SYNTHESIS OF A NOVEL PENTACYCLE: 8-METHYL-10-PHENYLPYRAZOLO[4',3':5,6]-PYRANO[3,2-*c*]-[1,10]PHENANTHROLIN-7(10H)-ONE

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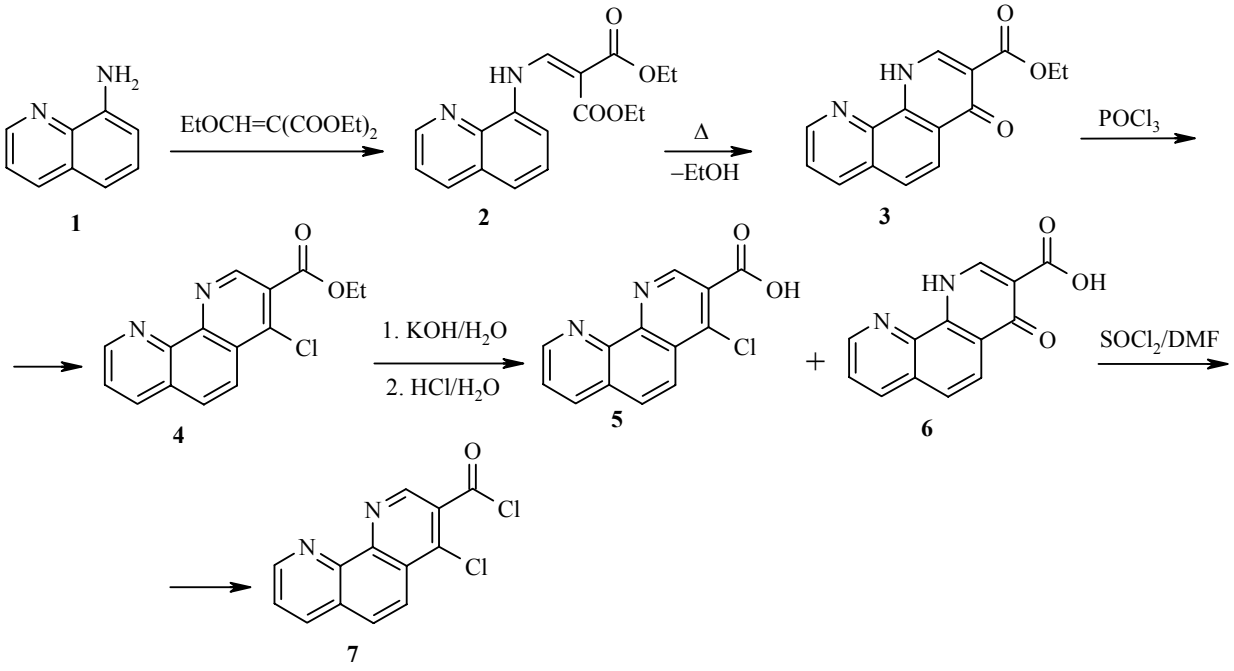
The title compound – a derivative of a hitherto unknown pentacyclic ring system – results from the reaction of 3-methyl-1-phenyl-2-pyrazolin-5-one and 4-chloro-1,10-phenanthroline-3-carbonyl chloride in the presence of $Ca(OH)_2$ in boiling 1,4-dioxane.

Keywords: pyrazolones, acylations, fused ring systems, NMR spectroscopy.

In the course of our investigations on novel heteroaromatic ring systems bearing a pyrano-[2,3-*c*]pyrazol-4(1H)-one moiety [1–5], we envisaged the synthesis of a new representative containing a 1,10-phenanthroline-ring system. Similarly to our previous works, the planned synthesis should include the selective C(4)-acylation of a pyrazolone (2-pyrazolin-5-one) with an appropriate *o*-haloarenecarbonyl chloride



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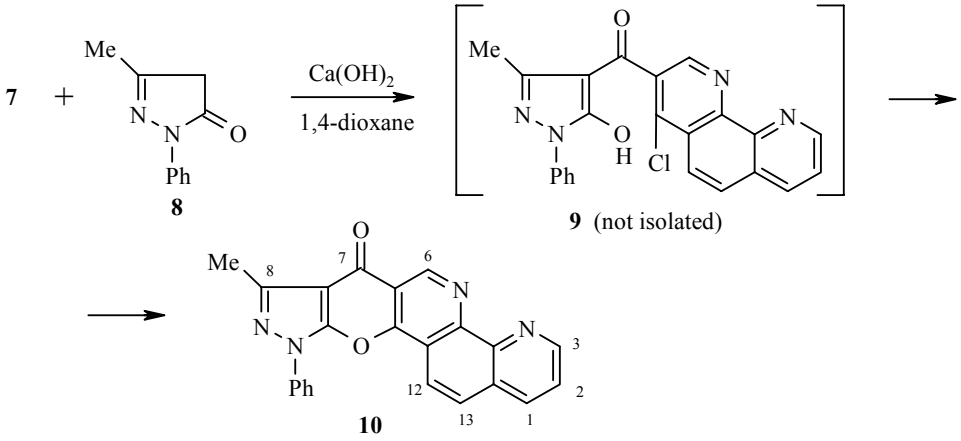
(i.e., 4-chloro-1,10-phenanthroline-3-carbonyl chloride (**7**)) under "Jensen" conditions ($Ca(OH)_2$, refluxing 1,4-dioxane) [6] and subsequent cyclization of the resulting ketone to form the central pyrone moiety.

The preparation of that acid chloride – key intermediate **7** – was accomplished *via* a multi-step procedure. According to [7], the reaction of 8-aminoquinoline (**1**) with diethyl ethoxymethylenemalonate gave enamine **2**, which was cyclized into the phenanthroline derivative **3** in hot diphenyl ether. Subsequent treatment of **3** with thionyl chloride/DMF converted the oxygen function in position 4 into a chlorine substituent (compound **4**) [8].

Saponification of ester **4** by treatment with aqueous KOH resulted in a precipitate, which after acidification should give the desired *o*-chlorocarboxylic acid **5**. However, NMR spectroscopic analysis (in DMSO-d_6 due to solubility reasons) of the thus obtained product revealed a mixture of initially two species **5** and **6**, with the amount of compound **5** rapidly decreasing for the benefit of compound **6**. Obviously, in polar DMSO-d_6, always containing more or less trace water, the chloro group of compound **5** is replaced by an OH function resulting in the formation of compound **6**, which is present as phenanthrolin-4-one. As this process occurred relatively fast, only ^{1}H NMR data could be acquired from compound **5**. Fortunately, when the raw material resulting from the saponification reaction was treated with $SOCl_2$ the acid chloride **7** was formed as the sole product, which was immediately employed in the next reaction step without any further purification.

Finally, the pyrazolone **8** was reacted with the acid chloride **7** in the presence of $Ca(OH)_2$ in boiling 1,4-dioxane. The thus obtained solid turned out to be already the desired pentacyclic title compound **10**, which was proved by means of C,H,N-analysis and MS, IR, ^{1}H, and ^{13}C NMR spectra. As expected, due to fact that the chloro atom in position 4 of the phenanthroline system is located in an "activated" position, the cyclization occurred under the conditions of the acylation reaction and thus no intermediate 4-aroylpyrazol-5-ol (**9**) could be isolated [1, 2, 4, 5].

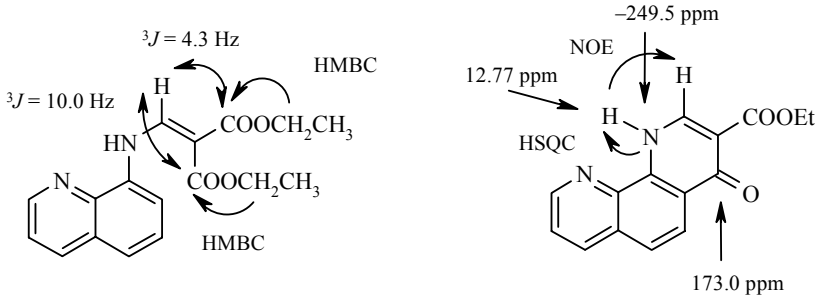


All the compounds prepared except the intermediate acid chloride **7** were thoroughly investigated with respect to their NMR spectra. Thus, unambiguous assignment of all proton, carbon, and nitrogen resonances was carried out by combined application of different standard NMR methods [9]. Moreover, many ^{13}C, ^{1}H coupling constants could be unequivocally assigned using 2D (δ, *J*) INEPT spectra with selective excitation [10]. Thus, for instance, the two ethyl ester moieties at the exocyclic double bond of compound **2** could be distinguished considering the vicinal $^3J_{CO,=CH}$ coupling constants: Whereas the (*Z*)-ester carbonyl-C resonance showed such a coupling of 10.0 Hz, the corresponding (*E*)-C=O signal was split with 4.3 Hz, indicating the *cis* position of the coupled nuclei in the latter case.

The NMR spectra of compound **3** clearly revealed this compound to exist solely as phenanthrolin-4-one and not as 4-hydroxyphenanthroline in DMSO-d_6 solution. This assignment was based on the following criteria:

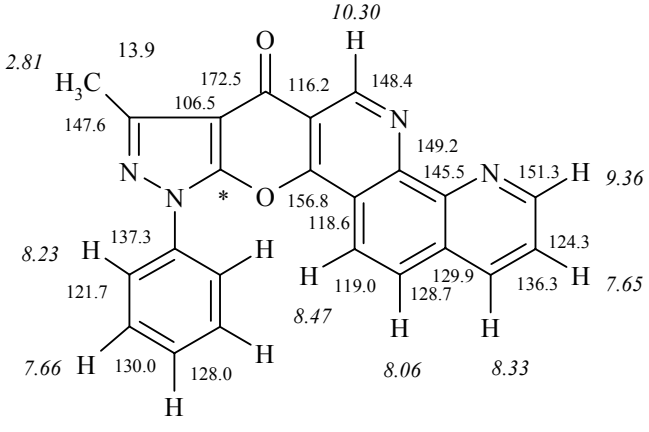
The relatively large chemical shift of C-4 (δ 173.0 ppm), indicating this carbon to be a carbonyl-type C-atom, a pronounced NOE on the signal due to H-2 upon irradiation of the resonance of the acidic proton, and mainly the low-field chemical shift of N-1 (δ −249.5 ppm) – which cannot be a pyridine-type N-atom – and its correlation to the acidic H (δ 12.77 ppm) in an ^{15}N, ^{1}H HSQC experiment. In comparison, the ^{15}N chemical shift of N-1 in the "aromatic" 4-chlorophenathroline **4** is -82.4 ppm. On basis of similar criteria the phenanthrolin-4-one structure of the acid **6** was proved.

Selected NMR data of compounds **2** and **3**



2 ($CDCl_3$) **3** (DMSO-d_6)

Selected NMR data of compound **10**



10 (pyridine-d_5)

* not found

The title compound **10** turned out to have a very limited solubility. Thus, in DMSO-d_6 solution only a ^{1}H NMR spectrum could be taken in a long-time run. However, a slightly better solubility in pyridine-d_5 permitted the unequivocal identification of all ^{13}C resonances.

EXPERIMENTAL

Melting points were determined on a Reichert–Kofler hot-stage microscope and are uncorrected. Mass spectra were obtained on a Shimadzu QP 1000 instrument (EI, 70 eV). IR spectra were recorded on a Perkin–Elmer FTIR 1605 spectrophotometer. Elemental analyses were performed at the Microanalytical Laboratory,

University of Vienna. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian UnityPlus 300 spectrometer at 28°C or on a Bruker Avance 500 spectrometer at 293 K. The center of the solvent signal was used as an internal standard which was related to TMS with δ = 7.26 (^{1}H in $CDCl_3$), δ = 2.49 (^{1}H in DMSO-d_6), δ_{H-4} = 7.55 (^{1}H in pyridine-d_5), δ = 77.0 (^{13}C in $CDCl_3$), δ = 39.5 (^{13}C in DMSO-d_6), and δ_{C-4} = 135.5 ppm (^{13}C in pyridine-d_5). The digital resolutions were 0.2 Hz/data point in the ^{1}H NMR spectra and 0.4 Hz/data point in the ^{13}C NMR spectra (^{1}H broadband decoupling or gated decoupling). ^{15}N NMR spectra were obtained on a Bruker Avance 500 instrument with a "directly" detecting broadband observe probe and were referenced against external nitromethane (coaxial capillary). Systematic names were generated with ACD/Name [11] according to the IUPAC recommendations and were also checked manually to ensure correct use of nomenclature within this publication [12]. Compound **8** was purchased from Sigma-Aldrich, Germany. Product yields were not optimized.

Diethyl [(quinolin-8-ylamino)methylidene]propanedioate (**2**). This compound was prepared similarly to a known procedure [7] starting of 8-aminoquinoline (**1**) (5.02 g, 35 mmol) and diethyl ethoxymethylenemalonate (7.53 g, 35 mmol) to yield 9.56 g (87%) of compound **2** as green-brownish needles; mp 111–112°C (mp 110–112°C [7]). IR spectrum (KBr), ν, cm^{-1}: 1683, 1645. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 12.32 (1H, d, $^{3}J_{NH,=CH}$ = 14.4, NH); 8.93 (1H, dd, $^{3}J_{2,3}$ = 4.2, $^{4}J_{2,4}$ = 1.7, H-2); 8.77 (1H, d, $^{3}J_{CH,NH}$ = 14.4, =CH); 8.14 (1H, dd, $^{3}J_{3,4}$ = 8.3, $^{4}J_{4,2}$ = 1.7, H-4); 7.51 (2H, m, H-5,6); 7.50 (1H, t, H-7); 7.46 (1H, dd, $^{3}J_{3,2}$ = 4.2, $^{3}J_{3,4}$ = 8.3, H-3); 4.41 (2H, q, $^{3}J_{OCH2,CH3}$ = 7.1, (*Z*)-ester OCH_2); 4.29 (2H, q, $^{3}J_{OCH2,CH3}$ = 7.1, (*E*)-ester OCH_2); 1.44 (3H, t, $^{3}J_{CH3,OCH2}$ = 7.1, (*Z*)-ester CH_3); 1.36 (3H, t, $^{3}J_{CH3,OCH2}$ = 7.1, (*E*)-ester CH_3). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 167.7 ($^{3}J_{CO,=CH}$ = 10.0, $^{3}J_{CO,OCH2}$ = 3.0, (*Z*)-ester CO); 166.1 ($^{3}J_{CO,=CH}$ = 4.3, $^{3}J_{CO,OCH_2}$ = 3.1, (*E*)-ester CO); 149.4 (^{1}J = 180.0, $^{2}J_{C-2,H-3}$ = 3.7, $^{3}J_{C-2,H-4}$ = 7.7, C-2); 148.8 (^{1}J = 167.9, =CH); 138.7 (C-8a); 136.0 (C-8); 135.9 (C-4); 128.6 (C-4a); 126.6 (C-6); 122.4 (C-5); 122.1 (^{1}J = 164.3, $^{2}J_{C-3,H-2}$ = 9.0, C-3); 110.3 (C-7); 95.4 (C(COOEt)$_2$); 60.4 (^{1}J = 147.5, $^{2}J_{O\underline{C}H2,C\underline{H}3}$ = 4.4, (*Z*)-ester OCH_2); 60.1 (^{1}J = 147.1, $^{2}J_{O\underline{C}H2,C\underline{H}3}$ = 4.4, (*E*)-ester OCH_2); 14.4 (^{1}J = 126.7, $^{2}J_{\underline{C}H3,OC\underline{H}2}$ = 2.7, (*E*)-ester CH_3); 14.3 (^{1}J = 126.9, $^{2}J_{\underline{C}H3,OC\underline{H}2}$ = 2.7, (*Z*)-ester CH_3). ^{15}N NMR spectrum (50 MHz, $CDCl_3$), δ, ppm: −87.1 (N-1); -260.5 (NH). Mass spectrum, *m/z* (I_{rel}, %): 314 $[M]^+$ (9), 241 (81), 213 (27), 196 (26), 195 (26), 169 (25), 168 (100), 155 (33), 140 (23), 129 (38), 128 (36), 101 (20).

Ethyl 4-oxo-1,4-dihydro-1,10-phenanthroline-3-carboxylate (**3**). This compound was prepared similarly to a known procedure [7] starting from 4.06 g (13 mmol) of compound **2** to yield 1.87 g (54%) of oxo ester **3** as a beige powder; mp 242–246°C (mp 237–241°C [7]). IR spectrum (KBr), ν, cm^{-1}: 1706, 1631. ^{1}H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 12.77 (1H, s, NH); 9.03 (1H, dd, $^{3}J_{9,8}$ = 4.3, $^{4}J_{9,7}$ = 1.6, H-9); 8.51 (1H, s, H-2); 8.50 (1H, dd, $^{3}J_{7,8}$ = 7.8, $^{4}J_{7,9}$ = 1.6, H-7); 8.18 (1H, d, $^{3}J_{5,6}$ = 8.8, H-5); 7.83 (1H, d, $^{3}J_{6,5}$ = 8.8, H-6); 7.78 (1H, dd, $^{3}J_{8,7}$ = 7.8, $^{4}J_{8,9}$ = 4.3, H-8); 4.24 (2H, q, $^{3}J_{OCH2,CH3}$ = 7.1, OCH_2); 1.28 (3H, t, $^{3}J_{CH3,OCH2}$ = 7.1, CH_3). ^{13}C NMR spectrum (75 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 173.0 ($^{3}J_{C-4,H-2}$ = 6.6, $^{3}J_{C-4,H-5}$ = 3.2, C-4); 164.5 ($^{3}J_{CO,CH2}$ = 3.3, $^{3}J_{CO,H-2}$ = 3.7, CO); 149.9 (^{1}J = 180.9, $^{2}J_{C-9,H-8}$ = 3.7, $^{3}J_{C-9,H-7}$ = 7.6, C-9); 143.8 (^{1}J = 179.8, C-2); 138.6 ($^{3}J_{C-10a,H-9}$ = 12.2, $^{3}J_{C-10a,H-6}$ = 6.5, $^{3}J_{C-10a,H-7}$ = 5.8, C-10a); 136.6 (^{1}J = 165.6, $^{3}J_{C-7,H-6}$ = 4.2, $^{3}J_{C-7,H-9}$ = 5.8, C-7); 136.0 ($^{3}J_{C-10b,H-5}$ = 7.1, C-10b); 129.0 ($^{2}J_{C-6a,H-6}$ = 1.9, $^{2}J_{C-6a,H-7}$ = 1.5, $^{3}J_{C-6a,H-5}$ = 9.7, $^{3}J_{C-6a,H-8}$ = 7.5, $^{4}J_{C-6a,H-9}$ = 1.3, C-6a); 126.0 ($^{3}J_{C-4a,H-6}$ = 8.7, C-4a); 124.2 (^{1}J = 166.5, $^{2}J_{C-8,H-9}$ = 8.8, C-8); 123.4 (^{1}J = 164.4, $^{2}J_{C-6,H-5}$ = 1.7, $^{3}J_{C-6,H--7}$ = 4.7, C-6); 122.4 (^{1}J = 164.5, $^{2}J_{C-5,H-6}$ = 1.6, C-5); 112.6 (C-3); 59.7 (^{1}J = 147.5, $^{2}J_{O\underline{C}H2,C\underline{H}3}$ = 4.4, OCH_2); 14.3 (^{1}J = 126.7, $^{2}J_{\underline{C}H3,OC\underline{H}2}$ = 2.6, CH_3). ^{15}N NMR spectrum (50 MHz, DMSO-d_6), δ, ppm: -83.4 (N-10); -249.5 (N-1). Mass spectrum, *m/z* (I_{rel}, %): 268 $[M]^+$ (15), 223 (20), 222 (17), 196 (100), 168 (33), 140 (46).

Ethyl 4-chloro-1,10-phenanthroline-3-carboxylate (4) was prepared similarly to a known procedure [8] starting of compound **3** (3.99 g, 15 mmol) and $SOCl_2$ (15 ml) to yield 3.99 g (93%) as a beige solid; mp 112-116°C (mp 121°C [13]). IR spectrum (KBr), ν, cm^{-1}: 1709. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 9.38 (1H, s, H-2); 9.17 (1H, dd, $^{3}J_{9,8}$ = 4.3, $^{4}J_{9,7}$ = 1.7, H-9); 8.27 (1H, d, $^{3}J_{5,6}$ = 9.1, H-5); 8.20 (1H, dd, $^{3}J_{7,8}$ = 8.0, $^{4}J_{7,9}$ = 1.7, H-7); 7.84 (1H, d, $^{3}J_{6,5}$ = 9.1, H-6); 7.63 (1H, dd, $^{3}J_{8,7}$ = 8.0, $^{3}J_{8,9}$ = 4.3, H-8); 4.49 (1H, q,

$^3J_{OCH2,CH3}$ = 7.1, OCH_2); 1.44 (1H, t, $^3J_{CH3,OCH2}$ = 7.1, CH_3). ^{13}C NMR spectrum (75 MHz, $CDCl_3$): δ, ppm (*J*, Hz): 164.4 ($^3J_{CO,OCH2}$ = 3.2, $^3J_{CO,H-2}$ = 2.2, CO); 151.0 (^1J = 181.1, $^2J_{C-9,H-8}$ = 3.5, $^3J_{C-9,H-7}$ = 7.6, C-9); 150.0 (*J* = 188.0, C-2); 147.9 ($^3J_{C-4,H-2}$ = 13.4, $^2J_{C-4,H-5}$ = 5.8, $^3J_{C-4,H-6}$ = 1.0, C-4); 145.3 ($^3J_{C-10a,H-6}$ = 6.4, $^3J_{C-10a,H-7}$ = 5.6, $^3J_{C-10a,H-9}$ = 10.8, C-10a); 142.7 ($^3J_{C-10b,H-2}$ = 8.0, $^3J_{C-10b,H-5}$ = 5.0, C-10b); 135.9 (*J* = 163.1, $^3J_{C-7,H-6}$ = 4.7, $^3J_{C-7,H-9}$ = 5.8, C-7); 129.1 ($^2J_{C-6a,H-6}$ = 2.3, $^2J_{C-6a,H-7}$ = 1.2, $^3J_{C-6a,H-5}$ = 9.5, $^3J_{C-6a,H-8}$ = 7.4, C-6a); 128.2 (^1J = 162.8, $^3J_{C-6,H-7}$ = 5.1, C-6); 126.5 ($^3J_{C-4a,H-6}$ = 9.4, C-4a); 125.1 ($^2J_{C-3,H-2}$ = 8.1, C-3); 124.0 (^1J = 164.9, $^3J_{C-8,H-9}$ = 9.1, C-8); 122.4 (^1J = 165.8, C-5); 62.2 (^1J = 148.5, $^2J_{OCH2,CH3}$ = 4.4, OCH_2); 14.1 (^1J = 127.4, $^2J_{CH3,OCH2}$ = 2.6, CH_3). ^{15}N NMR spectrum (50 MHz, DMSO-d_6): δ, ppm: −75.6 (N-10); −82.4 (N-1). Mass spectrum, *m/z* (I_{rel}, %): 288 $[M]^+$ (22), 286 $[M]^+$ (60), 243 (20), 242 (25), 241 (100), 213 (82), 178 (35), 151 (61), 75 (24).

4-Chloro-1,10-phenanthroline-3-carboxylic acid (**5**). Compound **4** (573 mg, 2 mmol) was dissolved in DME (30 ml), and aqueous KOH (40%, 30 ml) was added. The reaction mixture was stirred overnight. Then, the formed precipitate was filtered off, treated with 1N HCl, and filtered off again and dried to obtain 358 mg of the beige mixture of compounds **5** and **6;** mp 310–314°C. During the recording of the NMR spectra in DMSO-d_6, hydrolysis of compound **5** was observed. Compound **5**: ^{1}H NMR spectrum (500 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 9.44 (1H, s, H-2), 9.38 (1H, m, H-9), 9.36 (1H, m, H-7), 8.40 (1H, m, H-8), 8.58 (1H, d, $^3J_{5,6}$ = 9.3, H-5), 8.48 (1H, d, $^3J_{5,6}$ = 9.3, H-6), 4.82 (1H, br. s, COOH). Mass spectrum, *m/z* (I_{rel}, %): 260 $[M]^+$ (18), 258 $[M]^+$ (38), 241 (38), 196 (83), 168 (87), 140 (37), 111 (26), 98 (43), 97 (30), 81 (33), 69 (71), 57 (66), 55 (71), 45 (58), 43 (100), 41 (62). HRMS (EI, 70 eV), *m/z*: Found: 258.0202 $[M]^+$. $C_{13}H_7ClN_2O_2$. Calculated: 258.0196.

Compound **6** [13]: ^{1}H NMR spectrum (500 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 13.84 (2H, 2s, NH); 9.14 (1H, dd, $^3J_{9,8}$ = 4.3, $^4J_{9,7}$ = 1.6, H-9); 8.73 (1H, s, H-2); 8.62 (1H, dd, $^3J_{7,8}$ = 8.3, $^4J_{7,9}$ = 1.6, H-7); 8.24 (1H, d, $^3J_{5,6}$ = 8.9, H-5); 8.03 (1H, d, $^3J_{6,5}$ = 8.9, H-6); 7.91 (1H, dd, $^3J_{8,7}$ = 8.3, $^3J_{8,9}$ = 4.3, H-8); 4.82 (1H, br. s, COOH). ^{13}C NMR spectrum (125 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 177.9 ($^3J_{C-4,H-2}$ = 6.4, $^3J_{C-4,H-5}$ = 3.3, C-4); 166.2 ($^3J_{CO,H-2}$ = 3.5, CO); 150.7 (^1J = 181.7, $^2J_{C-9,H-8}$ = 3.6, $^3J_{C-9,H-7}$ = 7.6, C-9); 143.8 (^1J = 182.8, C-2); 138.4 ($^3J_{C-10a,H-9}$ = 12.3, $^3J_{C-10a,H-6}$ = 6.5, $^3J_{C-10a,H-7}$ = 5.8, $^4J_{C-10a,H-5}$ = 1.0, C-10a); 137.1 ($^3J_{C-10b,H-5}$ = 7.0, C-10b); 137.0 (^1J = 166.6, $^3J_{C-7,H-9}$ = 6.1, $^3J_{C-7,H-6}$ = 4.5, C-7); 129.7 ($^2J_{C-6a,H-6}$ = 2.4, $^3J_{C-6a,H-5}$ = 9.6, $^3J_{C-6a,H-8}$ = 7.5, C-6a); 125.4 (^1J = 167.5, $^3J_{C-6,H-7}$ = 4.6, C-6); 125.2 (^1J = 166.9, $^2J_{C-8,H-9}$ = 8.9, C-8); 123.6 ($^3J_{C-4a,H-6}$ = 8.8, C-4a); 121.3 (^1J = 168.2, C-5); 110.5 (C-3). ^{15}N NMR spectrum (50 MHz, DMSO-d_6), δ, ppm: −83.4 (N-10); −236.9 (N-1).

4-Chloro-1,10-phenanthroline-3-carbonyl chloride (**7**) [13]. The crude mixture resulting from saponification of ester **4** (compound **5** or a mixture of compounds **5** and **6**) was suspended in $SOCl_2$ (15 ml), and DMF (3 drops) was added. The reaction mixture was refluxed for 3 h. After cooling to room temperature, the solvent was evaporated under reduced pressure to give the crude acid chloride **7**, which was used in the following acylation reaction without further purification.

8-Methyl-10-phenylpyrazolo[4',3':5,6]pyrano[3,2-*c*][1,10]phenanthrolin-7(10H)-one (**10**). Under stirring, to a suspension of 3-methyl-1-phenyl-2-pyrazolin-5-one (**8**) (174 mg, 1 mmol) and $Ca(OH)_2$ (148 mg, 2 mmol) in dioxane (1 ml) was added the crude acid chloride **7** (277 mg, 1 mmol) in dioxane (2 ml) and the mixture was refluxed for 3 h. After cooling to room temperature, 2N HCl (3 ml) and H_2O (5 ml) were added. After 20 h, the precipitate was filtered off and washed with H_2O to obtain the target compound **10**. An analytical sample was recrystallized from ethanol and DMF. Yield 151 mg (40%); beige–pale brownish powder; mp > 340°C. IR spectrum (KBr), ν, cm^{-1}: 1664. ^{1}H NMR spectrum (500 MHz, DMSO-d_6): δ, ppm (*J*, Hz): 9.70 (1H, s, H-6); 9.21 (1H, dd, $^3J_{3,2}$ = 4.2, $^4J_{3,1}$ = 1.4, H-3); 8.63 (1H, dd, $^3J_{1,2}$ =8.1, $^4J_{1,3}$ = 1.4, H-1); 8.38 (1H, d, $^3J_{12,13}$ = 9.1, H-12); 8.29 (1H, d, $^3J_{13,12}$ = 9.1, H-13); 8.04 (2H, m, H-2,6, Ph); 7.89 (1H, dd, $^3J_{2,3}$ = 4.2, $^3J_{2,1}$ = 8.1, H-2); 7.74 (2H, m, H-3,5, Ph); 7.55 (1H, m, H-4, Ph); 2.65 (3H, s, CH_3). ^{1}H NMR spectrum (500 MHz, pyridine-d_5): δ, ppm (*J*, Hz): 10.30 (1H, s, H-6); 9.36 (1H, dd, $^3J_{3,2}$ = 4.1, $^4J_{3,1}$ = 1.7, H-3); 8.47 (1H, d, $^3J_{12,13}$ = 9.0, H-12); 8.33 (1H, dd, $^3J_{1,2}$ = 8.1, $^4J_{1,3}$ = 1.7, H-1); 8.23 (2H, m, H-2,6, Ph); 8.06 (1H, d, $^3J_{13,12}$ = 9.0, H-13); 7.66 (2H, m, H-3,5, Ph); 7.65 (1H, dd, $^3J_{2,3}$ = 4.1, $^3J_{2,1}$ = 8.1, H-2); 7.46 (1H, m, H-4, Ph); 2.81 (3H, s, CH_3). ^{13}C NMR spectrum (125 MHz, pyridine-d_5): δ, ppm: 172.5 (C-7); 156.8 (C-11a); 151.3 (C-3); 149.2 (C-4b);

148.4 (C-6); 147.6 (C-8); 145.5 (C-4a); 137.3 (C-1, Ph); 136.3 (C-1); 130.0 (C-3,5, Ph); 129.9 (C-13a); 128.7 (C-13); 128.0 (C-4, Ph); 124.3 (C-2); 121.7 (C-2,6, Ph); 119.0 (C-12); 118.6 (C-11b); 116.2 (C-6a); 106.5 (C-7a); 13.9 (CH_3); C-10a was not found. Mass spectrum, *m/z* (I_{rel}, %): 379 $[M + 1]^+$ (15), 378 $[M]^+$ (100), 189 (12), 155 (13), 91 (24), 77 (63), 51 (29). HRMS (EI, 70 eV), *m/z*: Found: 378.1120 $[M]^+$. $C_{23}H_{14}N_4O_2$. Calculated: 378.1117. Found, %: C 71.88; H 3.91; N 14.26. $C_{23}H_{14}N_4O_2 \cdot \frac{1}{3}H_2O$. Calculated, %: C 71.87; H 3.85; N 14.58.

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