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Polyfunctional pyrazoles

11*. Synthesis of 5-aroylpyrano[3,4-*c*]pyrazol-7(2*H*)-ones

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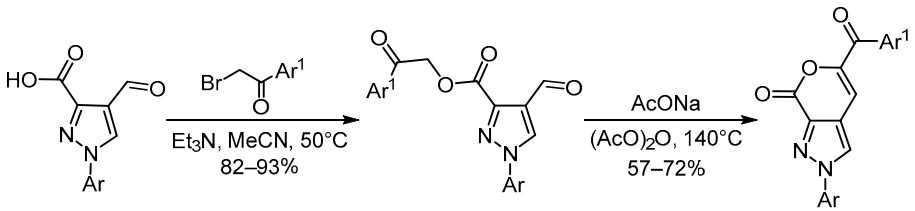


Aroylmethyl esters of 4-formylpyrazole-3-carboxylic acids underwent intramolecular cyclocondensation in the presence of sodium acetate in refluxing acetic anhydride, giving moderate yields of 5-aroylpyrano[3,4-*c*]pyrazol-7(2*H*)-ones.

Keywords: aroylmethyl esters, 5-aroylpyrano[3,4-*c*]pyrazoles, 4-formylpyrazole-3-carboxylic acids, intramolecular cyclocondensation.

Isocoumarins (2-benzopyran-1*H*-ones) belong to a class of lactone structures with a major synthetic potential and a broad range of biological activity.[2–4] Particularly mentioned in the series of functionally substituted isocoumarins should be their 3-carbonyl derivatives, in particular 3-acylisocoumarins, which represent convenient precursors for the preparation of certain natural compounds.[5–7] No less significant are 3-aroylisocoumarins, some of which have been characterized with antimicrobial and analgesic activity.[8–11]

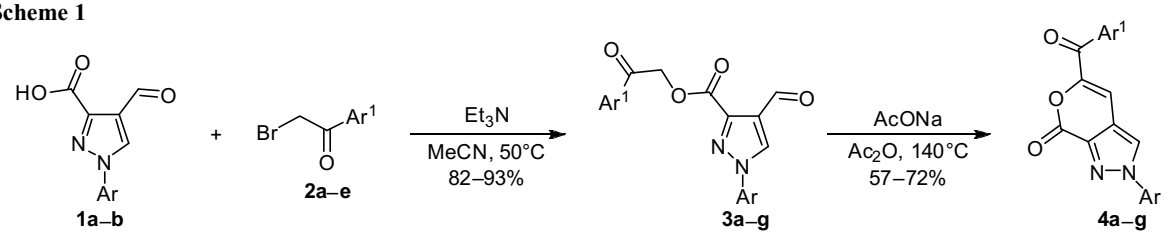
In contrast to isocoumarins, their heteroannulated analogs remain practically unexplored. Only a single report has been published on the synthesis of pyrano[2,3-*c*]-azepines,[12] along with two publications describing the preparation of pyrano[3,4-*c*]pyrazoles[13] and pyrano[4,3-*c*]-pyrazoles *via* acetylenation and subsequent cyclization of isomeric 4-iodo-1-methylpyrazole-3- and 4-iodo-1-methylpyrazole-5-carboxylic acids with copper acetylides in pyridine. The method is limited to only a few examples and has not found further practical applications.[14]

This report is devoted to the development of a method for the synthesis of pyrano[3,4-*c*]pyrazole system functionalized at position 5 with an aroyl substituent. The starting materials used for this purpose were our previously described[15] 1-aryl-4-formylpyrazole-3-carboxylic acids **1a**,**b** (Scheme 1). The initial attempts of using carboxylic acid **1a** in condensation reaction with phenacyl bromide (**2a**) under conditions suitable for the preparation of 3-aroylisocoumarins (anhydrous K_2CO_3, refluxing in methyl ethyl ketone[8] or DBU, heating in benzene at 60°C[16]) did not produce the expected result. In the first case, only the respective aroylmethyl ester **3a** was isolated in 52% yield, while in the second case the reaction did not proceed at all.

We demonstrated the suitability of a two-stage procedure for the synthesis of the target pyranopyrazoles. The first stage involved alkylation of carboxylic acids **1a**,**b** with bromomethyl aryl ketones **2a**–**e** in MeCN, while using Et_3N as a base. Heating the reagents for 2 h at 50°C allowed to obtain the aroylmethyl esters of 4-formylpyrazole-3-carboxylic acids **3a**–**g** in 82–93% yields. The following attempts to achieve intramolecular cyclocondensation of compound **3a** under alkaline conditions for the purpose of converting it to pyrano[3,4-*c*]pyrazole **4a** were unsuccessful when using KOH in EtOH, as well as MeONa or *t*-BuOK in MeOH. In all of these cases, only carboxylic acid **1a** was isolated as a hydrolysis product.

* For Communication 11, see [1].

Scheme 1



1a Ar = Ph, **b** Ar = 4-BrC_6H_4

2 a Ar^1 = Ph, **b** Ar^1 = 3-BrC_6H_4, **c** Ar^1 = 3-ClC_6H_4, **d** Ar^1 = 4-ClC_6H_4, **e** Ar^1 = 4-FC_6H_4

3, **4 a** Ar = Ar^1 = Ph; **b** Ar = Ph, Ar^1 = 3-BrC_6H_4; **c** Ar = Ph, Ar^1 = 3-ClC_6H_4; **d** Ar = Ph, Ar^1 = 4-ClC_6H_4; **e** Ar = Ph, Ar^1 = 4-FC_6H_4; **f** Ar = 4-BrC_6H_4, Ar^1 = 4-ClC_6H_4; **g** Ar = 4-BrC_6H_4, Ar^1 = 4-FC_6H_4

However, a successful result was obtained when the process was performed in acetic anhydride medium in the presence of an equimolar amount of anhydrous sodium acetate. It was found that refluxing esters **3a**–**g** in acetic anhydride in the presence of sodium acetate for 4 h resulted in the formation of pyran ring and provided compounds **4a**–**g** in 57–72% yields, as well as generated some unidentified by-products.

The structures of the intermediate products **3a**–**g**, as well as the target compounds **4a**–**g** were confirmed by a set of physicochemical analytical methods. The condensation of aroylpyran ring in this process was evidenced by the appearance of strong IR absorption bands due to the presence of aroyl and lactone groups in the range of 1659–1662 and 1754–1761 cm^{-1}, respectively. At the same time, ^{13}C NMR spectra featured the signals of C-3a carbon atom at 120–121 ppm, C-4 atom at 107–108 ppm, C-5 atom at 133–137 ppm, C-7 atom at 154–155 ppm, and C-7a atom at 138 ppm.

Thus, we have developed a convenient method for the synthesis of previously unknown 5-aroylpyrano[3,4-*c*]-pyrazol-7(2*H*)-ones, based on intramolecular condensation of the respective aroylmethyl esters of 4-formylpyrazole-3-carboxylic acids in an acetic anhydride – sodium acetate system.

Experimental

IR spectra were recorded on a Bruker Vertex 70 instrument in KBr pellets. ^1H and ^{13}C NMR spectra were acquired on a Varian VXR-400 spectrometer (400 and 100 MHz, respectively) in pulse Fourier transform mode in DMSO-d_6 solution. The signal positions were determined on δ scale relative to the residual solvent signal (2.49 ppm for ^1H nuclei). The assignment of carbon atom signals was based on using the APT method. Mass spectra were recorded on an Agilent LC/MSD SL instrument; Zorbax SB-C18 column, 4.6 × 15 mm, 1.8 μm (PN 82(c)75-932); solvent system component A: MeCN–H_2O, 95:5, 0.1% CF_3COOH, component B: 0.1% CF_3COOH; flow rate 3 ml/min; injection volume 1 μl; UV detection at 215, 254, 285 nm; chemical ionization at atmospheric pressure, reagent – HCOOH, *m*/*z* scanning range 80–1000. Elemental analysis was performed on a PerkinElmer CHN Analyzer at the analytical laboratory of the Institute of Organic Chemistry, National Academy of Sciences of Ukraine. Melting points were determined on a Kofler bench and were not corrected.

Preparation of aroylmethyl esters of 4-formyl-1-phenylpyrazole-3-carboxylic acids 3a–g (General method). A solution of carboxylic acid **1a**,**b** (0.01 mol) in MeCN (15 ml) was treated first by the addition of Et_3N (1.00 g, 0.01 mol), followed by addition of the appropriate bromomethyl aryl ketone **2a**–**e** (0.01 mol). The reaction mixture was stirred for 1 h at room temperature and 2 h at 50°C. The reaction mixture was cooled to room temperature and poured into ice water (100 ml). The precipitate that formed was filtered off, washed with water (2×25 ml), dried, and crystallized from EtOH.

2-Oxo-2-phenylethyl 4-formyl-1-phenyl-1*H*-pyrazole-3-carboxylate (3a). Yield 2.75 g (82%), colorless crystals, mp 168–170°C. IR spectrum, ν, cm^{-1}: 1677 (C=O), 1701 (C=O), 1724 (C=O). ^1H NMR spectrum, δ, ppm: 5.87 (2H, s, CH_2); 7.45–7.74 (6H, m, H Ph); 7.99 (2H, d, *J* = 7.6, H Ph); 8.02 (2H, d, *J* = 7.6, H Ph); 9.25 (1H, s, H-5); 10.36 (1H, s, CH=O). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 67.5 (CH_2); 119.6 (CH); 125.2 (C); 127.6 (CH); 128.1 (CH); 128.7 (CH); 129.5 (CH); 131.3 (CH); 133.7 (C); 134.1 (CH); 138.2 (C); 143.0 (C); 160.4 (C=O); 185.4 (CH=O); 192.1 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 335 $[M+H]^+$ (100). Found, %: C 68.11; H 4.31; N 8.49. $C_{19}H_{14}N_2O_4$. Calculated, %: C 68.26; H 4.22; N 8.38.

2-(3-Bromophenyl)-2-oxoethyl 4-formyl-1-phenyl-1*H*-pyrazole-3-carboxylate (3b). Yield 3.60 g (87%), colorless crystals, mp 158–160°C. IR spectrum, ν, cm^{-1}: 1678 (C=O), 1705 (C=O), 1727 (C=O). ^1H NMR spectrum, δ, ppm: 5.89 (2H, s, CH_2); 7.46–7.65 (4H, m, H Ar); 7.91–8.20 (4H, m, H Ar, H Ph); 8.19 (1H, s, H-2 Ph); 9.30 (1H, s, H-5); 10.34 (1H, s, CH=O). ^{13}C NMR spectrum, δ, ppm: 67.3 (CH_2); 119.9 (CH); 122.1 (C); 125.1 (C); 126.8 (CH); 128.2 (CH); 129.7 (CH); 130.0 (CH); 130.7 (CH); 131.6 (CH); 135.7 (C); 136.6 (CH); 138.2 (C); 142.9 (C); 160.1 (C=O); 185.4 (CH=O); 191.4 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 413 $[M(^{79}Br)+H]^+$ (100), 415 $[M(^{81}Br)+H]^+$ (80). Found, %: C 55.45; H 3.21; N 6.62. $C_{19}H_{13}BrN_2O_4$. Calculated, %: C 55.23; H 3.17; N 6.78.

2-(3-Chlorophenyl)-2-oxoethyl 4-formyl-1-phenyl-1*H*-pyrazole-3-carboxylate (3c). Yield 3.14 g (85%), colorless crystals, mp 171–173°C. IR spectrum, ν, cm^{-1}: 1680 (C=O), 1704 (C=O), 1725 (C=O). ^1H NMR spectrum, δ, ppm: 5.89 (2H, s, CH_2); 7.46–7.81 (5H, m, H Ph); 7.99–8.06 (4H, m, H Ar); 9.29 (1H, s, H-5); 10.35 (1H, s, CH=O). ^{13}C NMR spectrum, δ, ppm: 67.6 (CH_2); 119.7 (CH); 125.2 (C); 126.6 (CH); 127.2 (CH); 128.4 (CH); 129.5 (CH); 130.8 (CH); 131.5 (CH); 133.6 (CH); 133.9

(C); 135.5 (C); 138.3 (C); 143.0 (C); 160.2 (C=O); 184.7 (CH=O); 191.4 (C=O). Mass spectrum, *m/z* (I_{rel},%): 369 $[M+H]^+$ (100). Found, %: C 61.63; H 3.44; N 7.75. $C_{19}H_{13}ClN_2O_4$. Calculated, %: C 61.88; H 3.55; N 7.60.

2-(4-Chlorophenyl)-2-oxoethyl 4-formyl-1-phenyl-1*H*-pyrazole-3-carboxylate (3d). Yield 3.43 g (93%), colorless crystals, mp 188–190°C. IR spectrum, ν, cm^{-1}: 1675 (C=O), 1700 (C=O), 1728 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 5.86 (2H, s, CH_2); 7.43–7.67 (5H, m, H Ph); 7.99 (2H, d, *J* = 8.0, H Ar); 8.04 (2H, d, *J* = 8.0, H Ar); 9.27 (1H, s, H-5); 10.34 (1H, s, CH=O). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 67.4 (CH_2); 119.6 (CH); 125.2 (C); 128.5 (CH); 129.0 (CH); 129.7 (C); 129.8 (CH); 131.6 (C); 132.4 (CH); 138.2 (C); 143.0 (C); 160.2 (C=O); 185.6 (CH=O); 191.3 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 369 $[M+H]^+$ (100). Found, %: C 61.67; H 3.69; N 7.78. $C_{19}H_{13}ClN_2O_4$. Calculated, %: C 61.88; H 3.55; N 7.60.

2-(4-Fluorophenyl)-2-oxoethyl 4-formyl-1-phenyl-1*H*-pyrazole-3-carboxylate (3e). Yield 3.17 g (90%), colorless crystals, mp 178–180°C. IR spectrum, ν, cm^{-1}: 1676 (C=O), 1703 (C=O), 1727 (C=O). ^1H NMR spectrum, δ, ppm: 5.87 (2H, s, CH_2); 7.41–7.60 (5H, m, H Ph); 7.97–8.02 (2H, m, H Ar); 8.11–8.15 (2H, m, H Ar); 9.30 (1H, s, H-5); 10.35 (1H, s, CH=O). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 67.2 (CH_2); 116.1 (CH); 120.0 (CH); 125.1 (C); 128.3 (CH); 129.4 (CH); 130.4 (C); 130.6 (CH, d, $^2J_{CF}$ = 26.3); 131.4 (CH); 138.2 (C); 143.0 (C); 160.2 (C=O); 165.3 (C, d, $^1J_{CF}$ = 251.3); 185.4 (CH=O); 190.7 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 353 $[M+H]^+$ (100). Found, %: C 64.56; H 3.79; N 8.11. $C_{19}H_{13}FN_2O_4$. Calculated, %: C 64.77; H 3.72; N 7.95.

2-(4-Chlorophenyl)-2-oxoethyl 1-(4-bromophenyl)-4-formyl-1*H*-pyrazole-3-carboxylate (3f). Yield 3.78 g (84%), colorless crystals, mp 155–157°C. IR spectrum, ν, cm^{-1}: 1679 (C=O), 1701 (C=O), 1729 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 5.87 (2H, s, CH_2); 7.67 (2H, d, *J* = 8.4, H Ar); 7.79 (2H, d, *J* = 8.4, H Ar); 7.97 (2H, d, *J* = 8.4, H Ar); 8.04 (2H, d, *J* = 8.4, H Ar); 9.32 (1H, s, H-5); 10.33 (1H, s, CH=O). ^{13}C NMR spectrum, δ, ppm: 67.5 (CH_2); 121.3 (C); 121.7 (CH); 125.3 (C); 128.9 (CH); 129.7 (CH); 131.8 (CH); 132.4 (C); 132.5 (CH); 137.5 (C); 139.0 (C); 143.2 (C); 160.2 (C=O); 185.9 (CH=O); 191.3 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 448 $[M(^{79}Br)+H]^+$ (100), 450 $[M(^{81}Br)+H]^+$ (85). Found, %: C 51.23; H 2.81; N 6.35. $C_{19}H_{12}BrClN_2O_4$. Calculated, %: C 50.98; H 2.70; N 6.26.

2-(4-Fluorophenyl)-2-oxoethyl 1-(4-bromophenyl)-4-formyl-1*H*-pyrazole-3-carboxylate (3g). Yield 3.75 g (87%), colorless crystals, mp 162–164°C. IR spectrum, ν, cm^{-1}: 1677 (C=O), 1702 (C=O), 1727 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 5.87 (2H, s, CH_2); 7.45 (2H, d, *J* = 8.2, H Ar); 7.98 (2H, d, *J* = 8.4, H Ar); 8.12 (2H, d, *J* = 8.4, H Ar); 8.13–8.16 (2H, m, H Ar); 9.32 (1H, s, H-5); 10.33 (1H, s, CH=O). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 67.5 (CH_2); 116.0 (CH, d, $^2J_{CF}$ = 22.1); 121.3 (C), 121.7 (CH); 125.3 (C); 130.5 (C); 131.0 (CH, d, $^3J_{CF}$ = 9.1); 131.9 (CH); 132.6 (CH); 137.5 (C); 143.2 (C); 160.2 (C=O); 165.2 (C, d, $^1J_{CF}$ = 230.2); 185.9 (CH=O); 190.8 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 431 $[M(^{79}Br)+H]^+$ (100), 433 $[M(^{81}Br)+H]^+$ (85). Found, %: C 53.16; H 2.89; N 6.63. $C_{19}H_{12}BrFN_2O_4$. Calculated, %: C 52.92; H 2.81; N 6.50.

Preparation of 5-aroylpyrano[3,4-*c*]pyrazol-7(2*H*)-ones 4a–g (General method). A mixture of ester **3a**–**g** (2 mmol) and anhydrous sodium acetate (0.17 g, 2 mmol) in acetic anhydride (10 ml) was refluxed for 4 h. The solvent was removed by distillation at reduced pressure, the residue was worked up with water (40 ml), the solids were filtered off, dried, and crystallized from EtOH.

2-Phenyl-(5-phenylcarbonyl)pyrano[3,4-*c*]pyrazol-7(2*H*)-one (4a). Yield 0.38 g (60%), light-yellow powder, mp 181–183°C. IR spectrum, ν, cm^{-1}: 1660 (C=O), 1752 (C=O). ^1H NMR spectrum, δ, ppm: 7.46–7.81 (7H, m, H Ph, H-4); 7.90–8.04 (4H, m, H Ph); 9.10 (1H, s, H-3). ^{13}C NMR spectrum, δ, ppm: 108.9 (C-4); 120.2 (CH); 122.0 (C-3a); 127.4 (C-3); 128.3 (CH); 128.9 (CH); 129.2 (CH); 129.7 (CH); 132.7 (CH); 136.0 (C-5); 138.2 (C), 138.7 (C-7a); 148.3 (C); 154.9 (C=O); 184.8 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 317 $[M+H]^+$ (100). Found, %: C 72.33; H 3.94; N 9.01. $C_{19}H_{12}N_2O_3$. Calculated, %: C 72.15; H 3.82; N 8.86.

5-[(3-Bromophenyl)carbonyl]-2-phenylpyrano[3,4-*c*]-pyrazol-7(2*H*)-one (4b). Yield 0.45 g (57%), light-yellow powder, mp 200–202°C. IR spectrum, ν, cm^{-1}: 1659 (C=O), 1761 (C=O). ^1H NMR spectrum, δ, ppm: 7.47–7.64 (5H, m, H Ar, H-4); 7.87–8.05 (5H, m, H Ar); 9.09 (1H, s, H-3). ^{13}C NMR spectrum, δ, ppm: 109.2 (C-4); 120.0 (CH); 121.6 (C-3a); 121.9 (C); 127.5 (C-3); 128.1 (CH); 128.8 (CH); 129.5 (CH); 130.2 (CH); 131.4 (CH); 135.1 (C-5); 137.7 (CH); 138.1 (C); 138.6 (C-7a); 147.9 (C); 154.7 (C=O); 186.8 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 395 $[M(^{79}Br)+H]^+$ (80), 397 $[M(^{81}Br)+H]^+$ (100). Found, %: C 57.91; H 2.73; N 6.95. $C_{19}H_{11}BrN_2O_3$. Calculated, %: C 57.74; H 2.81; N 7.09.

5-[(3-Chlorophenyl)carbonyl]-2-phenylpyrano[3,4-*c*]-pyrazol-7(2*H*)-one (4c). Yield 0.43 g (62%), light-yellow powder, mp 203–205°C. IR spectrum, ν, cm^{-1}: 1660 (C=O), 1755 (C=O). ^1H NMR spectrum, δ, ppm: 7.48–8.01 (10H, m, H Ar, H-4); 9.11 (1H, s, H-3). ^{13}C NMR spectrum, δ, ppm: 109.2 (C-4); 120.3 (CH); 121.8 (C-3a); 127.4 (CH); 127.6 (C-3); 128.8 (CH); 129.8 (CH); 130.4 (CH); 132.5 (CH); 133.2 (C-5); 137.9 (C); 138.1 (C-7a); 138.6 (C); 138.8 (CH); 145.9 (C); 154.5 (C=O); 186.4 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 351 $[M+H]^+$ (100). Found, %: C 65.29; H 3.26; N 7.81. $C_{19}H_{11}ClN_2O_3$. Calculated, %: C 65.06; H 3.16; N 7.99.

5-[(4-Chlorophenyl)carbonyl]-2-phenylpyrano[3,4-*c*]-pyrazol-7(2*H*)-one (4d). Yield 0.48 g (68%), light-yellow crystals, mp 240–242°C. IR spectrum, ν, cm^{-1}: 1659 (C=O), 1756 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 7.42–7.69 (6H, m, H Ph, H-4); 7.93 (2H, d, *J* = 7.6, H Ar); 7.98 (2H, d, *J* = 7.6, H Ar); 9.06 (1H, s, H-3). ^{13}C NMR spectrum, δ, ppm: 108.9 (C-4); 120.2 (CH); 120.4 (C-3a); 121.9 (CH); 127.4 (C-3); 128.5 (CH); 128.9 (CH); 131.2 (CH); 134.7 (C-5); 138.1 (C-7a); 138.6 (C); 148.1 (C); 154.8 (C=O); 185.2 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 351 $[M+H]^+$ (100). Found, %: C 65.24; H 3.06; N 7.86. $C_{19}H_{11}ClN_2O_3$. Calculated, %: C 65.06; H 3.16; N 7.99.

5-[(4-Fluorophenyl)carbonyl]-2-phenylpyrano[3,4-*c*]-pyrazol-7(2*H*)-one (4e). Yield 0.43 g (64%), light-yellow powder, mp 218–220°C. IR spectrum, ν, cm^{-1}: 1660 (C=O), 1761 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.42–7.69 (6H, m, H Ph, H-4); 7.86–8.02 (4H, m, H Ar); 9.09 (1H, s, H-3). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 108.8 (C-4); 115.3 (CH, d, $^2J_{CF}$ =26); 120.0 (CH); 121.9 (C-3a); 127.2 (CH); 128.7 (C-3); 129.5 (CH); 132.2 (CH); 133.8 (C-5); 138.0 (C); 138.6 (C-7a); 154.7 (C=O); 164.5 (C, d, $^1J_{CF}$ = 262); 186.2 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 335 $[M+H]^+$ (100). Found, %: C 68.01; H 3.25; N 8.54. $C_{19}H_{11}FN_2O_3$. Calculated, %: C 68.26; H 3.32; N 8.38.

2-(4-Bromophenyl)-5-[(4-chlorophenyl)carbonyl]-pyrano[3,4-*c*]pyrazol-7(2*H*)-one (4f). Yield 0.62 g (72%), light-yellow crystals, mp 243–245°C. IR spectrum, ν, cm^{-1}: 1662 (C=O), 1760 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.54 (1H, s, H-4); 7.64 (2H, d, *J* = 8.4, H Ar); 7.80 (2H, d, *J* = 8.4, H Ar); 7.94 (4H, s, H Ar); 9.05 (1H, s, H-3). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 108.9 (C-4); 120.1 (C-3a); 120.5 (CH); 121.7 (C); 127.6 (C-3); 128.3 (CH); 129.2 (CH); 130.9 (C); 132.4 (CH); 134.9 (C-5); 138.1 (C-7a); 138.4 (C), 147.8 (C); 155.0 (C=O); 184.9 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 430 $[M(^{79}Br)+H]^+$ (85), 432 $[M(^{81}Br)+H]^+$ (100). Found, %: C 53.22; H 2.30; N 6.41. $C_{19}H_{10}BrClN_2O_3$. Calculated, %: C 53.11; H 2.35; N 6.52.

2-(4-Bromophenyl)-5-[(4-fluorophenyl)carbonyl]pyrano[3,4-*c*]pyrazol-7(2*H*)-one (4g). Yield 0.56 g (68%), light-yellow powder, mp 237–239°C. IR spectrum, ν, cm^{-1}: 1661 (C=O), 1754 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.39 (2H, d, *J* = 8.0, H Ar); 7.53 (1H, s, H-4); 7.79 (2H, d, *J* = 8.4, H Ar); 7.94–8.02 (4H, m, H Ar); 9.06 (1H, s, H-3). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 108.3 (C-4); 115.4 (CH, d, $^2J_{CF}$ = 19.4); 121.6 (C-3a); 121.9 (C), 122.1 (CH); 127.4 (C-3); 132.2 (CH); 132.6 (CH); 134.6 (C-5), 137.8 (C); 138.2 (C-7a); 148.4 (C); 154.8 (C=O); 162.3 (C, d, $^1J_{CF}$ = 227.2); 153.6 (C=O); 184.7 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 413 $[M(^{79}Br)+H]^+$ (100), 415 $[M(^{81}Br)+H]^+$ (85). Found, %: C 55.48; H 2.30; N 6.99. $C_{19}H_{10}BrFN_2O_3$. Calculated, %: C 55.23; H 2.44; N 6.78.

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