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*Research Article*

# NiO Nanoparticles: An Efficient Catalyst for the Multicomponent One-Pot Synthesis of Novel Spiro and Condensed Indole Derivatives

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An efficient catalytic protocol for the synthesis of novel spiro[indoline-3,4′-pyrano[2,3-c]thiazole]carbonitriles and condensed thiazolo[5′′,4′′:5′,6′]pyrano[4′,3′:3,4]furo[2,3-b]indole derivatives is developed in a one-pot three-component approach involving substituted 1H-indole-2,3-diones, activated methylene reagent, and 2-thioxo-4-thiazolidinone under conventional heating and microwave irradiation. This paper describes the use of NiO nanoparticles as catalyst for the synthesis of novel spiro and condensed indole derivatives by Knoevenagel condensation followed by Michael addition. The advantageous features of this methodology are operational simplicity, high yield processing, and easy handling. The particle size of NiO nanoparticle was determined by XRD. After reaction course, NiO nanoparticles can be recycled and reused without any apparent loss of activity.

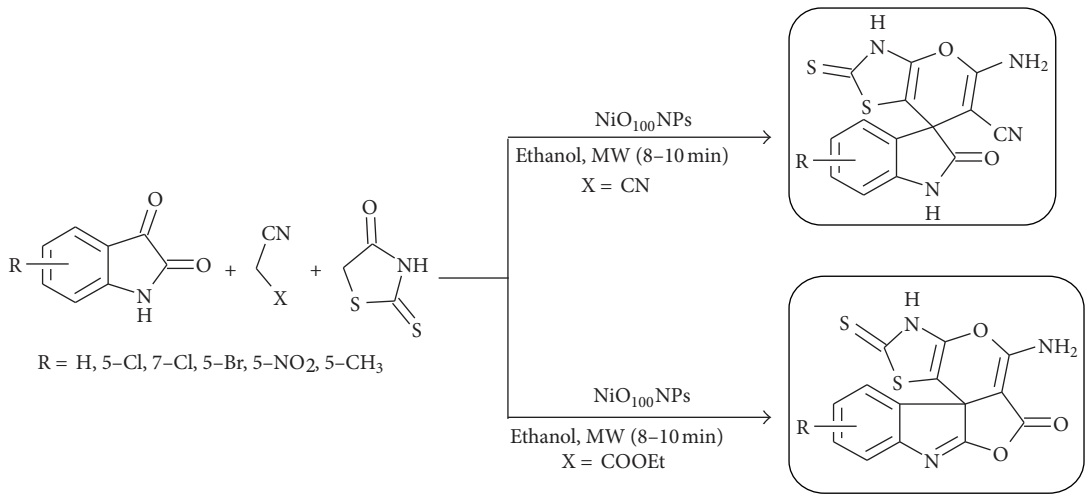
## 1. Introduction

Catalysis lies at the heart of countless chemical protocols. The presence of a catalyst is mainly required by both modern organic synthesis and fine chemical industries. Nowadays, it plays a key role in the production of chemicals and materials as catalytic reactions occur under milder conditions compared to noncatalytic reactions [1–3]. Intensive studies have been recently focused on the development of catalytic systems owing to their importance in synthetic organic chemistry. One of the most attractive synthetic strategies favoured by organic chemists is the use of heterogeneous catalyst in increasing the efficiency of a wide range organic synthesis [4].

In recent times, transition metal nanoparticles are attracting a great deal of attention in almost any scientific and technological field, including catalysis [5, 6]. Several reports [7–9] showed an amazing level of their performance as catalysts in terms of selectivity, reactivity, and improved yields of products. In addition, the high surface-to-volume ratio of nanoparticles provides a larger number of active sites per unit area compared to their heterogeneous counterparts. Thus, there has been a considerable increase in the interest in nanoparticles catalysis because of their high efficiency under environmentally benign reaction conditions [10–12]. Metal oxides represent a broad class of materials that have been researched extensively due to their interesting magnetic, electronic, and catalytic properties [13–16].

One possibility to extend the application of metal oxides as catalysts is to tailor their sizes in nanodimensions and hence their surface chemistry and catalytic properties. Recently, NiO nanoparticles have been employed as heterogeneous catalysts for various organic transformations [17]. An increasing number of examples are available in the literature where Nickel-based nanoparticles have been used as catalysts during organic transformations [18, 19]. Since these nanoparticles are often recovered easily by simple workup, which prevent contamination of products, they may be considered as promising, safe, and reusable catalysts compared to traditional catalysts.

Indole and its derivatives are known as an important class of heterocyclic compounds in the pharmaceutical industry as well as in synthetic chemistry [20–23]. On the other hand, the spirooxindole unit is privileged heterocyclic motif that forms




Scheme 1: Synthesis of spiro and condensed indole derivatives.

the core of a large family of alkaloid and natural products with strong bioactivity profiles and significant structural properties [24–31].

Among nitrogen-containing heterocyclic compounds, thiazoles are of immense interest to medicinal and industrial chemists due to their diverse biological activities such as antiglutamate, antiparkinson [32], antimicrobial [33], anthelmintic, anti-inflammatory [34], antihyperlipidemic, antihypertension and antioxidant properties as well as inhibition of enzymes such as acetylcholine esterase [35], aldose reductase [36], lipoxygenase [37], ATPase [38], and HCV helicase [39]. In general, heterocyclic systems encompassing pyran unit have found application as pharmaceuticals, agrochemicals, and veterinary products [40]. Further, pyrano thiazoles [41–46] also possess wide range of bioactivity. It has been observed that the incorporation of more than one bioactive heterocyclic moiety into a single framework may result into the production of novel heterocycles with enhanced bioactivity. There are only few reports [47–49] available in the literature on the synthesis of pyranothiazoles but literature survey reveals no report on the synthesis of title novel nucleus so far.

Keeping in view of diverse biological activities associated with spiroindoles and pyrano thiazoles, it was thought to construct a novel system which may combine these bioactive rings together in a single molecular framework to see the additive effects towards their biological activities. Earlier [50, 51], we studied the reaction of 1H-indol-2,3-diones and malononitrile with 1-phenyl-2-thiohydantoin and 2-pyrrolidone under conventional heating and microwave irradiation but the reaction of 1H-indol-2,3-diones and malononitrile/ethyl cyanoacetate with 2-thioxo-4-thiazolidinone has not been studied so far. Hence, as a part of our ongoing program to develop efficient and robust methods for the preparation of biologically relevant compounds [52–57], we have developed a facile and efficient catalytic approach for the multicomponent one-pot synthesis of novel spiro[indoline-pyranothiazole]carbonitriles (Scheme 1). The overall process involves the Knoevenagel condensation of 2-thioxo-4-thiazolidinone with 1H-indole-2,3-dione followed by "in situ" Michael addition of malononitrile in single operation.

In yet another attempt, we explored the reaction of 1H-indole-2,3-dione and 2-thioxo-4-thiazolidinone with ethyl-cyanoacetate in absolute ethanol in the presence of NiO nanoparticles under microwave irradiation. The reaction surprisingly lead to the exclusive synthesis of 11-amino-2-thioxo-10-oxo-thiazolo[5″,4″:5′,6′]pyrano[4′,3′:3,4]furo[2,3-b]indole instead of the expected spiro compound in contrast to the earlier reports [58, 59] of the formation of spiroindoles in the reaction of 3-carboethoxycyanomethylene-2H-indol-2-ones with cyclic ketones under classical conditions but similar [60] to the results reported by us in the reaction of 3-carboethoxycyanomethylene-2H-indol-2-ones with 1-phenyl-2-thiohydantoin leading to the synthesis of condensed indole derivatives. The formation of condensed product was assumed to involve the cycloaddition of less acidic indole-OH on the ester group of the intermediate spiro compound to form final isolated product (Scheme 2).

To the best of our knowledge, there is no report available in the literature describing the use of NiO nanoparticles as catalysts for the synthesis of spiro and condensed indole derivatives (Table 1). Here, we have used a combination of microwave conditions and NiO nanocatalyst to standardize the right conditions for the above reaction. The effectiveness of the process was studied by comparing the results obtained with and without catalyst under normal conditions (Table 2). Nanoparticle is considered to be more reacting because it offers higher surface area and low coordinating sites. The surface area of the catalyst increases tremendously when size decreases to nanolevels which are responsible for the higher catalytic activity and hence enhanced yields (Table 3).

Table 1: Synthesis of Spiro and condensed indole derivatives under microwave irradiation using $Ni_{100}$ nanoparticles.

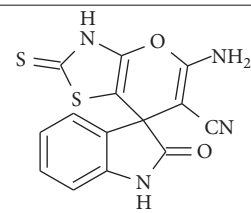
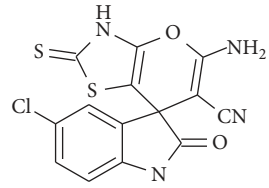
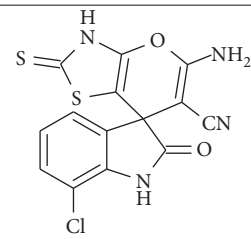
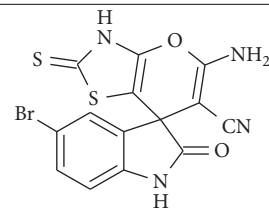
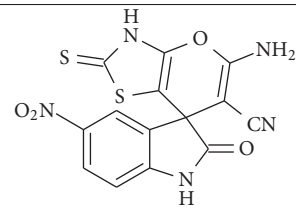
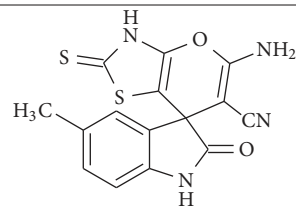
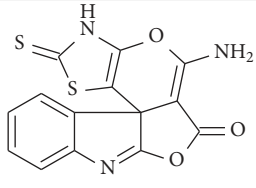
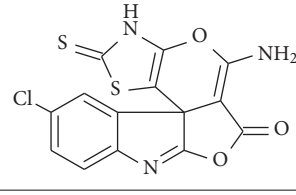
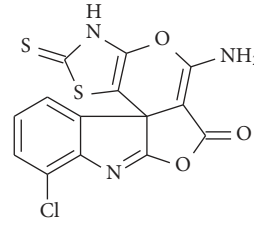
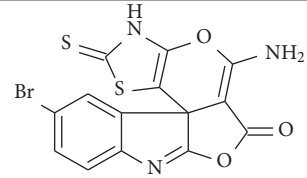
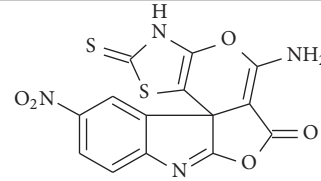
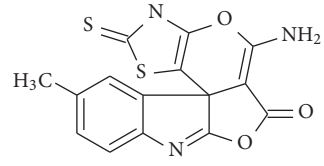
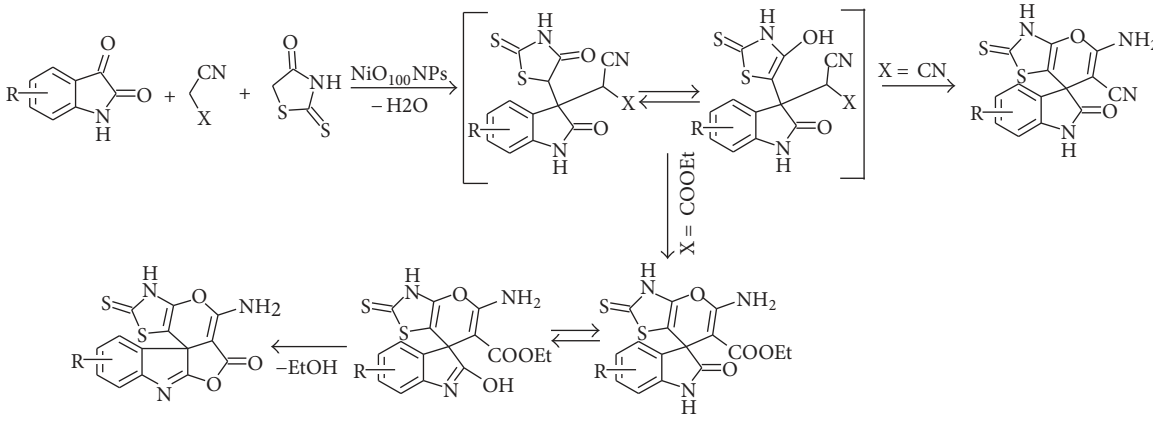
| Entry | R | X | Time (min.) | Product | Yield (%) $NiO_{100}$/Piperidine | MP (°C) |
|---|---|---|---|---|---|---|
| 5a | H | CN | 8 |  | 90/75 | 298 |
| 5b | 5-Cl | CN | 8 |  | 87/72 | 310 |
| 5c | 7-Cl | CN | 9 |  | 87/74 | 275 |
| 5d | 5-Br | CN | 8 |  | 88/72 | 270 |
| 5e | 5-$NO_2$ | CN | 10 |  | 90/72 | 340 |
| 5f | 5-$CH_3$ | CN | 8 |  | 88/70 | 315 |
| 5g | H | COOEt | 8 |  | 89/74 | 332 |
| 5h | 5-Cl | COOEt | 9 |  | 87/73 | 288 |

Table 1: Continued.

| Entry | R | X | Time (min.) | Product | Yield (%) $NiO_{100}$/Piperidine | MP (°C) |
|---|---|---|---|---|---|---|
| 5i | 7-Cl | COOEt | 10 |  | 88/73 | 226 |
| 5j | 5-Br | COOEt | 9 |  | 88/72 | 347 |
| 5k | 5-$NO_2$ | COOEt | 9 |  | 84/74 | 265 |
| 5l | 5-$CH_3$ | COOEt | 10 |  | 87/71 | 356 |

$NiO_{100}$ is the nanoparticle calcined at 100°C.



Scheme 2: Plausible Mechanism for the reaction of 1H-indole-2,3-dione and malononitrile with 2-thioxo-4-thiazolidinone.

## 2. Results and Discussion

As a part of our ongoing interest aimed at developing new synthetic strategies for heterocyclic framework, the reaction of 1H-indole-2,3-dione, malononitrile/ethylcyanoacetate, and 2-thioxo-4-thiazolidinone was examined in the presence of catalytic amount (20 mg) of NiO nanoparticle under microwave irradiation to give novel spiro[indoline-3,4′-pyrano[2,3-c]thiazole] carbonitrile and condensed thiazolo[5′′, 4′′:5′,6′]pyrano[4′,3′:3,4]furo[2,3-b]indole derivatives.

After some preliminary experiments, we found that a mixture of 1H-indole-2,3-dione malononitrile/ethylcyanoacetate and 2-thioxo-4-thiazolidinone in the presence of NiO nanoparticle afforded products in excellent yield (84–90%)

Table 2: Comparison of catalytic activity of $NiO_{100}$ nanoparticle with piperidine in the synthesis of compound 5a and 5g by conventional and microwave irradiation methods.

| Entry | Conditions | Type of catalysts | Reaction time (hr/min.) | Yield (%) |
|---|---|---|---|---|
| 5a | MW | No catalyst | 30 min. | 40 |
| | MW | Piperidine | 16 min. | 75 |
| | MW | $NiO_{100}$ | 8 min. | 90 |
| | Δ | No catalyst | 30 hrs | 35 |
| | Δ | Piperidine | 13 hrs | 52 |
| | Δ | $NiO_{100}$ | 8 hrs | 67 |
| 5g | MW | No catalyst | 30 min. | 32 |
| | MW | Piperidine | 16 min. | 74 |
| | MW | $NiO_{100}$ | 8 min. | 89 |
| | Δ | No catalyst | 30 hrs | 25 |
| | Δ | Piperidine | 14 hrs | 50 |
| | Δ | $NiO_{100}$ | 9 hrs | 65 |

Table 3: Comparison of catalytic activity of NiO nanoparticle calcined at 100°C ($NiO_{100}$), 200°C ($NiO_{200}$), 400°C ($NiO_{400}$) in the synthesis of the compound 5a under conventional heating and microwave irradiation methods.

| Entry | Type of catalyst | Time (hr/min.) | | Yield (%) | | Particle size (nm) |
|---|---|---|---|---|---|---|
| | | Δ | MW | Δ | MW | |
| 1 | $NiO_{100}$ | 8 hrs | 8 min. | 67 | 90 | 9.7 |
| 2 | $NiO_{200}$ | 12 hrs | 13 min. | 60 | 82 | 18 |
| 3 | $NiO_{400}$ | 16 hrs | 17 min. | 53 | 78 | — |

Table 4: Optimization of reaction conditions[a].

| Entry | Catalysts (mg) | Yield (%) |
|---|---|---|
| 1 | 10 | 83 |
| 2 | 20 | 90 |
| 3 | 30 | 90 |

[a]The reaction was carried out with 1H-indole-2,3-dione, malononitrile and 2-thioxo-4-thiazolidinone under microwave irradiation.

(Table 1) and with piperidine catalyst, the product formed with yields ranging between 72 and 75%.

In order to confirm the effective involvement of NiO nanoparticle during this transformation, we carried out the model reaction without any catalyst. In the absence of NiO nanoparticle, the reaction was incomplete even after 30 minutes of microwave irradiation though small amount of compound (40%) (Table 2) was observed. To verify the specific effect of microwaves, we also performed the experiment under conventional heating without using any catalyst. The synthesis of compound was carried out by refluxing for 30 hrs resulting in 25–35% yields while under microwave irradiation for 30 min. compound was obtained in 32–40% yields. It showed that microwave irradiation was found to have a beneficial effect on the synthesis of spiro/condensed indole derivatives (Table 2).

Encouraged by these results, we have extended this reaction to variously substituted 1H-indole-2,3-diones under similar conditions to furnish the respective spiro/condensed indole derivatives in excellent yields (84–90%) without the formation of any side products (Table 1). Compounds were also synthesized under conventional heating using piperidine/NiO nanoparticle catalyst but yield of the product was found to be low as compared to that obtained with microwave heating and it was observed that better yield was obtained in the presence of NiO nanoparticles even under conventional heating (Table 2).

To find the most effective catalyst for the synthesis of novel spiro and condensed indole derivatives under microwave irradiation, NiO nanoparticles obtained were calcined at different temperatures and their catalytic effect was studied. It was observed that particle size increased with increase in calcinations temperature from 100°C to 400°C and hence catalytic activity reduced (Table 3). When the reaction was carried out in the presence of 100°C calcined NiO nanoparticles, yield obtained was much higher (90%) as compared to that carried out in the presence of 200°C (82%) and 400°C (78%) calcined nanoparticles under microwave irradiation (Table 3). This may be due to decrease in surface area of NiO nanoparticle.

Further, we have also emphasized the amount of 100°C calcined NiO nanoparticle to be used in this condensation reaction (Table 4). Adding 30 mg of 100°C calcined NiO nanoparticle to the system under similar conditions resulted in obvious acceleration but the yield was not improved. While increasing the amount of NiO nanoparticle from 10 mg to 20 mg the reaction resulted in the formation of final compound in 83% and 90%, respectively. Thus best results were obtained when 20 mg of NiO nanoparticle was used. A higher amount of catalyst did not improve the results to an appreciable extent.

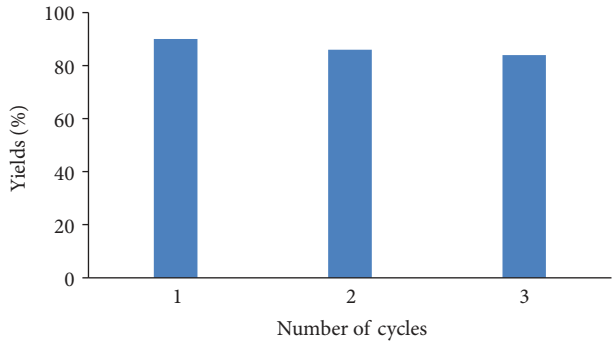



Figure 1: Recyclability of NiO nanoparticles.

Reusability (and hence recyclability) is one of the important properties of this catalyst. In this study, the catalyst was recovered by filtration from the reaction mixture and reused during three consecutive runs without any apparent loss of activity for the same reaction Figure 1.

The syntheses of the NiO nanoparticles were performed according to a literature method developed by Sun and Sirringhaus [61] with slight modification. The structure of NiO nanoparticles has been studied at room temperature by using X-ray diffraction pattern. Figure 2 shows XRD pattern of NiO nanoparticles calcined at 100°C. As reported in the literature [62], variation of ageing temperature has a profound effect on the unit cell lattice of metal oxide nanoparticles. Table 3 shows how variation of this parameter affects particle size. The particle sizes were calculated from X-ray diffraction images of NiO powders using Scherrer formula [63]:

$$D = \frac{K\lambda}{\beta \cos\theta}, \quad (1)$$

where $K$ is constant, $\lambda$ is wavelength of X-rays employed radiation, $\beta$ is full width at half max (FWHM), and $\theta$ is the diffraction angle.

A conceivable mechanism for the formation of the product would be as follows. The NiO nanoparticle facilitates the Knoevenagel-type coupling through Lewis acid sites ($Ni^{+2}$) [4] coordinated to the oxygen of carbonyl groups. On the other hand, NiO nanoparticles can activate methylene compounds so that deprotonation of the C–H bond occurs in the presence of Lewis basic sites ($O^{-2}$). As a result, the formation of spiro indole derivatives proceeds by activation of reactants through both Lewis acids and basic sites of NiO nanoparticles. The formation of condensed product was assumed to involve the cycloaddition of less acidic indole-OH on the ester group of the intermediate spiro compound to form final isolated product (Scheme 2).

## 3. Conclusion

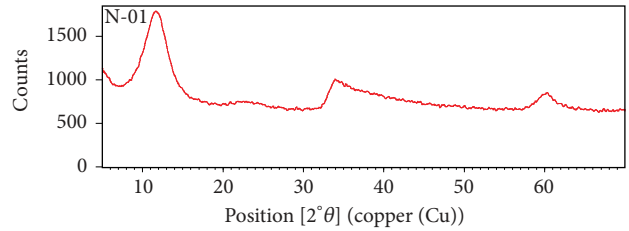
In conclusion, we have demonstrated a novel and highly efficient catalytic approach for the synthesis of structurally complex and diverse spiro and condensed indole derivatives catalyzed effectively by NiO nanoparticles involving Michael and Knoevenagel condensation. NiO nanoparticles are well characterized by XRD technique. This method offers several advantages including avoidance of harmful organic solvents, high yield, short reaction time, a simple work-up procedure, ease of separation, and recyclability of the catalyst, as well as ability to tolerate a wide variety of substitutions in the components.

## 4. Experimental Section

*4.1. General.* Reagents and solvents were obtained from commercial sources and used without further purification. Melting points were determined on a Toshniwal apparatus. The spectral analyses of synthesized compounds have been carried out at SAIF, Punjab University, Chandigarh. Purity of all compounds was checked by TLC using "G" coated glass plates and n-hexane: ethyl acetate (7 : 3) as eluent. IR spectra were recorded in KBr on a Perkin Elmer Infrared RXI FTIR spectrophotometer and $^1$HNMR spectra were recorded on Bruker Avance II 400 NMR Spectrometer using DMSO-$d_6$ and $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference standard. The obtained products were identified from their spectral ($^1$HNMR, $^{13}$C NMR, and IR) data. The microwave-assisted reactions were carried out in a Catalysts Systems Scientific Multimode MW oven attached with a magnetic stirrer and reflux condenser, operating at 700 W generating 2450 MHz frequency.

*4.2. General Procedure for the Synthesis of NiO Nanoparticles.* NiO precursors were synthesized by the sol-gel reaction and then calcined to obtain NiO nanoparticles. Firstly, nickel acetate ($Ni(Ac)_2$ 0.646 g, 2.6 mmol) and 250 $\mu$L of water were added in to a flask containing 42 mL of methanol. The solution was heated to 60°C with magnetic stirring. Potassium hydroxide (KOH, 0.485 g) was dissolved into 23 mL of methanol as the stock solution that was dropped into the flask within 10–15 min. At a constant temperature of 60°C, it took 2 hrs and 15 min. A small amount of water was found helpful to increase the NiO nanocrystal growth rate. To grow the nanorods, the solution was condensed to about 10 mL. This was found helpful before further heating to decrease the growth time of the nanorods. Then it was reheated for another 5 hrs before stopping the heating and stirring. The upper fraction of the solution was removed after 30 min. Methanol (50 mL) was added to the solution and stirred for 5 min. The upper fraction of the solution was discarded again after 30 min. This process was repeated twice. After being dried under vacuum, the precursors were calcined in oven at various temperatures (100°C, 200°C, and 400°C) for 2 hrs and then NiO nanoparticles were obtained.

*4.3. Regeneration of Catalyst.* To examine the reusability, the catalyst recovered by filtration from the reaction mixture after dilution with ethyl acetate was reused as such for subsequent experiments (up to three cycles) under similar reaction conditions. The observed fact that yields of the product remained comparable in these experiments (Figure 1) established the recyclability and reusability of the catalyst without any significant loss of activity.




| Pos. (°2Th.) | FWHM (°2Th.) | *d*-spacing (Å) | Rel. Int. (%) | Area (cts∗°2Th.) |
|---|---|---|---|---|
| 11.6450 | 1.4691 | 7.59942 | 100.00 | 829.18 |
| 34.0614 | 1.1880 | 2.63223 | 57.83 | 258.50 |
| 60.2907 | 0.3628 | 1.53513 | 50.65 | 103.70 |

FIGURE 2: XRD pattern of $NiO_{100}$ nanoparticle.

*4.4. General Procedure for the Synthesis of Compounds 5 and 6 under Microwave Irradiation.* An equimolar mixture (1 mmol) of 1H-indole-2,3-dione (0.147 g), malononitrile (0.066 g)/ethylcynoacetate (0.113 g) and 2-thioxo-4-thiazolidinone (0.133 g), in absolute ethanol (15 mL) in the presence of piperidine (2-3 drops)/$NiO_{100}$ (20 mg) was charged into a glass microwave vessel and refluxed inside a microwave oven at 420 Watts for 16–18 min./8–10 min., respectively. Progress of the reaction was monitored by TLC. After completion of the reaction, reaction mixture was cooled to room temperature and the excess solvent was evaporated on rota-evaporator to give a solid, which was dried and recrystallised from ethyl acetate.

*4.5. Characterization Data*

*4.5.1. 6′-Amino-2′-thioxo-2-oxo-1′H-spiro[indoline-3,4′-pyrano[2,3-c]thiazole]-5′-carbonitrile(***5a***).* Brown solid, mp 296–298°C, Yield ($NiO_{100}$/Piperidine) 90/75%, 0.269/0.246 g; IR (KBr) $\nu$ 3400, 3265, 3059, 3008, 2220, 1710, 1300 $cm^{-1}$; $^1$HNMR (400 MHz, DMSO) $\delta$ 11.21 (s. 1H, NH indole), 7.94 (s, 2H, $NH_2$), 6.93–8.75 (m, 4H, Ar-H), 2.88 (s, 1H, NH) ppm; $^{13}$CNMR (400 MHz, DMSO): 193.96, 185.54, 169.63, 161.47, 144.95, 142.98, 137.79, 129.74, 127.17, 121.28, 119.08, 77.27, 61.05, 59.42, 45.26 ppm. Anal. Calcd for $C_{14}H_8N_4O_2S_2$: C, 51.21; H, 2.46; N, 17.06. Found: C, 51.38; H, 2.48; N, 17.03; MS: $[M]^+$ at *m/z* 328.01.

*4.5.2. 6′-Amino-2′-thioxo-5-chloro-2-oxo-1′H-spiro[indoline-3,4′-pyrano[2,3-c]thiazole]-5′-carbonitrile(***5b***).* Brown solid, mp 310–312°C, Yield ($NiO_{100}$/Piperidine) 87/72%, 0.315/0.262 g; IR (KBr) $\nu$ 3450, 3225, 3052, 3028, 2120, 1685, 1320 $cm^{-1}$; $^1$HNMR (400 MHz, DMSO) $\delta$ 11.12 (s. 1H, NH indole), 8.78 (s, 2H, $NH_2$), 6.99–8.02 (m, 3H, Ar-H), 2.82 (s, 1H, NH) ppm; $^{13}$CNMR (400 MHz, DMSO): 189.88, 153.55, 150.67, 150.67, 147.04, 144.56, 129.69, 121.54, 120.56, 105.99, 77.06, 61.02, 56.26, 44.92 ppm. Anal. Calcd for $C_{14}H_7ClN_4O_2S_2$: C, 46.35; H, 1.94; N, 15.44. Found: C, 46.35; H, 1.92; N, 15.47; MS: $[M]^+$ at *m/z* 361.97.

*4.5.3. 6′-Amino-2′-thioxo-7-chloro-2-oxo-1′H-spiro[indoline-3,4′-pyrano[2,3-c]thiazole]-5′-carbonitrile(***5c***).* Brown solid, mp 275–277°C, Yield ($NiO_{100}$/Piperidine) 87/74%, 0.315/0.269 g; IR (KBr) $\nu$ 3310, 3115, 3039, 3020, 2215, 1720, 1340 $cm^{-1}$. $^1$HNMR (400 MHz, DMSO) $\delta$ 11.58 (s. 1H, NH indole), 7.19 (s, 2H, $NH_2$), 6.97–8.63 (m, 3H, Ar-H), 2.98 (s, 1H, NH) ppm; $^{13}$CNMR (400 MHz, DMSO) $\delta$ 193.12, 188.22, 169.41, 160.26, 142.46, 141.76, 135.34, 126.13, 121.04, 114.71, 77.64.08, 56.83, 44.33 ppm. Anal. Calcd for $C_{14}H_7ClN_4O_2S_2$: C, 46.35; H, 1.94; N, 15.44. Found: C, 46.14; H, 1.96; N, 15.41; MS: $[M]^+$ at *m/z* 361.97.

*4.5.4. 6′-Amino-2′-thioxo-5-bromo-2-oxo-1′H-spiro[indoline-3,4′-pyrano[2,3-c]thiazole]-5′-carbonitrile(***5d***).* Brown solid, mp 270–272°C, Yield ($NiO_{100}$/Piperidine) 88/72%, 0.360/0.294 g; IR (KBr) $\nu$ 3410, 3132, 3019, 3012, 2235, 1690, 1335 $cm^{-1}$. $^1$HNMR (400 MHz, DMSO) $\delta$ 11.04 (s. 1H, NH indole), 8.02 (s, 2H, $NH_2$), 6.87–8.53 (m, 3H, Ar-H), 2.93 (s, 1H, NH) ppm; $^{13}$CNMR (400 MHz, DMSO) 192.23, 183.71, 166.42, 143.32, 140.11, 131.44, 124.92, 122.11, 118.12, 111.76, 78.04, 64.25, 59.06, 44.17 ppm. Anal. Calcd for $C_{14}H_7BrN_4O_2S_2$: C, 41.48; H, 1.73; N, 13.76. Found: C, 41.48; H, 1.70; N, 13.74; MS: $[M]^+$ at *m/z* 405.92.

*4.5.5. 6′-Amino-2′-thioxo-5-nitro-2-oxo-1′H-spiro[indoline-3,4′-pyrano[2,3-c]thiazole]-5′-carbonitrile(***5e***).* Brown solid, mp 340–342°C, Yield ($NiO_{100}$/Piperidine) 90/72%, 0.337/0.269 g; IR (KBr) $\nu$ 3410, 3132, 3021, 3112, 2225, 1693, 1320 $cm^{-1}$. $^1$HNMR (400 MHz, DMSO) $\delta$ 11.01 (s. 1H, NH indole), 8.01 (s, 2H, $NH_2$), 6.83–8.43 (m, 3H, Ar-H), 2.83 (s, 1H, NH) ppm. $^{13}$CNMR (400 MHz, DMSO) 191.25, 185.62, 164.30, 143.51, 141.73, 135.81, 126.17, 121.45, 117.33, 78.54, 61.07, 59.31, 42.27 ppm. Anal. Calcd for $C_{14}H_7N_5O_4S_2$: C, 45.04; H, 1.89; N, 18.76. Found: C, 45.22; H, 1.91; N, 18.73; MS: $[M]^+$ at *m/z* 372.99.

*4.5.6. 6′-Amino-2′-thioxo-5-methyl-2-oxo-1′H-spiro[indoline-3,4′-pyrano[2,3-c]thiazole]-5′-carbonitrile(***5f***).* Brown

solid, mp 315–317°C, Yield ($NiO_{100}$/Piperidine) 88/70%, 0.301/0.241 g; IR (KBr) $\nu$ 3350, 3125, 3042, 3088, 2120, 1689, 1330 $cm^{-1}$. $^1$HNMR (400 MHz, DMSO) $\delta$ 10.91 (s. 1H, NH indole), 8.65 (s, 2H, $NH_2$), 6.81–8.02 (m, 3H, Ar-H), 3.37 (s, 3H, $CH_3$), 2.81 (s, 1H, NH) ppm; $^{13}$CNMR (400 MHz, DMSO) 191.54, 183.42, 169.55, 144.07, 141.52, 137.92, 126.76, 120.04, 117.15, 77.78, 62.22, 59.64, 45.33 ppm. Anal. Calcd for $C_{15}H_{10}N_4O_2S_2$: C, 52.62; H, 2.94; N, 16.36. Found: C, 52.83; H, 2.92; N, 16.39; MS: $[M]^+$ at *m/z* 342.02.

*4.5.7. 11-Amino-2-thioxo-10-oxo-thiazolo[5′′,4′′:5′,6′]pyrano[4′,3′:3, 4]furo[2,3-b]indole(***5g**). Brown solid, mp 332–334°C, Yield ($NiO_{100}$/Piperidine) 89/74%, 0.293 g/0.241; IR (KBr) $\nu$ 3430, 3225, 3059, 3018, 1710, 1320 $cm^{-1}$; $^1$HNMR (400 MHz, DMSO) $\delta$ 11.11 (s. 1H, NH indole), 7.24 (s, 2H, $NH_2$), 6.91–8.15 (m, 4H, Ar-H), 2.70 (s, 1H, NH) ppm; $^{13}$CNMR (400 MHz, DMSO) 192.49, 168.41, 142.73, 131.47, 127.33, 123.64, 120.87, 111.34, 77.88, 35.95, 30.03 ppm. Anal. Calcd for $C_{14}H_7N_3O_3S_2$: C, 51.05; H, 2.14; N, 12.76. Found: C, 50.87; H, 2.13; N, 12.79; MS: $[M]^+$ at *m/z* 328.99.

*4.5.8. 11-Amino-2-thioxo-5-chloro-10-oxo-thiazolo[5′′,4′′:5′,6′]pyrano[4′,3′:3, 4]furo[2,3-b]indole(***5h**). Brown solid, mp 288–291°C, Yield ($NiO_{100}$/Piperidine) 87/73%, 0.319/0.267 g; IR (KBr) $\nu$ 3330, 3231, 3039, 3018, 1710, 1340 $cm^{-1}$; $^1$HNMR (400 MHz, DMSO) $\delta$ 11.24 (s. 1H, NH indole), 7.34 (s, 2H, $NH_2$), 6.82–8.05 (m, 3H, Ar-H), 2.98 (s, 1H, NH). $^{13}$CNMR (400 MHz, DMSO) 193.26, 169.41, 167.43, 142.97, 131.43, 126.04, 123.25, 121, 111.64, 78.74, 39.05 ppm. Anal. Calcd for $C_{14}H_6ClN_3O_3S_2$: C, 46.22; H, 1.66; N, 11.55. Found: C, 46.05; H, 1.64; N, 11.52; MS: $[M]^+$ at *m/z* 362.95.

*4.5.9. 11-Amino-2-thioxo-7-chloro-10-oxo-thiazolo[5′′,4′′:5′,6′]pyrano[4′,3′:3, 4]furo[2,3-b]indole(***5i**). Brown solid, mp 226–228°C, Yield ($NiO_{100}$/Piperidine) 88/73%, 0.325/0.267 g; IR (KBr) $\nu$ 3430, 3231, 3039, 3018, 1690, 1330 $cm^{-1}$; $^1$HNMR (400 MHz, DMSO) $\delta$ 11.50 (s. 1H, NH indole), 7.54 (s, 2H, $NH_2$), 6.91–8.17 (m, 3H, Ar-H), 2.82 (s, 1H, NH) ppm; $^{13}$CNMR (400 MHz, DMSO) 191.52, 161.75, 159.02, 142.15, 134.06, 123.66, 120.34, 112.35, 76.56, 38.46 ppm. Anal. Calcd for $C_{14}H_6ClN_3O_3S_2$: C, 46.22; H, 1.66; N, 11.55. Found: C, 46.40; H, 1.64; N, 11.57; MS: $[M]^+$ at *m/z* 362.95.

*4.5.10. 11-Amino-2-thioxo-5-bromo-10-oxo-thiazolo[5′′,4′′:5′,6′]pyrano[4′,3′:3, 4]furo[2,3-b]indole(***5j**). Brown solid, mp 347-348°C, Yield (%) ($NiO_{100}$/Piperidine) 88/72%, 0.360/0.295 g; IR (KBr) $\nu$ 3423, 3231, 3029, 3078, 1692, 1340 $cm^{-1}$; $^1$HNMR (400 MHz, DMSO) $\delta$ 11.51 (s. 1H, NH indole), 7.13 (s, 2H, $NH_2$), 6.98–8.63 (m, 3H, Ar-H), 2.81 (s, 1H, NH) ppm; $^{13}$CNMR (400 MHz, DMSO) 193.02, 167.35, 161.64, 154.83, 143.57, 137.01, 126, 121.08, 117.24, 76.52. 38.50 ppm. Anal. Calcd for $C_{14}H_6BrN_3O_3S_2$: C, 41.19; H, 1.48; N, 10.29. Found: C, 41.40; H, 1.50; N, 10.26; MS: $[M]^+$ at *m/z* 406.90.

*4.5.11. 11-Amino-2-thioxo-5-nitro-10-oxo-thiazolo[5′′,4′′:5′,6′]pyrano[4′,3′:3, 4]furo[2,3-b]indole(***5k**). Brown solid, mp 265–267°C, Yield ($NiO_{100}$/Piperidine) 84/74%, 0.315/0.278 g; IR (KBr) 3421, 3248, 3039, 3098, 1702, 1335 $cm^{-1}$; $^1$HNMR (400 MHz, DMSO) $\delta$ 11.18 (s. 1H, NH indole), 8.22 (s, 2H, $NH_2$), 6.72–8.57 (m, 3H, Ar-H), 2.90 (s, 1H, NH); $^{13}$CNMR (400 MHz, DMSO) 192.38, 165.21, 160.53, 159.02, 143.76, 138.43, 126.87, 121.48, 111.56, 77.23, 36.17 ppm. Anal. Calcd for $C_{14}H_6N_4O_5S_2$: C, 44.92; H, 1.62; N, 14.94. Found: C, 44.72; H, 1.64; N, 14.94; MS: $[M]^+$ at *m/z* 373.98.

*4.5.12. 11-Amino-2-thioxo-5-methyl-10-oxo-thiazolo[5′′,4′′:5′,6′]pyrano[4′,3′:3, 4]furo[2,3-b]indole(***5l**). Brown solid, mp 356°C, Yield ($NiO_{100}$/Piperidine) 87/71%, 0.30/0.245 g; IR (KBr) 3411, 3228, 3013, 3090, 1720, 1320 $cm^{-1}$; $^1$H NMR (400 MHz, DMSO) $\delta$ 10.18 (s. 1H, NH indole), 7.44 (s, 2H, $NH_2$), 6.98–8.84 (m, 3H, Ar-H), 3.01 (s, 3H, $CH_3$), 2.81 (s, 1H, NH) ppm; $^{13}$CNMR (400 MHz, DMSO) 195.22, 167.47, 162.88, 131.12, 127.88, 123.72, 118.44, 110.47, 78.45, 40.46, 34.42, 24.77 ppm. Anal. Calcd for $C_{15}H_9N_3O_3S_2$: C, 52.47; H, 2.64; N, 12.24. Found: C, 52.65; H, 2.66; N, 12.27; MS: $[M]^+$ at *m/z* 343.01.

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