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SnO nanoparticles as efficient catalyst for the one-pot synthesis chromeno[2,3-b]pyridines and 2-amino-3,5-dicyano-6-sulfanyl pyridines

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SnO nanoparticles as an efficient catalyst have been used for the preparation of chromeno[2,3-b]pyridines and 2-amino-3,5-dicyano-6-sulfanyl pyridines under reflux conditions in ethanol in good to excellent yields. This flexible and nano-catalytic procedure showed good recyclability and provides cleaner condensation reaction in a short reaction time.

1. Introduction

The pyridine ring system is a structural component of a large number of biologically active compounds. Heterocycles with pyridine moiety exhibit various pharmacological such as anti-bacterial,[1] anticancer,[2] antiprion[3] potassium channel opening,[4] IKK-binhibitors,[5] potent inhibitor of HIV-1 integrase,[6] activities. Among the pyridine derivatives, 2-amino-3,5-dicyano-6-sulfanyl pyridines exhibit a broad range of biological properties such as treatment of the Hepatitis B Foundation infections,[7] Creutzfeldt–Jacob disease, Parkinson's disease, hypoxia/ischemia, asthma, kidney disease, epilepsy and cancer.[8-10] Condensed pyridines are known for versatile biological activities, for example chromeno [2,3-b]pyridines have a number of pharmacological properties. Chromenopyridines are fused heterocyclic compounds that exhibit antibacterial (including antitubercular),[11] anti-proliferative (cytotoxic activity against the human solid tumor HT-29 cell lines),[12] antirheumatic,[13]cancer chemopreventive and chemother-apeutic agent,[14] antimyopic,[15] antihistaminic,[16] and antiasthmatic[17] activities. Several compounds derived from these libraries were identified as inhibit mitogen-activated protein kinase-activated protein kinase 2 (MK-2) and suppress the expression of TNFα in U937 cells[18] and possessing gastric antisecretory activity in the rat and dog.[19] Some other examples of chromenopyridine derivatives such prominent drug molecules as a mlexanox (trade name Aphthasol) is an antiallergic and topical antiulcer agent and prosnoprofen (as NSAIDs) have been reported (Fig. 1).

<Fig. 1>

Synthesis of bioactive compounds should be facile, flexible, rapid and practical in organic synthesis. Therefore, looking for efficient and concise methods for the synthesis of pyridines is an interesting challenge. Multi-component reactions (MCRs) present a wide range of possibilities for molecular diversity per step with a minimum of synthetic time, outlay, labour and waste production.[20-25] Chromeno [2,3-b]pyridines show interesting characteristics which make them attractive targets for the synthesis *via* MCRs. Consequently, MCRs have been paid much attention by synthetic organic chemists worldwide.

Similarly nanoparticles have undergone extensive examination in the past decade. Due to their insolubility in reaction solvents renders them easily separable from the reaction mixture. Heterogeneous catalysis offers several advantages over the homogeneous counterpart, such as easy recovery, simple recycling without losing their activity and enhanced stability of the catalyst which can make synthetic processes cheaper, safer and greener.[26-32] Therefore, the possibility of performing multicomponent reactions under mild conditions with a heterogeneous catalyst could enhance their effectiveness from economic and ecological points of view.

We wish to report herein a highly efficient procedure for the preparation of chromeno[2,3-b]pyridines and 2-amino-3,5-dicyano-6-sulfanyl pyridines using SnO nanoparticles as an efficient and reusable heterogeneous catalyst under reflux conditions in ethanol (Scheme 1). A number of methods have been developed for the synthesis of chromeno [2,3-b] pyridines and 2-amino-3,5-dicyano-6-sulfanyl pyridines using MCRs in the presence of few catalysts such as Et_3N (under reflux conditions in ethanol),[33] K_2CO_3 (EtOH:H_2O, reflux).[34]

<Scheme 1>

2. Results and discussion

The first step entails the synthesis of highly stable SnO nanoparticles. The catalyst was prepared by co-precipitation technique and microwave radiation. For more investigation of the influence of microwave irradiation in this reaction, the synthesis of SnO nanoparticle was compared in two times. The precipitate dispersed in water kept under irradiation of microwave for 18 min and 12 min (Microwave power was maintained at 600 W). Particle size of SnO nanoparticles, was investigated by XRD pattern. The crystallite size diameter (D) of the SnO nanoparticles has been calculated by Debye–Scherrer equation ($D = K\lambda/\beta\cos\theta$), where FWHM (full-width at half-maximum or half-width) is in radians and Θ is the position of the maximum of diffraction peak ,K is the so-called shape factor, which usually takes a value about 0.9, and λ is the X-ray wavelength. Crystallite size of SnO has been found to be 28 nm for 18 min and 40 nm for 12 min. The XRD pattern of the SnO nanoparticles was shown in Fig. 2 (under irradiation of microwave for 18 min). The results show that SnO nanoparticles were obtained with an average diameter of 26-28 nm as confirmed by XRD analysis. The morphology and particle size of SnO nanoparticles, was investigated by scanning electron microscopy (SEM) (Fig. 3). The SEM images show particles with diameters in the range of nanometers.

<Fig. 2>

<Fig. 3>

Initially, we had explored and optimized different reaction parameters for the synthesis of 2-amino-3,5-dicyano-6-sulfanyl pyridines by the condensation reaction of 4-nitrobenzaldehyde (1 mmol), 2.2 mmol of malononitrile and 1 mmol of thiophenol as a model reaction. Meanwhile, we investigated the reaction of salicylaldehydes, thiols and 2 equiv of malononitrile in the presence of different catalysts for the synthesis of chromeno [2,3-b] pyridines. As given in Table 2, the solvent has a great effect on the acceleration of the reactions. Several reactions were scrutinized using various solvents such as EtOH, CH_3CN, water, DMF and $CHCl_3$. The best results were obtained under reflux conditions in ethanol and found that the reaction gave satisfying results in the presence of SnO nanoparticles at 6 mol% which gave excellent yields of products (Table 1 and 2). The polarity, dipole moment, polarizability and hydrogen bonding of a solvent determine what type of compounds it is able to dissolve. In this reaction, the use of polar solvents favours the reaction mechanism. The catalyst showed best activity in ethanol compared to other organic solvents such as DMF, CH_3CN, and $CHCl_3$. The dielectric constant of solvents was listed in Table 2. The ethanol with dielectric constant 24.5 carried out reactions in good to excellent yields. Therefore, the use of polar solvents with moderate dielectric constant favours the condensation reactions. Also, the activity and stability of the SnO nanoparticles and those metal oxides in ethanol is maximum compared to other solvents. The model reactions was carried out in the presence of various catalysts such as metal oxide (MgO, CaO, CuO, ZrO_2, SnO) and $InCl_3$, CuCl, $SnCl_2$ and $CuSO_4$. When the reaction was carried out using CuO, MgO and SnO NPs as the catalyst, the product could be obtained in moderate to good yield. The acidity or basicity of those metal oxides or salts can be determined with the help of a very weak basic molecule which is only adsorbed on Lewis centres very weakly. The surface of a metal oxide consists of ordered arrays of acid-base centres. The cationic metal centres act as Lewis acid sites while the anionic oxygen centres act as Lewis bases. The strong solid acids or bases usually give higher activities in condensation reactions. We propose that SnO NPs have highly effective catalytic behaviour because of the surface properties that include $Sn^{2}+$ as acid and $O^{2}-$ as base that accelerate the reaction rate. These complementary interactions between reactants and catalyst lead to an increase in the rate of reaction. Size of prepared SnO nanoparticles in the presence of microwave was reduced until 28 nm, and specific surface area was increased about 35 m^2/g. Table 3 shows that the influence of particles size on the activity of the SnO nanoparticles in the synthesis of 6-sulfanyl pyridines and chromenopyridines. As expected, the increased surface area due to small particle size increased reactivity of catalyst. This factor is responsible for the accessibility of the substrate molecules on the catalyst surface. However, the activity of solid catalysts is influenced by the acid-base properties and many other factors such as geometric structure (particularly pore structure), the distribution of sites and the polarity of the surface sites.[28]

We also investigated recycling of the SnO NPs as catalyst under reflux conditions in ethanol. The results showed that SnO NPs can be reused several times without noticeable loss of catalytic activity (Yields 92 to 86%) (Fig. 4). The catalyst could be reused for five times with a minimal loss of activity. Perhaps, activity of SnO NPs is decreased by the number of the regeneration.The morphology and particle size of SnO nanoparticle was investigated by scanning electron microscopy (SEM) before use and after reuse of five times with images shown in figure 5. The SEM of SnO nanoparticles before and after the reaction showed identical shape. Interestingly, the morphology of the nanoparticles remained unchanged before and after reaction. We believe that, this is also the possible reason for the extreme stability of the SnO nanoparticles presented herein.

<Table 1>

<Table 2>

<Table 3>

<Fig. 4>

<Fig. 5>

To study the scope of this reaction, we next utilized various aldehydes and thiols in four-component reactions under reflux conditions in ethanol (Table 4).

<Table 4>

As represented in Table 4, these products precipitate from refluxing ethanolic solutions and are isolated by easy filtration.

The proposed mechanism for the preparation of 2-amino-3,5-dicyano-6-sulfanyl pyridines is shown in Scheme 2. Initially, we assumed that the reaction occurs via a Knoevenagel condensation between malononitrile and aldehyde. Then, the subsequent Michael-type addition of the second molecule of malononitrile to the Knoevenagel adduct and thiolate addition to C≡N of the adduct and cyclization to dihydropyridine which upon aromatization and oxidation (air) under the reaction conditions leads to pyridine. In this mechanism the SnO NPs act as Lewis solid acid and activate the C=O group for better reaction with nucleophiles.

<Scheme 2>

A possible mechanism for the formation of chromeno [2,3-b] pyridines is shown in Scheme 3. Thus, salicylaldehyde reacts with 1 equiv of malononitrile to form iminochromene **H**. This compound undergoes addition with thiophenol to afford phenylsulfanylchromene **I**. Finally, when **I** is treated with another equivalent of malononitrile, chromenopyridine **P** forms in good to excellent yield. Also, the in the present reaction SnO NPs may play as Lewis solid acids. The increased surface area due to small particle size increased reactivity. So, we were encouraged to use SnO NPs in the following optimization of the reaction conditions.

<Scheme 3>

This flexible and nano-catalytic procedure showed good recyclability and provides cleaner condensation reaction in a short reaction time and excellent yields. Nanoparticles exhibit good catalytic activity due to their large surface area and active sites which are mainly responsible for their catalytic activity. These advances have opened the door for the design of fresh nanocatalysts for particular applications in synthetic chemistry.

3. Experimental

3.1. Chemicals and apparatus

All reagents and solvents were purchased from Merck (Germany) and Aldrich and used without further purification. Melting points were determined on Electro thermal 9200.^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance-400 MHz. NMR spectra were obtained in $CDCl_3$and DMSO-d_6 solution and are reported as parts per million (ppm) downfield from tetramethylsilane as internal standard. The IR spectra were recorded on FT-IR Magna 550 apparatus using with KBr plates. EIMS (70 eV) was performed by Finnigan-MAT-8430 mass spectrometer in m/z. The elemental analyses (C. H. N) of the samples were performed using a LECO CHNS 923 analyser.Surfacearea was determined by nitrogen adsorption measurement (Micrometrics ASAP-2000). Powder X-ray diffraction (XRD) of SnO nanoparticles was carried out on a Philips diffractometer of X'pert Company with monochromatized Cu Kα radiation (λ = 1.5406 Å). Microscopic morphology was visualized by SEM (LEO 1455VP).

3.2. Preparation of SnO nanoparticles

Tin oxide nanoparticles were prepared according to the procedure reported in the literature.[35] A 100 ml aqueous solution of 10^{-2} M is prepared by dissolving 0.225 g of tin (II) chloride ($SnCl_2.2H_2O$) in dilute HCl. The solution was continuously stirred and diluted NH_4OH was added drop-wise to obtain a precipitate. The solution pH increased to 5. The precipitate was washed several times to remove excess ions. The precipitate dispersed in water kept under irradiation of microwave for 18 min. The sample is characterised by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

3.3. General procedure for the preparation of 2-amino-3,5-dicyano-6-sulfanyl pyridines

SnO nanoparticles (6 mol%) were added to a mixture of aldehyde (1 mmol) and malononitrile (2.2 mmol) in 5 mL ethanol and the reaction mixture was stirred for 10 min at 60°C. Then, the desired thiol (1 mmol) was added to the solution and the solution was refluxed. Progress of the reaction was continuously monitored by thin-layer chromatography. When the reaction was completed, the mixture was cooled to room temperature and centrifuged to separate the catalyst. The solvent was evaporated under vacuum and the solid obtained was recrystallized from ethanol to afford the pure pyridines. The products were characterized by IR, NMR analysis and elemental analysis.

3.4. General procedure for the preparation of chromeno [2,3-b] pyridines

To a mixture of a selected salicylaldehyde (1.5 mmol), malononitrile (3 mmol) and a desired thiol (1.5 mmol) in 5 mL of anhydrous ethanol was added SnO NPs (6 mmol%). The resulting mixture was refluxed for 50–60 min and then allowed to cool toroom temperature. The formed precipitate was isolated by

filtration. The product was dissolved in DMF (3 mL) and the catalyst was filtered. Then, 4 mL water was added to the filtrate which resulted in the crystallization of the product. The resulting crystalline structure was filtered and dried with a vacuum pump. The structures of the products were fully established on the basis of their ^{1}H NMR, ^{13}C NMR and FT-IR spectra.

3.5. Spectral data

2-Amino-4-(4-methoxyphenyl)-6-(p-tolylthio)pyridine-3,5-dicarbonitrile (5a). Yellow solid; mp 229–231°C; FT-IR (KBr): (ν_{max}/cm^{-1}): 3462, 3332, 2218, 1632, 1544; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.43 (s, 3H, CH_3), 3.88 (s, 3H, OCH_3), 5.47 (s, 2H, NH_2), 7.04-7.06 (d, 2H, J = 8 Hz, Ar-H), 7.28 (d, 2H, Ar-H), 7.42 (d, 2H, J= 7.8 Hz, ArH), 7.51-7.53 (d, 2H, *J*= 8Hz, ArH);^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.4, 55.6, 87.1, 94.8, 114.3, 115.6, 124.1, 126.1, 130.3, 130.4, 135.3, 139.7, 158.2, 160.2, 161.2, 165.1, 167.4; MS (EI,70 eV): *m/z* 372 (M^+), Anal. Calcd for $C_{21}H_{16}N_4OS$: C, 67.72; H, 4.33; N, 15.04%. Found: C, 67.62; H, 4.39; N, 15.14%.

2-Amino-4-(4-methoxyphenyl)-6-(phenylthio)pyridine-3,5-dicarbonitrile (5b). Yellow solid; mp 240–242°C; FT-IR (KBr): (ν_{max}/cm^{-1}): 3438, 3329, 2217, 1640, 1545; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.86 (s, 3H, OCH_3), 6.81 (s, 2H, NH_2), 7.04 (d, 2H, J=7.6 Hz,Ar-H), 7.42-7.51 (m, 5H, Ar-H), 7.54 (d, 2H, J= 7.6 Hz, Ar-H), ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 55.5, 86.3, 93.6, 114.2, 115.6, 129.3, 129.6, 130.8, 131.1, 133.2, 135.7, 157.6, 158.9, 159.9, 161.4, 166.9; MS (EI,70 eV): *m/z* 358 (M^+), Anal. Calcd for $C_{20}H_{14}N_4OS$: C, 67.02,H, 3.94; N, 15.63%. Found: C, 67.11; H, 3.85; N, 15.52%.

2-Amino-4-(3-nitrophenyl)-6-(phenylsulfanyl)-3,5-pyridine dicarbonitrile (5c). Yellow solid, mp 218–220 °C; FT-IR (KBr): (ν_{max}/cm^{-1}): 3447, 3315, 2218, 1626, 1523, 1349; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.38 (s, 2H, NH_2), 7.50–7.57(m, 5H, Ar–H), 7.38-7.72 (m, 3H, Ar–H), 8.44 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 87.4, 95.9, 114.8, 115.2, 127.1, 128.4, 129.3, 129.9, 131.2, 133.2, 135.8, 136.1, 137.2, 158.4, 159.3, 164.1, 169.5; MS (EI, 70 eV): *m/z* 373 (M^+), HR MS calc. for $C_{19}H_{11}N_5O_2S$: 373.0633, found: 373.0631; Anal. Calcd for $C_{19}H_{11}N_5O_2S$: C, 61.12; H, 2.97; N, 18.76%. Found: C, 61.21; H, 2.91; N, 18.68%.

2-Amino-4-(4-chlorophenyl)-6-((4-methoxybenzyl)thio)-3,5-pyridinedicarbonitrile (5d). Yellow solid, mp 237–239 °C;FT-IR (KBr): (ν_{max}/cm^{-1}): 3322, 2214, 1626, 1543, 1482, 1243,^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.71 (s, 3H, OCH_3), 4.43 (s, 2H, CH_2), 6.84–6.86 (d,*J*=8.4, 2H, Ar–H), 7.41–7.43 (d, *J*=8.2, 2H, Ar–H),7.54–7.56 (d,*J*=8.4, 2H, Ar–H), 7.61–7.63 (d,*J*=8.2, 2H, Ar–H), 8.06 (s, 2H, NH_2).^{13}C NMR (100 MHz,DMSO-d_6): δ (ppm) 33.3, 55.5, 86.3, 93.6, 114.2, 114.9, 115.6, 129.3, 129.6, 130.8, 131.1, 133.2, 135.7, 157.6, 158.9, 159.9, 169.8; MS (EI, 70 eV): m/z 406 (M^+), Anal. Calcd for $C_{21}H_{15}ClN_4OS$: C, 61.99; H, 3.72; N, 13.77%. Found: C, 61.83; H, 3.80; N, 13.86%.

2-Amino-4-(4-nitrophenyl)-6-(*p*-tolylthio)pyridine-3,5-dicarbonitrile(5e). Yellow solid, mp 301–303°C; FT-IR (KBr): (ν_{max}/cm^{-1}): 3472,3332, 3218, 2215, 1626, 1541, 1509, 1344, 1262,^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.40 (s, 3H, CH_3), 5.50 (s, 2H,NH_2), 7.26–7.28 (d,J= 7.6, 2H , Ar-H), 7.43–7.45 (d,J=7.8, 2H, Ar-H), 7.66–7.68 (d, J = 7.6, 2H , Ar-H),8.39–8.41 (d, J= 7.8, 2H , Ar-H);^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 18.9, 86.8, 96.2, 115.1, 116.9, 125.3, 131.3,132.9, 134.1, 134.9, 135.5, 136.2, 137.3, 156.1, 158.2,165.1. MS (EI, 70 eV): m/z 387 (M^+), Anal. Calcd for $C_{20}H_{13}N_5O_2S$: C, 62.01; H, 3.38; N, 18.08%. Found: C, 61.83; H, 3.26; N, 18.15%.

2-Amino-4-phenyl-6-(*p*-tolylthio)pyridine-3,5-dicarbonitrile (5f). Yellow solid,mp 248–250 °C; FT-IR (KBr): (ν_{max}/cm^{-1}): 3446, 3314, 2219, 1627, 1522;^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.34 (s, 3H, CH_3), 7.27 (d, J= 7.9, 2H, Ar-H), 7.45 (d, 2H,J= 7.9,Ar-H), 7.49 (m,5H, Ar-H), 7.80 (s, 2H, NH_2);^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 21.4, 87.2, 95.7, 114.8, 115.2, 123.5, 128.4, 129.9, 130.1, 130.9, 133.2, 135.6, 140.3, 158.3, 159.3, 169.5, MS (EI, 70 eV): *m/z* 342 (M^+), HR MS calc. for $C_{20}H_{14}N_4S$: 342.0939; found: 342.0949; Anal. Calcd for $C_{20}H_{14}N_4S$: C, 70.15; H, 4.12; N, 16.36%. Found: C, 70.09; H, 4.21; N, 16.31%.

2-amino-6-(phenylthio)-4-*m*-tolylpyridine-3,5-dicarbonitrile (5g). Colorless solid; mp 278-280 °C,IR (KBr) (ν_{max}/cm^{-1}): 3420, 3339, 3219, 2214, 1621; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) δ 2.44 (s, 3H), 7.32-7.74 (m, 6H), 7.45-7.55 (m, 3H)7.63 (s, 2H, NH_2), ^{13}C NMR (100 MHz,DMSO-d_6): δ (ppm) 15.1, 87.6, 94.1, 115.9, 116.0, 126.0, 128.1, 129.7, 130.1, 130.3, 130.5,131.3, 132.2, 133.5, 135.6, 142.7, 158.6, 160.6. MS (EI, 70 eV): *m/z* 342 (M^+), Anal. Calcd for $C_{20}H_{14}N_4S$: C, 70.15; H, 4.12; N, 16.36 %.Found: C, 70.18; H, 4.15; N 16.32 %.

2-Amino-6-phenylsulfanyl-4-*p*-tolyl-pyridine-3,5-dicarbonitrile (5h)Colourless solid, mp 206-207°C, IR (KBr) (ν_{max}/cm^{-1}): 3441, 3339, 3216, 2214, 1627,1544, 1522, 1265;^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.52 (s, 3H), 7.33-7.75 (m, 6H), 7.46-7.55 (m, 3H),7.63 (s, 2H, NH_2),^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm)14.9, 87.6, 94.1, 115.9, 116.0, 126.0, 126.2, 128.1, 129.7, 130.1, 130.3, 130.5, 135.6, 142.7, 158.6, 160.6. MS (EI, 70 eV): *m/z* 342 (M^+), Anal. Calcd for $C_{20}H_{14}N_4S$: C, 70.15; H, 4.12; N, 16.36 %. Found: C, 70.17; H, 4.18; H, 16.39 %.

2-Amino-4-(4-chlorophenyl)-6-phenylsulfanylpyridine-3,5-dicarbonitrile (5i) Colourless solid,mp221-222°C, IR (KBr) (ν_{max}/cm^{-1}): 3487, 3344, 3222, 2926,2214, 1633, 1545;^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.45–7.50 (m, 3H, Ar-H), 7.57 (d, 2H,*J*=8.0Hz, Ar-H), 7.59 (d, 2H, *J*=8.0Hz, Ar-H), 7.64 (d, 2H, J=8.0Hz, Ar-H) 7.83 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 87.5, 93.7, 115.2, 115.5, 127.3, 129.2, 129.5, 129.8, 130.8, 133.1, 135.2, 135.7, 157.8, 159.9, 166.6. MS (EI, 70 eV): *m/z* 362 (M^+), HRMS m/z (ESI) calcd for $C_{19}H_{12}N_4SCl$ $(M+H)^+$ 363.0471, found 363.0481. Anal. Calcd for $C_{19}H_{11}ClN_4S$: C, 62.89; H, 3.06; N, 15.44%.Found: C, 62.85; H, 3.11; N 15.48 %.

2-Amino-4-(4-hydroxy-phenyl)-6-phenylsulfanyl-pyridine-3,5-dicarbonitrile (5j) Colourless solid, mp 315-317°C, IR (KBr) (ν_{max}/cm^{-1}): 3648, 3498, 3367, 3237, 2222, 2217, 1632;^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) δ 6.94 (d, *J*= 8.5 Hz, 2H), 7.39 (d, *J*= 8.5 Hz, 2H), 7.52 (m, 3H), 7.60 (m, 2H), 7.69 (s, 2H),

10.05 (bs, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 93.7, 96.9, 115.6, 115.9, 116.0, 124.5, 127.5, 129.8, 130.1, 130.7, 135.2, 159.1, 159.8, 160.3, 166.5; MS (EI, 70 eV): m/z 344 (M^+), Anal. Calcd for $C_{19}H_{12}N_4OS$: C, 66.26; H, 3.51; N, 16.27%.Found: C, 66.10; H, 3.62; N, 16.22 %.

2-Amino-4-(4-nitro-phenyl)-6-phenylsulfanyl-pyridine-3,5-dicarbonitrile(5k) Colourless solid, mp 289-290 °C, IR (KBr) (v_{max}/cm^{-1}): 3407, 3328, 3235, 2228, 2214, 1645, 1555;^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm)7.47-7.49 (m, 3H), 7.56-7.59 (m, 2H), 7.85 (d, *J*= 8.5 Hz, 2H), 7.91 (s, 2H, NH_2), 8.39 (d, *J*= 8.5 Hz, 2H);^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm)87.2, 93.3, 114.9, 115.3, 124.2, 127.2, 129.8, 130.1, 130.5, 135.1, 140.5,148.9, 157.0, 159.8, 166.5; MS (EI, 70 eV): *m/z* 373 (M^+), Anal. Calcd for $C_{19}H_{11}N_5O_2S$: C, 61.12; H, 2.97; N, 18.76%Found: C, 61.05; H, 2.78; N, 18.91%.

2-Amino-4-(4-bromophenyl)-6-phenylsulphanylpyridine-3,5-dicarbonitrile (5l) Colourless solid, mp 255-257 °C;IR (KBr) (v_{max}/cm^{-1}): 3442, 3338, 3222, 2219, 1629,1555, 1531, 1459;^{1}HNMR (400 MHz, DMSO-d_6): δ (ppm) 7.54–7.62 (m, 5H), 7.80–7.82(m, 4H), 7.87 (s, 2H, NH_2);^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 85.6, 92.1, 113.5, 113.4, 120.6, 125.9, 127.1, 128.0, , 129.5, 131.9, 133.5, 134.3, 158.3, 159.8, 166.5; MS (EI, 70 eV): m/z 405 (M^+), HRMS calc. For $C_{19}H_{11}BrN_4S$: 405.9888, found: 405.9885. Anal. Calcd for $C_{19}H_{11}BrN_4S$: C, 56.03; H, 2.72; N, 13.76%.Found: C, 56.08; H, 2.78; N 13.68%.

2,4-Diamino-5-phenylsulfanyl-5H-chromeno [2,3-b] pyridine-3-carbonitrile (6a). Yellow solid, mp 220-222°C,IR (KBr) (v_{max}/cm^{-1}): 3355, 3429, 2203, 1400-1623; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.73 (s, 1H), 6.50 (2H, s), 6.74-6.78 (3H, m), 6.94 (s, 2H), 7.05-7.11 (3H, m), 7.15-7.30 (m, 3H);^{13}C NMR (100MHz, DMSO-d_6): δ (ppm)43.12, 70.8, 86.90, 116.01, 116.5, 121.5, 123.9, 128.60, 128.64, 129.50, 129.70, 134.2, 137.7, 150.90, 156.40, 159.7, 160.90. MS (EI, 70 eV): *m/z* 346 (M^+), HRMS m/z (ESI) calcd for $C_{19}H_{15}N_4OS$ $(M+H)^+$ 347.0966, found 347.0958. Anal. Calcd. For $C_{19}H_{14}N_4OS$: C, 65.88; H, 4.074; N, 16.17;Found C, 65. 82; H, 4.09; N, 16.07%.

2,4-Diamino-5-(4-methylphenylsulfanyl)-5H-chromeno[2,3-b]pyridine-3-carbonitrile(6b). Yellow solid, mp 223–225 °C;IR (KBr) (v_{max}/cm^{-1}): 3457, 3349, 2198, 1400-1623. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.19 (s, 3H), 5.66 (s, 1H), 6.46 (br s, 2H), 6.61 (d, J=7.9Hz, 2H), 6.79 (d, J=7.9Hz, 1H), 6.90 (m, 4H), 7.11; (d,J=6.8Hz, 1H), 7.19 (d,J=7.3Hz, 2H).^{13}C NMR (100MHz, DMSO-d_6): δ (ppm) 21.2, 43.11, 70.8, 86.3, 115.7, 116.4, 121.8, 123.6, 127.0, 128.2, 128.6, 129.8, 136.9, 138.3, 151.33, 156.3, 160.08, 160.25 MS (EI, 70 eV): *m/z* 360 (M^+), HR MS ESI $[M+H]^+$calcd. for $C_{20}H_{17}N_4OS$ 361.1123; found 361.1132. Anal. Calcd. For$C_{20}H_{16}N_4OS$: C, 66.64; H, 4.47; N, 15.54; Found C, 66.59; H, 4.51; N, 15.48%

2,4-Diamino-5 (benzylthio)-5H-chromeno[2,3-b]pyridine-3-carbonitrile (6c). Yellow solid**,** mp175–177 °C;IR (KBr) (v_{max}/cm^{-1}): 3377, 3439, 2200, 1400, 1605; ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.49 (ABq, 2H, J=12Hz), 5.48 (1H), 6.55 (bs, 2H), 6.83 (bs, 2H), 7.03–7.21 (m, 7H), 7.33 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d6): δ (ppm) 35.02, 44.01, 70.90, 87.01, 117.6, 118.3, 119.3, 122.8, 124.2, 124.3, 129.6, 133.2, 133.3, 136.6, 143.7, 152.9, 159.9, 160.2. MS (EI, 70 eV): m/z 360 (M^+), HRMS m/z (ESI) calcd for $C_{20}H_{17}N_4OS$ $(M+H)^+$ 361.1123, found 361.1129. Anal. CalcdFor $C_{20}H_{16}N_4OS$: C, 66.64; H, 4.47; N, 15.54;Found C, 66. 48; H, 4.58; N,15.39%.

5- ((furan-2-yl) methylthio) -2,4-diamino - 5H-chromeno [2,3-b] pyridine-3-carbonitrile(6d). Yellow solid, mp 200–201°C;IR (KBr) (v_{max}/cm^{-1}): 3386, 3440, 2203, 1397, 1612;^{1}H NMR (400 MHz, DMSO-d_6): δ 3.51 (ABq, 2H, *J*=12Hz), 5.46 (1H), 5.99 (1H), 6.23 (s, 1H), 6.55 (bs, 2H), 6.79 (bs, 2H), 7.10(d, 1H, *J*=8Hz), 7.17 (t, 1H, *J*=8Hz), 7.24(s, 1H), 7.31(t, 2H, *J*= 8Hz); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 25.9, 36.03, 71.0, 87.9, 107.8, 111.0, 116.5, 116.9, 129.0, 129.7, 133.8, 142.7, 149.4, 151.2, 157.1, 160.03, 160.10. MS (EI, 70 eV): m/z 350 (M^+), HRMS m/z (ESI) calcd for $C_{18}H_{15}N_4O_2S$ $(M+H)^+$ 351.0915, found 351.0913. Anal. Calcd For $C_{18}H_{14}N_4O_2S$: C, 61.70; H, 4.03; N, 15.99 Found C, 61.62; H, 4.10; N, 15.91%.

2,4-Diamino-5-(benzylthio)-7-bromo-5H-chromeno[2,3-b] pyridine-3-carbonitrile(6e). Yellow solid.mp 206–208°C, IR (KBr) (v_{max}/cm^{-1}): 3315, 3441, 2189, 1403, 1653;^{1}H NMR (400 MHz, DMSO-d_6) δ 4.06–4.45 (AB q, 2H, J=12Hz), 4.67 (1H), 6.48 (s, 1H), 6.88–6.90 (m, 5H), 7.37 (m,6H); ^{13}C NMR (100 MHz, DMSO-d_6)δ (ppm) 33.34, 35.78, 71.21 87.22, 116.46, 118.79, 120.90, 121.60, 124.41, 128.60, 129.79, 131.05, 137.53, 137.96, 148.22, 152.75, 160.44, 160.80. MS (EI, 70 eV): m/z 439 (M^+), Anal. Calcd For $C_{20}H_{15}N_4OSBr$: C, 54.68; H, 3.44; N, 12.75;Found C, 54.55; H, 3.52; N, 12.61%.

5-((furan-2-yl)methylthio)-2,4-diamino-7-bromo-5H- chromeno[2,3-b] pyridine-3-carbonitrile (6f). Yellow solid.mp 225–227 °C, IR (KBr)(v_{max}/cm^{-1}): 3311, 3442, 2194, 1404, 1655;^{1}H NMR (400 MHz, DMSO-d_6) δ 4.14–4.56 (ABq, 2H, J=12Hz), 4.89 (1H), 6.34 (s, 1H), 6.46 (d, J= 8.3Hz,1H), 6.78-6.95 (m, 6H), 7.39 (d, 1H, J=9Hz), 7.62 (d, 1H); ^{13}C NMR (100 MHz, DMSO-d_6)δ (ppm) 28.64, 36.31, 54.27, 84.86, 108.77, 111.49, 116.50, 118.87, 119.41, 124.14, 125.50, 131.12, 131.89, 143.26, 148.21, 150.72, 155.24, 160.5.MS (EI, 70 eV): m/z 427, 429 (M^+), Anal. Calcd For $C_{18}H_{13}N_4O_2SBr$: C, 50.39; H, 3.05; N, 13.06;Found C, 50.35; H, 2.97; N, 13.01%.

4. Conclusions

In conclusion, we have developed a flexible, green and highly efficient protocol for the synthesis of chromeno [2,3-b] pyridines and 2-amino-3,5-dicyano-6-sulfanyl pyridines using SnO nanoparticles under reflux conditions in ethanol. These heterocyclic compounds will provide promising candidates for chemical biology and drug discovery. The advantages offered by this method include, easy workup, the employment of a cost-effective catalyst, short reaction times, excellent yields and the use of ethanol as a solvent that is considered to be relatively environmentally benign.

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Table1. Optimization for the synthesis 6-sulfanyl pyridines[a](5) and chromenopyridines[b](6) by various catalysts in ethanol under reflux conditions

Entry	catalyst	(mol%)	Yields 5a/6a (%)[c]
1	-------	------	20/17
2	MgO	15	55/44
3	CuCl	10	42/32
4	CuO	10	40/22
5	$InCl_3$	5	24/27
6	ZrO_2	10	49/33
7	CaO	5	54/38
8	$CuSO_4$	10	30/18
9	$SnCl_2$	10	40/35
10	SnO NPs	3	82/79
11	**SnO NPs**	**6**	**92/88**
12	SnO NPs	9	92/89

[a]1 mmol of 4-nitrobenzaldehyde, 2.2 mmol of malononitrile and 1 mmol of thiophenol
[b] Salicyladehyde (1.5 mmol), malononitrile (3 mmol) and benzenethiol (1.5 mmol)
[c] Isolated yields

Table 2. Synthesis of 6-sulfanyl pyridines [a] (5) and chromenopyridines [b] (6) using different solvents with SnO NPs (6 mol%)

Entry	Solvent	Dielectric constant	Time5a/6a (min)	Yields 5a/6a (%)[c]
1	H_2O (80 °C)	≈80	200/140	55/42
2	CH_3CN (reflux)	37.5	150/100	70/64
3	DMF (reflux)	38	160/110	65/60
4	$CHCl_3$ (reflux)	4.81	260/180	31/38
5	EtOH (45 °C)	≈24.5	130/98	69/60
6	**EtOH (reflux)**	**24.5**	**99/54**	**92/88**

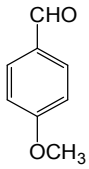
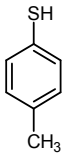
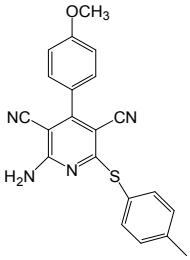
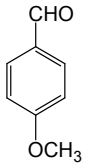
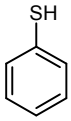
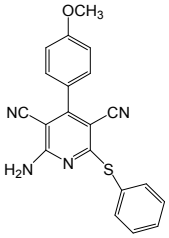
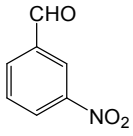
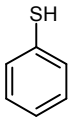
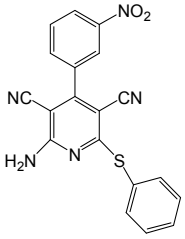
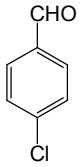
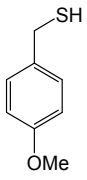
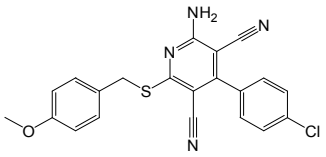
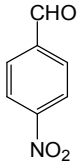
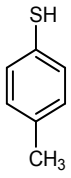
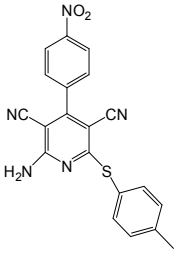
[a] 1mmol of 4-nitrobenzaldehyde, 2.2 mmol of malononitrile and 1 mmol of thiophenol
[b] Salicyladehyde (1.5 mmol), malononitrile (3 mmol) and benzenethiol (1.5 mmol)
[c] Isolated yields

Table 3. Effect of different size of the catalyst for the synthesis 6-sulfanyl pyridines[a] (5) andchromenopyridines[b]

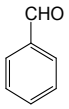
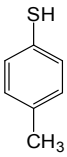
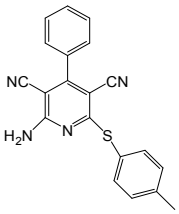
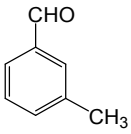
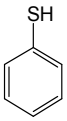
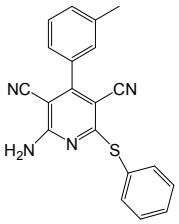
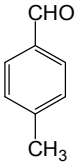
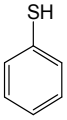
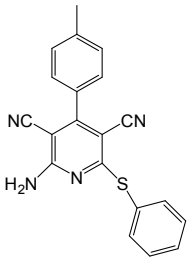
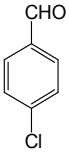
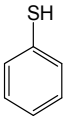
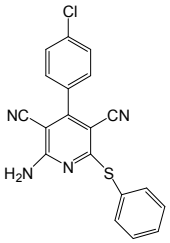
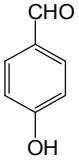
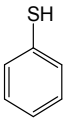
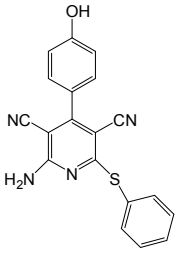
Entry	Catalyst	surface area	Time 5a/6a (min)	Yield 5a/6a (%)[c]
1	SnO bulk	0.93 m^2/g	190/120	63/56
2	**SnO 28 nm**	**35 m^2/g**	**99/54**	**92/88**
3	SnO 40 nm	29.9 m^2/g	106/65	89/85
4	SnO 82 nm	16.2 m^2/g	116/73	83/81

[a]1mmol of 4-nitrobenzaldehyde, 2.2 mmol of malononitrile and 1 mmol of thiophenol
[b]salicyladehyde (1.5 mmol), malononitrile (3 mmol) and benzenethiol (1.5 mmol)
[c] Isolated yields

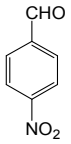
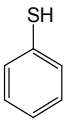
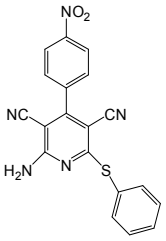
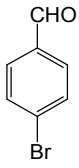
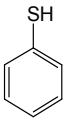
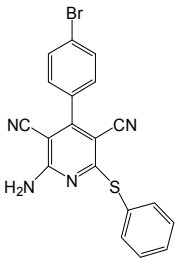
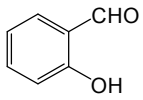
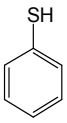
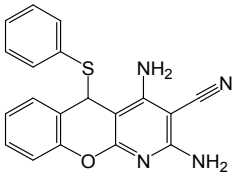
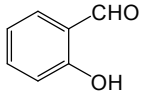
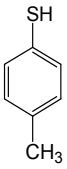
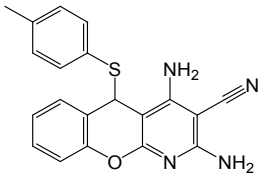
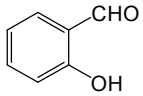
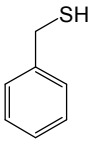
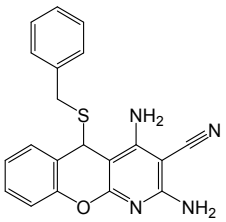
Table 4. Synthesis of 2-amino-3,5-dicyano-6-sulfanyl pyridinesandchromeno [2,3-b] pyridines using SnO nanoparticles.

Entry	Aldehyde	Thiols	Product of 5a-l and 6a-f	Time(min)	Yield (%)[a]	M.P °C.[ref]
1				110	84	229-231[26]
2				125	83	240-242[26]
3				132	79	218-220[26]
4				141	80	237-239[26]
5				99	92	301-303[26]

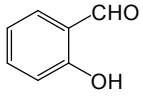
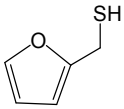
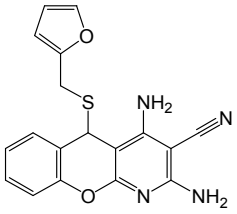
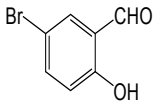
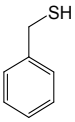
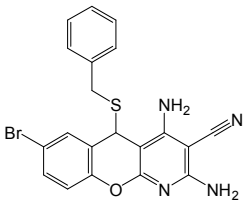
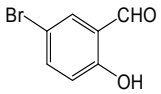
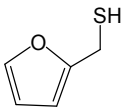
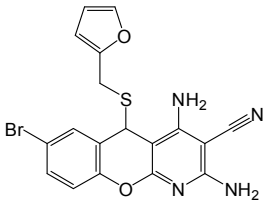
(Continued)

Entry	Aldehyde	Thiols	Product of 5a-l and 6a-f	Time(min)	Yield (%)[a]	M.P.°C[ref]
6				103	89	248-250[26]
7				115	81	278-280[36]
8				112	85	206-207[37]
9				100	89	221-222[37]
10				142	79	315-317[37]

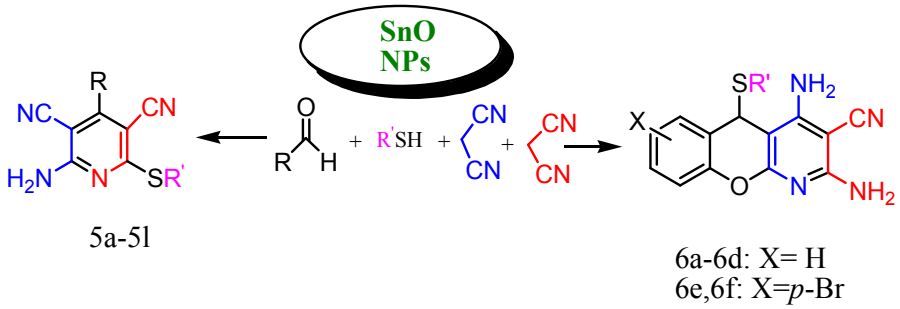
(Continued)

Entry	Aldehyde	Thiols	Product of 5a-l and 6a-f	Time(min)	Yield (%)[a]	M.P.°C [ref]
11				98	92	289-290[37]
12				104	85	255-257[36]
13				54	88	220-222[34]
14				57	85	223-225[34]
15				62	80	173-175

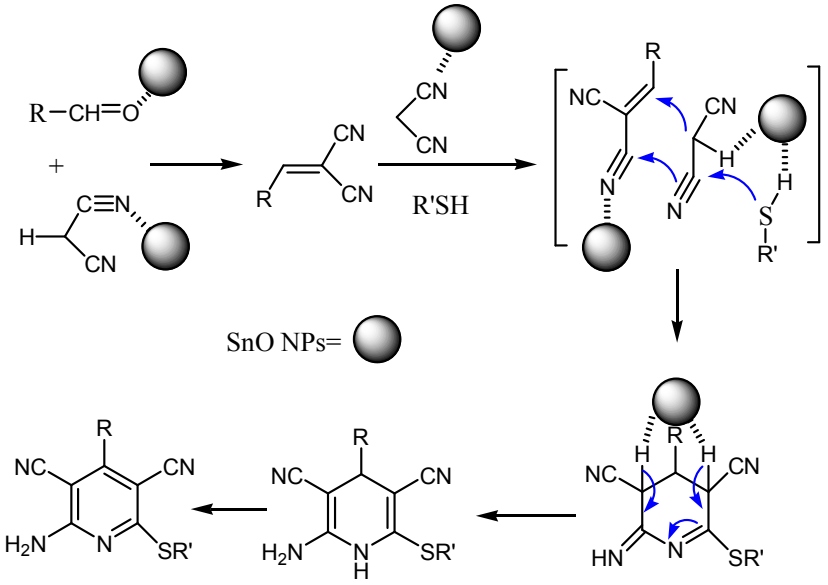
(Continued)

Entry	Aldehyde	Thiols	Product of 5a-l and 6a-f	Time(min)	Yield (%)[a]	M.P.[ref]
16				63	81	200-202
17				56	83	206-208[27]
18				57	85	225-227[27]

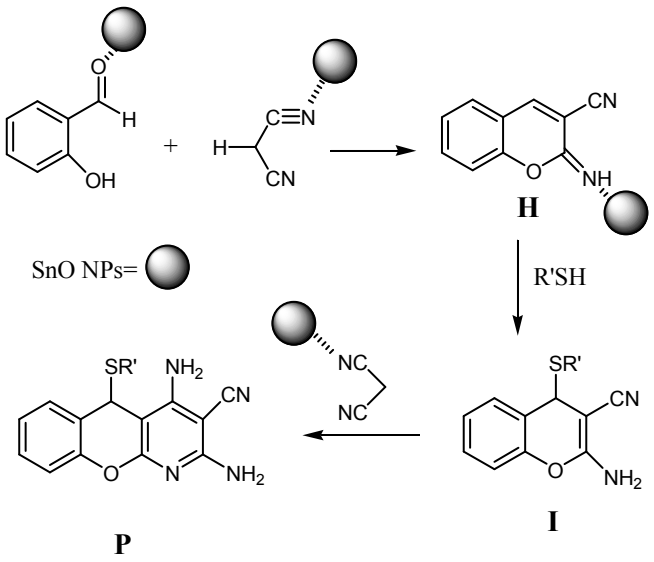
[a]Isolated yields



Scheme 1. Synthesis of chromeno [2,3-b] pyridines and 2-amino-3,5-dicyano-6-sulfanyl pyridines using SnO nanoparticles.



Scheme 2. Possible mechanism of the one-pot reactionforthe preparation of2-amino-3,5-dicyano-6-sulfanyl pyridines.



Scheme 3. Proposed reaction pathway for the synthesis of chromeno [2,3-b] pyridines

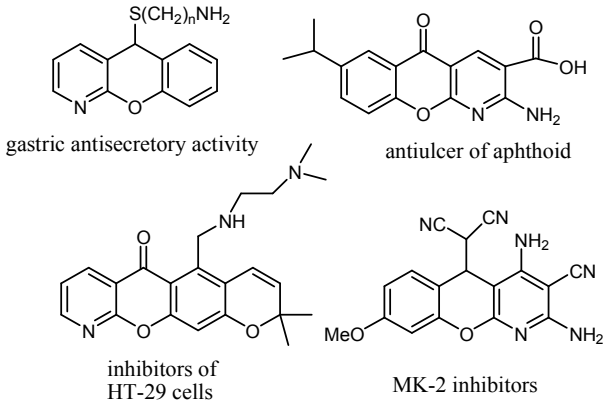


Fig. 1. Biologically important chromenopyridines

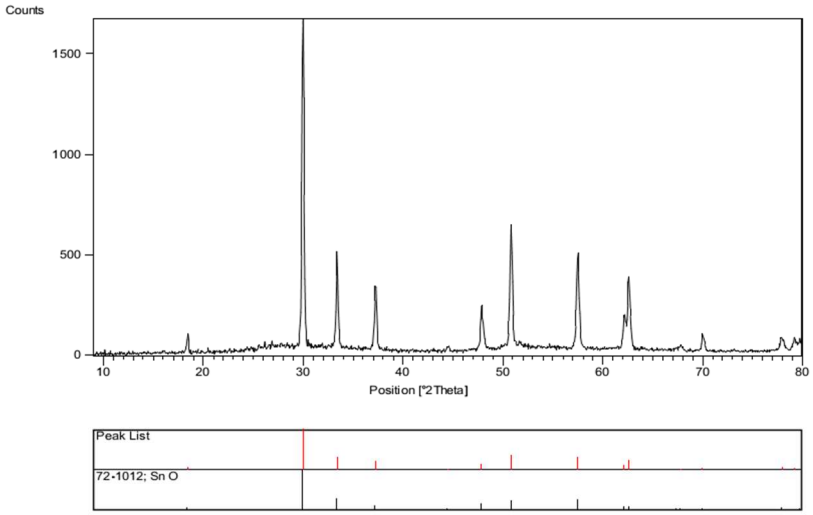


Fig.2. XRD pattern of the SnO nanoparticles

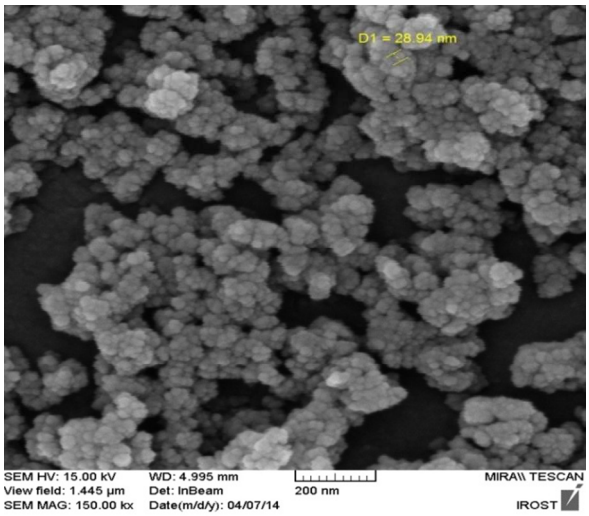


Fig.3. SEM image of the SnO nanoparticles

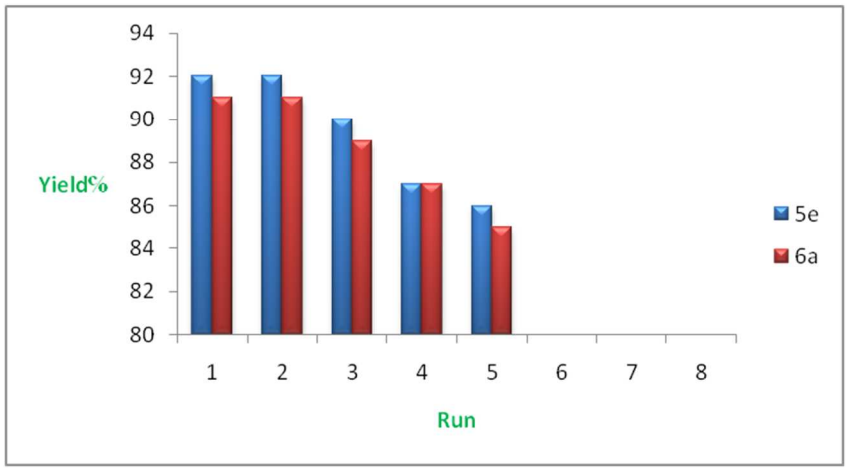
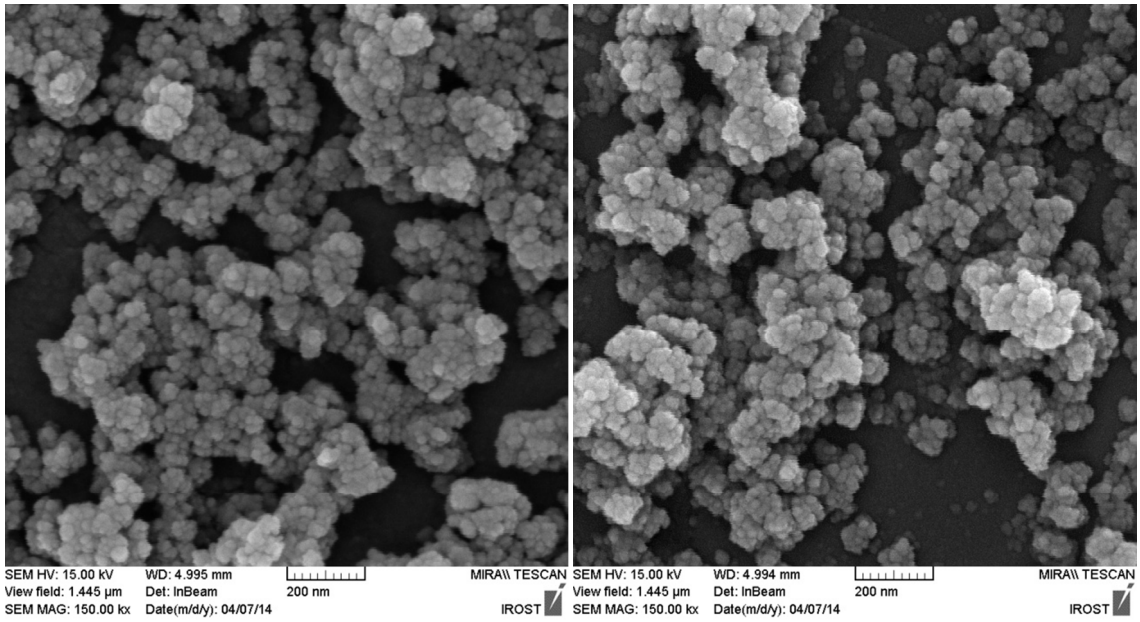


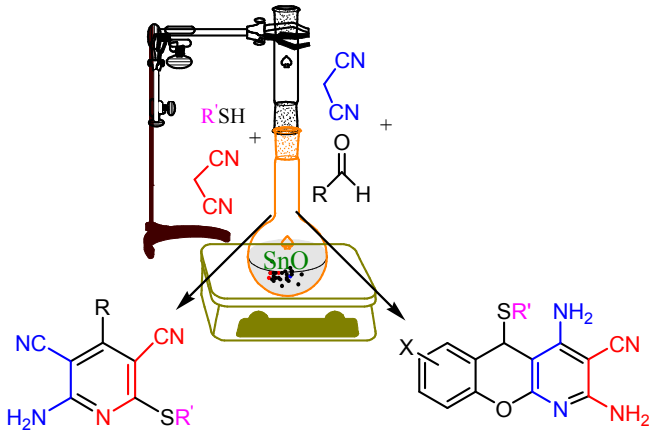
Fig 4. Reusability of SnO nanoparticles catalyst for the preparation of 5e and 6a



a. Before use b. After reuse of five time

Fig 5. SEM of SnO nanoparticles

Graphical abstract



R= Ar R= *o*-OH-Ar

A flexible and highly efficient protocol for the synthesis of chromenopyridines and sulfanyl pyridines using nanoSnOhas been developed.