Synthesis of Some New 1-Acyl-5-aryl-3-(5-methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-4,5-dihydro-1*H*-pyrazole

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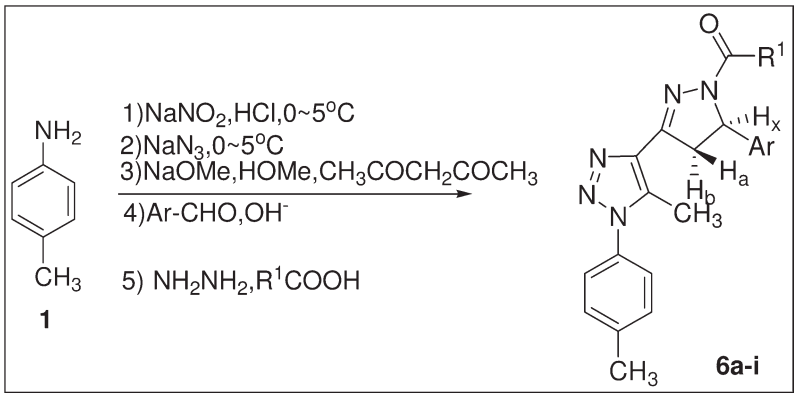

Some new compounds (*E*)-3-aryl-1-(5-methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-prop-2-en-1-ones **5a–e** were prepared by 1-(5-methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-ethanone and various aromatic aldehydes. Then one pot reaction was happened by compounds **5a–e** with hydrazine hydrate in acetic acid or propionic acid, respectively, to give the title compounds 1acyl-5-aryl-3-(5-methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-4,5-dihydro-1*H*-pyrazoles **6a–i**. All structures were established by MS, IR, CHN, ^{1}H-NMR and ^{13}C-NMR spectral data.

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INTRODUCTION

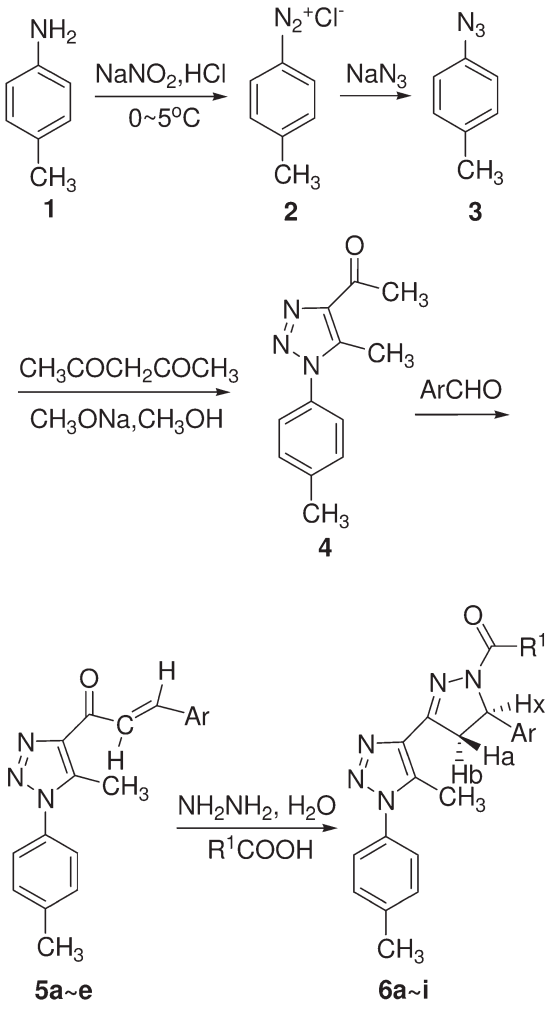
Among infectious diseases, tuberculosis (TB) is considered to be one of the most dangerous chronic communicable diseases with over 2 million casualties annually in the world [1]. At the same time, the emergence of AIDS which reduced emphasis on tuberculosis control programs contributed to the disease's resurgence in industrialized countries [2]. Resistance of *Mycobacterium tuberculosis* (MTB) strains to antimycobacterial agents is also an increasing problem worldwide [3–5]. However, the key problem in the chemotherapy of tuberculosis is no new powerful anti-TB drugs with new mechanism of action have been developed in recent years. Thus, the exploitation of new anti-TB drugs that are effective against a persistent MTB infection is urgently desired. Literature survey reveals that pyrazoline derivatives possess the various biological activities such as anti-bacterial and anti-fungal [6], anti-diabetic [7], anti-inflammatory [8], and are also active against many mycobacterials [9–13]. Therefore, we have synthesized some new (*E*)-3-aryl-1-(5-methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-prop-2-en-1-ones and 1-acyl-5-aryl-3-(5-methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-4,5-dihydro-1*H*-pyrazoles and the steps are shown in Scheme 1. All structures are established by MS, IR, CHN, ^{1}H-NMR, and ^{13}C-NMR spectral data.

RESULTS AND DISCUSSION

The compounds (*E*)-3-aryl-1-(5-methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-prop-2-en-1-one **5a–e** were prepared by the Claisen-Schmidt condensation reaction of 1-(5-methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-ethanone and some aromatic aldehydes. The target compounds 1-acyl-5-aryl-3-(5-methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-4,5-dihydro-1*H*-pyrazoles **6a–e** were prepared from **5a–e**, hydrazine and acetic/propionic acid by sequence reactions involving in intermolecular conjugated addition, hydrazone formation and *N*-acylation [14].

In their IR spectral, $\nu_{c=o}$ vibration bands are at 1648–1666 cm^{-1} in **5a–e**, and 1654–1665cm^{-1} in **6a–i**. Moreover, $\nu_{C=N}$

Scheme 1



5a Ar=C_6H_5 ; **5b** Ar=3-ClC_6H_4 ; **5c** Ar=3-$CH_3OC_6H_4$; **5d** Ar=2-furanyl ; **5e** Ar=4-$(CH_3)_2NC_6H_4$; **6a** Ar=C_6H_5 ; R^1=CH_3 ; **6b** Ar=C_6H_5 ; R^1=C_2H_5 ; **6c** Ar= 3-ClC_6H_4 ; R^1=CH_3 ; **6d** Ar=3-ClC_6H_4 ; R^1=C_2H_5 ; **6e** Ar= 3-$CH_3OC_6H_4$; R^1=CH_3 ; **6f** Ar=3-$CH_3OC_6H_4$; R^1=C_2H_5 ; **6g** Ar=2-furanyl ; R^1=CH_3 ; **6h** Ar=4-$(CH_3)_2NC_6H_4$; R^1=CH_3 ; **6i** Ar=4-$(CH_3)_2NC_6H_4$; R^1= C_2H_5.

stretching bands are shown in the region 1592–1611 cm^{-1} in **5a–e** and 1571–1605 cm^{-1} in the pyrazoline ring **6a–i** [15–18]. The ^{1}H-NMR spectrum of **6a** showed a singlet signal at δ 2.35 ppm corresponding to the acetyl group in accordance with the reported data [19]. The chemical shifts of H_a and H_b protons are discernible in the regions δ 3.40–3.55 and 3.70–3.95 ppm as double doublets, respectively, in the pyrazoline ring. The H_X proton is observed at δ 5.45–5.62 ppm as double doublets (J_{ab} = 4.50–4.80 Hz, J_{bx} = 18.2–18.6 Hz, J_{xa} = 11.5–11.7 Hz).

In summary, a series of pyrazoline derivatives were conveniently prepared by a simple synthetic method from aromatic amine. Its structure was characterized by MS, IR, CHN, ^{1}H-NMR, and ^{13}C-NMR spectral data.

EXPERIMENTAL

All melting points were determined on a XT4-100x Kofler melting point apparatus and are uncorrected. IR spectra were obtained in KBr discs on a Shimadzu IR-435 spectrometer. MS were performed on a HP-5988A spectrometer (EI at 70 eV). ^{1}H-NMR and ^{13}C-NMR spectroscopy ($CDCl_3$) was recorded on Avance Mercury plus-300 instrument with TMS as an internal standard. Elemental analysis was carried out on a Yanaco CHN Corder MT-3 analyzer.

1-Azido-4-methylbenzene 3. Compound **3** was prepared by the method reported in the literature [20,21].

1-(5-Methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-ethanone 4. Compound **4** was prepared by the reaction of 1-azido-4-methylbenzene **3** with pentane-2,4-dione [22]. A cold solution of CH_3ONa (0.23 mol, in 120 mL absolute methanol) was added to the mixture of pentane-2,4-dione (17 mL) and 1-azido-4-methylbenzene (about 0.15 mol) and stirred for 1 h at 0–5°C. Then the mixture was heated under reflux on an oil-bath for 10 h. Finally, the mixture was acidified with concentrated hydrochloric acid. Compound **4** was separated and crystallized from methanol. Yield is 52.6%, mp 106–107°C ^{1}H-NMR ($CDCl_3$): 2.45 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 2.73 (s, 3H, CH_3CO), 7.343 (s, 4H, Ar).

General method for the synthesis of (*E*)-3-aryl-1-(5-methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-prop-2-en-1-one 5a–e. A mixture of the aromatic aldehyde (0.012 mol) and compound **4** (0.01 mol) dissolved in ethanol (70 mL) was added slowly to an aqueous solution of potassium hydroxide (0.0128 mol) in water (10 mL) [21,23]. The reaction mixture was stirred in crushed-ice bath for 2 h, stirred at 20–25°C for 4 h. The mixture was filtrated and the solid was washed with cold water and cold alcohol. The product was crystallized from ethanol to give **5a–e**. All the products were new compounds, which were characterized by IR, ^{1}H-NMR, and mass spectral data.

(E)-1-(5-Methyl-1-p-tolyl-1H-1,2,3-triazol-4-yl)-3-phenylprop-2-en-1-one 5a. White powder, yield 90%, mp 173–175°C (Lit 178–180°C) [21].

(E)-3-(3-Chlorophenyl)-1-(5-methyl-1-p-tolyl-1H-1,2,3-triazol-4-yl)-2-en-1-one 5b. White powder, yield 88%, mp 144–146°C, IR (KBr, cm^{-1}): 1664 (C=O), 1611 (C=N), 979, 997, 1034, 1074, 1110 (N—N=N), 899, 855, 838, 815, 789, 684 (Ph-H); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.479 (s, 3H, CH_3), 2.666 (s, 3H, Ar_1-CH_3), 7.342–7.410 (m, 6H, Ar_1 and Ar_2-H), 7.581–7.608 (m, 1H Ar_2-H), 7.721 (s, 1H, Ar_2-2-H), 7.809–7.862 (d, 1H, J = 15.6Hz, C=CH—CO), 8.080–8.132 (d, 1H, J = 15.6Hz, CH=C—CO); ^{13}C-NMR δ 183.98, 151.02, 143.72, 141.73, 140.36, 138.65, 136.72, 134.83, 132.74, 130.18, 130.06, 128.31, 126.83, 125.03, 124.18, 21.23, 10.29; MS (EI, 70 eV) (*m/z*, %) 337 ($M^{+\cdot}$, 1.3%), 339 (M+2, 0.4), 281 (21.9), 228 (30.0), 165 (44.2), 132 (95.0), 91 (100), 65 (71.3). Anal. Calcd for $C_{19}H_{16}ClN_3O$: C, 67.56; H, 4.77; N, 12.44; Found: C, 67.86; H, 4.90; N, 12.02.

(E)-3-(3-Methoxyphenyl)-1-(5-methyl-1-p-tolyl-1H-1,2,3-triazol-4-yl)-2-en-1-one 5c. White powder, yield 91%, mp 177–

178°C, IR(KBr, cm^{-1}): 1657 (C=O), 1592 (C=N), 974, 995, 1011, 1033, 1113 (N—N=N), 813, 733 (Ph-H); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.476 (s, 3H, CH_3), 2.661 (s, 3H, Ar_1-CH_3), 3.877 (s, 3H, O—CH_3), 6.966 (s, 1H, Ar_2-2-H), 7.241–7.270 (d, 2H, J = 8.7Hz, Ar_2-4,6-H), 7.323–7.352 (d, 1H, J = 8.7Hz, Ar_2-5-H), 7.368 (s, 4H, Ar_1-H), 7.870–7.923 (d, 1H, J = 15.9Hz, C=CH—CO), 8.068–8.120 (d, 1H, J = 15.9Hz, CH=C—CO); ^{13}C-NMR δ 184.26, 159.83, 143.82, 143.48, 140.29, 138.50, 136.21, 132.77, 130.15, 129.78, 125.01, 123.09, 121.65, 116.73, 112.91, 55.30, 21.19, 10.59; MS (EI, 70 eV) (*m/z*, %): 333 ($M^{+\cdot}$, 12.6), 334 (M+1, 4.3), 304 (4.0), 277 (17.2), 262 (23.6), 247 (6.2), 224 (56.9), 161 (69.9), 145 (31.3), 132 (60.0), 91 (100), 65 (67.0). Anal. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.60; Found: C, 71.88; H, 5.64; N, 12.28.

(E)-3-(Furan-2-yl)-1-(5-methyl-1-p-tolyl-1H-1,2,3-triazol-4-yl)-2-en-1-one 5d. White powder, yield 92%, mp 188–189°C, IR (KBr, cm^{-1}): 1661 (C=O), 1598 (C=N), 1036, 1013, 993, 976 (N—N=N), 877, 860, 822, 771, 698 (Ph-H); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.472 (s, 3H, CH_3), 2.650 (s, 3H, Ar_1-CH_3), 6.512–6.529 (dd, 1H, J = 1.8Hz, J = 3.3Hz furan-4), 6.770–6.781 (d, 1H, J = 3.3Hz, furan-3), 7.333- 7.362 (d, 2H, J = 8.7Hz, Ar_1-3,5-H), 7.362–7.399 (d, 2H, J = 8.7Hz, Ar_1-2,6-H), 7.552–7.556 (d, 1H, J = 1.8Hz, furan-5), 7.671–7.723 (d, 1H, J = 15.6Hz, C=CH—CO), 7.980–7.927 (d, 1H, J = 15.6Hz, CH=C—CO); ^{13}C-NMR δ 184.16, 151.79, 145.01, 143.83, 140.22, 138.29, 132.83, 130.13, 129.60, 125.02, 120.86, 115.89, 112.52, 21.20, 10.25; MS (EI, 70 eV) (*m/z*, %): 293 ($M^{+\cdot}$, 10.9), 294 (M+1, 2.5), 265 (2.1), 237 (17.4), 222 (2.6), 210 (8.1), 132 (57.3), 91 (64.9), 65 (100), 51 (32), 39 (52). Anal. Calcd for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33; Found: C, 69.45; H, 5.33; N, 14.52.

(E)-3-[4-(Dimethylamino)phenyl]-1-(5-methyl-1-p-tolyl-1H-1,2,3–triazol-4-yl)prop-2-en-1-one 5e. White powder, yield 86%, mp 210–212°C, IR (KBr, cm^{-1}): 1648 (C=O), 1611 (C=N), 1034, 1017, 996, 981 (N—N=N), 891, 819, 798, 703 (Ph-H); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.472 (s, 3H, CH_3), 2.657 (s, 3H, Ar_1-CH_3), 3.056 (s, 6H, $N(CH_3)_2$), 6.696–6.725 (d, 2H, J = 8.7Hz, Ar_2-3,5-H), 7.366 (b, 4H, Ar_1-2,3,5,6-H), 7.626–7.657 (d, 2H, J = 8.7Hz, Ar_2-2,6-H), 7.911 (s, 2H, CH=CH); ^{13}C-NMR δ 184.35, 151.97, 144.48, 144.22, 140.10, 137.90, 132.99, 130.70, 130.11, 126.57, 125.06, 117.76, 111.71, 40.08, 21.22, 10.29; MS (EI, 70 eV) (*m/z*, %): 346 ($M^{+\cdot}$, 11.6), 347 (M+1 1.4), 318 (3.4), 290 (5.2), 275 (2.3), 237 (5.0), 174 (8.2), 158 (7.4), 144 (16.1), 132 (100), 91 (63.5), 65 (28.9), 44 (42.1). Anal. Calcd for $C_{21}H_{22}N_4O$: C, 72.81; H, 6.40; N, 16.17; Found: C, 72.25; H, 6.55; N, 15.97.

General method for the synthesis of 1-acyl-5-aryl-3-(5-methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-4,5-dihydro-1*H*-pyrazoles 6a–i. A mixture of compound **5** (0.01 mol), hydrazine hydrate (0.03 mol), acetic acid or propionic acid (50 mL) was refluxed for 3 h, then poured into crushed-ice [24]. The precipitate was separated by filtration, washed with water and the crude products **6a–i** were obtained, which were crystallized from ethanol. All the products were new compounds.

1-Acetyl-3-(5-methyl-1-p-tolyl-1H-1,2,3-triazol-4-yl)-5-phenyl-4,5-dihydro-1H-pyrazole 6a. White powder, yield 67.5%, mp 183–185°C, IR(KBr, cm^{-1}): 1655 (C=O), 1571 (C=N), 1090, 1031, 999, 956 (N—N=N), 870, 822, 750, 700 (Ph-H); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.389 (s, 3H, $COCH_3$), 2.473 (s, 3H, CH_3), 2.63 (s, 3H, Ar_1-CH_3), 3.476–3.552 (dd, 1H, $J_{A,X}$ = 4.8Hz, $J_{A,B}$ = 18.6Hz, H_A), 3.903–4.005 (dd, 1H, $J_{B,X}$ = 11.7Hz, $J_{A,B}$ = 18.6Hz, H_B), 5.560–5.615 (dd, 1H, $J_{A,X}$ = 4.8Hz, $J_{B,X}$ = 11.7Hz, H_X), 7.235–7.401 (m, 9H, Ar_1-H and Ar_2-H); ^{13}C-NMR δ 168.46, 149.38, 141.44, 140.09, 137.79, 133.34, 133.05, 130.11, 128.71, 127.50, 125.53, 124.84, 58.77, 43.27, 21.84, 21.16, 10.33; MS (EI, 70 eV) (*m/z*, %): 359 ($M^{+\cdot}$, 6.3), 360 (M+1, 1.3), 331 (0.25), 288 (3.4), 260 (3.6), 244 (2.9), 212 (4.9), 184 (3.2), 169 (4.7), 145 (6.9), 128 (6.2), 115 (6.2), 104 (3.4), 91 (27.1), 43 (100). Anal. Calcd for $C_{21}H_{21}N_5O$: C, 70.17; H, 5.89; N, 19.48; Found: C, 69.80; H, 5.78; N, 19.87.

3-(5-Methyl-1-p-tolyl-1H-1,2,3-triazol-4-yl)-5-phenyl-1-propionyl-4,5-dihydro-1H-pyrazole 6b. White powder, yield 56%, mp 116–118°C, IR (KBr, cm^{-1}): 1654 (C=O), 1605 (C=N), 1079, 1038, 1000, 978, 953 (N—N=N), 847, 822, 763, 700 (Ph-H); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.170–1.220 (t, 3H, J = 7.5Hz, $COCH_2CH_3$), 2.476 (s, 3H, CH_3), 2.633 (s, 3H, Ar_1-CH_3), 2.732–2.807 (q, 2H, J = 7.5Hz, $COCH_2CH_3$), 3.459–3.537 (dd, 1H, $J_{A,X}$ = 4.8Hz, $J_{A,B}$ = 18.6Hz, H_A), 3.891–3.992 (dd, 1H, $J_{B,X}$ = 11.7Hz, $J_{A,B}$ = 18.6Hz, H_B), 5.543–5.599 (dd, 1H, $J_{A,X}$ = 4.8Hz, $J_{B,X}$ = 11.7Hz, H_X), 7.117–7.402 (m, 9H, Ar_1-H and Ar_2-H); ^{13}C-NMR δ 171.46, 149.44, 143.43, 143.17, 140.47, 134.07, 130.80, 130.56, 129.30, 127.66, 125.78, 125.52, 59.48, 43.87, 27.85, 21.01, 10.39, 8.88; MS (EI, 70 eV) (*m/z*, %): 373 ($M^{+\cdot}$, 7.9), 345 (0.23), 289 (7.9), 260 (5.4), 244 (3.3), 212 (5.6), 184 (4.4), 169 (5.1), 157 (3.5), 91 (37.8), 77 (9.7), 57 (100). Anal. Calcd for $C_{22}H_{23}N_5O$: C, 70.76; H, 6.21; N, 18.75; Found: C, 70.88; H, 6.18; N, 18.86.

1-Acetyl-5-(3-chlorophenyl)-3-(5-methyl-1-p-tolyl-1H-1,2,3-triazol-4-yl)-4,5-dihydro-1H-pyrazole 6c. White powder, yield 86%, mp 158–159°C, IR(KBr, cm^{-1}): 1660 (C=O), 1595 (C=N), 1092, 1037, 1002, 973, 960 (N—N=N), 867, 822, 786, 693 (Ph-H); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.400 (s, 3H, $COCH_3$), 2.478 (s, 3H, CH_3), 2.637 (s, 3H, Ar_1-CH_3), 3.441–3.518 (dd, 1H, $J_{A,X}$ = 4.5Hz, $J_{A,B}$ = 18.6Hz, H_A), 3.913–4.014 (dd, 1H, $J_{B,X}$ = 11.7Hz, $J_{A,B}$ = 18.6Hz, H_B), 5.519–5.573 (dd, 1H, $J_{A,X}$ = 4.5Hz, $J_{B,X}$ = 11.7Hz, H_X), 7.148–7.177 (dd, 1H, J_1 = 1.8Hz, J_2 = 6.9Hz, Ar_2-5-H), 7.204 (m, Ar_2-6-H), 7.241–7.254 (q, 1H, J = 1.8Hz, Ar_2-4-H), 7.261 (m, 1H, Ar_2-2-H), 7.341–7.360 (d, 2H, J = 5.7Hz, Ar_1-3,5-H), 7.379–7.408 (d, 2H, J = 5.7Hz, Ar_1-2,6-H); ^{13}C-NMR δ 168.58, 149.34, 143.53, 140.19, 137.63, 134.62, 133.51, 133.05, 130.17, 130.09, 127.81, 125.63, 124.89, 124.02, 58.32, 43.22, 21.84, 21.21, 10.38; MS (EI, 70 eV) (*m/z*, %): 393 ($M^{+\cdot}$, 4.2), 395 (M+2, 1.3), 365 (1.9), 323 (2.6), 294 (1.9), 258 (1.4), 244 (1.5), 91 (22.9), 43 (100). Anal. Calcd for $C_{21}H_{20}ClN_5O$: C, 64.04; H, 5.12; N, 17.78; Found: C, 63.89; H, 5.32; N, 17.53.

5-(3-Chlorophenyl)-3-(5-methyl-1-p-tolyl-1H-1,2,3-triazol-4-yl)-1-propionyl-4,5-dihydro-1H-pyrazole 6d. Orange yellow powder, yield 83.5%, mp 110–112°C, IR (KBr, cm^{-1}): 1663 (C=O), 1595 (C=N), 1080, 1039, 1002, 976 (N—N=N), 860, 819, 784, 691 (Ph-H); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.148–1.197 (t, 3H, J = 7.5Hz, $COCH_2CH_3$), 2.476 (s, 3H, CH_3), 2.632 (s, 3H, Ar_1-CH_3), 2.745–2.803 (q, 2H, J = 7.5Hz, $COCH_2CH_3$), 3.431–3.490 (dd, 1H, $J_{A,X}$ = 4.8Hz, $J_{A,B}$ = 18.6Hz, H_A), 3.906–3.981 (dd, 1H, $J_{B,X}$ = 11.7Hz, $J_{A,B}$ = 18.6Hz, H_B), 5.503–5.545 (dd, 1H, $J_{A,X}$ = 4.8Hz, $J_{B,X}$ = 11.7Hz, H_X), 7.144–7.167 (dd, 1H, J_1 = 1.6Hz, J_2 = 8.7Hz, Ar_2-5-H), 7.201–7.197 (d, 1H, J = 1.6Hz, Ar_2-6-H), 7.233–7.247 (dd, 1H, J_1 = 1.6HZ, J_2 = 4Hz, Ar_2-4-H), 7.262 (s, 1H, Ar_2-2-H), 7.344–7.366 (d, 2H, J = 8.8Hz, Ar_1-3,5-H), 7.378–7.400 (d, 2H, J = 8.8Hz, Ar_1-2,6-H); ^{13}C-NMR δ 171.92, 149.02, 143.67, 140.05, 137.59, 134.45, 133.38, 132.95, 130.06, 130.00, 127.63, 125.57, 124.76, 123.91, 58.37, 43.89, 27.39, 21.09, 10.28, 8.70; MS (EI,

70 eV) (*m/z*, %): 407 ($M^{+\cdot}$, 5.5), 409(M+2, 1.5), 379 (2.3), 323 (9.8), 294 (4.8), 212 (10.3), 145 (10.3), 91 (30.2), 57 (100), 45 (78.9). Anal. Calcd for $C_{22}H_{22}ClN_5O$: C, 64.78; H, 5.44; N, 17.17; Found: C, 64.89; H, 5.51; N, 16.89.

1-Acetyl-5-(3-methoxyphenyl)-3-(5-methyl-1-p-tolyl-1H-1,2,3-triazol-4-yl)-4,5-dihydro-1H-pyrazole 6e. Gray powder, yield 59.5%, mp 185–187°C, IR(KBr, cm^{-1}): 1654 (C=O), 1583 (C=N), 1112, 1088, 1025, 1003, 959 (N—N=N), 875, 823 (Ph-H); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.390 (s, 3H, $COCH_3$), 2.466 (s, 3H, CH_3), 2.624 (s, 3H, Ar_1-CH_3), 3.451–3.529 (dd, 1H, $J_{A,X}$ = 4.8Hz, $J_{A,B}$ = 18.2Hz, H_A), 3.785(s, 3H, O—CH_3), 3.886–3.988 (dd, 1H, $J_{B,X}$ = 11.7Hz, $J_{A,B}$ = 18.2Hz, H_B), 5.526–5.580 (dd, 1H, $J_{A,X}$ = 4.8Hz, $J_{B,X}$ = 11.7Hz, H_X), 6.776–6.790 (m, 2H, *J* = 2.1Hz, Ar_2-4,6-H), 6.825–6.850 (d, 1H, *J* = 7.5Hz, Ar_2-5-H), 7.212–7.267 (dd, 1H, *J* = 7.5Hz, 2.1Hz, Ar_2-2-H), 7.333–7.396 (q, 4H, *J* = 8.1Hz, Ar_1-H); ^{13}C-NMR δ 168.50, 159.86, 149.45, 143.16, 140.16, 137.85, 133.39, 133.14, 130.18, 129.91, 124.92, 117.76, 112.57, 111.59, 58.78, 55.17, 43.37, 21.90, 21.24, 10.41; MS (EI, 70 eV) (*m/z*, %): 389 ($M^{+\cdot}$, 5.1), 361 (0.4), 212 (2.4), 184 (3.3), 169 (5.2), 145 (10.1), 121 (16.2), 91 (18.4), 65 (12.2), 43 (100). Anal. Calcd for $C_{22}H_{23}N_5O_2$: C, 67.85; H, 5.95; N, 17.98; Found: C, 67.55; H, 5.78; N, 17.37.

5-(3-Methoxyphenyl)-3-(5-methyl-1-p-tolyl-1H-1,2,3-triazol-4-yl)-1-propionyl-4,5-dihydro-1H-pyrazole 6f. Light gray powder, yield 68.4%, mp 128–130°C, IR(KBr, cm^{-1}): 1659 (C=O), 1591 (C=N), 1034, 1002, 976 (N—N=N), 859, 825, 800, 741 (Ph-H); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.176–1.227 (t, 3H, *J* = 7.5Hz, $COCH_2CH_3$), 2.466 (s, 3H, CH_3), 2.622 (s, 3H, Ar_1-CH_3), 2.735–2.812 (q, 2H, *J* = 7.5Hz, $COCH_2CH_3$), 3.433–3.509 (dd, 1H, $J_{A,X}$ = 4.8Hz, $J_{A,B}$ = 18.2Hz, H_A), 3.779(s, 3H, O—CH_3), 3.865–3.972 (dd, 1H, $J_{B,X}$ = 11.7Hz, $J_{A,B}$ = 18.2Hz, H_B), 5.508–5.563 (dd, 1H, $J_{A,X}$ = 4.8Hz, $J_{B,X}$ = 11.7Hz, H_X), 6.768–6.790(m, 2H, *J* = 2.2Hz, Ar_2-4,6-H), 6.819–6.845 (d, 1H, *J* = 7.8Hz, Ar_2-5-H), 7.206–7.263 (dd, 1H, *J* = 7.8Hz, 2.2Hz, Ar_2-2-H), 7.331–7.394 (q, 4H, *J* = 8.1Hz, Ar_1-H); ^{13}C-NMR δ 171.85, 159.73, 149.11, 143.30, 140.02, 137.81, 133.25, 133.02, 130.06, 129.79, 124.79, 117.65, 112.49, 111.38, 58.81, 55.01, 43.04, 27.46, 21.11, 10.29, 8.81; MS (EI, 70 eV) (*m/z*, %): 403 ($M^{+\cdot}$, 12.9), 404 (M+1, 3.1), 318 (6.8), 290 (4.7), 212 (7.3), 184 (5.0), 169 (7.1), 145 (21.3), 121 (43.6), 91 (49.6), 57 (100). Anal. Calcd for $C_{23}H_{25}N_5O_2$: C, 68.47; H, 6.25; N, 17.36; Found: C, 68.64; H, 6.37; N, 17.02.

1-Acetyl-5-(furan-2-yl)-3-(5-methyl-1-p-tolyl-1H-1,2,3-triazol-4-yl)-4,5-dihydro-1H-pyrazole 6g. Orange yellow powder, yield 56%, mp 163–165°C, IR(KBr, cm^{-1}): 1670 (C=O), 1592 (C=N), 1071, 1035, 1004, 977, 959 (N—N=N), 854, 821, 757, 697 (Ph-H); ^{1}H-NMR (300 MHz, $CDCl_3$), δ 2.354 (s, 3H, $COCH_3$), 2.474 (s, 3H, CH_3), 2.608 (s, 3H, Ar_1-CH_3), 3.771–3.798 (d, 2H, *J* = 8.1Hz, furan-3,5), 5.651–5.705 (t, 1H, *J* = 8.1Hz, furan-4), 6.323–6.350 (d, 2H, *J* = 8.1Hz, Ar_1-3,5-H), 7.265–7.370 (b, 5H, Ar_2-H and Ar_1-2,6-H); ^{13}C-NMR δ 168.99, 152,36, 149.96, 142.32, 140.52, 138.13, 133.81, 133.49, 130.55, 125.29, 110.80, 107.95, 52.62, 39.64, 22.27, 21.59, 10.74; MS (EI, 70 eV) (*m/z*, %): 349 ($M^{+\cdot}$, 9.15), 350 (M+1, 2.2), 279 (10.5), 261 (7.0), 220 (5.4), 191 (5.7), 169 (6.5), 145 (6.8), 135 (9.8), 91 (22.9), 43 (100). Anal. Calcd for $C_{19}H_{19}N_5O_2$: C, 65.32; H, 5.48; N, 20.04; Found: C, 65.88; H, 5.63; N, 19.87.

1-Acetyl-5-(4-dimethylaminophenyl)-3-(5-methyl-1-p-tolyl-1H-1,2,3-triazol-4-yl)-4,5-dihydro-1H-pyrazole 6h. White powder, yield 74%, mp 162–164°C, IR (KBr, cm^{-1}): 1660 (C=O), 1576 (C=N), 1092, 1063, 1039, 1003 (N—N=N), 868, 818 (Ph-H); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.353 (s, 3H, $COCH_3$), 2.473 (s, 3H, CH_3), 2.626 (s, 3H, Ar_1-CH_3), 2.918 (s, 6H, $N(CH_3)_2$), 3.492–3.568 (dd, 1H, $J_{A,X}$ = 4.5Hz, $J_{A,B}$ = 18.3Hz, H_A), 3.845–3.946 (dd, 1H, $J_{B,X}$ = 11.7Hz, $J_{A,B}$ = 18.3Hz, H_B), 5.489–5.542 (dd, 1H, $J_{A,X}$ = 4.8Hz, $J_{B,X}$ = 11.7 Hz, H_X), 6.666–6.694 (d, 2H, *J* = 8.4Hz, Ar_2-3,5-H), 7.137–7.166 (d, 2H, *J* = 8.4Hz, Ar_2-2,6-H), 7.339–7.367 (d, 2H, *J* = 8.4Hz, Ar_1-3,5-H), 7.375–7.403 (d, 2H, *J* = 8.4Hz, Ar_1-2,6-H); ^{13}C-NMR δ 168.35, 149.94, 149.42, 140.02, 137.95, 133.20, 133.08, 130.08, 129.30, 126.68, 124.83, 112.56, 58.37, 42.94, 40.47, 21.90, 21.15, 10.33; MS (EI, 70 eV) (*m/z*, %): 402 ($M^{+\cdot}$, 1.57), 279 (5.14), 261 (37.4), 220 (24.7), 191 (35.9), 135 (58.3), 9 1(19.7), 57 (100). Anal. Calcd for $C_{23}H_{26}N_6O$: C, 68.63; H, 6.51; N, 20.88; Found: C, 68.45; H, 6.64; N, 20.25.

5-(4-Dimethylaminophenyl)-3-(5-methyl-1-p-tolyl-1H-1,2,3-triazol-4-yl)-1-propionyl-4,5-dihydro-1H-pyrazole 6i. Orange yellow powder, yield 79%, mp 141–143°C, IR(KBr, cm^{-1}): 1665 (C=O), 1571 (C=N), 1095, 1064, 1040, 1002, 978 (N—N=N), 852, 818 (Ph-H); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.173 (t, 3H, *J* = 5.4Hz, $COCH_2CH_3$), 2.473 (s, 3H, CH_3), 2.622 (s, 3H, Ar_1-CH_3), 2.735 (q, 2H, *J* = 5.4Hz, $COCH_2CH_3$), 2.923 (s, 6H, $N(CH_3)_2$), 3.481–3.544 (dd, 1H, $J_{A,X}$ = 4.5Hz, $J_{A,B}$ = 18.3Hz, H_A), 3.839–3.943 (dd, 1H, $J_{B,X}$ = 11.7Hz, $J_{A,B}$ = 18.3Hz, H_B), 5.474–5.515 (dd, 1H, $J_{A,X}$ = 4.5Hz, $J_{B,X}$ = 11.7Hz, H_X), 6.658–6.686 (d, 2H, *J* = 8.4Hz, Ar_2-3,5-H), 7.131–7.159 (d, 2H, *J* = 8.4Hz, Ar_2-2,6-H), 7.339–7.367 (d, 2H, *J* = 8.4Hz, Ar_1-3,5-H), 7.373–7.401 (d, 2H, *J* = 8.4Hz, Ar_1-2,6-H); ^{13}C-NMR δ 171.76, 149.95, 149.17, 140.04, 138.13, 133.15, 130.12, 129.58, 126.78, 124.89, 112.63, 58.58, 42.73, 40.53, 27.57, 21.20, 10.38, 8.86; MS (EI, 70 eV) (*m/z*, %): 416 ($M^{+\cdot}$, 7.94), 417 (M+1, 2.07), 218 (23.9), 203 (24.6), 189 (57.5), 134 (100), 91 (44.5), 57 (78.7). Anal. Calcd for $C_{24}H_{28}N_6O$: C, 69.21; H, 6.78; N, 20.18; Found: C, 69.45; H, 6.87; N, 19.84.

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