Solvent and substituent effects on the electronic spectra of 3-arylazo-imidazo[1,2-*b*]pyrazolo[4,3-*d*]-pyridazines

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A series of new 3-arylazo-6-methyl-2,8,9-triphenyl-8*H*-imidazo[1,2-*b*]pyrazolo[4,3-*d*]pyridazines was prepared *via* reaction of hydrazonoyl halides with 3-hydrazonoacetyl-4-cyano-1,5-diphenylpyrazole. The structures of the compounds prepared were confirmed by spectral and elemental analyses. The solvatochromic and substituent effects on the absorption spectra of these azo dyes were interpreted by correlation of absorption frequencies with Kamlet–Taft and Hammett equations, respectively.

Keywords: arylazoheterocycles, pyrazole, hydrazonoyl bromides, imidazo[1,2-*b*]pyrazolo[4,3-*d*]-pyridazines

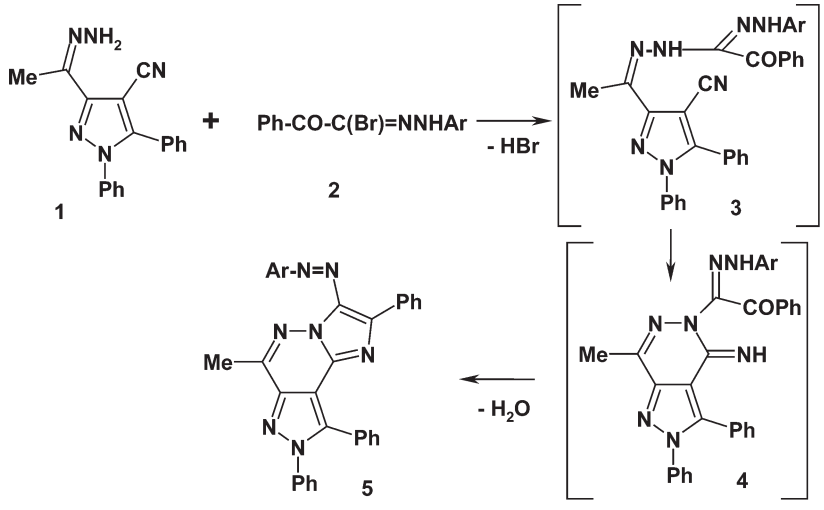
Over the past five years, we have explored the utility of hydrazonoyl halides in the synthesis of aryl- and heteroarylazo derivatives of heterocyclic compounds and studied their azo-hydrazone tautomerism.[1–8] Many such colourants have found numerous applications including hair dyes, disperse dyes, ink-jet inks and laser materials.[9,10] In this work, a series of 10 3-arylazo-8H-imidazo[1,2-*b*]pyrazolo[4,3-*d*]pyridazine derivatives **5a–j** were synthesised and their electronic absorption spectra have been recorded in the region 200–800 nm in five different solvents. Our intention was to shed some light on the effects of solvents and substituents on their absorption spectra *via* the application of the Kamlet–Taft and Hammett equations, respectively.[11,12]

Results and discussion

The required hydrazonoyl bromides **2a–j**[13–16] and 3-hydrazonoacetyl-4-cyano-1,5-diphenylpyrazole **1**[17] were prepared as previously reported. When equimolar quantities of **1** and each of the hydrazonoyl bromides **2** were refluxed in 1,4-dioxane in the presence of triethylamine, a single product was obtained in each case as evidenced by TLC analysis of the crude product. The structures of the compounds prepared were elucidated on the basis of their microanalyses and spectral data (MS, IR, ^{1}H NMR). Such results (see Experimental) indicated that the products isolated from the studied reactions are the respective tricyclic arylazo compounds **5** (Scheme 1). For example, their IR spectra revealed the absence of the bands due to the carbonyl and nitrile groups present in the putative intermediates **3** and **4** (Scheme 1). The ^{1}H NMR spectra of **5** exhibited a common signal assignable to the 6-methyl group in the range δ 2.56–2.82.

To account for the formation of the products **5**, it is suggested, as depicted in Scheme 1, that the reactions start with the formation of the substitution intermediates **3**. The latter undergo two successive *in situ* cyclisations to furnish the respective 3-arylazo-8*H*-imidazo[1,2-*b*]pyrazolo[4,3-*d*]-pyridazines **5** as the end products (Scheme 1).

The UV-Vis absorption spectra of the dyes prepared **5a–j** were recorded over the range 200–800 nm using a series of five solvents of different polarities at a concentration of 1×10^{-6} mol L^{-1}. Each of the dyes gave two absorption bands in all of the solvents employed. The results are summarised in Table 1. As shown, each compound exhibits an intense absorption band in the region 400–450 nm. Such data indicate that the electronic absorption spectra of compounds **5** are typical of azo chromophores.[8,18,19]



Ar = XC_6H_4

X : **a**, 4-MeO; **b**, 4-Me; **c**, H; **d**, 4-Cl; **e**, 3-Cl; **f**, 3-Br;

g, 4-EtOOC; **h**, 3-NO_2; **i**, 4-MeCO; **j**, 4-NO_2

Scheme 1

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Table 1 Electronic absorption spectral data of compounds **5a–j** in various solvents

Compd	Solvent/λ_{max} (log ε)				
	Ethanol	1,4-Dioxane	Chloroform	Methanol	Acetonitrile
5a	405(4.14); 306 (4.22)	405 (4.13); 299 (4.50)	410 (4.08); 298 (4.62)	401 (4.33); 300 (5.20)	405 (4.13); 303 (4.48)
5b	405(3.94); 302 (4.60)	404 (3.71); 290 (5.22)	423 (3.57); 300 (4.53)	401 (4.34); 228 (5.60)	400 (3.50); 296 (4.28)
5c	405(4.29); 304 (4.35)	405 (4.25); 301 (4.50)	409 (4.30); 298 (4.59)	399 (4.51); 228 (5.69)	405 (4.26); 300 (4.49)
5d	412(4.34); 305 (4.01)	413 (4.35); 300 (4.42)	416 (4.16); 298 (4.61)	411 (4.15); 230 (5.22)	413 (4.30); 300 (4.45)
5e	412(4.41); 304 (4.03)	412 (4.36); 299 (4.42)	415 (4.37); 294 (4.42)	410 (4.41); 300 (4.67)	411 (4.40); 300 (4.41)
5f	412(4.23); 305 (4.13)	412 (4.18); 293 (4.26)	416 (4.21); 288 (4.57)	411 (4.20); 300 (4.71)	412 (4.18); 300 (4.26)
5g	415(4.04); 312 (4.20)	422 (4.06); 300 (4.51)	425 (4.04); 288 (4.61)	415 (3.89); 300 (4.52)	422 (4.03); 300 (4.54)
5h	417(4.27); 304 (4.05)	417 (4.25); 290 (4.53)	420 (4.28); 292 (4.60)	416 (4.27); 268 (5.04))	416 (4.26); 300 (4.25)
5i	427(4.19); 307 (3.95)	426 (4.15); 296 (4.36)	429 (4.13); 298 (4.34)	428 (3.82); 300 (4.21)	425 (4.11); 303 (4.20)
5j	441(4.46); 303 (4.21)	441 (4.46); 292 (4.53)	448 (4.43); 288 (4.58)	438 (4.55), 348 (4.60)	440 (4.47); 306 (4.31)

As shown in Table 1, the absorption bands for all of the compounds **5** suffer small solvent shifts, a behaviour which is expected for local electronic transitions corresponding to π–π* transitions. The highest bathochromic shift was obseved in methanol for all compounds. In addition, the visible spectra of the compounds having electron withdrawing substituents such as **5d–j** exhibit large bathochromic shift in all solvents used (Table 1).

The effect of solvent polarity and hydrogen bonding on absorption spectra of the studied compounds **5** were examined by means of the linear solvation energy relation (LSER) namely Kamlet–Taft equation [Eqn (1)].[11,12]

$$\tilde{\upsilon} = \upsilon^{\circ} + s\pi^* + b\beta + a\alpha \quad (1)$$

where π* is the measure of solvent dipolarity/polarisabilty, β is the scale of the solvent hydrogen bond acceptor (HBA), basicities, α is the scale of the solvent hydrogen-bond donor (HBD) acidities and υ° is the regression value of the solute property in the reference solvent cyclohexane. The regression coefficients s, b and a in Eqn (1) measure the relative susceptibilities of the solvent-dependent solute property (absorption frequencies) to the indicated solvent parameters. The values of the solvent parameters are given in Table 2.

The results of multiple linear regression analysis of the data by Eqn (1), are given in Table 3. As shown, the values (0.988–0.784) of the correlation coefficient (r) indicate that the absorption frequencies for the azo compounds **5a–j** in the selected solvents show satisfactory correlation with the solvent parameters π*, β and α. The degree of success of Eqn (1) is shown in Fig. 1 by means of a plot of υ_{max} calculated versus υ_{max} observed in 1,4-dioxane (Table 4). Furthermore, as the coefficients of the solvent parameters measure the relative susceptibilities of the solvent-dependent solute property namely the absorption frequencies to the solvent parameters, it is clear that the negative sign of the α-coefficient indicates a bathochromic shift and the positive sign of the β-coefficient indicates a hypsochromic shift. The percentage contributions of solvatochromic parameters for the azo dyes **5** are depicted in Table 5. As shown for almost all compounds, most of the solvatochromism is due to the solvent polarity and basicity rather than the solvent acidity.

As shown in Table 6, the absorption spectra of the compounds **5a–j** in a given solvent depend upon the nature of the substituents. For example, in methanol compounds **5** exhibit bathochromic shifts ($\Delta\lambda_{max}$) whose magnitude depends on the nature of the substituent present. In order to rationalise these results, the λ_{max} values of the series **5a–j** were correlated to Hammett constants. In such a correlation, the enhanced substituent constants $\sigma^{-}_{(X)}$ were used for the *para*-substituents as they are in direct conjugation with the azo chromophore.

Table 2 Solvent parameters[13]

Solvent	π*	β	α
Ethanol	0.54	0.77	0.83
1,4-Dioxane	0.55	0.37	0.0
Chloroform	0.58	0.0	0.44
Methanol	0.60	0.62	0.93
Acetonitrile	0.75	0.31	0.19

Table 4 Experimental and calculated values of υ_{max} of compounds **5a–j** in 1,4-dioxane

Compound	υ_{max} Calcd (10^{13}) Hz	υ_{max} exptl.(10^{13}) Hz
5a	73.94	74.17
5b	73.95	74.26
5c	73.83	74.07
5d	72.66	72.73
5e	72.82	72.9
5f	72.82	72.9
5g	71.1	71.17
5h	71.96	72.03
5i	70.45	70.42
5j	67.88	68.03

Table 3 Regression fits to solvatochromic parameters [Eqn (1)][a,b]

Compd	Equation	
5a	$\upsilon_{max} = (72.380 + 1.78\pi^* + 1.582\beta - 0.028\alpha)10^{13}$	r = 0.787; ±s = 0.749
5b	$\upsilon_{max} = (66.383 + 9.71\pi^* + 6.003\beta - 1.855\alpha)10^{13}$	r = 0.948; ±s = 1.034
5c	$\upsilon_{max} = (71.872 + 2.552\pi^* + 1.485\beta + 0.339\alpha)10^{13}$	r = 0.784; ±s = 0.813
5d	$\upsilon_{max} = (71.612 + 1.099\pi^* + 1.197\beta - 0.195\alpha)10^{13}$	r = 0.935; ±s = 0.233
5e	$\upsilon_{max} = (71.47 + 1.672\pi^* + 1.150\beta - 0.222\alpha)10^{13}$	r = 0.9067; ±s = 0.280
5f	$\upsilon_{max} = (71.53 + 1.438\pi^* + 1.355\beta - 0.448\alpha)10^{13}$	r = 0.933; ±s = 0.255
5g	$\upsilon_{max} = (70.03 + 0.571\pi^* + 2.052\beta + 0.625\alpha)10^{13}$	r = 0.988; ±s = 0.231
5h	$\upsilon_{max} = (70.69 + 1.563\pi^* + 1.126\beta - 0.289\alpha)10^{13}$	r = 0.938; ±s = 0.211
5i	$\upsilon_{max} = (69.13 + 1.821\pi^* + 0.879\beta - 0.638\alpha)10^{13}$	r = 0.975; ±s = 0.125
5j	$\upsilon_{max} = (65.683 + 2.753\pi^* + 1.869\beta - 0.345\alpha)10^{13}$	r = 0.902; ±s = 0.469

[a] r, Correlation coefficient; [b] ±s, standard error of the estimate.

Table 5 Percentage contribution of solventochromic parameters[a]

Compd	$P\pi^*$(%)	$P\beta$ (%)	$P\alpha$ (%)
5a	52.50	46.66	0.826
5b	55.28	34.15	10.55
5c	58.31	33.93	7.76
5d	44.10	48.04	7.85
5e	54.92	37.77	7.29
5f	44.36	41.8	13.82
5g	17.59	63.16	19.24
5h	52.48	37.8	9.71
5i	54.54	26.33	19.11
5j	55.42	37.62	6.95

[a] *P*i (%) = i (100)/[s + b + a].

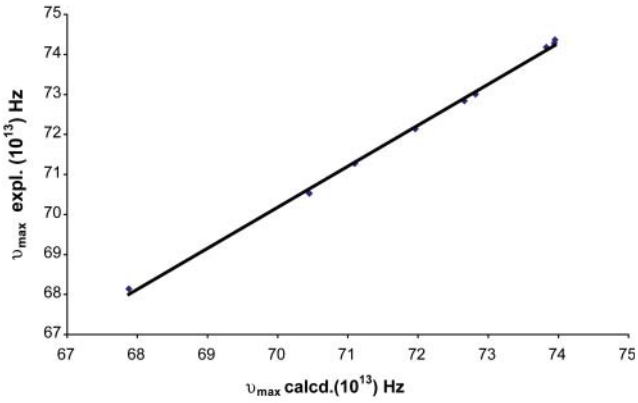

Fig. 1 The plot of υ_{max} observed against υ_{max} calculated from Eqn (1) for compound **5** in different solvents (data from Table 4).

Table 6 Substituent effects on electronic absorption spectra of compounds **5a–j** in methanol

Compound	λ_{max}	X	$\Delta\lambda_{max}$ [a]	σ_X^-
5a	401	4-MeO	+2	–0.27
5b	401	4-Me	+2	–0.17
5c	399	H	0.0	0.0
5d	411	4-Cl	+12	0.23
5e	410	3-Cl	+11	0.37
5f	411	3-Br	+12	0.39
5g	415	4-EtOOC	+16	0.68
5h	416	3-NO_2	+17	0.71
5i	428	4-Ac	+29	0.84
5j	438	4-NO_2	+39	1.28

[a] $\Delta\lambda_{max} = \lambda_{max}$ (**5**) – λ_{max} (**5**$_c$).

The results of such a correlation are shown in Fig. 2. The equation of the regression line is :

$$\lambda_{max\ (X)} = 403.1 + 24.23\ \sigma^-_{(X)}$$

with correlation coefficient r = 0.952 and standard deviation s = ± 3.99. This finding indicates that in the π–π* transition of the azo chromophore, the negative charge is largely localised on the N-atom adjacent to the benzene ring bearing the substituent.

Experimental

Melting points were determined on a Gallenkamp apparatus. IR spectra were recorded in potassium bromide using Perkin-Elmer FTIR 1650 and Pye-Unicam SP300 IR spectrophotometers. The ^{1}H NMR spectra were recorded in DMSO-d_6 on a Varian Mercury VXR-300 spectrometer (300 MHz for ^{1}H NMR), JEOL – ECA 500 MHz or JEOL JNM-LA400 for 400 MHz FT NMR Spectrometers. Mass spectra were recorded on a GCMS-QP 1000 EX Shimadzu and GCMS 5988-A HP spectrometers. Electronic absorption spectra were recorded on Perkin-Elmer Lambada 40 spectrophotometer. Elemental analyses were carried out at the Microanalytical Laboratory of Cairo University, Giza, Egypt. The hydrazonoyl bromides **2**[13–16] and 3-hydrazonoacetyl-4-cyano-1,5-diphenylpyrazole **1**.[17]

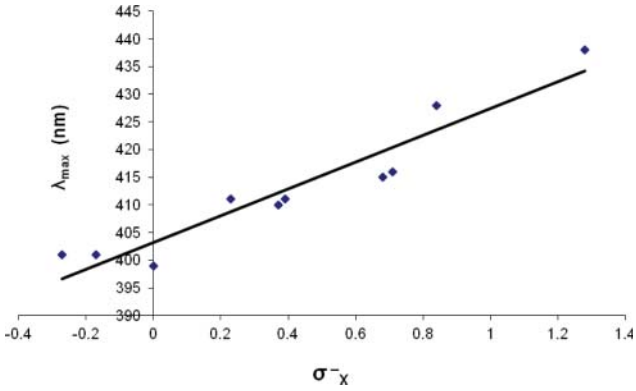

Fig. 2 Relation between λ_{max} and $\sigma^-_{(X)}$ for compounds **5a–j** in methanol (data from Table 6)

Reaction of compounds **1** *with hydrazonoyl bromides* (**2**): To a mixture of 3-hydrazonoacetyl-4-cyano-1,5-diphenylpyrazole (**1**) (0.75 g, 2.5 mmol) and the appropriate hydrazonoyl bromide (**2**) (2.5 mmol) in 1,4-dioxane (20 mL) was added triethylamine (0.35 mL). The mixture was refluxed for 10 h, then cooled. The solution was poured onto ice. The solid produced was collected by filtration and crystallised from the appropriate solvent to give the corresponding compound **5**.

*3-[4-Methoxyphenylazo]-6-methyl-2,8,9-triphenyl-8*H-*imidazo-[1,2*-b*]pyrazolo[4,3*-d*]pyridazine* (**5a**): Brown solid, (0.76 g, 64%), m.p. 214–216 °C (ethanol). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.74 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 7.35–7.64 (m, 15H, ArH), 7.81 (d, *J* = 8.0 Hz, 2H, ArH), 8.12 (d, *J* = 8.0 *Hz*, 2H, ArH); IR (KBr) ν_{max} 3066, 2931, 2835, 1593, 1496 cm^{-1}. MS *m/z* (%) 535 (M$^+$, 7), 377 (15), 97 (28), 84 (28), 77 (28), 73 (44), 72 (39), 55 (100). Anal. Calcd for $C_{33}H_{25}N_7O$ (535.21): C, 74.0; H, 4.70; N, 18.31. Found: C, 74.08; H, 4.81; N, 18.07%.

*6-Methyl-3-[4-methylphenylazo]-2,8,9-triphenyl-8*H-*imidazo[1,2*-b*]pyrazolo[4,3*-d*]pyridazine* (**5b**): Red solid, (0.65 g, 55%), m.p. 96–98 °C (1,4-dioxane-ethanol). ^{1}H NMR (DMSO-d_6, 500 MHz) δ 2.05 (s, 3H, CH_3), 2.79 (s, 3H, CH_3), 7.0 (d, *J* = 8.0 Hz, 2H, ArH), 7.67–7.36 (m, 15H, ArH), 7.94 (d, *J* = 8.0 Hz, 2H, ArH); IR (KBr) ν_{max} 3055, 2916, 2854, 1600, 1492, 1438, 1369, 1326 cm^{-1}. MS *m/z* (%) 519 (M$^+$, 31), 518 (33), 416 (38), 376 (36), 361 (47), 106 (43), 105 (38), 91 (51), 77 (100). Anal. Calcd for $C_{33}H_{25}N_7$ (519.22): C, 76.28; H, 4.85; N, 18.87. Found: C, 76.41; H, 5.04; N, 18.67%.

*6-Methyl-3-phenylazo-2,8,9-triphenyl-8*H-*imidazo[1,2*-b*]pyrazolo-[4,3*-d*]pyridazine* (**5c**):[16] Dark orange crystals (0.85 g, 67%), m.p. 230–232 °C (1,4-dioxane). ^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.56 (s, 3H, CH_3), 7.43–8.22 (m, 20H, ArH); IR (KBr) ν_{max} 1595, 1537, 1492 cm^{-1}. ^{13}C NMR (DMSO-d_6, 300 MHz) δ 17.6,109.1, 114.0,120.6, 120.7,121.8, 125.6, 126.2, 127.0, 128.1, 128.2, 128.8, 129.1, 129.2, 129.3, 129.4, 129.5, 130.3, 133.3, 138.2, 138.9, 148.0, 150.1, 153.5. MS *m/z* (%) 505 (M, 19), 504 (18), 476 (11), 252 (3), 180 (7), 77 (100). Anal. Calcd for $C_{32}H_{23}N_7$ (505.57): C, 76.02; H, 4.59; N, 19.39. Found: C, 76.11; H, 4.42; N, 19.25%.

*3-[4-Chlorophenylazo]-6-methyl-2,8,9-triphenyl-8*H-*imidazo[1,2*-b*]-pyrazolo[4,3*-d*]pyridazine* (**5d**): Red solid, (0.78 g, 66%), m.p. 232–234 °C (1,4-dioxane-ethanol). ^{1}H NMR (DMSO-d_6, 500 MHz) δ 2.72 (s, 3H, CH_3), 7.38–7.61 (m, 15H, ArH), 7.76 (d, *J* = 8.0 Hz, 2H, ArH), 8.12 (d, *J* = 8.0 Hz, 2H, ArH); IR (KBr) ν_{max} 3058, 1631, 1596, 1488, 1373, 1323 cm^{-1}. MS *m/z* (%) 541 (M$^+$+2, 17), 540 (M$^+$+1, 29), 539 (M$^+$, 52), 538 (56), 537 (42), 416 (36), 415 (23), 400 (18), 270 (16), 180 (23), 127 (23), 111 (22), 77 (100). Anal. Calcd for $C_{32}H_{22}ClN_7$(539.02): C, 71.17; H, 4.11; N, 18.16. Found: C, 7099; H, 4.32; N, 18.43%.

*3-[3-Chlorophenylazo]-6-methyl-2,8,9-triphenyl-8*H-*imidazo[1,2*-b*]pyrazolo[4,3*-d*]pyridazine* (**5e**): Red solid, (0.81 g, 69%), m.p. 156–158 °C (1,4-dioxane-ethanol). ^{1}H NMR (DMSO-d_6, 500 MHz) δ 2.80

(s, 3H, CH_3), 7.47–7.79 (m, 19H, ArH); IR (KBr) ν_{max} 3062, 2912, 2854, 1631, 1596, 1488, 1369, 1326 cm^{-1}. MS *m/z* (%) 541 (M^++2, 4), 540 (M^++1, 15), 539 (M^+, 28), 539 (45), 538 (41), 537 (38), 510 (37), 509 (28), 416 (21), 400 (18), 270 (20), 180 (29), 111 (20), 77 (100). Anal. Calcd for $C_{32}H_{22}ClN_7$(539.02): C, 71.17; H, 4.11; N, 18.16. Found: C, 71.30; H, 4.03; N, 17.98%.

*3-[3-Bromophenylazo]-6-methyl-2,8,9-triphenyl-8*H-*imidazo[1,2*-b*]-pyrazolo[4,3*-d*]pyridazine* (**5f**): Red solid, (0.69 g, 59%), mp. 178-180 °C (1,4-dioxane-ethanol). ^{1}H NMR (DMSO-d_6, 500 MHz) δ 2.80 (s, 3H, CH_3), 7.44-7.91 (m, 19H, ArH); IR (KBr) ν_{max} 3058, 2854, 1593, 1535, 1489, 1435, 1369, 1323, 1254 cm^{-1}. MS *m/z* (%) 585 (M^++2, 22), 584 (M^++1, 22), 583 (M^+, 22), 401 (22), 283 (22), 248 (22), 147 (41), 122 (37), 117 (48), 116 (33), 113 (37), 104 (48), 101 (33), 99 (41), 98 (37), 94 (48), 92 (56), 89 (41), 86 (67), 79 (44), 78 (37), 77 (63), 60 (100). Anal. Calcd for $C_{32}H_{22}BrN_7$ (583.47): C, 65.76; H, 3.79; N, 16.78. Found: C, 65.85; H,4.03; N, 16.94%.

*3-[4-Ethoxycarbonylphenylazo]-6-methyl-2,8,9-triphenyl-8*H-*imidazo[1,2*-b*]pyrazolo[4,3*-d*]pyridazine* (**5g**): Red solid, (087 g, 74%), m.p. 193–195 °C (1,4-dioxane-ethanol). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 0.97 (t, *J* = 7.0 Hz, 3H, CH_3), 2.75 (s, 3H, CH_3), 4.68 (q, *J* = 7.0 Hz, 2H, CH_2), 7.12 (d, *J* = 8.0 Hz, 2H, ArH), 7.34–7.96 (m, 15H, ArH), 8.08 (d, *J* = 8.0 Hz, 2H, ArH); IR (KBr) ν_{max} 3062, 2923, 2808, 1725, 1596, 1539, 1373, 1323, 1249 cm^{-1}. MS *m/z* (%) 577 (M^+, 10), 576 (11), 301 (43), 131 (46), 120 (75), 105 (57), 104 (46), 91 (32), 90 (39), 77 (46), 75 (32), 60 (100), 59 (54). Anal. Calcd for $C_{35}H_{27}N_7O_2$ (577.63): C, 72.78; H, 4.71; N, 16.97. Found: C, 72.56; H, 4.66; N, 17.03%.

*6-Methyl-3-[3-nitrophenylazo]-2,8,9-triphenyl-8*H-*imidazo[1,2*-b*]-pyrazolo[4,3*-d*]pyridazine* (**5h**): Red solid, (0.82 g, 70%), m.p. 226–228 °C (1,4-dioxane-ethanol). ^{1}H NMR (DMSO-d_6, 500 MHz) δ 2.82 (s, 3H, CH_3), 7.49–8.30 (m, 19H, ArH); IR (KBr) ν_{max} 3059, 2851, 1632, 1597, 1524, 1485, 1439, 1323, 1258 cm^{-1}. MS *m/z* (%) 552 (M^++2, 29), 167 (29), 150 (33), 149 (52), 132 (29), 121 (43), 83 (67), 71 (81), 57 (100). Anal. Calcd for $C_{32}H_{22}N_8O_2$ (550.57): C, 69.81; H, 4.03; N, 20.35. Found: C, 69.67; H, 4.22; N, 20.25%.

*3-[4-Acetylphenylazo]-6-methyl-2,8,9-triphenyl-8*H-*imidazo[1,2*-b*]-pyrazolo[4,3*-d*]pyridazine* (**5i**): Orange solid, (0.91 g, 77%), m.p. 130–132 °C (ethanol). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.38 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 7.35–7.75 (m, 15H, ArH), 7.72 (d, *J* = 8.0 Hz, 2H, ArH), 8.09 (d, *J* = 8.0 Hz, 2H, ArH); IR (KBr) ν_{max} 3067, 2974, 2882, 1690, 1663, 1597, 1493, 1373, 1326, 1254 cm^{-1}. MS *m/z* (%) 548 (M^++1, 4), 547 (M^+, 6), 416 (33), 404 (53), 389 (78), 120 (48), 105 (60), 77 (100). Anal. Calcd for $C_{34}H_{25}N_7O$ (547.61) C, 74.57; H, 4.60; N, 17.90. Found: C, 74.52; H, 4.35; N, 17.72%.

*6-Methyl-3-[4-nitrophenylazo]-2,8,9-triphenyl-8*H-*imidazo[1,2*-b*]-pyrazolo[4,3*-d*]pyridazine* (**5j**): Red solid, (0.86 g, 73%), m.p. 272–274 °C (1,4-dioxane-ethanol). ^{1}H NMR (DMSO-d_6, 500 MHz) δ 2.80 (s, 3H, CH_3), 7.20-8.40 (m, 19H, ArH); IR (KBr) ν_{max} 3063, 2851, 1632, 1593, 1504, 1435, 1377, 1327, 1254 cm^{-1}. MS *m/z* (%) 550 (M^+, 34), 549 (40), 549 (57), 548 (49), 476 (26), 416 (60), 415 (40), 195 (31), 180 (37), 138 (51), 105 (37), 92 (60), 77 (100). Anal. Calcd for $C_{32}H_{22}N_8O_2$(550.57): C, 69.81; H, 4.03; N, 20.35. Found: C, 70.06; H, 4.12; N, 20.59%.

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