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CHLOROTRIMETHYLSILANE MEDIATED SYNTHESIS OF 5-(2-HYDROXYBENZOYL)PYRIMIDINES FROM 3-FORMYLCHROMONES

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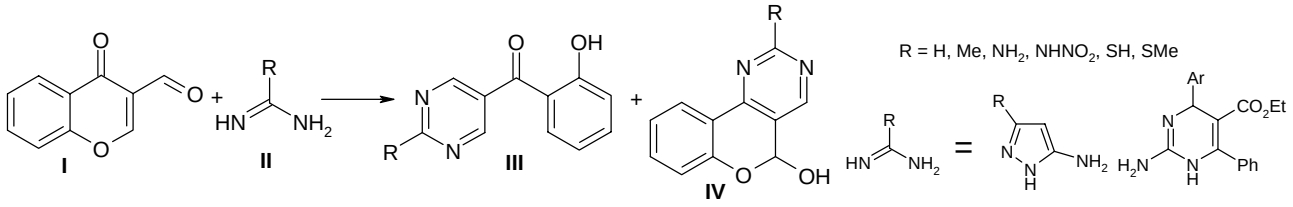
Abstract – The recyclization of 3-formylchromones with a variety of 1,3-*NCN*-binucleophiles promoted by chlorotrimethylsilane was investigated. A simple and flexible general procedure for the synthesis of series of 5-(2-hydroxybenzoyl)pyrimidines and their heterofused analogues was proposed. A set of pyrimidines was obtained in high preparative yields.

INTRODUCTION

Pyrimidines are useful class of organic compounds.[1,2] The pyrimidine scaffold plays an important role as a component of antiviral,[3] antibacterial,[4a] antimicrobial,[4b] anti-inflammatory,[4c] antifungal,[4d] antiparasitic,[4e] antimalarial,[4f,4g] antiprotozoal,[5a] antihypotensive,[5b] antiproliferative,[5c] anxiolytic,[5d] anorectic,[5e] fungistatic[5f] agents etc. Therefore, the search for effective methods for synthesis of pyrimidine libraries for high-throughput screening remains an actual problem. Although various methods have been developed for pyrimidine synthesis[1,2] novel methods are still desired.[6] One of methods to obtain the pyrimidine core is based on the reaction of 1,3-*NCN*-binucleophiles (amidines, guanidines etc) with various 1,3-dicarbonyl compounds as 1,3-*CCC*-bielectrophiles.[7] 3-Formylchromones **I** were used as 1,3-*CCC*-bielectrophiles as well.[8-10] Amidines,[9a-d] guanidine,[9d-h] nitroguanidine,[9f] thiourea,[9f] 2-methylisothiourea sulfate,[9h] *N*-unsubstituted aminopyrazoles,[10a-c] 2-amino-4-aryl-6-phenyl-1,4-dihydro-pyrimidine-5-carboxylic acid ethyl ester[10d] and *N*-triphenylphosphoranylidene benzamidine were used as 1,3-*NCN*-binucleophiles **II** in the reactions with 3-formylchromones **I**.[10e] The main problem is the fact

that 3-formylchromone **I** possess three electrophilic centers: C-4, formyl group at C-3 and unsaturated C-2 carbon atom, what leads to the formation of mixtures of 5-(2-hydroxybenzoyl)pyrimidines **III** and 5-hydroxybenzopyrano[4,3-*d*]pyrimidines **IV** (Scheme 1) in most of cases.



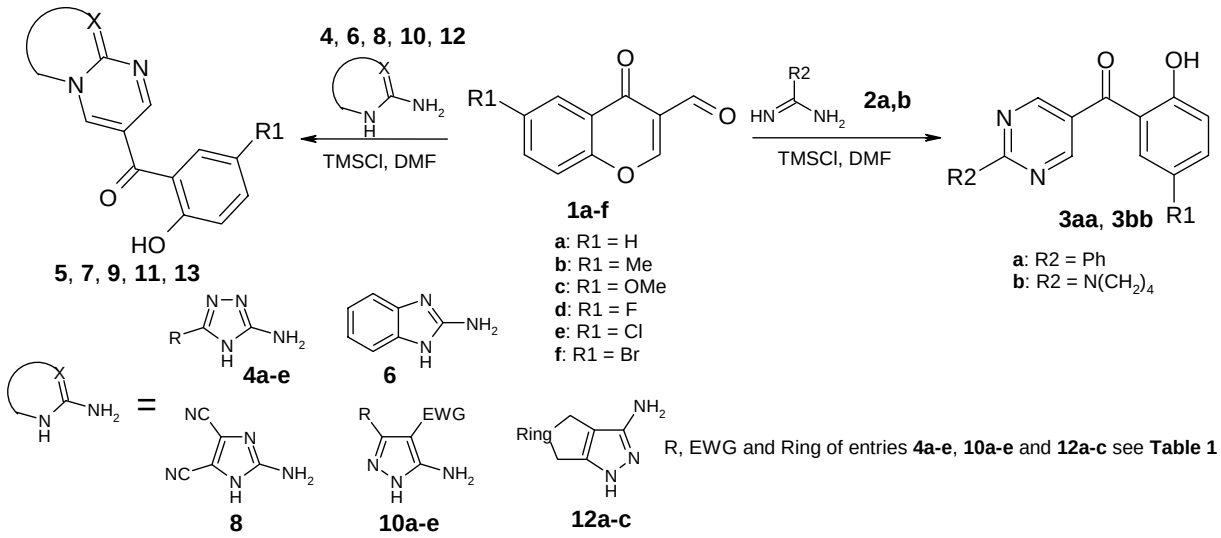
Scheme 1

During the course of our 3-formylchromone recyclization studies involving [3+3] cyclocondensation of 3-formylchromones with acetic acid amides[11a] which have an electron-withdrawing group at α-position, various π-electron-rich amino heterocycles and donor anilines,[11b] and various benzimidazoles, bearing CH_2-group at the 2-nd position,[11c] we explored the formation of 5-(2-hydroxybenzoyl) substituted pyrimidines *via* coupling of 3-formylchromone **1** with various amidines and their heterocyclic analogues.

RESULTS AND DISCUSSION

We have demonstrated in our earlier studies that chlorotrimethylsilane (TMSCl) is a convenient condensating agent for the recyclization of 3-formylchromones afford regioselective formation of 2-hydroxybenzoyl derivatives of nitrogen heterocycles,[11] as well as for other condensations of carbonyl compounds.[12] Therefore we decided to use TMSCl as a promoter and water scavenger in the reactions with various amidines and their heterocyclic analogues.

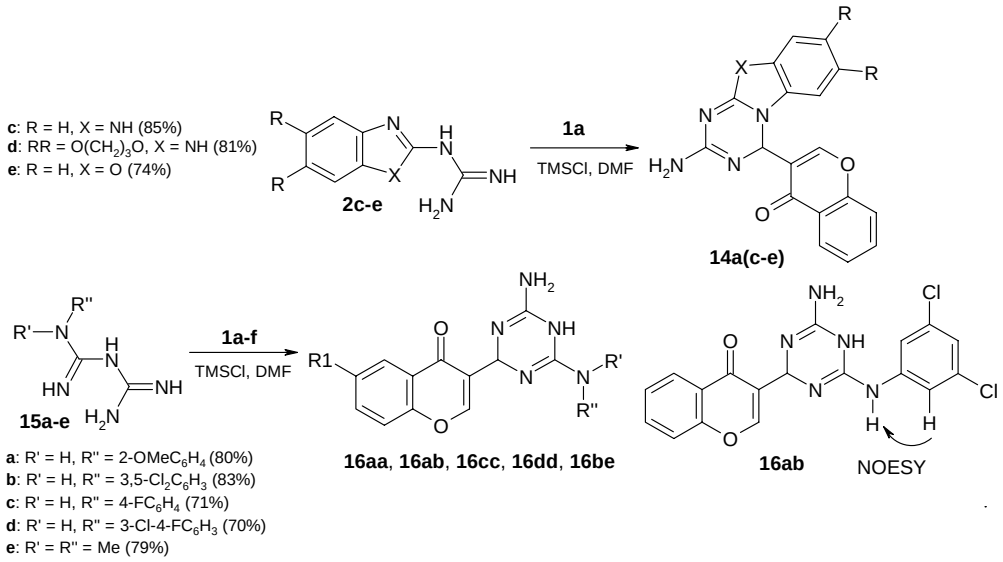
3-Formylchromones **1** react with equimolar amount of benzamidine **2a** or pyrrolidine-1-carboxamidine sulfate **2b** in DMF solution at 100 °C in the presence of 3 equivalents of chlorotrimethylsilane (TMSCl) giving 5-(2-hydroxybenzoyl)pyrimidines **3a** and **3b** as single products of recyclization in preparative yields (Scheme 2, Table 1). Aminotriazoles **4a-e** react with 3-formylchromones as 1,3-*NCN*-binucleophiles forming [1,2,4]triazolo[1,5-*a*]pyrimidines **5**.[13] 1*H*-Benzimidazole-2-amine **6** and 2-amino-1*H*-imidazole-4,5-dicarbonitrile **8** react similar affording pyrimido[1,2-*a*]benzimidazole **7b** and imidazo[1,2-*a*]pyrimidine **9a**, respectively. 1*H*-Pyrazole-5-amines **10a-e** containing nitrile or carbethoxy group at 4-position which prevents the reaction with 3-formylchromone **1** on carbon atom, forming pyrazolo[1,5-*a*]pyrimidines **11**. Reactions of 1*H*-indazole-3-amine **12a** with 1,3-*CCC*-bielectrophiles are poorly studied; but under the conditions found both mentioned compound and its heterocyclic analogues react with 3-formylchromone **1** forming compounds **13**. The duration of the reflux (6 to 12 hours) was found to be important for the purity of the final products.



Scheme 2

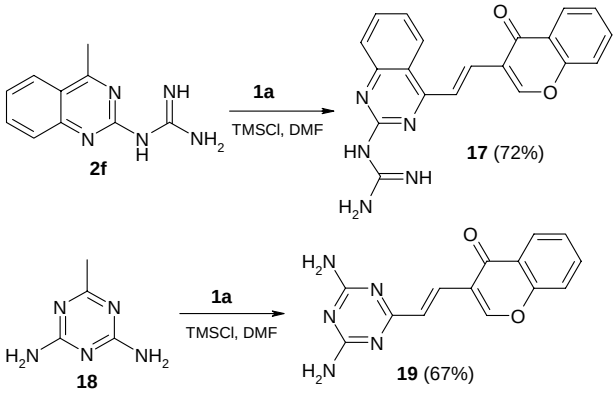
NMR spectra indicate the exclusive formation of 2-hydroxybenzoyl derivatives of pyrimidine; the formation of 5-hydroxybenzopyrano[4,3-*d*]pyrimidines **IV** was not detected. This conclusion is based on the observation of typical pyrimidine-ring shift values of δ ~ 8.0-9.0 ppm and ~9.1-9.6 ppm with coupling constant $^4J_{HH}$ ~ 0.8-2.3 Hz; on the presence of signal of carbonyl carbon atom in ^{13}C NMR spectra at δ ~ 191.6-194.0 ppm; and on the appearance of signal of carbon atom bounded to hydroxyl group at δ ~ 157.2-158.4 ppm in ^{13}C NMR spectra. The indirect confirmations are the presence of wide absorption band at 3600-3300 cm^{-1} in IR spectrum corresponding to valence vibrations of hydroxyl group, and intensive peak at ~ 1630 cm^{-1} corresponding to valence vibrations of carbonyl group.

In the case of *N*-1*H*-benzimidazol-2-ylguanidines **2c**,**d** and *N*-1,3-benzoxazol-2-ylguanidine **2e**, [5+1]cyclization takes place leading to the formation of 2-amino[1,3,5]triazin-4*H*-chromen-4-ones **14a(c-e)** (Scheme 3). In this case 3-formylchromone **1** react as a usual aldehyde.[14] *N*-Arylimidodicarbonimidic diamides **15a-d** and *N*,*N*-dimethylimidodicarbonimidic diamide **15e** react similar to *N*-1*H*-benzimidazol-2-ylguanidines **2c**,**d** and *N*-1,3-benzoxazol-2-ylguanidine **2e** forming 3-(4,6-diamino-2,5-dihydro-1,3,5-triazin-2-yl)-4*H*-chromen-4-ones[15] **16(a-d)(a-e)** (Scheme 3). It should be noted that compound **16** have structure with exocyclic aniline fragment that was confirmed by NOESY experiments on compound **16ab** of this series.[15]



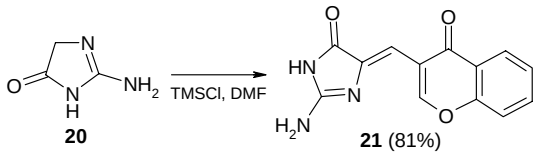
Scheme 3

The fact that *N*-(4-methylquinazolin-2-yl)guanidine **2f** reacts with 3-formylchromone **1a** on methyl group forming *N*-{4-[(*E*)-2-(4-oxo-4*H*-chromen-3-yl)vinyl]quinazolin-2-yl}guanidine **17** appeared to be surprising (Scheme 4). The similar product, namely stirile **19** is formed by the reaction of 3-formylchromone **1a** with 6-methyl-1,3,5-triazine-2,4-diamine **18**.



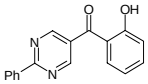
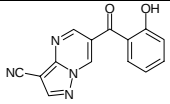
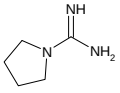
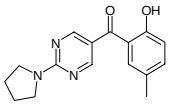
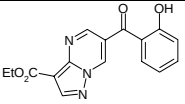
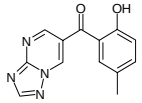
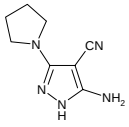
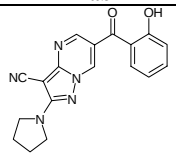
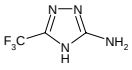
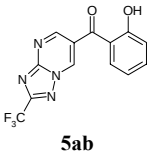
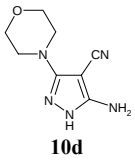
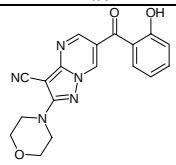
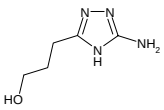
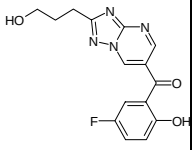
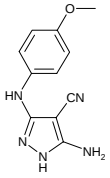
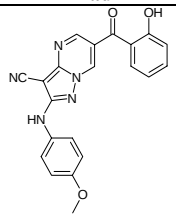
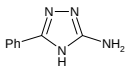
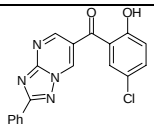
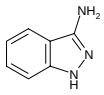
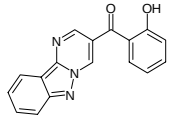
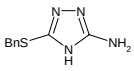
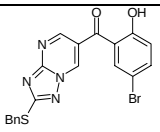
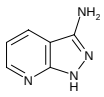
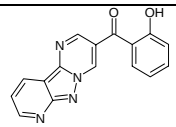
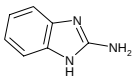
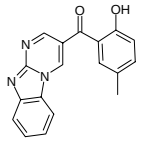
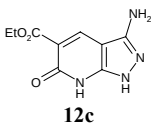
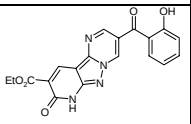
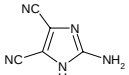
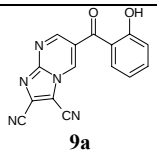
Scheme 4

2-Amino-3,5-dihydro-4*H*-imidazol-4-one **20** does not react with 3-formylchromone **1a** as 1,3-*NCN*-binucleophiles but on methylene group forming 2-amino-5-[(4-oxo-4*H*-chromen-3-yl)methylene]-3,5-dihydro-4*H*-imidazol-4-one **21** (Scheme 5).



Scheme 5

Table 1. TMSCl promoted synthesis of 5-(2-hydroxybenzoyl)pyrimidines

Entry	1	*NCN*-binucleophile	Product	Yield (%)[a]	Entry	1	*NCN*-binucleophile	Product	Yield (%)[a]
1	1a	 **2a**	 **3aa**	83	10	1a	 **10a**	 **11aa**	76
2	1b	 **2b**	 **3bb**	72	11	1a	 **10b**	 **11ab**	71
3	1b	 **4a**	 **5ba**	88	12	1a	 **10c**	 **11ac**	93
4	1a	 **4b**	 **5ab**	76	13	1a	 **10d**	 **11ad**	90
5	1d	 **4c**	 **5dc**	55	14	1a	 **10e**	 **11ae**	95
6	1e	 **4d**	 **5ed**	90	15	1a	 **12a**	 **13aa**	91
7	1f	 **4e**	 **5fe**	81	16	1a	 **12b**	 **13ab**	86
8	1b	 **6**	 **7b**	96	17	1a	 **12c**	 **13ac**	89
9	1a	 **8**	 **9a**	61					

[a]Yields refer to pure isolated products

In summary, we have elaborated an efficient methodology for the preparation of 5-(2-hydroxybenzoyl)pyrimidines and their heterofused analogues from 1,3-*NCN*-binucleophiles and 3-formylchromones using chlorotrimethylsilane as a promoter and water scavenger. The methodology is

applicable to a wide variety of amidines, guanidines and their heterocyclic analogues and delivers target products in good yields.

EXPERIMENTAL

General Data: All chemicals were obtained from commercially available sources (Aldrich, Fluka, Enamine Ltd.) and used without further purification. DMF was freshly distilled and dried by standard methods; monitoring of water concentration in solvents (the solvent contained < 0.05%, usually 0.02% of water) was performed using Mettler Toledo DL31 KF Titrator. All solvents for the crystallizations were used without additional purification.

Melting points were measured with a Buchi melting points apparatus and are uncorrected. ^{1}H NMR (400 MHz and 500 MHz) were recorded on a Varian Mercury-400 and Bruker Avance DRX-500 spectrometers with TMS as an internal standard. ^{13}C NMR (125 MHz) were recorded on a Bruker Avance DRX-500 spectrometer with TMS as an internal standard. NOESY experiments were recorded on a Bruker Avance drx 500 spectrometer. LC/MS spectra were recorded using chromatography/mass spectrometric system that consists of high-performance liquid chromatograph "Agilent 1100 Series" equipped with diode-matrix and mass-selective detector "Agilent LC/MSD SL". According to HPLC MS data all the synthesized compounds have purity > 95%. IR spectra were recorded on a Nexus-470 spectrometer for samples in KBr discs. Microanalyses were performed in the Microanalytical Laboratory of the Institute of Organic Chemistry, National Academy of Sciences of Ukraine. A Branson 2510E-MT ultrasonic bath was used.

General procedure for the preparation of pyrimidines

An appropriate amidines **2a-f**, **4a-e**, **6**, **8**, **10a-e**, **12a-c**, **15a-e**, **18**, **20** (2 mmol) and an appropriate 3-formylchromone **1a-f** (2 mmol) were placed in 15 mL pressure tube and dissolved in DMF (3 mL). Chlorotrimethylsilane (652 mg, 6 mmol) was added dropwise to the solution. The tube was thoroughly sealed and heated on a water-bath for 6-12 h. After cooling the flask was opened (*caution! Excessive pressure inside*); the reaction mixture was poured into water (15 mL) and allowed to stand at 20 °C in ultrasonic bath for 1h. The precipitate formed was filtered and washed with small amount of *i*-PrOH (2 mL). Recrystallization from an appropriate solvent yielded the target compounds **3**, **5**, **7**, **9**, **11**, **13**, **14**, **16**, **17**, **19**, **21**.

(2-Hydroxyphenyl)(2-phenylpyrimidin-5-yl)methanone (3aa)

Mp 131-132 °C (*i*-PrOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.01 (m, 2H, CH), 7.50-7.63 (m, 5H, CH), 8.47 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, CH), 9.11 (s, 2H, CH), 10.58 (s, 1H, OH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 117.6, 120.1, 124.0, 128.9, 129.4, 129.5, 131.6, 132.4, 135.2, 136.8, 157.8, 158.4, 165.5, 194.0. IR (KBr): ν = 3650-3200 (br, OH), 3070, 3030, 2926, 1626 (C=O), 1578, 1533, 1439, 1335, 1311, 1254, 1151, 933,

769, 752, 694. APSI MS: M^++1 = 277. Anal. Calcd for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.78; H, 4.49; N, 10.18.

(2-Hydroxy-5-methylphenyl)(2-pyrrolidin-1-ylpyrimidin-5-yl)methanone (3bb)

Mp 170-171 °C (*i*-PrOH). ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.94 (m, 4H, $2CH_2$), 2.23 (s, 3H, CH_3), 3.56 (m, 4H, $2NCH_2$), 6.85 (d, $^3J_{HH}$ = 8.4 Hz, 1H, CH), 7.15 (s, 1H, CH), 7.22 (d, $^3J_{HH}$ = 8.4 Hz, 1H, CH), 7.94 (s, 1H, CH), 8.59 (s, 1H, CH), 10.10 (br. s, 1H, OH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 20.4, 25.3, 47.3, 117.1, 119.9, 124.8, 128.5, 130.6, 134.3, 154.7, 160.4, 160.5, 193.1. APSI MS: M^++1 = 284. IR (KBr): ν = 3650-3270 (br, OH), 3032, 2964, 2920, 1626 (C=O), 1587, 1541, 1485, 1331, 1290, 1234, 1144, 1109, 951, 806, 785, 613. Anal. Calcd for $C_{16}H_{17}N_3O_2$: C, 67.83; H, 6.05; N, 14.83. Found: C, 67.97; H, 5.91; N, 14.75.

(2-Hydroxy-5-methylphenyl)([1,2,4]triazolo[1,5-*a*]pyrimidin-6-yl)methanone (5ba)

Mp 180-181 °C (EtOH). ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.26 (s, 3H, CH_3), 6.92 (d, $^3J_{HH}$ = 8.2 Hz, 1H, CH), 7.33 (d, $^3J_{HH}$ = 8.2 Hz, 1H, CH), 7.63 (s, 1H, CH), 8.83 (s, 1H, CH), 9.08 (d, $^4J_{HH}$ = 1.7 Hz, 1H, CH), 9.64 (d, $^4J_{HH}$ = 1.7 Hz, 1H, CH), 10.34 (s, 1H, OH). APSI MS: M^++1 = 255. Anal. Calcd for $C_{13}H_{10}N_4O_2$: C, 61.41; H, 3.96; N, 22.04. Found: C, 61.60; H, 3.84; N, 21.95.

(2-Hydroxyphenyl)[2-(trifluoromethyl)[1,2,4]triazolo[1,5-*a*]pyrimidin-6-yl]methanone (5ab)

Mp 169-170 °C (EtOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.03 (t, $^3J_{HH}$ = 8.0 Hz, 1H, CH), 7.17 (d, $^3J_{HH}$ = 8.0 Hz, 1H, CH), 7.55 (d, $^3J_{HH}$ = 8.0 Hz, 1H, CH), 7.66 (t, $^3J_{HH}$ = 8.0 Hz, 1H, CH), 9.24 (d, $^4J_{HH}$ = 1.4 Hz, 1H, CH), 9.89 (d, $^4J_{HH}$ = 1.4 Hz, 1H, CH), 10.67 (br. s, 1H, OH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 117.3 (q, $^1J_{CF}$ = 289.2 Hz), 117.8, 120.2, 123.0, 124.5, 129.1, 131.9, 135.5, 140.8 (q, $^3J_{CF}$ = 6.6 Hz), 152.4 (q, $^2J_{CF}$ = 38.9 Hz), 155.6, 158.1, 191.5. APSI MS: M^++1 = 309. Anal. Calcd for $C_{13}H_7F_3N_4O_2$: C, 50.66; H, 2.29; N, 18.18. Found: C, 50.44; H, 2.40; N, 18.27.

(5-Fluoro-2-hydroxyphenyl)[2-(3-hydroxypropyl)[1,2,4]triazolo[1,5-*a*]pyrimidin-6-yl]methanone (5dc)

Mp 170-171 °C (*i*-PrOH-hexane). ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.93 (quintet, $^3J_{HH}$ = 6.8 Hz, 2H, CH_2), 2.90 (t, $^3J_{HH}$ = 6.8 Hz, 2H, NCH_2), 3.46 (m, 1H, OH), 3.50 (m, 2H, OCH_2), 7.02 (m, 1H, CH), 7.35 (m, 2H, CH), 9.03 (d, $^4J_{HH}$ = 2.3 Hz, 1H, CH), 9.58 (d, $^4J_{HH}$ = 2.3 Hz, 1H, CH), 10.42 (s, 1H, OH). APSI MS: M^++1 = 317. Anal. Calcd for $C_{15}H_{13}FN_4O_3$: C, 56.96; H, 4.14; N, 17.71. Found: C, 56.82; H, 4.26; N, 17.75.

(5-Chloro-2-hydroxyphenyl)(2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidin-6-yl)methanone (5ed)

Mp 244-245 °C (EtOH). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.04 (d, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 7.52-7.56 (m, 2H, CH), 7.58 (m, 3H, CH), 8.24 (m, 2H, CH), 9.09 (d, $^4J_{HH}$ = 2.0 Hz, 1H, CH), 9.71 (d, $^4J_{HH}$ = 2.0 Hz, 1H, CH), 10.74 (s, 1H, OH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 119.6, 121.9, 123.7, 125.8, 127.5, 129.5,

129.6, 130.3, 131.7, 134.3, 140.2, 153.3, 155.9, 156.6, 167.1, 190.4. IR (KBr): ν = 3640-3300 (br, NH), 3057, 3026, 2962, 1616 (C=O), 1595, 1473, 1448, 1348, 1244, 1190, 930, 816, 719, 688. APSI MS: M^++1 = 351. Anal. Calcd for $C_{18}H_{11}ClN_4O_2$**:** C, 61.64; H, 3.16; Cl, 10.11; N, 15.97. Found: C, 61.50; H, 3.27; Cl, 10.15; N, 15.99.

[2-(Benzylthio)[1,2,4]triazolo[1,5-*a*]pyrimidin-6-yl](5-bromo-2-hydroxyphenyl)methanone (5fe)

Mp 225-226 °C (EtOH). ^{1}H NMR (500 MHz, DMSO-d_6) δ 4.60 (s, 2H, CH_2), 6.75 (d, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 7.25 (d, $^3J_{HH}$ = 8.1 Hz, 2H, CH), 7.32 (t, $^3J_{HH}$ = 8.1 Hz, 2H, CH), 7.56 (s, 1H, CH), 7.58 (s, 1H, CH), 7.82 (d, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 8.04 (t, $^3J_{HH}$ = 8.1 Hz, 1H, CH), 8.89 (s, 1H, CH), 9.34 (s, 1H, OH). APSI MS: M^++1 = 441. Anal. Calcd for $C_{19}H_{13}BrN_4O_2S$**:** C, 51.71; H, 2.97; Br, 18.11; N, 12.70; S, 7.27. Found: C, 51.58; H, 3.09; Br, 18.19; N, 12.74; S, 7.33.

(2-Hydroxy-5-methylphenyl)(pyrimido[1,2-*a*]benzimidazol-3-yl)methanone (7b)

Mp 255-256 °C (EtOH-DMF). ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.32 (s, 3H, CH_3), 7.08 (d, $^3J_{HH}$ = 8.4 Hz, 1H, CH), 7.22-7.30 (m, 2H, CH), 7.44 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, CH), 7.51 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, CH), 7.62-7.69 (m, 2H, CH), 8.97 (d, $^4J_{HH}$ = 1.2 Hz, 1H, CH), 9.89 (d, $^4J_{HH}$ = 1.2 Hz, 1H, CH), 10.26 (br. s, 1H, OH). APSI MS: M^++1 = 304. Anal. Calcd for $C_{18}H_{13}N_3O_2$: C, 71.28; H, 4.32; N, 13.85. Found: C, 71.10; H, 4.45; N, 13.93.

6-(2-Hydroxybenzoyl)imidazo[1,2-*a*]pyrimidine-2,3-dicarbonitrile (9a)

Mp 269-270 °C (*i*-PrOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.10 (d, $^3J_{HH}$ = 8.4 Hz, 1H, CH), 7.24 (t, $^3J_{HH}$ = 8.4 Hz, 1H, CH), 7.67 (t, $^3J_{HH}$ = 8.4 Hz, 1H, CH), 7.87 (d, $^3J_{HH}$ = 8.4 Hz, 1H, CH), 9.14 (d, $^4J_{HH}$ = 1.4 Hz, 1H, CH), 9.42 (d, $^4J_{HH}$ = 1.4 Hz, 1H, CH), 10.73 (s, 1H, OH). APSI MS: M^++1 = 290. Anal. Calcd for $C_{15}H_7N_5O_2$: C, 62.29; H, 2.44; N, 24.21. Found: C, 62.13; H, 2.62; N, 24.13.

6-(2-Hydroxybenzoyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (11aa)

Mp 155-156 °C (*i*-PrOH). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.01 (m, 2H, CH), 7.52 (t, $^3J_{HH}$ = 8.0 Hz, 1H, CH), 7.56 (d, $^3J_{HH}$ = 8.0 Hz, 1H, CH), 8.97 (s, 1H, CH), 9.03 (d, $^4J_{HH}$ = 1.4 Hz, 1H, CH), 9.57 (d, $^4J_{HH}$ = 1.4 Hz, 1H, CH), 10.58 (s, 1H, OH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 82.6, 113.3, 117.7, 120.2, 122.7, 123.9, 131.7, 135.3, 140.5, 150.3, 150.6, 154.2, 157.7, 191.7. IR (KBr): ν = 3640-3280 (br, OH), 3097, 3037, 2904, 2227 (C≡N), 1674 (C=O), 1585, 1522, 1462, 1373, 1333, 1271, 1215, 1138, 1009, 891, 768. APSI MS: M^++1 = 265. Anal. Calcd for $C_{14}H_8N_4O_2$**:** C, 63.64; H, 3.05; N, 21.20. Found: C, 63.50; H, 3.18; N, 21.23.

Ethyl 6-(2-hydroxybenzoyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (11ab)

Mp 156-157 °C (*i*-PrOH-hexane). ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.30 (t, $^3J_{HH}$ = 7.0 Hz, 3H, $CH_2\underline{CH_3}$), 4.29 (m, 2H, $\underline{CH_2}CH_3$), 7.01 (m, 2H, CH), 7.52 (t, $^3J_{HH}$ = 8.0 Hz, 1H, CH), 7.56 (d, $^3J_{HH}$ = 8.0 Hz, 1H, CH), 8.78 (s, 1H, CH), 9.02 (d, $^4J_{HH}$ = 1.5 Hz, 1H, CH), 9.45 (d, $^4J_{HH}$ = 1.5 Hz, 1H, CH), 10.79 (s, 1H,

OH). APSI MS: M^++1 = 312. Anal. Calcd for $C_{16}H_{13}N_3O_4$**:** C, 61.73; H, 4.21; N, 13.50. Found: C, 61.89; H, 4.05; N, 13.44.

6-(2-Hydroxybenzoyl)-2-pyrrolidin-1-ylpyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (11ac)

Mp 173-174 °C (EtOH-DMF). ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.97 (m, 4H, $2CH_2$), 3.57 (m, 4H, $2NCH_2$), 6.99 (m, 2H, CH), 7.48 (m, 2H, CH), 8.74 (d, $^4J_{HH}$ = 1.0 Hz, 1H, CH), 9.08 (d, $^4J_{HH}$ = 1.0 Hz, 1H, CH), 10.45 (s, 1H, OH). APSI MS: M^++1 = 334. Anal. Calcd for $C_{18}H_{15}N_5O_2$**:** C, 64.86; H, 4.54; N, 21.01. Found: C, 64.68; H, 4.65; N, 21.08.

6-(2-Hydroxybenzoyl)-2-morpholin-4-ylpyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (11ad)

Mp 183-184 °C (EtOH-DMF). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.59 (t, $^3J_{HH}$ = 5.0 Hz, 4H, $2NCH_2$), 3.76 (t, $^3J_{HH}$ = 5.0 Hz, 4H, $2OCH_2$), 6.96-7.03 (m, 2H, CH), 7.49 (m, 2H, CH), 8.81 (d, $^4J_{HH}$ = 0.8 Hz, 1H, CH), 9.15 (d, $^4J_{HH}$ = 0.8 Hz, 1H, CH), 10.50 (s, 1H, OH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 46.9, 65.9, 68.9, 114.7, 117.6, 120.1, 121.4, 124.2, 131.4, 134.8, 138.4, 152.6, 153.1, 157.2, 162.3, 191.6. IR (KBr): ν = 3650-3280 (br, OH), 3084, 2987, 2968, 2926, 2220 (C≡N), 1620 (C=O), 1578, 1481, 1448, 1335, 1252, 1157, 1113, 993, 866, 812, 760, 658. APSI MS: M^++1 = 350. Anal. Calcd for $C_{18}H_{15}N_5O_3$**:** C, 61.89; H, 4.33; N, 20.05. Found: C, 61.98; H, 4.20; N, 20.11.

6-(2-Hydroxybenzoyl)-2-[(4-methoxyphenyl)amino]pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (11ae)

Mp 232-233 °C (EtOH-DMF). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.73 (s, 3H, OCH_3), 6.91 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH), 7.01 (m, 2H, CH), 7.50 (m, 2H, CH), 7.63 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH), 8.82 (d, $^4J_{HH}$ = 1.7 Hz, 1H, CH), 9.17 (d, $^4J_{HH}$ = 1.7 Hz, 1H, CH), 9.58 (s, 1H, NH), 10.49 (s, 1H, OH). APSI MS: M^++1 = 386. Anal. Calcd for C21H15N5O3**:** C, 65.45; H, 3.92; N, 18.17. Found: C, 65.31; H, 4.03; N, 18.25.

(2-Hydroxyphenyl)(pyrimido[1,2-*b*]indazol-3-yl)methanone (13aa)

Mp 160-161 °C (EtOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.04 (m, 2H, CH), 7.36 (t, $^3J_{HH}$ = 8.5 Hz, 1H, CH), 7.54 (t, $^3J_{HH}$ = 7.8 Hz, 1H, CH), 7.60 (d, $^3J_{HH}$ = 7.8 Hz, 1H, CH), 7.70 (t, $^3J_{HH}$ = 8.5 Hz, 1H, CH), 7.85 (d, $^3J_{HH}$ = 8.5 Hz, 1H, CH), 8.28 (d, $^3J_{HH}$ = 8.5 Hz, 1H, CH), 8.96 (d, $^4J_{HH}$ = 1.9 Hz, 1H, CH), 9.56 (d, $^4J_{HH}$ = 1.9 Hz, 1H, CH), 10.54 (s, 1H, OH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 113.0, 116.8, 117.7, 120.1, 121.2, 122.1, 123.5, 124.3, 131.1, 131.6, 135.1, 137.4, 143.8, 146.3, 152.8, 157.6, 192.8. IR (KBr): ν = 3650-3140 (br, OH), 3057, 1641 (C=O), 1624, 1581, 1502, 1479, 1443, 1377, 1333, 1306, 1248, 1219, 1178, 1155, 1119, 1022, 881, 758, 723. APSI MS: M^++1 = 290. Anal. Calcd for $C_{17}H_{11}N_3O_2$**:** C, 70.58; H, 3.83; N, 14.52. Found: C, 70.45; H, 3.96; N, 14.47.

(2-Hydroxyphenyl)(pyrido[2',3':3,4]pyrazolo[1,5-*a*]pyrimidin-3-yl)methanone (13ab)

Mp 234-235 °C (EtOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.04 (m, 2H, CH), 7.40 (m, 1H, CH), 7.55 (t, $^3J_{HH}$ = 7.9 Hz, 1H, CH), 7.61 (d, $^3J_{HH}$ = 7.9 Hz, 1H, CH), 8.76 (d, $^3J_{HH}$ = 8.5 Hz, 1H, CH), 8.97 (m, 1H, CH), 9.05 (d, $^4J_{HH}$ = 2.0 Hz, 1H, CH), 9.66 (d, $^4J_{HH}$ = 2.0 Hz, 1H, CH), 10.59 (s, 1H, OH). ^{13}C NMR (125

MHz, DMSO-d_6) δ 106.2, 118.0, 118.4, 120.5, 124.4, 124.7, 131.5, 132.0, 135.6, 138.3, 143.5, 148.1, 156.0, 158.0, 161.7, 192.8. IR (KBr): ν = 3650-3100 (br, OH), 3074, 3030, 2924, 1633 (C=O), 1620, 1585, 1485, 1400, 1338, 1296, 1246, 1157, 816, 775. APSI MS: M^++1 = 291. Anal. Calcd for $C_{16}H_{10}N_4O_2$**:** C, 66.20; H 3.47; N 19.30. Found: C, 66.32; H, 3.40; N, 19.21.

Ethyl 3-(2-hydroxybenzoyl)-8-oxo-7,8-dihydropyrido[2',3':3,4]pyrazolo[1,5-*a*]pyrimidine-9-carboxylate (13ac)

Mp 291-292 °C (DMF-MeOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.30 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $CH_2\underline{CH_3}$), 4.24 (q, $^3J_{HH}$ = 7.1 Hz, 2H, $\underline{CH_2}CH_3$), 6.98-7.06 (m, 2H, CH), 7.53 (m, 2H, CH), 8.63 (s, 1H, CH), 8.93 (d, $^4J_{HH}$ = 1.8 Hz, 1H, CH), 9.44 (d, $^4J_{HH}$ = 1.8 Hz, 1H, CH), 10.54 (s, 1H, OH), 12.56 (s, 1H, NH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 14.6, 60.9, 95.3, 117.6, 118.1, 120.1, 122.2, 124.2, 131.5, 135.0, 136.6, 139.5, 145.1, 151.7, 156.0, 157.4, 160.7, 164.6, 191.8. IR (KBr): ν = 3454 (br, OH, NH), 3064, 3018, 2985, 2962, 1740 ($C=O_{ester}$), 1674, 1649, 1624, 1605, 1518, 1483, 1450, 1425, 1340, 1308, 1250, 1211, 1153, 1074, 903, 800, 766, 675. APSI MS: M^++1 = 379. Anal. Calcd for $C_{19}H_{14}N_4O_5$: C, 60.32; H, 3.73; N, 14.81. Found: C, 60.49; H, 3.60; N, 14.85.

3-(2-Amino-4,10-dihydro[1,3,5]triazino[1,2-*a*]benzimidazol-4-yl)-4*H*-chromen-4-one (14ac)

Mp 295-296 °C (EtOH-DMF). ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.89 (s, 1H, CH), 7.15 (t, $^3J_{HH}$ = 7.8 Hz, 1H, CH), 7.22 (t, $^3J_{HH}$ = 7.8 Hz, 1H, CH), 7.31 (d, $^3J_{HH}$ = 7.8 Hz, 1H, CH), 7.35 (d, $^3J_{HH}$ = 7.8 Hz, 1H, CH), 7.50 (t, $^3J_{HH}$ = 8.5 Hz, 1H, CH), 7.64 (br. s, 2H, NH_2), 7.72 (d, $^3J_{HH}$ = 8.5 Hz, 1H, CH), 7.85 (t, $^3J_{HH}$ = 8.5 Hz, 1H, CH), 7.96 (d, $^3J_{HH}$ = 8.5 Hz, 1H, CH), 8.95 (s, 1H, CH), 13.07 (br. s, 1H, NH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 62.6, 110.8, 112.0, 119.2, 119.4, 123.3, 124.0, 124.2, 125.3, 126.7, 128.0, 129.6, 135.5, 151.6, 156.1, 157.5, 158.3, 175.3. IR (KBr): ν = 3383 (NH), 3140 (br, NH), 2987, 2929, 1687, 1655, 1606, 1527, 1466, 1363, 1296, 762, 634. APSI MS: M^++1 = 332. Anal. Calcd for $C_{18}H_{13}N_5O_2$: C, 65.25; H, 3.95; N, 21.14. Found: C, 65.11; H, 4.11; N, 21.06.

3-(2-Amino-4,9,10,13-tetrahydro-8*H*-[1,4]dioxepino[2,3-*f*][1,3,5]triazino[1,2-*a*]benzimidazol-4-yl)-4*H*-chromen-4-one (14ad)

Mp >300 °C (EtOH-DMF). ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.02 (m, 2H, CH_2), 4.02 (m, 4H, $2OCH_2$), 6.73 (s, 1H, CH), 6.93 (d, $^4J_{HH}$ = 1.7 Hz, 1H, CH), 6.99 (d, $^4J_{HH}$ = 1.7 Hz, 1H, CH), 7.31 (br. s, 1H, NH), 7.50 (t, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 7.72 (d, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 7.84 (t, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 7.96 (d, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 8.76 (s, 1H, NH), 8.91 (s, 1H, CH), 12.88 (br. s, 1H, NH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 32.3, 62.6, 71.57, 71.62, 104.0, 105.0, 119.2, 119.3, 123.7, 124.1, 125.3, 125.4, 126.7, 135.6, 148.6, 149.3, 152.1, 156.2, 157.2, 158.2, 175.3. APSI MS: M^++1 = 404. Anal. Calcd for $C_{21}H_{17}N_5O_4$: C, 62.53; H, 4.25; N, 17.36. Found: C, 62.65; H, 4.14; N, 17.31.

3-(2-Amino-4*H*-[1,3,5]triazino[2,1-*b*][1,3]benzoxazol-4-yl)-4*H*-chromen-4-one (14ae)

Mp 257-258 °C (EtOH-DMF). ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.93 (s, 1H, CH), 7.32 (m, 2H, CH), 7.39 (m, 1H, CH), 7.51 (t, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 7.70 (m, 1H, CH), 7.75 (d, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 7.86 (t, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 7.97 (d, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 8.74 (s, 1H, NH), 9.05 (s, 1H, CH), 9.64 (s, 1H, NH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 63.7, 110.6, 111.6, 118.1, 119.4, 120.5, 123.8, 125.3, 125.8, 126.9, 127.2, 135.7, 144.1, 156.2, 158.2, 159.3, 164.0, 175.4. IR (KBr): ν = 3346 (NH), 3238 (NH), 3128, 2968, 2929, 1678, 1649, 1614, 1508, 1460, 1365, 1313, 1173, 1078, 827, 773, 741. APSI MS: M^++1 = 333. Anal. Calcd for $C_{18}H_{12}N_4O_3$: C, 65.06; H, 3.64; N, 16.86. Found: C, 64.92; H, 3.81; N, 16.79.

3-{4-Amino-6-[(2-methoxyphenyl)amino]-2,5-dihydro-1,3,5-triazin-2-yl}-4*H*-chromen-4-one (16aa)

Mp 259-260 °C (EtOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.91 (s, 3H, OCH_3), 5.75 (s, 1H, CH), 6.81-7.09 (m, 2H, CH), 7.20 (d, $^3J_{HH}$ = 8.2 Hz, 1H, CH), 7.30 (br. s, 1H, NH), 7.37 (t, $^3J_{HH}$ = 8.2 Hz, 1H, CH), 7.54 (t, $^3J_{HH}$ = 8.2 Hz, 1H, CH), 7.64 (d, $^3J_{HH}$ = 8.2 Hz, 1H, CH), 7.83 (t, $^3J_{HH}$ = 8.2 Hz, 1H, CH), 8.07 (d, $^3J_{HH}$ = 8.2 Hz, 1H, CH), 8.13 (br. s, 1H, NH), 8.38 (s, 1H, CH), 8.86 (br. s, 2H, NH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 56.6, 65.1, 113.7, 119.0, 120.7, 121.6, 124.0, 124.8, 125.5, 126.6, 130.2, 131.0, 131.6, 135.3, 155.4, 156.0, 157.4, 157.8, 175.3. APSI MS: M^++1 = 364. Anal. Calcd for $C_{19}H_{17}N_5O_3$: C, 62.80; H, 4.72; N, 19.27. Found: C, 62.93; H, 4.61; N, 19.21.

3-{4-Amino-6-[(3,5-dichlorophenyl)amino]-2,5-dihydro-1,3,5-triazin-2-yl}-4*H*-chromen-4-one (16ab)

Mp 266-267 °C (MeOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.99 (s, 1H, CH), 7.31 (t, $^4J_{HH}$ = 2.0 Hz, 1H, CH), 7.45 (br. s, 1H, NH), 7.56 (t, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 7.66 (d, $^4J_{HH}$ = 2.0 Hz, 2H, CH), 7.73 (d, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 7.88 (td, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, CH), 8.10 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, CH), 8.17 (br. s, 1H, NH), 8.48 (s, 1H, CH), 8.71 (s, 1H, NH), 8.88 (s, 1H, NH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 58.6, 119.1, 119.7, 122.5, 123.4, 123.9, 125.4, 126.6, 134.5, 135.4, 140.8, 155.5, 156.0, 156.3, 158.0, 175.8. IR (KBr): ν = 3367 (NH), 3153 (NH), 3089, 3026, 2976, 1647, 1620, 1599, 1572, 1556, 1531, 1466, 1406, 1315, 764. APSI MS: M^++1 = 402. APSI MS: M^++1 = 364. Anal. Calcd for $C_{18}H_{13}Cl_2N_5O_2$: C, 53.75; H, 3.26; Cl, 17.63; N, 17.41. Found: C, 53.88; H, 3.40; Cl, 17.52; N, 17.37.

3-{4-Amino-6-[(4-fluorophenyl)amino]-2,5-dihydro-1,3,5-triazin-2-yl}-6-methoxy-4*H*-chromen-4-one (16cc)

Mp 272-273 °C (EtOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.87 (s, 3H, OCH_3), 5.95 (s, 1H, CH), 7.18 (t, $^3J_{HF}$ = 9.0 Hz, 2H, CH), 7.35 (br. s, 1H, NH), 7.45-7.49 (m, 2H, CH), 7.55 (m, 2H, CH), 7.70 (m, 1H, CH), 8.43 (s, 1H, CH), 8.53 (s, 1H, NH), 8.75 (s, 1H, NH), 10.11 (s, 1H, NH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 56.3, 58.6, 105.2, 115.9 (d, $^2J_{CF}$ = 22.1 Hz), 120.8, 121.9, 124.4 (d, $^3J_{CF}$ = 7.5 Hz), 124.5,

124.6, 134.2, 151.1, 152.0, 155.6, 155.7, 156.5 (d, $^{1}J_{CF}$ = 238.4 Hz), 158.2, 175.6. APSI MS: M^{+}+1 = 382. Anal. Calcd for $C_{19}H_{16}FN_5O_3$: C, 59.84; H, 4.23; N, 18.36. Found: C, 60.01; H, 4.09; N, 18.30.

3-{4-Amino-6-[(3-chloro-4-fluorophenyl)amino]-2,5-dihydro-1,3,5-triazin-2-yl}-6-fluoro-4*H*-chromen-4-one (16dd)

Mp 273-274 °C (EtOH). ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.96 (s, 1H, CH), 7.37 (m, 1H, CH), 7.43 (m, 1H, CH), 7.78 (m, 2H, CH), 7.84 (m, 2H, CH), 8.03 (br. s, 1H, NH), 8.49 (s, 1H, CH), 8.62 (s, 1H, NH), 8.83 (s, 1H, NH), 10.33 (s, 1H, NH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 58.5, 110.0 (d, $^{2}J_{CF}$ = 23.9 Hz), 116.9 (d, $^{2}J_{CF}$ = 22.6 Hz), 117.3 (d, $^{2}J_{CF}$ = 22.2 Hz), 119.8 (d, $^{2}J_{CF}$ = 18.6 Hz), 121.4, 122.0 (d, $^{3}J_{CF}$ = 9.2 Hz), 122.4 (d, $^{3}J_{CF}$ = 8.4 Hz), 123.4, 123.7 (d, $^{3}J_{CF}$ = 7.1 Hz), 125.1 (d, $^{3}J_{CF}$ = 6.2 Hz), 135.3, 152.8, 154.3 (d, $^{1}J_{CF}$ = 243.2 Hz), 155.6, 157.2 (d, $^{1}J_{CF}$ = 242.4 Hz), 166.4, 175.2. APSI MS: M^{+}+1 = 404. Anal. Calcd for $C_{18}H_{12}ClF_2N_5O_2$: C, 53.54; H, 3.00; Cl, 8.78; N, 17.34. Found: C, 53.72; H, 3.11; Cl, 8.67; N, 17.27.

3-[4-Amino-6-(dimethylamino)-2,5-dihydro-1,3,5-triazin-2-yl]-6-methyl-4*H*-chromen-4-one (16be)

Mp 232-233 °C (EtOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.44 (s, 3H, CH_3), 3.04 (s, 6H, $N(CH_3)_2$), 5.84 (s, 1H, CH), 7.28 (br. s, 1H, NH), 7.61 (d, $^{3}J_{HH}$ = 8.5 Hz, 1H, CH), 7.68 (dd, $^{3}J_{HH}$ = 8.5 Hz, $^{4}J_{HH}$ = 1.7 Hz, 1H, CH), 7.87 (d, $^{4}J_{HH}$ = 1.7 Hz, 1H, CH), 8.35 (s, 1H, CH), 8.43 (s, 1H, NH), 8.54 (s, 1H, NH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 21.0, 37.4, 58.2, 118.9, 122.4, 123.6, 124.6, 136.1, 136.3, 154.6, 155.6, 156.4, 157.8, 175.8. IR (KBr): ν = 3311 (br, NH), 1682, 1632, 1481, 1354, 1292, 1171, 1117, 1063, 833, 802. APSI MS: M^{+}+1 = 300. Anal. Calcd for $C_{15}H_{17}N_5O_2$: C, 60.19; H, 5.72; N, 23.40. Found: C, 60.33; H, 5.57; N, 23.29.

***N*-{4-[(*E*)-2-(4-Oxo-4*H*-chromen-3-yl)vinyl]quinazolin-2-yl}guanidine hydrochloride (17)**

Mp 259-260 °C (MeCN). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.56 (t, $^{3}J_{HH}$ = 8.1 Hz, 1H, CH), 7.69 (m, 1H, CH), 7.74 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H, CH), 7.86 (t, $^{3}J_{HH}$ = 8.1 Hz, 1H, CH), 7.99 (s, 2H, CH), 8.09 (d, $^{3}J_{HH}$ = 15.4 Hz, 1H, CH), 8.17 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H, CH), 8.44 (br. s, 4H, NH), 8.47 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H, CH), 8.66 (d, $^{3}J_{HH}$ = 15.4 Hz, 1H, CH), 9.14 (s, 1H, CH), 11.07 (br. s, 1H, NH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 119.0, 119.6, 120.2, 121.7, 123.8, 125.4, 125.9, 126.6, 127.1, 127.3, 132.3, 135.1, 135.8, 150.5, 153.9, 155.7, 156.0, 159.5, 164.9, 175.8. IR (KBr): ν = 3277 (br, NH), 3047, 2929, 1697, 1655, 1630, 1612, 1541, 1500, 1466, 1319, 775, 760. APSI MS: M^{+}+1 = 358. Anal. Calcd for $C_{20}H_{16}ClN_5O_2$: C, 61.00; H, 4.09; Cl, 9.00; N, 17.78. Found: C, 61.16; H, 3.97; Cl, 8.88; N, 17.72.

3-[(*E*)-2-(4,6-Diamino-1,3,5-triazin-2-yl)vinyl]-4*H*-chromen-4-one (19)

Mp 243-244 °C (EtOH). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.54 (t, $^{3}J_{HH}$ = 8.5 Hz, 1H, CH), 7.68 (d, $^{3}J_{HH}$ = 15.6 Hz, 1H, CH), 7.75 (d, $^{3}J_{HH}$ = 8.5 Hz, 1H, CH), 7.81 (d, $^{3}J_{HH}$ = 15.6 Hz, 1H, CH), 7.88 (td, $^{3}J_{HH}$ = 8.5 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, CH), 7.89 (br. s, 2H, NH_2), 8.17 (dd, $^{3}J_{HH}$ = 8.5 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, CH), 8.31 (br. s, 2H, NH_2), 8.90 (s, 1H, CH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 118.9, 119.0, 124.0, 125.5,

126.0, 126.6, 134.1, 135.1, 155.6, 160.4, 162.8, 163.5, 175.8. IR (KBr): ν = 3354 (NH), 3319 (NH), 3151, 3078, 1686, 1649, 1630, 1578, 1460, 1348, 1300, 978, 791, 758, 704. APSI MS: M^++1 = 282. Anal. Calcd for $C_{14}H_{11}N_5O_2$: C, 59.78; H, 3.94; N, 24.90. Found: C, 59.98; H, 3.81; N, 24.78.

2-Amino-5-[(4-oxo-4*H*-chromen-3-yl)methylene]-3,5-dihydro-4*H*-imidazol-4-one (21)

Mp >300 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.33 (s, 1H, CH), 7.52 (t, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 7.68 (d, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 7.74 (br. s, 2H, NH_2), 7.83 (t, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 8.12 (d, $^3J_{HH}$ = 8.3 Hz, 1H, CH), 9.24 (s, 1H, CH), 10.77 (br. s, 1H, NH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 100.5, 119.0, 119.1, 120.0, 123.4, 125.9, 126.4, 135.1, 155.9, 159.1, 161.0, 171.1, 175.9. IR (KBr): ν = 3396 (br, NH), 3219 (NH), 3153, 3021, 2927, 1707, 1660, 1632, 1612, 1558, 1464, 1387, 1252, 1144, 764. APSI MS: M^++1 = 256. Anal. Calcd for $C_{13}H_9N_3O_3$: C, 61.18; H, 3.55; N, 16.46. Found: C, 61.07; H, 3.69; N, 16.40.

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