3-(3,5-Dimethyl-1\textit{H}-Pyrazol-1-yl)-3-Oxopropanenitrile as Precursor for Some New Mono-Heterocyclic and Bis-Heterocyclic Compounds

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Received September 8, 2015
DOI 10.1002/jhet.2578
Published online 22 December 2015 in Wiley Online Library (wileyonlinelibrary.com).

INTRODUCTION

In the last two decades, we have been involved in a program aiming to develop new simple procedures for the preparation of some new heterocyclic compounds of biological interest from laboratory available cheap starting materials [1–5].

In the recent years, attention has been increasingly paid to the synthesis of novel mono-heterocyclic and bis-heterocyclic derivatives expected to exhibit various biological activities [6–14]. In the light of these data and in continuation of our program, we have recently reported the synthesis of some new bis-heterocyclic compounds of biological interest [15–17]. Because of the increasing demand on such compounds, it was decided to synthesize a new group of functionally substituted bis-chromenes and bis-thiazole derivatives. 4-Acetylcyanoacetanilide seemed a good precursor to fulfill our objective as a starting compound.

RESULTS AND DISCUSSION

The reaction of 3-(3,5-dimethyl-1\textit{H}-pyrazol-1-yl)-3-oxopropanenitrile 1 with 4-aminoacetophenone in refluxing toluene results in the displacement of the 3,5-dimethylpyrazole moiety from substrate 1 to give \textit{N}(4-acetyl-phenyl)-2-cyanoacetamide 3 (Scheme 1). The structure of the reaction product was confirmed on the basis of its spectral and analytical data. The IR spectrum of compound 3 showed intense absorption bands at $\nu_{\text{stretch}} = 3317$, 2257, 1710, and 1680 cm$^{-1}$ due to NH, cyano group, and two carbonyl groups, respectively. The $^1$H-NMR spectrum of 3 showed three singlet signals at $\delta = 2.6$, 3.95, and 10.6 ppm assignable to methyl, methylene, and amino NH protons, respectively. The $^1$H-NMR spectrum of 3 showed three singlet signals at $\delta = 2.6$, 3.95, and 10.6 ppm assignable to methyl, methylene, and amino NH protons, respectively. The mass spectrum of 3 showed a molecular ion peak at $m/z = 202$.

Grinding of compound 3 with the aromatic aldehydes 4a–d in the presence of solid sodium hydroxide afforded
the corresponding arylidene derivatives 6a–d rather than chalcones 5a–d (Scheme 2). The structure of isolated products 6a–d was confirmed on the basis of their elemental analyses and spectroscopic data (IR, $^1$H NMR, and MS). The IR spectrum of product 6b taken as a typical example of the prepared series, showed absorption bands at $v_{\text{stretch}} = 3328, 2218, 1705,$ and 1685 cm$^{-1}$ corresponding to NH, CN, and CO groups, respectively. The $^1$H-NMR spectrum of 6b revealed the presence of two singlet signals assigned to the methyl and methoxy protons at $\delta = 2.60$ and 3.87 ppm, respectively. In addition, two singlet signals appeared at $\delta = 8.25$ and 10.57 ppm assigned for vinyl and NH protons. The mass spectrum together with the elemental analyses is in agreement with the proposed structure 6b (Experimental and Scheme 2).

On the other hand, grinding of 3 with o-hydroxybenzaldehyde derivatives 7a–c in presence of solid sodium hydroxide afforded yellow solid products of melting point above 300°C. The structure of these isolated products 9a–c was established based on their elemental analyses and spectral data. For example, the IR spectra of the isolated products did not reveal absorption band near $v_{\text{stretch}} \approx 2200$ cm$^{-1}$ assignable to cyano group and instead showed an absorption band near $v_{\text{max}} \approx 3290$ cm$^{-1}$ attributable to NH groups. The $^1$H-NMR spectra of the isolated products revealed a D$_2$O-exchangeable signal at $\delta = 2.34$ and 3.88 ppm due to the methyl and methoxy protons and other two singlets signals at $\delta = 8.16$ and 8.25 ppm due to the vinylic protons, respectively, in addition to D$_2$O-exchangeable signals at $\delta = 10.39$ and 11.0 ppm assignable to the amide protons, beside to the other expected signals for the aromatic protons. The mass spectra together with the elemental analyses are in agreement with structures 9a–c (Scheme 3).

Treatment of compound 3 with cyanoacetoxyhydrazide 10 in refluxing dioxane afforded compound 11 (Scheme 4). The IR spectrum of compound 11 showed absorption bands at $v_{\text{stretch}} = 3325, 3185, 2267,$ and 1674 cm$^{-1}$ due to NH, CN, and the amide carbonyl groups, respectively. The $^1$H-NMR spectrum of 11 showed singlet signals at $\delta = 2.23, 3.91, 4.22, 10.41,$ and 10.97 ppm due to methyl, two methylene, and two NH protons, respectively, beside to the expected signals for aromatic protons. The mass spectrum of 11 showed a molecular ion peak at $m/z = 283$.

Refluxing compounds 11 with various aromatic aldehydes 4a–d in 1:2 molar ratios in absolute ethanol containing few drops of piperidine gave the corresponding di-arylidene derivatives 12a–d (Scheme 5). The structure of the isolated products 12a–d was established based on their elemental analyses and spectral data. Thus, IR spectrum of the isolated product 12b (for example) showed absorption band at $v_{\text{stretch}} = 2200$ cm$^{-1}$ assignable to the cyano groups and an absorption band at $v_{\text{stretch}} = 3381$ cm$^{-1}$ attributable to the NH group. Its $^1$H-NMR spectrum revealed two singlet signals at $\delta = 2.34$ and 3.88 ppm due to the methyl and methoxy protons and other two singlets signals at $\delta = 8.16$ and 8.25 ppm due to the vinylic protons, respectively, in addition to D$_2$O-exchangeable signals at $\delta = 10.39$ and 11.0 ppm assignable to the amide protons, beside to the other expected signals for the aromatic protons. The mass spectra together with the elemental analyses are in agreement with structures 12.

On the other hand, condensation of 11 with twofold excess of o-hydroxybenzaldehydes 7a–c in absolute ethanol catalyzed by few drops of piperidine gave the colored products 13a–c (Scheme 6). The structure of the isolated products was established on their elemental analyses and spectral data. For example, the IR spectrum of the isolated product 13a showed absorption bands at $v_{\text{stretch}} = 3436–3316, 1680,$ and 1659 cm$^{-1}$ attributable to the NH and CO groups. Its $^1$H-NMR spectrum revealed three D$_2$O-exchangeable signals at $\delta = 8.59$ (1H), 9.23 (1H), and 12.93 (2H) ppm attributable to the NH groups, in addition to the other expected signals. The mass spectra together with the elemental analyses are in agreement with the proposed structures 13a–c.

Compound 11 undergoes the coupling reaction with aryldiazoion chloride 14a–d (twofold excess) to afford the corresponding di-arylhydrazono derivatives 15a–d (Scheme 7). The elemental analyses and spectral data of the products 15a–d are in full agreement with their proposed structures (cf. Experimental).

The reaction of compound 11 with phenyl isothiocyanate in DMF in presence of KOH followed by the addition of the

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Scheme 1

![Scheme 1](image1)

Scheme 2

![Scheme 2](image2)

Scheme 3

![Scheme 3](image3)
phenacyl bromides 17a–c to the reaction mixture led to the di-thiazole derivatives 18a–c (Scheme 8). The analytical and spectral data for compounds 18a–c are in full agreement with their proposed structures (cf. Experimental).

EXPERIMENTAL

Melting points were determined on an electrothermostat (9100) apparatus (Kleinfeld, Gehrden, Germany) and are uncorrected. IR spectra were recorded as KBr pellets on a Nicolet 205 spectrophotometer (Nicolet, Madison, WI, USA). The 1H-NMR spectra were taken on a Varian Gemini 300 MHz spectrometer (Varian Inc., Palo Alto, CA, USA) in DMSO-d6 using TMS as internal standard, and chemical shifts are expressed in δ (ppm) values. Mass spectra were taken on a Shimadzu GCMS-GB 1000 PX (Shimadzu, Kyoto, Japan; 70 eV). Elemental analyses and spectral measurements were carried out by the microanalytical center at Cairo University and the analytical laboratory of the institute of organic chemistry, Technical University of Dresden, Germany. The starting compound 1 was prepared according to the reported literature [18].

Synthesis of N-(4-acetylphenyl)-2-cyanoacetamide 3. To a hot solution of 3-(3,5-dimethyl-1H-pyrazol-1-yl)-3-oxopropanenitrile 1 (0.01 mol) in dry toluene (10 mL) was added 4-aminoacetophene (0.01 mol). The reaction mixture was refluxed until precipitation then left to cool. The solid precipitate so formed was collected by filtration and recrystallized from ethanol–dioxane mixture (1:1) as pale brown crystals, yield (91%), mp 225°C; νstretch/cm⁻¹ (KBr) 3317 (NH), 2257 (CN), 1710 and 1680 (CO); δH = 2.62 (s, 3H, CH₃), 3.95 (s, 2H, CH₂), 7.68–7.70 (dd, 2H, J = 1.8, 2.4 Hz, Ar), 7.93–7.95 (dd, 2H, J = 1.8, 2.4 Hz, Ar), 10.61 (s, 1H, NH). MS: m/z = 202 (27.9%), 190 (33.5%), 136 (40.7%), 69 (100%), 55 (63.5%). Anal. Calcd for C₁₁H₁₀N₂O₂: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.52; H, 5.1%; N, 14.13%.

Synthesis of compounds 6a–d. A mixture of N-(4-acetyl-phenyl)-2-cyanoacetamide 3 (0.01 mol) and sodium hydroxide (0.01 mol) was ground in a mortar till complete mixing then the aromatic aldehyde 4a–d were added with grinding for 24 hr. The reaction mixture was poured onto ice–water mixture acidified with concentrated hydrochloric acid. The solid products were collected by filtration, washed with water, and recrystallized from an ethanol–dioxane mixture (1:1).

N-(4-acetylphenyl)-2-cyano-3-phenylprop-2-enamide 6a. Yellow crystals, yield (92%), mp 210°C; νstretch/cm⁻¹ (KBr) 3318 (NH), 2240 (CN), 1691 and 1580 (CO); δH = 2.56 (s, 3H, CH₃), 4.35–7.18 (m, 9H, Ar), 8.33 (s, 1H, CH), 10.74 (s, 1H, NH). Anal. Calcd for C₁₈H₁₄N₂O₂: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.66; H, 5.06; N, 9.89%.

N-(4-acetylphenyl)-2-cyano-3-(4-methoxyphenyl)prop-2-enamide 6b. Yellow crystals, yield (90%), mp 240°C; νstretch/cm⁻¹ (KBr) 3328 (NH), 2218 (CN), 1705 and 1620 cm⁻¹ (CO); δH = 2.56 (s, 3H, CH₃), 3.90 (s, 3H, OCH₃), 7.38–7.70 (m, 9H, Ar), 8.20 (s, 1H, CH), 10.74 (s, 1H, NH). Anal. Calcd for C₁₉H₁₆N₂O₃: C, 73.63; H, 4.96; N, 9.89%. Found: C, 73.96; H, 4.86; N, 9.96%.

Journal of Heterocyclic Chemistry DOI 10.1002/jhet
recrystallized from dimethylformamide (DMF). The solid was collected by filtration, washed with water, and recrystallized from ethanol.

N-(4-acetylphenyl)-3-(4-chlorophenyl)-2-cyano-3-prop-2-enamide 6c. Whitish brown crystals, yield (91%), mp 254°C; δ(C) 3190 (NH), 1702 and 1661 (CO); δ(H) 3.25 (s, 3H, CH3), 6.81 (dd, 2H, J = 3.9, 4.8 Hz, Ar), 7.66–7.69 (dd, 2H, J = 3.9, 4.8 Hz, Ar), 7.91–7.96 (m, 4H, Ar), 8.0 (s, 1H, CH), 10.61 (s, 1H, NH). Anal. Calcd for C18H13ClN2O2 (320.34): C, 66.57; H, 4.08; N, 9.45; S, 10.82. Found: C, 65.03; H, 5.17; N, 9.43%.

N-(4-acetylphenyl)-2-cyano-3-(thiophen-2-yl)prop-2-enamide 6d. Brown crystals, yield (89%), mp 250°C; δ(C) 3320 (NH), 2246 (CN), 1697 and 1653 (CO); δ(H) 2.60 (s, 3H, CH3), 3.87 (s, 3H, OCH3), 7.16–8.05 (m, 8H, Ar), 8.25 (s, 1H, CH), 10.57 (s, 1H, NH). Anal. Calcd for C19H16N2O3 (320.34): C, 71.24; H, 4.03; N, 8.05 (m, 8H, Ar), 8.25 (s, 1H, CH), 10.57 (s, 1H, NH). Anal. Calcd for C19H16N2O3 (320.34): C, 71.24; H, 4.03; N, 8.05%.

Synthesis of compounds 9a–c. A mixture of compound 3 (0.01 mol) was refluxed with cyanoacetic acid hydrizide (0.01 mol) in dry dioxane for 7 h. The solid so formed was collected by filtration, washed with ethanol, and recrystallized from ethanol–dioxane mixture (1:1) as pale brown crystals, yield (61%), mp 250°C; δ(C) 3320 (NH), 2246 (CN), 1674 and 1600 (CO); δ(H) = 2.23 (s, 3H, CH3), 3.91 (s, 2H, CH2), 4.22 (s, 2H, CH2), 7.57–7.81 (dd, 4H, J = 8.4, 8.7 Hz, Ar), 10.41 (s, 1H, NH), 10.97 (s, 1H, NH). MS: m/z = 283 (M+, 64.5%), 243 (50.4%), 216 (47.5%), 215 (55.3%), 186 (33.3%), 174 (48.2%), 146 (42.6%), 119 (69.5%), 118 (84.4%), 107 (34.8%), 91 (79.4%), 90 (42.6%), 68 (100%), 65 (87.9%), 64 (49.6%), 63 (44.0%). Anal. Calcd for C14H13N5O2: C, 59.36; H, 4.63; N, 24.72. Found: C, 59.55; H, 4.80; N, 24.96%.

Synthesis of compounds 11a–d. A mixture of compound 11 (0.01 mol) with the aromatic aldehydes 4b–d (0.02 mol) was refluxed in ethanol in presence of few drops of piperidine for 2 h. The solid so formed was collected by filtration, washed with ethanol, and recrystallized from ethanol–dioxane mixture.

2-Cya-no-N-(4-(1-(2-(2-cyano-3-phenyl-acryloyl)-hydrazono)-ethyl)-phenyl)-3-hydroxy-2-imino-2H-chromene-3-carboxamide 9a. Brown crystals, yield (82%), mp 235°C; δ(C) 3349 (OH), 3290 (NH), 1697 and 1653 (CO); δ(H) = 3.28 (s, 3H, CH3), 6.66–8.22 (m, 7H, Ar), 8.0 (s, 1H, CH), 9.54 (s, 1H, NH), 10.21 (s, 1H, NH); 11.50 (s, 1H, OH). Anal. Calcd for C19H14N2O4 (322.31): C, 67.07; H, 4.38; N, 8.69. Found: C, 67.26; H, 4.56; N, 8.42%.

N-(4-Acetylphenyl)-8-bromo-2-imino-2H-chromene-3-carboxamide 9c. Yellowish brown crystals, yield (97%), mp > 300°C; δ(C) 3200 (NH), 1705 and 1662 (CO); δ(H) = 3.25 (s, 3H, CH3), 6.81–8.06 (m, 7H, Ar), 8.23 (s, 1H, CH), 9.52 (s, 1H, NH), 10.22 (s, 1H, NH). Anal. Calcd for C18H13BrN2O3 (385.21): C, 56.12; H, 3.40; Br, 20.74; N, 7.27. Found: C, 56.32; H, 3.59; Br, 20.91; N, 7.51%.

Synthesis of 2-cyano-N-(4-(1-(2-cyanoacetyl)hydrazinylidene)ethyl)-phenyl)-acacetamide 11. Compound 3 (0.01 mol) was refluxed with cyanoacetic acid hydrizide (0.01 mol) in dry dioxane for 7 h. The solid so formed was collected by filtration, washed with ethanol, and recrystallized from ethanol–dioxane mixture (1:1) as pale brown crystals, yield (61%), mp 250°C; δ(C) 3320 (NH), 2246 (CN), 1674 and 1600 (CO); δ(H) = 2.23 (s, 3H, CH3), 3.91 (s, 2H, CH2), 4.22 (s, 2H, CH2), 7.57–7.81 (dd, 4H, J = 8.4, 8.7 Hz, Ar), 10.41 (s, 1H, NH), 10.97 (s, 1H, NH). MS: m/z = 283 (M+, 64.5%), 243 (50.4%), 216 (47.5%), 215 (55.3%), 186 (33.3%), 174 (48.2%), 146 (42.6%), 119 (69.5%), 118 (84.4%), 107 (34.8%), 91 (79.4%), 90 (42.6%), 68 (100%), 65 (87.9%), 64 (49.6%), 63 (44.0%). Anal. Calcd for C14H13N5O2: C, 59.36; H, 4.63; N, 24.72. Found: C, 59.55; H, 4.80; N, 24.96%.
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(3, 1H, NH), 10.55 (s, 1H, NH). MS: \( m/z = 459 \) (M+, 11.1%), 371 (17%), 370 (10.1%), 303 (15%), 274 (10.4%), 156 (100%), 155 (37.8%), 127 (10.8%), 128 (92.3%), 102 (28.8%), 91 (24.6%), 77 (52.7%). Anal. Calcd for \( \text{C}_{28}\text{H}_{21}\text{N}_{5}\text{O}_{2} \): C, 73.19; H, 4.61; N, 15.24.

2-Cyano-N-[1-(2-cyano-3-(4-methoxy-phenyl)-acryloyl]-hydrazono}-ethyl)-phenyl]-2H-chromene-3-carboxamide 13a. Yellow crystals, yield (89%), mp 268°C; \( \nu_{\text{stretch}}/\text{cm}^{-1} \) (KBr) 3376 (NH), 2210 (CN), 1698 and 1584 (CO); \( \delta_{\text{H}} = 2.32 \) (s, 3H, CH3), 7.32 (s, 1H, CH), 7.51–7.82 (m, 10H, Ar), 8.35 (s, 1H, CH), 8.51 (s, 1H, NH), 10.73 (s, 1H, NH). Anal. Calcd for \( \text{C}_{30}\text{H}_{25}\text{N}_{5}\text{O}_{4} \): C, 69.35; H, 4.85; N, 13.48. Found: C, 69.53; H, 5.04; N, 13.74%.

3-(4-Chloro-phenyl)-N-[4-(4-chloro-phenyl)-2-cyano-3-phenyl]-hydrazono)-ethyl)-phenyl]-2-cyanoacrylamide 12b. Yellow crystals, yield (54%), mp 273°C; \( \nu_{\text{stretch}}/\text{cm}^{-1} \) (KBr) 3374 (NH), 2202 (CN), 1682 and 1573 (CO); \( \delta_{\text{H}} = 2.32 \) (s, 3H, CH3), 7.32 (s, 1H, CH), 7.46–8.01 (m, 12H, Ar), 8.20 (s, 1H, CH), 8.34 (s, 1H, NH), 10.62 (s, 1H, NH). Anal. Calcd for \( \text{C}_{28}\text{H}_{19}\text{Cl}_{2}\text{N}_{5}\text{O}_{2} \) (528.39): C, 63.65; H, 3.62; Cl, 13.42; N, 13.25. Found: C, 63.83; H, 3.81; Cl, 13.61; N, 13.51.

2-Cyano-N-[4-(2-cyano-2-phenyl-3-(4-methoxy-phenyl)-hydrazono)-ethyl]-phenyl]-2-cyanoacrylamide 12d. Yellowish green crystals, yield (70%), mp 253°C; \( \nu_{\text{stretch}}/\text{cm}^{-1} \) (KBr) 3376 (NH), 2210 (CN), 1698 and 1584 (CO); \( \delta_{\text{H}} = 2.32 \) (s, 3H, CH3), 7.32 (s, 1H, CH), 7.51–7.82 (m, 10H, Ar), 8.35 (s, 1H, CH), 8.51 (s, 1H, NH), 10.73 (s, 1H, NH). Anal. Calcd for \( \text{C}_{28}\text{H}_{21}\text{N}_{5}\text{O}_{2} \) (471.55): C, 63.11; H, 3.63; N, 14.85; S, 13.60. Found: C, 63.31; H, 3.81; N, 15.09; S, 13.94%.

Synthesis of compounds 13a–c. A mixture of compound 11 (0.01 mol) with the o-hydroxybenzaldehyde derivatives 7a–c (0.02 mol) was refluxed in ethanol in presence of few drops piperidine for 6h. The solid products so formed were collected by filtration, washed with ethanol, and recrystallized from dimethylformamide (DMF).

2-Imino-N-[4-(1-(2-imino-2H-chromene-3-carbonyl) hydrazono)-ethyl)-phenyl]-2H-chromene-3-carboxamide 13a. Yellow crystals, yield (89%), mp > 300°C; \( \nu_{\text{stretch}}/\text{cm}^{-1} \) (KBr) 3436–3316 (NH), 1680 and 1659 (CO); \( \delta_{\text{H}} = 3.29 \) (s, 3H, CH3), 7.26–7.86 (m, 12H, Ar), 8.55 (s, 2H, 2CH), 8.59 (s, 1H, NH), 9.23 (s, 1H, NH), 12.93 (s, 2H, 2NH). Anal. Calcd for \( \text{C}_{28}\text{H}_{24}\text{N}_{12} \): C, 64.82; H, 4.31; N, 14.25. Found: C, 64.82; H, 4.50; N, 14.51.

7-Hydroxy-N-[4-(1-(2-hydroxy-2-imino-2H-chromene-3-carbonyl)-hydrazono)-ethyl)-phenyl]-2-imino-2H-chromene-3-carboxamide 13b. Yellow crystals, yield (83%), mp > 300°C; \( \nu_{\text{stretch}}/\text{cm}^{-1} \) (KBr) 3423 (OH), 3320–3184 (NH), 1673 and 1595 (CO); \( \delta_{\text{H}} = 3.30 \) (s, 3H, CH3), 6.60 (s, 2H, OH), 6.74 (s, 1H, CH), 7.57–7.89 (m, 10H, Ar), 8.48 (s, 1H, CH), 8.50 (s, 1H, NH), 9.03 (s, 1H, NH), 10.43 (s, 1H, NH), 13.52 (s, 1H, NH). Anal. Calcd for \( \text{C}_{28}\text{H}_{23}\text{N}_{12} \): C, 64.24; H, 4.04; N, 13.38. Found: C, 64.24; H, 4.16; N, 13.66%.

8-bromo-N-{4-(1-(2-(8-bromo-2-imino-2H-chromene-3-carbonyl)-hydrazono)-ethyl)-phenyl]-2-imino-2H-chromene-3-carboxamide 13c. Yellow crystals, yield (76%), mp > 300°C; \( \nu_{\text{stretch}}/\text{cm}^{-1} \) (KBr) 3410–3315 (NH), 1681 and 1660 (CO); \( \delta_{\text{H}} = 3.29 \) (s, 3H, CH3), 7.08–7.97 (m, 11H, Ar and CH), 8.50 (s, 1H, CH), 8.80 (s, 1H, NH), 9.50 (s, 1H, NH), 10.50 (s, 1H, NH), 13.44 (s, 1H, NH). Anal. Calcd for \( \text{C}_{28}\text{H}_{19}\text{Br}_{2}\text{N}_{5}\text{O}_{4} \) (649.29): C, 51.80; H, 2.95; Br, 24.61; N, 10.79. Found: C, 51.61; H, 3.13; Br, 24.91; N, 11.04%.

Synthesis of 2-(2-(2-(2-(2-cyano-2-phenyl-hydrazono)-acetyl)-ethyl)-phenyl)-diazinyl)-2-oxo-N-arylacetoyl-

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(CN), 1728 (CO); δH = 2.33 (s, 3H, CH3), 7.08–7.49 (m, 10H, Ar and 2NH), 7.68–8.21 (m, 4H, Ar), 10.35 (s, 1H, NH), 10.98 (s, 1H, NH). Anal. Calcd for C28H19Cl2N4O2S2 (540.39): C, 55.91; H, 3.22; Cl, 8.82; N, 12.17; S, 8.41%. Found: C, 55.72; H, 3.42; Cl, 8.62; N, 11.92; S, 7.79. Found: C, 64.41; H, 3.72; Cl, 8.82; N, 12.17; S, 8.01%.

**Synthesis of the compounds 18a–c.** Equimolar amounts of compound 11 (0.01 mol) and potassium hydroxide (0.02 mol) in dimethylformamide (DMF; 10 ml) were stirred at room temperature till complete dissolution of potassium hydroxide followed by the addition of phenyl isothiocyanate (0.02 mol) with stirring for 1 h. Finally, phenacyl bromides 17a–c (0.02 mol) were added with stirring for more 1 h. The solid products so formed were collected by filtration and recrystallized from dioxane–ethanol mixture (1:1).

2-Cyano-N-[4-[[2-cyano-2-(3,4-diphenyl-3H-thiazol-2-ylidene)-acyethyl]hydrazono]-ethyl]phenyl]-2-cyanoacetamide 18c. Brown crystals, yield (54%), mp > 300°C; νstretch/cm⁻¹ (KBr) 3315–3208 (NH), 2220 (CN), 1630 (CO); δH = 2.32 (s, 3H, CH3), 6.73 (s, 1H, CH), 6.81–7.71 (m, 21H, Ar and CH), 7.75–7.81 (m, 4H, Ar), 10.18 (s, 1H, NH), 10.8 (s, 1H, NH). Anal. Calcd for C44H31N7O2S2 (753.89): C, 70.66; H, 4.14; N, 13.01; S, 8.51. Found: C, 70.84; H, 4.32; N, 12.78; S, 8.21. Found: C, 70.30; H, 4.14; N, 13.01; S, 8.51. Found: C, 70.84; H, 4.32; N, 12.78; S, 8.21.

2-Cyano-N-[4-[[2-cyano-2-(3-phenyl-4-(4-methylphenyl)thiazol-2(3H)-ylidene)-acetyl]hydrazono]-ethyl]phenyl]-2-(3,4-diphenyl-3H-thiazol-2-ylidene)-acetamide 18b. Brown crystals, yield (61%), mp > 300°C; νstretch/cm⁻¹ (KBr) 3338–3222 (NH), 2238 (CN), 1723 (CO); δH = 2.29 (s, 3H, CH3), 2.38 (s, 6H, 2CH3), 7.012 (s, 1H, CH), 7.24–7.87 (m, 19H, Ar and CH), 8.03–8.79 (m, 4H, Ar), 10.45 (s, 1H, NH), 10.91 (s, 1H, NH). Anal. Calcd for C46H35N7O2S2 (781.95): C, 70.66; H, 4.14; N, 13.01; S, 8.51. Found: C, 70.84; H, 4.32; N, 12.78; S, 8.41%.

References and Notes