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Nano-Co-[4-chlorophenyl-salicylaldimine-pyranopyrimidine dione]Cl_2 as a new Schiff base complex and catalyst for the one-pot synthesis of some 4*H*-pyrimido[2,1-*b*]benzazoles

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Abstract

Nano-Co-[4-clolorophenyl-salsylaldimine-pyranopyrimidine dione]Cl_2 {Nano-[Co-4CSP]Cl_2} was prepared and fully characterized as a new nano-Schiff base complex. Nano-[Co-4CSP]Cl_2 was successfully used as an efficient catalyst for the synthesis of some 4*H*-pyrimido[2,1-b]benzazoles such as 4*H*-pyrimido[2,1-b]benzothiazoles and 4*H*-pyrimido[2,1-b]benzimidazoles.

Keywords Nano-[Co-4CSP]Cl_2 · Pyrano[2,3-*d*]pyrimidine dione · 4*H*-pyrimido[2,1-*b*]benzazole · Schiff base

Introduction

4*H*-pyrimido[2,1-*b*]benzazole derivatives such as 4*H*-pyrimido[2,1-*b*]benzothiazoles and 4*H*-pyrimido[2,1-*b*]benzimidazoles are important biological fused heterocyclic compounds which are prepared by the multi-component Biginelli-type reaction [1]. In this kind reaction, Biginelli-like compounds such as 4*H*-pyrimido[2,1-*b*]benzazoles were prepared by the condensation reaction of ethyl acetoacetate with various aldehyde and 2-aminobenzothiazole or 2-aminobenzimidazole, like thiourea or urea in Biginelli reaction, to prepare 4*H*-pyrimido[2,1-*b*]benzothiazoles and 4*H*-pyrimido[2,1-b]benzimidazoles, respectively [1]. This condensation as a multi-component reaction through the direct synthesis of target product, without the

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preparation of side products, has some important advantages such as increasing of the yield and decreasing of reaction time, waste of energy, materials and solvents [2–6].

4*H*-pyrimido[2,1-*b*]benzazoles have the ability to prepare the various drugs and applied as anti-tumor [7], anti-inflammatory [8], anti-bacterial [9] and anti-fungal compounds [10]. Various methods have been reported for the preparation of 4*H*-pyrimido[2,1-*b*]benzazole derivatives in the presence of different catalysts such as Fe_3O_4@nano-cellulose/TiCl [11], TMGT [1], iron fluoride [12], nano-Fe_3O_4@SiO_2–$TiCl_3$ [6], chitosan [13], nano-$TiCl_2$/cellulose [14], H_3PO_4–Al_2O_3 [15] and acetic acid [16]. But, according to the importance of these compounds, new and useful methods are still needed to prepare these significant compounds.

Pyrano[2,3-*d*]pyrimidine diones have important biological properties such as antitumor [17], antibacterial [18], antihypertensive [19], bronchodilators [20] and antiallergic [21, 22]. Because of the significant biological properties of these compounds, in continuous to our previous researches on the synthesis of new Schiff base complexes based on pyranopyrazole derivatives as amine [21, 23–28], we have synthesized a derivative of pyrano[2,3-*d*]pyrimidine diones, namely 7-amino-5-(4-chlorophenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1*H*-pyrano[2,3-d]pyrimidine-6-carbonitrile and reacted with salicylaldehyde and $Co(Cl)_2{\cdot}6H_2O$ to give nano-Co-[4-clolorophenyl-salsylaldimine-pyranopyrimidinedione]Cl_2 {Nano-[Co-4CSP]Cl_2} as a new Schiff base complex (Fig. 1) and successfully applied as a catalyst for the synthesis of some 4*H*-pyrimido[2,1-*b*]benzazole derivatives (Scheme 1).

Experimental

Procedure for the synthesis of [4CSP]

A mixture of 7-amino-5-(4-chlorophenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1*H*-pyrano[2,3-*d*]pyrimidine-6-carbonitrile as an amine (1 mmol), salicylaldehyde (1.2 mmol) and

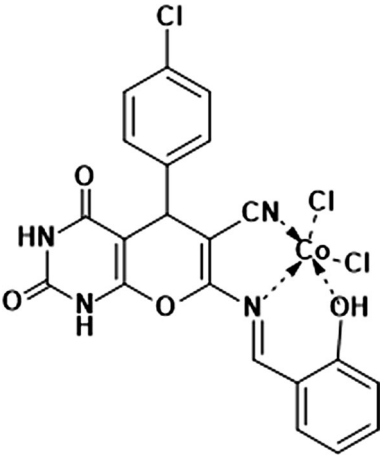
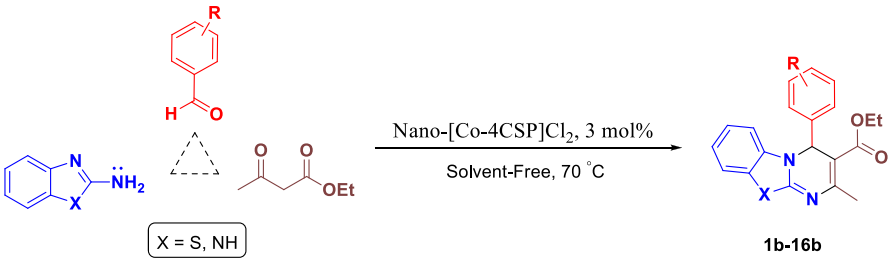


Fig. 1 The proposed structure of nano-[Co-4CSP]Cl_2



Scheme 1 The preparation of 4*H*-pyrimido[2,1-*b*]benzazoles using nano-[Co-4CSP]Cl_2

acetic acid glacial as a catalyst (13 mol%) was added in a 25-mL round-bottomed flask connected to a reflux condenser and stirred at 110 °C for 48 h. After completion of the reaction, as monitored by TLC, the reaction mixture was washed with ethylacetate and hexane (7/3) (10 mL) for three times to purify (7E)-7-(2-hydroxybenzylideneamino)-5-(4-chlorophenyl)-2,3,4,5-tetrahydro-2,4-dioxo-1H pyrano[2,3-d]pyrimidine-6-carbonitrile (4CSP) as a Schiff base from excess salicylaldehyde.

Spectral data for [4CSP]

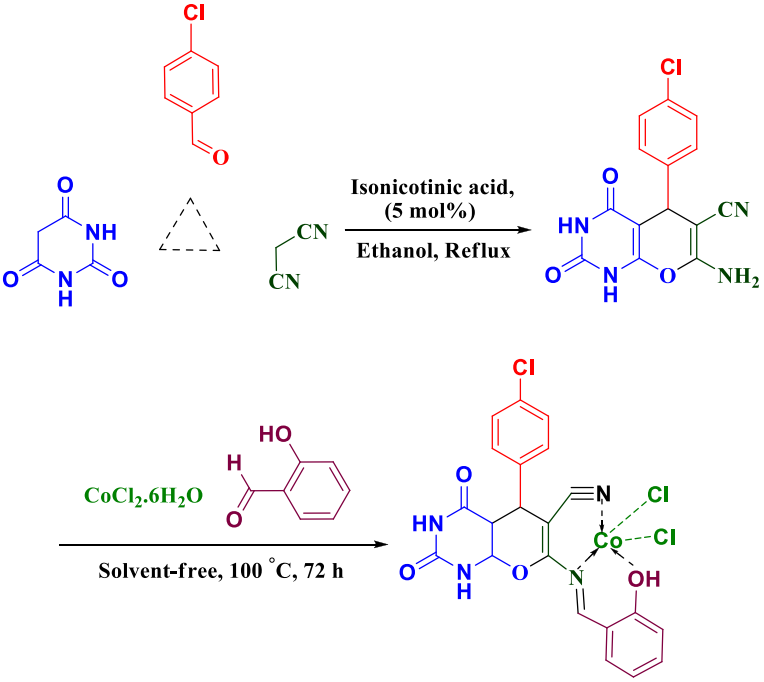
Yellow Solid; M.p.: 233–235°°C; M.p.: 235–237 °C; Yield: 80%; IR (KBr, cm^{-1}): 3155, 3018, 2856, 1715, 1659, 1618, 756,550; ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 5.43 (s, 1H), 7.069, (t, J=7.60 Hz, 1H), 7.16–7.22 (m, 2H), 7.31–7.38 (m, 3H), 7.61 (dd, J=6.40, 1.2 Hz,1H), 7.69 (dd, J=6.00, 1.60 Hz, 1H), 10.08 (s,1H), 11.09 (d, J=6.80 Hz, 1H), 11.37 (s,1H), 12.06 (s, 1H); ^{13}CNMR (100 MHz, DMSO-d_6): δ (ppm) 31.3, 86.7, 116.1, 119.8, 121.2, 123.7, 125.4, 128.3, 129.3, 131.9, 133.6, 136.3, 148.2, 149.6, 154.8, 157.6, 163.1, 191.3, 197.1.

Procedure for the synthesis of nano-Co-[4-clolorophenyl-salsylaldimine-pyranopyrimidine dione]Cl_2 {Nano-[Co-4CSP]Cl_2}

7-Amino-5-(4-chlorophenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1*H*-pyrano[2,3-*d*] pyrimidine-6-carbonitrile as an amine (1 mmol) and $Co(Cl)_2{\cdot}6H_2O$ (1 mmol) were added to a 25-mL round-bottomed flask containing salicylaldehyde (1.2 mmol) which connected to a reflux condenser and stirred at 100 °C for 72 h. After this time, the reaction mixture was washed by ethylacetate and hexane (7/3) (10 mL) for three times to purify nano-Co-[4-clolorophenyl-salsylaldimine-pyranopyrimidine dione]Cl_2 {Nano-[Co-4CSP]Cl_2} in 80% of yield (Scheme 2).

General procedure for the synthesis of 4*H*-pyrimido[2,1-b]benzazole derivatives

A mixture of aromatic aldehyde, (1 mmol), ethyl acetoacetate (1 mmol, 0.13 g), 2-aminobenzothiazole (1 mmol, 0.15 g) or 2-aminobenzimidazole (1 mmol,



Scheme 2 The preparation of nano-[Co-4CSP]Cl_2

0.133 g) and nano-[Co-4CSP]Cl_2 (0.164 g, 3 mol%) as a catalyst was added to 25-mL round-bottomed flask connected to a reflux condenser and stirred at 70 °C under solvent-free conditions. After the completion of the reaction, as monitored by TLC, the reaction mixture was extracted with warm ethanol (10 mL) and separated from the catalyst by simple filtration. Finally, the desired product was purified by the recrystallization in ethanol (90%). Note: Compound 1 was purified by plate chromatography. The spectral data of some prepared compounds are given in supporting information.

Selected spectral data of compounds

Ethyl-2-methyl-4-(phenyl)-4*H*-pyrimido[2,1-b] [1,3] benzothiazole-3-carboxylate (1)

Yellow Solid; M.p.: 179–181 °C; Yield: 87%; IR (KBr, cm^{-1}): 3043, 2968, 1670, 1589, 1462, 1244, 744, 543; ^{1}H-NMR: (250 MHz, DMSO-d_6): δ (ppm) 1.17 (s, 3H), 2.30 (s, 3H), 4.02 (s, 2H), 5.74 (s, 1H), 7.16–7.28 (m, 4H), 7.50 (d, $J = 6.75$ Hz, 1H), 7.60 (d, $J = 6.75$ Hz, 1H), 7.71 (d, $J = 6.75$ Hz, 1H); ^{13}CNMR: (62.5 MHz, DMSO-d_6): δ (ppm) 14.5, 23.6, 57.0, 59.9, 103.1, 112.7, 123.2, 124.4, 127.2, 127.4, 128.7, 129.0, 142.0, 154.5.

Ethyl-2-methyl-4-(2,4 dichloro-phenyl)-4*H*-pyrimido[2,1-b] [1,3] benzothiazole-3-carboxylate (2)

Yellow Solid; M.p.: 114–117 °C; Yield: 80%; IR (KBr, cm^{-1}): 3067, 2981, 1689, 1584, 1073, 1016, 746, 579; ^{1}H-NMR: (250 MHz, DMSO-d_6): δ (ppm) 1.08 (s, 3H), 3.30 (s, 3H), 4.01 (s, 2H), 6.77 (s, 1H), 7.16–7.28 (m, 4H), 7.50 (d, $J = 6.75$ Hz, 1H), 7.60 (d, $J = 6.75$ Hz, 1H), 7.71 (d, $J = 6.75$ Hz, 1H); ^{13}CNMR: (62.5 MHz, DMSO-d_6): δ (ppm) 14.5, 23.8, 56,0, 59.9, 101.8, 111.8, 122.9, 123.4, 124.7, 127.3, 129.3, 130.0, 131.1, 132.7, 137.9, 141.6, 155.3, 163.1, 165.6.

Ethyl-2-methyl-4-(3-hydroxy-phenyl)-4*H*-pyrimido[2,1-b] [1,3] benzothiazole-3-carboxylate (3)

White Solid; M.p.: 260–261 °C; Yield: 85%; IR (KBr, cm^{-1}): 3048, 2980, 2864, 2933, 1686, 1510, 1100,754, 552; ^{1}H-NMR: (250 MHz, DMSO-d_6): δ (ppm) 1.18 (s, 3H), 2.28 (s, 3H), 4.04 (s, 2H), 6.34 (s, 1H)), 6.57 (d, $J = 6.75$ Hz, 1H), 6.77–6.84 (m, 2H), 7.02 (d, $J = 6.75$ Hz, 1H) 7.16 (d, $J = 6.00$ Hz 1H), 7.31 (s, 3H), 7.70 (d, $J = 7.00$ Hz, 1H), 9.40 (s,1H); ^{13}CNMR: (62.5 MHz, DMSO-d_6): δ (ppm) 14.5, 23.6, 56.9, 59.9, 103.2, 112.7, 114.0, 115.7, 118.1, 123.2, 124.4, 127.2, 129.8, 138.0, 143.2, 154.2, 158.0, 163.0, 166.0.

Ethyl-2-methyl-4-(2,4-dichloro-phenyl)-4*H*-pyrimido[2,1-b] [1,3] benzoimidazole-3-carboxylate (12)

White Solid; M.p.: 280 °C; Yield: 72%; IR (KBr, cm^{-1}): 3235, 2931, 1698, 1656, 1618, 729, 465; ^{1}H-NMR (500 MHz, DMSO-d_6): δ (ppm) 1.13 (t, $J = 6.85$ Hz, 3H), 2.53(s, 3H), 4.03 (s, 2H), 6.76 (s, 1H), 7.00 (d, $J = 7.90$ Hz, 1H), 7.09 (t, $J = 7.30$ Hz, 2H), 7.18 (d, $J = 7.80$ Hz, 1H), 7.40 (d, $J = 7.50$ Hz, 1H), 7.51–7.58 (m, 1H), 11.04 (s, 1H); ^{13}CNMR (125 MHz, DMSO-d_6): δ (ppm) 14.0, 18.7, 53.2, 59.3, 109.1, 117.0, 120.4, 122.0, 128.0, 128.9, 131.5, 132.6, 133.2, 142.1, 145.1, 147.6, 164.8.

Ethyl-2-methyl-4-(3-nitro-phenyl)-4*H*-pyrimido[2,1-b] [1,3] benzoimidazole-3-carboxylate (15)

White Solid; M.p.: 261–262 °C; Yield: 68%; IR (KBr, cm^{-1}): 3232, 2978, 1706, 1659, 1617, 1528, 1236, 737; 477; ^{1}H-NMR (500 MHz, DMSO-d_6): δ (ppm) 1.18 (t,, $J = 7.00$ Hz,3H), 2.52 (s, 3H), 4.04 (q, $J = 5.50$ Hz, 2H), 6.68 (s, 1H), 6.97 (t, $J = 7.65$ Hz, 1H), 7.07(t, $J = 7.35$ Hz, 1H), 7.33 (d, $J = 7.85$ Hz, 1H), 7.38 (d, $J = 7.90$ Hz, 1H), 7.59 (t, $J = 7.80$ Hz, 1H), 7.77 (d, $J = 7.40$ Hz, 1H), 8.08 (d, $J = 8.15$ Hz, 1H), 8.30(s, 1H), 10.99 (s, NH); ^{13}CNMR (125 MHz, DMSO-d_6):

δ (ppm) 13.9, 18.7, 55.1, 59.8, 97.0, 109.8, 116.9, 120.4, 121.8, 122.0, 122.8, 130.2, 131.3, 133.5, 142.2, 144.2, 145.3, 147.5, 147.6, 164.9.

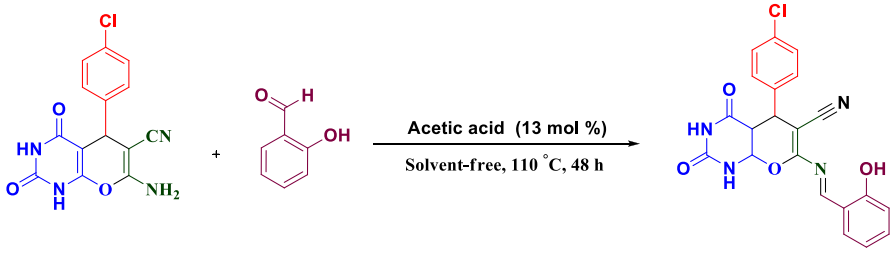
Ethyl-2-methyl-4-(4-chloro-phenyl)-4*H*-pyrimido[2,1-b] [1,3] benzoimidazole-3-carboxylate (16)

White Solid; M.p.: 290–292 °C; Yield: 85%; IR (KBr, cm^{-1}): 3235, 3103, 2928, 1695, 1656, 1617, 701, 517; ^{1}H-NMR (250 MHz, DMSO-d_6): δ (ppm) 1.11 (s, 3H), 2.44 (s, 3H), 4.00 (s, 2H), 6.41 (s, 1H), 6.57 (d, J = 6.75 Hz, 1H), 6.89–7.34 (m, 9H), 10.88 (s,1H); ^{13}CNMR (125 MHz, DMSO-d_6): δ (ppm) 14.4, 19.0, 55.7, 59.8, 97.9, 110.2, 117.2, 120.6, 122.3, 128.8, 129.4, 131.8, 132.7, 141.4, 142.7, 145.8, 147.2, 165.5.

Results and discussion

7-Amino-5-(4-chlorophenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1*H*-pyrano[2,3-*d*]pyrimidine-6-carbonitrile as a pyrano[2,3-d]pyrimidine dione compound was synthesized by the reaction of barbituric acid, 4-chlorobenzaldehyde, malononitrile using isonicotinic acid as a catalyst. Then, the prepared compound as an amine was reacted with salicylaldehyde and $Co(Cl)_2{\cdot}6H_2O$ at 100 °C for 72 h to give nano-Co-[4-clolorophenyl-salsylaldimine-pyranopyrimidine dione]Cl_2 {Nano-[Co-4CSP]Cl_2} (Scheme 2). The structure of nano-[Co-4CSMP]Cl_2 was studied by various analyses such as FT-IR, TGA, DTG, SEM, BET and mass to confirm the chemical structure, available chemical elements, thermal stability, morphology, size of particles and active surface area of the synthesized nano-Schiff base complex.

To investigate the structure of Schiff base compound (4CSP), at first, by the reaction of 7-amino-5-(4-chlorophenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1*H*-pyrano[2,3-*d*] pyrimidine-6-carbonitrile as an amine with salicylaldehyde in the presence of acetic acid as a mild catalyst, (7E)-7-(2-hydroxybenzylideneamino)-5-(4-chlorophenyl)-2,3,4,5-tetrahydro-2,4-dioxo-1H pyrano[2,3-d]pyrimidine-6-carbonitrile (4CSP) as a Schiff base was prepared individually at 110 °C after 48 h (Scheme 3). To show and confirm the preparation of Schiff base ligand, the structure of it was studied by



Scheme 3 The preparation of [4CSP]

FT-IR, ^{1}H-NMR and ^{13}CNMR spectra. The related spectra are given in supporting information.

In another procedure, to direct preparation of the Schiff base complex, by the reaction of the prepared pyrano[2,3-*d*]pyrimidine dione derivative with salicylaldehyde and $CoCl_2{\cdot}6H_2O$, nano-[Co-4CSP]Cl_2 prepared in one step, the mass spectra of the complex, to show the preparation of nano-[Co-4CSP]Cl_2, were recorded and the exact mass of it was appeared at 549 m/z.

FT-IR spectrum of nano-[Co-4CSP]Cl_2 was studied, and a broad peak appeared at 3250–3500 cm^{-1} which could be related to O–H stretching and another peak at 1656 cm^{-1} could be corresponded to stretching mode of C=N bond in the structure of nano-[Co-4CSP]Cl_2 which coordinated with Cobalt (**II**) chloride (Fig. 2). The peak at 1710 cm^{-1} is related to stretching of C=O group in the structure of nano-[Co-4CSP]Cl_2. The peak related to cyano group (CN) is displayed in the structure of ligand (4CSP), due to interaction of nitrogen with cobalt in complex, weakened and appeared in 2237 cm^{-1}. According to that, the existence of important functional groups in nano-[Co-4CSP]Cl_2 was approved by FT-IR spectrum.

To illustrate the presence of the desired elements in the structure of complex, energy-dispersive X-ray spectroscopy (EDX) from nano-[Co-4CSP]Cl_2 was studied and the expected elements in the complex were approved (Fig. 3). As it is shown in Fig. 3, it indicates that carbon, oxygen, nitrogen, chlorine and cobalt were presented in nano-[Co-4CSP]Cl_2.

To find the morphology and the particle size of nano-[Co-4CSP]Cl_2, the scanning electron microscope (SEM) micrographs of nano-[Co-4CSP]Cl_2 was checked out and showed that the synthesized particles were prepared in size less than 100 nm (Fig. 4).

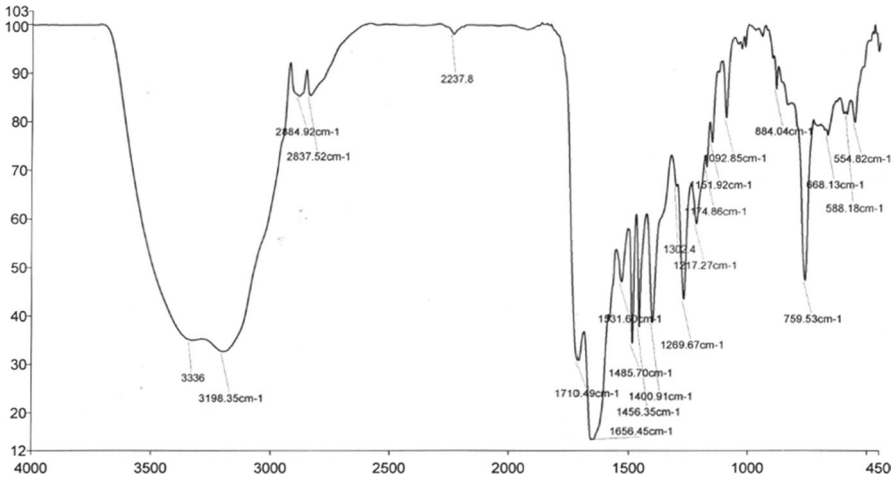


Fig. 2 FT-IR spectrum of nano-[Co-4CSP]Cl_2

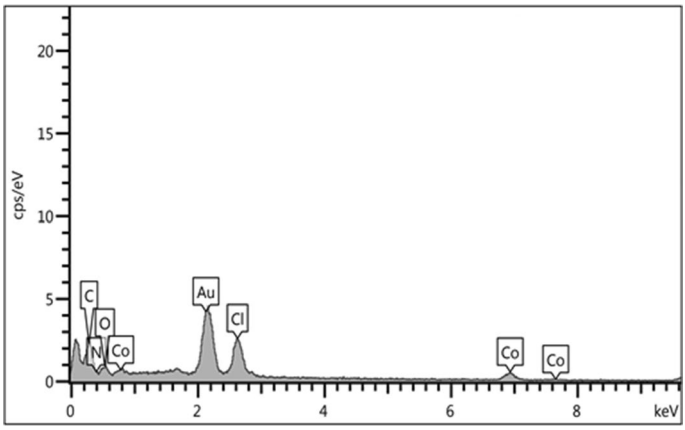


Fig. 3 Energy-dispersive X-ray spectroscopy (EDX) of nano-[Co-4CSP]Cl_2

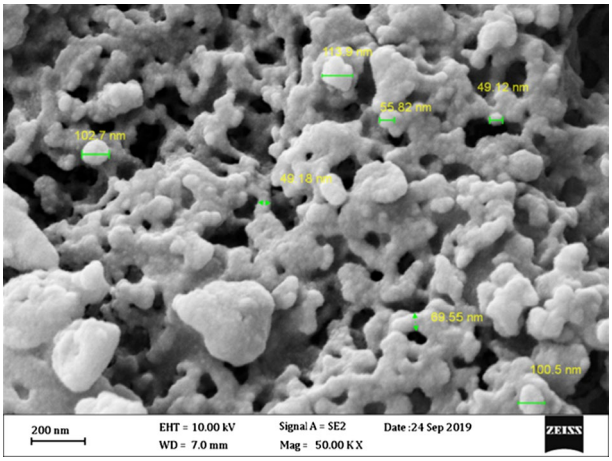


Fig. 4 SEM micrograph of nano-[Co-4CSP]Cl_2

Table 1 Specific surface area (BET), mean pore diameter and total pore volume of nano-[Co-4CSP]Cl_2

Sample	Specific surface area ($m^2\ g^{-1}$)	Mean pore diameter (nm)	Total pore volume ($cm^3\ g^{-1}$)
Nano-[Co-4CSMP]Cl_2	11.64	45.71	0.13

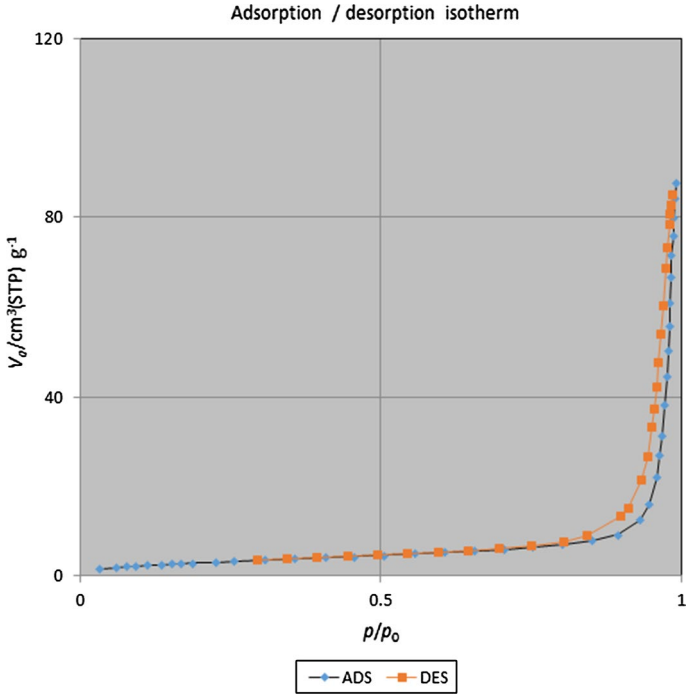


Fig. 5 N_2 adsorption–desorption isotherms of nano-[Co-4CSP]Cl_2

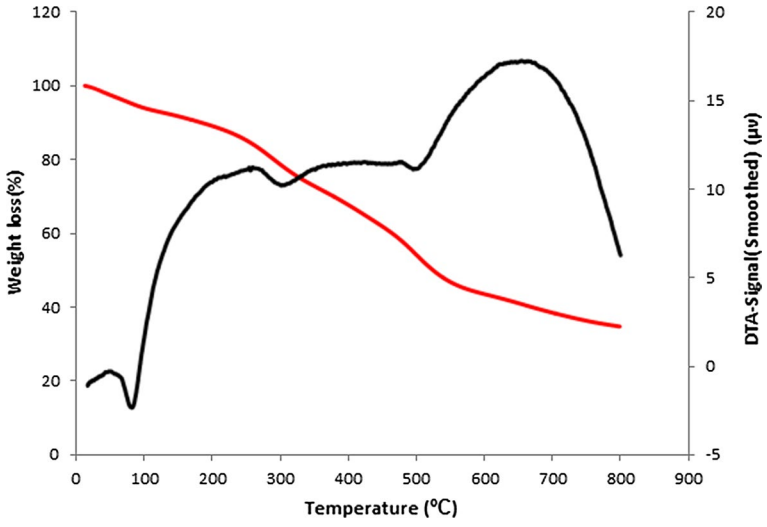


Fig. 6 Thermal gravimetric analysis (TGA) of nano-[Co-4CSP]Cl_2 at range of 25–800 °C

Because of the porous structure of catalyst particles, to display the effective surface of complex for the catalysis of the reactions, the volume and size of the cavities included in nano-[Co-4CSP]Cl_2 were studied. The specific surface area, mean pore diameter and total pore volume of nano-[Co-4CSP]Cl_2 are 11.64 $m^2\ g^{-1}$, 45.71 nm and 0.13 $cm^3\ g^{-1}$, respectively (Table 1, Fig. 5).

To indicate the temperature range for the application of nano-[Co-4CSP]Cl_2 in the chemical reactions and thermal stability of it, thermal gravimetric analysis (TGA) and differential thermal gravimetric (DTG) of the complex were investigated and displayed that it could be used in the temperature range up to 200 °C without no particular changes in its structure (Fig. 6).

After the preparation and identification of nano-[Co-4CSP]Cl_2, the reaction of 2-aminobenzothiazole, benzaldehyde and ethyl acetoacetate was considered as a model reaction. This reaction was examined in the presence of various amounts of nano-[Co-4CSP]Cl_2 at range of 50–100 °C under solvent-free condition which the best result was obtained using 3 mol% of the catalyst at 70 °C (Table 2). Also, the model reaction was tested in some various solvents such as ethyl acetate, chloroform, dichloromethane and *n*-hexane in comparison with solvent-free condition which did not modify the yield of product and reaction time (Table 2). Moreover, the model reaction was tested in the presence of $CoCl_2$ as a catalyst in comparison with nano-[Co-4CSP]Cl_2 which did not have no acceptable result.

After the optimization of the reaction condition, to display the generality of the catalyst, a wide range of various aldehydes was used for the preparation of 4*H*-pyrimido[2,1-*b*]benzazoles. For this purpose, ethyl acetoacetate was reacted with various aldehyde and 2-aminobenzothiazole or 2-aminobenzimidazole to give 4*H*-pyrimido[2,1-*b*]benzothiazoles and 4*H*-pyrimido[2,1-*b*]benzimidazoles, respectively. The expected products were synthesized with high yields in good reaction times (Table 3).

In the purposed mechanism, which is supported by the previous literature [9–15, 29–31], ethyl acetoacetate reacted with aldehyde which was activated by the catalyst to give Knoevenagel product. Then, 2-aminobenzothiazole was

Table 2 Effect of catalyst amounts, temperature and solvents on the reaction between 2-aminobenzothiazole, benzaldehyde and ethyl acetoacetate

Mol% of catalyst	Solvent	Temp. (°C)	Time (min)	Yield[a] (%)
1	–	70	60	60
3	–	70	60	87
5	–	70	60	87
3	–	50	60	80
3	–	100	60	87
3	Ethyl acetate	Reflux	60	75
3	Chloroform	Reflux	60	50
3	Dichloromethane	Reflux	60	60
3	*n*-Hexane	Reflux	60	10

[a]Isolated yield

Table 3 The preparation of 4*H*-pyrimido[2,1-*b*]benzazoles

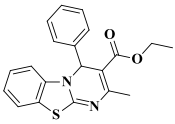
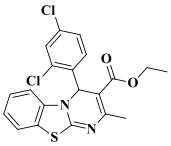
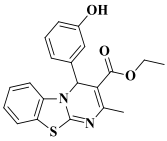
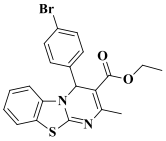
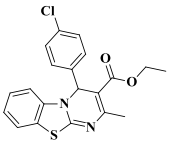
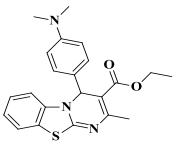
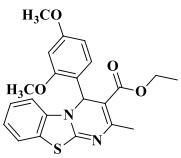
Entry	Product	Time (min)	Yield[a] (%)	M.p. °C (Lit.)[ref]
1	 (1b)	60	87	179–181 (175–178)[9]
2	 (2b)	120	80	114–117 (112–116)[9]
3	 (3b)	90	85	260–261 (259–261)[9]
4	 (4b)	150	81	110–114 (107–109)[9]
5	 (5b)	120	79	138–140 (140–142)[9]
6	 (6b)	120	78	174–177 (–)[13]
7	 (7b)	120	79	164–165 (164–166)[9]

Table 3 (continued)

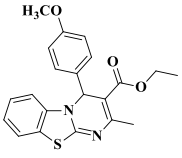
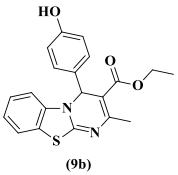
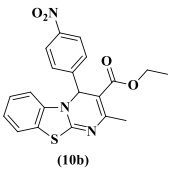
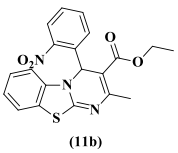
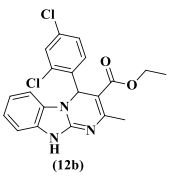
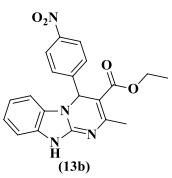
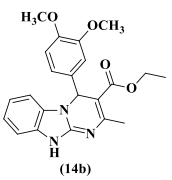
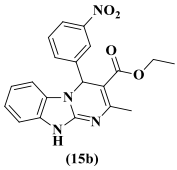
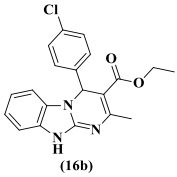
Entry	Product	Time (min)	Yield[a] (%)	M.p. °C (Lit.)[ref]
8	 (8b)	60	86	128–130 (130–132)[30]
9	 (9b)	40	76	220–223 (218–222)[9]
10	 (10b)	70	85	152–154 (153–156)[9]
11	 (11b)	45	86	161–163 (160–164)[9]
12	 (12b)	100	72	280 (> 300)[31]
13	 (13b)	120	82	230 (225)[1] (dec)
14	 (14b)	110	79	259–261(261.3–261.9)[29]

Table 3 (continued)

Entry	Product	Time (min)	Yield[a] (%)	M.p. °C (Lit.)[ref]
15	 (15b)	10	68	291–292 (294–297)[31]
16	 (16b)	90	85	290–292 (291.4–292.2)[29]

The reaction was carried out at 70 °C under solvent-free conditions

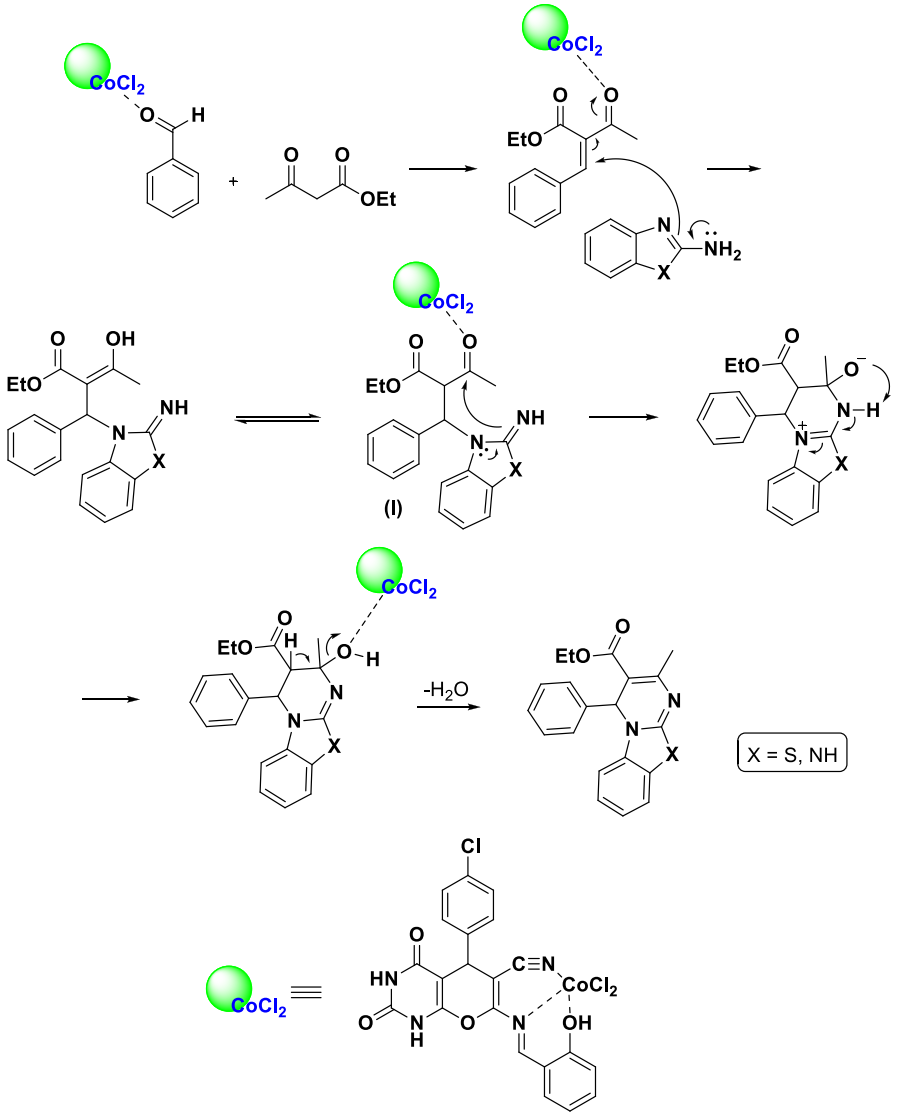
[a]Isolated yield

reacted with Knoevenagel product to furnish intermediate (**I**). Afterward, by the intranucleophilic attack to carbonyl group in intermediate (**I**) which was activated by the catalyst and removing of one molecule of H_2O in the last step, the desired product was prepared (Scheme 4).

To investigate the reusability of the catalyst, the reaction of 2-aminobenzothiazole, benzaldehyde and ethyl acetoacetate, as a model reaction, was studied in the presence of the reuse catalyst. In this regard, after the completion of the reaction, the reaction mixture was extracted by warm ethanol and separated from the catalyst by simple filtration. The separated catalyst was washed with ethyl acetate, dried and successfully reused for four times (Fig. 7).

Conclusions

In summary, nano-Co-[4-clolorophenyl-salsylaldimine-pyranopyrimidinedione]Cl_2 {Nano-[Co-4CSP]Cl_2} as a novel Schiff base complex and catalyst was synthesized and identified by various techniques such as IR, SEM, EDX, TGA, DTA and BET as well as mass analysis. The prepared nano-Schiff base complex and catalyst were successfully used for the synthesis of some 4*H*-pyrimido[2,1-*b*]benzazoles including 4*H*-pyrimido[2,1-*b*]benzothiazoles and 4*H*-pyrimido[2,1-*b*]benzimidazoles.



Scheme 4 The offered mechanism for the synthesis of 4*H*-pyrimido[2,1-*b*]benzazoles

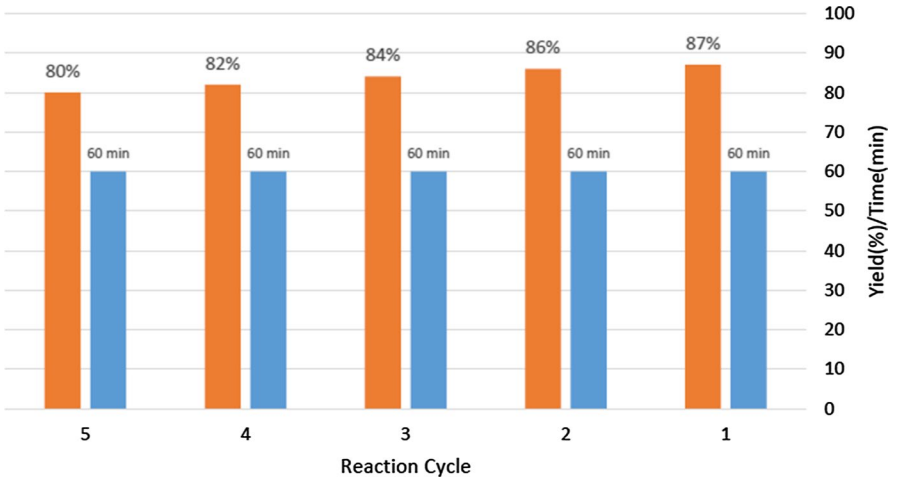


Fig. 7 The condensation of 2-aminobenzothiazole with benzaldehyde and ethyl acetoacetate in the presence of reused catalyst

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