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A novel and efficient approach for the synthesis of new halo substituted 2-arylpyrazolo[4,3-*c*] coumarin derivatives

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ABSTRACT

A convenient protocol for the efficient synthesis of 2-arylpyrazolo[4,3-c]coumarins is described. The synthesis route involves molecular iodine catalyzed oxidative cyclization of 1-phenyl-3-(2'-hydroxyaryl)-4-formyl pyrazoles in dimethylsulfoxide. During the lactonisation of 4-formylpyrazoles, we found that iodine was incorporated into the unsubstituted O/P position of the 3-(2'-hydroxyaryl) group. Under similar conditions *o*-allyloxy derivative of pyrazoles gave same corresponding lactone derivatives by deallylation, lactonisation, and iodination in one step.

1. Introduction

The diverse biological activities of natural and synthetic coumarins as coagulants [1] and antithrombotics [2] are well known. Some of the coumarins are reported as anti HIV agents [3] and antioxidants [4]. Many coumarin derivatives are known as free radical scavengers [5]. Recent work demonstrated that novobiocin was observed to be a DNA-gyrase inhibitor [6] that binds to the C-terminal nucleotide binding region of heat shock protein-90 [7]. They have also found to posses vasorelaxant [8], anti-inflammatory [9] and antitumor [10] activity. The incorporation of a fused heterocyclic moiety in parent coumarin alters its properties and converts it into important derivatives [11,12]. Large numbers of heterocyclic fused and heterocyclic substituted coumarin derivatives is used as drugs and dyes [13,14].

The literature reports a short number of synthetic routes for 2-arylpyrazolo[4,3-c]coumarins (2-arlychromeno[4,3-c]pyrazol-4(2*H*)-ones), such as cyclization of the 3-hydrazone-4-chloro or 4-hydroxy coumarins, which were relatively unstable and give a mixture of isomeric 1-aryl and 2-arylpyrazolo[4,3-c]coumarins [15,16]. These compounds were studied for binding studies interaction with the central benzodiazepine receptor [17].

Considering the activity profile of the 2-arylpyrazolo[4,3-c]coumarins, we decided to synthesis a new series of halo substituted 2-arylpyrazolo[4,3-c]coumarin derivatives. In this account, we describe a new synthetic route for the synthesis of the title compounds from the corresponding 3-(2-hydroxyaryl)-1-phenyl-1*H*-pyrazole-4-carbaldehydes (**3**) and 3-(2-(allyloxyaryl)-1-phenyl-1*H*-pyrazole-4-carbaldehydes (**4**) by using iodine in dimethylsulfoxide. The use of iodine for synthetic purpose has gained significant importance. The negligible toxicity associated with iodine, in conjunction with ease of handling, readily availability, low cost and mild reaction conditions employed has resulted in its application in an increasing number of diverse transformations [18-28]. In continuation of our research programme using I_2/DMSO as an efficient catalytic system for oxidation of pyrazoline to pyrazole [29], deallylation and preparation of flavones from 2'-allyloxychalcones [30] and oxidation of dihydroflavone [31], here, we wish to report some new halo substituted 2-arylpyrazolo[4,3-c]coumarins under mild condition. To the best of our knowledge, there are no earlier reports for I_2/DMSO as an efficient catalytic system for the synthesis of 2-arylpyrazolo[4,3-c]coumarins.

2. Experimental

2.1. Instrumentation

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian VXR 300 instrument at 293 K in DMSO-d_6. Chemical shift values were recorded in δ units (ppm) relative to Me_4Si as internal standard. Melting points were determined by using a Buchi melting point apparatus. Infrared spectra (IR) were recorded using KBr pellets on a Perkin-Elmer 240C analyzer. Mass spectra were recorded in an AE-IMS-30 spectrometer. Thin layer chromatography (TLC) was performed on silica gel 60 PF_{254} plates or aluminium oxide plates from Merck. Elemental analyses were performed on a Thermo Flash EA 1112 analyzer.

2.2. Synthesis

2.2.1. General procedure for the preparation of substituted acetophenones (1a-g)

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Parent 5-chloro-2-hydroxyacetophenone, 5-bromo-2-hydroxyacetophenone, 3-chloro-2-hydroxyacetophenone, 3,5-dichloro-2-hydroxyacetophenone, and 5-methyl-2-hydroxy-acetophenone were synthesized from *p*-chloro, *p*-bromo, *o*-chloro, 2,4-dichloro and *p*-cresol phenols respectively, by Fries-rearrangement using acetyl chloride and $AlCl_3$ [32]. 3,5-dibromo-2-hydroxyacetophenone and 3-bromo-5-methyl-2-hydroxyacetophenone were also synthesized by the bromination (bromine in acetic acid) method [32].

2.2.2. General procedure for the preparation of phenyl hydrazones (2a-g)

To a solution of the appropriate 2-hydroxyacetophenone derivatives (24 mmol) in 40 mL methanol, phenyl hydrazine (24 mmol) was added and refluxed for two hours. After cooling the reaction mixture the phenyl hydrazone derivatives was crystallized and filtered, the yield was 91-94 %.

5-Chloro-2-hydroxy acetophenone phenylhydrazone (**2a**): Yield: 91%. M.p.: 169-171 °C (170 °C [33]). FT-IR (KBr, ν, cm^{-1}): 3355, 1601. ^{1}H NMR (300 MHz, $CDCl_3$): 2.30 (s, 3H), 6.93-7.03 (m, 4H), 7.16 (dd, 1H J_1 = 8.4 Hz, J_2 = 2.4 Hz), 7.29-7.36 (m, 4H), 12.49 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 16.2, 115.4, 118.3, 119.8, 120.6, 128.1, 129.8, 130.5, 133.8, 145.1, 160.4, 170.1. MS (EI, m/z): 262 (M+2), 260 (M^+), 243. Anal. Calcd. for $C_{14}H_{13}N_2OCl$: C, 64.61; H, 5.00; N, 10.76. Found: C, 64.72; H, 4.93; N, 10.68%.

5-Bromo-2-hydroxy acetophenone phenylhydrazone (**2b**): Yield: 93%. M.p.: 163-164 °C (164 °C [33]). FT-IR (KBr, ν, cm^{-1}): 3358, 1600. ^{1}H NMR (300 MHz, $CDCl_3$): 2.32 (s, 3H), 7.01 (d, 1H, J = 7.5 Hz), 7.08-7.12 (m, 3H), 7.21 (dd, 1H, J_1 = 7.8 Hz, J_2 = 2.7 Hz), 7.24-7.34 (m, 3H), 7.44 (d, 1H, J = 2.7 Hz), 12.61 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 15.8, 114.9, 117.1, 119.4, 119.8, 121.5, 128.2, 136.3, 137.1, 145.4, 159.2, 168.2. MS (EI, m/z): 306 (M+2), 304 (M^+). Anal. Calcd. for $C_{14}H_{13}N_2OBr$: C, 55.26; H, 4.27; N, 9.21. Found: C, 55.31; H, 4.22; N, 9.11%.

3-Chloro-2-hydroxyacetophenone phenylhydrazone (**2c**): Yield: 92%. M.p.: 146-148 °C. FT-IR (KBr, ν, cm^{-1}): 3325, 1601. ^{1}H NMR (300 MHz, $CDCl_3$): 2.34 (s, 3H), 6.81 (t, 1H, J = 8.1 Hz), 6.94 (t, 1H, J = 7.2 Hz), 7.31 (d, 2H, J = 8.1 Hz), 7.27-7.33 (m, 4H), 12.63 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 16.1, 115.3, 119.2, 120.3, 122.8, 125.6, 129.7, 129.8, 134.5, 144.2, 158.6, 169.3. MS (EI, m/z): 262 (M+2), 260 (M^+). Anal. Calcd. for $C_{14}H_{13}N_2OCl$: C, 64.61; H, 5.00; N, 10.76. Found: C, 64.56; H, 4.94; N, 10.81%.

3,5-Dichloro-2-hydroxy acetophenone phenylhydrazone (**2d**): Yield: 93%. M.p.: 132-134 °C (133 °C [15]). FT-IR (KBr, ν, cm^{-1}): 3344, 1604. ^{1}H NMR (300 MHz, $CDCl_3$): 2.33 (s, 3H), 6.96 (t, 1H, J = 7.5 Hz), 7.02 (d, 2H, J = 7.5 Hz), 7.28-7.33 (m, 4H), 7.39 (d, 1H, J = 2.1 Hz), 13.18 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 15.9, 115.9, 119.8, 122.0, 126.7, 129.3, 129.5, 129.8, 135.6, 144.8, 157.8, 168.8. MS (EI, m/z): 296 (M+2), 294(M^+). Anal. Calcd. for $C_{14}H_{12}N_2OCl_2$: C, 57.14; H, 4.08; N, 9.52. Found: C, 57.27; H, 4.11; N, 9.61%.

3,5-Dibromo-2-hydroxy acetophenone phenylhydrazone (**2e**): Yield: 93%. M.p.: 151-152 °C. FT-IR (KBr, ν, cm^{-1}): 3358, 1608. ^{1}H NMR (300 MHz, $CDCl_3$): 2.34 (s, 3H), 6.99 (t, 1H, J = 8.1 Hz), 7.09 (d, 2H, J = 7.1 Hz), 7.31 (s, 1H), 7.32-7.36 (m, 3H), 7.48 (d, 1H, J = 2.4 Hz), 12.87 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 16.1, 115.9, 116.0, 119.1, 119.4, 124.2, 128.1, 134.2, 139.3, 143.9, 159.1, 169.2. MS (EI, m/z): 386 (M+4), 384 (M+2), 382(M^+). Anal. Calcd. for $C_{14}H_{12}N_2OBr_2$: C, 43.97; H, 3.14; N, 7.32. Found: C, 44.08; H, 3.20; N, 7.42%.

3-Bromo-5-chloro-2-hydroxy acetophenone phenylhydrazone (**2f**): Yield: 93%. M.p.: 144-145 °C. FT-IR (KBr, ν, cm^{-1}): 3346, 1599. ^{1}H NMR (300 MHz, $CDCl_3$): 2.32 (s, 3H), 6.98 (t, 1H, J = 7.2 Hz), 7.04 (d, 2H, J = 7.2 Hz), 7.29 (s, 1H), 7.32-7.34 (m, 3H), 7.47 (d, 1H, J = 2.4 Hz), 13.36 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 15.8, 114.1, 116.3, 118.1, 120.0, 128.2, 128.3, 128.6, 133.5, 142, 158.2, 169.1. MS (EI, m/z): 342 (M+4), 340 (M+2), 338 (M^+). Anal. Calcd. for $C_{14}H_{12}N_2OBrCl$: C, 49.70; H, 3.55; N, 8.28. Found: C, 49.75; H, 3.61; N, 8.34%.

3-Bromo-5-methyl-2-hydroxy acetophenone phenyl hydrazone (**2g**): Yield: 93%. M.p.: 171-173 °C. FT-IR (KBr, ν, cm^{-1}): 3344, 1597. ^{1}H NMR (300 MHz, $CDCl_3$): 2.29 (s, 3H), 2.32 (s, 3H), 6.95 (t, 1H, J = 7.5 Hz), 7.04 (d, 2H, 8.4 Hz), 7.16 (s, 1H), 7.26-7.31 (m, 3H), 7.32 (d, 1H, J = 1.8 Hz), 13.17 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 16.1, 22.9, 112.6, 115.8, 117.0, 122.1, 128.3, 128.9, 134.0, 138.2, 142.4, 157.7, 169.4. MS (EI, m/z): 320 (M+2), 318 (M^+). Anal. Calcd. for $C_{15}H_{15}N_2OBr$: C, 56.60; H, 4.71; N, 8.80. Found: C, 56.71; H, 4.67; N, 8.69%.

2.2.3. General procedure for the preparation of 3-aryl-1-phenyl-1H-pyrazole-4-carbaldehyde (3a-g)

The derivatives of 2-hydroxyacetophenone phenyl hydrazone (0.01 mol) was dissolved in DMF (15 mL) and then $POCl_3$ (0.03 mol) was added drop wise at 0 °C. After a complete addition of $POCl_3$, the reaction mixture warmed at room temperature and heated at 60-70 °C for 2.5-3 h.The reaction was poured onto crushed ice and then neutralized with 10% aqueous NaOH solution. The precipitate was filtered, strongly washed with water and crystallized from ethanol.

3-(5-chloro-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (**3a**): Yield: 84%. M.p.: 132-134 °C. FT-IR (KBr, ν, cm^{-1}): 3450, 1683, 1657. ^{1}H NMR (300 MHz, $CDCl_3$): 7.02 (d, 1H, J = 8.4 Hz), 7.25 (dd, 1H, J_1 = 8.7 Hz, J_2 = 2.4 Hz), 7.43 (t, 1H, J = 7.2 Hz), 7.54 (t, 2H, J = 7.8 Hz), 7.69 (d, 2H, J = 7.8 Hz), 8.07 (d, 1H, J = 2.1Hz), 8.56 (s, 1H), 10.14 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 116.4, 118.5, 119.3, 122.8, 124.2, 128.4, 129.0, 129.7, 130.6, 133.5, 137.6, 150.9, 154.4, 183.2. MS (EI, m/z): 298 (M^+). Anal. Calcd. for $C_{16}H_{11}N_2O_2Cl$: C, 64.42; H, 3.69; N, 9.39. Found: C, 63.91; H, 3.58; N, 9.44%.

3-(5-bromo-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (**3b**): Yield: 86%. M.p.: 133-134 °C. FT-IR (KBr, ν, cm^{-1}): 3454, 1683, 1598. ^{1}H NMR (300 MHz, $CDCl_3$): 7.01 (d, 1H, J = 8.7 Hz), 7.42-7.49 (m, 2H), 7.57 (t, 2H, J = 8.4Hz), 7.72 (d, 2H, J = 8.4 Hz), 8.23 (s, 1H), 8.59 (s, 1H), 10.18 (s, 1H), 10.20 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 117.2, 117.7, 118.0, 119.2, 124.8, 128.4, 131.2, 131.4, 133.7, 134.6, 141.8, 151.8, 153.6, 183.4. MS (EI, m/z): 342 (M^+). Anal. Calcd. for $C_{16}H_{11}N_2O_2Br$: C, 56.14; H, 3.21; N, 8.18. Found: C, 56.23; H, 3.28; N, 8.23%.

3-(3-Chloro-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (**3c**): Yield: 85%. M.p.: 149-150 °C. FT-IR (KBr, ν, cm^{-1}): 3448, 1693, 1664. ^{1}H NMR (300 MHz, $CDCl_3$): 6.97 (t, 1H, J = 7.8 Hz), 7.41-7.45 (m, 2H), 7.53 (t, 2H, J = 7.5 Hz), 7.71 (d, 2H, J = 8.1 Hz), 7.98 (d, 1H, J = 7.8 Hz), 8.58 (s, 1H), 10.13 (s, 1H), 10.65 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 116.6, 119.2, 119.5, 121.9, 123.0, 128.2, 128.4, 129.8, 131.2, 133.4, 137.7, 151.4, 151.7, 183.5. MS (EI, m/z): 298 (M^+). Anal. Calcd. for $C_{16}H_{11}N_2O_2Cl$: C, 64.42; H, 3.69; N, 9.39. Found: C, 64.65; H, 3.74; N, 9.33%.

3-(3,5-Dichloro-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (**3d**): Yield: 88%. M.p.: 166-167 °C. FT-IR (KBr, ν, cm^{-1}): 3444, 1687, 1654. ^{1}H NMR (300 MHz, $CDCl_3$): 7.44-7.47 (m, 2H), 7.54 (t, 2H, J = 7.5Hz), 7.70 (d, 2H, J = 7.5 Hz), 8.18 (s, 1H), 8.54 (s, 1H), 10.11 (s, 1H), 10.79 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 117.4, 119.5, 122.7, 123.2, 124.4, 127.9, 128.8, 130.0, 130.8, 134.2, 137.7, 150.4, 150.8, 183.0. MS (EI, m/z): 332 (M^+). Anal. Calcd. for $C_{16}H_{10}N_2O_2Cl_2$: C, 57.83; H, 3.01; N, 8.43. Found: C, 57.76; H, 3.02; N, 8.58%.

3-(3,5-dibromo-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (**3e**): Yield: 87%. M.p.: 172-173 °C. FT-IR (KBr, ν, cm^{-1}): 3360, 1689, 1661. ^{1}H NMR (300 MHz, $CDCl_3$): 7.49 (t, 1H, J = 8.7Hz), 7.56 (t, 2H, J = 8.7 Hz), 7.72 (d, 2H, J = 8.4 Hz), 7.75 (d, 1H, J = 2.4 Hz), 8.37 (d, 1H, J = 2.4 Hz), 8.60 (s, 1H), 10.14 (s, 1H), 10.96 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 116.4, 117.1, 117.4, 121.3, 127.2, 128.4, 131.5, 132.1, 135.8, 136.4, 141.9, 151.6, 152.8, 183.8. MS (EI, m/z): 424 (M+4), 422 (M+2), 420

(M^+). Anal. Calcd. for $C_{16}H_{10}N_2O_2Br_2$: C, 45.71; H, 2.38; N, 6.66. Found: C, 45.82; H, 2.35; N, 6.71%.

3-(3-Bromo-5-chloro-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (**3f**): Yield: 84%. M.p.: 175-176 °C. FT-IR (KBr, ν, cm^{-1}): 3344, 1685, 1649. ^{1}H NMR (300 MHz, $CDCl_3$): 7.48 (t, 1H, *J* = 7.2 Hz), 7.57 (t, 2H, *J* = 7.2 Hz), 7.59 (d, 1H, *J* = 2.4 Hz), 7.74 (d, 2H, *J* = 7.2 Hz), 8.26 (d, 1H, *J* = 2.4 Hz), 8.61 (s, 1H), 10.16 (s, 1H), 10.96 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 117.2, 117.6, 119.2, 125.2, 128.4, 129.3, 131.4, 131.6, 132.1, 132.9, 139.7, 152.5, 154.7, 184.1. MS (EI, m/z): 380 (M+4), 376 (M^+). Anal. Calcd. for $C_{16}H_{10}N_2O_2BrCl$: C, 51.06; H, 2.65; N, 7.44. Found: C, 51.15; H, 2.60; N, 7.51%.

3-(3-Bromo-5-methyl-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (**3g**): Yield: 85%. M.p.: 159-160 °C. FT-IR (KBr, ν, cm^{-1}): 3489 (OH), 1680, 1645. ^{1}H NMR (300 MHz, $CDCl_3$): 2.36 (s, 3H), 7.44-7.46 (m, 2H), 7.54 (t, 2H, *J* = 7.2 Hz), 7.72-7.75 (m, 3H), 8.59 (s, 1H), 10.17 (s, 1H), 10.40 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 22.8, 116.1, 115.5, 119.3, 123.7, 128.2, 131.4, 132.1, 133.0, 134.7, 135.3, 141.2, 151.0, 151.8, 182.8. MS (EI, m/z): 358 (M+2), 356 (M^+). Anal. Calcd. for $C_{17}H_{13}N_2O_2Br$: C, 57.30; H, 3.65; N, 7.85. Found: C, 57.49; H, 3.71; N, 7.93%.

2.2.4. General procedure for the preparation of 3-(2-(allyloxy aryl)-1-phenyl-1H-pyrazole-4-carbaldehyde (4a-g)

To a solution of 3-aryl-4-formylpyrazole (3.5 mmol) in DMSO (10 mL), K_2CO_3 (8 mmol) and ally bromide (3.55 mmol) was added. The reaction mixture was stirred at room temperature for 4h. Then the reaction mixture was poured onto crushed ice. The precipitation was filtered and crystallized by methanol.

3-(2-(allyloxy)-5-chlorophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (**4a**): Yield: 87%. M.p.: 121-123 °C. FT-IR (KBr, ν, cm^{-1}): 1672, 1650. ^{1}H NMR (300 MHz, $CDCl_3$): 4.55 (d, 2H, *J* = 5.1 Hz), 5.24 (d, 1H, *J* = 10.8 Hz), 5.31 (d, 1H, *J* = 17.1 Hz), 5.93 (m, 1H), 6.95 (d, 1H, *J* = 8.7 Hz), 7.36-7.41 (m, 2H), 7.51 (t, 2H, *J* = 8.4 Hz), 7.62 (d, 1H, *J* = 2.4 Hz), 7.77 (d, 2H, *J* = 8.7 Hz), 8.51 (s, 1H), 9.82 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 69.5, 113.7, 118.0, 119.4, 122.3, 123.2, 126.1, 127.7, 129.1, 129.5, 130.2, 130.9, 132.0, 138.9, 150.4, 154.5, 185.9. MS (EI, m/z): 338 (M^+). Anal. Calcd. for $C_{19}H_{15}N_2O_2Cl$: C, 67.45; H, 4.43; N, 8.28. Found: C, 67.58; H, 4.31; N, 8.35%.

3-(2-(allyloxy)-5-bromophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (**4b**): Yield: 89%. M.p.: 128-129 °C. FT-IR (KBr, ν, cm^{-1}): 1675, 1658. ^{1}H NMR (300 MHz, $CDCl_3$): 4.58 (d, 2H, *J* = 5.4 Hz), 5.21 (d, 1H, *J* = 10.5 Hz), 5.40 (d, 1H, *J* = 17.4 Hz), 5.91 (m, 1H), 6.88 (d, 1H, *J* = 8.7 Hz), 7.32-7.41 (m, 2H), 7.50 (t, 2H, *J* = 8.4 Hz), 7.74 (d, 1H, *J* = 2.4 Hz), 7.86 (d, 2H, *J* = 8.4 Hz), 8.53 (s, 1H), 9.79 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 70.1, 112.3, 115.9, 118.1, 119.2, 122.1, 122.8, 129.5, 129.8, 130.5, 132.0, 135.7, 135.8, 140.3, 150.6, 155.3, 186.4. MS (EI, m/z): 384 (M+2), 382 (M^+); Anal. Calcd. for $C_{19}H_{15}N_2O_2Br$: C, 59.68; H, 3.92; N, 7.32. Found: C, 60.08; H, 4.09; N, 7.18%.

3-(2-(allyloxy)-3-chlorophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (**4c**): Yield: 88%. M.p.: 92-94 °C. FT-IR (KBr, ν, cm^{-1}): 1678, 1635. ^{1}H NMR (300 MHz, $CDCl_3$): 4.32 (d, 2H, *J* = 6 Hz), 5.01 (d, 1H, *J* = 10.5 Hz), 5.19 (d, 1H, *J* = 16.8 Hz), 5.82 (m, 1H), 7.21 (t, 1H, *J* = 7.8 Hz), 7.42 (t, 1H, *J* = 7.5 Hz), 7.50-7.57 (m, 4H), 7.79 (d, 2H, *J* = 7.5 Hz), 8.54 (s, 1H), 9.85 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 68.4, 114.3, 119.1, 120.4, 123.7, 124.8, 125.1, 129.3, 129.5, 129.8, 131.7, 132.8, 134.6, 138.8, 151.6, 155.5, 186.8. MS (EI, m/z): 338 (M^+). Anal. Calcd. for $C_{19}H_{15}N_2O_2Cl$: C, 67.45; H, 4.43; N, 8.28. Found: C, 67.15; H, 4.39; N, 8.31%.

3-(2-(allyloxy)-5,3-dichlorophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (**4d**): Yield: 90%. M.p.: 114-116 °C. FT-IR (KBr, ν, cm^{-1}): 1674, 1598. ^{1}H NMR (300 MHz, $CDCl_3$): 4.28 (d, 2H, *J* = 5.7 Hz), 5.11 (d, 1H, *J* = 10.2 Hz), 5.18 (d, 1H, *J* = 17.4 Hz), 7.41 (t, 1H, *J* = 7.2 Hz), 7.51-7.57 (m, 4H), 7.78 (d, 2H, *J* = 7.5 Hz), 8.54 (s, 1H), 9.84 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 70.1, 115.3, 115.6, 120.5, 122.8, 125.7, 126.8, 126.9, 128.0, 131.2, 132.3, 133.0, 136.8, 140.3, 151.2, 157.1, 188.2. MS (EI, m/z): 372 (M^+). Anal. Calcd. for $C_{19}H_{14}N_2O_2Cl_2$: C, 61.29; H, 3.76; N, 7.52. Found: C, 61.46; H, 3.66; N, 7.68%.

3-(2-(allyloxy)-5,3-dibromophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (**4e**): Yield: 91%. M.p.: 118-120 °C. FT-IR (KBr, ν, cm^{-1}): 1681, 1601. ^{1}H NMR (300 MHz, $CDCl_3$): 4.32 (d, 2H, *J* = 6 Hz), 5.02 (d, 1H, *J* = 10.5 Hz), 5.24 (d, 1H, *J* = 17 Hz), 7.45 (t, 1H, *J* = 7.5 Hz), 7.51 (d, 1H, *J* = 2.4 Hz), 7.53-7.61 (m, 3H), 7.78 (d, 2H, *J* = 7.5 Hz), 8.54 (s, 1H), 9.84 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 68.8, 112.0, 115.4, 118.4, 120.2, 122.3, 126.4, 128.9, 130.0, 132.8, 135.7, 136.5, 137.1, 143.1, 149.7, 150.1, 184.3. MS (EI, m/z): 464 (M+4), 462 (M+2), 460 (M^+). Anal. Calcd. for $C_{19}H_{14}N_2O_2Br_2$: C, 49.56; H, 3.04; N, 6.08. Found: C, 49.14; H, 3.12; N, 6.26%.

3-(2-(allyloxy)-3-bromo-5-chlorophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (**4f**): Yield: 89%. M.p.: 112-114 °C. FT-IR (KBr, ν, cm^{-1}): 1669, 1604. ^{1}H NMR (300 MHz, $CDCl_3$): 4.31 (d, 2H, *J* = 5.7 Hz), 5.14 (d, 1H, *J* = 10.4 Hz), 5.21 (d, 1H, *J* = 17.8 Hz), 7.43 (t, 1H, *J* = 7.6 Hz), 7.53-7.59 (m, 4H), 7.81 (d, 2H, *J* = 7.8 Hz), 8.59 (s, 1H), 9.87 (s, 1H). ^{13}C NMR (75 M Hz, $CDCl_3$): 74.9, 116.7, 118.6, 118.8, 119.5, 122.9, 128.0, 128.3, 129.3, 129.6, 130.2, 132.2, 133.8, 138.8, 149.7, 152.4, 185.8. MS (EI, m/z): 420 (M+4), 418 (M+2), 416 (M^+). Anal. Calcd. for $C_{19}H_{14}N_2O_2BrCl$: C, 54.80; H, 3.36; N, 6.73. Found: C, 55.03; H, 3.40; N, 6.51%.

3-(2-(allyloxy)-3-bromo-5-methylphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (**4g**): Yield: 91%. M.p.: 102-104 °C. FT-IR (KBr, ν, cm^{-1}): 1672, 1614. ^{1}H NMR (300 MHz, $CDCl_3$): 2.38 (s, 3H), 4.24 (d, 2H, *J* = 6 Hz), 5.09 (d, 1H, *J* = 10.8 Hz), 5.18 (d, 1H, *J* = 16.8 Hz), 5.81 (m, 1H), 7.40-7.42 (m, 2H), 7.49-7.54 (m, 2H), 7.78 (d, 2H, *J* = 8.1 Hz), 8.53 (s, 1H), 9.84 (s, 1H). ^{13}C NMR (75 M Hz, $CDCl_3$): 24.1, 69.3, 114.3, 115.1, 119.4, 119.8, 123.2, 128.3, 129.6, 131.4, 131.5, 134.0, 134.7, 134.9, 139.9, 150.8, 156.2, 184.8. MS (EI, m/z): 398 (M+2), 396 (M^+). Anal. Calcd. for $C_{20}H_{17}N_2O_2Br$: C, 60.60; H, 4.29; N, 7.07. Found: C, 60.56; H, 4.28; N, 7.11%.

2.2.5. General procedure for the preparation of substituted of 2-arylpyrazolo[4,3-c]coumarin derivatives (5a-g)

To a solution of 3-(2-hydroxyaryl)-1-phenyl-1*H*-pyrazole-4-carbaldehydes (**3a-g**) (1 mmol) or 3-(2-(allyloxyaryl)-1-phenyl-1*H*-pyrazole-4-carbaldehydes (**4a-g**) (1 mmol) in DMSO (10 mL), iodine (10 mol%) and 4-5 drops of concentrated H_2SO_4 was added. Then reaction mixture was heated at 120 °C. After the completion of the reaction (checked by TLC), the contents were cooled to room temperature and poured into ice-cooled water. The separated solid was filtered and washed with cooled dilute sodium thiosulphate solution. Finally the obtained product was crystallized from DMF to give product **5a-g**.

8-chloro-2-phenylchromeno[4,3-c]pyrazol-4(2H)-one (**5a**): FT-IR (KBr, ν, cm^{-1}): 1734. ^{1}H NMR (300 MHz, DMSO-d_6): 7.35 (d, 1H, *J* = 8.7 Hz, C_6-H), 7.44-7.50 (m, 2H, C_7-H & Ph-H), 7.57 (t, 2H, *J* = 7.8 Hz, Ph-H), 7.84 (d, 2H, *J* = 8.4 Hz, Ph-H), 8.17 (d, 1H, *J* = 2.7 Hz, C_9-H), 8.69 (s, 1H, C_3-H). ^{13}C NMR (75 MHz, DMSO-d_6): 109.1, 116.3, 120.8, 125.9, 127.1, 127.9, 128.9, 129.1, 130.9, 132.2, 140.2, 150.1, 150.9, 157.7. MS (EI, m/z): 296 (M^+). Anal. Calcd. for $C_{16}H_9N_2O_2Cl$. C, 64.86; H, 3.04; N, 9.45. Found: C, 63.94; H, 3.01; N, 9.57%.

8-bromo-2-phenylchromeno[4,3-c]pyrazol-4(2H)-one (**5b**): FT-IR (KBr, ν, cm^{-1}): 1741. ^{1}H NMR (300 MHz, DMSO-d_6): 7.38 (d, 1H, *J* = 8.1 Hz, C_6-H), 7.49-7.54 (m, 2H, C_7-H & Ph-H), 7.59 (t, 2H, *J* = 7.8 Hz, Ph-H), 7.81 (d, 2H, *J* = 8.4 Hz, Ph-H), 8.35 (d, 1H, *J* = 2.9 Hz, C_9-H), 8.71(s, 1H, C_3-H). ^{13}C NMR (75 MHz, DMSO-d_6): 106.9, 115.1, 119.0, 123.8, 127.3, 129.5, 129.8, 131.3, 132.4,

135.5, 141.2, 148.1, 151.6, 159.8. MS (EI, m/z): 340 (M^+). Anal. Calcd. for $C_{16}H_9N_2O_2Br$. C, 56.47; H, 2.64; N, 8.23. Found: C, 56.31; H, 2.71; N, 8.09%.

6-chloro-2-phenylchromeno[4,3-c]pyrazol-4(2H)-one (**5c**): FT-IR (KBr, ν, cm^{-1}): 1740. ^1H NMR (300 MHz, DMSO-d_6): 7.21 (t, 1H, *J* = 8.1 Hz, C_8-H), 7.38-7.43 (m, 2H, C_7-H & Ph-H), 7.60 (t, 2H, *J* = 8.1 Hz, Ph-H), 7.84 (d, 2H, *J* = 8.4 Hz, Ph-H), 8.15 (dd, 1H, J_1=8.1 Hz, J_2= 2.4 Hz, C_9-H), 8.66 (s, 1H, C_3-H). ^{13}C NMR (75 MHz, DMSO-d_6): 105.1, 119.0, 121.4, 128.2, 128.8, 129.1, 130.4, 131.1, 132.0, 132.8, 141.4, 149.2, 152.3, 157.8. MS (EI, m/z): 296 (M^+). Anal. Calcd. for $C_{16}H_9N_2O_2Cl$. C, 64.86; H, 3.04; N, 9.45. Found: C, 66.09; H, 2.98; N, 9.59%.

6,8-Dichloro-2- phenylchromeno[4,3-c]pyrazol-4(2H)-one (**5d**): FT-IR (KBr, ν, cm^{-1}): 1747. ^1H NMR (300 MHz, DMSO-d_6): 7.49 (t, 1H, *J* = 7.5 Hz, Ph-H), 7.56-7.61 (m, 3H, C_7-H & Ph-H), 7.84 (d, 2H, *J* = 7.8 Hz, Ph-H), 8.10 (d, 1H, *J* = 2.4 Hz, C_9-H), 8.72 (s, 1H, C_3-H). ^{13}C NMR (75 MHz, DMSO-d_6): 110.2, 118.1, 121.8, 128.3, 131.2, 132.0, 132.5, 132.9, 133.2, 134.8, 141.2, 147.3, 153.0, 159.9. MS (EI, m/z): 330 (M^+). Anal. Calcd. for $C_{16}H_8N_2O_2Cl_2$. C, 58.18; H, 2.42; N, 8.48. Found: C, 58.34; H, 2.61; N, 8.11%.

6,8-Dibromo-2-phenylchromeno[4,3-c]pyrazol-4(2H)-one (**5e**): FT-IR (KBr, ν, cm^{-1}): 1766. ^1H NMR (300 MHz, DMSO-d_6): 7.49 (t, 1H, *J* = 7.5 Hz, Ph-H), 7.58 (t, 2H, *J* = 7.5 Hz, Ph-H), 7.83 (d, 2H, *J* = 7.8 Hz, Ph-H), 7.88 (d, 1H, *J* = 2.1 Hz, C_7-H), 8.29 (d, 1H, *J* = 2.1 Hz, C_9-H), 8.71 (s, 1H, C_3-H). ^{13}C NMR (75 MHz, DMSO-d_6): 107.8, 116.1, 121.4, 124.6, 127.8, 131.0, 132.2, 132.8, 134.3, 137.4, 139.9, 149.6, 152.9, 161.2. MS (EI, m/z): 418 (M^+). Anal. Calcd. for $C_{16}H_8N_2O_2Br_2$. C, 45.93; H, 1.91; N, 6.69. Found: C, 46.12; H, 1.83; N, 6.78%.

6-Bromo-8-chloro-2-phenylchromeno[4,3-c]pyrazol-4(2H)-one (**5f**): FT-IR (KBr, ν, cm^{-1}): 1759. ^1H NMR (300 MHz, DMSO-d_6): 7.49 (t, 1H, *J* = 7.5 Hz, Ph-H), 7.59 (t, 2H, *J* = 7.5 Hz, Ph-H), 7.75 (d, 1H, *J* = 2.4 Hz, C_7-H), 7.85 (d, 2H, *J* = 7.5 Hz, Ph-H), 8.15 (d, 1H, *J* = 2.4, C_9-H), 8.72 (s, 1H, C_3-H). ^{13}C NMR (75 MHz, DMSO-d_6): 109.2, 119.4, 121.5, 127.9, 129.1, 130.5, 130.7, 131.9, 132.6, 135.8, 142.8, 149.6, 151.0, 157.5. MS (EI, m/z): 374 (M^+). Anal. Calcd. for $C_{16}H_8N_2O_2BrCl$. C, 51.33; H, 2.13; N, 7.48. Found: C, 51.64; H, 2.34; N, 7.31%.

6-Bromo-8-methyl-2-phenylchromeno[4,3-c]pyrazol-4(2H)-one (**5g**): FT-IR (KBr, ν, cm^{-1}): 1741. ^1H NMR (300 MHz, DMSO-d_6): 2.44 (s, 3H, CH_3), 7.46 (t, 1H, *J* = 7.2 Hz, Ph-H), 7.54- 7.59 (m, 3H, C_7-H & Ph-H), 7.84 (d, 2H, *J* = 7.5 Hz, Ph-H), 7.95 (d, 1H, *J* = 1.2 Hz, C_9-H), 8.69 (s, 1H, C_3-H). ^{13}C NMR (75 MHz, DMSO-d_6): 25.1, 110.9, 117.4, 122.1, 127.9, 130.3, 131.2, 131.7, 132.0, 134.7, 139.9, 140.8, 148.4, 150.4, 157.1. MS (EI, m/z): 354 (M^+). Anal. Calcd. for $C_{17}H_{11}N_2O_2Br$. C, 57.62; H, 3.10; N, 7.90. Found: C, 57.41; H, 2.93; N, 7.61%.

2.2.6. General procedure for the preparation of substituted of 2-arylpyrazolo [4, 3-c] coumarin derivatives (6a-c)

To a solution of 3-(2-hydroxyaryl)-1-phenyl-1*H*-pyrazole-4-carbaldehydes (**3a-c**) (1 mmol) or 3-(2-(allyloxyaryl)-1-phenyl-1*H*-pyrazole-4-carbaldehydes (**4a-c**) (1 mmol) in DMSO (20 mL), iodine (1.2 equivalent) and 4-5 drops of concentrated H_2SO_4 was added. Then the reaction mixture was heated at 120 ^oC. After the completion of the reaction (checked by TLC), the contents were cooled to room temperature and poured into ice-cooled water. The separated solid was filtered and washed with cooled dilute sodium thiosulphate solution. Finally the obtained product was crystallized from DMF to give product **6a-c**.

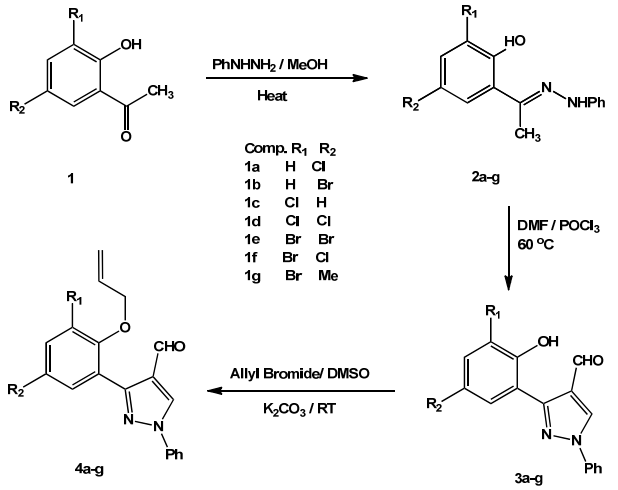
8-Chloro-6-iodo-2-phenylchromeno[4,3-c]pyrazol-4(2H)-one (**6a**): FT-IR (KBr, ν, cm^{-1}): 1745. ^1H NMR (300 MHz, DMSO-d_6): 7.48 (t, 1H, *J* = 7.5 Hz, Ph-H), 7.57 (t, 2H, *J* = 7.5 Hz, Ph-H), 7.83 (d, 2H, *J* = 8.4 Hz, Ph-H), 7.94 (d, 1H, *J* = 2.4 Hz, C_7-H), 8.16 (d, 1H, *J* = 2.4 Hz, C_9-H), 8.71 (s, 1H, C_3-H). ^{13}C NMR (75 MHz, DMSO-d_6): 87.3, 108.8, 115.6, 119.9, 121.7, 128.5, 129.3, 129.7, 131.3, 138.5, 138.8, 147.5, 150.9, 155.7. MS (EI, m/z): 422 (M^+). Anal. Calcd. for $C_{16}H_8N_2O_2ClI$. C, 45.49; H, 1.89; N, 6.63. Found: C, 45.61; H, 2.01; N, 6.31%.

8-Bromo-6-iodo-2-phenylchromeno[4,3-c]pyrazol-4(2H)-one (**6b**): FT-IR (KBr, ν, cm^{-1}): 1743. ^1H NMR (300 MHz, DMSO-d_6): 7.47 (t, 1H, *J* = 7.8 Hz, Ph-H), 7.57 (t, 2H, *J* = 7.8 Hz, Ph-H), 7.83 (d, 2H, *J* = 7.8 Hz, Ph-H), 8.08 (d, 1H, *J* = 2.4 Hz, C_7-H), 8.31 (d, 1H, *J* = 2.1 Hz, C_9-H), 8.70 (s, 1H, C_3-H). ^{13}C NMR (75 MHz, DMSO-d_6): 87.9, 108.2, 115.4, 115.6, 119.3, 124.2, 129.7, 130.1, 130.9, 138.1, 141.2, 148.1, 151.8, 156.3. MS (EI, m/z): 466 (M^+). Anal. Calcd. for $C_{16}H_8N_2O_2BrI$. C, 41.20; H, 1.71; N, 6.00. Found: C, 41.51; H, 1.87; N, 6.24%.

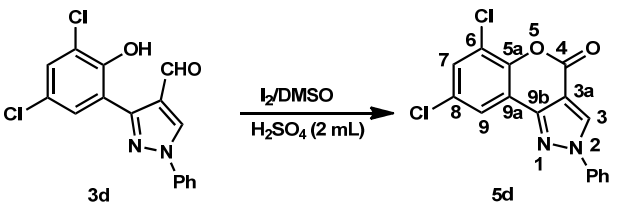
6-Chloro-8-iodo-2-phenylchromeno[4,3-c]pyrazol-4(2H)-one (**6c**): FT-IR (KBr, ν, cm^{-1}): 1749. ^1H NMR (300 MHz, DMSO-d_6): 7.48-7.51 (m, 1H, Ph-H), 7.58 (t, 2H, *J* = 7.2 Hz, Ph-H), 7.87 (d, 1H, *J* = 1.8 Hz, C_7-H), 7.92 (d, 2H, *J* = 7.2 Hz, Ph-H), 8.42 (d, 1H, *J* = 2.1 Hz, C_9-H), 9.01 (s, 1H, C_3-H). ^{13}C NMR (75 MHz, DMSO-d_6): 87.5, 109.5, 115.8, 120.8, 121.0, 128.3, 131.4, 131.6, 131.8, 138.6, 138.9, 148.0, 148.9, 156.0. MS (EI, m/z): 422 (M^+). Anal. Calcd. for $C_{16}H_8N_2O_2ClI$. C, 45.49; H, 1.89; N, 6.63. Found: C, 45.41; H, 1.81; N, 6.59%.

3. Results and discussion

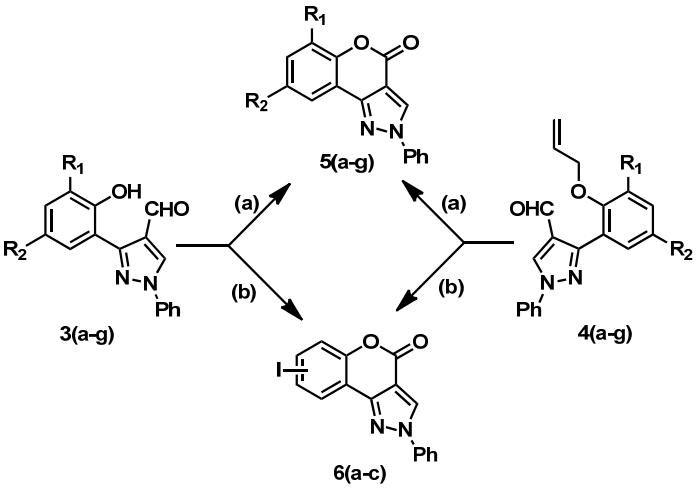
The overall synthetic route utilized for the preparation of the target pyrazolocoumarin is depicted in Scheme 1 and Scheme 2. Our approach to the synthesis of the target molecule, started from the condensation of halo substituted *o*-hydroxyacetophenones, **1a-g**, with phenyl hydrazine to efficiently provide the hydrazones, **2a-g**. These derivatives were purified and transformed into the corresponding 3-(2-hydroxyaryl)-1-phenyl-1*H*-pyrazole-4-carbaldehydes, **3a-g**, by using the Vilsmeier reagent (according to method of Rathelot *et. al.* [34]). The 3-(2-(allyloxyaryl)-1-phenyl-1*H*-pyrazole-4-carbaldehydes, **4a-g**, were readily prepared from **3a-g** using the ally bromide in DMSO (Scheme 1). These key intermediate substituted pyrazole-4-carbaldehydes (**3a-g** & **4a-g**) were required for the synthesis of 2-arylpyrazolo[4,3-*c*]coumarins.



Scheme 1



Scheme 2



	R_1	R_2		R_1	R_2		R_1	R_2		R_1	R_2
3a	H	Cl	**4a**	H	Cl	**5a**	H	Cl	**6a**	I	Cl
3b	H	Br	**4b**	H	Br	**5b**	H	Br	**6b**	I	Br
3c	Cl	H	**4c**	Cl	H	**5c**	Cl	H	**6c**	Cl	I
3d	Cl	Cl	**4d**	Cl	Cl	**5d**	Cl	Cl			
3e	Br	Br	**4e**	Br	Br	**5e**	Br	Br			
3f	Br	Cl	**4f**	Br	Cl	**5f**	Br	Cl			
3g	Br	Me	**4g**	Br	Me	**5g**	Br	Me			

(a) I_2 (10 mol %) /DMSO, conc. H_2SO_4, 120 °C, 5-7 h.
(b) I_2 (1.2 equiv.)/DMSO, conc. H_2SO_4, 120 °C, 3-4 h.

Scheme 3

Initially, we attempted the oxidative cyclization of 3-(3,5-dichloro-2-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde, **3d**, using iodine (5%) in dimethylsulfoxide in the presence of H_2SO_4 at 60 °C as per our known procedures for the flavone synthesis [23]. The product was not appearing even after 30 h. Showing that the formyl group of the pyrazole is not reactive. Actually the reaction rate depended on the catalyst amount and temperature (Scheme 2, Table 1). The best condition was obtained, using of 10% iodine in DMSO in the presence of catalytic amount of H_2SO_4 at 120 °C, and the reaction went to completion within 5 h and the corresponding product **5d** was obtained in 92% yield (Table 1). Encouraged based on these results, various 4-formylpyrazoles were converted to the corresponding coumarins in 87-94 % yield (Scheme 3, Table 2). The reaction probably proceeds via formation of hemiacetals by the reaction of 4-formyl group and phenol, and the oxidation of hemiacetal to lactone by molecular iodine in dimethylsulfoxide.

Table 1. Effect of the catalyst iodine and temperature on the synthesis of 6,8-dichloro-2-phenylchromeno[4,3-c]pyrazol-4(2*H*)-one (**4d**).

Entry	Mol (%)	Temp (°C)	Time (h)	Yield (%)
1	5	RT	30	NR
2	10	RT	30	NR
3	15	RT	30	NR
4	20	RT	30	NR
5	5	60	30	NR
6	10	60	30	NR
7	15	60	30	NR
8	20	60	26	20
9	5	120	20	60
10	10	120	5	92

RT: Room temperature.
NR: No Reaction.

According to our research in deallylation of 2'-allyloxychalcones [30], we attempted to apply this reagent for 3-(2-(allyloxyaryl)-1-phenyl-1*H*-pyrazole-4-carbaldehydes, **4a-g**. In this case also **4a-g** interestingly easily under went to deallylation as well as cyclization, and gave the corresponding pyrazolocoumarin (Scheme 3).

Table 2. Physico-chemical data of 2-arylpyrazolo[4,3-c]coumarins.

Entry	R_1	R_2	M.p. (°C)	Yield (%)	Time (h)
5a	H	Cl	189-190	89 [a], 91 [b]	7
5b	H	Br	196-197	91 [a], 89 [b]	6.5
5c	Cl	H	183-184	93 [a], 88 [b]	7
5d	Cl	Cl	233-234	92 [a], 88 [b]	5
5e	Br	Br	248-249	88 [a], 89 [b]	5
5f	Br	Cl	258-259	92 [a], 87 [b]	5.5
5g	Br	Me	254-255	94 [a], 88 [b]	5
6a	I	Cl	203-204	87 [a], 87 [b]	3.5
6b	I	Br	259-260	89 [a], 87 [b]	3
6c	Cl	I	208-209	91 [a], 86 [b]	4

[a] Yield of cyclization of 3a-g.
[b] Yield of cyclization of 4a-g.

On the other hand the excess in mol% of iodine (1.2 equiv.) on the mono substituted compounds of **3a-g** & **4a-g** leads to iodination at the phenol ring (Entry **6a**, **6b** and **6c**, Table 2, Scheme 3). If the para position in the phenol moiety is blocked the iodination takes place at the ortho position (Entry **6a**, **6b**, Table 2), while if the ortho position is blocked the iodination takes place at the para position (Entry **6c**, Table 2). The structure of the synthesized compounds was confirmed on the basis of spectroscopic methods. Lower amount of iodine (30%, 50%) gave the mixture of iodosubstituted and unsubstituted products. While in other prazoles were already substituted at both positions in the phenol moiety hence no iodination observed.

4. Conclusion

In summary, we have developed a simple and convenient method for the synthesis of 2-arylpyrazolo[4,3-c]coumarins using I_2/DMSO as an efficient catalytic system. The present methodology is clean; eliminates the toxic metal oxidant,

shorter reaction times, high yields, easy of workup and more applicable for the medicinal as well as pharmaceutical chemist.

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