HETEROCYCLES, Vol. 96, No. 2, 2018, pp. 233 - 253. © 2018 The Japan Institute of Heterocyclic Chemistry
Received, 27th November, 2017, Accepted, 30th December, 2017, Published online, 15th January, 2018
DOI: 10.3987/COM-17-13844

ONE-POT THREE-COMPONENT SYNTHESIS OF NOVEL PYRAZOLE-2,3-PYRROLEDICARBOXYLIC ACID 2,3-DIESTERS

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Abstract – A facile synthesis of a series of pyrazol-3-one derivatives containing dihydropyrrole moiety using an efficient three-component reaction with 4-(dicyanomethylene)-3*H*-pyrazol-3-ones, acetylenic esters, and anilines is reported. The reaction is moderate to good yielding, tolerant towards a variety of amines, and provides access to novel pyrazole-2,3-pyrroledicarboxylic acid 2,3-diesters in a single step. All the synthesized compounds were characterized by spectroscopic analysis.

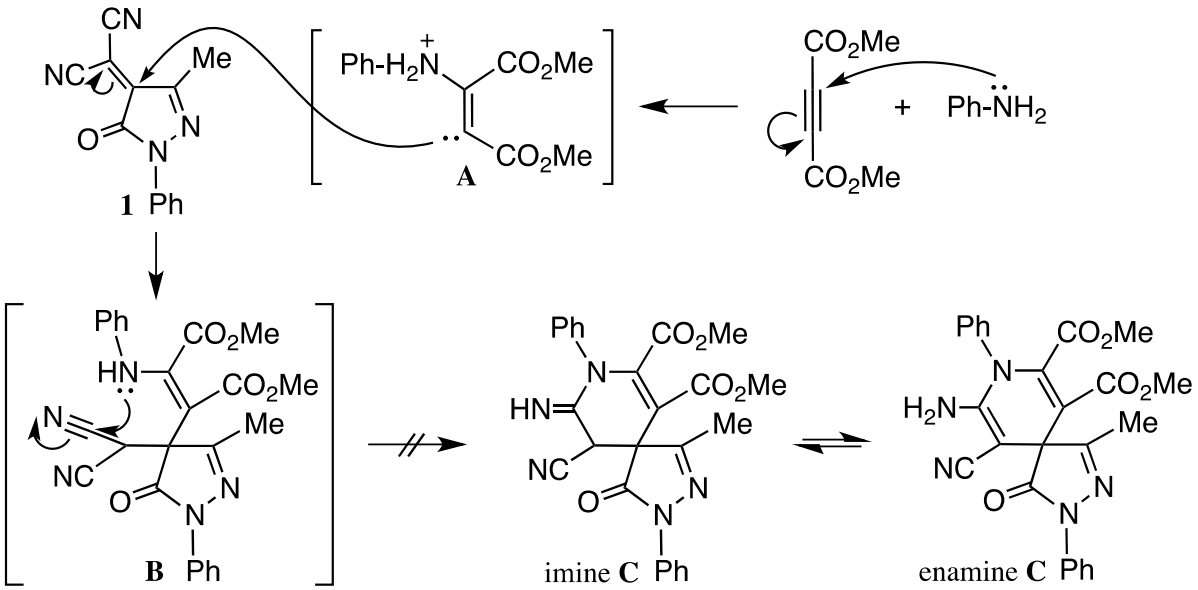
INTRODUCTION

Heterocyclic compounds form by far the largest of the classical divisions of organic chemistry. They are of immense importance not only both biologically and industrially but also to the functioning of any developed human society as well. The majority of pharmaceutical products that mimic natural products with biological activity are heterocyclic compounds. Most of the significant advances against disease have been made by designing and testing new structures, which are often heteroaromatic derivatives. In addition, a number of pesticides, antibiotics, alkaloids, and cardiac glycosides are heterocyclic natural products of significance for human and animal health. Therefore, a huge number of combinations of carbon, hydrogen, and heteroatoms can be designed, providing compounds with the most diverse physical, chemical, and biological properties.[1]

Among nitrogen-containing heterocyclic compounds, the pyarzole moiety is an important pharmacophore, which is found in a large number of biologically active molecules. Pyrazole derivatives are known to exhibit a wide spectrum of biological activities such as antipyretic, anti-inflammatory, antiviral, antimicrobial, hypoglycemic, antihypertensive, antioxidant, and antitumor activities.[2] Hence, there have been many attempts to develop alternative methods for the synthesis of pyrazole derivatives.[3] On the other hand, pyridine and dihydropyridine derivatives are also important because of their incidence in

nature and biological properties such as calcium antagonists, antitubercular agents, and possess antidiabetic activities.[4] For the reasons given above, a large number of general methods for the preparation of pyridine derivatives have recently reported.[5]

Spiro compounds are well known to possess varied biological activities[6] and hence their synthesis has always been a challenge and of attraction to organic chemists.[7] Among them, in the literature there is not much research related to the synthesis of spiro pyrazole derivatives,[8] even though they also have biological activities, including action on antimicrobial, analgesic, and antitumor properties.[8b,9] Over the past decade, we have reported some exciting synthetic strategies for the synthesis of this exclusive class of spiro pyrazole derivatives.[10] Hence, we are interested in developing a novel route for the synthesis of spiro pyrazole derivatives. Although we tried to directly construct different derivatives of spiro pyrazole through multicomponent reactions[11] of 4-(dicyanomethylene)-3*H*-pyrazol-3-one **1**,[12] dimethyl acetylene-dicarboxylate (DMAD), and aniline according to the method reported procedure[11a] by Kiruthika *et al.*, those attempts failed (Scheme 1). In the case of this reaction, we hypothesized that the zwitterionic intermediate **A**[11a] formed in situ from DMAD and aniline would play a key role in the formation of Michael adduct **B**. Unfortunately, the reaction mode was completely changed and the expected spiro compound **C** was not observed at all. This result indicates that this type of straightforward preparation of spiro compounds by the three-component reaction is not easy.



Scheme 1

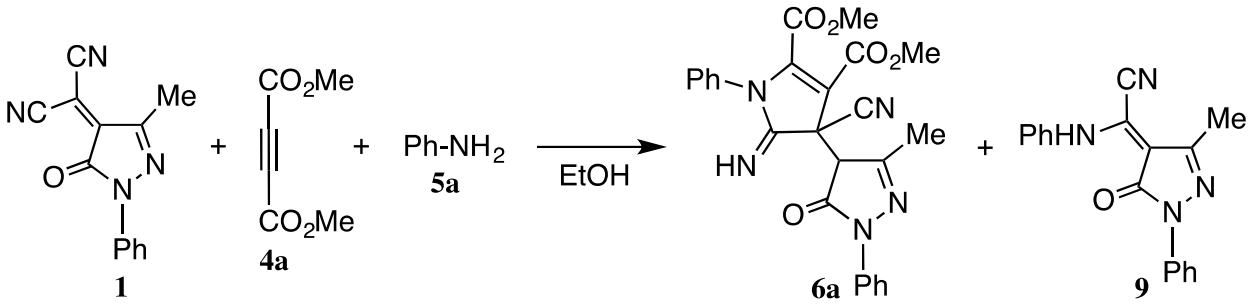
Interestingly, during the aforementioned three-component reaction, we found the reaction condition under which the pyrazole derivatives containing dihydropyrrole moiety could be isolated. In this research, we decided to extend our studies to synthesize different derivatives of pyrazole through multicomponent

reactions of 4-(dicyanomethylene)-3*H*-pyrazol-3-ones, acetylenic esters, and anilines, which might have useful biological activities and now report the results of our investigation.

RESULTS AND DISCUSSION

To access the desired pyrazole derivative containing dihydropyrrole moiety **6a**, we examined the optimization of the three-component reaction with 4-(dicyanomethylene)-3*H*-pyrazol-3-one **1**, DMAD, and aniline in EtOH (Table 1). The substrate **1** was prepared by the treatment of 2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-one with tetracyanoethylene according to the method reported procedure.[12]

Table 1. Optimization of the reaction conditions

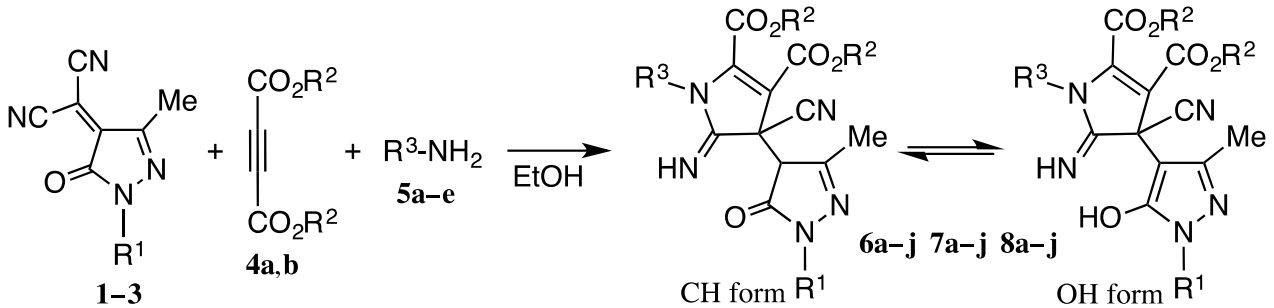


Entry	Ratio of **1**/**4a**/**5a**	Temp. (˚C)	Time (h)	Yield (%)[a] of **6a**/**9**
1	1.0/1.0/1.0	rt	24	52/20
2	1.0/1.5/1.5	rt	24	53/18
3	1.0/1.5/1.0	rt	24	70/trace
4	1.0/1.5/1.0	rt	48	61/trace
5	1.0/1.5/1.0	80	12	none
6	1.0/1.5/1.0	5	48	59/trace
7	1.0/2.0/1.0	rt	48	59/trace
8	1.0/2.0/1.5	rt	48	64/trace

[a] Isolated yield.

We carried out several experiments on **6a**, testing different reaction conditions, *e.g.* the ratio of the substrate **1** to **4a** and **5a**, reaction temperature, and reaction time. The results suggested that a lower reaction temperature such as at 5 ˚C or at room temperature could lead to higher yields of **6a** with a longer reaction time (entries 3 and 6–8). Conducting the reaction under stronger reaction conditions such as at 80 ˚C proved detrimental to the yield (entry 5). In addition, the reaction was sensitive to the ratio of **4a** to **5a**. When the same equivalent amount of **4a** to **5a** was employed, the undesired product **9** was obtained as a minor product (entries 1 and 2). In this case, it seems that the substrate **1** was reacted with

Table 2. Substrate scope of the three-component reaction for pyrazole-2,3-pyrroledicarboxylates[a]



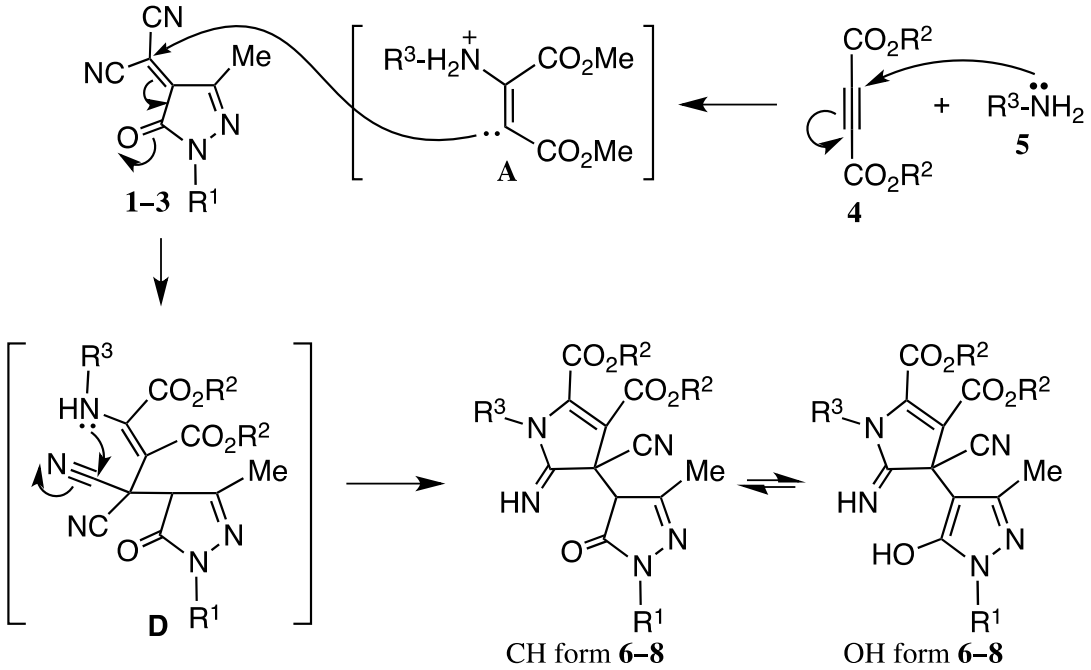
Entry	Substrate	R^1	R^2	R^3	Product	Yield (%)[b]
1	**1**	Ph	Me	Ph	**6a**	70
2	**1**	Ph	Me	4-Me-C_6H_4	**6b**	81
3	**1**	Ph	Me	4-Et-C_6H_4	**6c**	63
4	**1**	Ph	Me	4-*n*-Pr-C_6H_4	**6d**	73
5	**1**	Ph	Me	4-MeO-C_6H_4	**6e**	77
6	**1**	Ph	Et	Ph	**6f**	71
7	**1**	Ph	Et	4-Me-C_6H_4	**6g**	73
8	**1**	Ph	Et	4-Et-C_6H_4	**6h**	65
9	**1**	Ph	Et	4-*n*-Pr-C_6H_4	**6i**	62
10	**1**	Ph	Et	4-MeO-C_6H_4	**6j**	78
11	**2**	4-Me-C_6H_4	Me	Ph	**7a**	40
12	**2**	4-Me-C_6H_4	Me	4-Me-C_6H_4	**7b**	47
13	**2**	4-Me-C_6H_4	Me	4-Et-C_6H_4	**7c**	51
14	**2**	4-Me-C_6H_4	Me	4-*n*-Pr-C_6H_4	**7d**	56
15	**2**	4-Me-C_6H_4	Me	4-MeO-C_6H_4	**7e**	72
16	**2**	4-Me-C_6H_4	Et	Ph	**7f**	53
17	**2**	4-Me-C_6H_4	Et	4-Me-C_6H_4	**7g**	53
18	**2**	4-Me-C_6H_4	Et	4-Et-C_6H_4	**7h**	52
19	**2**	4-Me-C_6H_4	Et	4-*n*-Pr-C_6H_4	**7i**	57
20	**2**	4-Me-C_6H_4	Et	4-MeO-C_6H_4	**7j**	78
21	**3**	4-NO_2-C_6H_4	Me	Ph	**8a**	56
22	**3**	4-NO_2-C_6H_4	Me	4-Me-C_6H_4	**8b**	73
23	**3**	4-NO_2-C_6H_4	Me	4-Et-C_6H_4	**8c**	65
24	**3**	4-NO_2-C_6H_4	Me	4-*n*-Pr-C_6H_4	**8d**	63
25	**3**	4-NO_2-C_6H_4	Me	4-MeO-C_6H_4	**8e**	70
26	**3**	4-NO_2-C_6H_4	Et	Ph	**8f**	48
27	**3**	4-NO_2-C_6H_4	Et	4-Me-C_6H_4	**8g**	67
28	**3**	4-NO_2-C_6H_4	Et	4-Et-C_6H_4	**8h**	67
29	**3**	4-NO_2-C_6H_4	Et	4-*n*-Pr-C_6H_4	**8i**	67
30	**3**	4-NO_2-C_6H_4	Et	4-MeO-C_6H_4	**8j**	68

[a] Reactions were carried out with **1**–**3** (1 mmol), **4** (1.5 mmol), and **5** (1 mmol) in EtOH (20 mL) at rt for 24 h.
[b] Isolated yield.

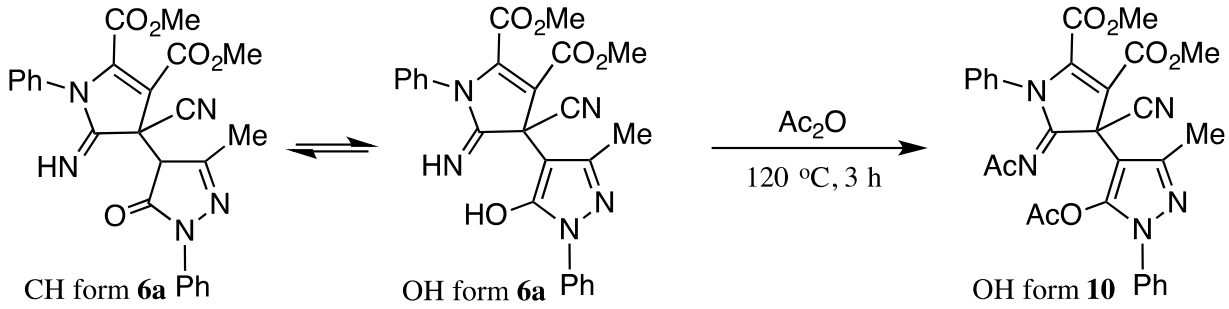
aniline to give the 4-(phenylaminocyanomethylene)-3*H*-pyrazol-3-one **9** of condensation by hydrogen cyanide elimination.[12b] Considering all these results, the optimal reaction conditions were obtained when a mixture of **4a** (1.5 equiv.) and **5a** (1.0 equiv.) in EtOH at room temperature for 1 h and then the reaction mixture was treated with **1** at room temperature for 24 h, the pyrazole-2,3-pyrroledicarboxylic acid 2,3-dimethyl ester **6a** was obtained in 70% yield (entry 3). With the optimal reaction conditions in hand, we constructed a series of pyrazole-2,3-pyrroledicarboxylates by use of the three-component reaction. Consequently, various derivatives of acetylenic esters **4a**,**b** and anilines **5a**–**e** were reacted under the optimized conditions and the expected compounds **6a**–**j**, **7a**–**j**, and **8a**–**j** were obtained in moderate to good yields. The results are listed in Table 2. In a three-component reaction using compound **2** as the substrate, the expected products **7** were obtained in somewhat lower yields (entries 11–14 and 16–19). The reason for this change of behavior is not very clear at present, but for one explanation, it is assumed that the electron density of the dicyanomethylene moiety would be increased by the electron-donating effect of the methyl group substituted at the 4-position of the phenyl group. Therefore, a nucleophilic attack of zwitterionic intermediates **A** to compound **2** may be less likely to occur. On the other hand, when 4-methoxyaniline was used in this reaction, the expected products were obtained in higher yields (entries 5, 10, 15, 20, 25, and 30). In this case, it seems that the key zwitterionic intermediates **A** could be easily formed because of the electron-donating effect of the 4-methoxy group. In these reactions, spiro pyrazol-3-one derivatives containing dihydropyridine moiety such as compounds **C** were not detected. The reason for this change of behavior is not clear at present.

These products **6**–**8** gave satisfactory elemental analyses and spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, and MS) consistent with their assigned structures (see experimental section). Interestingly, the IR spectra of **6**–**8** show the presence of a single isomer of CH form, whereas the NMR spectra of **6**–**8** in DMSO-d_6 indicate that **6**–**8** exist almost exclusively as a single isomer of OH form. For example, IR spectrum of **6a** displays bands in the range of 3282 cm^{-1} because of an imino group, a band at 2251 cm^{-1} because of a nonconjugated cyano group, and three bands at 1751, 1704, and 1646 cm^{-1} because of two esters and an amido carbonyl groups. The ^{1}H NMR spectrum of **6a** exhibits two three-proton singlets at δ 3.63 and δ 3.64 assignable to two esters methyl protons and two D_2O exchangeable one-proton broad singlets at δ 9.76 and δ 11.83 assignable to the imino and hydroxyl protons. The ^{13}C NMR spectrum of **6a** shows a signal at δ 44.9 because of the quaternary carbon, two signals at δ 52.4 and 53.9 because of two esters methyl carbons, a signal at δ 98.2 because of the pyrazole C-4 carbon, a signal at δ 116.8 because of the cyano carbon, a signal at δ 160.4 because of the pyrazole C-5 carbon, two signals at δ 161.0 and 161.3 because of two esters carbonyl carbons, and a signal at δ 163.1 because of the imino carbon.

A plausible reaction mechanism for the formation of pyrazole-2,3-pyrroledicarboxylates **6**–**8** is depicted in Scheme 2. Anilines **5** probably add on to acetylenic esters **4** to afford the key zwitterionic intermediates **A**, which undergo Michael addition with **1**–**3** to form the Michael adducts **D**. The intramolecular cyclization of **D** easily occurs via a nucleophilic addition of the amino group to the cyano group and then the corresponding pyrazole-2,3-pyrroledicarboxylates **6**–**8** would be produced. To our knowledge, this type of multicomponent reaction has not been described previously.



Scheme 2



Scheme 3

To conform the structure of the pyrazole-2,3-pyrroledicarboxylic acid 2,3-diester derivatives, we carried out the acetylation of **6a** (Scheme 3). Thus, thermal treatment of **6a** with acetic anhydride at 120 ˚C for 3 h afforded the diacetylated compound **10** (70%), which was characterized by IR, ^{1}H NMR, ^{13}C NMR, MS,

and elemental analysis (see experimental section). For example, IR spectrum of **10** displays a band at 2250 cm^{-1} because of a nonconjugated cyano group, a band at 1792 cm^{-1} because of an *O*-acetylated carbonyl group, and a band at 1679 cm^{-1} because of an *N*-acetylated carbonyl group. In the case of this reaction, mono-acetylated compound could not be isolated.

In conclusion, we have demonstrated new one-pot three-component reaction for the synthesis of pyrazole-2,3-pyrroledicarboxylic acid 2,3-diesters employing 4-(dicyanomethylene)-3*H*-pyrazol-3-ones, acetylenic esters, and anilines. The zwitterionic intermediates formed in situ from acetylenic esters and amines play a key role in the formation of pyrazol-3-ones containing dihydropyrrole moiety. Pyrrole and its derivatives are ever present in nature.[13a] Moreover, the pyrrole skeleton can be found in several marketed drugs, such as atorvastatin, aloracetam, elopiprazole, isamoltane, and ketorolac.[13b] Furthermore, some of these compounds are useful intermediates in the synthesis of biologically important naturally occurring alkaloids and synthetic heterocyclic derivatives.[13c-k] Pyrazole and pyrrole derivatives are important building blocks for the preparation of biologically active compounds with interest in medicinal chemistry. Further synthetic applications for novel pyrazole derivatives containing heterocyclic skeleton are in progress.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were recorded on a Thermo Fisher Scientific Nicolet iS5 FT-IR spectrometer equipped with an iD7 diamond ATR accessory. The ^{1}H and ^{13}C NMR spectra were measured with a JEOL JNM-ECZ600R/S1 spectrometer at 600.17 and 150.91 MHz, respectively. The ^{1}H and ^{13}C chemical shifts (δ) are reported in parts per million (ppm) relative to TMS as internal standard. Positive FAB MS spectra were obtained on a JEOL JMS-700T spectrometer. Elemental analyses were performed on YANACO MT-6 CHN analyzer. The substrates **1**,[12] **2**,[12] and **3** were prepared in this laboratory according to the method reported procedure.

2-[1,5-Dihydro-3-methyl-1-(4-nitrophenyl)-5-oxo-4*H*-pyrazol-4-ylidene]propanedinitrile (3): Purple prisms (84%), mp 168–170 ˚C ($CHCl_3$/petroleum ether); IR (ATR): ν 2232 (CN), 1730 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$): δ 2.62 (s, 3H, pyrazole 3-Me), 8.07–8.10 (m, 2H, Ph-H), 8.29–8.32 (m, 2H, Ph-H); ^{13}C NMR ($CDCl_3$): δ 15.1 (pyrazole 3-Me), 92.1 [=*C*$(CN)_2$], 109.0, 110.2 [=C(*C*N)$_2$], 118.1, 125.2, 141.1 (Ph-C), 144.8 (pyrazole C-4), 145.1 (Ph-C), 147.1 (pyrazole C-3), 158.0 (pyrazole C-5); MS: *m/z* 282 $[M+H]^+$; high-resolution MS: Calcd for $C_{13}H_8N_5O_3$ 282.0627, Found 282.0616. Anal. Calcd for $C_{13}H_7N_5O_3 \cdot 0.15H_2O$: C, 54.99; H, 2.59; N, 24.67. Found: C, 55.00; H, 2.63; N, 24.75.

General procedure for the preparation of compounds 6a–j, 7a–j, and 8a–j from 1–3, 4a,b, and 5a–e. A mixture of **4a** (0.213 g, 1.5 mmol) or **4b** (0.255 g, 1.5 mmol) and/or **5a** (0.093 g, 1 mmol), **5b** (0.107 g, 1 mmol), **5c** (0.121 g, 1 mmol), **5d** (0.135 g, 1 mmol), or **5e** (0.123 g, 1 mmol) in EtOH (20 mL)

was stirred at rt for 1 h. To the resulting mixture, **1** (0.236 g, 1 mmol), **2** (0.250 g, 1 mmol), or **3** (0.281 g, 1 mmol) was added and then the mixture was stirred at rt for 24 h. Further processing of the resulting mixture is described in the following paragraphs.

(A) To a reaction mixture, cold H_2O was added with stirring. The resulting mixture was extracted with $CHCl_3$ (150 mL). The extract was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was recrystallized from acetone/petroleum ether to afford **6a**–**j** and **7a**–**j**.

(B**)** The precipitate was collected by filtration, washed with Et_2O, dried, and recrystallized from an appropriate solvent to give **8a**–**j**.

4-Cyano-4-(4,5-dihydro-3-methyl-5-oxo-1-phenyl-1*H*-pyrazol-4-yl)-4,5-dihydro-5-imino-1-phenyl-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-dimethyl ester (6a): Colorless prisms (0.331 g, 70%), mp 187–189 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3282 (NH), 2251 (CN), 1751, 1704, 1646 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 2.49 (s, 3H, pyrazole 3-Me), 3.63, 3.64 (s, 6H, $2CO_2Me$), 7.19–7.21 (m, 1H, Ph-H), 7.41–7.47 (m, 7H, Ph-H), 7.65–7.67 (m, 2H, Ph-H), 9.76 (br, 1H, NH), 11.83 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.2 (pyrazole 3-Me), 44.9 (pyrrole C-4), 52.4, 53.9 ($2CO_2\mathit{Me}$), 98.2 (pyrazole C-4), 102.3 (pyrrole C-3), 116.8 (CN), 119.3, 125.7, 128.2, 129.4, 129.6, 129.8, 135.2, 136.9 (Ph-C), 148.0 (pyrazole C-3), 150.4 (pyrrole C-2), 160.4 (pyrazole C-5), 161.0, 161.3 ($2\mathit{C}O_2Me$), 163.1 (pyrrole C-5); MS: *m/z* 472 $[M+H]^+$. Anal. Calcd for $C_{25}H_{21}N_5O_5$: C, 63.69; H, 4.49; N, 14.85. Found: C, 63.67; H, 4.33; N, 14.80.

4-Cyano-4-(4,5-dihydro-3-methyl-5-oxo-1-phenyl-1*H*-pyrazol-4-yl)-4,5-dihydro-5-imino-1-(4-methylphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-dimethyl ester (6b): Colorless prisms (0.394 g, 81%), mp 157–159 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3255 (NH), 2252 (CN), 1749, 1703, 1655 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 2.31 (s, 3H, 4-Me-C_6H_4), 2.48 (s, 3H, pyrazole 3-Me), 3.64 (s, 6H, $2CO_2Me$), 7.15–7.52 (m, 7H, Ph-H), 7.60–7.66 (m, 2H, Ph-H), 9.70 (br, 1H, NH), 11.86 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.2 (pyrazole 3-Me), 21.3 (4-Me-C_6H_4), 44.8 (pyrrole C-4), 52.4, 53.8 ($2CO_2\mathit{Me}$), 98.4 (pyrazole C-4), 102.0 (pyrrole C-3), 116.9 (CN), 119.4, 125.7, 128.0, 129.6, 130.5, 132.4, 136.9, 139.2 (Ph-C), 148.0 (pyrazole C-3), 150.5 (pyrrole C-2), 160.4 (pyrazole C-5), 161.1, 161.4 ($2\mathit{C}O_2Me$), 163.2 (pyrrole C-5); MS: *m/z* 486 $[M+H]^+$; high-resolution MS: Calcd for $C_{26}H_{24}N_5O_5$ 486.1777, Found 486.1781. Anal. Calcd for $C_{26}H_{23}N_5O_5 \cdot 0.1H_2O$: C, 64.08; H, 4.80; N, 14.37. Found: C, 64.06; H, 4.89; N, 14.11.

4-Cyano-1-(4-ethylphenyl)-4-(4,5-dihydro-3-methyl-5-oxo-1-phenyl-1*H*-pyrazol-4-yl)-4,5-dihydro-5-imino-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-dimethyl ester (6c): Colorless needles (0.314 g, 63%), mp 167–169 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3263 (NH), 2254 (CN), 1750, 1712, 1658 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 1.17 (t, J = 7.6 Hz, 3H, 4-$\mathit{Me}CH_2$-C_6H_4), 2.49 (s, 3H, pyrazole 3-Me), 2.61 (q, J = 7.6 Hz, 2H, 4-Me$\mathit{CH_2}$-C_6H_4), 3.64 (s, 6H, $2CO_2Me$), 7.18–7.53 (m, 7H, Ph-H), 7.57–7.74 (m, 2H,

Ph-H), 9.71 (br, 1H, NH), 11.82 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.1 (pyrazole 3-Me), 15.8 (4-*Me*CH_2-C_6H_4), 28.4 (4-Me*C*H_2-C_6H_4), 44.9 (pyrrole C-4), 52.4, 53.8 (2CO_2*Me*), 98.4 (pyrazole C-4), 102.1 (pyrrole C-3), 116.9 (CN), 119.3, 125.6, 128.1, 129.1, 129.6, 132.7, 136.9, 145.1 (Ph-C), 148.0 (pyrazole C-3), 150.4 (pyrrole C-2), 160.5 (pyrazole C-5), 161.1, 161.3 (2*C*O_2Me), 163.2 (pyrrole C-5); MS: *m/z* 500 $[M+H]^+$. Anal. Calcd for $C_{27}H_{25}N_5O_5$: C, 64.92; H, 5.04; N, 14.02. Found: C, 64.97; H, 4.89; N, 14.02.

4-Cyano-4-(4,5-dihydro-3-methyl-5-oxo-1-phenyl-1*H*-pyrazol-4-yl)-4,5-dihydro-5-imino-1-(4-propylphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-dimethyl ester (6d): Colorless prisms (0.373 g, 73%), mp 180–182 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3255 (NH), 2249 (CN), 1747, 1709, 1657 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 0.86 (t, *J* = 7.6 Hz, 3H, 4-*Me*CH_2CH_2-C_6H_4), 1.57 (sext, *J* = 7.6 Hz, 2H, 4-MeC*H*$_2$$CH_2$-$C_6H_4$), 2.48 (s, 3H, pyrazole 3-Me), 2.56 (t, *J* = 7.6 Hz, 2H, 4-MeCH_2C*H*$_2$-C_6H_4), 3.63, 3.66 (s, 6H, 2CO_2Me), 7.18–7.47 (m, 7H, Ph-H), 7.62–7.66 (m, 2H, Ph-H), 9.70 (br, 1H, NH), 11.75 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.2 (pyrazole 3-Me), 14.1 (4-*Me*CH_2CH_2-C_6H_4), 24.4 (4-Me*C*H_2CH_2-C_6H_4), 37.4 (4-MeCH_2*C*H_2-C_6H_4), 44.9 (pyrrole C-4), 52.4, 53.8 (2CO_2*Me*), 98.3 (pyrazole C-4), 102.2 (pyrrole C-3), 116.9 (CN), 119.4, 125.7, 128.0, 129.6, 129.7, 132.7, 137.0, 143.6 (Ph-C), 147.9 (pyrazole C-3), 150.5 (pyrrole C-2), 160.3 (pyrazole C-5), 161.1, 161.3 (2*C*O_2Me), 163.1 (pyrrole C-5); MS: *m/z* 514 $[M+H]^+$. Anal. Calcd for $C_{28}H_{27}N_5O_5$: C, 65.49; H, 5.30; N, 13.64. Found: C, 65.33; H, 5.17; N, 13.61.

4-Cyano-4-(4,5-dihydro-3-methyl-5-oxo-1-phenyl-1*H*-pyrazol-4-yl)-4,5-dihydro-5-imino-1-(4-methoxyphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-dimethyl ester (6e): Colorless prisms (0.387 g, 77%), mp 172–174 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3276, 3251 (NH), 2248 (CN), 1750, 1700, 1654, 1639 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 2.48 (s, 3H, pyrazole 3-Me), 3.63 (s, 6H, 2CO_2Me), 3.75 (s, 3H, 4-*Me*O-C_6H_4), 7.00–7.05 (m, 2H, Ph-H), 7.18–7.21 (m, 1H, Ph-H), 7.34–7.44 (m, 4H, Ph-H), 7.60–7.72 (m, 2H, Ph-H), 9.67 (br, 1H, NH), 11.78 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.2 (pyrazole 3-Me), 44.7 (pyrrole C-4), 52.3, 53.8 (2CO_2*Me*), 55.9 (4-*Me*O-C_6H_4), 98.4 (pyrazole C-4), 101.8 (pyrrole C-3), 115.1 (Ph-C), 116.9 (CN), 119.4, 125.7, 127.5, 129.6, 129.8, 137.0 (Ph-C), 147.9 (pyrazole C-3), 150.7 (pyrrole C-2), 160.0 (Ph-C), 160.4 (pyrazole C-5), 161.1, 161.4 (2*C*O_2Me), 163.4 (pyrrole C-5); MS: *m/z* 502 $[M+H]^+$. Anal. Calcd for $C_{26}H_{23}N_5O_6$: C, 62.27; H, 4.62; N, 13.97. Found: C, 62.30; H, 4.65; N, 13.82.

4-Cyano-4-(4,5-dihydro-3-methyl-5-oxo-1-phenyl-1*H*-pyrazol-4-yl)-4,5-dihydro-5-imino-1-phenyl-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-diethyl ester (6f): Colorless prisms (0.357 g, 71%), mp 128–130 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3294 (NH), 2251 (CN), 1738, 1707, 1643 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 0.96, 1.11 (t, *J* = 6.9 Hz, 6H, 2CO_2CH_2*Me*), 2.49 (s, 3H, pyrazole 3-Me), 4.03–4.14 (m, 4H, 2CO_2C*H*$_2$Me), 7.18–7.23 (m, 1H, Ph-H), 7.37–7.52 (m, 7H, Ph-H), 7.63–7.66 (m, 2H, Ph-H),

9.68 (br, 1H, NH), 11.71 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.3 (pyrazole 3-Me), 13.9, 14.5 (2CO_2CH_2*Me*), 44.9 (pyrrole C-4), 60.9, 63.0 (2CO_2*C*H_2Me), 98.4 (pyrazole C-4), 102.3 (pyrrole C-3), 116.9 (CN), 119.5, 125.7, 128.5, 129.6, 129.8, 130.0, 135.1, 137.0 (Ph-C), 148.0 (pyrazole C-3), 150.4 (pyrrole C-2), 160.3 (pyrazole C-5), 160.4, 160.9 (2*C*O_2CH_2Me), 163.2 (pyrrole C-5); MS: *m/z* 500 $[M+H]^+$; high-resolution MS: Calcd for $C_{27}H_{26}N_5O_5$ 500.1934, Found 500.1942. Anal. Calcd for $C_{27}H_{25}N_5O_5 \cdot 0.7H_2O$: C, 63.32; H, 5.20; N, 13.67. Found: C, 63.39; H, 5.16; N, 13.70.

4-Cyano-4-(4,5-dihydro-3-methyl-1-phenyl-5-oxo-1*H*-pyrazol-4-yl)-4,5-dihydro-5-imino-1-(4-methylphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-diethyl ester (6g): Colorless needles (0.373 g, 73%), mp 167–169 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3264 (NH), 2253 (CN), 1744, 1703, 1655 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 1.00, 1.11 (t, *J* = 6.9 Hz, 6H, 2CO_2CH_2*Me*), 2.31 (s, 3H, 4-*Me*-C_6H_4), 2.48 (s, 3H, pyrazole 3-Me), 4.03–4.13 (m, 4H, 2CO_2C*H*$_2$Me), 7.18–7.34 (m, 5H, Ph-H), 7.41–7.44 (m, 2H, Ph-H), 7.61–7.68 (m, 2H, Ph-H), 9.64 (br, 1H, NH), 11.75 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.3 (pyrazole 3-Me), 14.0, 14.5 (2CO_2CH_2*Me*), 21.3 (4-*Me*-C_6H_4), 44.9 (pyrrole C-4), 60.8, 63.0 (2CO_2*C*H_2Me), 98.3 (pyrazole C-4), 102.1 (pyrrole C-3), 117.0 (CN), 119.4, 125.7, 128.3, 129.6, 130.3, 132.4, 137.0, 139.2 (Ph-C), 147.9 (pyrazole C-3), 150.5 (pyrrole C-2), 159.8 (pyrazole C-5), 160.5, 160.9 (2*C*O_2CH_2Me), 163.2 (pyrrole C-5); MS: *m/z* 514 $[M+H]^+$. Anal. Calcd for $C_{28}H_{27}N_5O_5$: C, 65.49; H, 5.30; N, 13.64. Found: C, 65.56; H, 5.36; N, 13.61.

4-Cyano-1-(4-ethylphenyl)-4-(4,5-dihydro-3-methyl-5-oxo-1-phenyl-1*H*-pyrazol-4-yl)-4,5-dihydro-5-imino-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-diethyl ester (6h): Colorless needles (0.341 g, 65%), mp 164–165 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3254 (NH), 2254 (CN), 1745, 1702, 1655 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 0.97, 1.12 (t, *J* = 6.9 Hz, 6H, 2CO_2CH_2*Me*), 1.15 (t, *J* = 7.6 Hz, 3H, 4-*Me*CH_2-C_6H_4), 2.49 (s, 3H, pyrazole 3-Me), 2.61 (q, *J* = 7.6 Hz, 2H, 4-MeC*H*$_2$-C_6H_4), 4.03–4.13 (m, 4H, 2CO_2C*H*$_2$Me), 7.18–7.44 (m, 7H, Ph-H), 7.57–7.73 (m, 2H, Ph-H), 9.65 (br, 1H, NH), 11.80 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.3 (pyrazole 3-Me), 13.9, 14.5 (2CO_2CH_2*Me*), 16.0 (4-*Me*CH_2-C_6H_4), 28.4 (4-Me*C*H_2-C_6H_4), 44.9 (pyrrole C-4), 60.8, 62.9 (2CO_2*C*H_2Me), 98.4 (pyrazole C-4), 102.0 (pyrrole C-3), 116.9 (CN), 119.3, 125.6, 128.4, 129.0, 129.6, 132.6, 137.0, 145.2 (Ph-C), 148.0 (pyrazole C-3), 150.6 (pyrrole C-2), 160.3 (pyrazole C-5), 160.4, 160.9 (2*C*O_2CH_2Me), 163.3 (pyrrole C-5); MS: *m/z* 528 $[M+H]^+$. Anal. Calcd for $C_{29}H_{29}N_5O_5$: C, 66.02; H, 5.54; N, 13.27. Found: C, 65.94; H, 5.50; N, 13.22.

4-Cyano-4-(4,5-dihydro-3-methyl-5-oxo-1-phenyl-1*H*-pyrazol-4-yl)-4,5-dihydro-5-imino-1-(4-propylphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-diethyl ester (6i): Colorless needles (0.337 g, 62%), mp 161–162 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3252 (NH), 2254 (CN), 1748, 1702, 1662 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 0.85 (t, *J* = 7.6 Hz, 3H, 4-*Me*CH_2CH_2-C_6H_4), 0.95, 1.11 (t, *J* = 6.9 Hz, 6H, 2CO_2CH_2*Me*), 1.56 (sext, *J* = 7.6 Hz, 2H, 4-MeC*H*$_2CH_2$-C_6H_4), 2.49 (s, 3H, pyrazole 3-Me), 2.56 (t, *J* = 7.6 Hz, 2H, 4-MeCH_2C*H*$_2$-C_6H_4), 4.03–4.13 (m, 4H, 2CO_2C*H*$_2$Me), 7.18–7.44 (m, 7H, Ph-H),

7.61–7.70 (m, 2H, Ph-H), 9.65 (br, 1H, NH), 11.83 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.3 (pyrazole 3-Me), 13.9 (CO_2CH_2*Me*), 14.0 (4-*Me*CH_2CH_2-C_6H_4), 14.5 (CO_2CH_2*Me*), 24.5 (4-Me*C*H_2CH_2-C_6H_4), 37.4 (4-MeCH_2*C*H_2-C_6H_4), 44.9 (pyrrole C-4), 60.8, 62.9 (2CO_2*C*H_2Me), 98.4 (pyrazole C-4), 102.0 (pyrrole C-3), 116.9 (CN), 119.3, 125.6, 128.3, 129.6, 132.8, 137.0, 143.7 (Ph-C), 148.0 (pyrazole C-3), 150.6 (pyrrole C-2), 160.1 (pyrazole C-5), 160.4, 160.9 (2*C*O_2CH_2Me), 163.3 (pyrrole C-5); MS: *m/z* 542 $[M+H]^+$; high-resolution MS: Calcd for $C_{30}H_{32}N_5O_5$ 542.2403, Found 542.2408. Anal. Calcd for $C_{30}H_{31}N_5O_5 \cdot 0.2H_2O$: C, 66.09; H, 5.81; N, 12.85. Found: C, 66.05; H, 5.72; N, 12.81.

4-Cyano-4-(4,5-dihydro-3-methyl-5-oxo-1-phenyl-1*H*-pyrazol-4-yl)-4,5-dihydro-5-imino-1-(4-methoxyphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-diethyl ester (6j): Colorless prisms (0.413 g, 78%), mp 153–155 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3274 (NH), 2247 (CN), 1743, 1712, 1650, 1636 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 0.99, 1.11 (t, *J* = 6.9 Hz, 6H, 2CO_2CH_2*Me*), 2.48 (s, 3H, pyrazole 3-Me), 3.75 (s, 3H, 4-*Me*O-C_6H_4), 4.03–4.13 (m, 4H, 2CO_2C*H*$_2$Me), 7.01–7.05 (m, 2H, Ph-H), 7.18–7.21 (m, 1H, Ph-H), 7.35–7.44 (m, 4H, Ph-H), 7.63–7.69 (m, 2H, Ph-H), 9.62 (br, 1H, NH), 11.77 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.3 (pyrazole 3-Me), 14.0, 14.5 (2CO_2CH_2*Me*), 44.8 (pyrrole C-4), 56.0 (4-*Me*O-C_6H_4), 60.8, 62.9 (2CO_2*C*H_2Me), 98.5 (pyrazole C-4), 101.7 (pyrrole C-3), 114.9 (Ph-C), 117.0 (CN), 119.4, 125.6, 127.4, 129.7, 130.1, 137.0 (Ph-C), 147.9 (pyrazole C-3), 150.6 (pyrrole C-2), 160.0 (Ph-C), 160.3 (pyrazole C-5), 160.5, 160.9 (2*C*O_2CH_2Me), 163.5 (pyrrole C-5); MS: *m/z* 530 $[M+H]^+$; high-resolution MS: Calcd for $C_{28}H_{28}N_5O_6$ 530.2040, Found 530.2045. Anal. Calcd for $C_{28}H_{27}N_5O_6 \cdot 0.2H_2O$: C, 63.08; H, 5.18; N, 13.14. Found: C, 63.01; H, 4.95; N, 13.10.

4-Cyano-4-[4,5-dihydro-3-methyl-1-(4-methylphenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1-phenyl-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-dimethyl ester (7a): Colorless prisms (0.194 g, 40%), mp 159–161 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3392 (NH), 2247 (CN), 1746, 1701, 1653 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 2.27 (s, 3H, 4-*Me*-C_6H_4), 2.47 (s, 3H, pyrazole 3-Me), 3.63, 3.64 (s, 6H, 2CO_2Me), 7.22–7.26 (m, 2H, Ph-H), 7.34–7.54 (m, 7H, Ph-H), 9.72 (br, 1H, NH), 11.70 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.2 (pyrazole 3-Me), 21.0 (4-*Me*-C_6H_4), 44.9 (pyrrole C-4), 52.4, 53.8 (2CO_2*Me*), 98.0 (pyrazole C-4), 102.5 (pyrrole C-3), 116.9 (CN), 119.6, 128.2, 129.4, 129.7, 130.0, 134.6, 135.0 (Ph-C), 147.4 (pyrazole C-3), 150.4 (pyrrole C-2), 160.4 (pyrazole C-5), 161.1, 161.3 (2*C*O_2Me), 163.1 (pyrrole C-5); MS: *m/z* 486 $[M+H]^+$. Anal. Calcd for $C_{26}H_{23}N_5O_5$: C, 64.32; H, 4.78; N, 14.43. Found: C, 64.27; H, 4.82; N, 14.25.

4-Cyano-4-[4,5-dihydro-3-methyl-1-(4-methylphenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1-(4-methylphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-dimethyl ester (7b): Colorless needles (0.237 g, 47%), mp 155–157 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3278 (NH), 2249 (CN), 1753, 1704, 1665, 1631 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 2.28, 2.31 [s, 6H, 2(4-*Me*-C_6H_4)], 2.46 (s, 3H, pyrazole 3-Me), 3.63 (s, 6H, 2CO_2Me), 7.22–7.34 (m, 6H, Ph-H), 7.51–7.54 (m, 2H, Ph-H), 9.72 (br, 1H,

NH), 11.70 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.2 (pyrazole 3-Me), 21.0, 21.3 [2(4-*Me*-C_6H_4)], 44.9 (pyrrole C-4), 52.3, 53.8 (2CO_2*Me*), 98.2 (pyrazole C-4), 102.2 (pyrrole C-3), 116.9 (CN), 119.6, 128.0, 129.9, 130.3, 132.4, 134.6, 135.0, 139.0 (Ph-C), 147.3 (pyrazole C-3), 150.6 (pyrrole C-2), 160.4 (pyrazole C-5), 161.1, 161.4 (2*C*O_2Me), 163.3 (pyrrole C-5); MS: *m/z* 500 $[M+H]^+$. Anal. Calcd for $C_{27}H_{25}N_5O_5$: C, 64.92; H, 5.04; N, 14.02. Found: C, 64.91; H, 5.12; N, 13.73.

4-Cyano-1-(4-ethylphenyl)-4-[4,5-dihydro-3-methyl-1-(4-methylphenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-dimethyl ester (7c): Colorless prisms (0.261 g, 51%), mp 167–169 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3294 (NH), 2245 (CN), 1745, 1704, 1650 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 1.16 (t, *J* = 7.6 Hz, 3H, 4-*Me*CH_2-C_6H_4), 2.27 (s, 3H, 4-*Me*-C_6H_4), 2.46 (s, 3H, pyrazole 3-Me), 2.61 (q, *J* = 7.6 Hz, 2H, 4-MeC*H*$_2$-C_6H_4), 3.63 (s, 6H, 2CO_2Me), 7.22–7.36 (m, 6H, Ph-H), 7.51–7.54 (m, 2H, Ph-H), 9.68 (br, 1H, NH), 11.73 (br, 1H, NH); ^{13}C NMR (DMSO-d_6): δ 12.2 (pyrazole 3-Me), 15.8 (4-*Me*CH_2-C_6H_4), 21.0 (4-*Me*-C_6H_4), 28.4 (4-Me*C*H_2-C_6H_4), 44.9 (pyrrole C-4), 52.3, 53.8 (2CO_2*Me*), 98.3 (pyrazole C-4), 102.3 (pyrrole C-3), 116.9 (CN), 119.5, 128.0, 129.1, 129.9, 132.7, 134.6, 135.0, 145.0 (Ph-C), 147.3 (pyrazole C-3), 150.5 (pyrrole C-2), 160.2 (pyrazole C-5), 161.1, 161.4 (2*C*O_2Me), 163.4 (pyrrole C-5); MS: *m/z* 514 $[M+H]^+$. Anal. Calcd for $C_{28}H_{27}N_5O_5$: C, 65.49; H, 5.30; N, 13.64. Found: C, 65.58; H, 5.47; N, 13.49.

4-Cyano-4-[4,5-dihydro-3-methyl-1-(4-methylphenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1-(4-propylphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-dimethyl ester (7d): Colorless needles (0.294 g, 56%), mp 150–151 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3291 (NH), 2249 (CN), 1751, 1714, 1648 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 0.86 (t, *J* = 7.6 Hz, 3H, 4-*Me*CH_2CH_2-C_6H_4), 1.57 (sext, *J* = 7.6 Hz, 2H, 4-MeC*H*$_2$$CH_2$-$C_6H_4$), 2.27 (s, 3H, 4-*Me*-$C_6H_4$), 2.46 (s, 3H, pyrazole 3-Me), 2.55 (t, *J* = 7.6 Hz, 2H, 4-MeCH_2C*H*$_2$-C_6H_4), 3.62, 3.63 (s, 6H, 2CO_2Me), 7.22–7.35 (m, 6H, Ph-H), 7.50–7.53 (m, 2H, Ph-H), 9.70 (br, 1H, NH), 11.74 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.2 (pyrazole 3-Me), 14.1 (4-*Me*CH_2CH_2-C_6H_4), 21.0 (4-*Me*-C_6H_4), 24.4 (4-Me*C*H_2CH_2-C_6H_4), 37.4 (4-MeCH_2*C*H_2-C_6H_4), 44.9 (pyrrole C-4), 52.3, 53.8 (2CO_2*Me*), 98.2 (pyrazole C-4), 102.3 (pyrrole C-3), 116.9 (CN), 119.5, 127.9, 129.7, 129.9, 132.7, 134.6, 135.0, 143.5 (Ph-C), 147.3 (pyrazole C-3), 150.5 (pyrrole C-2), 160.2 (pyrazole C-5), 161.1, 161.3 (2*C*O_2Me), 163.2 (pyrrole C-5); MS: *m/z* 528 $[M+H]^+$. Anal. Calcd for $C_{29}H_{29}N_5O_5$: C, 66.02; H, 5.54; N, 13.27. Found: C, 66.02; H, 5.40; N, 13.45.

4-Cyano-4-[4,5-dihydro-3-methyl-1-(4-methyphenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1-(4-methoxylphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-dimethyl ester (7e): Colorless needles (0.370 g, 72%), mp 153–155 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3273 (NH), 2249 (CN), 1747, 1716, 1654 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 2.27 (s, 3H, 4-*Me*-C_6H_4), 2.46 (s, 3H, pyrazole 3-Me), 3.63 (s, 6H, 2CO_2Me), 3.75 (s, 3H, 4-*Me*O-C_6H_4), 7.00–7.04 (m, 2H, Ph-H), 7.22–7.40 (m, 4H, Ph-H), 7.51–7.54 (m, 2H, Ph-H), 9.64 (br, 1H, NH), 11.75 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.2

(pyrazole 3-Me), 21.0 (4-*Me*-C_6H_4), 44.8 (pyrrole C-4), 52.3, 53.8 ($2CO_2$*Me*), 55.9 (4-*Me*O-C_6H_4), 98.4 (pyrazole C-4), 101.8 (pyrrole C-3), 115.0 (Ph-C), 116.9 (CN), 119.5, 127.5, 129.8, 129.9, 134.6, 135.0 (Ph-C), 147.3 (pyrazole C-3), 150.7 (pyrrole C-2), 160.0 (Ph-C), 160.4 (pyrazole C-5), 161.1, 161.4 ($2CO_2$Me), 163.5 (pyrrole C-5); MS: *m/z* 516 $[M+H]^+$; high-resolution MS: Calcd for $C_{27}H_{26}N_5O_6$ 516.1883, Found 516.1891. Anal. Calcd for $C_{27}H_{25}N_5O_6 \cdot 0.6H_2O$: C, 61.61; H, 5.02; N, 13.31. Found: C, 61.56; H, 4.84; N, 13.03.

4-Cyano-4-[4,5-dihydro-3-methyl-1-(4-methylphenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1-phenyl-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-diethyl ester (7f): Colorless prisms (0.273 g, 53%), mp 132–135 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3294 (NH), 2249 (CN), 1739, 1709, 1643, 1629 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 0.96, 1.11 (t, *J* = 6.9 Hz, 6H, $2CO_2CH_2$*Me*), 2.27 (s, 3H, 4-*Me*-C_6H_4), 2.47 (s, 3H, pyrazole 3-Me), 4.03–4.13 (m, 4H, $2CO_2CH_2$Me), 7.22–7.26 (m, 2H, Ph-H), 7.41–7.53 (m, 7H, Ph-H), 9.66 (br, 1H, NH), 11.65 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.3 (pyrazole 3-Me), 13.9, 14.5 ($2CO_2CH_2$*Me*), 21.0 (4-*Me*-C_6H_4), 44.9 (pyrrole C-4), 60.9, 63.0 ($2CO_2CH_2$Me), 98.3 (pyrazole C-4), 102.4 (pyrrole C-3), 116.9 (CN), 119.6, 128.5, 129.5, 129.7, 130.0, 134.6, 135.0 (Ph-C), 147.4 (pyrazole C-3), 150.3 (pyrrole C-2), 159.9 (pyrazole C-5), 160.4, 160.9 ($2CO_2CH_2$Me), 163.2 (pyrrole C-5); MS: *m/z* 514 $[M+H]^+$; high-resolution MS: Calcd for $C_{28}H_{28}N_5O_5$ 514.2090, Found 514.2095. Anal. Calcd for $C_{28}H_{27}N_5O_5 \cdot 0.65H_2O$: C, 64.03; H, 5.43; N, 13.33. Found: C, 64.07; H, 5.29; N, 13.32.

4-Cyano-4-[4,5-dihydro-3-methyl-1-(4-methylphenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1-(4-methylphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-diethyl ester (7g): Colorless needles (0.279 g, 53%), mp 135–137 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3247 (NH), 2250 (CN), 1749, 1699, 1671 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 1.00, 1.11 (t, *J* = 6.9 Hz, 6H, $2CO_2CH_2$*Me*), 2.27, 2.30 [s, 6H, 2(4-*Me*-C_6H_4)], 2.46 (s, 3H, pyrazole 3-Me), 4.03–4.12 (m, 4H, $2CO_2CH_2$Me), 7.22–7.34 (m, 6H, Ph-H), 7.50–7.53 (m, 2H, Ph-H), 9.60 (br, 1H, NH), 11.62 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.3 (pyrazole 3-Me), 14.0, 14.5 ($2CO_2CH_2$*Me*), 21.0, 21.3 [2(4-*Me*-C_6H_4)], 44.9 (pyrrole C-4), 60.8, 63.0 ($2CO_2CH_2$Me), 98.3 (pyrazole C-4), 102.1 (pyrrole C-3), 117.0 (CN), 119.6, 128.3, 129.9, 130.2, 132.4, 134.7, 135.0, 139.1 (Ph-C), 147.4 (pyrazole C-3), 150.5 (pyrrole C-2), 159.6 (pyrazole C-5), 160.5, 160.9 ($2CO_2CH_2$Me), 163.3 (pyrrole C-5); MS: *m/z* 528 $[M+H]^+$; high-resolution MS: Calcd for $C_{29}H_{30}N_5O_5$ 528.2247, Found 528.2266. Anal. Calcd for $C_{29}H_{29}N_5O_5 \cdot 0.5H_2O$: C, 64.91; H, 5.64; N, 13.05. Found: C, 64.95; H, 5.47; N, 13.00.

4-Cyano-1-(4-ethylphenyl)-4-[4,5-dihydro-3-methyl-1-(4-methylphenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-diethyl ester (7h): Colorless needles (0.280 g, 52%), mp 162–164 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3250 (NH), 2251 (CN), 1741, 1706, 1655 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 0.96, 1.11 (t, *J* = 6.9 Hz, 6H, $2CO_2CH_2$*Me*), 1.15 (t, *J* = 7.6 Hz,

3H, 4-*Me*CH_2-C_6H_4), 2.28 (s, 3H, 4-*Me*-C_6H_4), 2.46 (s, 3H, pyrazole 3-Me), 2.61 (q, *J* = 7.6 Hz, 2H, 4-Me*C*H_2-C_6H_4), 4.03–4.14 (m, 4H, $2CO_2CH_2$Me), 7.13–7.40 (m, 6H, Ph-H), 7.51–7.56 (m, 2H, Ph-H), 9.62 (br, 1H, NH), 11.66 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.3 (pyrazole 3-Me), 13.9, 14.5 ($2CO_2CH_2$*Me*), 16.0 (4-*Me*CH_2-C_6H_4), 21.0 (4-*Me*-C_6H_4), 28.4 (4-Me*C*H_2-C_6H_4), 44.9 (pyrrole C-4), 60.8, 62.9 ($2CO_2$*C*H_2Me), 98.2 (pyrazole C-4), 102.1 (pyrrole C-3), 116.9 (CN), 119.5, 128.3, 128.9, 129.9, 132.7, 134.7, 134.9, 145.3 (Ph-C), 147.4 (pyrazole C-3), 150.5 (pyrrole C-2), 159.8 (pyrazole C-5), 160.5, 160.9 ($2CO_2CH_2$Me), 163.4 (pyrrole C-5); MS: *m/z* 542 $[M+H]^+$; high-resolution MS: Calcd for $C_{30}H_{32}N_5O_5$ 542.2403, Found 542.2419 Anal. Calcd for $C_{30}H_{31}N_5O_5 \cdot 0.45H_2O$: C, 65.55; H, 5.85; N, 12.74. Found: C, 65.55; H, 5.64; N, 12.75.

4-Cyano-4-[4,5-dihydro-3-methyl-1-(4-methylphenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1-(4-propylphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-diethyl ester (7i): Colorless prisms (0.318 g, 57%), mp 156–157 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3261 (NH), 2250 (CN), 1751, 1707, 1659 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 0.85 (t, *J* = 7.6 Hz, 3H, 4-*Me*CH_2CH_2-C_6H_4), 0.95, 1.11 (t, *J* = 6.9 Hz, 6H, $2CO_2CH_2$*Me*), 1.56 (sext, *J* = 7.6 Hz, 2H, 4-Me*C*H_2CH_2-C_6H_4), 2.28 (s, 3H, 4-*Me*-C_6H_4), 2.46 (s, 3H, pyrazole 3-Me), 2.56 (t, *J* = 7.6 Hz, 2H, 4-MeCH_2*C*H_2-C_6H_4), 4.03–4.13 (m, 4H, $2CO_2$*C*H_2Me), 7.09–7.41 (m, 6H, Ph-H), 7.51–7.57 (m, 2H, Ph-H), 9.62 (br, 1H, NH), 11.72 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.3 (pyrazole 3-Me), 13.9 (4-*Me*CH_2CH_2-C_6H_4), 14.0, 14.4 ($2CO_2CH_2$*Me*), 21.0 (4-*Me*-C_6H_4), 24.5 (4-Me*C*H_2CH_2-C_6H_4), 37.4 (4-MeCH_2*C*H_2-C_6H_4), 44.9 (pyrrole C-4), 60.8, 62.9 ($2CO_2$*C*H_2Me), 98.3 (pyrazole C-4), 102.1 (pyrrole C-3), 116.9 (CN), 119.5, 128.3, 129.5, 129.9, 132.8, 134.7, 134.9, 143.5 (Ph-C), 147.4 (pyrazole C-3), 150.6 (pyrrole C-2), 159.9 (pyrazole C-5), 160.4, 160.9 ($2CO_2CH_2$Me), 163.4 (pyrrole C-5); MS: *m/z* 556 $[M+H]^+$; high-resolution MS: Calcd for $C_{31}H_{34}N_5O_5$ 556.2560, Found 556.2563. Anal. Calcd for $C_{31}H_{33}N_5O_5 \cdot 0.35H_2O$: C, 66.26; H, 6.04; N, 12.46. Found: C, 66.30; H, 5.95; N, 12.34.

4-Cyano-4-[4,5-dihydro-3-methyl-1-(4-methylphenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1-(4-methoxyphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-diethyl ester (7j): Colorless needles (0.426 g, 78%), mp 161–163 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 3267 (NH), 2249 (CN), 1749, 1701, 1641, 1636 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ 1.00, 1.11 (t, *J* = 6.9 Hz, 6H, $2CO_2CH_2$*Me*), 2.28 (s, 3H, 4-*Me*-C_6H_4), 2.47 (s, 3H, pyrazole 3-Me), 3.75 (s, 3H, 4-*Me*O-C_6H_4), 4.04–4.13 (m, 4H, $2CO_2$C*H*$_2$Me), 7.02–7.10 (m, 2H, Ph-H), 7.18–7.41 (m, 4H, Ph-H), 7.51–7.54 (m, 2H, Ph-H), 9.59 (br, 1H, NH), 11.75 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.2 (pyrazole 3-Me), 14.0, 14.5 ($2CO_2CH_2$*Me*), 21.0 (4-*Me*-C_6H_4), 44.8 (pyrrole C-4), 56.0 (4-*Me*O-C_6H_4), 60.8, 62.9 ($2CO_2$*C*H_2Me), 98.3 (pyrazole C-4), 101.7 (pyrrole C-3), 114.9 (Ph-C), 117.0 (CN), 119.4, 127.6, 129.9, 130.2, 134.7, 134.9 (Ph-C), 147.4 (pyrazole C-3), 150.8 (pyrrole C-2), 159.9 (pyrazole C-5), 160.1 (Ph-C), 160.5, 160.9 ($2CO_2CH_2$Me),

163.6 (pyrrole C-5); MS: *m/z* 544 $[M+H]^+$. Anal. Calcd for $C_{29}H_{29}N_5O_6$: C, 64.08; H, 5.38; N, 12.88. Found: C, 63.88; H, 5.37; N, 12.83.

4-Cyano-4-[4,5-dihydro-3-methyl-1-(4-nitrophenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1-phenyl-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-dimethyl ester (8a): Yellow needles (0.288 g, 56%), mp 196–198 ˚C (dec.) ($CHCl_3$/MeOH); IR (ATR): ν 3252 (NH), 2253 (CN), 1745, 1709, 1658 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ 2.51 (s, 3H, pyrazole 3-Me), 3.63, 3.64 (s, 6H, $2CO_2Me$), 7.42–7.53 (m, 5H, Ph-H), 7.97–8.03 (m, 2H, Ph-H), 8.28–8.34 (m, 2H, Ph-H), 9.84 (br, 1H, NH), 11.97 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.6 (pyrazole 3-Me), 44.9 (pyrrole C-4), 52.5, 53.9 ($2CO_2\mathit{Me}$), 98.3 (pyrazole C-4), 102.7 (pyrrole C-3), 116.5 (CN), 118.2, 125.6, 128.2, 129.7, 130.0, 134.5, 142.3, 143.6 (Ph-C), 150.0 (pyrrole C-2), 150.8 (pyrazole C-3), 160.6 (pyrazole C-5), 160.8, 161.2 ($2\mathit{C}O_2Me$), 162.9 (pyrrole C-5); MS: *m/z* 517 $[M+H]^+$; high-resolution MS: Calcd for $C_{25}H_{21}N_6O_7$ 517.1472, Found 517.1470. Anal. Calcd for $C_{25}H_{20}N_6O_7 \cdot 0.5H_2O$: C, 57.14; H, 4.03; N, 15.99. Found: C, 57.06; H, 3.88; N, 15.85.

4-Cyano-4-[4,5-dihydro-3-methyl-1-(4-nitrophenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1-(4-methylphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-dimethyl ester (8b): Yellow needles (0.387 g, 73%), mp 170–172 ˚C (dec.) ($CHCl_3$/petroleum ether); IR (ATR): ν 3281 (NH), 2255 (CN), 1743, 1710, 1659 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ 2.32 (s, 3H, 4-Me-C_6H_4), 2.50 (s, 3H, pyrazole 3-Me), 3.64 (s, 6H, $2CO_2Me$), 7.28–7.34 (m, 4H, Ph-H), 8.00–8.04 (m, 2H, Ph-H), 8.28–8.32 (m, 2H, Ph-H), 9.83 (br, 1H, NH), 11.83 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.6 (pyrazole 3-Me), 21.3 (4-Me-C_6H_4), 44.9 (pyrrole C-4), 52.4, 53.9 ($2CO_2\mathit{Me}$), 97.9 (pyrazole C-4), 102.5 (pyrrole C-3), 116.5 (CN), 118.1, 125.6, 128.0, 130.5, 131.8, 139.4, 142.4, 143.5 (Ph-C), 150.1 (pyrrole C-2), 150.7 (pyrazole C-3), 160.8 (pyrazole C-5), 160.9, 161.2 ($2\mathit{C}O_2Me$), 163.2 (pyrrole C-5); MS: *m/z* 531 $[M+H]^+$; high-resolution MS: Calcd for $C_{26}H_{23}N_6O_7$ 531.1628, Found 531.1618. Anal. Calcd for $C_{26}H_{22}N_6O_7 \cdot 0.6H_2O$: C, 57.69; H, 4.32; N, 15.53. Found: C, 57.66; H, 4.13; N, 15.50.

4-Cyano-1-(4-ethylphenyl)-4-[4,5-dihydro-3-methyl-1-(4-nitrophenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-dimethyl ester (8c): Yellow needles (0.352 g, 65%), mp 178–179 ˚C (dec.) ($CHCl_3$/petroleum ether); IR (ATR): ν 3267 (NH), 2245 (CN), 1743, 1708, 1655 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ 1.17 (t, J = 7.6 Hz, 3H, 4-$\mathit{Me}CH_2$-C_6H_4), 2.50 (s, 3H, pyrazole 3-Me), 2.62 (q, J = 7.6 Hz, 2H, 4-Me$\mathit{C}H_2$-C_6H_4), 3.63, 3.64 (s, 6H, $2CO_2Me$), 7.31–7.35 (m, 4H, Ph-H), 7.98–8.01 (m, 2H, Ph-H), 8.30–8.32 (m, 2H, Ph-H), 9.83 (br, 1H, NH), 11.98 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.6 (pyrazole 3-Me), 15.8 (4-$\mathit{Me}CH_2$-C_6H_4), 28.4 (4-Me$\mathit{C}H_2$-C_6H_4), 44.9 (pyrrole C-4), 52.5, 53.9 ($2CO_2\mathit{Me}$), 98.0 (pyrazole C-4), 102.6 (pyrrole C-3), 116.5 (CN), 118.1, 125.6, 128.0, 129.3, 132.0, 142.3, 143.6, 145.5 (Ph-C), 150.1 (pyrrole C-2), 150.8 (pyrazole C-3), 160.6 (pyrazole C-5), 160.9, 161.2 ($2\mathit{C}O_2Me$), 163.1 (pyrrole C-5); MS: *m/z* 545 $[M+H]^+$. Anal. Calcd for $C_{27}H_{24}N_6O_7$: C, 59.56; H, 4.44; N, 15.43. Found: C, 59.48; H, 4.46; N, 15.39.

4-Cyano-4-[4,5-dihydro-3-methyl-1-(4-nitrophenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1-(4-propylphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-dimethyl ester (8d): Yellow needles (0.353 g, 63%), mp 173–175 ˚C (dec.) ($CHCl_3$/petroleum ether); IR (ATR): ν 3291, 3276 (NH), 2247 (CN), 1750, 1715, 1661 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ 0.86 (t, J = 7.6 Hz, 3H, 4-*Me*CH_2CH_2-C_6H_4), 1.58 (sext, J = 7.6 Hz, 2H, 4-Me*C*H_2CH_2-C_6H_4), 2.50 (s, 3H, pyrazole 3-Me), 2.57 (t, J = 7.6 Hz, 2H, 4-MeCH_2*C*H_2-C_6H_4), 3.62, 3.64 (s, 6H, 2CO_2Me), 7.29–7.35 (m, 4H, Ph-H), 7.98–8.01 (m, 2H, Ph-H), 8.30–8.32 (m, 2H, Ph-H), 9.83 (br, 1H, NH), 11.98 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.6 (pyrazole 3-Me), 14.1 (4-*Me*CH_2CH_2-C_6H_4), 24.4 (4-Me*C*H_2CH_2-C_6H_4), 37.4 (4-MeCH_2*C*H_2-C_6H_4), 44.9 (pyrrole C-4), 52.5, 53.9 (2CO_2*Me*), 98.2 (pyrazole C-4), 102.6 (pyrrole C-3), 116.5 (CN), 118.1, 125.6, 127.9, 129.9, 132.0, 142.3, 143.6, 144.0 (Ph-C), 150.0 (pyrrole C-2), 150.8 (pyrazole C-3), 160.5 (pyrazole C-5), 160.8, 161.2 (2*C*O_2Me), 163.2 (pyrrole C-5); MS: *m/z* 559 $[M+H]^+$. Anal. Calcd for $C_{28}H_{26}N_6O_7$: C, 60.21; H, 4.69; N, 15.05. Found: C, 60.00; H, 4.76; N, 15.03.

4-Cyano-4-[4,5-dihydro-3-methyl-1-(4-nitrophenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1-(4-methoxyphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-dimethyl ester (8e): Yellow needles (0.380 g, 70%), mp 176–178 ˚C (dec.) ($CHCl_3$/petroleum ether); IR (ATR): ν 3273 (NH), 2247 (CN), 1751, 1715, 1664 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ 2.49 (s, 3H, pyrazole 3-Me), 3.63, 3.64 (s, 6H, 2CO_2Me), 3.76 (s, 3H, 4-*Me*O-C_6H_4), 7.02–7.05 (m, 2H, Ph-H), 7.37–7.40 (m, 2H, Ph-H), 8.00–8.05 (m, 2H, Ph-H), 8.27–8.33 (m, 2H, Ph-H), 9.86 (br, 1H, NH), 11.89 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.7 (pyrazole 3-Me), 44.9 (pyrrole C-4), 52.5, 53.9 (2CO_2*Me*), 56.0 (4-*Me*O-C_6H_4), 97.8 (pyrazole C-4), 102.5 (pyrrole C-3), 115.2 (Ph-C), 116.5 (CN), 118.1, 125.6, 126.6, 129.8, 142.5, 143.5 (Ph-C), 150.2 (pyrrole C-2), 150.7 (pyrazole C-3), 160.2 (Ph-C), 160.4 (pyrazole C-5), 160.8, 161.2 (2*C*O_2Me), 163.7 (pyrrole C-5); MS: *m/z* 547 $[M+H]^+$; high-resolution MS: Calcd for $C_{26}H_{23}N_6O_8$ 547.1577, Found 547.1583. Anal. Calcd for $C_{26}H_{22}N_6O_8 \cdot 0.2H_2O$: C, 56.77; H, 4.10; N, 15.28. Found: C, 56.73; H, 4.04; N, 15.24.

4-Cyano-4-[4,5-dihydro-3-methyl-1-(4-nitrophenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1-phenyl-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-diethyl ester (8f): Yellow needles (0.262 g, 48%), mp 162–164 ˚C (dec.) ($CHCl_3$/petroleum ether); IR (ATR): ν 3297 (NH), 2257 (CN), 1745, 1704, 1662 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ 0.96, 1.11 (t, J = 6.9 Hz, 3H, 2CO_2CH_2*Me*), 2.51 (s, 3H, pyrazole 3-Me), 4.04–4.14 (m, 4H, 2CO_2C*H*$_2$Me), 7.44–7.54 (m, 5H, Ph-H), 8.00–8.04 (m, 2H, Ph-H), 8.30–8.32 (m, 2H, Ph-H), 9.82 (br, 1H, NH), 11.94 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.7 (pyrazole 3-Me), 13.9, 14.4 (2CO_2CH_2*Me*), 45.0 (pyrrole C-4), 61.0, 63.0 (2CO_2*C*H_2Me), 98.3 (pyrazole C-4), 102.7 (pyrrole C-3), 116.6 (CN), 118.1, 125.6, 128.4, 129.8, 130.0, 134.5, 142.4, 143.6 (Ph-C), 149.9 (pyrrole C-2), 150.8 (pyrazole C-3), 159.9 (pyrazole C-5), 160.2, 160.8 (2*C*O_2CH_2Me), 163.0 (pyrrole C-5); MS: *m/z* 545 $[M+H]^+$; high-resolution MS: Calcd for $C_{27}H_{25}N_6O_7$ 545.1785, Found 545.1804. Anal. Calcd for $C_{27}H_{24}N_6O_7 \cdot 0.35H_2O$: C, 58.87; H, 4.52; N, 15.26. Found: C, 58.87; H, 4.43; N, 15.24.

4-Cyano-4-[4,5-dihydro-3-methyl-1-(4-nitrophenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1-(4-methylphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-diethyl ester (8g): Yellow needles (0.373 g, 67%), mp 185–186 ˚C (dec.) ($CHCl_3$/petroleum ether); IR (ATR): ν 3298, 3280 (NH), 2249 (CN), 1751, 1707, 1661 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ 1.00, 1.11 (t, J = 6.9 Hz, 6H, $2CO_2CH_2$*Me*), 2.32 (s, 3H, 4-*Me*-C_6H_4), 2.50 (s, 3H, pyrazole 3-Me), 4.03–4.13 (m, 4H, $2CO_2CH_2$Me), 7.29–7.33 (m, 4H, Ph-H), 8.00–8.04 (m, 2H, Ph-H), 8.31–8.34 (m, 2H, Ph-H), 9.81 (br, 1H, NH), 11.92 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.7 (pyrazole 3-Me), 14.0, 14.5 ($2CO_2CH_2$*Me*), 21.3 (4-*Me*-C_6H_4), 45.0 (pyrrole C-4), 61.0, 63.0 ($2CO_2CH_2$Me), 98.2 (pyrazole C-4), 102.5 (pyrrole C-3), 116.5 (CN), 118.1, 125.6, 128.2, 130.4, 131.7, 139.5, 142.4, 143.5 (Ph-C), 150.1 (pyrrole C-2), 150.8 (pyrazole C-3), 159.6 (pyrazole C-5), 160.2, 160.8 ($2CO_2CH_2$Me), 163.2 (pyrrole C-5); MS: *m/z* 559 $[M+H]^+$. Anal. Calcd for $C_{28}H_{26}N_6O_7$: C, 60.21; H, 4.69; N, 15.05. Found: C, 60.21; H, 4.69; N, 14.93.

4-Cyano-1-(4-ethylphenyl)-4-[4,5-dihydro-3-methyl-1-(4-nitrophenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-diethyl ester (8h): Yellow needles (0.386 g, 67%), mp 175–177 ˚C (dec.) ($CHCl_3$/petroleum ether); IR (ATR): ν 3293 (NH), 2251 (CN), 1755, 1711, 1660 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ 0.96, 1.11 (t, J = 6.9 Hz, 6H, $2CO_2CH_2$*Me*), 1.16 (t, J = 7.6 Hz, 3H, 4-*Me*CH_2-C_6H_4), 2.50 (s, 3H, pyrazole 3-Me), 2.62 (q, J = 7.6 Hz, 2H, 4-Me*C*H_2-C_6H_4), 4.03–4.13 (m, 4H, $2CO_2CH_2$Me), 7.32–7.36 (m, 4H, Ph-H), 7.98–8.04 (m, 2H, Ph-H), 8.31–8.33 (m, 2H, Ph-H), 9.80 (br, 1H, NH), 11.93 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.7 (pyrazole 3-Me), 13.9, 14.4 ($2CO_2CH_2$*Me*), 16.0 (4-*Me*CH_2-C_6H_4), 28.4 (4-Me*C*H_2-C_6H_4), 45.0 (pyrrole C-4), 61.0, 63.0 ($2CO_2CH_2$Me), 98.2 (pyrazole C-4), 102.6 (pyrrole C-3), 116.5 (CN), 118.1, 125.6, 128.3, 129.3, 132.0, 142.4, 143.6, 145.7 (Ph-C), 150.0 (pyrrole C-2), 150.8 (pyrazole C-3), 160.0 (pyrazole C-5), 160.2, 160.7 ($2CO_2CH_2$Me), 163.4 (pyrrole C-5); MS: *m/z* 573 $[M+H]^+$. Anal. Calcd for $C_{29}H_{28}N_6O_7$: C, 60.83; H, 4.93 N, 14.68. Found: C, 60.83; H, 4.91; N, 14.55.

4-Cyano-4-[4,5-dihydro-3-methyl-1-(4-nitrophenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1-(4-propylphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-diethyl ester (8i): Yellow needles (0.391 g, 67%), mp 179–181 ˚C (dec.) ($CHCl_3$/petroleum ether); IR (ATR): ν 3275 (NH), 2247 (CN), 1743, 1704, 1662 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ 0.85 (t, J = 7.6 Hz, 2H, 4-*Me*CH_2CH_2-C_6H_4), 0.94, 1.11 (t, J = 6.9 Hz, 6H, $2CO_2CH_2$*Me*), 1.57 (sext, J = 7.6 Hz, 2H, 4-Me*C*H_2CH_2-C_6H_4), 2.50 (s, 3H, pyrazole 3-Me), 2.56 (t, J = 7.6 Hz, 2H, 4-$MeCH_2C$*H*$_2$-C_6H_4), 4.03–4.13 (m, 4H, $2CO_2C$*H*$_2$Me), 7.30–7.36 (m, 4H, Ph-H), 7.99–8.02 (m, 2H, Ph-H), 8.30–8.34 (m, 2H, Ph-H), 9.78 (br, 1H, NH), 11.92 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.7 (pyrazole 3-Me), 13.9 (4-*Me*CH_2CH_2-C_6H_4), 14.0, 14.4 ($2CO_2CH_2$*Me*), 24.5 (4-Me*C*H_2CH_2-C_6H_4), 37.4 (4-$MeCH_2$*C*H_2-C_6H_4), 45.0 (pyrrole C-4), 61.0, 63.0 ($2CO_2CH_2$Me), 97.7 (pyrazole C-4), 102.5 (pyrrole C-3), 116.5 (CN), 118.1, 125.6, 128.2, 129.8, 131.9, 142.5, 143.5, 144.1

(Ph-C), 150.2 (pyrrole C-2), 150.8 (pyrazole C-3), 159.7 (pyrazole C-5), 160.2, 160.7 (2*C*O_2CH_2Me), 163.3 (pyrrole C-5); MS: *m/z* 587 $[M+H]^+$. Anal. Calcd for $C_{30}H_{30}N_6O_7$: C, 61.43; H, 5.15; N, 14.33. Found: C, 61.26; H, 5.16; N, 14.20.

4-Cyano-4-[4,5-dihydro-3-methyl-1-(4-nitrophenyl)-5-oxo-1*H*-pyrazol-4-yl]-4,5-dihydro-5-imino-1-(4-methoxyphenyl)-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-diethyl ester (8j): Yellow needles (0.389 g, 68%), mp 182–183 ˚C (dec.) ($CHCl_3$/MeOH); IR (ATR): ν 3291 (NH), 2249 (CN), 1753, 1710, 1659 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ 0.99, 1.11 (t, *J* = 6.9 Hz, 6H, 2CO_2CH_2*Me*), 2.50 (s, 3H, pyrazole 3-Me), 3.76 (s, 3H, 4-*Me*O-C_6H_4), 4.03–4.13 (m, 4H, 2CO_2CH_2Me), 7.02–7.04 (m, 2H, Ph-H), 7.37–7.41 (m, 2H, Ph-H), 7.99–8.02 (m, 2H, Ph-H), 8.27–8.31 (m, 2H, Ph-H), 9.77 (br, 1H, NH), 11.83 (br, 1H, OH); ^{13}C NMR (DMSO-d_6): δ 12.8 (pyrazole 3-Me), 14.0, 14.4 (2CO_2CH_2*Me*), 44.9 (pyrrole C-4), 56.0 (4-*Me*O-C_6H_4), 61.0, 63.0 (2CO_2*C*H_2Me), 98.0 (pyrazole C-4), 102.4 (pyrrole C-3), 115.2 (Ph-C), 116.5 (CN), 118.0, 125.6, 126.7, 130.0, 142.6, 143.5 (Ph-C), 150.2 (pyrrole C-2), 150.7 (pyrazole C-3), 160.2 (Ph-C), 160.3 (*C*O_2CH_2Me), 160.5 (pyrazole C-5), 160.8 (*C*O_2CH_2Me), 163.8 (pyrrole C-5); MS: *m/z* 575 $[M+H]^+$; high-resolution MS: Calcd for $C_{28}H_{27}N_6O_8$ 575.1890, Found 575.1893. Anal. Calcd for $C_{28}H_{26}N_6O_8 \cdot 0.5H_2O$: C, 57.63; H, 4.66; N, 14.40. Found: C, 57.67; H, 4.42; N, 14.33.

The preparation of diacetylated compound 10 from 6a and acetic anhydride. A mixture of **6a** (0.471 g, 1 mmol) and Ac_2O (2 mL) was stirred at 120 ˚C for 3 h. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel with $CHCl_3$ as the eluent to afford 4-[5-(acetyloxy)-3-methyl-1-phenyl-1*H*-pyrazol-4-yl]-5-(acetylimino)-4-cyano-4,5-dihydro-1-phenyl-1*H*-pyrrole-2,3-dicarboxylic acid 2,3-dimethyl ester (**10**): this compound was obtained as colorless prisms (0.389 g, 70%), mp 156–157 ˚C (dec.) (acetone/petroleum ether); IR (ATR): ν 2250 (CN), 1792, 1749, 1703, 1679 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ 1.70 (s, 3H, NCOMe), 2.25 (s, 3H, OCOMe), 2.38 (s, 3H, pyrazole 3-Me), 3.64, 3.68 (s, 6H, 2CO_2Me), 7.37–7.44 (m, 3H, Ph-H), 7.48–7.54 (m, 7H, Ph-H); ^{13}C NMR (DMSO-d_6): δ 13.8 (pyrazole 3-Me), 20.5 (OCO*Me*), 25.7 (NCO*Me*), 43.8 (pyrrole C-4), 53.0, 54.5 (2CO_2*Me*), 99.9 (pyrazole C-4), 106.1 (pyrrole C-3), 114.1 (CN), 122.7, 127.9, 128.7, 130.3, 130.5, 130.7, 133.4, 137.3 (Ph-C), 141.9 (pyrazole C-5), 146.9 (pyrazole C-3), 148.5 (pyrrole C-5), 151.9 (pyrrole C-2), 160.0, 160.2 (2*C*O_2Me), 167.7 (O*C*OMe), 180.2 (N*C*OMe); MS: *m/z* 556 $[M+H]^+$. Anal. Calcd for $C_{29}H_{25}N_5O_7$: C, 62.70; H, 4.54; N, 12.61. Found: C, 62.68; H, 4.62; N, 12.53.

ACKNOWLEDGEMENTS

The authors thank Hiroshi Hanazono for obtaining MS spectra and Junko Honda for her valuable help with elemental analyses.

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