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LETTERS TO THE EDITOR

Synthesis of 1,2,3-triazolo[1,5-*a*]pyridin-8-ium-3-olates

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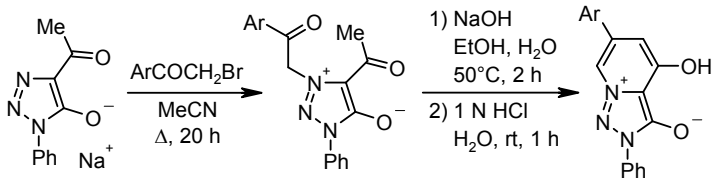


Alkylation of sodium 4-acetyl-1-phenyl-1,2,3-triazol-5-olate with α-bromoacetophenones was shown to occur at position 3 of the heterocycle, with the formation of 1,2,3-triazol-3-ium-5-olates. Intramolecular crotonic condensation of the latter led to the formation of 1,2,3-triazolo[1,5-*a*]pyridin-8-ium-3-olates.

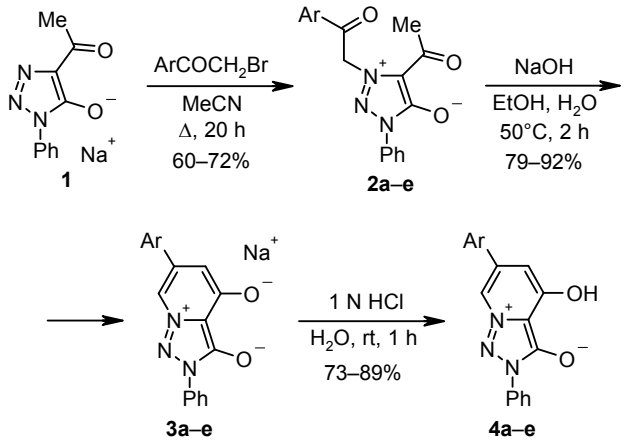
Keywords: azoles, fused heterocycles, mesoionic heterocycles, pyridines, 1,2,3-triazoles, 1,2,3-triazol-3-ium-5-olates, alkylation, crotonic condensation, heterocyclization.

Mesoionic 1,2,3-triazolium-5-olates, in particular their fused analogs, represent a little known class of heterocyclic compounds.[1] At the same time, these compounds have been characterized with regard to various biological effects: herbicidal,[2,3] antitumor,[4] and other types of activity.[5–6] There are two main approaches to the synthesis of fused mesoionic 1,2,3-triazolium-5-olates: intramolecular acylation of triazenes, obtained by azo coupling of cyclic α-amino acids with aromatic and heterocyclic diazonium salts,[1,2,7–10] or intramolecular condensation of mesoionic 1,2,3-triazoles, containing suitable substituents at the ring positions 3 and 4.[6,11–13]

We used the second approach for the synthesis of a new heterocyclic system, 1,2,3-triazolo[1,5-*a*]pyridin-8-ium-3-olates. The reaction of sodium 4-acetyl-1-phenyl-1*H*-1,2,3-triazol-5-olate[14] (**1**) with α-bromoacetophenones allowed us to synthesize the 1,2,3-triazol-3-ium-5-olates **2a**–**e** (Scheme 1). The X-ray structural analysis data for compound **2a** (Fig. 1) confirmed that the alkylation had occurred at position 3 of the triazole ring.

Triazolium-5-olates **2a**–**e** underwent intramolecular crotonic condensation in the presence of NaOH in aqueous alcohol solution, giving the triazolopyridiniumolate sodium salts **3a**–**e**. Acidification of aqueous suspension of the latter gave the triazolopyridiniumolates **4a**–**e**.

Scheme 1



a Ar = Ph, **b** Ar = 4-MeC_6H_4, **c** Ar = 4-$MeOC_6H_4$, **d** Ar = 4-$EtOC_6H_4$, **e** Ar = 4-ClC_6H_4

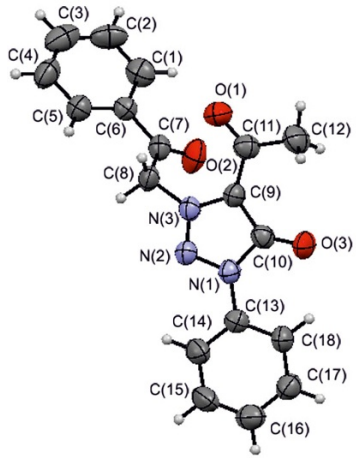


Figure 1. Molecular structure of compound **2a** with atoms represented by thermal vibration ellipsoids of 50% probability.

It should be noted that triazolopyridiniumolates **4a–e**, in particular their sodium salts **3a–e**, rapidly decomposed in DMSO or DMF solutions.

Thus, in this work we propose a convenient method for the synthesis of 4-hydroxy-1,2,3-triazolo[1,5-*a*]pyridin-8-ium-3-olates and their sodium salts.

IR spectra were recorded on a Bruker Alpha spectrometer (ATR, ZnSe). ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance II spectrometer (400 and 100 MHz, respectively) in DMF-d_7 (the ^{13}C NMR spectrum of compound **3a**) and in DMSO-d_6 (the rest of the NMR spectra), with TMS as internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP-2010 Plus GC-MS instrument (EI ionization, 70 eV). Elemental analysis was performed on a PE 2400 Series II CHNS-analyzer. Melting points were determined on a Stuart SMP3 apparatus and were reported uncorrected. The reaction progress and the individuality of the synthesized compounds were monitored by TLC on Silufol UV-254 plates, eluent 1:9 EtOH–$CHCl_3$, visualization under UV light.

4-Acetyl-3-(2-aryl-2-oxoethyl)-1-phenyl-1*H*-1,2,3-triazol-3-ium-5-olates 2a–e (General method). The corresponding α-bromoacetophenone (2.2 mmol) was added to a solution of sodium 4-acetyl-1-phenyl-1*H*-1,2,3-triazol-5-olate (**1**) (500 mg, 2.2 mmol) in anhydrous MeCN (15 ml). The mixture was refluxed for 20 h, cooled; the solvent was removed under vacuum, the obtained residue was recrystallized from a 3:1 mixture of H_2O–EtOH.

4-Acetyl-3-(2-oxo-2-phenylethyl)-1-phenyl-1*H*-1,2,3-triazol-3-ium-5-olate (2a). Yield 460 mg (65%), sand colored powder, mp 115–117°C. IR spectrum, ν, cm^{-1}: 687, 767, 1142, 1231, 1318, 1342, 1359, 1394, 1410, 1460, 1638, 1674 (C=O), 1705 (C=O), 2919–3036 (CH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.44 (3H, s, CH_3); 6.35 (2H, s, CH_2); 7.53 (1H, ddd, *J* = 7.5, *J* = 7.4, *J* = 1.9, H Ph); 7.61–7.66 (4H, m, H Ph); 7.78 (1H, ddd, *J* = 7.4, *J* = 7.7, *J* = 1.2, H Ph); 7.95 (2H, br. d, *J* = 7.4, H Ph); 8.09 (2H, br. d, *J* = 7.2, H Ph). ^{13}C NMR spectrum, δ, ppm: 27.8 (CH_3); 61.1 (CH_2); 116.6, 121.9, 128.8, 129.3, 129.5, 130.0, 134.5, 134.9, 135.1 (C Ar); 156.8 (C-5 triazole); 185.9 (C=O); 190.7 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 322 $[M+H]^+$ (4), 321 $[M]^+$ (16), 146 (16), 119 (12), 105 (75), 91 (15), 77 (100), 51 (23), 43 (45). Found, %: C 67.14; H 4.47; N 12.96. $C_{18}H_{15}N_3O_3$. Calculated, %: C 67.28; H 4.71; N 13.08.

4-Acetyl-3-[2-(4-methylphenyl)-2-oxoethyl]-1-phenyl-1*H*-1,2,3-triazol-3-ium-5-olate (2b). Yield 500 mg (68%), light-yellow powder, mp 134–135°C. IR spectrum, ν, cm^{-1}: 665, 756, 971, 1136, 1229, 1309, 1402, 1457, 1593, 1639, 1673 (C=O), 1699 (C=O), 2925–3087 (CH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.43 (3H, s, CH_3); 2.44 (3H, s, CH_3); 6.30 (2H, s, CH_2); 7.44 (2H, d, *J* = 8.0, HAr); 7.52 (1H, dd, *J* = 7.4, *J* = 7.5, H Ph); 7.63 (2H, dd, *J* = 7.5, *J* = 8.1, H Ph); 7.94–7.99 (4H, m, H Ar, H). ^{13}C NMR spectrum, δ, ppm: 21.8 (CH_3); 27.9 (CH_3); 61.0 (CH_2); 116.7, 121.9, 128.9, 129.2, 130.0 (2C), 132.0, 135.1, 145.5 (C Ar); 156.8 (C-5 triazole); 185.9 (C=O); 190.1 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 336 $[M+H]^+$ (3), 335 $[M]^+$ (15), 160 (7), 133 (7), 119 (100), 105 (18), 91 (29), 77 (60), 65 (12), 51 (13), 43 (34). Found, %: C 67.96; H 5.17; N 12.44. $C_{19}H_{17}N_3O_3$. Calculated, %: C 68.05; H 5.11; N 12.53.

4-Acetyl-3-[2-(4-methoxyphenyl)-2-oxoethyl]-1-phenyl-1*H*-1,2,3-triazol-3-ium-5-olate (2c). Yield 479 mg (62%), yellow-brown crystals, mp 164–165°C. IR spectrum, ν, cm^{-1}: 762, 832, 964, 1025, 1174, 1234, 1394, 1460, 1573, 1597, 1644, 1674 (C=O), 1693 (C=O), 2915–3085 (CH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.41 (3H, s, CH_3); 3.87 (3H, s, OCH_3); 6.25 (2H, s, CH_2); 7.12 (2H, d, *J* = 8.9, H Ar); 7.49 (1H, dd, *J* = 7.5, *J* = 7.4, HPh); 7.60 (2H, dd, *J* = 7.5, *J* = 8.1, H Ph); 7.93 (2H, d, *J* = 7.5, H Ph); 8.03 (2H, d, *J* = 8.9, H Ar). ^{13}C NMR spectrum, δ, ppm: 27.8 (CH_3); 56.2 (OCH_3); 60.8 (CH_2); 114.8, 116.7, 121.8, 127.3, 129.2, 130.0, 131.2, 135.1, 156.8 (C Ar); 164.6 (C-5 triazole); 185.9 (C=O); 188.9 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 352 $[M+H]^+$ (2), 351 $[M]^+$ (11), 136 (9), 135 (100), 121 (12), 107 (6), 92 (7), 78 (6), 77 (50), 51 (9), 43 (21). Found, %: C 64.58; H 5.05; N 12.11. $C_{19}H_{17}N_3O_4$. Calculated, %: C 64.95; H 4.88; N 11.96.

4-Acetyl-3-[2-(4-ethoxyphenyl)-2-oxoethyl]-1-phenyl-1*H*-1,2,3-triazol-3-ium-5-olate (2d). Yield 485 mg (60%), light-yellow powder, mp 169–170°C. IR spectrum, ν, cm^{-1}: 602, 667, 761, 838, 968, 1139, 1173, 1237, 1392, 1459, 1560, 1573, 1644, 1672 (C=O), 1695 (C=O), 2887–3176 (CH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.38 (3H, t, *J* = 7.0, $OCH_2C\underline{H}_3$); 2.43 (3H, s, $COCH_3$); 4.18 (2H, q, *J* = 7.0, $OC\underline{H}_2CH_3$); 6.28 (2H, s, $C\underline{H}_2COAr$); 7.13 (2H, d, *J* = 8.9, H Ar); 7.52 (1H, dd, *J* = 7.4, *J* = 7.4, H Ph); 7.63 (2H, dd, *J* = 7.4, *J* = 7.6, H Ph); 7.94 (2H, d, *J* = 7.6, HPh); 8.04 (2H, d, *J* = 8.9, H Ar). ^{13}C NMR spectrum, δ, ppm: 14.9 (CH_3); 27.8 (CH_3); 60.8 (CH_2); 64.3 (OCH_2); 115.1, 116.7, 121.9, 127.1, 129.2, 130.0, 131.2, 135.1, 156.8 (C Ar); 163.9 (C-5 triazole); 185.9 (C=O); 188.9 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 366 $[M+H]^+$ (3), 365 $[M]^+$ (14), 150 (10), 149 (100), 135 (5), 121 (42), 107 (14), 93 (11), 77 (51), 65 (11), 51 (9), 43 (27). Found, %: C 65.70; H 5.13; N 11.42. $C_{20}H_{19}N_3O_4$. Calculated, %: C 65.74; H 5.24; N 11.50.

4-Acetyl-3-[2-(4-chlorophenyl)-2-oxoethyl]-1-phenyl-1*H*-1,2,3-triazol-3-ium-5-olate (2e). Yield 564 mg (72%), yellow crystals, mp 128–129°C. IR spectrum, ν, cm^{-1}: 759, 833, 1095, 1139, 1228, 1354, 1391, 1401, 1460, 1632, 1680 (C=O), 1701 (C=O), 2951–3066 (CH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.44 (3H, s, CH_3); 6.31 (2H, s, CH_2); 7.53 (1H, dd, *J* = 7.4, *J* = 7.5, H Ph); 7.63 (2H, dd, *J* = 7.0, *J* = 8.1, H Ph); 7.71 (2H, d, *J* = 8.6, H Ar); 7.95 (2H, d, *J* = 7.7, H Ph); 8.10 (2H, d, *J* = 8.6, H Ar). ^{13}C NMR spectrum, δ, ppm: 27.8 (CH_3); 61.0 (CH_2); 116.5, 121.9, 129.3, 129.6, 130.1, 130.7, 133.3, 135.0, 139.8, 156.8 (C Ar); 185.9 (C=O); 189.9 (C=O). Mass spectrum, *m/z* (I_{rel},%): 358 $[M(^{37}Cl)+H]^+$ (3), 357 $[M(^{37}Cl)]^+$ (12), 356 $[M(^{35}Cl)+H]^+$ (8), 355 $[M(^{35}Cl)]^+$ (35), 182 (5), 180 (15), 141 (20), 139 (64), 125 (10), 113 (5), 111 (16), 105 (22), 77 (100), 51 (14), 43 (50). Found, %: C 60.35; H 3.86; N 11.64. $C_{18}H_{14}ClN_3O_3$. Calculated, %: C 60.77; H 3.97; N 11.81.

Sodium 2,6-diaryl-2*H*-1,2,3-triazolo[1,5-*a*]pyridin-8-ium-3,4-bis(olates) 3a–e (General method). A solution of compound **2a–e** (1.2 mmol) in EtOH (15 ml) was treated with NaOH (70 mg, 1.8 mmol) dissolved in minimum amount of H_2O. The reaction mixture was heated at 50°C for 2 h, resulting in the formation of a precipitate. The mixture was then cooled to room temperature, the precipitate was filtered off, washed with water, and dried.

Sodium 2,6-diphenyl-2*H*-1,2,3-triazolo[1,5-*a*]pyridin-8-ium-3,4-bis(olate) (3a). Yield 330 mg (84%), yellow

powder, mp >320°C. IR spectrum, ν, cm^{-1}: 690, 744, 830, 927, 1167, 1231, 1360, 1408, 1488, 1526, 1587, 1632, 3062–3600 (CH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.02 (1H, s, H-5); 7.23 (1H, dd, *J* = 7.4, *J* = 7.4, H Ph); 7.31–7.44 (5H, m, H Ph); 7.49 (1H, s, H-7); 7.57 (2H, d, *J* = 7.2, H Ph); 8.13 (2H, d, *J* = 8.3, H Ph). ^{13}C NMR spectrum, δ, ppm: 102.9; 118.3; 120.2; 126.0; 127.1; 128.2; 129.0 (2C); 137.7; 139.0; 139.5; 154.4; 162.5; 166.6. Found, %: C 66.24; H 3.68; N 13.02. $C_{18}H_{12}N_3NaO_2$. Calculated, %: C 66.46; H 3.72; N 12.92.

Sodium 6-(4-methylphenyl)-2-phenyl-2*H*-1,2,3-triazolo-[1,5-*a*]pyridin-8-ium-3,4-bis(olate) (3b). Yield 370 mg (92%), yellow powder, mp >320°C. IR spectrum, ν, cm^{-1}: 690, 753, 820, 927, 1169, 1234, 1313, 1359, 1399, 1417, 1489, 1538, 1587, 1633, 3209–3496 (CH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.35 (3H, s, CH_3); 5.89 (1H, s, H-5); 7.25 (2H, d, *J* = 7.9, H Ph); 7.30 (1H, dd, *J* = 7.4, *J* = 7.4, H Ph); 7.48–7.58 (5H, m, H-7, H Ar, H Ph); 8.12 (2H, d, *J* = 8.7, H Ar). Found, %: C 66.97; H 4.28; N 12.49. $C_{19}H_{14}N_3NaO_2$. Calculated, %: C 67.25; H 4.16; N 12.38.

Sodium 6-(4-methoxyphenyl)-2-phenyl-2*H*-1,2,3-triazolo[1,5-*a*]pyridin-8-ium-3,4-bis(olate) (3c). Yield 337 mg (79%), yellow powder, mp >320°C. IR spectrum, ν, cm^{-1}: 752, 826, 929, 1049, 1227, 1252, 1290, 1398, 1426, 1489, 1516, 1627, 3106–3350 (CH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.80 (3H, s, OCH_3); 5.87 (1H, s, H-5); 6.99 (2H, d, *J* = 8.7, H Ar); 7.29 (1H, dd, *J* = 7.4, *J* = 7.4, HPh); 7.50 (2H, dd, *J* = 7.4, *J* = 7.8, H Ph); 7.53 (1H, s, H-7); 7.59 (2H, d, *J* = 8.7, H Ar); 8.12 (2H, d, *J* = 7.8, H Ph). ^{13}C NMR spectrum, δ, ppm: 55.1 (OCH_3); 99.5; 104.0; 114.1; 117.6; 119.6; 125.6; 127.7; 128.9; 130.5; 136.8; 138.4; 153.7; 159.3; 167.2. Found, %: C 63.95; H 3.80; N 11.68. $C_{19}H_{14}N_3NaO_3$. Calculated, %: C 64.23; H 3.97; N 11.83.

Sodium 6-(4-ethoxyphenyl)-2-phenyl-2*H*-1,2,3-triazolo-[1,5-*a*]pyridin-8-ium-3,4-bis(olate) (3d). Yield 375 mg (85%), bright-yellow powder, mp >320°C. IR spectrum, ν, cm^{-1}: 752, 825, 926, 1048, 1226, 1253, 1359, 1398, 1426, 1488, 1515, 1587, 1608, 1633, 3228–3385 (CH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.35 (3H, t, *J* = 6.9, $OCH_2C\underline{H}_3$); 4.06 (2H, q, *J* = 6.9, $OC\underline{H}_2CH_3$); 5.93 (1H, s, H-5); 6.96 (2H, d, *J* = 8.6, H Ar); 7.29 (1H, dd, *J* = 7.3, *J* = 7.3, H Ph); 7.51 (2H, dd, *J* = 7.3, *J* = 7.9, H Ph); 7.54 (1H, s, H-7); 7.57 (2H, d, *J* = 8.6, H Ar); 8.12 (2H, d, *J* = 7.9, H Ph). ^{13}C NMR spectrum, δ, ppm: 15.1 (CH_3); 63.7 (CH_2); 100.9; 104.5; 115.2; 118.1; 120.2; 126.1; 128.2; 129.3; 130.9; 137.4; 139.0; 154.2; 159.1; 167.6. Found, %: C 64.94; H 4.80; N 11.15. $C_{20}H_{16}N_3NaO_3$. Calculated, %: C 65.04; H 4.37; N 11.38.

Sodium 6-(4-chlorophenyl)-2-phenyl-2*H*-1,2,3-triazolo-[1,5-*a*]pyridin-8-ium-3,4-bis(olate) (3e). Yield 392 mg (91%), dark-yellow powder, mp >320°C. IR spectrum, ν, cm^{-1}: 754, 816, 927, 1359, 1393, 1416, 1489, 1537, 1586, 1633, 3022–3472 (CH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.98 (1H, br. s, H-5); 7.30 (1H, dd, *J* = 7.2, *J* = 7.3, HPh); 7.45–7.51 (4H, m, H Ar); 7.65 (1H, s, H-7); 7.68 (2H, d, *J* = 7.2, H Ph); 8.09 (2H, d, *J* = 7.7, H Ph). ^{13}C NMR spectrum, δ, ppm: 99.5; 114.7; 120.2; 126.7; 128.6; 128.7; 129.0; 129.1; 133.5; 135.2; 135.3; 136.0; 139.0; 136.2. Found, %: C 60.18; H 3.20; N 11.46. $C_{18}H_{11}ClN_3NaO_2$. Calculated, %: C 60.10; H 3.08; N 11.68.

2,6-Diaryl-4-hydroxy-2*H*-1,2,3-triazolo[1,5-*a*]pyridin-8-ium-3-olates 4a–e (General method). A suspension of salt **3a–e** (0.74 mmol) in H_2O (20 ml) was acidified with 1 N HCl to pH 1–3. The reaction mixture was maintained at room temperature for 1 h, the precipitate was filtered off, washed with water, and dried.

4-Hydroxy-2,6-diphenyl-2*H*-1,2,3-triazolo[1,5-*a*]pyridin-8-ium-3-olate (4a). Yield 185 mg (82%), yellow powder, mp 240–242°C. IR spectrum, ν, cm^{-1}: 689, 751, 831, 924, 1157, 1315, 1364, 1414, 1489, 1550, 1593, 1643, 2546–3062 (CH, OH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.52 (1H, d, *J* = 1.0, H-5); 7.38 (1H, dd, *J* = 7.4, *J* = 7.4, H Ph); 7.45–7.58 (5H, m, H Ph); 7.72 (2H, d, *J* = 6.9, H Ph); 8.08 (2H, d, *J* = 7.6, H Ph); 8.42 (1H, d, *J* = 1.0, H-7); 11.31 (1H, br. s, OH). ^{13}C NMR spectrum, δ, ppm: 100.0; 101.4; 112.9; 113.6; 120.9; 127.4; 129.6; 129.7 (2C); 136.1; 136.7; 137.1; 151.5; 154.2. Mass spectrum, *m*/*z* (I_{rel}, %): 304 $[M+H]^+$ (5), 303 $[M]^+$ (24), 198 (52), 170 (44), 142 (22), 140 (8), 116 (22), 115 (100), 105 (8), 89 (6), 77 (84), 63 (5), 51 (30). Found, %: C 70.99; H 4.31; N 13.47. $C_{18}H_{13}N_3O_2$. Calculated, %: C 71.28; H 4.32; N 13.85.

4-Hydroxy-6-(4-methylphenyl)-2-phenyl-2*H*-1,2,3-triazolo[1,5-*a*]pyridin-8-ium-3-olate (4b). Yield 209 mg (89%), sand colored powder, mp 252–253°C. IR spectrum, ν, cm^{-1}: 688, 755, 790, 830, 1155, 1174, 1231, 1248, 1309, 1406, 1426, 1489, 1519, 1555, 1606, 1633, 2623–3062 (CH, OH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.37 (3H, s, CH_3); 6.52 (1H, d, *J* = 0.7, H-5); 7.33 (2H, d, *J* = 8.0, H Ar); 7.39 (1H, dd, *J* = 7.4, *J* = 7.4, HPh); 7.56 (2H, dd, *J* = 8.2, *J* = 7.7, H Ph); 7.61 (2H, d, *J* = 8.1, H Ar); 8.09 (2H, d, *J* = 7.7, H Ph); 8.39 (1H, d, *J* = 0.7, H-7); 11.28 (1H, br. s, OH). ^{13}C NMR spectrum, δ, ppm: 21.2 (CH_3); 101.4; 112.5; 113.5; 120.8; 127.2; 127.4; 129.6; 130.2; 133.2; 136.7; 137.0; 139.2; 151.5; 154.1. Mass spectrum, *m*/*z* (I_{rel}, %): 319 $[M+2H]^+$ (1), 318 $[M+H]^+$ (10), 317 $[M]^+$ (44), 212 (91), 184 (59), 156 (34), 140 (10), 129 (98), 115 (20), 105 (7), 91 (6), 77 (100), 65 (6), 51 (30). Found, %: C 71.87; H 4.40; N 13.12. $C_{19}H_{15}N_3O_2$. Calculated, %: C 71.91; H 4.76; N 13.24.

4-Hydroxy-6-(4-methoxyphenyl)-2-phenyl-2*H*-1,2,3-triazolo[1,5-*a*]pyridin-8-ium-3-olate (4c). Yield 190 mg (77%), yellow powder, mp 247–248°C. IR spectrum, ν, cm^{-1}: 754, 925, 1120, 1405, 1427,1490, 1520, 1555, 1635, 2649–3061 (CH, OH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.81 (3H, s, OCH_3); 6.50 (1H, d, *J* = 1.0, H-5); 7.07 (2H, d, *J* = 8.8, H Ar); 7.38 (1H, dd, *J* = 7.4, *J* = 7.4, H Ph); 7.55 (2H, dd, *J* = 8.3, *J* = 7.6, H Ph); 7.61 (2H, d, *J* = 8.7, H Ar); 8.08 (2H, d, *J* = 7.6, H Ph); 8.37 (1H, d, *J* = 1.0, H-7); 11.23 (1H, br. s, OH). ^{13}C NMR spectrum, δ, ppm: 55.8 (OCH_3); 101.4; 101.2; 112.1; 113.4; 115.1; 120.8; 127.3; 128.2; 128.7; 129.7; 136.7; 151.5; 154.7; 160.6. Mass spectrum, *m*/*z* (I_{rel}, %): 334 $[M+H]^+$ (4), 333 $[M]^+$ (21), 288 (48), 200 (30), 185 (8), 172 (12), 169 (4), 157 (4), 146 (11), 145 (36), 140 (6), 131 (10), 115 (15), 102 (13), 77 (100), 63 (5), 51 (33). Found, %: C 68.38; H 4.22; N 12.39. $C_{19}H_{15}N_3O_3$. Calculated, %: C 68.46; H 4.54; N 12.61.

6-(4-Ethoxyphenyl)-4-hydroxy-2-phenyl-2*H*-1,2,3-triazolo[1,5-*a*]pyridin-8-ium-3-olate (4d). Yield 188 mg (73%), dark-yellow powder, mp 250–251°C. IR spectrum, ν, cm^{-1}: 753, 823, 922, 1044, 1153, 1180, 1228, 1252, 1406, 1487, 1518, 1556, 1606, 1625, 2631–3044 (CH, OH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.36 (3H, t, *J* = 6.9,

$OCH_2C\underline{H}_3$); 4.09 (2H, q, J = 6.9, $OC\underline{H}_2CH_3$); 6.49 (1H, s, H-5); 7.05 (2H, d, J = 8.6, H Ar); 7.38 (1H, dd, J = 7.4, J = 7.4, H Ph); 7.56 (2H, dd, J = 7.4, J = 7.8, H Ph); 7.65 (2H, d, J = 8.6, H Ar); 8.09 (2H, d, J = 7.8, H Ph); 8.39 (1H, s, H-7); 10.00–12.00 (1H, br. s, OH). ^{13}C NMR spectrum, δ, ppm: 15.1 (CH_3); 63.7 (CH_2); 100.0; 101.3; 111.6; 115.5; 120.7; 127.3; 128.1; 128.6; 129.6; 136.7; 136.8; 140.2; 151.6; 159.8. Mass spectrum, *m*/*z* (I_{rel}, %): 349 $[M+2H]^+$ (2), 348 $[M+H]^+$ (11), 347 $[M]^+$ (45), 243 (16), 242 (100), 215 (7), 214 (49), 186 (22), 159 (16), 158 (28), 140 (6), 132 (18), 131 (58), 130 (10), 115 (6), 105 (8), 103 (22), 102 (9), 78 (8), 77 (98), 76 (5), 51 (22). Found, %: C 68.69; H 4.64; N 11.89. $C_{20}H_{17}N_3O_3$. Calculated, %: C 69.15; H 4.93; N 12.10.

6-(4-Chlorophenyl)-4-hydroxy-2-phenyl-2*H*-1,2,3-triazolo[1,5-*a*]pyridin-8-ium-3-olate (4e). Yield 192 mg (77%), sand colored powder, mp 252–253°C. IR spectrum, ν, cm^{-1}: 754, 830, 925, 1092, 1161, 1316, 1391, 1427, 1489, 1545, 1594, 1636, 2650–3069 (CH, OH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.53 (1H, s, H-5); 7.39 (1H, dd, J = 7.3, J = 7.4, H Ar); 7.53–7.59 (4H, m, H Ar); 7.74 (2H, d, J = 8.3, H Ar); 8.08 (2H, d, J = 8.0, H Ar); 8.44 (2H, d, J = 0.7, H-7); 10.00–12.50 (1H, br. s, OH). ^{13}C NMR spectrum, δ, ppm: 101.2; 113.0; 113.7; 120.9; 120.7; 127.4; 129.2; 129.6; 129.7; 134.4; 135.0; 135.8; 136.6; 151.5; 154.3. Mass spectrum, *m*/*z* (I_{rel},%): 339 $[M(^{37}Cl)]^+$ (9), 338 $[M(^{35}Cl)+H]^+$ (7), 337 $[M(^{35}Cl)]^+$ (32), 234 (26), 232 (75), 206 (149), 204 (45), 176 (14), 169 (12), 151 (9), 149 (40), 140 (25), 114 (11), 105 (9), 78 (10), 77 (100), 63 (6), 52 (11), 51 (37), 50 (10), 39 (29). Found, %: C 63.87; H 3.66; N 12.28. $C_{18}H_{12}ClN_3O_2$. Calculated, %: C 64.01; H 3.58; N 12.44.

X-Ray structural analysis of compound 2a was performed on an Xcalibur S automated four-circle X-ray diffractometer by using the standard procedure (MoKα radiation, graphite monochromator, ω/2θ-scanning). A yellow prismatic crystal with dimensions of 0.4×0.3×0.25 mm was used for the analysis of compound **2a** ($C_{18}H_{15}N_3O_3$, M 321.33). The crystal at 295(2) K was rhombic; space group $P2_12_12_1$; unit cell parameters: a 8.0484(12), b 8.1876(8), c 23.784(3) A; Z 4; d_{calc} 1.362 g/cm^3; μ 0.095 mm^{-1}. A total of 8547 reflections were collected in the range of $2.63 < \theta < 26.37°$, of which 3064 were independent (R_{int} 0.0688), including 1812 reflections with $I > 2\sigma(I)$. No correction for absorption was used. The structure was solved and refined with the SHELX[15] software suite by using anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were placed at calculated positions and were included in the refinement according to the "rider" model in isotropic approximation with dependent thermal parameters. The final structural refinement parameters: R_1 0.0414, wR_2 0.0761 (by reflections with $I > 2\sigma(I)$), R_1 0.0784, wR_2 0.0811 (by all reflections) with the robustness parameter S 1.001. The maximum/minimum residual electron density peaks were 0.131/–0.195 $\bar{e}Å^{-3}$. The atomic coordinates and temperature factors were deposited at the Cambridge Crystallographic Data Center (deposit CCDC 1030491).

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