mixture was vigorously stirred at 0 °C for 5 min, the organic phase was then separated, and the mother liquor was extracted with EtOAc (5×30 mL). The combined organic phases were washed with cooled water (1×50 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was evaporated *in vacuo* at 40 °C.

To isolate compound **4a**, THF was evaporated from the reaction mixture at ~20 °C. The formed precipitate was filtered off, washed with water (3×20 mL), and dried in air. The residues were purified using flash chromatography with the following eluents: EtOAc—$CHCl_3$ (1 : 2) for **4a**; EtOAc—hexane (1 : 30—1 : 10) for **4b**; $CHCl_3$—hexane (1 : 1—2 : 1) for **4c**; and CH_2Cl_2—hexane (1 : 3—2 : 1) for **4d**. After that, the corresponding product was washed with cooled hexane (0 °C, 3×2 mL, to remove small amounts of impurity **1a**), dried in a stream of argon, and compounds **4a—d** were thus isolated.

1-(3-*tert*-Butyl-4-hydroxy-8-methylpyrazolo[5,1-*c*][1,2,4]-triazin-1(4*H*)-yl)-2,2,2-trifluoroethanone (4a). White powder, m.p. 180—190 °C (decomp.), the yield of 0.38 g (95%). UV (MeOH), λ_{max}/nm (lgε): 252 (3.943), 278 (4.002). UV (CH_3CN), λ_{max}/nm (lgε): 242 (4.068), 278 (4.002). IR (KBr), ν/cm^{-1}: 3101 (OH), 2977, 2938, 2872, 2835 (CH), 2709, 1743 (CO), 1633, 1585, 1518, 1477, 1453, 1412, 1399, 1363, 1309, 1260, 1239, 1207, 1176 (CF_3), 1104, 1060, 1010, 921, 882, 857, 833, 790, 741, 706, 658, 632, 571, 530, 493, 445. ^{1}H NMR (300 MHz, DMSO-d_6), δ: 1.27 (s, 9 H, Bu^t); 2.09 (s, 3 H, C(8)C<u>H</u>$_3$); 6.32 (d, 1 H, C(4)<u>H</u>, *J* = 8.2 Hz); 7.52 (s, 1 H, C(7)<u>H</u>); 7.65 (d, 1 H, C(4)O<u>H</u>, *J* = 8.5 Hz). ^{19}F NMR (282 MHz, DMSO-d_6), δ: −68.90 (s, 3 F, C<u>F</u>$_3$CON(1)). ^{13}C NMR (APT, 75 MHz, DMSO-d_6), δ: 10.26 (C(8)<u>C</u>H$_3$); 27.59 (C(<u>C</u>H$_3$)$_3$); 37.00 (<u>C</u>(CH$_3$)$_3$); 70.14 (<u>C</u>(4)H); 104.39 (C(8)); 110.15, 113.96, 117.76, 121.56 (q, <u>C</u>F$_3$CON(1), *J* = 286.6 Hz); 128.54 (C(8a)); 141.24 (<u>C</u>(7)H); 150.77, 151.26, 151.76, 152.25 (q, CF$_3$<u>C</u>ON(1), *J* = 37.7 Hz); 161.66 (C(3)). MS: found *m/z* (I_{rel} (%)) 305.1224 [M + H] (100). $C_{12}H_{15}F_3N_4O_2$. Calculated: M + H = 305.1220.

1-(3-*tert*-Butyl-8-methyl-4-methoxypyrazolo[5,1-*c*][1,2,4]-triazin-1(4*H*)-yl)-2,2,2-trifluoroethanone (4b). Colorless crystals, m.p. 105—110 °C (decomp.), the yield of 0.34 g (81%). UV (CH_3CN), λ_{max}/nm (lgε): 252 (4.021), 274 (4.156). IR (neat), ν/cm^{-1}: 2978, 2955, 2936, 2874, 2853, 2835 (CH), 1734 (CO), 1625, 1585, 1506, 1466, 1425, 1398, 1371, 1353, 1265, 1237, 1200, 1177 (CF_3), 1111, 1094, 1075, 1044, 1022, 999, 953, 937, 856, 837, 792, 746, 732, 701, 667, 652, 635, 570, 549, 533, 473, 452, 433. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.31 (s, 9 H, Bu^t); 2.20 (s, 3 H, C(8)C<u>H</u>$_3$); 3.41 (s, 3 H, OC<u>H</u>$_3$); 5.93 (s, 1 H, C(4) <u>H</u>); 7.44 (s, 1 H, C(7)<u>H</u>). ^{19}F NMR (282 MHz, $CDCl_3$), δ: −69.88 (s, 3 F, C<u>F</u>$_3$CON(1)). ^{13}C NMR (APT, 75 MHz, $CDCl_3$, two components of the CF$_3$<u>C</u>O quadruplet were not observed), δ: 10.84 (C(8)<u>C</u>H$_3$); 27.88 (C(<u>C</u>H$_3$)$_3$); 37.51 (<u>C</u>(CH$_3$)$_3$); 56.22 (O<u>C</u>H$_3$); 77.46 (<u>C</u>(4)H); 105.81 (C(8)); 110.44, 114.24, 118.04, 121.84 (q, <u>C</u>F$_3$CON(1), *J* = 286.8 Hz); 129.51 (<u>C</u>(8a)); 142.48 (<u>C</u>(7)H); 152.55, 153.06 (q, <u>C</u>F$_3$CON(1), *J* = 37.9 Hz); 158.77 (<u>C</u>(3)). MS: found *m/z* (I_{rel} (%)) 319.1382 [M + H] (100), 341.1196 [M + Na] (20). $C_{13}H_{17}F_3N_4O_2$. Calculated: M + H = = 319.1376, M + Na = 341.1196.

1-(3-*tert*-Butyl-4-mercapto-8-methylpyrazolo[5,1-*c*][1,2,4]-triazin-1(4*H*)-yl)-2,2,2-trifluoroethanone (4c). White powder, m.p. 55—60 °C (decomp.), the yield of 0.33 g (78%). IR (neat), ν/cm^{-1}: 3414 (SH), 3095, 2984, 2972, 2941, 2906, 2872 (CH), 2547, 1718 (CO), 1617, 1587 (C=N), 1505, 1478, 1466, 1458, 1430, 1397, 1370, 1362, 1258, 1235, 1204, 1171 (CF_3), 1104, 1091, 1041, 1018, 997, 969, 941, 906, 853, 825, 786, 736, 724, 700, 658, 639, 619, 566, 531, 451. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.39 (s, 9 H, Bu^t); 2.21 (s, 3 H, C(8)C<u>H</u>$_3$); 2.78 (d, 1 H, C(4) S<u>H</u>, *J* = 7.5 Hz); 6.32 (d, 1 H, C(4)<u>H</u>, *J* = 7.5 Hz); 7.43 (s, 1 H, <u>C</u>(7)−<u>H</u>). ^{19}F NMR (282 MHz, $CDCl_3$), δ: −70.22 (s, 3 F, C<u>F</u>$_3$CON(1)). ^{13}C NMR (APT, 75 MHz, $CDCl_3$, three components of the CF$_3$<u>C</u>O quadruplet were not observed), δ: 11.04 (C(8)<u>C</u>H$_3$); 28.84 (C(<u>C</u>H$_3$)$_3$); 38.07 (<u>C</u>(CH$_3$)$_3$); 50.57 (<u>C</u>(4)H); 106.67 (C(8)); 110.49, 114.30, 118.10, 121.90 (q, <u>C</u>F$_3$CON(1), *J* = 286.7 Hz); 129.11 (<u>C</u>(8a)); 143.16 (<u>C</u>(7)H); 152.57 (q, CF$_3$<u>C</u>ON(1)); 162.33 (<u>C</u>(3)). MS: found *m/z* (I_{rel} (%)) 321.1005 [M + H] (100), 343.0826 [M + Na] (40). $C_{12}H_{15}F_3N_4OS$. Calculated: M + H = 321.0991, M + Na = 343.0811.

1-(3-*tert*-Butyl-4-ethylthio-8-methylpyrazolo[5,1-*c*][1,2,4]-triazin-1(4*H*)-yl)-2,2,2-trifluoroethanone (4d). Colorless crystals, m.p. 140—150 °C (sublimation), the yield of 0.38 g (83%). UV (THF), λ_{max}/nm (lgε): 246 (3.940), 284 (3.764). IR (neat), ν/cm^{-1}: 2975, 2958, 2935, 2906, 2877 (CH), 1722 (CO), 1586, 1507, 1478, 1458, 1425, 1395, 1372, 1353, 1261, 1233, 1200, 1176 (CF_3), 1088, 1041, 998, 917, 852, 825, 801, 768, 746, 726, 701, 657, 637, 613, 568, 532, 487, 451. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.25 (t, 3 H, SCH$_2$C<u>H</u>$_3$, *J* = 7.4 Hz); 1.38 (s, 9 H, Bu^t); 2.19 (s, 3 H, C(8)C<u>H</u>$_3$); 2.80—2.50 (diastereotopic m, 2 H, SC<u>H</u>$_2$CH$_3$); 6.15 (s, 1 H, C(4)<u>H</u>); 7.40 (s, 1 H, C(7)<u>H</u>). ^{19}F NMR (282 MHz, $CDCl_3$), δ: −70.07 (s, 3 F, C<u>F</u>$_3$CON(1)). ^{13}C NMR (APT, 75 MHz, $CDCl_3$, two components of the CF$_3$<u>C</u>O quadruplet were not observed), δ: 10.91 (C(8)<u>C</u>H$_3$); 13.96 (SCH$_2$<u>C</u>H$_3$); 25.57 (S<u>C</u>H$_2$CH$_3$); 28.96 (C(<u>C</u>H$_3$)$_3$); 37.98 (<u>C</u>(CH$_3$)$_3$); 56.39 (<u>C</u>(4)H); 106.53 (C(8)); 110.55, 114.35, 118.16, 121.95 (q, <u>C</u>F$_3$CON(1), *J* = 286.6 Hz); 129.15 (<u>C</u>(8a)); 142.35 (<u>C</u>(7)H); 152.90, 153.35 (q, CF$_3$<u>C</u>ON(1), *J* = 33.4 Hz); 161.52 (<u>C</u>(3)). MS: found *m/z* (I_{rel} (%)) 349.1297 [M + H] (100), 371.1112 [M + Na] (30). $C_{14}H_{19}F_3N_4OS$. Calculated: M + H = 349.1304, M + Na = 371.1124.

Single crystal X-ray diffraction analysis of compound **4d**. Crystals of compound **4d** ($C_{14}H_{19}F_3N_4OS$, M = 348.39, μ = 0.233 mm^{-1}, d_{calc} = 1.391 g cm^{-3}) at 120 K triclinic, space group $P\bar{1}$, *a* = 9.0928(6), *b* = 9.9948(7), and *c* = 10.9181(8) Å, α = 96.3559(13)°, β = 103.9402(13)°, γ = 116.7910(12)°, *V* = 831.65(10) Å^3, *Z* = 2. The crystal was grown in ethyl acetate. The intensities of 16754 reflections for the crystal of compound **4d** were measured on a Bruker APEX II CCD diffractometer (λ(MoKa) = 0.71072 Å, θ = 1.99—29.00°), and 4430 independent reflections (R_{int} = 0.0257) were used in the further refinement.

The structure was solved by the direct method and refined by the least-squares method in the anisotropic full-matrix approximation on F^2_{hkl}. Positions of the hydrogen atoms were geometrically calculated and refined in the isotropic approximation according to the riding model. Final values of the uncertainty factors were wR_2 = 0.0878 and GOOF = 1.014 for all the independent reflections (R_1 = 0.0315 was calculated on *F* for 3830 observed reflections with $I > 2\sigma(I)$). All the calculations were performed using the SHELXTL software package.[24] The coordinates of atoms and full structural data were deposited with the Cambridge Structural Databank (CCDC 1875748; www.ccdc.ac.uk).

***tert*-Butyl 3-*tert*-butyl-4-hydroxypyrazolo[5,1-*c*][1,2,4]triazin-1(4*H*)-carboxylate (5).** ^{1}H NMR (300 MHz, DMSO-d_6,

20 °C), δ: 7.55 (d, 1 H, C(7)H, *J* = 1.9 Hz); 7.34 (d, 1 H, OH, *J* = 7.9 Hz); 6.27—6.23 (m, 2 H, C(4)H + C(8)H); 1.55 (s, 9 H, Bu^{t}O); 1.27 (s, 9 H Bu^{t}C(3)). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C), δ: 7.57 (s, 1 H, C(7)H); 7.3—6.4 (br.s, 1 H, OH); 6.47—6.42 (m, 2 H, C(4)H + C(8)H); 1.65 (s, 9 H, Bu^{t}O); 1.40 (s, 9 H, Bu^{t}C(3)). ^{1}H NMR (300 MHz, CF_3CO_2H (0.03 mL)—$CDCl_3$ (0.6 mL)—**5** (20 mg), −20 °C), δ: 11.00 (br.s, ~ 6 H, CF_3CO_2H + OH); 8.02 (d, 1 H, C(7)H, *J* = 2.3 Hz); 6.82 (d, 1 H, C(8)H, *J* = 2.0 Hz); 6.67 (s, 1 H, C(4)H); 1.67 (s, 9 H, Bu^{t}O); 1.38 (s, 9 H, Bu^{t}C(3)).

***tert*-Butyl 3-*tert*-butyl-4-(ethylthio)pyrazolo[5,1-*c*][1,2,4]triazin-1(4*H*)-carboxylate (7).** Under an argon atmosphere, $(CF_3CO_2)O$ (0.50 mL, 3.60 mmol) was added in one portion to a cooled (to −(50—45) °C, external cooling with a heptane—liquid N_2 mixture) solution of compound **5** (0.4 g, 1.36 mmol) in THF (20 mL). The resulting mixture was stirred for 10 min at the same temperature, and cooled EtSH (0 °C, 3 mL, 41.6 mmol) was added dropwise within 3 min under vigorous stirring. Then the cooling bath was removed, and the reaction mixture was stirred for 15 min at −50 → −20 °C. After that, crystalline $KHCO_3$ (5 g, 50 mmol) was added in one portion, and the resulting mixture was stirred for 30 min at −20 °C → 0 °C. Then, EtOAc (100 mL) and cooled water (0 °C, 100 mL) were subsequently added, and the mixture was vigorously stirred at 0 °C for 5 min. The organic phase was separated, and the mother liquor was extracted with EtOAc (3×25 mL). The combined organic phases were washed with cooled water (100 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was evaporated in vacuo at 25 °C. The residue was purified using flash chromatography (eluent was EtOAc—hexane, 1 : 20—1 : 10). Compound **7** was isolated as white powder, m.p. 77.6—78.1 °C, the yield of 0.39 g (85%). UV (H_2O), λ_{max}/nm (logε): 255.0 (3.175). IR (neat), ν/cm^{-1}: 2960 (CH), 1751 (CO), 1543, 1499, 1453, 1408, 1368, 1327, 1276, 1230, 1146, 1109, 1058, 996, 912, 848, 789, 772, 681, 640, 619, 579. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.21 (t, 3 H, SCH_2CH_3, *J* = 7.4 Hz); 1.39 (s, 9 H Bu^{t}C(3)); 1.63 (s, 9 H, Bu^{t}O); 2.75—2.50 (diastereotopic m, 2 H, SCH_2CH_3); 6.16 (s, 1 H, C(4)H); 6.31 (d, 1 H, C(8)H, *J* = 2.0 Hz); 7.52 (d, 1 H, C(7)H, *J* = 2.0 Hz). ^{13}C NMR (APT, 151 MHz, $CDCl_3$), δ: 13.46 (SCH_2CH_3), 25.23 (SCH_2CH_3), 27.65, 28.74 (2 C(CH_3)$_3$), 36.94 (C(3)C(CH_3)$_3$), 54.97 (C(4)H), 83.35 (OC(CH_3)$_3$), 93.24 (C(8)H), 134.60 (C(8a)), 139.87 (C(7)H), 149.10 (C(3)), 152.69 (CO_2Bu^t). MS: found *m*/*z* (I_{rel} (%)) 339.1843 [M + H] (25), 361.1662 [M + Na] (100), 377.1396 [M + K] (1). $C_{16}H_{26}N_4O_2S$. Calculated: M + H = 339.1849, M + Na = 361.1669, M + K = = 377.1408.

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