Heterocyclic Synthesis with \(\omega\)-bromoacetophenone: Synthesis of Some New Pyrazole, Pyridazine and Furan Derivatives

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Síntesis heterocíclica con \(\omega\)-bromoacetofenona: Síntesis de nuevos derivados de pirazol, piridazina y furano

RESUMEN
Los derivados de \(p\)-bromofenacilnitrilo \(3a,b\) reaccionan con derivados de hidrazina bajo diferentes condiciones para dar los dianimopirazoles \(4a,b\), las piridazin-6-iminas \(5a,b\) y los 5-aminopirazoles \(11a,b\). Al calentar a refluxo \(5a\) en una mezcla etanol / ácido clorhídrico, éste se transforma en la piridazin-6-ona \(6\) mientras que, bajo las mismas condiciones de reacción, \(5b\) experimenta contracción de anillo con eliminación de fenilhidrazina rindiendo el derivado de furano \(7\). El compuesto \(7\) también se puede obtener a partir de \(3a\) calentando este producto a refluxo en etanol usando catalizador de trietilamina. El fenacilcianoacetato de etilo \(3b\) reacciona con hidrazo de hidrazina y fenilhidrazina para dar los derivados de 4-fenacilpirazol \(11a,b\), respectivamente. El compuesto \(3b\) rinde una mezcla de los dos derivados de furano \(12\) y \(13\) al calentarlo a refluxo en etanol usando catalizador de trietilamina. Además, el compuesto \(3b\) experimenta la reacción de acoplamiento con las sales de diazonio aromáticas \(14a-d\) para dar los derivados de pirazol \(16a-d\), presumiblemente por los correspondientes derivados hidrazo \(15a-d\).


SUMMARY
\(p\)-Bromophenacetonitrile derivatives \(3a,b\) react with hydrazine derivatives under different conditions to afford the dianimopyrazoles \(4a,b\), the pyridazine-6-imines \(5a,b\), and 5-aminopyrazoles \(11a,b\). Refluxing of \(5a\) in ethanol/hydrochloric acid mixture furnished its transformation into the pyridazine-6-one \(6\) while \(5b\) under the same reaction conditions, underwent ring contraction expelling phenyl hydrazine to afford the furan derivative \(7\). Compound \(7\) could also be obtained from \(3a\) upon reflux in ethanol catalyzed by triethylamine. Ethyl phenacylcyanocetate \(3b\) reacts with hydrazine hydrate and phenylhydrazine to afford the 4-phenacylpyrazole derivatives \(11a,b\) respectively. Compound \(3b\) afforded a mixture of the two furan derivatives \(12\) and \(13\) upon reflux in ethanol catalyzed by triethylamine. Compound \(3b\) also undergoes the coupling reaction with the aromatic diazonium salts \(14a-d\) to afford the pyrazole derivatives \(16a-d\) presumibly via the hydrazo derivatives \(15a-d\) respectively.

Key words: \(p\)-Bromophenacetonitriles. Pyridazineimines. Pyridazinone. 3,5-Diaminopyrazoles. Furans.

RESUM
Els derivats de \(p\)-bromofenacilnitril \(3a,b\) reaccionen amb derivats d'hidrazina sota diferents condicions per donar les dianimopirazoles \(4a,b\), les piridazin-6-imines \(5a,b\) i les 5-aminopirazoles \(11a,b\). L’escalfament a reflux de \(5a\) en una barreja etanol / acid clorhídric el transforma en la piridazin-6-ona \(6\) mentre que, sota les mateixes condicions de reacció, \(5b\) experimenta contracció d’anell amb eliminació de fenilhidrazina rendint el derivat de furà \(7\). El compost \(7\) també es pot obtenir a partir de \(3a\) en escalfar aquest producte a reflux en etanol emprant catalitzador de trietilamina. El fenacilcianoacetat d’etil \(3b\) reacciona amb hidrat d’hidrazina i fenilhidrazina per donar els derivats de 4-fenacilpirazol \(11a,b\), respectivament. El compost \(3b\) rendeix una barreja dels dos derivats de furà \(12\) i \(13\) en ésser escalfat a reflux en etanol emprant catalitzador de trietilamina. A més, el compost \(3b\) experimenta la reacció d’acoblament amb les sales de diazoni aromàtiques \(14a-d\) per donar els derivats de pirazol \(16a-d\), presumiblement via els corresponents derivats hidrazo \(15a-d\).


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INTRODUCTION

Nitriles are versatile synthones for a wide variety of heterocyclic compounds that are interesting as pharmaceuticals, pesticides and dyes. Pyridazine derivatives have received considerable attention in recent decades due to their biological activity as antiplatelet agents, inhibitors of glycogen synthase kinase and antimicrobial agents.

Recently aminopyrazoles were found to be potentially useful to prevent protein aggregation which is the first phase of Alzheimer. Substituted furans also served as building blocks in material sciences.

In the last two decades we have been involved in a program aiming to develop new simple routes for the synthesis of heterocyclic compounds of biological interest. Recently some new bromo-substituted pyridazine, pyrazole and furan derivatives were required for biological evaluation.

RESULTS AND DISCUSSION

\(p\)-Bromophenacyl malononitrile \(3a\) and ethyl \(p\)-bromophenacyl cyanoacetate \(3b\) were prepared from the reaction of \(p\)-bromophenacyl bromide \(1\) with malononitrile \(2a\) or the sodium salt of ethyl cyanoacetate \(2b\) respectively according to literature procedures (Scheme 1).

\(p\)-Bromophenacyl malononitrile \(3a\) reacts with hydrazines to afford different products according to the reaction conditions. Thus it reacts with hydrazine hydrate at room temperature to afford a yellow crystalline product of \(mp. 252^\circ C\). Elemental analysis of this product showed that it is 1:1 adduct. The IR spectrum of the isolated products showed absorption bands at \(\nu_{max} 3352, 3215, 3078\) and \(1658 \text{cm}^{-1}\) corresponding to \(\text{NH, NH}_{2}\) and \(\text{CO}\) groups, respectively and no cyano absorption bands were revealed. The \(^1\text{H NMR}\) spectrum of the isolated product revealed a singlet (2H) at \(\delta = 3.55 \text{ppm}\), a broad singlet (4H, D\(_2\)O exchangeable) at \(8.50 \text{ppm}\) attributable to two \(\text{NH}_{2}\) and a singlet (1H, D\(_2\)O exchangeable) at \(10.16 \text{ppm}\) due to \(\text{NH}\), beside the other aromatic signals. The mass spectrum showed two molecular ion peaks at \(m/z 293 (M^+ - 1)\) and \(295 (M^+ + 1)\). Based on these spectral as well as elemental analytical data the diaminopyrazole structure \(4a\) was assigned to this product (cf. experimental & Scheme 1). Similarly, the reaction of \(3a\) with phenyl hydrazine under the same reaction conditions afforded the corresponding N-phenylpyrazole derivative \(4b\). Elemental analysis and spectral data agree with structure \(4b\).

The reaction of \(3a\) with hydrazine hydrate in refluxing ethanol catalyzed by few drops of triethylamine afforded another pale yellow solid product with \(mp. 310^\circ C\). The IR
spectrum of this isolated product revealed absorption bands at \( \delta = 3280, 3120 \) and 2231 \( \text{cm}^{-1} \), attributable to NH and CN groups, respectively, and no carbonyl absorption bands appeared. The \(^1\)H NMR spectrum of this reaction product revealed a multiplet (2H) at \( \delta = 1.78 \text{ ppm, a signal (dd, 1H)} \) at \( \delta = 2.44-2.54 \text{ ppm, and two D}_2\text{O exchangeable singlet signals at } 7.50 \text{ and 11.46 ppm (1H) attributable to the ring NH, NH}_2 \text{ and OH beside carbonyl absorption bands at } \delta = 1685 \text{ and 1666 cm}^{-1} \text{ respectively.} \)

The \(^1\)H NMR spectrum of 11a revealed four singlets at \( \delta = 3.53 \) (2H), 3.72 (2H), 4.66 (1H) and 11.35 (1H) ppm attributable to NH, CH\(_2\), OH and NH beside two doublets at \( \delta = 7.50-7.64 \text{ ppm (4H) for the aromatic protons.} \)

On the other hand compound 3b reacts with hydrazines to afford the 4-phenacylpyrazole derivatives 11a,b (Scheme 2). The IR spectra of both compounds showed a broad absorption bands at \( \nu = 3425-3157 \text{ cm}^{-1} \) assignable to the ring NH, NH\(_2\) and OH beside carbonyl absorption bands at \( \nu = 1685 \text{ and 1666 cm}^{-1} \text{ respectively.} \)

The \(^1\)H NMR spectrum of 11a,b revealed four singlets at \( \delta = 3.53 \) (2H), 3.72 (2H), 4.66 (1H) and 11.35 (1H) ppm attributable to NH, CH\(_2\), OH and NH beside two doublets at \( \delta = 7.50-7.64 \text{ ppm (4H) for the aromatic protons.} \)

The reaction of 1 with phenyl hydrazine in refluxing ethanol catalyzed by triethylamine afforded a new colorless solid product. The IR spectrum of this product showed the absorption bands at \( \nu = 3182 \text{ and 2215 cm}^{-1} \text{, corresponded to NH and CN groups, respectively.} \)

The \(^1\)H NMR spectrum of this reaction product revealed a multiplet (2H) at \( \delta = 1.78 \text{ ppm, a signal (dd, 1H)} \) at \( \delta = 2.44-2.54 \text{ ppm, and only one D}_2\text{O exchangeable singlet at } 11.50 \text{ ppm (1H) attributable to the imine NH, beside other aromatic signals at their proper position.} \)

The mass spectrum of this product showed correct molecular ion peaks at \( m/z = 276, 278 \text{ (M}^-1 \text{ and M}^+1\text{. Based on the above data the imino-pyridazine structure 5a was assigned for this product (cf. experimental, Scheme 1).} \)

The reaction of 3a with phenyl hydrazine in refluxing ethanol catalyzed by triethylamine afforded a new colorless solid product. The IR spectrum of this product showed the absorption bands at \( \nu = 3182 \text{ and 2215 cm}^{-1} \text{, corresponded to NH and CN groups, respectively.} \)

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The mass spectrum of this product showed correct molecular ion peaks at \( m/z = 276, 278 \text{ (M}^-1 \text{ and M}^+1\text{. Based on the above data the imino-pyridazine structure 5a was assigned for this product (cf. experimental, Scheme 1).} \)

The appearance of the methylene protons as multiplets and of the methine protons as doublet of doublet in the 1H NMR spectra of compounds 5a and 5b as well as 6 is presumably attributed to the non chemical equivalence of the two methylene protons which are axial and equatorial in a chair form of diazacyclohexenes.

This behavior of 3a towards hydrazines is in agreement with our recently reported behavior of phenacylmalononitrile towards the same reagents.

Compounds 5a,b were refluxed in ethanol / conc. HCl mixture (4:1 by volume) aiming to transform them to the corresponding pyridazine derivatives. However, only 5a could undergo this transformation and compound 6 was obtained. Under these conditions compound 5b has afforded light brown crystals of mp. 240°C. The IR spectrum of this product did not show any NBOH carbonyl absorption band but absorption bands at \( \nu = 3410, 3313 \text{ and 2217 cm}^{-1} \text{, attributable to the imine NH, beside other aromatic signals at their proper position.} \)

The mass spectrum of this product showed correct molecular ion peaks at \( m/z = 276, 278 \text{ (M}^-1 \text{ and M}^+1\text{. Based on the above data the imino-pyridazine structure 5a was assigned for this product (cf. experimental, Scheme 1).} \)

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This behavior of 3a towards hydrazines is in agreement with our recently reported behavior of phenacylmalononitrile towards the same reagents.

On the other hand compound 3b reacts with hydrazines to afford the 4-phenacylpyrazole derivatives 11a,b (Scheme 2). The IR spectra of both compounds showed a broad absorption bands at \( \nu = 3425-3157 \text{ cm}^{-1} \) assignable to the ring NH, NH\(_2\) and OH beside carbonyl absorption bands at \( \nu = 1685 \text{ and 1666 cm}^{-1} \text{ respectively.} \)

The \(^1\)H NMR spectrum of 11a revealed four singlets at \( \delta = 3.53 \) (2H), 3.72 (2H), 4.66 (1H) and 11.35 (1H) ppm attributable to NH, CH\(_2\), OH and NH beside two doublets at \( \delta = 7.50-7.64 \text{ ppm (4H) for the aromatic protons.} \)

Compound 3b has afforded a mixture of two compounds with overall yield of 76% (1:1 ratio) upon reflux in ethanol catalyzed by triethylamine. These were separated and identified as the furan derivatives 12 and 13. Compound 12 is assumed to be formed via cyclization with loss of ethanol.

This compound was prepared according to ref. 12. The IR spectra showed the absorption bands at \( \nu = 3182 \text{ and 2215 cm}^{-1} \) and the presence of OH in the \(^1\)H NMR spectrum. Compound 13 on the other hand, is formed apparently via cyclization with the cyano group. Again in this case no cyano absorption band in the IR spectrum while the ester carbonyl absorption band is clearly defined at 1712 cm\(^{-1}\), the characteristic ethoxy protons are also revealed in the \(^1\)H NMR spectrum.

Aroyl pyrazoles are interesting compounds from the point of view of biological activity studies as well as their further transformations. Therefore it was planned to obtain 4-bromophenacyl pyrazolyl ketones from 3a,b via their azo/hydrzo derivatives of the type 15 (Scheme 2) which then can be cyclized into the desired compounds. Therefore we carried out the coupling reaction of 3a and 3b with aromatic diazonium salts. Unfortunately we could not isolate any products from 3a; while 3b underwent a successful azocoupling reaction to afford highly colored products.

It was thought that we have obtained the azo derivatives 15a-d or their hydrazo tautomers, however the IR spectra did not show ester carbonyl absorptions and the \(^1\)H NMR spectra did not reveal the usual quartet and triplet signals of the ester group, or the hydrazo NH proton singlet.

All analytical and spectral data are in complete agreement with the pyrazole structures 16a-d which were assigned for these products. Furthermore the \(^13\)C NMR spectrum of 16a as a representative example revealed 13 signals which are applicable to this structure (cf. Scheme 2 & experimental).

**EXPERIMENTAL SECTION**

Melting points were measured on an Electrothermal (9100) apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Perkin Elmer 1430 spectrophotometer. The \(^1\)H and \(^13\)C NMR spectra were taken on a Varian Gemini 300 MHz spectrometer in DMSO-d\(_6\) using TMS as internal standard and chemical shifts are expressed in \( \delta \) ppm values. Mass spectra were taken on a Shimadzu GCMS-GC 1000 FX (70 ev). Elemental analyses were carried out at the Micro-analytical Center at Caro University.

0-p-Bromophenacylitrile derivatives 3a,b (General Procedure).

These compounds were prepared according to literature procedure, 3a according to ref. 10 and 3b according to ref. 10.
Preparation of 3,5-diaminopyrazole derivatives 4a,b:
(General Procedure).
A mixture of 3a (0.01 mol) and hydrazine hydrate or phenyl hydrazine (0.015 mol) is warmed under dry conditions on a water bath until a homogenous solution is obtained. The solid mass formed on standing at room temperature was triturated with ethanol then poured onto cold water acidified by few drops of conc. HCl. The solid products so formed were filtered off and recrystallized from ethanol / dimethylformamide (DMF) mixture (4:1).

1-(4-Bromophenyl)-2-(3,5-diamino-1H-pyrazol-4-yl)-ethanone 4a:
Yellow powder, mp. 252°C, 63% yield. $\nu_{\text{max}}$ (KBr) 3352, 3215, 3078 (NH$_2$ & NH) and 1658 (CO) cm$^{-1}$. $\delta$H (300 MHz, DMSO-d$_6$) 3.55 (s, 2H, CH$_2$), 7.55-7.64 (2d, 4H, arom.), 8.50 (br., 4H, 2NH$_2$), 10.16 (s, 1H, NH). Anal. Calcd. for (C$_{11}$H$_{11}$BrN$_4$O) C, 44.77; H, 3.76; Br, 27.07; N, 18.98. Found: C, 44.61; H, 3.58; Br, 27.24; N, 18.78.

1-(4-Bromophenyl)-2-(3,5-diamino-1-phenyl-1H-pyrazol-4-yl)-ethanone 4b:
Brownish yellow powder, mp. 225°C, 65% yield. $\nu_{\text{max}}$ (KBr) 3311-3135 (NH$_2$) and 1661 (CO) cm$^{-1}$. $\delta$H (300 MHz, DMSO-d$_6$) 3.65 (s, 2H, CH$_2$), 7.15-7.68 (m, 9H, arom.), 8.1 (br. s., 2H, NH$_2$), 8.15 (br. s, 2H, NH$_2$). Anal. Calcd. for (C$_{17}$H$_{15}$BrN$_4$O) C, 55.00; H, 4.07; Br, 21.52; N, 15.09. Found: C, 54.80; H, 4.20; Br, 21.30; N, 15.40.

Preparation of 3-(4-bromophenyl)-2,3,4,5-tetrahydro-6-iminopyridazine-5-carbonitriles 5a,b:
(General Procedure).
To a solution of 3a (0.01 mol) in ethanol (20 mL) was added 0.01 mol of either hydrazine hydrate or phenyl hydrazine. The reaction mixture was refluxed for 2h in each case, left overnight. The reaction mixture is poured on ice cold water and acidified with dil. HCl till just neutral. The precipitated solid was filtered off and recrystallized from acetic acid.

6-(4-bromophenyl)-3-imino-2,3,4,5-tetrahydro-pyridazine-4-carbonitrile 5a:
Pale yellow powder, mp. 310°C, 73% yield. $\nu_{\text{max}}$ (KBr) 3311-3135 (NH$_2$) and 1661 (CO) cm$^{-1}$. $\delta$ (300 MHz, DMSO-d$_6$) 3.65 (s, 2H, CH$_2$), 7.55-7.64 (2d, 4H, arom.), 8.50 (br., 4H, 2NH$_2$), 10.16 (s, 1H, NH). Anal. Calcd. for (C$_{17}$H$_{15}$BrN$_4$O) C, 55.00; H, 4.07; Br, 21.52; N, 15.09. Found: C, 54.80; H, 4.20; Br, 21.30; N, 15.40.

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Preparation of 3-(4-bromophenyl)-2,3,4,5-tetrahydro-6-iminopyridazine-5-carbonitriles 5a,b:
(General Procedure).
To a solution of 3a (0.01 mol) in ethanol (20 mL) was added 0.01 mol of either hydrazine hydrate or phenyl hydrazine. The reaction mixture was refluxed for 2h in each case, left overnight. The reaction mixture is poured on ice cold water and acidified with dil. HCl till just neutral. The precipitated solid was filtered off and recrystallized from acetic acid.

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Pale yellow powder, mp. 310°C, 73% yield. $\nu_{\text{max}}$ (KBr) 3311-3135 (NH$_2$) and 1661 (CO) cm$^{-1}$. $\delta$ (300 MHz, DMSO-d$_6$) 3.65 (s, 2H, CH$_2$), 7.55-7.64 (2d, 4H, arom.), 8.50 (br., 4H, 2NH$_2$), 10.16 (s, 1H, NH). Anal. Calcd. for (C$_{17}$H$_{15}$BrN$_4$O) C, 55.00; H, 4.07; Br, 21.52; N, 15.09. Found: C, 54.80; H, 4.20; Br, 21.30; N, 15.40.

Preparation of 3-(4-bromophenyl)-2,3,4,5-tetrahydro-6-iminopyridazine-5-carbonitriles 5a,b:
(General Procedure).
To a solution of 3a (0.01 mol) in ethanol (20 mL) was added 0.01 mol of either hydrazine hydrate or phenyl hydrazine. The reaction mixture was refluxed for 2h in each case, left overnight. The reaction mixture is poured on ice cold water and acidified with dil. HCl till just neutral. The precipitated solid was filtered off and recrystallized from acetic acid.
6-(4-Bromophenyl)-3-amino-2-phenyl-2,3,4,5-tetrahydro-pyridazine-4-carbonitrile 5b:

Yellow powder, mp. 235°C, 78% yield. ν∞ (KBr) 3182 (NH) and 2215 (CN) cm⁻¹. δ∞ (300 MHz, DMSO-d₆) 1.75-1.84 (m, 2H, CH₂), 2.45-2.56 (dd, 1H, CH), 6.65-7.55 (m, 9H, arom.). 8.1 (s, 2H, NH₂). Anal. Calcd. for (C₁₇H₁₃BrN₄) C, 57.81; H, 2.50; Br, 30.26; N, 11.40. Found: C, 50.16; H, 3.74; Br, 25.54; N, 4.72.

Preparation of 4-amino-6-(4-bromophenyl)-furo[2,3-d]pyrimidine 10:

A solution of 7 (0.01 mol) in 20 mL formamide was refluxed for 6 h, and then left to cool overnight. The brown precipitated solid was filtered off and recrystallized from ethanol / DMF mixture. Brown amorphous solid, mp. 290°C, 61% yield. ν∞ (KBr) 3330-3210 (NH) cm⁻¹. δ∞ (300 MHz, DMSO-d₆) 6.65 (s, 1H, furan H) 6.45 (s, 1H, CH pyrimidine), 7.35 (d, 2H, arom.), 7.58 (2H, arom.), 8.1 (s, 2H, NH), Anal. Calcd. for (C₁₃H₁₂BrNO₃) C, 49.68; H, 2.78; Br, 25.74; N, 14.48. Found: C, 49.50; H, 2.50; Br, 27.40; N, 14.60.

Preparation of 5-amino-pyrazole derivatives 11a,b (General Procedure).

To a solution of 3b (3.1 g; 0.01 mol) in dioxan (20 mL) was added 0.01 mol of either hydrazine hydrate or phenyl hydrazine. The reaction mixture was refluxed for 2h in each case, left overnight where dark yellow crystalline products appeared. The products were filtered off and recrystallized from ethanol.

2-(5-Amino-3-hydroxy-1H-pyrazol-4-yl)-1-(4-bromophenyl) ethanone 11a:

Dark yellow crystals, mp. 185°C, 60% yield. ν∞ (KBr) 3425, 3225, 3157 (OH, NH & NH) and 1685 (CO) cm⁻¹. δ∞ (300 MHz, DMSO-d₆) 3.72 (s, 2H, CH₂), 3.53 (br., 2H, NH), 4.66 (s, 1H, OH), 7.50&7.64 (2d, 4H, arom.), 11.35 (s, 1H, NH). Anal. Calcd. for (C₁₉H₁₈BrN₂O) C, 44.62; H, 3.40; Br, 26.98; N, 14.19. Found: C, 44.70; H, 3.50; Br, 27.20; N, 14.30.

3-(4-Bromo-benzoyl)-5-hydroxy-1-phenyl-1H-pyrazole-4-carbonitrile 16a:

Light brown crystals, mp. 260°C, 70% yield. ν∞ (KBr) 3340 (OH), 2223 (CN) cm⁻¹. δ∞ (300 MHz, DMSO-d₆) 6.79-7.93 (m, 9H, arom.), 11.74 (s, 1H, OH) δ∞ (300 MHz, DMSO-d₆) 112.80(s), 113.57(s), 114.63(d), 123.24(s), 126.06(d), 126.66(s), 129.37(d), 131.55(d), 132.28(d), 136.96(a), 142.59(a), 153.72(a), 161.97(a). Anal. Calcd. for (C₁₉H₁₈BrN₂O) C, 55.46; H, 2.74; Br, 21.70; N, 11.41. Found: C, 55.13; H, 2.55; Br, 21.49; N, 11.74.
d) 2.35 (s, 3H, CH₃), 7.23-7.80 (4d, 8H, arom.), 11.76 (s, 1H, OH). Anal. Calcd. for (C₁₈H₁₂BrN₃O₂) C, 56.56; H, 3.16; Br, 20.91; N, 10.99. Found: C, 56.25; H, 3.42; Br, 20.45; N, 10.58.

3-(4-Bromo-benzoyl)-5-hydroxy-1-(4-methoxy-phenyl)-1H-pyrazole-4-carbonitrile 16c:
Dark violet crystals, mp. 250 ºC, 72% yield. δδH (300 MHz, DMSO-d₆) 3.74 (s, 3H, OCH₃), 6.94-7.91 (4d, 8H, arom.), 11.81 (s, 1H, OH). Anal. Calcd. for (C₁₈H₁₂BrN₃O₃) C, 54.29; H, 3.04; Br, 20.07; N, 10.55. Found: C, 54.61; H, 3.27; Br, 20.30; N, 10.73.

3-(4-Bromo-benzoyl)-1-(4-chloro-phenyl)-5-hydroxy-1H-pyrazole-4-carbonitrile 16d:
Red crystals, mp. 294 ºC, 75% yield. δδH (300 MHz, DMSO-d₆) 7.24-7.73 (4d, 8H, arom.), 11.75 (s, 1H, OH). Anal. Calcd. for (C₁₇H₉BrClN₃O₂) C, 50.71; H, 2.25; Br, 19.85; Cl, 8.81; N, 10.44. Found: C, 50.42; H, 2.37; Br, 19.46; Cl, 9.07; N, 10.58.

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