A facile entry for synthesis of 3-arylazo derivatives of [1,2,4]triazolo[4,3-*a*] benzimidazole and [1,2,4]triazolo[3,4-*b*]quinazolin-5-one

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A simple synthetic strategy is described for synthesis of hitherto unreported 3-arylazo derivatives of both [1,2,4]triazolo[4,3-*a*]benzimidazole and [1,2,4]triazolo[3,4-*b*]quinazolin-5-one **6** and **7**, respectively. This strategy utilises reactions of 3-chloro-1,5-diarylformazans **1** with 2-mercaptobenzimidazole **2** and 2,3-dihydro-2-thioxoquinazolin-4(1*H*)-one **4** or their 2-methylthio derivatives **3** and **5**, respectively. A plausible reaction mechanism is suggested for the formation of the isolated products **6** and **7**.

Keywords: 3-arylazo heterocycles, [1,2,4]triazolo[4,3-*a*]benzimidazole, [1,2,4]triazolo[3,4-*b*]quinazolin-5-one

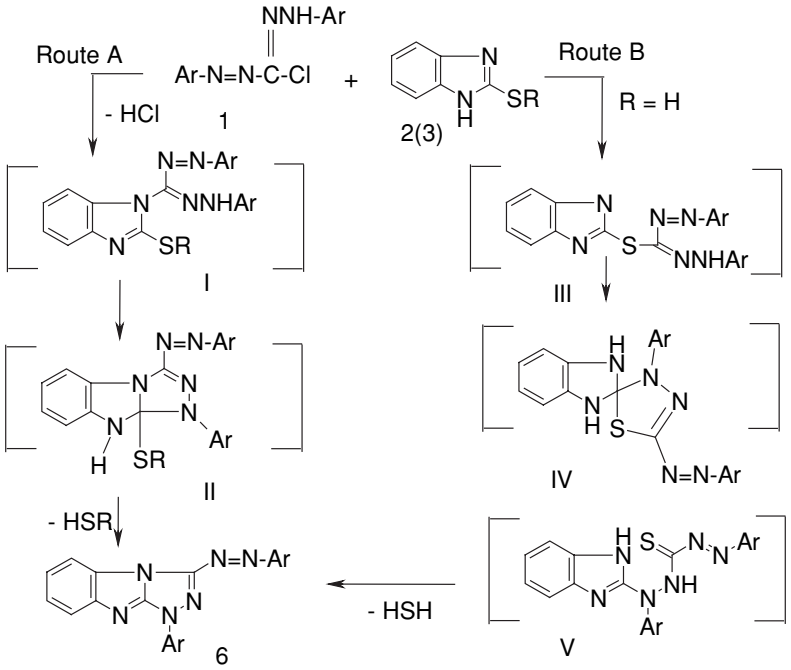
While numerous arylazoheterocycles have been reported, the title arylazo derivatives have been unknown[1] although the parent ring systems have been reported since 1959 and 1986.[2] In continuation of our synthetic and mechanistic studies on 1, 5-diaryl-3-chloroformaqzans **1**,[3] we report the use of the latter as precursors for one-pot synthesis of 3-arylazo derivatives of both [1,2,4]triazolo[4,3-*a*]benzimidazole and [1,2,4]triazolo [3,4-*b*]quinazolin-5-one **6** (Scheme 1) and **7** (Scheme 2). The interest in the synthesis of new arylazo heterocycles is because many such compounds are being evaluated and patented for potential use in various sectors of industry including hair dyeing,[4] thermal transfer printing,[5] non-linear optics,[6] disperse dyes,[7] pigments,[8] dyeing polyesters[9] and ink-jet inks.[10]

Results and discussion

The starting reagents 3-chloro-1,5-diarylformazans **1**,[1] 2-mercaptobenzimidazole **2**,[11] its 2-methylthio- derivative **3**,[12] 2,3-dihydro-2-thioxoquinazolin-4(1*H*)-one **4**[13] and its 2-methylthio derivative **5**[14] were prepared by known methods.

Refluxing of **2** with each of **1a–f** in chloroform in the presence of triethylamine until hydrogen sulfide ceased to evolve and working up the reaction mixture gave, in each case, one product as evidenced by TLC analysis. On the basis of spectral (MS, IR and ^{1}H NMR) (see Experimental) and elemental analyses, the products isolated from the reactions of **2** with **1a–f** were assigned the 3-arylazo[1,2,4] triazolo[4,3-*a*]benzimidazole structures **6a–f**, respectively (Scheme 1). Such structure assignment was substantiated by ^{13}C NMR spectra. For example, the ^{13}C NMR spectrum of **6a** reveals, as expected, 18 signals.

To account for the formation of **6** in the studied reactions of **2** with the formazans **1a–f**, the two possible pathways A and B depicted in Scheme 1 were considered. Thus, it is suggested that the reactions start with the initial formation of the amidrazone derivatives **I** which subsequently undergo cyclisation with concurrent elimination of hydrogen sulfide to give **6** as end products (Route A, Scheme 1). Alternatively, reactions of **2** with **1** may start with the formation of the thiohydrazonate esters **III**, which undergo *in situ* Smiles

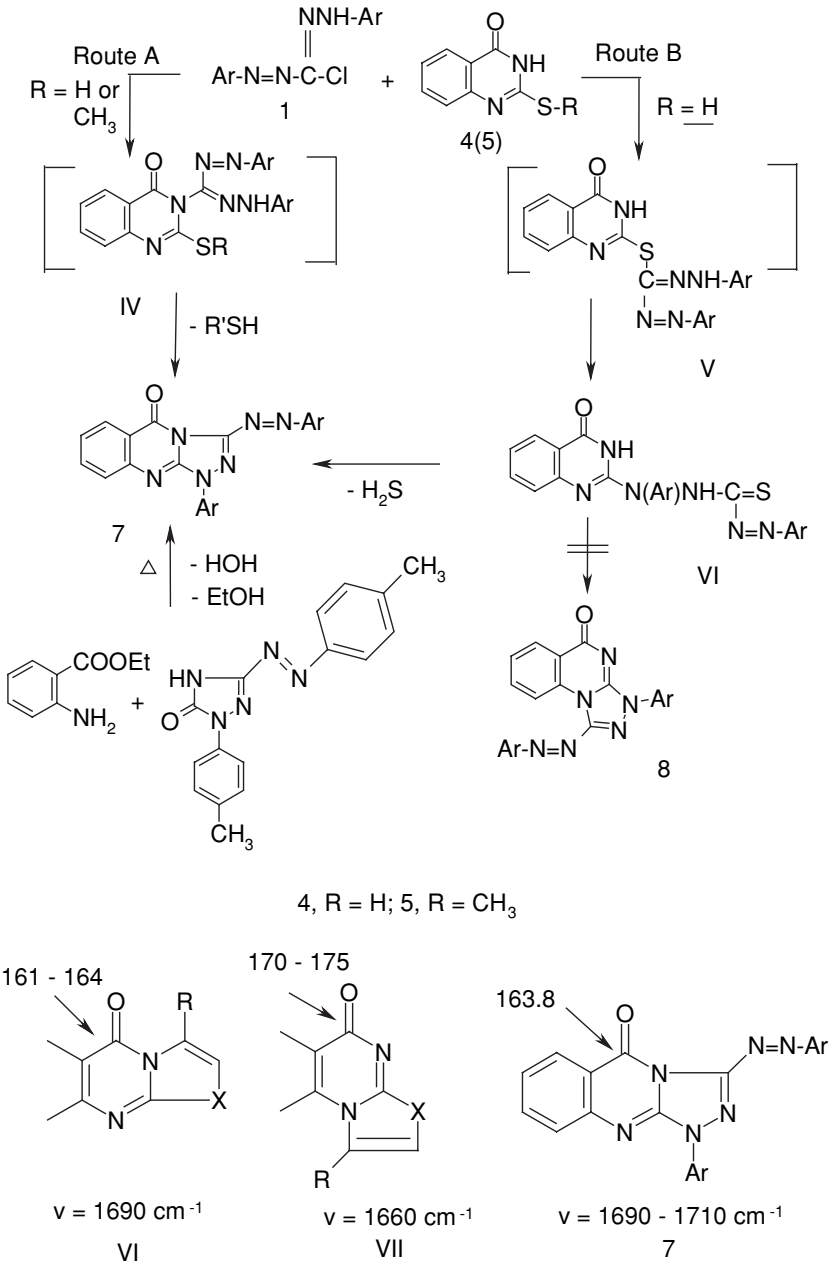


2, R = H; **3**, R = CH_3

Ar = XC_6H_4; **a**, 4-Me; **b**, H: **c**, 4-Cl; **d**, 3-Cl; **e**, 3-NO_2; **f**, 4-NO_2

Scheme 1

* Correspondent.



Scheme 2

rearrangement[15] under the reaction conditions employed to afford the corresponding thiohydrazides **V**. Then, the latter thiohydrazides undergo cyclisation as soon as they are formed with concurrent elimination of hydrogen sulfide to give **6** as the end products (Route B, Scheme 1). All attempts to isolate any of the latter intermediates **I, III** or **V** failed, however. Presumably, such intermediates are consumed under the employed reaction conditions as soon as they are formed.

To distinguish between these two alternative pathways, the reactions of **3** with **1a–f** were examined. Thus, refluxing a mixture of **3** with each of **1a–f** in chloroform in the presence of triethylamine afforded, in each case, one product. The isolated products proved identical in all respects (m.p., mixed m.p., IR) with those obtained above from reactions of **2** with **1** (Scheme 1). As compound **3** cannot form thiohydrazonates with **1**, it is not unreasonable to conclude that route A in Scheme 1 is the most plausible mechanism for the studied reactions of **1** with either **2** or **3**.

Next, reactions of **4** and **5** each with **1** were examined. Refluxing **1** and **4** in chloroform in the presence of triethylamine for 8 h and work up the reaction mixture gave, in each case, one isolable product as evidenced by TLC analysis. Similar results were obtained when **1** was refluxed with **5** under the same reaction conditions. The mass spectra and elemental analysis data of the products isolated were compatible with either the linear [1,2,4]triazolo[3,4-*b*]quinazolin-5-one structure **7** and not the angular isomeric [1,2,4]triazolo[4.3-*a*]quinazolin-9-one structure **8** (Scheme 2). The differentiation between these two isomeric structures was made on the basis of their ^{13}C NMR and IR spectra and by alternate synthesis. Thus, the ^{13}C NMR spectra of the isolated products showed the signal due to the carbonyl carbon at δ values in the range 163.8 – 167.4. Such data are consistent with the linear structure **7**, as they are similar to those reported for 1,2,4-triazolo[4,3-*a*]pyrimidin-5-one derivatives **VI** (δ 161–164) and different from those of 1,2,4-triazolo[4,3-*a*]pyrimidin-7-one analogues **VII** (δ 170–175).[16] Furthermore, the IR spectra of the isolated products are also consistent with their assigned structure **7**. For example, their IR spectra exihibit in each case a characteristic carbonyl absorption band in the region

Table 1 Electronic absorption spectra of the products **6** and **7** in dioxane

Compd. no.	λ_{max} (log ε)	Compd. no.	λ_{max} (log ε)
6a	390 (4.83), 295 (4.80)	**7a**	410 (4.25), 310 (4.61)
6b	400 (4.26), 300 (4.61)	**7b**	435 (4.80), 280 (4.93)
6c	420 (4.65), 310 (4.74)	**7c**	430 (4.63), 295 (4.85)
6d	421 (4.59), 310 (4.55)	**7d**	460 (4.16), 285 (5.10)
6e	445 (4.65), 290 (4.73)	**7e**	455 (4.40), 300 (4.72)
6f	450 (4.62), 300 (4.75)	**7f**	480 (4.54), 315 (4.71)

1680–1700 cm^{-1}. Such finding is compatible with the assigned linear structure **7** rather the non-linear structure **8** (Scheme 2). This is because the characteristic stretching frequencies of the carbonyl groups of the structures of type **VI** and **VII** were reported to be near 1690 and 1660 cm^{-1}, respectively.[16]

The assigned structure **7** was further confirmed by alternate synthesis of **7a** as a typical example of the series prepared. Thus, reaction of ethyl anthranilate with 1-(*p*-tolyl)-3-(*p*-tolyl)azo-1,2,4-triazol-5(4*H*)-one **9** at reflux gave a product which proved identical in all respects (m.p., mixed m.p. and IR) with **7a** obtained above from the reaction of **1a** with **5** (Scheme 2).

The mechanism for the formation of the products **7** in the studied reactions of **1** with the methylthio derivative **5** is straight forward. As depicted in Scheme 2, it is suggested that the reactions start with the initial formation of the amidrazone intermediates **IV** which cyclise *in situ* with concurrent elimination of CH_3SH to form the respective products **7** (Route A, Scheme 1). The nucleophilic attack by N3 rather than N1 of **5,** in the reaction of **1** with **5**, is consistent with the literature reports which indicate that the 2-substituted-4(3*H*)-quinazolinone tautomeric form is more stable than the isomeric 2-substituted-4(1*H*)-quinazolinone form.[17] Furthermore, on the basis of our finding that the products **7** are formed by reactions of **1** with either the thione **4** or its methylthio derivatives **5**, it is not unreasonable to conclude that the pathway (route A, Scheme 2) is also the most plausible mechanism for the studied reactions of **1** with **4**.

Finally, as shown in Table 1, the electronic absorption spectra of both series of products **6** and **7** in dioxane showed in each case two bands in the reagions 400–480 and 315–280 nm characteristic to their azo chromphore.

In conclusion, the studied reactions provide a facile synthetic strategy for 3-arylazo-1,2,4-triazolo[4,3-*a*]benzimidazoles **6** and 3-arylazo-1,2,4-triazolo[3,4-*b*]quinazolines **7**.

Experimental

Melting points were measured on an electrothermal Gallenkamp melting point apparatus and are uncorrected. The ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6 with tetramethylsilane (TMS) as an internal standard using 300 MHz Varian Gemini spectrometer. The IR spectra were measured on a Fourier Transform and Pye Unicam Infrared spectrophotometers using potassium bromide wafer. Mass spectra were recorded on a GCMS-QP 1000 EX spectrometer at an ionizing potential of 70 eV. Elemental microanalyses were carried out at the Microanalytical Laboratory of Cairo University, Giza, Egypt. The identification of compounds from different experiments were secured by mixed m.p.'s and superimposable IR spectra. 3-Chloro-1,5-diarylformazans **1** were prepared by coupling of the corresponding diazotized anilines with potassium chloromalonate as previously described.[1] 2-Mercaptobenzimidazole **2**,[11] its 2-methylthio-derivative **3**,[12] 2,3-dihydro-2-thioxoquinazolin-4(1*H*)-one **4**[13] and its methylthio derivative **5**[14] were prepared as previously described.

Synthesis of 1-Aryl-3-arylazo[1,2,4]triazolo[4,3-a] benzimidazoles **6a–f**: To a solution of the appropriate 3-chloro-1,5-diarylformazan **1** (0.005 mol) and 2-mercaptobenzimidazole **2** (0.005 mol) in chloroform (40 ml) was added tiethylamine (0.7 ml, 0.007 mol). The resulting mixture was refluxed till hydrogen sulfide ceased to evolve, then cooled. The precipitated solid triethylamine hydrochloride was filtered off. The excess solvent was distilled and the residue was triturated with few drops of methanol or petroleum ether (40–60°C) where it solidified. The solid product was filtered and crystallised from ethanol to give the respective derivative [1,2,4]triazolo [4,3-*a*]benzimidazole 6 as reddish brown solid.

Repitition of the above procedure using ethanol as solvent and **3** *in lieu* of **2** and work up the reaction mixture after methanethiol ceased to evolve afforded the respective arylazo derivative **6**.

The compounds **6a–f** prepared together with their physical constants are listed below.

1-(4-Methylphenyl)-3-(4-methylphenylazo)[1,2,4]Triazolo[4,3-a] benzimidazole (**6a**): Yield 55 %; m.p. 268–270°C; IR (KBr) υ (cm^{-1}) 1604, 1555; ^1H NMR (DMSO-d_6) δ 2.40 (s, 3H), 2.42 (s, 3H), 7.29 (td, *J*=8, 1.2 Hz, 1H), 7.43 (td, *J*=8, 1.2 Hz, 1H), 7.46 (d, *J*=8 Hz, 2H), 7.51 (d, *J*=8 Hz, 2H), 7.74 (d, *J*=8 Hz, 2H), 7.70 (dd, *J*=8, 1.2 Hz, 1H), 8.10 (d, *J*=8 Hz, 2H), 8.32 (dd, *J*=8, 1.2 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 21.3, 21.9, 116.7, 124.5, 127.6, 129.3, 129.6, 129.9, 130.2, 130.3, 131.0, 131.8, 132.0, 132.8, 136.6, 144.2, 145.6, 149.9; MS *m/z* (%) 366 (M+, 7.3), 263 (0.4), 116 (3.2), 159(0.5), 144 (0.3), 119 (12); Anal. Calcd. for $C_{22}H_{18}N_6$ (366.4): C, 72.11, H, 4.95; N, 22.93, Found: C, 72.09, H, 4.76, N, 22.91 %.

1-Phenyl-3-phenylazo[1,2,4]triazolo[4,3-a]benzimidazole (**6b**): 60 % yield, m.p. 233–235°C; IR (KBr) υ (cm^{-1}) 1600, 1540; ^1H NMR (DMSO-d_6) δ 7.35 – 7.68 (m, 10H), 7.29 (td, *J*=8, 1.2 Hz, 1H), 7.43 (td, *J*=8, 1.2 Hz, 1H), 7.70 (dd, *J*=8, 1.2 Hz, 1H), 8.32 (dd, *J*=8, 1.2 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 113.5, 120.9, 123.6, 125.3, 128.1, 128.4, 128.5, 129.7, 129.9, 130.1, 130.6, 131.8, 132.0, 139.0, 147.7, 150.9; MS *m/z* (%) 338 (M^+, 58.1), 249 (6.0) 116 (2.0), 144 (0.7), 131 (0.4), 105 (21.5); Anal. Calcd. for $C_{20}H_{14}N_6$ (338.3): C, 70.99, H, 4.17; N, 24.84, Found: C, 70.81, H, 4.15, N, 24.80 %.

1-(4-Chlorophenyl)-3-(4-chlorophenylazo)[1,2,4]triazolo[4,3-a] benzimidazole (**6c**): Yield 58 %, m.p. 248–250°C; IR (KBr) υ (cm^{-1}) 1624, 1585; ^1H NMR(DMSO-d_6) δ 7.29 (td, *J*=8, 1.2 Hz, 1H), 7.43 (td, *J*=8, 1.2 Hz, 1H), 7.51 (d, *J*=8 Hz, 2H), 7.69 (d, *J*=8 Hz, 2H), 7.70 (dd, *J*=8, 1.2 Hz, 1H), 7.74 (d, *J*=8 Hz, 2H), 8.23 (d, *J*=8 Hz, 2H), 8.32 (dd, *J*=8, 1.2 Hz, 1H); MS *m/z* (%) 407 (M^+, 23.1), 283 (0.2) 116 (0.5), 181 (2.0), 166 (0.5), 140 (2.0); Anal. Calcd. for $C_{20}H_{12}Cl_2N_6$ (407.2): C, 58.98, H, 2.97; N, 20.64, Found: C, 58.94, H, 2.93, N, 20.66 %.

1-(3-Chlorophenyl)-3-(3-chlorophenylazo)[1,2,4]triazolo[4,3-a] benzimidazole (**6d**): Yield 54%; m.p. 224–225°C;; IR (KBr) υ (cm^{-1}) 1606, 1560; ^1H NMR(DMSO-d_6) δ 7.09–7.76 (m, 10H), 7.70 (dd, *J*=8, 1.2 Hz, 1H), 8.32 (dd, *J*=8, 1.2 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 117.5, 118.7, 119.6, 121.4, 121.8, 123.6, 123.7, 123.9, 124.2, 124.9, 126.0, 128.8, 129.3, 129.5, 129.7, 130.1, 131.2, 142.4, 145.1, 152.7; MS *m/z* (%) 407 (M^+, 9.3), 283 (3.5) 116 (2.1), 181 (0.2), 166 (1.5), 140 (2.5); Anal. Calcd. for $C_{20}H_{12}Cl_2N_6$ (407.2): C, 58.98, H, 2.97; N, 20.64, Found: C, 58.67, H, 2.95, N, 20.67, %.

1-(3-Nitrophenyl)-3-(3-nitrophenylazo)[1,2,4]triazolo[4,3-a] benzimidazole (**6e**): Yield 60%, m.p. 227–229°C; IR (KBr) υ (cm^{-1}) 1600, 1542; ^1H NMR (DMSO-d_6) δ 7.12–7.66 (m, 10H), 7.70 (dd, *J*=8, 1.2 Hz, 1H), 8.32 (dd, *J*=8, 1.2 Hz, 1H); MS *m/z* (%) 428 (M^+, 5.5), 293 (1.0) 116 (0.5), 190 (7.0), 177 (2,0), 150 (2.0); Anal. Calcd. for $C_{20}H_{12}N_8O_4$ (428.3): C, 56.08, H, 2.82; N, 26.16, Found: C, 56.08, H, 2.82, N, 26.13 %.

1-(4-Nitrophenyl)-3-(4-nitrophenylazo)[1,2,4]triazolo[4,3-a] benzimidazole (**6f**): Yield 50 %, m.p. 279–280°C; IR (KBr) υ (cm^{-1}) 1616, 1577; ^1H NMR (DMSO-d_6) δ 7.29 (td, *J*=8, 1.2 Hz, 1H), 7.43 (td, *J*=8, 1.2 Hz, 1H), 7.48 (d, *J*=6 Hz, 2H), 7.55 (d, *J*=6 Hz, 2H), 7.68 (d, *J*=6 Hz, 2H), 7.70 (dd, *J*=8, 1.2 Hz, 1H), 7.72 (d, *J*=6 Hz, 2H), 8.32 (dd, *J*=8, 1.2 Hz, 1H); MS *m/z* (%) 428 (M^+, 15), 293 (0.1) 116 (0.5), 190 (2.5), 177 (0.3), 150 (0.2); Anal., Calcd. for $C_{20}H_{12}N_8O_4$ (428.3): C, 56.08, H, 2.82; N, 26.16 Found: C, 56.20, H, 2.74, N, 26.16 %.

Preparation of 1-(4-methylphenyl)-3-(4-methylphenylazo)-1,2, 4-triazol-5(4H)-one (**9**)

General procedure: A mixture of 3-chloro-1,5-di(4-methylphenyl) formazan (0.86 g, 0.003 mole) and potassium cyanate (0.65 g, 0.008 mole) in methanol (40 ml) was refluxed for 3 h, then hydrochloric acid (1 ml) was added to the mixture, and refluxing was continued for a further 30 min. The excess solvent was distilled, then cooled. The crude solid reside was collected and crystallised from ethanol to give **9**, Yield 55%, m.p. > 300 °C; IR (KBr) υ (cm^{-1}) 1707, 3426; ^1H NMR (DMSO-d_6) δ 2.50(s, 3H), 2.52(s, 3H), 7.53–7.76(m), 12.56(s, 1H), Anal. Calcd. for $C_{16}H_{15}N_5O$ (293.33): C, 65.52, H, 5.15; N, 23.88 Found: C, 65.55, H, 5.21, N, 23.85 %.

Synthesis of 1-Aryl-3-arylazo[1,2,4]triazolo[3,4-b]quinazolin-5-ones (**7a–f**)

Method A: To a solution of the appropriate 3-chloro-1,5-diarylformazan **1** (0.005 mol) and 2,3-dihydro-2-thioxoquinazolin-4(1*H*)-one **4** (0.89 g, 0.005 mol) in chloroform (40 ml) was added tiethylamine (0.7 ml, 0.007 mol). The resulting mixture was refluxed till hydrogen sulfide ceased to evolve, then cooled. The precipitated solid triethylamine hydrochloride was filtered off. The excess solvent was distilled and the residue was triturated with few drops of methanol or petroleum ether (40–60°C) where it solidified. The solid product was filtered and crystallised from ethanol to give the respective derivative [1,2,4]triazolo[*3,4-b*]quinazolin-5-one **7**.

Repitition of the above procedure using **5** *in lieu* of **4** and work up the reaction mixture after methanethiol ceased to evolve afforded the respective arylazo derivative **7**.

Method B: A mixture of equimolar quantities of methyl anthranilate (1.5 g, 0.01 mol), the appropriate triazolinone **9** (0.01 mol) and conc. sulfuric acid (0.5 ml) was heated for 2 h, then cooled. The crude product was collected, washed with water, dried and finally crystallised from the appropriate solvent to give the respective derivative of **7** which was found to be identical in all respects with that one obtained by the foregoing procedure.

The compounds **7a–f** prepared together with their physical constants are listed below.

1-(4-Methylphenyl)-3-(4-methylphenylazo)[1,2,4]triazolo[3,4-b]-quinazolin-5-one (**7a**): Yield 66 %, m.p. 141°C; IR (KBr) υ (cm^{-1}) 1720, 1600, 1560; ^{1}H NMR (DMSO-d_6) δ 2.40 (s, 6H), 7.44 (td, *J*=9, 1.2Hz, 1H), 7.46 (d, *J*=8 Hz, 2H), 7.51 (d, *J*=8 Hz, 2H), 7.74 (d, *J*=8 Hz, 2H), 7.87 (td, *J*=9.0, 1.2 Hz, 1H), 8.10 (d, *J*=8 Hz, 2H), 8.22 (dd, *J*=9, 1.2 Hz, 1H), 8.30 (dd, *J*=9, 1.2 Hz, 1H); δ^{13}C (DMSO-d_6) 21.3, 21.9, 124.4, 124.9, 127.3, 129.3, 129.7, 131.1, 131.3, 133.3, 136.3, 136.9, 138.4, 144.3, 145.6, 149.9, 152.5, 159.6, 163.8.; MS *m/z* (%) 394 (M^+, 12.4), 290 (1.6) 142 (3.5), 159 (5.9), 145 (8.1), 119 (19.6); Anal. Calcd. For $C_{23}H_{18}N_6O$ (394.4): C, 70.04, H, 4.60; N, 21.30, Found: C, 70.00, H, 5.00, N, 21.20 %.

1-Phenyl-3-phenylazo[1,2,4]triazolo[3,4-b]quinazolin-5-one (**7b**): Yield 62 %, m.p. 151°C; IR (KBr) υ (cm^{-1}) 1705, 1620, 1550; ^{1}H NMR (DMSO-d_6) δ 7.44 (td, *J*=9, 1.2, 1H), 7.74–7.80 (m, 10H), 7.87 (td, *J*=9.0, 1.2 Hz, 1H), 8.22 (dd, *J*=9, 1.2 Hz, 1H), 8.30 (dd, *J*=9, 1.2 Hz, 1H); MS *m/z* (%) 366 (M^+, 27.4), 261 (7.9) 142 (5.9), 145 (18.5), 131 (7.9), 105 (30.1); Anal. Calcd. for $C_{21}H_{14}N_6O$ (366.4): C, 68.84, H, 3.85; N, 22.94, Found: C, 69.00, H, 3.80, N, 23.00 %.

1-(4-Chlorophenyl)-3-(4-chlorophenylazo)[1,2,4]triazolo[3,4-b]-quinazolin-5-one (**7c**): Yield 61 %, m.p. 275°C; IR (KBr) υ (cm^{-1}) 1700, 1610, 1540; ^{1}H NMR (DMSO-d_6) δ 7.44 (td, *J*=9, 1.2, 1H), 7.51 (d, *J*=8 Hz, 2H), 7.69 (d, *J*=8 Hz, 2H), 7.74 (d, *J*=8 Hz, 2H), 7.87 (td, *J*=9.0, 1.2 Hz, 1H), 8.22 (dd, *J*=9, 1.2 Hz, 1H), 8.23 (d, *J*=8 Hz, 2H), 8.30 (dd, *J*=9, 1.2 Hz, 1H); MS *m/z* (%) 435 (M^+, 22.0), 310 (1.8) 142 (1.5), 181 (2.5), 166 (1.3), 140 (3.7); Anal. Calcd. for $C_{21}H_{12}Cl_2N_6O$ (435.3): C, 57.95, H, 2.78; N, 19.31, Found: C, 57.93, H, 2.50, N, 19.40 %.

1-(3-Chlorophenyl)-3-(3-chlorophenylazo)[1,2,4]triazolo[3,4-b]-quinazolin-5-one (**7d**): Yield 60%, m.p. 240°C; IR (KBr) υ (cm^{-1}) 1700, 1630, 1580; ^{1}H NMR (DMSO-d_6) δ 7.44 (td, *J*=9, 1.2, 1H), 7.54-7.65 (m, 4H), 7.09–7.76 (m, 4H), 7.87 (td, *J*=9.0, 1.2 Hz, 1H), 8.22 (dd, *J*=9, 1.2 Hz, 1H), 8.30 (dd, *J*=9, 1.2 Hz, 1H); MS *m/z* (%) 435 (M^+, 2.0), 310 (1.8) 142 (4.6), 181 (4.0), 166 (5.0), 140 (6.1); Anal. Calcd. for $C_{21}H_{12}Cl_2N_6O$ (435.3): C, 57.95, H, 2.78; N, 19.31, Found: C, 57.70, H, 2.60, N, 19.30 %.

1-(3-Nitrophenyl)-3-(3-nitrophenylazo)[1,2,4]triazolo[3,4-b]-quinazolin-5-one (**7e**): Yield 69%, m.p. 184–185°C; IR (KBr) υ (cm^{-1}) 1690, 1620, 1530; ^{1}H NMR (DMSO-d_6) δ 7.12–7.66 (m, 9H), 7.87 (td, *J*=9.0, 1.2 Hz, 1H), 8.22 (dd, *J*=9, 1.2 Hz, 1H), 8.30 (dd, *J*=9, 1.2 Hz, 1H); MS *m/z* (%) 456 (M^+, 7.9), 321 (11.2) 142 (4.6), 190 (4.6), 177 (5.1), 150 (38.5); Anal. Calcd. for $C_{21}H_{12}N_8O_5$ (456.4): C, 55.27, H, 2.65; N, 24.55, Found: C, 55.50, H, 2.70, N, 24.40 %.

1-(4-Nitrophenyl)-3-(4-nitrophenylazo)[1,2,4]triazolo[3,4-b]-quinazolin-5-one (**7f**): Yield 70 %, m.p. 156–157°C; IR (KBr) υ (cm^{-1}) 1700, 1600, 1530; ^{1}H NMR (DMSO-d_6) δ 7.44 (td, *J*=9, 1.2Hz, 1H), 7.48 (d, *J*=6 Hz, 2H), 7.55 (d, *J*=6 Hz, 2H), 7.68 (d, *J*=6 Hz, 2H), 7.72 (d, *J*=6 Hz, 2H), 7.87 (td, *J*=9.0, 1.2 Hz, 1H), 8.22 (dd, *J*=9, 1.2 Hz, 1H), 8.30 (dd, *J*=9, 1.2 Hz, 1H); MS *m/z* (%) 456 (M^+, 11.7), 321 (19.1) 142 (3.5), 190 (3.7), 177 (5.2), 150 (3.1); Anal. Calcd. for $C_{21}H_{12}N_8O_5$ (456.4): C, 55.27, H, 2.65; N, 24.55 %, Found: C, 55.20, H, 2.90, N, 24.60 %.

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