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A FACILE SYNTHESIS OF IMIDAZO[1,5-*b*]PYRIDAZINES FROM 3-FORMYLCHROMONES

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Abstract – The recyclization of 3-formylchromones promoted by chlorotrimethylsilane with 1-amino-1*H*-imidazoles results in a set of imidazo[1,5-*b*]pyridazines is obtained in high preparative yields. It's found that the reaction is sensitive to the structure of *NNC*-binucleophiles.

INTRODUCTION

Imidazo[1,5-*b*]pyridazines **1** were used for the treatment of neuropathic pain, psychiatric and mood disorders such as, schizophrenia, anxiety, depression, panic;[1a] psoriasis, lung diseases, and peripheral vascular diseases;[1b] diabetes.[1c] They have been also shown to possess high antiviral[2] and anti-HIV activities.[3]

This research was undertaken in order to develop facile and efficient method for the synthesis of novel functionally diverse imidazopyridazines[4] through the reaction of hydrazones of formylchromones.

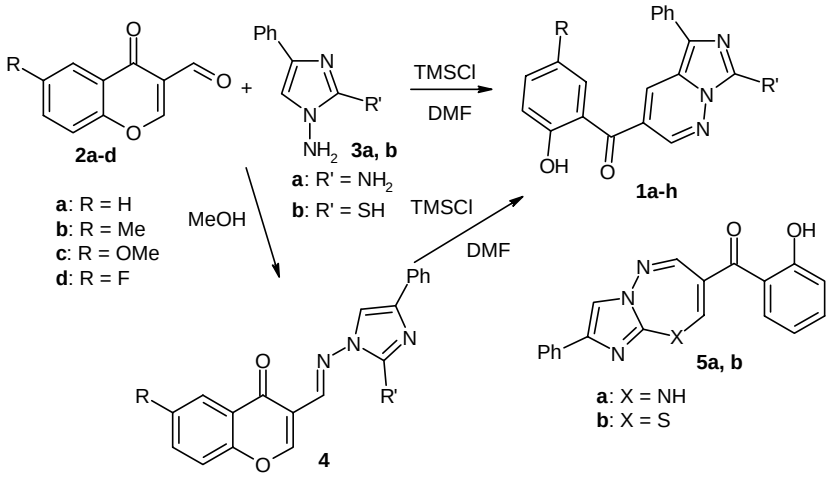
RESULTS AND DISCUSSION

Previously we have shown that [3+3] cyclocondensation of 3-formylchromones **2** with substituted acetamides,[5a] π-electron-rich amino heterocycles, donor anilines,[5b] and benzimidazoles,[5c] led to the formation of 3-(2-hydroxybenzoyl) substituted pyridines.

We have also demonstrated that chlorotrimethylsilane (TMSCl) is a convenient condensing agent for the recyclization of 3-formylchromones affording regioselective formation of 2-hydroxybenzoyl derivatives

of nitrogen heterocycles,[5] as well as for other condensations of carbonyl compounds.[6] Therefore it was decided to use TMSCl as a promoter and water scavenger in the reactions of 3-formylchromones **2** with 1-amino-1*H*-imidazoles **3** that could lead to imidazo[1,5-*b*]pyridazines **1**.

3-Formylchromone **2a** reacted with 4-phenyl-1*H*-imidazole-1,2-diamine **3a** (DMF, 100 °C) in the presence of 4 eq. TMSCl to give compound **1a** in 96% yield (Scheme 1, Table 1). 9*H*-Imidazo[1,2-*b*][1,2,4]triazepine **5a** were not formed which is a surprising result considering that other 1,3-*CCC*-bielectrophiles (1,3-diketones etc), react with diamine **3a** to give mixtures of compounds of types **1** and **5**.[4c,d] The use of thiol **3b** in this reaction gave imidazo[1,5-*b*]pyridazine **1e** in 85% yield and no imidazo[2,1-*b*][1,3,4]thiadiazepine **5b** was detected.[7] The nature of the substituent in the aromatic ring in 3-formylchromone **2** virtually didn't effect the yield and proceeding of the reaction.



Scheme 1

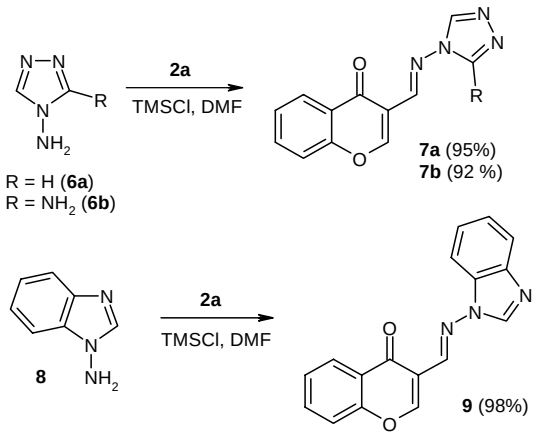
Table 1. Yields, melting points and MS data for imidazo[1,5-*b*]pyridazines **1a-h**.

Entry	1	R	R'	Yield (%)[a]	Mp (°C, solvent)[b]	M+1	Entry	1	R	R'	Yield (%)[a]	Mp (°C, solvent)	M+1
1	**1a**	H	NH_2	96	225-226 (MeOH-DMF)	331	5	**1e**	H	SH	85	279-280 (MeOH-DMF)	348
2	**1b**	Me	NH_2	95	232-233 (MeOH-DMF)	345	6	**1f**	Me	SH	84	274-275 (MeOH-DMF)	362
3	**1c**	OMe	NH_2	92	211-212 (EtOH-DMF)	361	7	**1g**	OMe	SH	81	269-270 (EtOH-DMF)	378
4	**1d**	F	NH_2	90	248-249 (EtOH-DMF)	349	8	**1h**	F	SH	85	284-285 (EtOH-DMF)	366

[a]Yields refer to pure isolated product.
[b]Melting points are uncorrected.

It seems likely that the reaction of compounds **2** and **3** initially generates intermediate hydrazones **4**. These compounds can be obtained through the reaction of 3-formylchromone **2a** with 1-amino-4-phenyl-1*H*-imidazoles **3a**,**b** under mild conditions (methanol, 20 °C) and can be quantitatively transformed into targeted imidazo[1,5-*b*]pyridazines **1a** and **1e** upon refluxing in DMF in the presence of TMSCl (Scheme 1).

The reaction of 4-amino-4*H*-1,2,4-triazoles[8] **6a**,**b** or 1-amino-1*H*-benzimidazole[9] **8** with 3-formylchromone **2a** in DMF in the presence of TMSCl at 100 °C led to hydrazones **7** and **9** which did not undergo the cyclization reaction. The latter can be explained by low nucleophilicity of the carbon atoms in triazole and benzimidazole rings (Scheme 2). Compounds **7** and **9** remained intact upon 30 h reflux and microwave irradiation (30 min, 220 °C) of their DMF solutions in the presence of 2 molar equivalents of $ZnCl_2$.



Scheme 2

The structure and composition of the compounds obtained were confirmed by NMR, IR-spectroscopy, mass spectrometry and elemental analysis.

In summary, an efficient methodology has been elaborated for preparative synthesis of imidazo[1,5-*b*]pyridazines from 3-formylchromones and 1-amino-1*H*-imidazoles using TMSCl as an efficient promoter and water scavenger.

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 crystallization were used without additional purification. All procedures were carried out under open atmosphere with no precautions taken to exclude ambient moisture. 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. 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 and ^{1}H NMR 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. Microwave irradiation experiments were performed using Emrys Creator EXP.

General procedure for the preparation of imidazo[1,5-*b*]pyridazines 1.

1-Amino-1*H*-imidazole **3a**,**b** (2 mmol) and 3-formylchromone **2a-d** (2 mmol) were placed in 15 mL pressure tube and dissolved in DMF (3 mL). Chlorotrimethylsilane (869 mg, 8 mmol) was added dropwise to the solution. The tube was thoroughly sealed and heated on a water-bath for 6-12 h (6 h for **3a**, 12 h for **3b**). 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 an ultrasonic bath for 1 h. The precipitate formed was filtered off and washed with *i*-PrOH (2 mL). Compounds **1a-h** were puridied by recrystallization from an appropriate solvent (Table 1).

Hydrazones **7a**,**b** and **9** were obtained by the same procedure.

(7-Amino-5-phenylimidazo[1,5-*b*]pyridazin-3-yl)(2-hydroxyphenyl)methanone (1a)

^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.91 (s, 2H, NH_2), 6.93-7.01 (m, 2H, CH), 7.32 (t, $^3J_{H,H}$ = 7.8 Hz, 1H, CH), 7.39-7.47 (m, 4H, CH), 7.75 (d, $^3J_{H,H}$ = 7.8 Hz, 2H, CH), 8.19 (d, $^4J_{H,H}$ = 1.8 Hz, 1H, CH), 8.23 (d, $^4J_{H,H}$ = 1.8 Hz, 1H, CH), 10.29 (1H, s, OH). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 116.5, 116.9, 117.1, 119.9, 125.4, 126.7, 128.3, 129.5, 130.7, 132.4, 133.4, 134.0, 136.2, 144.1, 146.6, 156.2, 191.7. IR (KBr) ν = 3429 (br, NH), 3331 (br, OH), 3051, 3035, 1647 (C=O), 1618, 1589, 1551, 1485, 1394, 1201, 1161, 930, 806, 762, 750, 688 cm^{-1}. Anal. Calcd for $C_{19}H_{14}N_4O_2$: C, 69.08; H, 4.27; N, 16.96. Found: C, 68.94; H, 4.38; N, 16.90.

(7-Amino-5-phenylimidazo[1,5-*b*]pyridazin-3-yl)(2-hydroxy-5-methylphenyl)methanone (1b)

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.23 (s, 3H, CH_3), 6.90 (d, $^3J_{H,H}$ = 8.8 Hz, 1H, CH), 6.95 (br. s, 2H, NH_2), 7.20 (s, 1H, CH), 7.22 (d, $^3J_{H,H}$ = 8.8 Hz, 1H, CH), 7.33 (t, $^3J_{H,H}$ = 8.4 Hz, 1H, CH), 7.44 (t, $^3J_{H,H}$ = 8.4 Hz, 2H, CH), 7.77 (d, $^3J_{H,H}$ = 8.4 Hz, 2H, CH), 8.18 (d, $^4J_{H,H}$ = 1.4 Hz, 1H, CH), 8.22 (d, $^4J_{H,H}$ = 1.4 Hz, 1H, CH), 10.03 (s, 1H, OH). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 20.4, 116.6, 116.95, 117.0, 125.2, 126.7, 128.3, 128.6, 129.5, 130.7, 132.4, 134.02, 134.04, 136.0, 144.2, 146.6, 153.9, 191.7. Anal. Calcd for $C_{20}H_{16}N_4O_2$: C, 69.76; H, 4.68; N, 16.27. Found: C, 69.85; H, 4.53; N, 16.35.

(7-Amino-5-phenylimidazo[1,5-*b*]pyridazin-3-yl)(2-hydroxy-5-methoxyphenyl)methanone (1c)

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.71 (s, 3H, OCH_3), 6.91 (br. s, 2H, NH_2), 6.92 (m, 2H, CH), 7.02 (dd, $^3J_{H,H}$ = 9.0 Hz, $^4J_{H,H}$ = 3.0 Hz, 1H, CH), 7.32 (t, $^3J_{H,H}$ = 7.9 Hz, 1H, CH), 7.43 (t, $^3J_{H,H}$ = 7.9 Hz, 2H, CH), 7.76 (d, $^3J_{H,H}$ = 7.9 Hz, 2H, CH), 8.20 (d, $^4J_{H,H}$ = 2.0 Hz, 1H, CH), 8.22 (d, $^4J_{H,H}$ = 2.0 Hz, 1H, CH), 9.78 (s, 1H, OH). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 56.0, 114.3, 116.6, 116.8, 118.1, 119.8, 125.7, 126.7, 128.4, 129.5, 132.5, 134.0, 136.2, 144.2, 146.6, 149.8, 152.7, 191.2. Anal. Calcd for $C_{20}H_{16}N_4O_3$: C, 66.66; H, 4.48; N, 15.55. Found: C, 66.80; H, 4.35; N, 15.61.

(7-Amino-5-phenylimidazo[1,5-*b*]pyridazin-3-yl)(5-fluoro-2-hydroxyphenyl)methanone (1d)

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.95 (br. s, 2H, NH_2), 6.98 (m, 1H, CH), 7.19 (dd, $^3J_{H,F}$ = 8.8 Hz, $^4J_{H,H}$ = 3.1 Hz, 1H, CH), 7.26 (m, 1H, CH), 7.33 (t, $^3J_{H,H}$ = 8.0 Hz, 1H, CH), 7.43 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, CH), 7.76 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, CH), 8.18 (d, $^4J_{H,H}$ = 1.9 Hz, 1H, CH), 8.22 (d, $^4J_{H,H}$ = 1.9 Hz, 1H, CH), 10.17 (s, 1H, OH). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 116.3 (d, $^2J_{C,F}$ = 23.0 Hz), 116.4, 116.6, 118.4 (d, $^3J_{C,F}$ = 6.6 Hz), 119.7 (d, $^2J_{C,F}$ = 23.0 Hz), 126.6 (d, $^3J_{C,F}$ = 6.6 Hz), 126.8, 128.4, 129.5, 132.6, 133.9, 136.7, 144.0, 146.8, 152.0 (d, $^4J_{C,F}$ = 1.8 Hz), 155.8 (d, $^1J_{C,F}$ = 236.2 Hz), 190.0 (d, $^4J_{C,F}$ = 1.8 Hz). Anal. Calcd for $C_{19}H_{13}FN_4O_2$: C, 65.51; H, 3.76; N, 16.08. Found: C, 65.69; H, 3.65; N, 16.01.

(2-Hydroxyphenyl)(7-mercapto-5-phenylimidazo[1,5-*b*]pyridazin-3-yl)methanone (1e)

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.97 (t, $^3J_{H,H}$ = 8.1 Hz, 1H, CH), 7.00 (d, $^3J_{H,H}$ = 8.1 Hz, 1H, CH), 7.42-7.49 (m, 3H, CH), 7.51 (t, $^3J_{H,H}$ = 7.9 Hz, 2H, CH), 7.70 (d, $^3J_{H,H}$ = 7.9 Hz, 2H, CH), 8.13 (d, $^4J_{H,H}$ = 1.9 Hz, 1H, CH), 8.41 (d, $^4J_{H,H}$ = 1.9 Hz, 1H, CH), 10.43 (s, 1H, OH), 14.27 (s, 1H, SH). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 117.4, 118.8, 120.1, 123.2, 124.3, 125.0, 127.3, 127.5, 129.78, 129.83, 131.3, 131.9, 134.5, 145.9, 157.0, 157.7, 191.7. IR (KBr) ν = 3650-3150 (br, OH, NH), 3062, 3010, 2924, 1621 (C=O), 1587, 1481 (C=S), 1385, 1236, 1219, 1192, 1163, 1043, 926, 758, 715 cm^{-1}. Anal. Calcd for $C_{19}H_{13}N_3O_2S$: C, 65.69; H, 3.77; N, 12.10; S, 9.23. Found: C, 65.53; H, 3.92; N, 12.17; S, 9.15.

(2-Hydroxy-5-methylphenyl)(7-mercapto-5-phenylimidazo[1,5-*b*]pyridazin-3-yl)methanone (1f)

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.23 (s, 3H, CH_3), 6.88 (d, $^3J_{H,H}$ = 8.5 Hz, 1H, CH), 7.18-7.30 (m, 2H, CH), 7.46 (t, $^3J_{H,H}$ = 8.0 Hz, 1H, CH), 7.52 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, CH), 7.68 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, CH), 8.14 (d, $^4J_{H,H}$ = 1.2 Hz, 1H, CH), 8.41 (d, $^4J_{H,H}$ = 1.2 Hz, 1H, CH), 10.25 (br. s, 1H, OH), 14.34 (s, 1H, SH). Anal. Calcd for $C_{20}H_{15}N_3O_2S$: C, 66.47; H, 4.18; N, 11.63; S, 8.87. Found: C, 66.63; H, 4.02; N, 11.72; S, 8.81.

(2-Hydroxy-5-methoxyphenyl)(7-mercapto-5-phenylimidazo[1,5-*b*]pyridazin-3-yl)methanone (1g)

^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.73 (s, 3H, OCH_3), 6.90 (d, $^3J_{H,H}$ = 8.8 Hz, 1H, CH), 6.98 (d, $^4J_{H,H}$ = 2.4 Hz, 1H, CH), 7.08 (dd, $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,H}$ = 2.4 Hz, 1H, CH), 7.45 (t, $^3J_{H,H}$ = 8.0 Hz, 1H, CH), 7.50 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, CH), 7.72 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, CH), 8.16 (d, $^4J_{H,H}$ = 1.5 Hz, 1H, CH), 8.42 (d, $^4J_{H,H}$ = 1.5 Hz, 1H CH), 10.02 (br. s, 1H, OH), 14.35 (s, 1H, SH). Anal. Calcd for $C_{20}H_{15}N_3O_3S$: C, 63.65; H, 4.01; N, 11.13; S, 8.50. Found: C, 63.84; H, 3.90; N, 11.07; S, 8.42.

(5-Fluoro-2-hydroxyphenyl)(7-mercapto-5-phenylimidazo[1,5-*b*]pyridazin-3-yl)methanone (1h)

^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.99 (m, 1H, CH), 7.22 (dd, $^3J_{H,F}$ = 8.8 Hz, $^4J_{H,H}$ = 3.0 Hz, 1H, CH), 7.26 (m, 1H, CH), 7.45 (t, $^3J_{H,H}$ = 8.0 Hz, 1H, CH), 7.51 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, CH), 7.70 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, CH), 8.14 (d, $^4J_{H,H}$ = 1.5 Hz, 1H, CH), 8.42 (d, $^4J_{H,H}$ = 1.5 Hz, 1H, CH), 10.35 (s, 1H, OH), 14.26 (s, 1H, SH). Anal. Calcd for $C_{19}H_{12}FN_3O_2S$: C, 62.46; H, 3.31; N, 11.50; S, 8.78. Found: C, 62.30; H, 3.47; N, 11.42; S, 8.85.

3-[(*E*)-(4*H*-1,2,4-Triazol-4-ylimino)methyl]-4*H*-chromen-4-one (7a)

Mp > 300 °C (EtOH). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.59 (t, $^3J_{H,H}$ = 8.3 Hz, 1H, CH), 7.77 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, CH), 7.89 (t, $^3J_{H,H}$ = 8.3 Hz, 1H, CH), 8.16 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, CH), 9.01 (s, 1H, CH), 9.03 (s, 1H, CH), 9.18 (s, 2H, CH). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 117.5, 119.3, 123.9, 125.8, 127.1, 135.6, 139.5, 151.8, 156.2, 158.4, 174.8. APSI MS: M^++1 = 241. Anal. Calcd for $C_{12}H_8N_4O_2$: C, 60.00; H, 3.36; N, 23.32. Found: C, 59.82; H, 3.50; N, 23.21.

3-{(*E*)-[(3-Amino-4*H*-1,2,4-triazol-4-yl)imino]methyl}-4*H*-chromen-4-one (7b)

Mp = 266-267 °C (EtOH). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.59 (t, $^3J_{H,H}$ = 8.3 Hz, 1H, CH), 7.79 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, CH), 7.90 (t, $^3J_{H,H}$ = 8.3 Hz, 1H, CH), 8.17 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, CH), 8.82 (s, 2H, NH_2), 9.01 (s, 1H, CH), 9.40 (s, 1H, CH), 9.41 (s, 1H, CH). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 117.3, 119.4, 123.9, 125.8, 127.2, 133.5, 135.6, 148.8, 150.3, 156.2, 159.4, 174.7. APSI MS: M^++1 = 256. Anal. Calcd for $C_{12}H_9N_5O_2$: C, 56.47; H, 3.55; N, 27.44. Found: C, 56.31; H, 3.73; N, 27.33.

3-[(*E*)-(1*H*-Benzimidazol-1-ylimino)methyl]-4*H*-chromen-4-one (9)

Mp > 300 °C (EtOH-DMF). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.48 (t, $^3J_{H,H}$ = 8.3 Hz, 1H, CH), 7.54 (t, $^3J_{H,H}$ = 8.3 Hz, 1H, CH), 7.61 (t, $^3J_{H,H}$ = 8.3 Hz, 1H, CH), 7.81 (m, 2H, CH), 7.92 (m, 2H, CH), 8.19 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, CH), 9.24 (s, 1H, CH), 9.25 (s, 1H, CH), 9.70 (s, 1H, CH). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 112.2, 117.7, 118.0, 119.4, 123.9, 125.4, 125.78, 125.84, 127.1, 131.3, 135.6, 136.0, 136.4, 151.6, 156.2, 158.8, 174.9. 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, 70.41; H, 3.97; N, 14.43.

General procedure for the preparation of hydrazones 4.

The mixture of 1-amino-1*H*-imidazole **3a**,**b** (2 mmol) and 3-formylchromone **2a-d** (2 mmol) in 8 ml MeOH was stirred 12 h at 20 °C. The precipitate formed was filtered off and washed with EtOH. Hydrazones **4** were puridied by recrystallization from MeOH-DMF (4:1).

3-{(*E*)-[(2-Amino-4-phenyl-1*H*-imidazol-1-yl)imino]methyl}-4*H*-chromen-4-one (4a)

Yield 97%. Mp = 214-215 °C (MeOH-DMF). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.91 (s, 2H, NH_2), 7.32 (t, $^3J_{H,H}$ = 8.0 Hz, 1H, CH), 7.42 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, CH), 7.57 (m, 2H, CH), 7.75 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, CH), 7.87 (t, $^3J_{H,H}$ = 8.2 Hz, 1H, CH), 8.15 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, CH), 8.22 (s, 1H, CH), 8.47 (s, 1H, CH), 9.23 (s, 1H, CH). APSI MS: M^++1 = 331. Anal. Calcd for $C_{19}H_{14}N_4O_2$: C, 69.08; H, 4.27; N, 16.96. Found: C, 69.27; H, 4.11; N, 16.90.

3-{(*E*)-[(2-Mercapto-4-phenyl-1*H*-imidazol-1-yl)imino]methyl}-4*H*-chromen-4-one (4e)

Yield 98%. Mp = 262-263 °C (MeOH-DMF). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.33 (t, $^3J_{H,H}$ = 8.2 Hz, 1H, CH), 7.44 (t, $^3J_{H,H}$ = 8.2 Hz, 2H, CH), 7.58 (t, $^3J_{H,H}$ = 8.2 Hz, 1H, CH), 7.78 (m, 3H, CH), 7.89 (t, $^3J_{H,H}$ = 8.2 Hz, 1H, CH), 8.17 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, CH), 8.37 (s, 1H, CH), 8.95 (s, 1H, CH), 9.18 (s, 1H, CH), 12.97 (s, 1H, SH). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 110.1, 118.2, 119.3, 123.9, 124.9, 125.8,

126.9, 128.0, 128.3, 128.7, 129.4, 135.4, 148.1, 156.3, 156.9, 161.9, 175.2. APSI MS: M^++1 = 348. Anal. Calcd for $C_{19}H_{13}N_3O_2S$: C, 65.69; H, 3.77; N, 12.10; S, 9.23. Found: C, 65.57; H, 3.90; N, 12.02; S, 9.26.

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