Facile bromination of the benzene ring during the cyclisation of the 1H-3-methyl-4-ethoxycarbonyl-5-arylidenehydrazonopyrazoles to the 3-substituted-aryl-1H-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazoles

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Abstract

1H-3-Substituted-aryl-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazoles 2, 3 were obtained by the action of the bromine on the 1H-3-methyl-4-ethoxycarbonyl-5-arylidenehydrazonopyrazoles 1 and were transformed, after hydrolysis-decarboxylation to 1H-3-substituted-aryl pyrazolo[3,2-c]-s-triazoles 5 in the azomethyne dyes 6.

Keywords: Bromination, hydrolysis-decarboxylation, 5-arylidenehydrazonopyrazoles, pyrazolo[3,2-c]-s-triazoles, azomethyne dyes

Introduction

3,6-Disubstituted pyrazolo[3,2-c]-s-triazoles were synthetised1 and utilized for the preparation of couplers for photographic materials2,3,4 and for their biological activity5. 1H-3-Substituted-aryl-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazoles 2 were prepared by the action of the bromine in acetic acid in the presence of anhydrous sodium acetate1 or by the action of lead tetraacetate in acetic acid6 on the 1H-3-methyl-4-ethoxycarbonyl-5-arylidenehydrazono-pyrazole 1 (Scheme 1).
Results and Discussion

The bromine action on the 1H-3-methyl-4-ethoxycarbonyl-5-arylidenehydrazono-pyrazole 1 in acetic acid in the presence of anhydrous sodium acetate led mainly to the pyrazolo-triazole 2a-e in the case of the substituents X=2-NO₂, Y=H b) X=4-NO₂ Y=H c) X=2-Cl Y=H d) X=4-CH₃ Y=H e) X=2OCH₃ Y=H f) X=2-OH Y=H g) X=4-OH Y=H h) X=3-OH Y=H i) X=2-OH Y=4-OH j) X=4-OCH₃ Y=H k)X=2-OCH₃ Y=4-OCH₃ m) X=4-OH Y=3,5-(t-C₄H₉)₂ n) X=2-OCH₃ Y=H Brₙ=(3)5-Br o) X=2-OH Y=H Brₙ=3,5-Br₂ p) X=4-OH Y=H Brₙ=3,5-Br₂ q) X=3-OH Y=H Brₙ=2,4,6-Br₃ s) X=2-OH Y=4-OH Brₙ=3,5-Br₂ t) X=4-OCH₃ Y=H Brₙ=3-Br u) X=2-OCH₃ Y=4-OCH₃ Brₙ=5-Br

Scheme 1

i = Br₂ / CH₃COOH / CH₃COONa ii = Pb(CH₃COO)₂ / CH₃COOH
X=2-NO₂ Y=H b) X=4-NO₂ Y=H c) X=2-Cl Y=H d) X=4-CH₃ Y=H e) X=2OCH₃ Y=H f) X=2-OH Y=H g) X=4-OH Y=H h) X=3-OH Y=H i) X=2-OH Y=4-OH j) X=4-OCH₃ Y=H k)X=2-OCH₃ Y=4-OCH₃ m) X=4-OH Y=3,5-(t-C₄H₉)₂ n) X=2-OCH₃ Y=H Brₙ=(3)5-Br o) X=2-OH Y=H Brₙ=3,5-Br₂ p) X=4-OH Y=H Brₙ=3,5-Br₂ q) X=3-OH Y=H Brₙ=2,4,6-Br₃ s) X=2-OH Y=4-OH Brₙ=3,5-Br₂ t) X=4-OCH₃ Y=H Brₙ=3-Br u) X=2-OCH₃ Y=4-OCH₃ Brₙ=5-Br

Also by the action of one equivalent of the bromine on the 1k, a mixture of 1k 2k and 3u was formed, whereas two equivalent of the bromine led to 3u. The two molecular peaks M⁺ (m/z) at
408, 410 confirmed the monobromination and $^1$H-NMR and $^{13}$C-NMR spectra proved the structure of the 3u.

In the case of the compounds 1f-i, which contains hydroxy groups, utilization of one equivalent of the bromine led to a mixture of compounds. Use of three equivalents of the bromine for 1f 1g 1i led to the dibrominated compounds 3o 3p 3s whereas the utilization of four equivalents of the bromine for 1h led to the tribrominated compound 3r. The dibromination was confirmed by the three molecular peaks M$^+$ (m/z) at 442, 444, 446 for 3o, M$^+$ (m/z) at 442, 444, 446 for 3p, M$^+$ (m/z) at 458, 460, 462 for 3s, and the tribromination by the four molecular peaks M$^+$ (m/z) at 520, 522, 524, 526 for 3r. The structures of the compounds 3o-s were confirmed also by $^1$H-NMR and $^{13}$C-NMR spectra.

The formation and the structure of compounds 3n-u were also confirmed by the synthesis and characterization of compounds 5n-u and of their azomethine dyes 6n-u. (Scheme2). The ethoxycarbonyl groups from the 3-substituted aryl-1H-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazoles 3n-u were eliminated by hydrolysis and decarboxylation to the 3-substituted aryl-1H-6-methyl-pyrazolo[3,2-c]-s-triazoles 5 which were converted to the azomethine dyes 6 by coupling with 2-methyl-4-N,N-diethylamino-aniline 7 in aqueous-alkaline K$_3$Fe(CN)$_6$ solution (Scheme 2).

Our preliminary experiments on the hydrolysis of the compounds 3n-u by heating them 30min at 100 °C with concentrated H$_2$SO$_4$, showed that the acids 4n-u contained variable amounts of the decarboxylated compounds 5n-u and in some cases, the starting material, the esters 3.

\[ C_2H_5OOC \quad H_2SO_4 \quad 80\% \quad / \quad CH_3COOH \quad 4-6 \quad h \quad reflux \quad ii=2,4-(CH_3)(NEt_2)C_6H_3NH_2 \quad 7 \quad / \quad K_3Fe(CN)_6 \quad /NH_4OH-C_2H_5OH \]

**Scheme 2**

This facile decarboxylation of the compounds 4 to 5 during the hydrolysis with concentrated H$_2$SO$_4$ determined us to try one-pot hydrolysis-decarboxylation of 3n-u to 5n-u by 4-6 hours of refluxing with a solution of 80% H$_2$SO$_4$ in acetic acid, method utilized by us for the previously described hydrolysis-decarboxylation of the compounds 2. The new compounds 5n-u were...
characterized by melting point, mass spectrometry, which confirmed the degree of brominating, IR, $^1$H-NMR and $^{13}$C-NMR spectroscopy. They were also characterized by coupling with 2-methyl-4-N,N-diethylamino-aniline 7 in the presence of potassium fericyanide in ethanol-ammonium hydroxide solution. The new azomethyne dyes 6 were characterized by mass spectrometry, UV−VIS, $^1$H-NMR and $^{13}$C-NMR spectroscopy. The preparation of the compounds 5t-6t and 6s were unsuccessful. A single alkaline-hydrolysis experiment of the compound 3f to 4f was successful and after the extension of the experiment to all the compounds 3 it will be reported.

**Experimental Section**

**General Procedures.** TLC was performed using aluminium plates precoated with silica gel 60 or 60 F$_{254}$ (Merck) and visualized by iodine or UV light (254 nm). Melting points were determined on a Böetius PHMK (Veb Analytik Dresden) apparatus. The NMR spectra were recorded on a Varian Gemini 300 and Bruker DRX 400 spectrometer at 25 °C, unless otherwise stated. $^1$H- and $^{13}$C-NMR signals were referenced to TMS and the solvent shift ((CD$_3$)$_2$SO $\delta$H 2.50 and $\delta$C 39.5). Coupling constants are given in Hz and without sign. The IR-spectra were recorded (KBr) on a Jasco FT/IR-410 instrument; the UV−VIS spectra were recorded (CH$_3$OH) on a M40 Karl Zeiss Jena instrument. Mass spectrometry was carried out on a Varian FINNIGAN MAT 212 instrument and the elementar analysis on the Perkin Elmer 240 instrument.

**Materials.** 1H-3-methyl-4-ethoxycarbonyl-5-aryllidene-hydrazono-pyrazoles 1e-k,m were obtained according to the literature.$^{1,7}$ The others materials were commercial samples. All organic solvents were of analytical quality and used as purchased. Solvent mixtures are defined by volume ratios (v/v).

**1H-3-Substituted aryl-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazoles 3n-u**
To a solution of 5 mmol 1H-3-methyl-4-ethoxycarbonyl-5-aryllidenehydrazono-pyrazole 1 e-k, m in 15-25 mL acetic acid was added
10 mmol anhydrous sodium acetate for the compounds 1m
20 mmol anhydrous sodium acetate for the compounds 1e, j, k
30 mmol anhydrous sodium acetate for the compounds 1f, g, i and
40 mmol anhydrous sodium acetate for the compounds 1h
After dissolution by heating of the anhydrous sodium acetate, the solution was cooled to room temperature (water bath) and a solution of
5 mmol Br$_2$ in 5 mL solution of acetic acid for the compounds 1m
10 mmol Br$_2$ in 10 mL solution of acetic acid for the compounds 1e, j, k
15 mmol Br$_2$ in 15 mL solution of acetic acid for the compounds 1f, g, i and
20 mmol Br$_2$ in 20 mL solution of acetic acid for the compounds 1h
was dropped during 10-15 minutes. The formed solution (suspension) was stirred to room temperature for 30 minutes and 1 hour to 100 °C (water bath). After cooling to room temperature, the suspensions were filtered to afford the compounds 3n,o,r-u or the solutions were precipitated in water to afford the compounds 2m 3p.

1H-3-(5-Bromo-2-methoxy)-phenyl-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazole (3n). White powder (yield 78%); mp186-188 °C (acetic acid); MS m/z: 378, 380(M+); IR ν 3227, 3077, 3037, 2978, 2929, 2909, 2843, 1715, 1627, 1596, 1501, 1275, 1217, 1159, 1098, 1014, 879, 808, 771, 727, 689, 621 cm⁻¹; Anal. Calcd for C_{15}H_{15}BrN_{4}O_{3}: C,47.51; H,3.99; N, 14.77; Found: C,47.43; H,4.05; N,14.74.

1H-3-(3,5-Dibromo-2-hydroxy)-phenyl-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazoles (3o). White powder (yield 88%); mp300-302 °C (acetic acid); MS m/z: 442, 444, 446 (M+); IR ν 3190, 3071, 2990, 2971, 1655, 1626, 1322, 1258, 1233, 1187, 1178, 1094, 1045, 1018, 645, 604 cm⁻¹; 1H-NMR δ 10.61 (1H, bs, NH), 8.58 (1H, d, \(J=2.0, \ 6´-H\)), 8.01 (1H, d, \(J=2.0, \ 4´-H\)), 4.34 (2H, q, \(J=7.1, \ CH_3-CH_2-O\)), 3.35 (1H, bs, OH), 2.60 (3H, s, CH_3-6-C), 1.42 (3H, t, \(J=7.1, \ CH_3-CH_2-O\)); 13C-NMR δ 162.99 (C=O), 160.83 (2´-C), 152.73 (7a-C), 148.79 (6-C), 137.35 (4´-C), 129.54 (6´-C), 114.02 (1´-C), 112.92 (5´-C), 112.03 (3´-C), 88.71 (7-C), 59.83 (CH_3-CH_2-O), 15.22 (CH_3-CH_2-O), 14.85 (CH_3-6-C), (Bruker DPX 300); Anal. Calcd. for C_{14}H_{12}Br_{2}N_{4}O_{3}: C,37.86; H,2.72; N,12.62; Found: C,37.83; H,2.85; N,12.57.

1H-3-(3,5-Dibromo-4-hydroxy)-phenyl-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazole (3p). Faintly violet powder (yield 84%); mp 216-217°C (ethanol); MS m/z: 442, 444, 446 (M+); IR ν 3470, 3256, 3078, 2980, 2932, 1702, 1658, 1621, 1326, 1232, 1172, 1103, 1022, 685, 652, 583 cm⁻¹; 1H-NMR δ 10.58 (1H, bs, NH), 8.11 (2H, s, 2´-H, 6´-H), 8.00 (1H, bs, OH), 4.23 (2H, q, \(J=7.1, \ CH_3-CH_2-O\)), 2.28 (3H, s, CH_3-6-C), 1.30 (3H, t, \(J=7.1, \ CH_3-CH_2-O\)); 13C-NMR δ 159.00 (7a-C), 161.43 (C=O), 151.00 (3-C), 137.00 (6-C), 129.46 (2´-C, 6´-C), 122.50 (1´-C), 112.17 (3´-C, 5´-C), 82.5 (7-C), 59.08 (CH_3-CH_2-O), 14.51 (CH_3-6-C), (Bruker AC 200); Anal. Calcd. for C_{14}H_{12}Br_{2}N_{4}O_{3}: C,37.86; H,2.72; N, 12.62; Found: C,37.83; H,2.85; N,12.57.

1H-3-(3,5-Dibromo-2,4-dihydroxy)-phenyl-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazole (3s). Faintly brown powder (yield 75%); mp 302-305 °C (ethanol); MS m/z:458, 460, 462(M+); IR ν 3493, 3263, 3188, 2988, 2935, 1651, 1616, 1322, 1213, 1174, 1105, 1026, 698, 657, 605 cm⁻¹; 1H-NMR δ 10.58 (1H, bs, NH), 8.11 (2H, s, 2´-H, 6´-H), 8.00 (1H, bs, OH), 4.23 (2H, q, \(J=7.1, \ CH_3-CH_2-O\)), 2.28 (3H, s, CH_3-6-C), 1.30 (3H, t, \(J=7.1, \ CH_3-CH_2-O\)); 13C-NMR δ 161.74 (C=O), 159.47 (4´-C), 153.50 (2´-C), 152.95 (7a-C), 148.68 (6-C), 136.56 (3-C), 128.71 (6´-C), 118.77 (1´-C), 104.37 (5´-C), 101.11 (3´-C), 86.75 (7-C), 59.09 (CH_3-CH_2-O), 14.33 (CH_3-CH_2-O), 14.32 (CH_3-6-C), (Bruker AC 200); Anal. Calcd. for C_{14}H_{12}Br_{2}N_{4}O_{4}: C,36.55; H,2.63; N, 12.18; Found: C,36.53; H,2.72; N,12.09.

1H-3-(3,5-Dibromo-2,4-dimethoxy)-phenyl-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazole (3u). White powder (yield 60%); mp 222-224°C (ethanol); MS m/z:408, 410(M+); IR ν 3430, 3151, 2978, 2938, 2845, 1700, 1619, 1605, 1506, 1369, 1277, 1210, 1160, 1096, 1021, 693, 570, 547 cm⁻¹; 1H-NMR (CDCl_3) δ 7.75 (1H, s, 6´-H), 6.82 (1H, s, 3´-H), 4.30 (2H, q, \(J=7.1, \ CH_3-CH_2-O\)), 3.95 (3H, s, CH_3-O), 3.88 (3H, s, CH_3-O), 2.32 (3H, s, CH_3-6-C), 1.29 (3H, t, \(J=7.1, \ CH_3-CH_2-O\)); 13C-NMR δ 162.63(C=O), 161.54 (4´-C), 158.45 (2´-C), 153.02 (3-C),
1H-3-(3-Bromo-4-methoxy)-phenyl-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazole (3t).

Faintly gray powder (yield 80%); mp 196-198 °C (acetic acid); MS m/z: 378, 380(M+); IR ν 3209, 3000, 2932, 2833, 1649, 1626, 1504, 1321, 1252, 1175, 1098, 1021, 1001, 739, 609, 520 cm−1; 1H-NMR δ 13.90 (1H, s, NH), 8.48 (1H, d, J=2.0, 2´-H), 8.27 (1H, dd, J=8.8, 2.0, 6´-H), 7.33 (1H, d, J=8.8, 5´-H), 4.24 (2H, q, J=7.1, CH3-CH2-O), 3.95 (3H, s, CH3O), 2.58 (3H, s, CH3-6-C), 1.33 (3H, t, J=7.1, CH3-CH2-O); 13C-NMR δ 162.06 (C=O), 159.15 (4´-C), 156.80 (7a-C), 147.89 (3-C), 137.05 (6-C), 130.00 (2´-C), 126.85 (6´-C), 118.84 (1´-C), 113.04 (5´-C), 111.01 (3´-C), 86.67 (7-C), 59.02 (CH3-CH2-O), 56.47 (CH3-O), 14.48 (CH3-6-C), 13.52 (CH3-6-C); Anal. Calcd. for C15H15BrN4O3: C, 47.51; H, 3.99; N, 14.77; Found: C, 47.48; H, 4.06; N, 14.69.

A small amount of the isomeric 1H-3-(2-bromo-4-methoxy)-phenyl-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazole was evidenced in the 400MHz spectra.

1H-3-(3-Hydroxy-2,4,6-tribromo)-phenyl-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazole (3r).

White powder (yield 50%); MS m/z: 520, 522, 524, 526(M+); IR ν 3497, 3173, 3074, 3005, 2940, 1660, 1616, 1328, 1223, 1181, 1117, 1094, 1016, 688, 672, 592 cm−1; 1H-NMR δ 10.78 (1H, bs, NH), 8.10 (1H, s, 5´-H), 3.38 (1H, bs, OH), 2.72 (2H, q, J=7.1, CH3-CH2-O), 2.42 (3H, s, CH3-6-C), 1.28 (3H, t, J=7.1, CH3-CH2-O); 13C-NMR δ 161.96 (C=O), 159.28 (3´-C), 151.54 (7a-C), 147.11 (3-C), 137.60 (6-C), 134.94 (5´-C), 127.94 (1´-C), 116.21 (6´-C), 116.17 (4´-C), 114.49 (2´-C), 87.00 (7-C), 59.14 (CH3-CH2-O), 14.55 (CH3-CH2-O), 14.55 (CH3-CH2-O). (Bruker AC 200); Anal. Calcd. for C14H11Br3N4O3: C, 32.15; H, 2.12; N, 10.71; Found: C, 32.13; H, 2.17; N, 10.69.

A small amount (up to 5%) of the 1H-3-(3-bromo-4-hydroxy-5-t-butyl)-phenyl-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazole was evidenced in the 400MHz spectra.

1H-3-(4-Hydroxy-3,5-di-t-butyl)-phenyl-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazole (2m).

Faintly yellow powder (yield 95%); mp 253-256 °C (benzene–petr. et.); MS m/z: 398(M+); IR ν 3605, 3447, 3144, 2958, 2874, 1713, 1669, 1622, 1319, 1240, 1223, 1198, 1159, 1099, 1024 cm−1; 1H-NMR δ 13.69 (1H, s, NH), 9.83 (1H, s, OH), 8.21 (2H, s, 2´-H, 6´-H), 4.30 (2H, q, J=7.1, CH3-CH2-O), 2.50 (3H, s, CH3-6-C), 1.46 (18H, s, t-Bu), 1.33 (3H, t, J=7.1, CH3-CH2-O); 13C-NMR δ 162.21 (C=O), 158.78 (7a-C), 156.00 (3-C), 147.94 (4´-C), 139.39 (3´-C), 139.36 (6-C), 122.92 (6´-C), 116.60 (1´-C), 86.41 (7-C), 58.96 (CH3-CH2-O), 34.69 (C-Me3), 30.04 (C-Me3), 14.80 (CH3-CH2-O), 14.50 (CH3-6-C).

A small amount (up to 5%) of the 1H-3-(bromo-4-hydroxy-5-t-butyl)-phenyl-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazole was evidenced in the 400 MHz spectra.

1H-3-Substituted aryl-6-methyl-pyrazolo[3,2-c]-s-triazoles (5n-u)

A mixture of 1mmol 1H-3-substituted aryl-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazoles 3n-u in 8 mL acetic acid and 2mL H2SO4 80% was refluxed for 4-7 h (TLC benzene / ethyl acetate 1:1). The reaction mixture was filtered, the solution precipitated in 50 mL water, neutralized with 10% NaOH solution, the suspension filtered and the products 5n-u recrystallised.
Preparation of the azomethyne dyes: 3-Substituted-phenyl-6-methyl-7-(2-methyl-4-diethylamino-phenyl-imino-pyrazolo-[3,2-c]-s-triazoles 6n-u

To a solution of 1mol of the compounds 5n-u and 1,1mmol 7 in 15-20 mL ethanol was dropped with stirring a solution of 4,4 mmol K$_3$Fe(CN)$_6$ in 10 mL water and 2 mL 25% ammonium hydroxide. After 10 minute stirring to room temperature the reaction mixture was poured into 100 mL water and filtered. The compounds 6n-u were recrystallised from CH$_3$COOC$_2$H$_5$—petroleum ether.

1H-3-(5-Bromo-2-methoxy)-phenyl-6-methyl-pyrazolo[3,2-c]-s-triazole (5n). White powder (yield 59%); MS m/z: 306, 308(M+); IR $\nu$: 3429, 3220, 3155, 3105, 3074, 3021, 2968, 2928, 2897, 2838, 1611, 1506, 1261, 1185, 1085, 1020, 695, 630, 563, 546 cm$^{-1}$; $^1$H-NMR (CDCl$_3$ with CF$_3$COOH) $\delta$ 7.87 (1H, d, $J$=2.50, 6´-H), 7.33 (1H, dd, $J$=2.50, 9.0, 4´-H), 7.03 (1H, d, $J$=9.0, 3´-H), 6.27 (1H, bs, 7-H), 3.95 (3H, s, OCH$_3$), 2.55 (3H, s, CH$_3$-6-C); $^{13}$C-NMR $\delta$ 161.65 (2´-C), 156.35 (7a-C), 154.50 (3-C), 148.12 (6-C), 137.49 (4´-C), 133.03 (6´-C), 120.21 (1´-C), 114.14 (3´-C), 108.88 (5´-C), 82.26 (7-C), 57.00 (CH$_3$O-2´C), 12.64 (CH$_3$-6C); Anal. Calcd. for C$_{12}$H$_{11}$BrN$_4$O: C,46.93; H,3.61; N, 18.24; Found: C,46.89; H,3.70; N,18.27.

6n. MS m/z: 480, 482(M+); $\lambda_{max}$: 558nm($\varepsilon$ 5,9x10$^4$); $^1$H-NMR (CDCl$_3$) $\delta$ 9.22 (1H, d, $J$=9.50, 14-H), 7.96 (1H, d, $J$=2.50, 6´-H), 7.55 (1H, dd, $J$=2.50, $J$=8.90, 4´-H), 6.93 (1H, d, $J$=8.90, 3´-H), 6.79 (1H, dd, $J$=3.00, $J$=9.50, 13-H), 6.63 (1H, d, $J$=3.00, 11-H), 3.89 (3H, s, OCH$_3$), 3.51 (4H, q, $J$=7.10, -N-CH$_2$-CH$_3$), 2.57 (3H, s, CH$_3$-6-C), 2.49 (3H, s, CH$_3$-10-C), 1.27 (6H, t, $J$=7.10, N-CH$_2$-CH$_3$); $^{13}$C-NMR $\delta$ 168.09 (7-C), 156.94 (2´-C), 153.00 (3-C), 151.62 (7a-C), 148.59 (6-C), 146.19 (12-C), 142.20 (9-C), 135.20 (1´-C), 130.34 (4´-C), 133.74 (6´-C), 127.05 (14-C), 116.75 (1´-C), 113.59 (3´-C), 112.80 (5´-C), 112.57 (11-C), 110.40 (13-C), 56.28 (CH$_3$O-), 45.01 (CH$_3$-CH$_2$-N), 19.45 (CH$_3$-10-C), 12.88 (CH$_3$-CH$_2$-N), 12.66 (CH$_3$-6-C); Anal. Calcd. for C$_{23}$H$_{25}$BrN$_6$O: C,57.39; H,5.23; N, 17.46; Found: C,57.32; H,5.28; N,17.39.

1H-3-(3,5-Dibromo-2-hydroxy)-phenyl-6-methyl-pyrazolo[3,2-c]-s-triazole (5o). White powder (yield 90%); mp235-237 °C (ethanol—water); MS m/z: 370, 372, 374(M+); IR $\nu$: 3595, 3407, 3143, 3075, 2976, 2927, 1607, 1237, 1188, 1103, 1032, 647, 618, 556cm$^{-1}$; $^1$H-NMR (CDCl$_3$ with CF$_3$COOH) $\delta$ 7.92 (1H, d, $J$=2.50, 6´-H), 7.89 (1H, d, $J$=2.50, $J$=8.90, 4´-H), 6.93 (1H, d, $J$=8.90, 3´-H), 6.79 (1H, dd, $J$=3.00, $J$=9.50, 13-H), 6.63 (1H, d, $J$=3.00, 11-H), 3.89 (3H, s, OCH$_3$), 3.51 (4H, q, $J$=7.10, -N-CH$_2$-CH$_3$), 2.57 (3H, s, CH$_3$-6-C); $^{13}$C-NMR $\delta$ 161.48 (2´-C), 155.10 (7a-C), 149.05 (6-C), 148.31 (3-C), 138.82 (4´-C), 131.60 (6´-C), 119.80 (1´-C), 114.38 (5´-C), 108.49 (7-C), 123.0 (CH$_3$-6-C); Anal. Calcd. for C$_{11}$H$_8$Br$_2$N$_4$O: C,35.51; H,2.17; N, 15.06; Found: C,35.49; H,2.22; N,15.02.

6o. MS m/z: 544, 546, 548(M+); $\lambda_{max}$: 576nm($\varepsilon$ 7,9x10$^4$); $^1$H-NMR (CDCl$_3$) $\delta$ 9.10 (1H, d, $J$=9.35, 14-H), 8.51 (1H, d, $J$=2.35, 6´-H), 7.76 (1H, d, $J$=2.35, 4´-H), 6.82 (1H, dd, $J$=9.35, $J$=2.90, 13-H), 6.62 (1H, d, $J$=2.90, 11-H), 3.51 (4H, q, N-CH$_2$-CH$_3$), 2.57 (3H, s, CH$_3$-6-C), 1.29 (6H, t, $J$=7.10, N-CH$_2$-CH$_3$); $^{13}$C-NMR $\delta$ 161.48 (2´-C), 155.10 (7a-C), 149.05 (6-C), 148.31 (3-C), 138.82 (4´-C), 131.60 (6´-C), 119.80 (1´-C), 114.38 (5´-C), 108.49 (3´-C), 86.05 (7-C), 12.30 (CH$_3$-6-C); Anal. Calcd. for C$_{11}$H$_8$Br$_2$N$_4$O: C,35.51; H,2.17; N, 15.06; Found: C,35.49; H,2.22; N,15.02.
1H-3-(3,5-Dibromo-4-hydroxy)-phenyl-6-methyl-pyrazolo[3,2-c]-s-triazole (5p). Brown powder (yield 41%); MS m/z: 370, 372, 374(M+); IR ν 3612, 3488, 3381, 3142, 3078, 2990, 2923, 1601, 1243, 1195, 1041, 1000, 678, 621, 558 cm⁻¹; ¹H-NMR (CDCl₃ with CF₃COOH) δ 8.02 (2H, s, 2´, 6´-H), 6.26 (1H, s, 7-H), 2.56 (3H, s, CH₃-6-C); ¹³C-NMR δ 162.10 (4´-C), 156.50 (7a-C), 153.30 (3-C), 149.10 (6-C), 130.67 (2´-C, 6´-C), 120.31 (1´-C), 108.99 (3´-C, 5´-C), 86.81 (7-C), 12.67 (CH₃-6-C); Anal. Calcd. for C₁₁H₈Br₂N₄O: C, 35.51; H, 2.17; N, 15.06; Found: C, 35.47; H, 2.25; N, 15.01.

6p. MS m/z: 544, 546, 548(M+); λ max: 572 nm (ε 3,5x10⁴); ¹H-NMR (CDCl₃) δ 8.98 (1H, d, J = 9.30, 14-H), 7.84 (2H, s, 2´, 6´-H), 6.83 (1H, dd, J = 9.30, J = 2.90, 13-H), 6.60 (1H, d, J = 2.90, 11-H), 3.51 (4H, q, J = 7.10, CH₂-CH₃), 2.53 (3H, s, CH₃-6-C), 1.28 (6H, t, J = 7.10, N-CH₂-CH₃); ¹³C-NMR δ 165.85 (7-C), 163.20 (3´-C), 152.80 (3-C), 151.60 (7a-C), 148.70 (6-C), 146.50 (12-C), 142.31 (9-C), 139.93 (10-C), 130.82 (2´-C, 6´-C), 126.80 (14-C), 119.50 (1´-C), 112.80 (11-C), 111.85 (3´-C, 5´-C), 109.85 (13´-C), 45.10 (CH₃-CH₂-N), 19.40 (CH₃-10-C), 12.81 (CH₃-CH₂-N), 12.65 (CH₃-6-C); Anal. Calcd. for C₂₂H₂₂Br₂N₆O: C, 48.37; H, 4.06; N, 15.38; Found: C, 48.32; H, 4.12; N, 15.33.

1H-3-(3-Hydroxy-2,4,6-tribromo)-phenyl-6-methyl-pyrazolo[3,2-c]-s-triazole (5r). White-pink powder (yield 40%); MS m/z: 448, 450, 452, 454(M+); IR ν 3556, 3320, 3159, 3074, 2980, 2928, 1599, 1335, 1225, 1176, 1099, 1065, 1014, 684, 656, 585 cm⁻¹; ¹H-NMR (CDCl₃ with CF₃COOH) δ 7.90 (1H, s, 5´-H), 6.27 (1H, s, 7-H), 2.56 (3H, s, CH₃-6-C); ¹³C-NMR δ 164.10 (3´-C), 155.37 (7a-C), 150.77 (3-C), 147.64 (6-C), 135.81 (5´-C), 124.01 (1´-C), 120.20 (6´-C), 115.31 (4´-C), 108.87 (2´-C), 85.90 (7-C), 12.81 (CH₃-6-C); Anal. Calcd. for C₁₁H₇Br₃N₄O: C, 29.30; H, 1.56; N, 12.43; Found: C, 29.25; H, 1.60; N, 12.36.

6r. MS m/z: 622, 624, 626, 628 (M+); λ max: 553 nm (ε 4,8x10⁴); ¹H-NMR (CDCl₃) δ 9.05 (1H, d, J = 9.30, 14-H), 8.15 (1H, s, 5´-H), 6.78 (1H, dd, J = 9.30, J = 2.90, 13-H), 6.56 (1H, d, J = 2.90, 11-H), 3.50 (4H, q, J = 7.10, N-CH₂-CH₃), 2.53 (3H, s, CH₃-6-C), 1.27 (6H, t, J = 7.10, N-CH₂-CH₃); ¹³C-NMR δ 164.10 (3´-C), 155.37 (7a-C), 150.77 (3-C), 147.64 (6-C), 135.81 (5´-C), 124.01 (1´-C), 120.20 (6´-C), 115.31 (4´-C), 108.87 (2´-C), 85.90 (7-C), 12.81 (CH₃-6-C); Anal. Calcd. for C₂₂H₂₁Br₃N₆O: C, 42.27; H, 1.39; N, 13.44; Found: C, 42.21; H, 1.45; N, 13.37.

1H-3-(3,5-Dibromo-2,4-dihydroxy)-phenyl-6-methyl-pyrazolo[3,2-c]-s-triazole (5s). Black powder (yield 76%); mp 145-147 °C (ethanol–water); MS m/z: 386, 388, 390 (M+); IR ν 3585, 3550, 3140, 3073, 2993, 2927, 1605, 1324, 1212, 1100, 1018, 695, 647, 551 cm⁻¹; ¹H-NMR (CDCl₃ with CF₃COOH) δ 7.67 (1H, s, 6´-H), 6.31 (1H, s, 7-H), 2.55 (3H, s, CH₃-6-C); ¹³C-NMR δ 167.62 (4´-C), 161.50 (2´-C), 156.42 (7a-H), 154.82 (3-C), 146.20 (6-C), 135.43 (6´-C), 115.32 (1´-C), 106.77 (5´-C), 101.20 (3´-C), 87.21 (7-C), 13.24 (CH₃-6-C); Anal. Calcd. for C₁₁H₉Br₂N₄O₂: C, 34.05; H, 2.08; N, 14.44; Found: C, 34.00; H, 2.12; N, 14.39.

1H-3-(5-Bromo-2,4-dimethoxy)-phenyl-6-methyl-pyrazolo[3,2-c]-s-triazole (5u). Grey powder (yield 83%); mp 240-242 °C (ethanol); MS m/z: 336, 338 (M+); IR ν 3368, 3061, 2941, 2838, 2749, 1605, 1280, 1213, 1173, 1092, 1017, 550 cm⁻¹; ¹H-NMR δ 7.26 (1H, s, 6´-H), 6.61
(1H, s, 3'-H), 5.56 (1H, s, 7-H), 3.98 (3H, s, CH3-O), 3.91 (3H, s, CH3-O), 2.43 (3H, s, CH3-6-C); 13C-NMR δ 162.00 (4´-C), 157.00 (2´-C), 156.50 (7a-C), 132.54 (6´-C), 132.50 (3´-C), 108.50 (1´-C), 98.28 (5´-C), 76.57 (7-C), 56.33 (CH3O), 56.32 (CH3O), 14.58 (CH3-6-C) (Bruker DPX 300); Anal. Calcd. for C13H13BrN4O2: C, 46.31; H, 3.89; N, 16.62; Found: C, 46.27; H, 3.96; N, 16.58.

6u. MS m/z: 510, 512(M+); λmax 576 nm; 1H-NMR (CDCl3) δ 9.08 (1H, d, J=9.35, 14-H), 7.32 (1H, s, 6'-H), 6.90 (1H, dd, J=9.30, J=2.90, 13-H), 6.72 (1H, s, 3'-H), 6.57 (1H, d, J=2.90, 11-H), 3.98 (3H, s, CH3-O), 3.51 (4H, q, J=7.10, N-CH2-CH3), 2.53 (3H, s, CH3-10-C), 2.43 (3H, s, CH3-6-C), 1.28 (6H, t, J=7.10, N-CH2-CH3); 13C-NMR δ 163.25 (7-C), 162.85 (4´-C), 157.43 (2´-C), 152.23 (3-C), 151.94 (7a-C), 148.22 (6-C), 146.73 (12-C), 142.11 (9-C), 135.22 (10-C), 132.68 (6´-C), 132.33 (3´-C), 125.47 (14-C), 112.63 (1´-C), 111.81 (11-C), 109.90 (13-C), 99.19 (5´-C), 57.05 (CH3O), 56.32 (CH3O), 45.14 (CH3-CH2=N), 19.36 (CH2-10-C), 13.90 (CH2-CH2-N), 13.21 (CH2-6-C); Anal. Calcd. for C24H27BrN6O2: C, 56.36; H, 5.32; N, 16.43; Found: C, 56.31; H, 5.38; N, 16.38 Anal. Calcd. for C24H27BrN6O2: C, 56.36; H, 5.32; N, 16.43; Found: C, 56.31; H, 5.38; N, 16.38.

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References