Synthesis of (3,5-Aryl/methyl-1*H*-pyrazol-1-yl)-(5-arylamino-2*H*-1,2,3-triazol-4-yl)methanone

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Some new (3,5-aryl/methyl-1*H*-pyrazol-1-yl)-(5-arylamino-2*H*-1,2,3-triazol-4-yl)methanones were synthesized and characterized by ^{1}H NMR, ^{13}C NMR, MS, IR spectra data and elemental analyses or high resolution mass spectra (HRMS). During the procedure, Dimroth rearrangement was used in this synthesis.

Keywords: 1*H*-Pyrazole; 2*H*-1,2,3-Triazole; Methanone; Synthesis; Dimroth rearrangement.

INTRODUCTION

The synthesis and research of biological activities of triazole derivatives have attracted much attention in recent years because a set of valuable pharmacological properties such as anti-inflammatory, anti-rhenmatic, analgesic and anti-psychotic activities. In addition, compounds of the pyrazole series have demonstrated their usefulness in pathological states, and cardiovascular and gastrointestinal disorders.[1-3] Based on these literature studies, the synthesis and research of biological activities of novel pyrazole derivatives are of great significance. At present, the heterocyclic derivatives with triazole and pyrazole nucleuses are being developed in good time.[4-6] In recent years, we have reported synthesis of some 7*H*-*s*-triazolo[3,4-b]-1,3,4-thiadiazine derivatives,[7] *N*-[1-(2,5-dichlorophenyl)-5-methyl-1,2,3-triazol-4-yl]carbamic acid ester derivatives[8] and 3,6-bis(1,2,3-triazolyl)-*s*-triazolo[3,4-b]-1,3,4-thiadiazole derivatives.[9] Thanks to these, we have synthesized some new (3,5-aryl/methyl-1*H*-pyrazol-1-yl)-(5-arylamino-2*H*-1,2,3-triazol-4-yl)methanones **6a-j**, **7a-d** in 60-96% yield. The route of these syntheses is in Scheme I.

The crystal structure of (5-methyl-3-phenyl-1*H*-pyrazol-1-yl)-[5-(*p*-tolylamino)-2*H*-1,2,3-triazol-4-yl]methanone **6b** was researched by single-crystal X-ray diffraction. The ORTEP drawing of the title compound **6b** showing the atom numbering scheme is shown in Fig. 1.

RESULTS AND DISCUSSION

The new [(5-arylamino)-2*H*-1,2,3-triazol-4-yl]-(5-methyl-3-substituted-1*H*-pyrazol-1-yl)-methanones **6a-e** and [(5-arylamino)-2*H*-1,2,3-triazol-4-yl]-(3-methyl-5-substituted-1*H*-pyrazol-1-yl)-methanones **7a-d** have been synthesized by reaction of benzoylacetone and compounds **5a-e** which were prepared by hydrazinolysis and Dimroth rearrangement of ethyl 5-amino-1-aryl-1*H*-1,2,3-triazol-4-carboxylate and hydrazine hydrate. They were separated completely by chromatographic column (silica gel, eluent for ethyl acetate: petroleum ether = 1:6) because of their distinction of polarity. During reaction of compound **5e** with benzoylacetone, product **6e** is primary. While acetylacetone reacts with compounds **5a-e**, products **6f-j** are

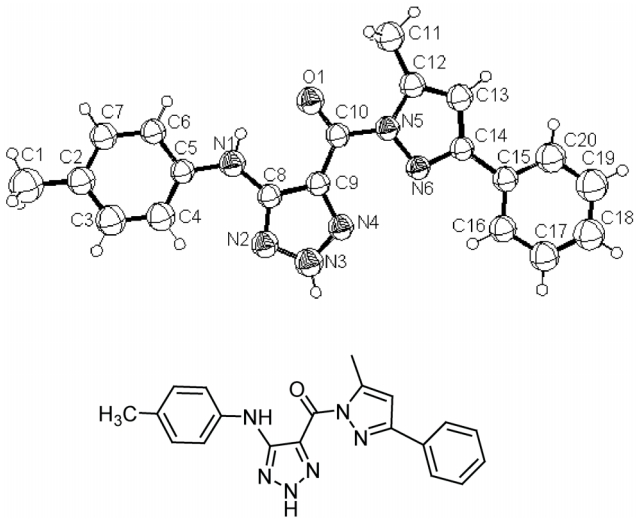
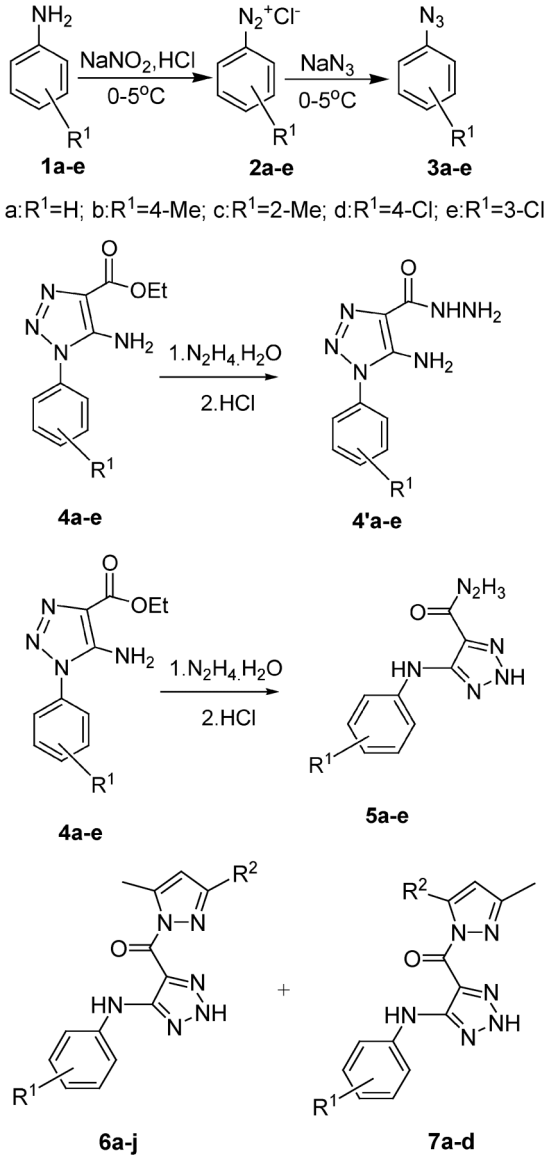


Fig. 1. ORTEP drawing of the title compound **6b** showing the atom numbering scheme.

Scheme I



given exclusively. To differentiate pairs of compounds **6a-e** and **7a-d**, compound **6b**' single-crystal structure and all of the compounds' ^{1}H NMR spectrum were performed. Actually, in the pyrazole ring of these compounds, chemical shifts of CH_3 at the 3- and 5-parts are different, one is in a range of 2.439-2.452 ppm, while the other is in an area of 2.770-2.794 ppm. 6b's correct structure is due to its crystal structure; consequently the 5-CH_3 chemical shift which is 2.782 ppm is determined. So we extrapolate that the 5-CH_3 chemical shift is in a range of 2.770-2.794 ppm and 3-CH_3 is in the region of 2.439-2.452 ppm. Finally, compounds **6a-e** and **7a-d** are distinguishable. In their ^{13}C NMR spectroscopy data of compounds **6a-e** and **7a-d**, chemical shift of 3-CH_3 in the pyrazole ring is at 13.80-13.95 ppm, and 5-CH_3 is in the region of 14.34-14.68 ppm.

The IR spectra data character of compounds **5a-e** are tip peaks at 3200-3450 and 1620-1660 cm^{-1} which could be found clearly. These peaks could be assigned respectively to NH or NH_2 and C=O. The vibration band of N-N=N is in the region 970-980 cm^{-1}. We investigated the MS spectra of **5a-e** and the results showed that compounds **5a-e** have weak molecular ion peaks.

The IR spectra data character of compounds **6a-j** and **7a-d** are tip peaks at 3300-3500 and 1640-1670 cm^{-1}. These peaks could be assigned respectively to NH and C=O. A chemical shift at 6.00-6.70 ppm can be assigned to the CH of the pyrazole ring, and usually the chemical shift of NH is at 8.40 ppm, but we cannot find the NH of the triazole ring. Further exploration is in progress.

We investigated the MS spectra of **6a-j** and **7a-d** and the results showed that compounds **6a-j** and **7a-d** have weak molecular ion peaks. While analyzing the cleavage fragments of the molecular ions, we found that the MS spectra of **6a-j** exhibit some important ion peaks at *m/z* 159, M-159, 97, M-97.

EXPERIMENTAL

All melting points are uncorrected and determined on an XT_4-100x microscopic melting point apparatus. IR spectra were obtained in KBr discs on a Nicolet NEXUS 670 FT-IR spectrometer. MS were performed on an HP-5988A spectrometer (EI at 70 eV). High resolution mass spectra (HRMS) were tested on Bruker Daltonics Apex2 47e ft-icr mass spectra apparatus. ^{1}H NMR spectroscopy ($CDCl_3$) was recorded on a Varian Mercury Plus-300 instrument with TMS as an internal standard. ^{13}C NMR spectroscopy was performed on a Bruker DRX-200 spectrometer. Elemental analyses were carried out on a Yanaco CHN Corder MT-3 analyzer.

Preparation of ethyl 5-amino-1-aryl-1*H*-1,2,3-triazol-4-carboxylates **4a-e** followed a method in the literature.[10-11]

Ethyl 5-amino-1-phenyl-1*H*-1,2,3-triazol-4-carboxylate 4a m.p. 125-126 °C (Lit.[10a] m.p. 124.5-125.5 °C)

Ethyl 5-amino-1-*p*-tolyl-1*H*-1,2,3-triazol-4-carboxylate 4b m.p. 151-152 °C (Lit.[10a] m.p. 152-153 °C)

Ethyl 5-amino-1-*o*-tolyl-1*H*-1,2,3-triazol-4-carboxylate 4c

Compound is white powder, m.p. 124-125 °C. ^{1}H

NMR ($CDCl_3$-*d*) (ppm), 1.426-1.473 (t, 3H, *J* = 7.2 Hz, CH_3), 2.163 (s, 3H, CH_3), 4.408-4.480 (q, 2H, *J* = 7.2 Hz, CH_2), 5.043 (b, 2H, NH_2), 7.296-7.321 (d, 1H, *J* = 7.5 Hz, Ar-H), 7.358-7.505 (m, 3H, Ar-H); MS *m/z*: 246 (M^+, 26.2), 247 (M+1, 4.0), 248 (M+2, 0.5), 201 (2.8), 172 (22.0), 157 (9.4), 145 (90.3), 118 (59.2), 91 (100). IR: 3366 (NH_2), 3289, 3223, 3173 (Ar-H), 2982, 2929 (CH_3), 1691 (s, C=O), 1639, 1571, 1514, 1410 (s, Ar or triazole ring), 974 (N=N-N) cm^{-1}. Anal. Calcd for $C_{12}H_{14}N_4O_2$: C, 58.53; H, 5.73; N, 22.75; Found: C, 58.40; H, 5.69; N, 22.62.

Ethyl 5-amino-1-(4-chlorophenyl)-1*H*-1,2,3-triazol-4-carboxylate 4d m.p. 165-166 °C (Lit.[10b] m.p. 165-167 °C)

Ethyl 5-amino-1-(3-chlorophenyl)-1*H*-1,2,3-triazol-4-carboxylate 4e m.p. 134-135 °C (Lit.[10b] m.p. 134-135 °C)

1. General synthesis of 5-arylamino-2*H*-1,2,3-triazol-4-carbohydrazides 5a-e

Ethyl 5-amino-1-arlyl-1*H*-1,2,3-triazol-4-carboxylate **4a-e** (0.003 mol) and hydrazine hydrate (0.012 mol) were added in a 100 mL flask; the mixture was heated at 80 °C for a hour, then refluxed in EtOH (25 mL) for 5-10 hours. The mixture was cooled to room temperature and the solid was filtered, washed with cool anhydrous ethanol and dried. The compound which Dimroth rearrangement hasn't happened was given. The filtrate was neutralized with diluted HCl, the solid was filtered and dried. Compounds **5a-e** were given.

5-Phenylamino-2*H*-1,2,3-triazol-4-carbohydrazide 5a

Compound is white powder, yield 41.3%, m.p. 179-180 °C. ^1H NMR (DMSO-d_6) (ppm), 4.509 (b, 2H, NH_2), 6.807-6.855 (t, 1H, *J* = 7.8 Hz, Ph), 7.157-7.210 (t, 2H, *J* = 7.8 Hz, Ph), 7.487-7.516 (d, 2H, *J* = 7.8 Hz, Ph), 8.444 (s, 1H, NH), 9.772 (b, 1H, NH); MS *m/z*: 218 (M^+, 93), 219 (M+1, 10.0), 187 (37), 161 (9), 132 (29), 104 (31), 77 (100). IR: 3370, 3320, 3248, 3206 (NH_2, -NH), 1625 (CO), 974 (N=N-N)cm^{-1}. Anal. Calcd for $C_9H_{10}N_6O$: C, 49.54; H, 4.62; N, 38.51; Found: C, 49.36; H, 4.51; N, 38.62.

5-*p*-Tolylamino-2*H*-1,2,3-triazol-4-carbohydrazide 5b

Compound is white powder, yield 35%, m.p. 199-200 °C. ^1H NMR (DMSO-d_6) (ppm), 2.241(s, 3H, CH_3), 4.506 (b, 2H, NH_2), 7.089-7.116 (d, 2H, *J* = 8.1 Hz, Ar-H), 7.403-7.430 (d, 2H, *J* = 8.1 Hz, Ar-H), 8.440 (s, 1H, NH), 9.771 (b, 1H, NH); MS *m/z*: 232 (M^+, 90), 233 (M+1, 10), 201 (51), 173 (20), 146 (35), 118 (40), 91 (100). IR: 3388, 3355, 3325, 3304 (NH, NH_2), 1641 (C=O), 974 (N=N-N) cm^{-1}. Anal. Calcd for $C_{10}H_{12}N_6O$: C, 51.72; H, 5.21; N, 36.19; Found: C, 51.91; H, 5.19; N, 36.05.

5-*o*-Tolylamino-2*H*-1,2,3-triazol-4-carbohydrazide 5c

Compound is white powder, yield 43%, m.p. 214-216 °C. ^1H NMR (DMSO-d_6) (ppm), 2.261 (s, 3H, CH_3), 4.501 (b, 2H, NH_2), 6.860-6.901 (m, 1H, Ar-H), 7.011-7.108 (m, 3H, Ar-H), 8.435 (s, 1H, NH), 9.769 (b, 1H, NH); MS *m/z*: 232 (M^+, 100), 233 (M+1, 12), 201 (60), 173 (18), 146 (27), 118 (41), 91 (86), 77 (35), 65 (62). IR: 3371, 3316 (NH_2, NH), 1621 (CO), 973 (N=N-N) cm^{-1}. Anal. Calcd for $C_{10}H_{12}N_6O$: C, 51.72; H, 5.21; N, 36.19; Found: C, 51.61; H, 5.29; N, 36.32.

5-(4-Chlorophenylamino)-2*H*-1,2,3-triazol-4-carbohydrazide 5d

Compound is white powder, yield 79.3%, m.p. 217-218 °C. ^1H NMR (DMSO-d_6) (ppm), 4.511 (b, 2H, NH_2), 7.213-7.241 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.486-7.514 (d, 2H, *J* = 8.4 Hz, Ar-H), 8.449 (s, 1H, NH), 9.775 (b, 1H, NH); MS *m/z*: 252 (M^+, 100), 253 (M+1, 12), 254 (M+2, 29), 221 (39), 195 (12), 166 (29), 138 (28), 111 (77), 102 (34), 75 (66), 63 (18). IR: 3390, 3352, 3308, 3267 (NH_2, NH), 1659 (CO), 970 (N=N-N) cm^{-1}. Anal. Calcd for $C_9H_9ClN_6O$: C, 42.78; H, 3.59; N, 33.26; Found: C, 42.93; H, 3.66; N, 33.03.

5-(3-Chlorophenylamino)-2*H*-1,2,3-triazol-4-carbohydrazide 5e

Compound is white needles, yield 73.8%, m.p. 218-219 °C. ^1H NMR (DMSO-d_6) (ppm), 4.511 (b, 2H, NH_2), 6.897-7.029 (t, 1H, Ar-H), 7.119-7.146 (d, 1H, *J* = 8.1 Hz, Ar-H), 7.364-7.391 (d, 1H, *J* = 8.1 Hz, Ar-H), 7.629 (s, 1H, Ar-H), 8.443 (b, 1H, NH), 9.768 (b, 1H, NH); MS *m/z*: 252 (M^+, 97), 253 (M+1, 12), 254 (M+2, 37.5), 221 (56), 193 (19), 166 (33), 138 (43), 113 (36), 111 (100), 102 (39), 75 (94), 63 (22). IR: 3348, 3323, 3266 (NH_2, NH), 1635 (CO), 972 (N=N-N) cm^{-1}. Anal. Calcd for $C_9H_9ClN_6O$: C, 42.78; H, 3.59; N, 33.26; Found: C, 42.96; H, 3.62; N, 33.50.

2. General synthesis of [(5-arylamino)-2*H*-1,2,3-triazol-4-yl]-(5-methyl-3-substituted-1*H*-pyrazol-1-yl)methanones 6a-j and [(5-arylamino)-2*H*-1,2,3-triazol-4-yl]-(3-methyl-5-substituted-1*H*-pyrazol-1-yl)methanones 7a-d

To add 5-arylamino-2*H*-1,2,3-triazol-4-carbohydrazide **5a-e** (3 mmol), 1,3-diketone (3 mmol) and EtOH (25 mL) in a 100 mL flask. When the mixture was controlled at 80 °C till completely dissolved under stirring, 5 drops of dilute HCl was added, and refluxed for 0.5-2 hours. The mixture was cooled to room temperature and the solid was filtered, washed with cool anhydrous ethanol and dried. The

solid was separated by chromatographic column (silica gel, eluent for ethyl acetate:petroleum ether = 1:6). The titled compounds **6a-j**, **7a-d** were given.

(5-Methyl-3-phenyl-1*H*-pyrazol-1-yl)-(5-phenylamino-2*H*-1,2,3-triazol-4-yl)methanone 6a

Compound is light yellow powder, yield 19.3%, m.p. 186-188 °C. ^{1}H NMR ($CDCl_3$-*d*) (ppm), 2.784 (s, 3H, CH_3), 6.619 (s, 1H, CH), 7.050-7.831 (m, 10H, Ph), 8.462 (b, 1H, NH); ^{13}C NMR ($CDCl_3$-*d*) (ppm), 14.68 (CH_3), 108.59 (CH), 117.88 (2CH), 120.29 (C), 121.95 (CH), 126.42 (2CH), 129.05 (2CH), 129.20 (2CH), 129.87 (CH), 130.85 (C), 139.94 (C), 146.28 (C), 155.18 (C), 155.76 (C), 156.92 (C=O); MS *m/z*: 344 ($M^{+\cdot}$, 12), 345 (M+, 3.2), 316 (6.5), 287 (5.0), 273 (1.7), 260 (3.1), 246 (2.3), 212 (3.3), 196 (5.7), 159 (69), 103 (48), 77 (100), 69 (55), 57 (56), 55 (49), 43 (45); IR: 3357, 3321 (b, NH), 3141, 3113 (Ar-H), 2924 (w, CH_3), 1665 (s, C=O), 1611 (s, triazole or pyrazole ring), 1576, 1520, 1469, 1440 (s, Ar), 1261 (s, C=N-N), 946 (w, N=N-N) cm^{-1}. Anal. Calcd for $C_{19}H_{16}N_6O$: C, 66.27; H, 4.68; N, 24.40; Found: C, 66.01; H, 4.46; N, 24.58.

(5-Methyl-3-phenyl-1*H*-pyrazol-1-yl)-[5-(*p*-tolyl-amino)-2*H*-1,2,3-triazol-4-yl]methanone 6b

Compound is light yellow powder, yield 39%, m.p. 170-171 °C. ^{1}H NMR ($CDCl_3$-*d*) (ppm), 2.341 (s, 3H, CH_3), 2.782 (s, 3H, CH_3), 6.616 (s, 1H, CH), 7.173-7.200 (d, 2H, *J* = 8.1 Hz, *p*-MeC_6H_4-H), 7.636-7.663 (d, 2H, *J* = 8.1 Hz, *p*-MeC_6H_4-H), 7.495-7.519 (m, 3H, Ph-H), 7.825-7.851 (d, 2H, Ph-H), 8.382 (b, 1H, NH); ^{13}C NMR ($CDCl_3$-*d*) (ppm), 14.60 (CH_3), 20.67 (CH_3), 108.42 (CH), 110.84 (C), 117.90 (2CH), 126.33 (2CH), 128.97 (2CH), 129.62 (2CH), 129.75 (CH), 130.83 (C), 131.36 (C), 137.39 (C), 146.14 (C), 154.98 (C), 155.28 (C), 156.80 (C=O); MS *m/z*: 358 ($M^{+\cdot}$, 27), 359 (M+1, 6.3), 330 (7.1), 301 (7.4), 212 (3.6), 159 (100), 117 (63), 91 (78), 77 (47), 65 (38), 57 (30), 51 (25), 43 (27), 39 (16); HRMS (ESI, $M^{+\cdot}$) calcd for $C_{20}H_{18}N_6O$ 358.1542, found 358.1537, 301.1481, 158.0837; IR: 3437, 3348 (b, NH), 3106 (Ar-H), 2922 (w, CH_3), 1661 (s, C=O), 1607 (s, triazole or pyrazole ring), 1570, 1510, 1448, 1408 (s, Ar), 1261 (m, C=N-N), 945 (w, N=N-N) cm^{-1}.

(5-Methyl-3-phenyl-1*H*-pyrazol-1-yl)-[5-(*o*-tolyl-amino)-2*H*-1,2,3-triazol-4-yl]methanone 6c

Compound is light yellow powder, yield 11%, m.p. 183-184 °C. ^{1}H NMR ($CDCl_3$-*d*) (ppm), 2.442 (s, 3H, CH_3), 2.794 (s, 3H, CH_3), 6.616 (s, 1H, CH), 6.984 (t, 1H, Phenyl), 7.315-7.421 (m, 3H, Ar-H), 7.496-7.514 (m, 3H, Ar-H), 7.834-7.853 (d, 2H, Ar-H), 8.462, 8.495 (b, 2H, NH); ^{13}C NMR ($CDCl_3$-*d*) (ppm), 14.66 (CH_3), 17.81 (CH_3), 108.47 (CH), 111.30 (C), 117.91 (CH), 121.92 (CH), 125.03 (C), 126.38 (2CH), 127.16 (CH), 129.02 (2CH), 129.82 (CH), 130.28 (CH), 130.87 (C), 138.34 (C), 146.27 (C), 155.11 (C), 155.41 (C), 156.96 (C=O); MS *m/z*: 358 ($M^{+\cdot}$, 18), 359 (M+1, 4.3), 330 (5.2), 315 (1), 301 (3.5), 287 (2.7), 260 (1.5), 212 (3), 200 (2.0), 184 (5.1), 172 (4.4), 159 (100), 117 (53), 91 (56), 77 (40), 65 (37); IR: 3474, 3338 (b, NH), 3060 (Ar-H), 2924 (w, CH_3), 1659 (s, C=O), 1618, 1596 (s, triazole or pyrazole ring), 1573, 1519, 1468, 1449, 1429 (s, Ar), 1261 (m, C=N-N), 943 (w, N=N-N) cm^{-1}. Anal. Calcd for $C_{20}H_{18}N_6O$: C, 67.02; H, 5.06; N, 23.45; Found: C, 67.13; H, 5.11; N, 23.34.

[5-(*p*-Chlorophenylamino)-2*H*-1,2,3-triazol-4-yl]-(5-methyl-3-phenyl-1*H*-pyrazol-1-yl)methanone 6d

Compound is light yellow powder, yield 21%, m.p. 209-211 °C. ^{1}H NMR ($CDCl_3$-*d*) (ppm), 2.778 (s, 3H, CH_3), 6.627 (s, 1H, CH), 7.313-7.342 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.499-7.524 (d, 3H, Ph), 7.706-7.735 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.825-7.850 (d, 2H, *J* = 7.5 Hz, Ph), 8.464 (b, 1H, NH); ^{13}C NMR ($CDCl_3$-*d*) (ppm), 14.68 (CH_3), 108.77 (CH), 111.32 (C), 119.05 (2CH), 126.46 (2CH), 126.80 (C), 129.14 (2*2CH), 129.99 (CH), 130.81 (C), 138.52 (C), 146.36 (C), 154.87 (C), 155.41 (C), 156.91 (C=O); MS *m/z*: 378 ($M^{+\cdot}$, 19), 381 (M+3, 0.4), 380 (M+2, 6.7), 379 (M+1, 4.5), 350 (6.7), 321 (4.1), 315 (3.2), 294 (2.3), 287 (5.8), 212 (3.9), 196 (5.8), 184 (5.6), 159 (100), 137 (38), 111 (28), 77 (39), 51 (26); IR: 3444, 3347 (NH), 3061 (m, Ar-H), 2924 (CH_3), 1653 (s, C=O), 1605 (s, triazole or pyrazole ring), 1570, 1522, 1490, 1448, 1408 (s, Ar), 1264 (C=N-N), 943 (N=N-N) cm^{-1}. Anal. Calcd for $C_{19}H_{15}ClN_6O$: C, 60.24; H, 3.99; N, 22.19; Found: C, 60.52; H, 3.87; N, 22.06.

[5-(*m*-Chlorophenylamino)-2*H*-1,2,3-triazol-4-yl]-(5-methyl-3-phenyl-1*H*-pyrazol-1-yl)methanone 6e

Compound is light yellow powder, yield 61%, m.p. 187-188 °C. ^{1}H NMR ($CDCl_3$-*d*) (ppm), 2.770 (s, 3H, CH_3), 6.619 (s, 1H, CH), 6.981-7.014 (dd, 1H, *J* = 8.7 Hz, *J* = 1.2 Hz, Ar^1-H), 7.249-7.303 (m, 1H, Ar^1-H), 7.497-7.536 (m, 3H, Ar^2-H), 7.588-7.616 (d, 1H, Ar^1-H), 7.821-7.848 (m, 2H, Ar^2-H), 7.880 (s, 1H, Ar^1-H), 8.487 (b, 1H, NH); ^{13}C NMR ($CDCl_3$-*d*) (ppm), 14.34 (CH_3), 108.80 (CH), 115.88 (CH), 117.75 (CH), 121.89 (CH), 126.48 (2CH), 129.11 (2CH), 130.00 (CH), 130.17 (CH), 130.74 (C),

134.90 (C), 141.73 (C), 146.07 (C), 146.16 (C), 154.67 (C), 155.45 (C), 156.93 (C=O); MS *m/z*: 378 ($M^{\ddagger}$, 17), 380 (M+2, 4.5), 379 (M+1, 3.5), 350 (7.7), 321 (5.0), 294 (2.7), 287 (8.0), 280 (1.3), 266 (0.5), 212 (6.0), 196 (7.5), 184 (10), 159 (100), 137 (39), 111 (48), 91 (12), 77 (57); IR: 3464, 3330 (b, NH), 3059 (Ar-H), 2922 (CH_3), 1648 (s, C=O), 1610, 1596 (s, triazole or pyrazole ring), 1566, 1519, 1472, 1452, 1423 (s, Ar), 1261 (b, C=N-N), 942 (w, N=N-N) cm^{-1}. Anal. Calcd for $C_{19}H_{15}ClN_6O$: C, 60.24; H, 3.99; Cl, 9.36; N, 22.19; O, 4.22; Found: C, 60.18; H, 3.94; N, 22.03.

(3,5-Dimethyl-1*H*-pyrazol-1-yl)-(5-phenylamino-2*H*-1,2,3-triazol-4-yl)methanone 6f

Compound is white powder, yield 95.7%, m.p. 196-198 °C. ^{1}H NMR ($CDCl_3$-*d*) (ppm), 2.350 (s, 3H, CH_3), 2.676 (s, 3H, CH_3), 6.100 (s, 1H, CH), 6.897-7.045 (t, 1H, *J* = 7.8 Hz, Ph), 7.338-7.391 (t, 2H, *J* = 7.8 Hz, Ph), 7.737-7.766 (d, 2H, *J* = 7.8 Hz, Ph), 8.409 (b, 1H, NH); ^{13}C NMR (DMSO-d_6) (ppm), 13.34 (CH_3), 13.84 (CH_3), 111.53 (CH), 116.95 (2CH *and* C), 120.73 (C), 128.95 (3CH), 140.89 (C), 144.39 (2C), 152.65 (C=O); MS *m/z*: 282 ($M^{\ddagger}$, 20), 283 (M+1, 4.1), 254 (12.7), 225 (3.8), 211 (2.1), 198 (9.3), 184 (4.4), 158 (5.0), 150 (4.0), 130 (8.4), 103 (46), 97 (100), 91 (3), 77 (51); IR: 3365 (s, NH), 3141, 3065 (Ar-H), 2930 (CH_3), 1662 (s, C=O), 1598 (s, triazole or pyrazole ring), 1569, 1488, 1462, 1428 (s, Ar), 1254 (b, C=N-N), 987, 971 (N=N-N) cm^{-1}. Anal. Calcd for $C_{14}H_{14}N_6O$: C, 59.56; H, 5.00; N, 29.77; Found: C, 59.42; H, 5.09; N, 29.98.

(3,5-Dimethyl-1*H*-pyrazol-1-yl)-[5-(*p*-tolylamino)-2*H*-1,2,3-triazol-4-yl]methanones 6g

Compound is light yellow powder, yield 84%, m.p. 191-193 °C. ^{1}H NMR ($CDCl_3$-*d*) (ppm), 2.331 (s, 3H, CH_3), 2.349 (s, 3H, CH_3), 2.671 (s, 3H, CH_3), 6.092 (s, 1H, CH), 7.157-7.184 (d, 2H, *J* = 8.1 Hz, Ar-H), 7.620-7.648 (d, 2H, *J* = 8.4 Hz, Ar-H), 8.329 (b, 1H, NH); ^{13}C NMR ($CDCl_3$-*d*) (ppm), 13.84 (CH_3), 14.40 (CH_3), 20.68 (CH_3), 111.25 (CH), 117.84 (2CH), 129.63 (2CH), 131.22 (C), 137.57 (C), 145.50 (2C), 153.65 (C), 155.14 (C), 156.79 (C=O); MS *m/z*: 296 ($M^{\ddagger}$, 9), 297 (M+1, 1.2), 268 (3.3), 239 (1.7), 225 (2.0), 212 (3.4), 198 (1.9), 172 (1.4), 145 (6.3), 133 (5.2), 117 (37), 97 (100), 91 (33), 65 (23); HRMS (ESI, $M^{\ddagger}$) calcd for $C_{15}H_{16}N_6O$ 296.1386, found 296.1380, 297.1418, 268.1322, 239.1300, 225.1144, 212.1202, 145.0780; IR: 3364 (NH), 3198, 3140 (Ar-H), 2922 (CH_3), 1663 (s, C=O), 1606 (s, triazole or pyrazole ring), 1569, 1511, 1447, 1411 (s, Ar), 1261 (m, C=N-N), 967 (N=N-N) cm^{-1}.

(3,5-Dimethyl-1*H*-pyrazol-1-yl)-[5-(*o*-tolylamino)-2*H*-1,2,3-triazol-4-yl]methanone 6h

Compound is light yellow powder, yield 85%, m.p. 205-206 °C. ^{1}H NMR ($CDCl_3$-*d*) (ppm), 2.362 (s, 3H, CH_3), 2.424 (s, 3H, CH_3), 2.686 (s, 3H, CH_3), 6.092 (s, 1H, CH), 6.938-6.985 (m, 1H, Ph-H), 7.198-7.297 (m, 3H, Ph-H), 8.417-8.495 (b, 2H, NH); ^{13}C NMR ($CDCl_3$-*d*) (ppm), 13.90 (CH_3), 14.46 (CH_3), 17.86 (CH_3), 111.27 (CH), 111.70 (C), 117.87 (CH), 122.93 (C), 125.00 (CH), 127.20 (CH), 130.29 (CH), 138.52 (C), 147.89 (C), 153.76 (C), 155.27 (C), 155.80 (C=O); MS *m/z*: 296 ($M^{\ddagger}$, 21), 297 (M+1, 4.4), 268 (7.2), 239 (2.0), 225 (3.9), 212 (1.5), 198 (4.3), 171 (2.7), 144 (16), 117 (52), 97 (100), 91 (39), 65 (35); IR: 3369 (b, NH), 3137, 2975 (Ar-H), 2926 (w, CH_3), 1661 (s, C=O), 1597 (s, triazole or pyrazole ring), 1571, 1515, 1472, 1431 (s, Ar), 1261 (s, C=N-N), 987, 967 (w, N=N-N) cm^{-1}. Anal. Calcd for $C_{15}H_{16}N_6O$: C, 60.80; H, 5.44; N, 28.36; Found: C, 60.99; H, 5.34; N, 28.20.

[5-(*p*-Chlorophenylamino)-2*H*-1,2,3-triazol-4-yl]-(3,5-dimethyl-1*H*-pyrazol-1-yl)methanone 6i

Compound is light yellow powder, yield 94.8%, m.p. 204-206 °C. ^{1}H NMR ($CDCl_3$-*d*) (ppm), 2.352 (s, 3H, CH_3), 2.667 (s, 3H, CH_3), 6.104 (s, 1H, CH), 7.295-7.301, 7.325-7.331 (q, 2H, *J* = 8.7 Hz, Ph-H), 7.688-7.694, 7.717-7.723 (q, 2H, *J* = 8.7 Hz, Ph-H); 8.409 (b, 1H, NH); ^{13}C NMR ($CDCl_3$-*d*) (ppm), 13.90 (CH_3), 14.42 (CH_3), 111.48 (CH), 118.94 (2CH), 126.62 (C), 129.11 (2CH), 137.07 (C), 138.71 (C), 145.66 (C), 153.95 (C), 154.60 (C), 156.27 (C=O); MS *m/z*: 316 ($M^{\ddagger}$, 8), 318 (M+2, 2.8), 317 (M+1, 1.7), 288 (4.3), 253 (3.8), 232 (2.8), 225 (7.6), 137 (27), 111 (22), 97 (100), 75 (29); IR: 3361 (b, NH), 3194 (Ar-H), 2925 (CH_3), 1660 (s, C=O), 1614 (s, triazole or pyrazole ring), 1567, 1515, 1492, 1454 (s, Ar), 1263 (s, C=N-N), 966 (w, N=N-N) cm^{-1}. Anal. Calcd for $C_{14}H_{13}ClN_6O$: C, 53.09; H, 4.14; N, 26.53; Found: C, 53.20; H, 4.05; N, 26.70.

[5-(*m*-Chlorophenylamino)-2*H*-1,2,3-triazol-4-yl]-(3,5-dimethyl-1*H*-pyrazol-1-yl)methanones 6j

Compound is light yellow powder, yield 91%, m.p. 203-204 °C. ^{1}H NMR ($CDCl_3$-*d*) (ppm), 2.356 (s, 3H, CH_3), 2.671 (s, 3H, CH_3), 6.107 (s, 1H, CH), 6.969-7.002 (t, 1H, Ph-H), 7.268-7.295 (d, 1H, *J* = 8.1 Hz, Ph-H), 7.577-7.604 (d, 1H, *J* = 8.1 Hz, Ph-H), 7.880 (s, 1H, Ph-H), 8.448 (b, 1H, NH); ^{13}C NMR (DMSO-d_6) (ppm), 13.25

(CH_3), 13.79 (CH_3), 111.41, 115.38, 116.17, 120.04, 130.04, 133.52, 142.20, 144.34, 152.67; MS *m/z*: 316 ($M^{+\cdot}$, 10), 318 (M+2, 3.4), 317 (M+1, 2.1), 288 (7.0), 225 (13), 137 (26), 111 (20), 97 (100), 75 (28), 54 (12), 42 (15); HRMS (ESI, $M^{+\cdot}$) calcd for $C_{14}H_{13}ClN_6O$ 316.0839, found 316.0834, 318.0793, 288.0777, 253.1094, 225.1150, 137.0046, 97.0778; IR: 3434, 3364 (b, NH), 3130, 2983 (Ar-H), 2926 (w, CH_3), 1662 (s, C=O), 1602 (s, triazole or pyrazole ring), 1564, 1511, 1480, 1453, 1422 (s, Ar), 1259 (s, C=N-N), 987, 965 (w, N=N-N) cm^{-1}.

(3-Methyl-5-phenyl-1*H*-pyrazol-1-yl)-(5-phenylamino-2*H*-1,2,3-triazol-4-yl)methanone 7a

Compound is light yellow powder, yield 77.5%, m.p. 167-168 °C. ^{1}H NMR ($CDCl_3$-*d*) (ppm), 2.448 (s, 3H, CH_3), 6.332 (s, 1H, CH), 6.996 (t, 1H, Ph), 7.299-7.352 (t, 2H, Ph), 7.479-7.489 (d, 5H, Ph), 7.671-7.696 (d, 2H, Ph), 8.239 (b, 1H, NH); ^{13}C NMR ($CDCl_3$-*d*) (ppm), 13.88 (CH_3), 112.39 (C), 112.99 (CH), 117.7 (2CH), 121.75 (CH), 128.02 (2CH), 128.89 (2CH), 129.03 (2CH), 129.12 (CH), 130.40 (C), 139.91 (C), 148.07 (C), 153.77 (C), 154.87 (C), 156.19 (C=O); MS *m/z*: 344 ($M^{+\cdot}$, 14), 345 (M+1, 2.6), 316 (8.5), 287 (5.4), 260 (2.8), 212 (1), 196 (1.2), 184 (6.4), 170 (1.5), 159 (100), 130 (15), 103 (49), 77 (71); HRMS (ESI, $M^{+\cdot}$) calcd for $C_{19}H_{16}N_6O$ 344.1386, found 344.1380, 316.1305, 287.1292, 196.0883, 159.0937; IR: 3356 (NH), 3132, 3058 (Ar-H), 2933 (w, CH_3), 1667 (s, C=O), 1600 (s, triazole or pyrazole ring), 1569, 1526, 1499, 1467, 1444 (s, Ar), 1237 (s, C=N-N), 980 (w, N=N-N) cm^{-1}.

(3-Methyl-5-phenyl-1*H*-pyrazol-1-yl)-[5-(*p*-tolylamino)-2*H*-1,2,3-triazol-4-yl]methanone 7b

Compound is light yellow powder, yield 34%, m.p. 179-180 °C. ^{1}H NMR ($CDCl_3$-*d*) (ppm), 2.305 (s, 3H, CH_3), 2.444 (s, 3H, CH_3), 6.324 (s, 1H, CH), 7.114-7.143 (d, 2H, *J* = 8.7 Hz, *p*-MeC_6H_4-H), 7.549-7.577 (d, 2H, *J* = 8.4 Hz, *p*-MeC_6H_4-H), 7.475 (s, 5H, Ph-H), 8.161 (b, 1H, NH); ^{13}C NMR ($CDCl_3$-*d*) (ppm), 13.94 (CH_3), 20.68 (CH_3), 111.32 (C), 112.95 (CH), 118.04 (2CH), 128.06 (2CH), 128.97 (2CH), 129.19 (CH), 129.60 (2CH), 130.47 (C), 131.38 (C), 137.41 (C), 148.08 (C), 153.65 (C), 155.26 (C), 155.92 (C=O); MS *m/z*: 358 ($M^{+\cdot}$, 8), 359 (M+1, 0.9), 330 (1.4), 301 (1), 232 (4.7), 188 (2.4), 158 (52), 117 (26), 91 (61), 77 (43), 65 (32), 57 (100), 51 (25), 43 (94), 39 (22); IR: 3359 (b, triazole-NH), 3210, 3135 (b, N-H···O=C), 2919 (w, CH_3), 1668 (s, C=O), 1613 (s, triazole or pyrazolering), 1570, 1512, 1444, 1409 (s, Ar), 1275 (b, C=N-N), 973 (m, N=N-N) cm^{-1}. Anal. Calcd for $C_{20}H_{18}N_6O$: C, 67.02; H, 5.06; N, 23.45; Found: C, 66.90; H, 5.00; N, 23.63.

(3-Methyl-5-phenyl-1*H*-pyrazol-1-yl)-[5-(*o*-tolylamino)-2*H*-1,2,3-triazol-4-yl]methanone 7c

Compound is light yellow powder, yield 53%, m.p. 170-172 °C. ^{1}H NMR ($CDCl_3$-*d*) (ppm), 2.276 (s, 3H, CH_3), 2.439 (s, 3H, CH_3), 6.331 (s, 1H, CH), 6.952 (m, 1H, Ar-H), 7.395-7.472 (m, 7H, Ar-H), 7.944 (m, 1H, Ar-H), 8.171 (b, 1H, NH), 8.332 (b, 1H, NH); ^{13}C NMR ($CDCl_3$-*d*) (ppm), 13.95 (CH_3), 17.82 (CH_3), 112.14 (C), 112.98 (CH), 118.45 (CH), 122.19 (CH), 125.75 (C), 127.04 (CH), 128.00 (2CH), 129.00 (2CH), 129.10 (CH), 130.31 (CH *and* C), 138.31 (C), 148.20 (C), 153.65 (C), 155.31 (C), 155.90 (C=O); MS *m/z*: 358 ($M^{+\cdot}$, 14), 359 (M+1, 2.6), 330 (6.0), 301 (1.7), 287 (1.9), 260 (0.7), 212 (2.3), 196 (1), 185 (5.1), 171 (4.3), 159 (100), 117 (54), 91 (55); IR: 3368, 3203 (b, NH), 3051, 2965 (Ar-H), 2923 (w, CH_3), 1665 (s, C=O), 1616, 1598 (s, triazole or pyrazole ring), 1571, 1503, 1468, 1444, 1427 (s, Ar), 1272, 1246 (C=N-N), 972 (N=N-N) cm^{-1}. Anal. Calcd for $C_{20}H_{18}N_6O$: C, 67.02; H, 5.06; N, 23.45; Found: C, 67.08; H, 5.14; N, 23.57.

[5-(*p*-Chlorophenylamino)-2*H*-1,2,3-triazol-4-yl]-(3-methyl-5-phenyl-1*H*-pyrazol-1-yl)methanone 7d

Compound is light yellow powder, yield 67%, m.p. 188-190 °C. ^{1}H NMR ($CDCl_3$-*d*) (ppm), 2.452 (s, 3H, CH_3), 6.338 (s, 1H, CH), 7.252-7.288 (d, 2H, *J* = 6.9 Hz, Ar-H), 7.475 (s, 5H, Ph), 7.624-7.653 (d, 2H, *J* = 6.9 Hz, Ar-H), 8.239 (b, 1H, NH); ^{13}C NMR (DMSO-d_6) (ppm), 13.80 (CH_3), 112.99 (C), 119.13 (CH), 124.71 (C), 128.49 (2CH *and* C), 128.84 (2CH), 128.93 (CH *and* C), 129.02 (2*2CH), 130.72 (C), 140.36 (C), 147.16 (C), 152.79 (C=O); MS *m/z*: 378 ($M^{+\cdot}$, 13), 380 (M+2, 5), 379 (M+1, 3), 350 (4.8), 321 (2.3), 315 (2.8), 294 (2), 287 (5.1), 212 (2.5), 196 (2.8), 184 (4.5), 170 (2.1), 159 (100), 137 (30), 111 (26); IR: 3572, 3363 (b, NH), 3143, 2968 (Ar-H), 2837 (w, CH_3), 1661 (s, C=O), 1601 (s, triazole or pyrazole ring), 1565, 1494, 1449, 1406 (s, Ar), 1280, 1237 (C=N-N), 978 (N=N-N) cm^{-1}. Anal. Calcd for $C_{19}H_{15}ClN_6O$: C, 60.24; H, 3.99; N, 22.19; Found: C, 60.06; H, 3.89; N, 22.35.

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