A Divergent Synthesis of Dihydropyridazinones, *N*-Substituted Dihydropyrazoles, and *O*-Substituted Pyrazoles

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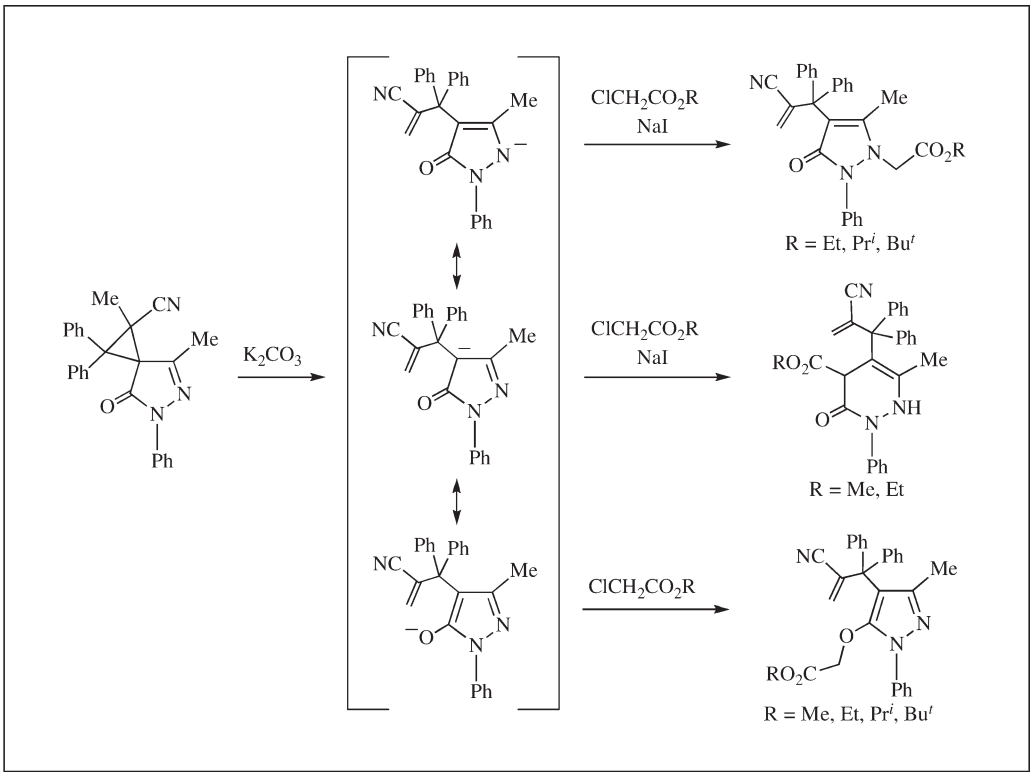


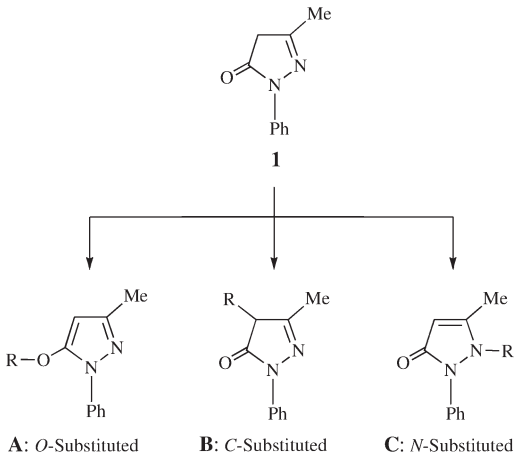
Dihydropyridazinones **4a**,**b**, *N*-substituted dihydropyrazoles **5b–d**, and *O*-substituted pyrazoles **6a–d** have been synthesized starting from spirocyclopropanepyrazole derivative **2**. Treatment of **2** with α-chloro esters, e.g., methyl chloroacetate, ethyl chloroacetate, isopropyl chloroacetate, and *tert*-butyl chloroacetate, in potassium carbonate/sodium iodide system caused ring opening and subsequent *C*- or *N*-attack nucleophilic substitution to give the corresponding dihydropyridazinones **4a**,**b** and *N*-substituted dihydropyrazoles **5b–d**. On the other hand, in the absence of sodium iodide, *O*-substituted pyrazoles **6a–d** were obtained from **2** *via* an *O*-attack nucleophilic substitution.

INTRODUCTION

The pyridazine nucleus and derived 3-oxo-derivatives, pyridazin-3(2*H*)-ones, are versatile pharmacophores in many biologically active molecules of contemporary interest [1–4]. For example, these molecules have been previously reported to be platelet aggregation inhibitor [5], α-adrenoceptor antagonists [6], and antisecretory/antiulcer agents [7]. In this context, the synthesis of pyridazin-3(2*H*)-ones continues to attract attention and provides an interesting challenge [8–11].

Pyrazole motif makes up the core structure of numerous biologically active compounds, including blockbuster drugs such as Celebrex [12] and Viagra [13], that find a wide range of applications in pharmaceutical [14–16]. Many synthetic methods for pyrazoles are available [17–23], among which notable methods involve the reactions between 1,3-difunctional compounds with hydrazines or their derivatives [24,25] and 1,3-dipolar cycloadditions of diazo compounds onto triple bonds [26–28]. Although the synthesis of functionalized pyrazoles such as *O*- and *C*-substituted pyrazoles (types A and B) starting from dihydropyrazole **1** has been reported [29–31], there are relatively few methods in the

Scheme 1



literature describing the selective preparation of *N*-substituted pyrazoles (type C) (Scheme 1). In connection with our current research interests in this area, we have reported the synthesis of *N*-acyl-1,2-dihydro-3*H*-pyrazol-3-ones through Lewis acid–mediated rearrangement of *O*-acyloxypyrazoles [32].

On the other hand, the utility of cyclopropane derivatives in organic synthesis has been recognized for their ready accessibility originating from the inherent ring strain that can lead to a variety of ring-opening reactions under the influence of a wide range of chemicals, for example, electrophiles, nucleophiles, and radicals [33–37]. In our recent work, we achieved the synthesis of spirocyclopropanepyrazoles, followed by the reaction of 4-arylidene-3*H*-pyrazol-3-one with α-chloro esters, e.g., methyl chloroacetate, ethyl chloroacetate, isopropyl chloroacetate, and *tert*-butyl chloroacetate [38]. More recently, we have also discussed the ring-opening reaction of spirocyclopropanepyrazoles in the presence of sodium hydride [39]. Thus, we hypothesized that if the *O*-, *C*-, or *N*-anion-containing intermediate could be produced readily from spirocyclopropanepyrazole derivative through a ring-opening reaction under appropriate reaction conditions, the synthesis of *O*-, *C*-, or *N*-substituted pyrazoles would then be possible.

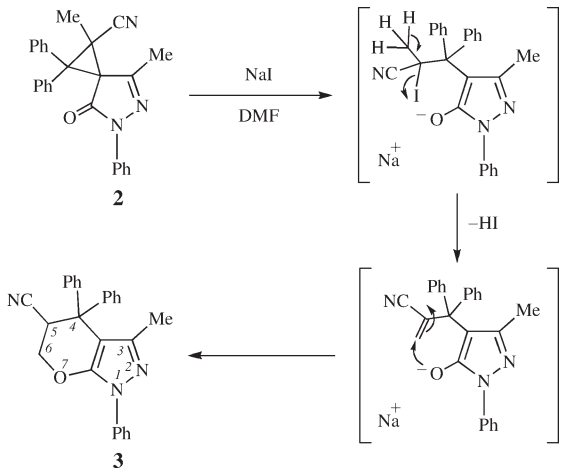
For these reasons, we focused our attention on the development of a new method for the preparation of substituted pyrazole derivatives; we now report our experimental results, a ring opening/nucleophilic substitution of spirocyclopropanepyrazole derivative with α-chloro esters in the presence of a base such as potassium carbonate.

RESULTS AND DISCUSSION

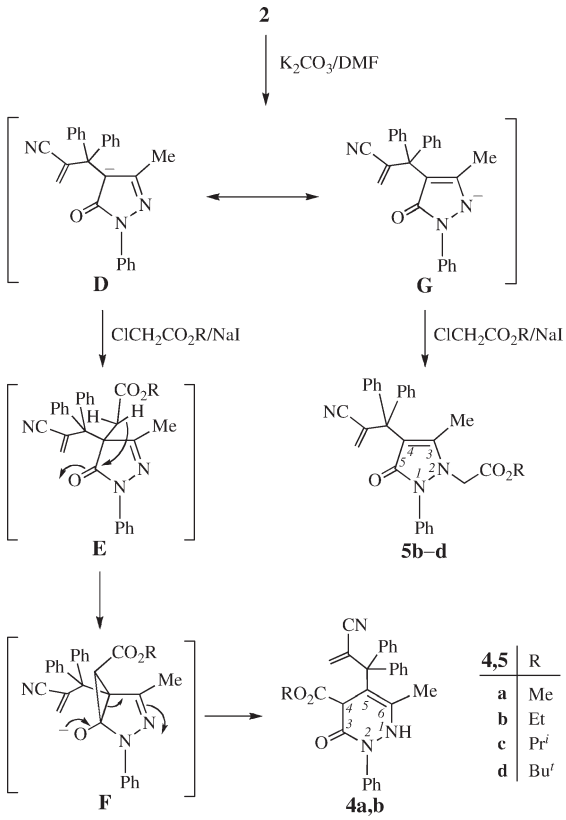
The starting material, spirocyclopropanepyrazole **2**, was prepared by treatment of 2,4-dihydro-5-methyl-2-phenyl-4-(diphenylmethylene)-3*H*-pyrazol-3-one and 2-chloropropionitrile according to our previous investigation [38]. In our initial studies, to check something about the reactivity of spirocyclopropanepyrazole **2**, we examined a sodium iodide–promoted ring transformation of **2**. Fortunately, we found the reaction condition under which pyrano[2,3-*c*]pyrazole derivative **3** could be isolated. Indeed, thermal treatment of **2** with sodium iodide in *N*,*N*-dimethylformamide caused a ring opening/recyclization to give the fused pyrazole derivative **3** in 78% yield (Scheme 2). The structure of **3** was confirmed by elemental analysis and spectroscopic data (^{1}H NMR, ^{13}C NMR, and mass). This result suggests that a ring-opening reaction of spirocyclopropanepyrazole **2** easily occurs in the presence of nucleophiles and then the intermediate anion would be produced. Moreover, in our previous article [39], we have shown that the ring-opening reaction of spirocyclopropanepyrazole derivatives with sodium hydride provided the corresponding ring-opened products.

With these results in hand, we next investigated a divergent method for the synthesis of pyrazole derivatives from spirocyclopropanepyrazole **2** in detail. When a mixture of **2**, methyl chloroacetate, and sodium iodide in the presence of potassium carbonate in *N*,*N*-dimethylformamide was stirred at 120°C for 1 h, the dihydropyridazinone **4a** was obtained in 38% yield as the only isolated product (Scheme 3 and entry 1 in Table 1). While, the reaction with isopropyl and/or *tert*-butyl chloroacetate afforded the corresponding *N*-substituted dihydropyrazoles **5c**,**d** in 62 and 45% yields, respectively (entries 3 and 4). In the case of ethyl chloroacetate, the reaction gave the *N*-substituted dihydropyrazole **5b** (38%) together with the dihydropyridazinone **4b** (15%) as minor product (entry 2). These products **4a**,**b** and **5b**–**d** gave satisfactory spectroscopic data consistent with their assigned structures (see Experimental section).

Scheme 2



Scheme 3



The IR spectra of **4a**,**b** display bands near 3230 cm^{-1} due to a secondary amino group near 2220 cm^{-1} due to a conjugated cyano group and in the range of 1605−1745 cm^{-1} due to two carbonyl groups, whereas those of **5b–d** show bands near 2225 cm^{-1} due to a conjugated cyano group and in the range of 1610−1750 cm^{-1} due to two carbonyl groups. The ^1H NMR spectra of **4a**,**b** in deuteriochloroform exhibit a one-proton singlet near δ 5.25 assignable to the 4-methine proton, a D_2O exchangeable signal near δ 5.3 attributable to the secondary amino proton, and two one-proton singlets near δ 6.0 due to the two olefin protons, whereas those of **5b–d** show a two-proton singlet near δ 4.3 due to the methylene protons and two one-proton singlets near δ 6.0 due to the two olefin protons. The ^{13}C NMR spectra of **4a**,**b** show a signal near δ 70 due to the 4-methine carbon and two signals near δ 162 and 172 due to the two carbonyl carbons, whereas those of **5b–d** show a signal near δ 48 due to the methylene carbon and two signals near δ 165 due to the two carbonyl carbons.

The reason for this change of behavior is not very clear at present. One explanation could rely on the fact that isopropyl and *tert*-butyl groups are well known as bulky substituents. When the substituent is a large group, such as isopropyl and *tert*-butyl groups, *N*-attack nucleophilic substitution is preferred, whereas *C*-attack nucleophilic substitution is preferred when the substituent is a relatively smaller group, such as methyl and ethyl. Therefore, it is proposed that a ring-opening reaction of **2** probably causes in the presence of potassium carbonate to give the intermediate *C*-anion **D**, which undergoes *C*-attack nucleophilic substitution to afford *C*-adduct **E**. Intramolecular nucleophilic addition of activated methylene group of **E** to carbonyl group readily occurs and then the fused pyrazole **F** would be produced. Thus, the dihydropyridazinones **4a**,**b** could be formed *via* a ring expansion of **F**. While in the reaction of isopropyl and/or *tert*-butyl chloroacetate, an isomerization of **D** to the intermediate *N*-anion **G** easily occurs, depending in a large part on the steric effects of the substituent on the ester group, and then *N*-substituted dihydropyrazoles **5b–d** would be produced from **G** through an *N*-attack nucleophilic substitution.

Furthermore, we found the reaction condition under which the *O*-substituted pyrazoles **6a–d** could be isolated. Thermal treatment of **2** with α-chloro esters in the presence of potassium carbonate, without sodium iodide, gave the corresponding *O*-substituted pyrazoles **6a–d** and *N*-substituted dihydropyrazoles **7a–d** (Scheme 4 and Table 2). Interestingly, in this reaction, the dihydropyridazinone derivative such as **4a**,**b** was not detected at all. The IR spectra of **6a–d** display bands near 2220 cm^{-1} due to a conjugated cyano group and in the range of 1745−1768 cm^{-1} due to a carbonyl group. The ^1H NMR spectra of **6a–d** in deuteriochloroform exhibit a two-proton singlet near δ 3.7 due to the methylene protons and two one-proton singlets near δ 6.0 due to the two olefin protons. The ^{13}C NMR spectra of **6a–d** show a signal near δ 70 due to the methylene carbon and a signal near δ 166 due to the ester carbonyl carbon. In addition, mass spectra and elemental analyses of the *N*-substituted pyrazole **5b** and *O*-substituted pyrazole **6b** point to the same molecular ion and elemental composition $C_{30}H_{27}N_3O_3$. By comparison of the NMR, mass spectra and elemental analyses of **5b–d** and **6a–d**, it seems that the structural assignments given to these compounds are correct (see Experimental section).

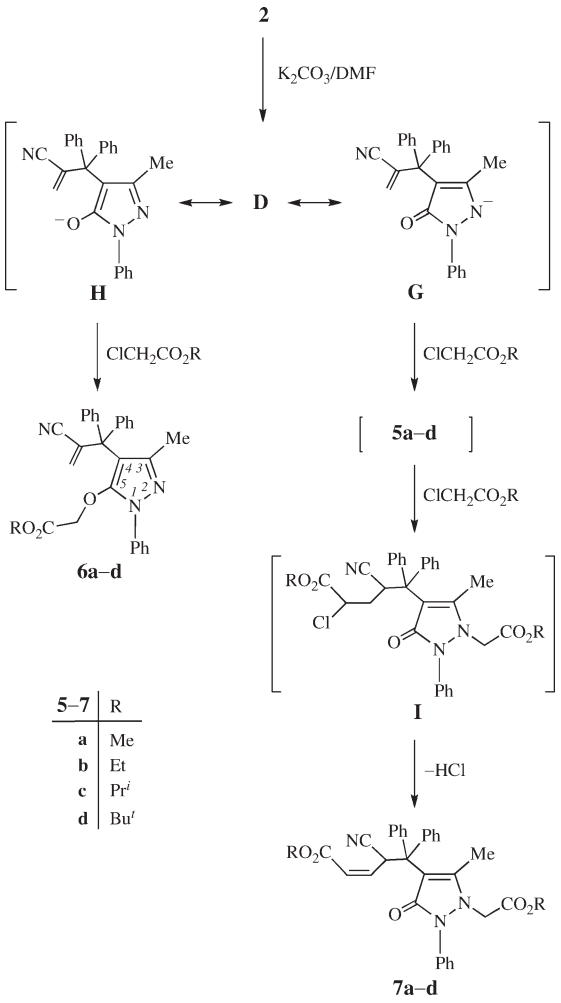
The formation of **6a–d** and **7a–d** could be explained by possible mechanism presented in Scheme 4. Thus, the reaction of spiro compound **2** with potassium

Table 1

Synthesis of **4a**,**b** and **5b–d** according to Scheme 3.

Entry	R	Products	Yields (%)
1	Me	**4a**	38
2	Et	**4b/5b**	15/38
3	Pr^i	**5c**	62
4	Bu^t	**5d**	59

Scheme 4



carbonate probably causes the ring opening of cyclopropane to give the intermediate *C*-anion **D**, which was followed by an isomerization to produce the *O*-anion **H** or *N*-anion **G** in the absence of sodium iodide, respectively. The *O*-anion **H** could then undergo an *O*-attack nucleophilic addition to afford the *O*-substituted pyrazoles **6a–d**. In the case of the *N*-anion **G**, an *N*-attack nucleophilic addition probably occurs and then could provide **5a–d**, which were followed by a Michael addition of activated methylene group of α-chloro esters to α,β-unsaturated nitrile of **5a–d**, giving the chlorine-containing compound **I**. Compounds **7a–d** would then be formed easily from **I** through an elimination of hydrogen chloride. On the basis of all of the above results, it make us believe that compared with a nitrogen atom, the relatively lower nucleophilicity of the oxygen atom made the transformation from **5** to **7** proceeded more efficiently in the absence of sodium iodide.

To confirm the structure of the dihydropyridazinone derivatives **4a**,**b**, we carried out the acetylation of **4a**,**b**.

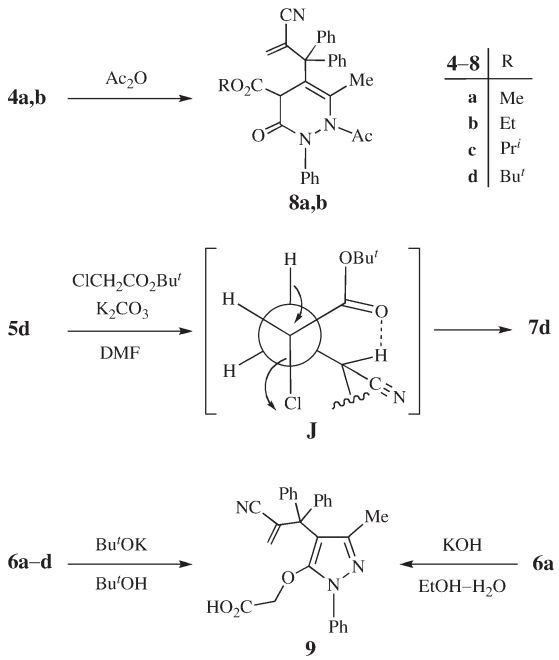
Table 2

Synthesis of **6a–d** and **7a–d** according to Scheme 4.

Entry	R	Products	Yields (%)
1	Me	**6a/7a**	42/38
2	Et	**6b/7b**	36/34
3	Pr^i	**6c/7c**	43/28
4	Bu^t	**6d/7d**	36/41

Thus, thermal treatment of **4a**,**b** with acetic anhydride in pyridine afforded the *N*-acetylated dihydropyridazinones **8a**,**b** (55, 35%), which were characterized by ^{1}H NMR, ^{13}C NMR, mass, IR, and elemental analyses (Scheme 5). Furthermore, to understand better the formation of **7d**, compound **5d** was reacted with *tert*-butyl chloroacetate in the presence of potassium carbonate to produce the corresponding *N*-substituted dihydropyrazole **7d** (72%), which was confirmed by direct comparison with an authentic sample prepared from **2** and *tert*-butyl chloroacetate as described above. In this reaction, the activated methylene group of *tert*-butyl chloroacetate could nucleophilically attack the α,β-unsaturated nitrile of **5d** to result in the formation of the intermediate Michael adduct **J**. The chlorine-containing compound **J** may be favored due to the hydrogen bond formed between hydrogen of methine proton and oxygen of ester carbonyl group. Thus, compound **7d** would then be formed easily from **J** *via* an elimination of hydrogen chloride. In deuteriochloroform, the NMR spectra indicate that compound **7d** existed as a geometrical single

Scheme 5



isomer of *Z* configuration. In addition, for product **7d**, a clear nuclear Overhauser effect was observed between two olefin protons of *Z* configuration.

Finally, on the basis of these results, we examined the conversion of the *O*-substituted pyrazoles **6a–d** into the fused pyrazole derivatives in the presence of a base. Although, we carried out several experiments on **6a–d**, testing different reaction conditions, e.g., time, solvent, and substrate/base molar ratio, those attempts were unacceptable with respect to yield. Contrary to our expectation, when **6a–d** were treated with potassium *tert*-butoxide in *tert*-butyl alcohol to result in the formation of the carboxylic acid **9** (41% from **6a**, 29% from **6b**, 26% from **6c**, and 48% from **6d**). To confirm the structure of **9**, we carried out the hydrolysis of compound **6a**. Thus, thermal treatment of **6a** with potassium hydroxide in aqueous ethanol afforded the carboxylic acid **9** in 56% yield. The melting point and IR spectrum of this compound coincided with those of samples prepared from **6a–d** in a potassium *tert*-butoxide/*tert*-butyl alcohol condition.

In conclusion, we have developed a novel method for the construction of dihydropyridazinones **4a**,**b**, *N*-substituted dihydropyrazoles **5b–d**, and *O*-substituted pyrazoles **6a**−**d**, proceeding by a ring opening and *C*-, *N*-, or *O*-attack nucleophilic substitution when spirocyclopropanepyrazole **2** are treated with α-chloro esters and potassium carbonate, with or without sodium iodide. Functionalized pyrazole derivatives are important synthons in organic synthesis and for the preparation of biologically active compounds with interest in medicinal chemistry. Further synthetic applications for pyridazine and pyrazole derivatives are in progress.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-A500 spectrometer at 500 and 125 MHz, respectively. The ^{1}H and ^{13}C chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane as internal standard. The positive FAB mass spectra were obtained on a JEOL JMS-700T spectrometer. The elemental analyses were performed on a YANACO MT-6 CHN analyzer.

The preparation of fused pyrazole 3 from 2 and sodium iodide. A mixture of **2** [38] (0.782 g, 2 mmol) and sodium iodide (0.600 g, 4 mmol) in *N*,*N*-dimethylformamide (5 mL) was stirred at 140°C for 1 h. After removal of the solvent *in vacuo*, cold water was added to the residue. The resulting mixture was extracted with chloroform (60 mL). The extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with chloroform as the eluent to give 3-methyl-1,4,4-triphenyl-1,4,5,6-tetrahydropyrano[2,3-*c*]pyrazole-5-carbonitrile (**3**). This compound was obtained as colorless prisms (0.607 g, 78%), mp 185−187°C (acetone-petroleum ether); IR (potassium bromide): ν 2242 cm^{-1} (CN); ^{1}H NMR (deuteriochloroform): δ 1.60 (s, 3H, 3-Me), 4.02 (dd, J = 2.4, 7.6 Hz, 1H, 5-H), 4.29 (dd, J = 7.6, 11.0 Hz, 1H, 6-H), 4.37 (dd, J = 2.4, 11.0 Hz, 1H, 6-H), 7.24–7.26 (m, 1H, Ph-H), 7.31–7.49 (m, 12H, Ph-H), 7.76–7.78 ppm (m, 2H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 14.2 (3-Me), 39.7 (C-5), 50.1 (C-4), 66.9 (C-6), 101.5 (C-3a), 117.5 (CN), 120.5, 126.0, 127.8, 128.1, 128.3, 128.7, 128.8, 129.0, 130.1, 138.2, 139.6, 141.3, (Ph-C), 147.5 (C-3), 148.3 ppm (C-7a); ms: *m*/*z* 392 [M + H]$^+$. Anal. Calcd. for $C_{26}H_{21}N_3O$: C, 79.77; H, 5.41; N, 10.73. Found: C, 79.77; H, 5.64; N, 10.61.

General procedure for the preparation of dihydropyridazinones 4a,b and *N*-substituted dihydropyrazoles 5b–d from 2 and α-chloro esters in the presence of sodium iodide and potassium carbonate. A mixture of **2** (0.391 g, 1 mmol), methyl chloroacatate (0.326 g, 3 mmol), ethyl chloroacatate (0.368 g, 3 mmol), isopropyl chloroacatate (0.410 g, 3 mmol) or *tert*-butyl chloroacatate (0.452 g, 3 mmol), sodium iodide (0.450 g, 3 mmol), and potassium carbonate (0.276 g, 2 mmol) in *N*,*N*-dimethylformamide (5 mL) was stirred at 120°C for 1 h. After removal of the solvent *in vacuo*, a saturated aqueous sodium thiosulfate solution (30 mL) was added to the residue with stirring and ice cooling. The resulting mixture was extracted with chloroform (60 mL). The extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with chloroform as the eluent and recrystallization from an appropriate solvent (a fractional recrystallization) to afford **4a**,**b** and **5b–d**.

1,2,3,4-Tetrahydro-6-methyl-3-oxo-2-phenyl-5-(α-methylene-β,β-diphenylpropanenitril-3-yl)-4-pyridazinecarboxylic acid methyl ester (4a). This compound was obtained as colorless needles (0.176 g, 38%), mp 216−217°C (chloroform-petroleum ether); IR (potassium bromide): ν 3232 (NH), 2220 (CN), 1742, 1613 cm^{-1} (C=O); ^{1}H NMR (deuteriochloroform): δ 1.56 (s, 3H, 6-Me), 3.92 (s, 3H, CO_2Me), 5.31 (s, 1H, 4-H), 5.33 (br. s, 1H, NH), 5.70 (s, 1H, olefin H), 5.85 (s, 1H, olefin H), 7.17–7.45 (m, 13H, Ph-H), 7.62–7.64 ppm (m, 2H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 21.3 (6-Me), 53.6 (CO_2*Me*), 58.9 [Ph_2*C*-C(CN)=CH_2], 69.8 (C-4), 109.7 (C-5), 119.8 (CN), 126.46, 126.49, 126.6, 126.7 (Ph-C), 127.5 [Ph_2C-C(CN)=*C*H_2], 127.85, 127.91, 128.2, 129.0, 129.3, 129.6, 130.0 (Ph-C), 132.2 [Ph_2C-*C*(CN)=CH_2], 141.0, 141.3, 143.1 (Ph-C), 155.2 (C-6), 162.1 (C-3), 172.3 ppm (C=O); ms: *m*/*z* 464 [M + H]$^+$. Anal. Calcd. for $C_{29}H_{25}N_3O_3 \cdot 0.15H_2O$: C, 74.71; H, 5.47; N, 9.01. Found: C, 74.72; H, 5.53; N, 8.91.

1,2,3,4-Tetrahydro-6-methyl-3-oxo-2-phenyl-5-(α-methylene-β,β-diphenylpropanenitril-3-yl)-4-pyridazinecarboxylic acid ethyl ester (4b). This compound was obtained as colorless needles (0.072 g, 15%), mp 215–216°C (chloroform-petroleum ether); IR (potassium bromide): ν 3275 (NH), 2226 (CN), 1733, 1609 cm^{-1} (C=O); ^{1}H NMR (deuteriochloroform): δ 1.37 (t, J = 7.0 Hz, 3H, CO_2CH_2*Me*), 1.54 (s, 3H, 6-Me), 4.32–4.41 (m, 2H, CO_2*C*H_2Me), 5.27 (s, 1H, 4-H), 5.33 (br. s, 1H, NH), 5.74 (s, 1H, olefin H), 5.89 (s, 1H, olefin H), 7.15–7.29 (m, 7H, Ph-H), 7.34–7.44 (m, 6H, Ph-H), 7.58–7.60 ppm (m, 2H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 14.1 (CO_2CH_2*Me*), 21.4 (6-Me), 58.9 [Ph_2*C*-C(CN)=CH_2], 63.1 (CO_2*C*H_2Me), 69.8 (C-4), 109.5 (C-5), 119.9 (CN), 126.39, 126.40, 126.6, 126.9, 127.8, 127.9 (Ph-C), 128.3 [Ph_2C-C(CN)=*C*H_2], 129.0, 129.36, 129.4, 130.0 (Ph-C), 131.7

[Ph_2C-*C*(CN)=CH_2], 141.2, 141.7, 143.5 (Ph-C), 155.2 (C-6), 162.1 (C-3), 171.6 ppm (C=O); ms: *m/z* 478 $[M + H]^+$. Anal. Calcd. for $C_{30}H_{27}N_3O_3 \cdot 0.2H_2O$: C, 74.89; H, 5.74; N, 8.73. Found: C, 74.74; H, 5.57; N, 8.94.

3-Methyl-4-(α-methylene-β,β-diphenylpropanenitril-3-yl)-5-oxo-1-phenyl-3-pyrazoline-2-acetic acid ethyl ester (5b). This compound was obtained as colorless prisms (0.181 g, 38%), mp 157–159°C (chloroform-petroleum ether); IR (potassium bromide): ν 2228 (CN), 1748, 1646 cm^{-1} (C=O); ^1H NMR (deuteriochloroform): δ 1.24 (t, *J* = 7.0 Hz, 3H, CO_2CH_2*Me*), 1.68 (s, 3H, pyrazoline 3-Me), 4.18 (q, *J* = 7.0 Hz, 2H, CO_2CH_2Me), 4.23 (s, 2H, NCH_2), 6.00 (s, 1H, olefin H), 6.11 (s, 1H, olefin H), 7.20–7.46 ppm (m, 15H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 13.8 (pyrazoline 3-Me), 14.2 (CO_2CH_2*Me*), 48.3 (NCH_2), 57.1 [Ph_2C-C(CN)=CH_2], 61.9 (CO_2CH_2Me), 112.1 (pyrazoline C-4), 119.4 (CN), 124.7, 126.9, 127.1 (Ph-C), 127.5 [Ph_2C-*C*(CN)=CH_2], 128.2, 129.3, 129.4 (Ph-C), 131.3 [Ph_2C-C(CN)=*C*H_2], 134.7, 141.4 (Ph-C), 154.8 (pyrazoline C-3), 164.7 (pyrazoline C-5), 166.5 ppm (C=O); ms: *m/z* 478 $[M + H]^+$. Anal. Calcd. for $C_{30}H_{27}N_3O_3$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.41; H, 5.75; N, 8.64.

3-Methyl-4-(α-methylene-β,β-diphenylpropanenitril-3-yl)-5-oxo-1-phenyl-3-pyrazoline-2-acetic acid isopropyl ester (5c). This compound was obtained as colorless prisms (0.305 g, 62%), mp 169–171°C (chloroform-petroleum ether); IR (potassium bromide): ν 2221 (CN), 1737, 1612 cm^{-1} (C=O); ^1H NMR (dimethyl sulfoxide-d_6): δ 1.16 (d, *J* = 6.4 Hz, 6H, CO_2CHMe_2), 1.66 (s, 3H, pyrazoline 3-Me), 4.41 (s, 2H, NCH_2), 4.94 (sep, *J* = 6.4 Hz, 1H, CO_2CHMe$_2$), 5.82 (s, 1H, olefin H), 6.16 (s, 1H, olefin H), 7.24–7.29 (m, 4H, Ph-H), 7.34–7.39 (m, 9H, Ph-H), 7.47–7.50 ppm (m, 2H, Ph-H); ^{13}C NMR (dimethyl sulfoxide-d_6): δ 13.3 (pyrazoline 3-Me), 21.3 (CO_2CHMe_2), 48.1 (NCH_2), 56.4 [Ph_2C-C(CN)=CH_2], 68.9 (CO_2CHMe$_2$), 109.9 (pyrazoline C-4), 119.1 (CN), 124.5, 125.9, 126.8, 126.9, 127.9 (Ph-C), 128.1 [Ph_2C-*C*(CN)=CH_2], 129.0, 129.1 (Ph-C), 130.5 [Ph_2C-C(CN)=*C*H_2], 134.6, 141.1 (Ph-C), 154.6 (pyrazoline C-3), 164.0 (pyrazoline C-5), 166.3 ppm (C=O); ms: *m/z* 492 $[M + H]^+$. Anal. Calcd. for $C_{31}H_{29}N_3O_3 \cdot 0.2H_2O$: C, 75.19; H, 5.98; N, 8.49. Found: C, 75.23; H, 5.99; N, 8.41.

3-Methyl-4-(α-methylene-β,β-diphenylpropanenitril-3-yl)-5-oxo-1-phenyl-3-pyrazoline-2-acetic acid tert-butyl ester (5d). This compound was obtained as colorless prisms (0.298 g, 59%), mp 171–173°C (chloroform-petroleum ether); IR (potassium bromide): ν 2226 (CN), 1746, 1664 cm^{-1} (C=O); ^1H NMR (dimethyl sulfoxide-d_6): δ 1.37 (s, 9H, CO_2CMe_3), 1.63 (s, 3H, pyrazoline 3-Me), 4.33 (s, 2H, NCH_2), 5.81 (s, 1H, olefin H), 6.16 (s, 1H, olefin H), 7.25–7.29 (m, 4H, Ph-H), 7.34–7.38 (m, 9H, Ph-H), 7.47–7.50 ppm (m, 2H, Ph-H); ^{13}C NMR (dimethyl sulfoxide-d_6): δ 13.2 (pyrazoline 3-Me), 27.5 (CO_2CMe_3), 48.7 (NCH_2), 56.5 [Ph_2C-C(CN)=CH_2], 82.1 (CO_2CMe_3), 109.7 (pyrazoline C-4), 119.1 (CN), 124.5, 126.8, 126.9, 127.9 (Ph-C), 128.1 [Ph_2C-*C*(CN)=CH_2], 129.1 (Ph-C), 130.6 [Ph_2C-C(CN)=*C*H_2], 134.7, 141.1 (Ph-C), 154.3 (pyrazoline C-3), 163.9 (pyrazoline C-5), 165.9 ppm (C=O); ms: *m/z* 506 $[M + H]^+$. Anal. Calcd. for $C_{32}H_{31}N_3O_3$: C, 76.02; H, 6.18; N, 8.31. Found: C, 76.06; H, 6.22; N, 8.20.

General procedure for the preparation of *O*-substituted pyrazoles 6a–d and *N*-substituted dihydropyrazoles 7a–d from 2 and α-chloro esters in the presence of potassium carbonate. A mixture of **2** (0.391 g, 1 mmol), methyl chloroacatate (0.326 g, 3 mmol), ethyl chloroacatate (0.368 g, 3 mmol), isopropyl chloroacatate (0.410 g, 3 mmol) or *tert*-butyl chloroacatate (0.452 g, 3 mmol), and potassium carbonate (0.276 g, 2 mmol) in *N*,*N*-dimethylformamide (5 mL) was stirred at 120°C for 1 h. After removal of the solvent *in vacuo*, cold water was added to the residue. The resulting mixture was extracted with chloroform (60 mL). The extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with chloroform as the eluent to yield **6a–d**. Further the elution gave **7a–d**.

{[3-Methyl-4-(α-methylene-β,β-diphenylpropanenitril-3-yl)-1-phenyl-1H-pyrazol-5-yl]oxy}acetic acid methyl ester (6a). This compound was obtained as colorless prisms (0.195 g, 42%), mp 126–128°C (chloroform-petroleum ether); IR (potassium bromide): ν 2224 (CN), 1762 cm^{-1} (C=O); ^1H NMR (deuteriochloroform): δ 1.72 (s, 3H, pyrazole 3-Me), 3.55 (s, 3H, CO_2Me), 3.72 (s, 2H, OCH_2), 5.96 (s, 1H, olefin H), 6.27 (s, 1H, olefin H), 7.27–7.43 (m, 13H, Ph-H), 7.69–7.71 ppm (m, 2H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 15.8 (pyrazole 3-Me), 51.8 (CO_2Me), 56.9 [Ph_2C-C(CN)=CH_2], 69.7 (OCH_2), 108.2 (pyrazole C-4), 119.4 (CN), 122.9, 127.3, 127.4, 128.1 (Ph-C), 129.1 [Ph_2C-*C*(CN)=CH_2], 129.2, 130.0 (Ph-C), 131.9 [Ph_2C-C(CN)=*C*H_2], 138.2, 140.8 (Ph-C), 148.7 (pyrazole C-3), 149.3 (pyrazole C-5), 167.1 ppm (C=O); ms: *m/z* 464 $[M + H]^+$. Anal. Calcd. for $C_{29}H_{25}N_3O_3$: C, 75.14; H, 5.44; N, 9.07. Found: C, 74.93; H, 5.49; N, 9.06.

{[3-Methyl-4-(α-methylene-β,β-diphenylpropanenitril-3-yl)-1-phenyl-1H-pyrazol-5-yl]oxy}acetic acid ethyl ester (6b). This compound was obtained as colorless prisms (0.172 g, 36%), mp 120–122°C (chloroform-petroleum ether); IR (potassium bromide): ν 2219 (CN), 1768 cm^{-1} (C=O); ^1H NMR (deuteriochloroform): δ 1.15 (t, *J* = 7.3 Hz, 3H, CO_2CH_2*Me*), 1.71 (s, 3H, pyrazole 3-Me), 3.70 (s, 2H, OCH_2), 4.03 (q, *J* = 7.3 Hz, 2H, CO_2CH_2Me), 5.96 (s, 1H, olefin H), 6.27 (s, 1H, olefin H), 7.27–7.42 (m, 13H, Ph-H), 7.70–7.72 ppm (m, 2H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 14.0 (CO_2CH_2Me), 15.8 (pyrazole 3-Me), 56.9 [Ph_2C-C(CN)=CH_2], 61.0 (CO_2CH_2Me), 69.8 (OCH_2), 108.3 (pyrazole C-4), 119.4 (CN), 122.8, 127.2, 127.4, 128.1 (Ph-C), 129.1 [Ph_2C-*C*(CN)=CH_2], 129.2, 130.0 (Ph-C), 131.8 [Ph_2C-C(CN)=*C*H_2], 138.1, 140.7 (Ph-C), 148.7 (pyrazole C-3), 149.3 (pyrazole C-5), 166.6 ppm (C=O); ms: *m/z* 478 $[M + H]^+$. Anal. Calcd. for $C_{30}H_{27}N_3O_3$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.55; H, 5.78; N, 8.83.

{[3-Methyl-4-(α-methylene-β,β-diphenylpropanenitril-3-yl)-1-phenyl-1H-pyrazol-5-yl]oxy}acetic acid isopropyl ester (6c). This compound was obtained as colorless needles (0.212 g, 43%), mp 124–126°C (chloroform-petroleum ether); IR (potassium bromide): ν 2223 (CN), 1756, 1740 cm^{-1} (C=O); ^1H NMR (deuteriochloroform) δ 1.14 (d, *J* = 6.4 Hz, 6H, CO_2CHMe_2), 1.72 (s, 3H, pyrazole 3-Me), 3.66 (s, 2H, OCH_2), 4.92 (sep, *J* = 6.4 Hz, 1H, CO_2CHMe$_2$), 5.96 (s, 1H, olefin H), 6.27 (s, 1H, olefin H), 7.25–7.43 (m, 13H, Ph-H), 7.72–7.73 ppm (m, 2H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 15.8 (pyrazole 3-Me), 21.6 (CO_2CHMe_2), 56.9 [Ph_2C-C(CN)=CH_2], 68.8 (CO_2CHMe$_2$), 69.8 (OCH_2), 108.3 (pyrazole C-4), 119.4 (CN), 122.6, 127.1, 127.4, 128.1 (Ph-C), 129.1 [Ph_2C-*C*(CN)=CH_2], 129.2, 130.0 (Ph-C), 131.8 [Ph_2C-C(CN)=*C*H_2], 138.2, 140.8 (Ph-C), 148.7 (pyrazole C-3), 149.2 (pyrazole C-5), 166.1 ppm (C=O); ms: *m/z* 492 $[M + H]^+$. Anal. Calcd. for $C_{31}H_{29}N_3O_3$: C, 75.74; H, 5.95; N, 8.55. Found: C, 75.84; H, 6.03; N, 8.54.

{[3-Methyl-4-(α-methylene-β,β-diphenylpropanenitril-3-yl)-1-phenyl-1H-pyrazol-5-yl]oxy}acetic acid tert-butyl ester (6d). This compound was obtained as colorless needles (0.182 g, 36%), mp 161–163°C (chloroform-petroleum ether); IR (potassium bromide): ν 2231 (CN), 1748 cm^{-1} (C=O); ^1H NMR (deuteriochloroform): δ 1.35 (s, 9H, CO_2CMe_3), 1.71 (s, 3H, pyrazole 3-Me), 3.60 (s, 2H, OCH_2), 5.96 (s, 1H, olefin H), 6.26 (s, 1H, olefin H), 7.25–7.43 (m, 13H, Ph-H), 7.72–7.74 ppm (m, 2H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 15.8 (pyrazole 3-Me), 27.9 (CO_2CMe_3), 56.9 [Ph_2C-C(CN)=CH_2], 67.0 (OCH_2), 82.0 (CO_2CMe_3), 108.4 (pyrazole C-4), 119.4 (CN), 122.6, 127.1, 127.4, 128.1 (Ph-C), 129.18 [Ph_2C-C(CN)=CH_2], 129.21, 130.0 (Ph-C), 131.7 [Ph_2C-C(CN)=CH_2], 138.2, 140.7 (Ph-C), 148.6 (pyrazole C-3), 149.3 (pyrazole C-5), 165.6 ppm (C=O); ms: *m/z* 506 $[M + H]^+$. Anal. Calcd. for $C_{32}H_{31}N_3O_3$: C, 76.02; H, 6.18; N, 8.31. Found: C, 76.06; H, 6.24; N, 8.29.

(Z)-4-Cyano-5-[3-methyl-2-(methoxycarbonylmethylene)-5-oxo-1-phenyl-3-pyrazolin-4-yl]-5,5-diphenyl-2-pentenoic acid methyl ester (7a). This compound was obtained as colorless needles (0.203 g, 38%), mp 209–210°C (acetone-petroleum ether); IR (potassium bromide): ν 2224 (CN), 1750, 1736, 1639 cm^{-1} (C=O); ^1H NMR (deuteriochloroform): δ 1.58 (s, 3H, pyrazoline 3-Me), 3.67, 3.89 (s, 6H, 2 × CO_2Me), 4.01 (d, J = 18.0 Hz, 1H, NCH_2), 4.35 (d, J = 18.0 Hz, 1H, NCH_2), 5.41 (s, 1H, methine H), 5.57 (s, 1H, olefin H), 5.80 (s, 1H, olefin H), 7.17–7.45 (m, 11H, Ph-H), 7.50–7.52 (m, 2H, Ph-H), 7.69–7.70 ppm (m, 2H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 19.3 (pyrazoline 3-Me), 51.6 (NCH_2), 52.6, 53.7 (2 × CO_2Me), 59.6 [Ph_2C-CH(CN)], 76.0 (methine C), 112.5 (pyrazoline C-4), 119.7 (CN), 126.5, 126.6 (olefin C), 126.7, 127.9, 129.1, 129.8, 130.4, 133.3, 140.6, 141.0, 143.4 (Ph-C), 154.7 (pyrazoline C-3), 161.8 (pyrazoline C-5), 168.9, 171.2 ppm (C=O); ms: *m/z* 536 $[M + H]^+$. Anal. Calcd. for $C_{32}H_{29}N_3O_5$: C, 71.76; H, 5.46; N, 7.85. Found: C, 71.75; H, 5.65; N, 7.73.

(Z)-4-Cyano-5-[2-(ethoxycarbonylmethylene)-3-methyl-5-oxo-1-phenyl-3-pyrazolin-4-yl]-5,5-diphenyl-2-pentenoic acid ethyl ester (7b). This compound was obtained as colorless needles (0.192 g, 34%), mp 124–126°C (chloroform-petroleum ether); IR (potassium bromide): ν 2224 (CN), 1743, 1638 cm^{-1} (C=O); ^1H NMR (deuteriochloroform): δ 1.15, 1.34 (t, J = 7.3 Hz, 6H, 2 × CO_2CH_2Me), 1.59 (s, 3H, pyrazoline 3-Me), 3.99 (d, J = 18.0 Hz, 1H, NCH_2), 4.13 (q, J = 7.3 Hz, 2H, CO_2CH_2Me), 4.36 (d, J = 18.0 Hz, 1H, NCH_2), 4.32–4.38 (m, 2H, CO_2CH_2Me), 5.39 (s, 1H, methine H), 5.62 (s, 1H, olefin H), 5.83 (s, 1H, olefin H), 7.18–7.52 (m, 13H, Ph-H), 7.66–7.68 ppm (m, 2H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 13.96, 14.0 (2 × CO_2CH_2Me), 19.4 (pyrazoline 3-Me), 52.0 (NCH_2), 59.6 [Ph_2C-CH(CN)], 61.9, 63.3 (2 × CO_2CH_2Me), 76.1 (methine C), 112.0 (pyrazoline C-4), 119.7 (CN), 126.5, 126.6 (olefin C), 126.8, 127.0, 127.8, 127.9, 129.0, 129.7, 130.3, 141.0, 141.2, 143.6 (Ph-C), 154.8 (pyrazoline C-3), 161.8 (pyrazoline C-5), 168.5, 170.7 ppm (C=O); ms: *m/z* 564 $[M + H]^+$. Anal. Calcd. for $C_{34}H_{33}N_3O_5$: C, 72.45; H, 5.90; N, 7.46. Found: C, 72.25; H, 6.09; N, 7.33.

(Z)-4-Cyano-5-[2-(isopropoxycarbonylmethylene)-3-methyl-5-oxo-1-phenyl-3-pyrazolin-4-yl]-5,5-diphenyl-2-pentenoic acid isopropyl ester (7c). This compound was obtained as colorless needles (0.166 g, 28%), mp 122–124°C (chloroform-petroleum ether); IR (potassium bromide): ν 2224 (CN), 1733, 1637 cm^{-1} (C=O); ^1H NMR (deuteriochloroform): δ 1.12, 1.15 (d, J = 6.1 Hz, 6H, CO_2CHMe_2), 1.32, 1.39 (d, J = 6.4 Hz, 6H, CO_2CHMe_2), 1.59 (s, 3H, pyrazoline 3-Me), 3.93 (d, J = 17.7 Hz, 1H, NCH_2), 4.33 (d, J = 17.7 Hz, 1H, NCH_2), 5.01, 5.13 (sep, J = 6.4 Hz, 2H, 2 × CO_2CHMe_2), 5.35 (s, 1H, methine H), 5.69 (s, 1H, olefin H), 5.88 (s, 1H, olefin H), 7.14–7.32 (m, 7H, Ph-H), 7.36–7.39 (m, 2H, Ph-H), 7.47–7.51 (m, 4H, Ph-H), 7.61–7.63 ppm (m, 2H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 19.6 (pyrazoline 3-Me), 21.56, 21.64, 21.7, 21.8 (2 × CO_2CHMe_2), 52.6 (NCH_2), 59.6 [Ph_2C-CH(CN)], 69.9, 71.8 (2 × CO_2CHMe_2), 76.2 (methine C), 111.5 (pyrazoline C-4), 119.9 (CN), 126.4, 126.5, 126.6, 127.0 (Ph-C), 127.8, 127.9 (olefin C), 128.9, 129.4, 130.2, 141.37, 141.43, 144.1 (Ph-C), 154.6 (pyrazoline C-3), 161.7 (pyrazoline C-5), 168.0, 169.8 ppm (C=O); ms: *m/z* 592 $[M + H]^+$. Anal. Calcd. for $C_{36}H_{37}N_3O_5 \cdot 0.2H_2O$: C, 72.63; H, 6.33; N, 7.06. Found: C, 72.59; H, 6.35; N, 7.08.

(Z)-5-[2-(Tert-butoxycarbonylmethylene)-3-methyl-5-oxo-1-phenyl-3-pyrazolin-4-yl]-4-cyano-5,5-diphenyl-2-pentenoic acid tert-butyl ester (7d). This compound was obtained as colorless needles (0.254 g, 41%), mp 149–151°C (chloroform-petroleum ether); IR (potassium bromide): ν 2224 (CN), 1737, 1639 cm^{-1} (C=O); ^1H NMR (deuteriochloroform): δ 1.35, 1.53 (s, 18H, 2 × CO_2CMe_3), 1.55 (s, 3H, pyrazoline 3-Me), 3.84 (d, J = 18.0 Hz, 1H, NCH_2), 4.28 (d, J = 18.0 Hz, 1H, NCH_2), 5.27 (s, 1H, methine H), 5.58 (s, 1H, olefin H), 5.83 (s, 1H, olefin H), 7.14–7.26 (m, 5H, Ph-H), 7.29–7.39 (m, 4H, Ph-H), 7.48–7.53 (m, 4H, Ph-H), 7.64–7.66 ppm (m, 2H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 19.5 (pyrazoline 3-Me), 28.0 (2 × CO_2CMe_3), 53.5 (NCH_2), 59.6 [Ph_2C-CH(CN)], 76.6 (methine C), 83.0, 84.7 (2 × CO_2CMe_3), 111.1 (pyrazoline C-4), 120.0 (CN), 122.8, 126.4, 126.6 (Ph-C), 127.0, 127.1 (olefin C), 127.2, 127.5, 127.8, 127.9, 128.8, 129.6, 130.5, 140.8, 141.6, 144.3 (Ph-C), 154.9 (pyrazoline C-3), 161.7 (pyrazoline C-5), 167.7, 169.7 ppm (C=O); ms: *m/z* 620 $[M + H]^+$. Anal. Calcd. for $C_{38}H_{41}N_3O_5 \cdot 0.8H_2O$: C, 71.97; H, 6.77; N, 6.63. Found: C, 71.97; H, 6.59; N, 6.63.

The preparation of *N*-acetylated dihydropyridazinones 8a,b from 4a,b and acetic anhydride. A mixture of **4a** (0.463 g, 1 mmol) or **4b** (0.477 g, 1 mmol) and acetic anhydride (0.306 g, 3 mmol) in pyridine (5 mL) was stirred at 100°C for 2 h. After removal of the solvent *in vacuo*, cold water was added to the residue. The resulting mixture was extracted with chloroform (60 mL). The extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with chloroform as the eluent to provide **8a**,**b**.

1-Acetyl-1,2,3,4-tetrahydro-6-methyl-3-oxo-2-phenyl-5-(α-methylene-β,β-diphenylpropanenitril-3-yl)-4-pyridazinecarboxylic acid methyl ester (8a). This compound was obtained as colorless prisms (0.278 g, 55%), mp 214–216°C (chloroform-petroleum ether); IR (potassium bromide): ν 2224 (CN), 1747, 1686, 1660 cm^{-1} (C=O); ^1H NMR (dimethyl sulfoxide-d_6): δ 1.76 (s, 3H, 6-Me), 2.21 (s, 3H, COMe), 3.86 (s, 3H, CO_2Me), 5.60 (s, 1H, olefin H), 6.00 (s, 1H, olefin H), 6.75 (s, 1H, 4-H), 7.27–7.47 ppm (m, 15H, Ph-H); ^{13}C NMR (dimethyl sulfoxide-d_6): δ 21.8 (6-Me), 23.1 ($COMe$), 53.5 (CO_2Me), 59.4 [Ph_2C-C(CN)=CH_2], 71.0 (C-4), 118.9 (CN), 125.3 (C-5), 126.5, 126.8, 127.00, 127.01, 127.9 (Ph-C), 128.0 [Ph_2C-C(CN)=CH_2], 128.1, 128.9, 129.1, 129.5 (Ph-C), 131.0 [Ph_2C-C(CN)=CH_2], 139.38, 139.40, 141.6 (Ph-C), 149.3 (C-6),

160.5 (C-3), 169.2, 169.9 ppm (C=O); ms: *m/z* 506 [M + H]$^+$. Anal. Calcd. for $C_{31}H_{27}N_3O_4 \cdot 1.0H_2O$: C, 71.11; H, 5.58; N, 8.03. Found: C, 71.16; H, 5.48; N, 7.80.

1-Acetyl-1,2,3,4-tetrahydro-6-methyl-3-oxo-2-phenyl-5-(α-methylene-β,β-diphenylpropanenitril-3-yl)-4-pyridazinecarboxylic acid ethyl ester (8b). This compound was obtained as colorless prisms (0.182 g, 35%), mp 212–214°C (chloroform-petroleum ether); IR (potassium bromide): ν 2224 (CN), 1751, 1688, 1656 cm^{-1} (C=O); ^{1}H NMR (dimethyl sulfoxide-d_6): δ 1.28 (t, J = 7.0 Hz, 3H, CO_2CH_2*Me*), 1.75 (s, 3H, 6-Me), 2.20 (COMe), 4.25–4.38 (m, 2H, CO_2CH_2Me), 5.60 (s, 1H, olefin H), 6.00 (s, 1H, olefin H), 6.71 (s, 1H, 4-H), 7.25–7.48 ppm (m, 15H, Ph-H); ^{13}C NMR (dimethyl sulfoxide-d_6): δ 13.7 (CO_2CH_2*Me*), 21.9 (6-Me), 23.1 (CO*Me*), 59.5 [Ph_2C-C(CN)=CH_2], 62.9 (CO_2CH_2Me), 70.9 (C-4), 119.0 (CN), 125.5 (C-5), 126.7, 126.9, 127.04, 127.07, 127.9, 128.0 (Ph-C), 128.2 [Ph_2C-C(CN)=CH_2], 128.9, 129.1, 129.5 (Ph-C), 131.0 [Ph_2C-C(CN)=CH_2], 139.4, 139.5, 141.7 (Ph-C), 149.3 (C-6), 160.5 (C-3), 168.7, 170.0 ppm (C=O); ms: *m/z* 520 [M + H]$^+$. Anal. Calcd. for $C_{32}H_{29}N_3O_4 \cdot 0.15H_2O$: C, 73.59; H, 5.65; N, 8.05. Found: C, 73.61; H, 5.77; N, 7.97.

The preparation of compound 7d from 5d and *tert*-butyl chloroacetate. A mixture of **5d** (0.505 g, 1 mmol), *tert*-butyl chloroacatate (0.452 g, 3 mmol), and potassium carbonate (0.276 g, 2 mmol) in *N*,*N*-dimethylformamide (5 mL) was stirred at 120°C for 1 h. After work-up as described for the preparation of **7a–d**, compound **7d** was obtained in 72% yield (0.446 g). The melting point and IR spectrum of this compound coincided with an authentic sample prepared from **2** and *tert*-butyl chloroacatate.

The preparation of carboxylic acid 9 from 6a–d and potassium *tert*-butoxide. A mixture of **6a–d** (1 mmol) and potassium *tert*-butoxide (0.112 g, 1 mmol) in *tert*-butyl alcohol (5 mL) was refluxed for 5 h. After removal of the solvent *in vacuo*, a 5% hydrochloric acid solution (20 mL) was added to the residue with stirring and ice cooling. The resulting mixture was extracted with chloroform (60 mL). The extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with chloroform as the eluent to afford {[3-methyl-4-(α-methylene-β,β-diphenylpropanenitril-3-yl)-1-phenyl-1*H*-pyrazol-5-yl]oxy}acetic acid (**9**) [from **6a**: 0.184 g (41%), from **6b**: 0.130 g (29%), from **6c**: 0.117 g (26%), and from **6d**: 0.216 g (48%)]. This compound was obtained as colorless needles, mp 80–83°C (chloroform-petroleum ether); IR (potassium bromide): ν 3447 (OH), 2224 (CN), 1744 cm^{-1} (C=O); ^{1}H NMR (deuteriochloroform): δ 1.72 (s, 3H, pyrazole 3-Me), 3.76 (s, 2H, OCH_2), 5.96 (s, 1H, olefin H), 6.26 (s, 1H, olefin H), 6.63 (br, 1H, CO_2H), 7.23–7.50 (m, 13H, Ph-H), 7.61–7.69 ppm (m, 2H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 15.7 (pyrazole 3-Me), 56.9 [Ph_2C-C(CN)=CH_2], 69.1 (OCH_2), 108.3 (pyrazole C-4), 119.4 (CN), 123.0, 127.5, 127.6, 128.2 (Ph-C), 128.9 [Ph_2C-C(CN)=CH_2], 129.4, 129.9 (Ph-C), 131.9 [Ph_2C-C(CN)=CH_2], 137.8, 140.6 (Ph-C), 148.79 (pyrazole C-3), 148.83 (pyrazole C-5), 169.8 ppm (C=O); ms: *m/z* 450 [M + H]$^+$. Anal. Calcd. for $C_{28}H_{23}N_3O_3 \cdot 0.4H_2O$: C, 73.64; H, 5.25; N, 9.20. Found: C, 73.75; H, 5.64; N, 8.89.

The preparation of carboxylic acid 9 from 6a and potassium hydroxide. A mixture of **6a** (0.463 g, 1 mmol) and potassium hydroxide (0.056 g, 1 mmol) in ethanol (5 mL) and water (2 mL) was refluxed for 5 h. After the same work-up as described for the preparation of **9** from **6a–d** and potassium *tert*-butoxide, carboxylic acid derivative **9** was obtained in 56% yield (0.252 g).

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