***Experimental section***

***(E)-N'-(2-cyano-1-(p-tolyl)-1H-benzo[f]chromen-3-yl)-N-(4-sulfamoylphenyl) formimid-amide 3***

A mixture of formimidate derivative **2** (3.68 g, 10 mmol) and sulfanilamide (1.7 g, 10 mmol) in dry pyridine (20 mL) was heated under reflux for 6 h. After cooling, the deposited solid was filtered off, washed with petroleum ether (40-60oC), and then crystallized from ethanol to yield **3** as white crystals, m.p. 210-212oC, yield; 70 %. IR (KBr, *ν*, cm-1): br.3194 (NH2, NH), 2185 (C≡N), 1652 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 2.13 (s, 3H, CH3), 6.03 (s, 1H, C4H-pyran), 6.61 (s, 1H, N=CH), 7.00-8.65 (m, 14H, Ar-H + 2H, NH2, exchangeable with D2O), 9.42 (s, 1H, NH, exchangeable with D2O). Anal. Calcd. for C28H22N4O3S (494.57): C, 68.00; H, 4.48; N, 11.33; S, 6.48. Found: C, 68.13; H, 4.56; N, 11.27; S, 6.45.

***3-amino-1-(p-tolyl)-1H-benzo[f]chromene-2-carbonitrile 1***

A mixture of formimidate derivative **2** (3.68 g, 10 mmol) and cyclohexylamine (0.9 mL, 10 mmol) in dioxane (30 mL) was heated at refluxing temperature for 6 h. The excess solvent was removed by distillation and the obtained solid was filtered off, dried and then crystallized from ethanol to give **1** as white crystals, m.p. 272-273oC, yield: 75 %. IR (KBr, *ν*, cm-1): 3425, 3335 (NH), 2186 (C≡N), 1642 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 2.19 (s, 3H, CH3), 5.25 (s, 1H, C4H-pyran), 6.95 (s, 2H, NH2, exchangeable with D2O), 7.04-7.94 (m, 10H, Ar-H). Anal. Calcd. for C28H27N3O (421.54): C, 79.78; H, 6.46; N, 9.97. Found: C, 71.81; H, 6.51; N, 10.02.

***N'-(2-cyano-1-(p-tolyl)-1H-benzo[f]chromen-3-yl)-N-(pyridin-3-yl)formimidamide 5***

A mixture of formimidate derivative **2** (3.68 g, 10 mmol) and 3-amino pyridine (0.9 g, 10 mmol) in dioxane (30 mL) was heated under reflux for 6 h. The excess solvent was removed by distillation and the obtained solid was filtered off, dried and then crystallized from ethanol to give **5** as white crystals, m.p. 222-224oC, yield: 85%. IR (KBr, *ν*, cm-1): br.3440 (NH), 2200 (C≡N), 1659 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 2.22 (s, 3H, CH3), 5.48, 5.51 (2s, 1H, C4H-pyran), 7.08-9.17 (m, 14H, Ar-H+ 1H olefinic), 10.58, 11.03 (2 brs, 2H, 2NH, exchangeable with D2O). Anal. Calcd. for C27H20N4O (416.48): C, 77.87; H, 4.84; N, 13.45. Found: C, 77.74; H, 4.90; N, 13.47.

***10-(pyridin-3-yl)-12-(p-tolyl)-10,12-dihydro-11H-benzo[5,6]chromeno[2,3-d]pyrimidin-11-imine 6***

A mixture of formimidate derivative **2** (3.68 g, 10 mmol) and 3-amino pyridine (0.9 g, 10 mmol) in dry pyridine (20 mL) was heated under reflux for 6 h. After cooling, the precipitated solid was filtered off, dried, and then crystallized from EtOH to give **6** as white crystals, m.p. 150-152oC, yield: 81%. IR (KBr, *ν*, cm-1): 3274 (NH), 1629 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 2.11 (s, 3H, CH3), 6.58 (s, 1H, C4H-pyran), 7.00-8.90 (m, 14H, ArH), 9.44 (s, 1H, N=CH), 10.36 (brs, 1H, C=NH, exchangeable with D2O). Anal. Calcd. for C27H20N4O (416.48): C, 77.87; H, 4.84; N, 13.45. Found: C, 77.81; H, 4.79; N, 13.38.

***(E)-N'-(2-cyano-1-(p-tolyl)-1H-benzo[f]chromen-3-yl)-N-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)formimidamide 7***

A mixture of formimidate derivative **2** (3.68 g, 10 mmol) and 4-aminoantipyrine (2 g, 10 mmol) in dry pyridine (20 mL) was refluxed for 6h. The formed solid was filtered off, dried, and then crystallized from ethanol to yield **7** as orange crystals, m.p. 178-180oC, yield: 77%. IR (KBr, *ν*, cm-1): br.3164 (NH), 2186 (C≡N), 1654 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 1.92 (s, 3H, CH3), 2.09 (s, 3H, CH3), 2.15 (s, 3H, NCH3), 5.24 (s, 1H, C4H-pyran), 6.34 (s, 1H, N=CH), 6.94-8.23 (m, 15H, ArH), 8.54 (brs, 1H, NH, exchangeable with D2O). Anal. Calcd. for C33H27N5O2 (525.61): C, 75.41; H, 5.18; N, 13.32. Found: C, 75.51; H, 5.23; N, 13.44.

***14-(p-tolyl)-14H-benzo[5,6]chromeno[3,2-e][1,2,4]triazolo[1,5-c]pyrimidin-2-amine 8***

A mixture of formimidate derivative **2** (3.68 g, 10 mmol) and thiosemicarbazide (0.9 g, 10 mmol) in dry pyridine (20 mL) was refluxed for 7h. The excess solvent was removed and the formed solid was filtered off, dried, and then crystallized from EtOH to give **8** as brown crystals, m.p. > 300oC, yield: 70%. IR (KBr, *ν*, cm-1): 3336, 3169 (NH2), 1663(C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 2.13 (s, 3H, CH3), 6.01 (s, 1H, C4H-pyran), 6.99-8.22 (m, 10H, Ar-H), 7.17 (brs, 2H, NH2, exchangeable with D2O), 8.22(s, 1H, N=CH). Anal. Calcd. for C23H17N5O (379.42): C, 72.81; H, 4.52; N, 18.46. Found: C, 72.87; H, 4.66; N, 18.52.

***N-((Z)-3-(2-((E)-((2-cyano-1-(p-tolyl)-1H-benzo[f]chromen-3-yl)imino)methyl)hydrazinyl)-1-(1,3-diphenyl-1H-pyrazol-4-yl)-3-oxoprop-1-en-2-yl)benzamide 9***

A mixture of formimidate derivative **2** (3.68 g, 10 mmol) and *N*-(1-(1,3-diphenyl-1H-pyrazol-4-yl)-3-hydrazinyl-3-oxoprop-1-en-2-yl)benzamide (4.2 g, 10 mmol) in dry pyridine (30 mL) was refluxed for 6 h. The excess solvent was removed and the formed solid was filtered off, dried, and then crystallized from EtOH to give **8** as pale yellow crystals, m.p. 244-246oC, yield: 78%. IR (KBr, *ν*, cm-1): br 3201 (NH2, NH), 2207 (C≡N), br 1680 (C=O), 1639 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 2.14 (s, 3H, CH3), 6.18 (s, 1H, C4H-pyran), 7.04-8.58 (m, 11H, Ar-H + 2H olefinic), 8.32, 8.80 and 9.96 (brs, 3H, 3NH, exchangeable with D2O). Anal. Calcd. for C47H35N7O3 (745.84): C, 75.69; H, 4.73; N, 13.15. Found: C, 75.71; H, 4.68; N, 13.22.

***2-(14-(p-tolyl)-14H-benzo[5,6]chromeno[3,2-e][1,2,4]triazolo[1,5-c]pyrimidin-2-yl)aceto-nitrile 10***

A mixture of formimidate derivative **2** (3.68 g, 10 mmol) and cyanoacetohydrazide (0.9 g, 10 mmol) in dioxane (30 mL) was at refluxing temperature for 12 h. The produced solid while reflux was filtered off, dried, and then crystallized from dioxane/DMF to yield **10** as pale yellow crystals, m.p. 290-292oC, yield: 85%. IR (KBr, *ν*, cm-1): 3060 (CH aromatic), 2850 (CH aliphatic), 2256 (C≡N), 1634 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 2.11 (s, 3H, CH3), 4.51 (s, 2H, CH2CN), 6.19 (s, 1H, C4H-pyran), 6.98-8.06 (m, 10H, Ar-H), 9.63 (s, 1H, N=CH pyrimidine). Anal. Calcd. for C25H17N5O (403.45): C, 74.43; H, 4.25; N, 17.36. Found: C, 74.22; H, 4.33; N, 17.41.

***(2Z,4E)-5-phenyl-2-(14-(p-tolyl)-14H-benzo[5,6]chromeno[3,2-e][1,2,4]triazolo[1,5-c] pyramid in-2-yl)penta-2,4-dienenitrile 11***

A mixture of compound **10** (2 g, 5 mmol) and cinnamaldehyde(0.66 mL, 5 mmol) in dioxane (20 mL) in the presence of catalytic amount of piperidine (0.5 mL) was heated under reflux for 4h. The yielded solid on hot was filtered off, dried, and then crystallized from dioxane to give **11** as yellow crystals, m.p. 146-148oC, yield: 65%. IR (KBr, *ν*, cm-1): 3057 (CH aromatic), 2845 (CH aliphatic), 2220 (C≡N), 1633 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 2.12 (s, 3H, CH3), 4.50, 6.33 (s, 2H, C4H-pyran), 7.00-8.65 (m, 18H, Ar-H+ olefinic protons), 9.69 (s, 1H, N=CH pyrimidine). Anal. Calcd. for C34H23N5O (517.59): C, 78.90; H, 4.48; N, 13.53. Found: C, 78.99; H, 4.35; N, 13.67.

***3-(4-chlorophenyl)-2-(14-(p-tolyl)-14H-benzo[5,6]chromeno[3,2-e][1,2,4]triazolo[1,5-c] pyrimidin-2-yl)acrylonitrile 13***

A mixture of compound **10** (2 g, 5 mmol) and 2-(4-chlorobenzylidene)malononitrile (0.9 g, 5 mmol) in dioxane (20 mL) in the presence of catalytic amount of piperidine (0.5 mL) was heated under reflux for 6h. After cooling, the formed solid was filtered off, dried, and crystallized from ethanol to give **13** as yellow crystals, m.p. >300oC, yield: 83%. IR (KBr, *ν*, cm-1): 3063 (CH aromatic), 2921 (CH aliphatic), 2196 (C≡N), 1635 (C=N). 1H NMR (400 MHz, CDCl3‐d6) *δ* (ppm): 2.10 (s, 3H, CH3), 6.31 (s, 2H, C4H-pyran), 7.05-8.45 (m, 14H, Ar-H+ 1H olefinic), 9.74 (s, 1H, N=CH pyrimidine). Anal. Calcd. for C32H20ClN5O (526.00): C, 73.07; H, 3.83; Cl, 6.74; N, 13.31. Found: C, 73.18; H, 3.90; Cl, 6.81; N, 13.38.

***4-amino-3-phenyl-5-(14-(p-tolyl)-14H-benzo[5,6]chromeno[3,2-e][1,2,4]triazolo[1,5-c] pyrimidin-2-yl)thiazole-2(3H)-thione 14***

A mixture of compound **10** (2 g, 5 mmol) and phenylisothiocyanate (0.7 mL, 5 mmol), elemental sulphur (0.2 g, 5 mmol) and triethylamine (0.5 mL) in absolute ethanol (20 mL) was heated under reflux for 6 h. The formed solid while reflux was filtered off, dried, and then crystallized from EtOH/Dioxane to give **14** as grey crystals, m.p. 158-160oC, yield: 63%. IR (KBr, *ν*, cm-1): 3442, 3318 (NH2), 1615 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 2.12 (s, 3H, CH3), 6.26 (s, 1H, C4H-pyran), 6.98 (brs, 2H, NH2, exchangeable with D2O), 7.00-8.04 (m, 15H, Ar-H), 9.79 (s, 1H, N=CH pyrimidine). Anal. Calcd. for C32H22N6OS2 (570.69): C, 67.35; H, 3.89; N, 14.73; S, 11.24. Found: C, 67.55; H, 3.72; N, 14.65; S, 11.33.

***General procedure for 15-19***

The cyanomethylene derivative **10** (2 g, 5 mmol) was added to a cold suspension of finely divided potassium carbonate (2.07 g, 15 mmol) and TBAB (0.97 g, 3 mmol) in dioxane (30 mL) with stirring for 15 minutes. Carbon disulphide (7 mL, 10 mmol) was added dropwise and then the mixture was allowed to stand overnight. chloroacetyl chloride, 1,2-dibromoethane, 1,3-dibromobropane, methyl iodide, and benzyl chloride (5 mmol) was added dropwise, stirred at room temperature for 3 h and then allowed to stand overnight. The reaction mixture was poured onto ice-cold water with stirring. The separated solid was filtered off, washed with water, dried and crystallized from suitable solvent to give **15-19**, respectively.

***2-(4-oxo-1,3-dithiolan-2-ylidene)-2-(14-(p-tolyl)-14H-benzo[5,6]chromeno[3,2-e][1,2,4] tri-azolo[1,5-c]pyrimidin-2-yl)acetonitrile 15:*** Yellow crystals, m.p. 210-212oC, yield: 75%. IR (KBr, *ν*, cm-1): 3061 (CH aromatic), 2919 (CH aliphatic), 2213 (C≡N), 1731 (C=O), 1635 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 2.12 (s, 3H, CH3), 4.51 (s, 2H, CH2CO), 6.25 (s, 1H, C4H-pyran), 7.00-8.10 (m, 10H, ArH), 9.64 (s, 1H, N=CH pyrimidine). Anal. Calcd. for C28H17N5O2S2 (519.60): C, 64.72; H, 3.30; N, 13.48; S, 12.34. Found: C, 64.76; H, 3.28; N, 13.51; S, 12.39.

***2-(1,3-dithiolan-2-ylidene)-2-(14-(p-tolyl)-14H-benzo[5,6]chromeno[3,2-e][1,2,4] triazolo [1,5-c]pyrimidin-2-yl)acetonitrile 16*:** Yellow crystals, m.p. 280-283oC, yield: 84%. IR (KBr, *ν*, cm-1): 3056 (CH aromatic), 2923 (CH aliphatic), 2208 (C≡N), 1634 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 2.12 (s, 3H, CH3), 3.79 (t, 2H, CH2), 3.87 (t, 2H, CH2), 6.17 (s, 1H, C4H-pyran), 6.99-8.01 (m, 10H, Ar-H), 9.58 (s, 1H, N=CH pyrimidine). Anal. Calcd. for C28H19N5OS2 (505.61): C, 66.51; H, 3.79; N, 13.85; S, 12.68. Found: C, 66.49; H, 3.82; N, 13.79; S, 12.70.

***3-bromopropyl2-cyano-2-(14-(p-tolyl)-14H-benzo[5,6]chromeno[3,2-e][1,2,4]triazolo[1,5-c]pyrimidin-2-yl)ethanedithioate 17:*** Yellow crystals, m.p. 220-224oC, yield: 74%. IR (KBr, *ν*, cm-1): 3056 (CH aromatic), 2959 (CH aliphatic), 2208 (C≡N), 1633 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 2.13 (s, 3H, CH3), 2.28 (m, 2H, CH2), 3.21 (t, 2H, SCH2), 3.24 (t, 2H, CH2Br), 4.51 (s, 1H, CHCN), 6.21 (s, 1H, C4H-pyran), 7.00-8.10 (m, 10H, ArH), 9.61 (s, 1H, N=CH pyrimidine). Anal. Calcd. for C29H22BrN5OS2 (600.55): C, 58.00; H, 3.69; Br, 13.31; N, 11.66; S, 10.68. Found: C, 58.09; H, 3.72; Br, 13.29; N, 11.80; S, 10.65.

***3,3-bis(methylthio)-2-(14-(p-tolyl)-14H-benzo[5,6]chromeno[3,2-e][1,2,4]triazolo[1,5-c] pyrimidin-2-yl)acrylonitrile 18:*** Yellow crystals, m.p. >300oC, yield: 63%. IR (KBr, *ν*, cm-1): 3061 (CH aromatic), 2962 (CH aliphatic), 2208 (C≡N), 1634 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 2.12 (s, 3H, CH3), 2.74 (s, 6H, 2CH3), 6.25 (s, 1H, C4H-pyran), 7.00-8.10 (m, 10H, ArH), 9.66 (s, 1H, N=CH pyrimidine). Anal. Calcd. for C28H21N5OS2 (507.63): C, 66.25; H, 4.17; N, 13.80; S, 12.63. Found: C, 66.29; H, 4.21; N, 13.92; S, 12.59.

***3,3-bis(benzylthio)-2-(14-(p-tolyl)-14H-benzo[5,6]chromeno[3,2-e][1,2,4]triazolo[1,5-c]pyrimidin-2-yl)acrylonitrile 19:*** Yellow crystals, m.p. 140-142oC, yield: 83%. IR (KBr, *ν*, cm-1): 3060 (CH aromatic), 2917 (CH aliphatic), 2209 (C≡N), 1632 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 2.13 (s, 3H, CH3), 4.35 (dd, 4H, 2CH2), 6.16 (s, 1H, C4H-pyran), 6.72-8.10 (m, 10H, ArH), 9.64 (s, 1H, N=CH pyrimidine). Anal. Calcd. for C40H29N5OS2 (659.83): C, 72.81; H, 4.43; N, 10.61; S, 9.72. Found: C, 72.78; H, 4.38; N, 10.52; S, 9.68.

***General procedure for 20-22***

The cyanomethylene derivative **10** (2 g, 5 mmol) was added to a cold suspension of finely divided potassium carbonate (2.07 g, 15 mmol) and TBAB (0.97 g, 3 mmol) in dioxane (30 mL) with stirring for 15 minutes. phenylisothiocyanate (1.35 g, 10 mmol) was added dropwise and then the mixture was allowed to stand overnight, diluted HCl, chloroacetyl chloride and methyl iodide (5 mmol) was added dropwise, stirred at room temperature for 3 h and then allowed to stand overnight. The reaction mixture was poured onto ice-cold water with stirring. The separated solid was filtered off, washed with water, dried and crystallized from suitable solvent to give **20-22**, respectively.

***3-mercapto-3-(phenylamino)-2-(14-(p-tolyl)-14H-benzo[5,6]chromeno[3,2-e][1,2,4] triazolo [1,5-c]pyrimidin-2-yl)acrylonitrile 20:*** Yellow crystals, m.p. 222-224oC, yield: 81%. IR (KBr, *ν*, cm-1): br.3200 (NH), 3053 (CH aromatic), 2960 (CH aliphatic), 2175 (C≡N), 1621 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 1.57 (brs, 1H, SH, exchangeable with D2O), 2.07 (s, 3H, CH3), 6.24 (s, 1H, C4H-pyran), 6.42-8.07 (m, 15H, ArH), 9.36 (s, 1H, N=CH pyrimidine), 11.78 (brs, 1H, NH, exchangeable with D2O). Anal. Calcd. for C32H22N6OS (538.63): C, 71.36; H, 4.12; N, 15.60; S, 5.95. Found: C, 71.40; H, 4.19; N, 15.68; S, 5.62.

***2-(5-oxo-3-phenylthiazolidin-2-ylidene)-2-(14-(p-tolyl)-14H-benzo[5,6]chromeno[3,2-e] [1,2,4]triazolo[1,5-c]pyrimidin-2-yl)acetonitrile 21:*** Yellow crystals, m.p. 122-124oC, yield: 83%. IR (KBr, *ν*, cm-1): 3062 (CH aromatic), 2963 (CH aliphatic), 2214 (C≡N), 1728 (C=O), 1634 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 2.12 (s, 3H, CH3), 4.29 (s, 2H, COCH2), 6.19 (s, 1H, C4H-pyran), 7.02-8.04 (m, 15H, ArH), 9.64 (s, 1H, N=CH pyrimidine). Anal. Calcd. for C34H22N6O2S (578.65): C, 70.57; H, 3.83; N, 14.52; S, 5.54. Found: C, 70.62; H, 3.87; N, 14.50; S, 5.63.

***3-(methylthio)-3-(phenylamino)-2-(14-(p-tolyl)-14H-benzo[5,6]chromeno[3,2-e][1,2,4] triazolo[1,5-c]pyrimidin-2-yl)acrylonitrile 22:*** Yellow crystals, m.p. > 300 oC, yield: 77%. IR (KBr, *ν*, cm-1): 3053 (CH aromatic), 2953 (CH aliphatic), 2203 (C≡N), 1633 (C=N). 1H NMR (400 MHz, DMSO‐d6) *δ* (ppm): 1.96 (s, 3H, CH3), 2.23 (s, 3H, SCH3), 6.29 (s, 1H, C4H-pyran), 6.51-8.03 (m, 15H, ArH), 9.61 (s, 1H, N=CH pyrimidine), 11.40 (s, 1H, NH, exchangeable with D2O). Anal. Calcd. for C33H24N6OS (552.66): C, 71.72; H, 4.38; N, 15.21; S, 5.80. Found: C, 71.69; H, 4.40; N, 15.26; S, 5.85