

# Nano $\text{MgBi}_2\text{O}_4$ : A Novel Green Catalyst for the One-step Cascade Condensation of Arylamines, Acetone and Isatins in Water

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MS received 10 July 2016; revised 18 August 2016; accepted 12 September 2016

**Abstract.** Nano-size  $\text{MgBi}_2\text{O}_4$  has been synthesized for the first time *via* a simple co-precipitation method using the surfactant *N*-cetyl-*N*, *N*, *N*-trimethylammonium bromide (CTAB). Fourier transform infrared (FT-IR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray powder diffraction (XRD) techniques were employed to characterize the nano-catalyst. Additionally, the reactivity of the prepared nanoparticles was investigated in the synthesis of 1'-aryl-2'-(2-oxoindolin-3-yl)spiro[indoline-3,5'-pyrroline]-2,3'-diones in a one-pot, one-step and pseudo four-component condensation of arylamine, acetone, and isatins at 50°C in water. Five new compounds were synthesized and identified. This procedure has various advantages such as, short reaction times, mild eco-friendly conditions and excellent yields to prepare a novel class of heteroaromatic compounds.  $\text{MgBi}_2\text{O}_4$  possess superior qualities such as easy and economic preparation procedure and handling, stability, and non-toxicity. Its reusability has also been examined upto 4 runs without activity loss.

**Keywords.**  $\text{MgBi}_2\text{O}_4$ ; spiro compound; multi-component reactions; green chemistry.

## 1. Introduction

Metal oxides play a critical role in different fields such as chemistry, physics and material science.<sup>1–4</sup> In technological applications, metal oxides are used in the manufacture of microelectronic circuits, sensors, piezoelectric devices, fuel cells, and coatings for the passivation of surfaces against corrosion.<sup>5–7</sup> Metal oxides are used for their acid/base properties in the context of catalysis. The key features essential for their application as acid/base catalysts is the coordination environment of surface and possessing s or p electrons in their valence orbitals.<sup>8</sup> They also demonstrate unequaled physical and chemical properties due to their limited size and a high density of corner or edge surface sites.<sup>9</sup> Liquid-solid transformations are possibly the most broadly used methods for the preparation of metal oxides in order to control morphological characteristics with certain chemical versatility.<sup>10</sup> Other than the above mentioned transformations, some other broadly used specific methods are: co-precipitation methods,<sup>11</sup> sol-gel processing,<sup>12</sup> microemulsion technique,<sup>13</sup> solvothermal methods,<sup>14</sup> and template/surface derivatized methods.<sup>15</sup>

The spirooxindole system is the core structure of many pharmacological agents and natural alkaloids.<sup>16,17</sup>

So, a variety methods have been reported for the synthesis of spirooxindole-fused heterocycles.<sup>18,19</sup> Recent synthetic methods to access spirocyclicoxindoles include cycloaddition,<sup>20,21</sup> Morita-Baylis Hillman reaction,<sup>22,23</sup> and other cyclization reactions such as photoinduced reactions,<sup>24</sup> and electrocyclization.<sup>25</sup>

In the past few years different multicomponent or domino reactions based on the versatile reactivity of isatins have been utilized for the preparation of various spirooxindoles.<sup>26–29</sup> Among the wide-spread functional groups which reacted with isatin core, arylamines are one of the important motifs. Yan and co-workers reported the preparation of cyclopentyl-fused spiro[dihydropyridine-oxindoles] by three-component reaction of arylamine, isatin and cyclopentane-1,3-dione.<sup>30</sup> Perumal and coworkers successfully reported the synthesis of spiro[indole-3,4'-pyridines] derivatives by four-component reaction of arylamines, acetylenedicarboxylates, malononitrile, and isatins.<sup>31</sup> The base promoted domino four-component reaction of hydrated hydrazine, dimethyl acetylenedicarboxylate, isatin and malononitrile or ethyl cyanoacetate in ethanol in the presence of triethylamine also afforded the polysubstituted spiro [indoline-3,4'-pyrano[2,3-c]pyrazole] derivatives.<sup>32</sup> Wet cyanuric chloride catalyzed the one-pot condensation of isatins, 3-methyl-1-phenyl-1H-pyrazol-5-amine and Meldrum's acid to afford spiro[pyrazolo[3,4-b]pyri-

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dine-4,3'-indoline] derivatives.<sup>33</sup> Pore and Mane prepared some fluorescent 1-H-spiro[indoline-1,2'-quinazoline]-3,4'(3'H)-diones *via* the sulphamic acid catalyzed reaction of isatins and anthranilamide in ethanol.<sup>34</sup> Recently, Yan *et al.*, reported the first synthesis of 1'-aryl-2'-(2-oxoindolin-3-yl)spiro[indoline-3,5'-pyrroline]-2,3'-diones *via* one-pot domino reaction of arylamines, acetone, and isatins in acetic acid.<sup>35</sup> Acetic acid seemed to be both promotor and also reaction medium. In continuation of research interest in N-containing heterocycles and nanocatalysts,<sup>36-47</sup> herein we prepared magnesium bismuth tetroxide ( $\text{MgBi}_2\text{O}_4$ ) as a novel nano compound by a simple co-precipitation method and characterized by SEM, FT-IR, XRD, and EDX techniques. The catalytic activity of the prepared nanocrystalline  $\text{MgBi}_2\text{O}_4$ , has been examined in the preparation of 1'-aryl-2'-(2-oxoindolin-3-yl)spiro[indoline-3,5'-pyrroline]-2,3'-diones *via* one-pot and one-step condensation of arylamines, acetone, and isatins at 50°C in water medium (Scheme 1). Five of the eight reported derivatives are new compounds.

## 2. Experimental

All chemicals were purchased from Merck, Aldrich and Alfa Aesar and were used as received. N-Benzylisatin was synthesized from isatin according to the reported procedure.<sup>48</sup> IR spectra were recorded from KBr disk using FT-IR Bruker Tensor 27 instrument. Melting points were determined on an Electrothermal 9200 analyzer and are uncorrected. <sup>1</sup>H NMR spectra were recorded with a Bruker drx (400 MHz) machine. Elemental analyses were determined using a Thermo-Finnigan Flash EA 1112 Series. Progress of the reaction was monitored by thin layer chromatography (TLC) technique using commercially available silica gel sheets. Preparative layer chromatography (PLC) carried out on 20 × 20 cm<sup>2</sup> plates, coated with a 1 mm

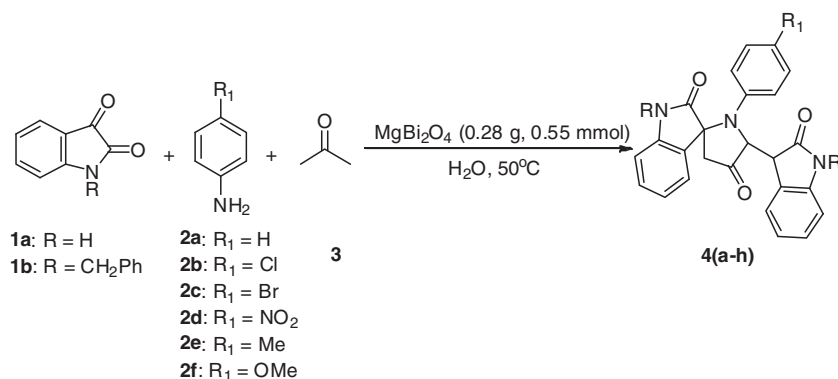
thick layer of Merck silica gel PF<sub>254</sub>, prepared by applying the silica as slurry and drying in air. The scanning electron microscope (SEM, model ZEISS AMA) was used to characterize the nanostructures. All products were characterized by their spectral and physical data. An ultrasound bath (Wise Clean, Korea) was used for sonication. The XRD pattern was obtained by an X-ray diffractometer, Philips (x'pert MPD, The Netherland) with  $\text{CuK}\alpha 1$  radiation, cobalt anode with wavelength 1.7889 Å at 40 kV and 40 mA. The centrifuge apparatus was a RST16 full digital model with rpm 300 cycle  $\text{min}^{-1}$ .

### 2.1 Preparation of Nano $\text{MgBi}_2\text{O}_4$

In a typical preparation, deionized water (100 mL) was added to stoichiometric amounts of magnesium nitrate hexahydrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) (4.0 mmol, 1.024 g) and bismuth nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ) (4.0 mmol, 1.940 g) and sonicated in ultrasound bath for 20 min. Then, *N*-cetyl-*N*, *N*, *N*-trimethylammonium bromide (CTAB) (2.0 g) was added and the pH of the solution adjusted to 9 by dropwise addition of concentrated ammonia under continuous stirring. After precipitation, the slurry was sonicated for another 30 min and subsequently refluxed at 80°C for 24 h under continuous stirring. Then the mixture was cooled to room temperature and centrifuged. The final product is dried at 100°C for 24 h and calcined at 800°C for 6 h. The pale yellow powder is nano-size magnesium bismuth tetroxide.

### 2.2 General procedure for the preparation of 1'-Aryl-2'-(2-oxoindolin-3-yl)spiro[indoline-3,5'-pyrroline]-2,3'-diones

A mixture of isatins **1** (2.0 mmol), arylamines **2** (1.0 mmol), acetone **3** (2.0 mL) and  $\text{MgBi}_2\text{O}_4$  (0.55 mmol,



**Scheme 1.** Synthesis of 1'-phenyl-2'-(2-oxoindolin-3-yl)spiro[indoline-3,5'-pyrroline]-2,3'-dione derivatives **4(a-h)** in the presence of nano  $\text{MgBi}_2\text{O}_4$ .

0.28 g) in water (5 mL) was stirred at 50°C for the desired reaction time. The progress of the reaction was monitored by TLC, (*n*-hexan/EtOAc, 1:1). After completion of the reaction, the mixture was extracted with CHCl<sub>3</sub> (2 × 10 mL). Purification of the product was gained by PLC eluted with *n*-hexan/EtOAc (1:1) to give dark yellow solids **4(a–h)** in 71–95% isolated yields. The characterization data of the new compounds are as follows.

**2.2a** *1'-Phenyl-2'-(2-oxoindolin-3-yl)spiro[indoline-3,5'-pyrroline]-2,3'-dione (4a): M.p. 224°C. FT-IR (KBr):  $\nu = 3380, 2924, 2855, 1726, 1621, 1467, 1375, 753 \text{ cm}^{-1}$ . <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  2.95–3.04 (m, 1H), 3.23–3.33 (m, 1H), 5.07 (d, *J* = 14.56 Hz, 1H), 5.98 (br s, 1H, NH), 6.44 (d, *J* = 13.72 Hz, 1H), 6.76 (d, *J* = 9.62 Hz, 2H), 6.86–6.91 (m, 2H), 6.98–7.07 (m, 1H), 7.13–7.28 (m, 8H), 10.23 (br s, 1H, NH) ppm. Anal. Calcd. for C<sub>25</sub>H<sub>19</sub>N<sub>3</sub>O<sub>3</sub>: C 73.33, H 4.67, N 10.26%. Found: C 72.87, H 4.53, N 10.05%.*

**2.2b** *1'-4-Bromoaniline-2'-(2-oxoindolin-3-yl)spiro[indoline-3,5'-pyrroline]-2,3'-dione (4c): M.p. 222°C. FT-IR (KBr):  $\nu = 3373, 3171, 2958, 2923, 2853, 1721, 1619, 1460, 754 \text{ cm}^{-1}$ . <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  2.98 (m, 1H), 3.31 (m, 1H), 4.45 (m, 2H), 6.08 (br s, 1H, NH), 6.75–6.88 (m, 4H), 6.88–7.01 (m, 1H), 7.15–7.18 (m, 3H), 6.24–7.26 (m, 4H), 10.28 (br s, 1H, NH) ppm. Anal. Calcd. for C<sub>25</sub>H<sub>18</sub>N<sub>3</sub>BrO<sub>3</sub>: C 61.48, H 3.71, N 8.60%. Found: C 61.21, H 3.67, N 8.21%.*

**2.2c** *1'-4-Nitroanilin-2'-(2-oxoindolin-3-yl)spiro[indoline-3,5'-pyrroline]-2,3'-dione (4d): M.p. 201°C. FT-IR (KBr):  $\nu = 3415, 2924, 2855, 1730, 1647, 1459, 1425, 1387, 1037, 875, 789, 467 \text{ cm}^{-1}$ . <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  2.98 (m, 1H), 3.28 (m, 1H), 4.11–4.13 (m, 2H), 5.98 (br s, 1H, NH), 6.76 (d, *J* = 10.12 Hz, 2H), 6.88 (t, *J* = 9.86 Hz, 2H), 7.15 (t, *J* = 9.90 Hz, 2H), 7.22 (d, *J* = 9.56 Hz, 2H), 7.64–7.72 (m, 4H), 10.23 (s, 1H, NH) ppm. Anal. Calcd. for C<sub>25</sub>H<sub>18</sub>N<sub>4</sub>O<sub>5</sub>: C 66.07, H 3.99, N 12.33%. Found: C 65.95, H 3.89, N 12.05%.*

**2.2d** *1'-4-Chlorophenyl-2'-(2-oxoindolin-1-benzyl-3-yl)spiro[indoline-3,5'-pyrroline]-2,3-dione (4g): M.p. 238–245°C. FT-IR (KBr):  $\nu = 3316, 2923, 2853, 1699, 1617, 1494, 1467, 1431, 1386, 1181, 1079, 1003, 755, 733 \text{ cm}^{-1}$ . <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  3.15 (d, *J* = 22.62 Hz, 1H), 3.42 (d, *J* = 22.67 Hz, 1H), 4.79 (d, *J* = 21.2 Hz, 2H), 4.81 (d, *J* = 21.04 Hz, 2H), 6.16–6.21 (m, 2H), 6.71 (d, *J* = 10.12 Hz, 2H), 6.94 (t, *J* = 9.72 Hz, 4H), 7.15 (t, *J* = 10.23 Hz, 4H), 7.24–7.31 (m, 10H), 7.41 (d, *J* = 9.57 Hz, 2H) ppm. Anal. Calcd.*

for C<sub>39</sub>H<sub>30</sub>N<sub>3</sub>ClO<sub>3</sub>: C 75.05, H 4.84, N 6.73%. Found: C 74.86, H 4.79, N 6.68%.

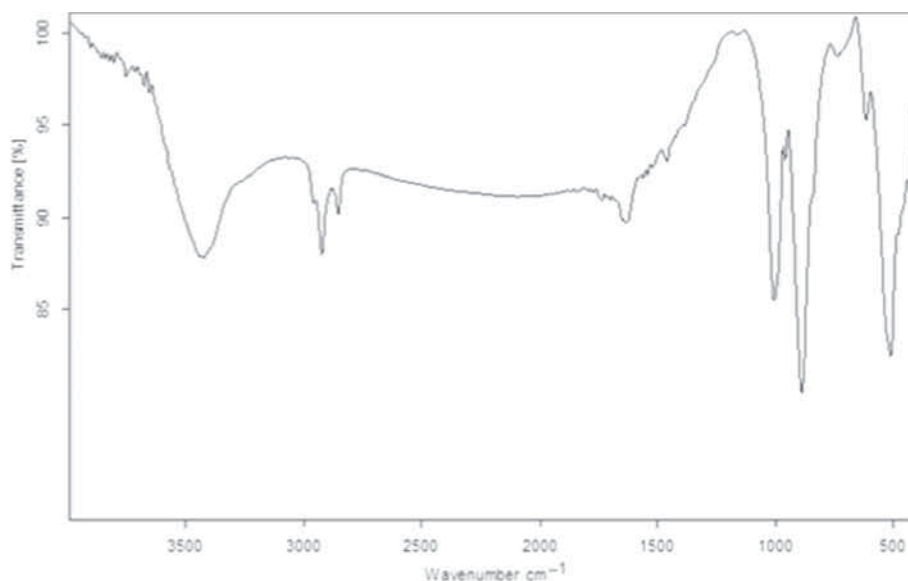
**2.2e** *1'-4-Bromo-2'-(2-oxoindolin-1-benzyl-3-yl)spiro[indoline-3,5'-pyrroline]-2,3'-dione (4h): M.p. 230°C. FT-IR (KBr):  $\nu = 3320, 2922, 2854, 1699, 1616, 1494, 1465, 1430, 1179, 1106, 754 \text{ cm}^{-1}$ . <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  3.12–3.18 (m, 2H), 3.47 (d, *J* = 14.17 Hz, 1H), 4.79 (d, *J* = 21.05 Hz, 1H), 4.89 (d, *J* = 21.18 Hz, 1H), 6.18–6.21 (m, 2H), 6.72 (d, *J* = 10.36 Hz, 2H), 7.15 (d, *J* = 10.18 Hz, 4H), 7.22–7.26 (m, 2H), 7.30–7.34 (m, 3H), 7.41 (d, *J* = 9.8 Hz, 2H) ppm. Anal. Calcd. for C<sub>39</sub>H<sub>30</sub>N<sub>3</sub>BrO<sub>3</sub>: C 70.06, H 4.52, N 6.28%. Found: C 69.94, H 4.60, N 6.08%.*

### 3. Results and Discussion

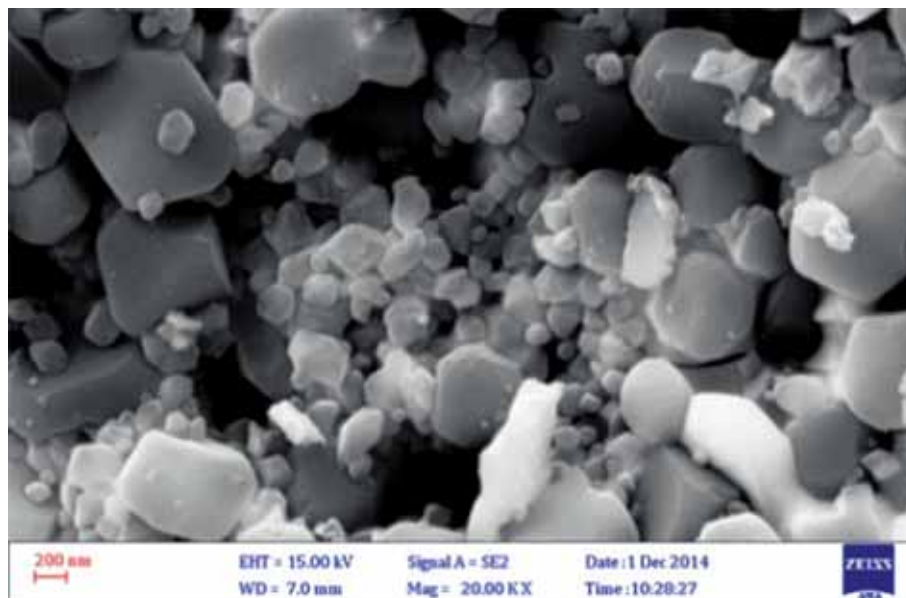
The FT-IR spectrum nano MgBi<sub>2</sub>O<sub>4</sub> at 450–4000 cm<sup>-1</sup> is shown in Figure 1. The broad band at 3424 cm<sup>-1</sup> shows the stretching vibration of hydroxyl group related to the adsorbed water on the catalyst surface. The peak at 1636 cm<sup>-1</sup> shows the bending vibration of water molecule. The major peaks at 880 and 512 cm<sup>-1</sup> are related to the characteristic absorption peaks of Mg-O and Bi-O vibrations, respectively. The bands in the region of 2923, 2853 cm<sup>-1</sup>, which belong to the symmetrical and unsymmetrical methylene groups of CTAB, are absent in the FT-IR spectra. The band at 1005 cm<sup>-1</sup> may belong to Mg-Bi vibration.

The SEM pattern of nano MgBi<sub>2</sub>O<sub>4</sub> is shown at Figure 2. This image reveals that the product consists of particles with the average size of 70–200 nm, with semi-spherical morphology. The wide range could be due to thermal variation or surfactant concentration change. Also, the average crystallite size is estimated using Scherrer formula ( $d = k\lambda/\beta \cos \theta$ ), where  $\lambda$  is the wavelength of the X-ray ( $\lambda = 1.78 \text{ \AA}$ ),  $k$  is a constant between 0.89 and 1.0, and  $\theta$  is the Bragg's diffraction angle. The  $\beta$  is sum of the  $\beta_{size}$ ,  $\beta_{ins}$  and  $\beta_{strain}$ . The  $\beta_{strain}$ , that identified the micro strain of crystal, is negligible. The instrumental broadening effect ( $\beta_{ins}$ ), which was measured by XRD instrument, is 0.0033 radian. Then the true value of  $\beta_{size}$  is calculated by  $\beta_{size} = \beta - \beta_{ins}$ . The mean crystal size is calculated as 63 nm which corresponds to the minimum size in the SEM image (70 nm, Figure 2). This calculation revealed that the CTAB amount, that could control the particle size, is suitable for the preparation of small nanoparticles.

EDX in Figure 3 shows that the catalyst is mainly made up of magnesium and bismuth. The weight percent of the product confirms the molecular formula of MgBi<sub>2</sub>O<sub>4</sub>. The amount of Au is negligible.



**Figure 1.** FT-IR spectrum of synthesized nano  $\text{MgBi}_2\text{O}_4$ .



**Figure 2.** SEM image of nano-size  $\text{MgBi}_2\text{O}_4$ .

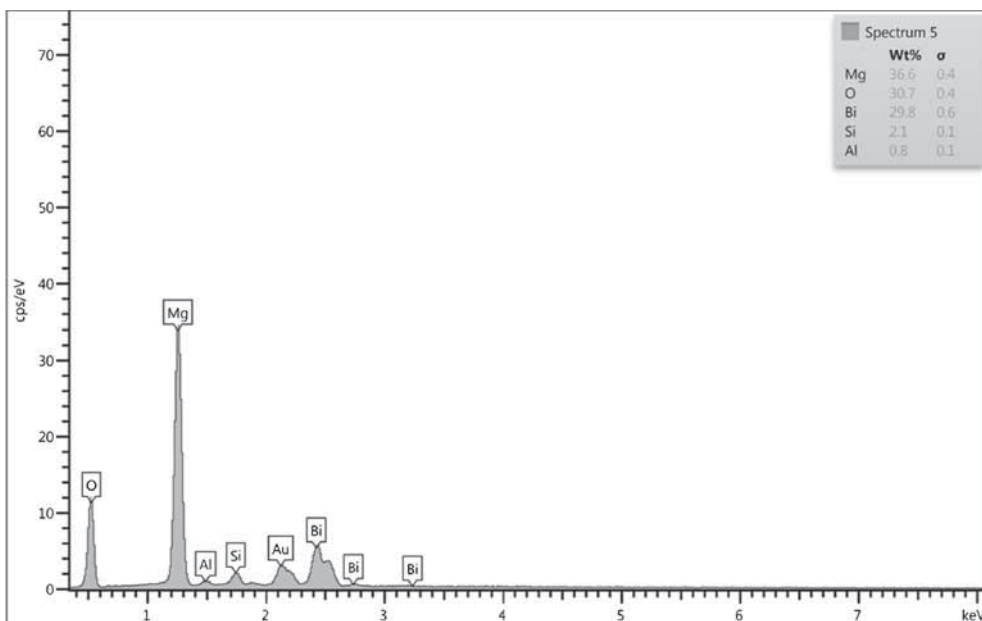
The morphology and phase identification of the synthesized nanocatalyst was investigated using XRD pattern (Figure 4). According to Figure 4, the peaks were observed at the scattering angles 32.03, 34.63, 36.85, 37.49, 39.17, 43.05, 44.11, 47.49, 58.27 and 63.03 degrees with related normalized intensities of 18.36, 16.80, 55.55, 62.22, 100, 14.40, 40.13, 21.125, 32.65, and 24.07, respectively. The impurities such as Au could change the peak locations.

In order to achieve the optimum conditions, the model condensation of isatin **1a** (2 mmol), 4-bromoaniline **2c** (1 mmol), and acetone **3** (2 mL) in the presence of  $\text{MgBi}_2\text{O}_4$  (0.55 mmol, 0.28 g) was chosen. Solvent and

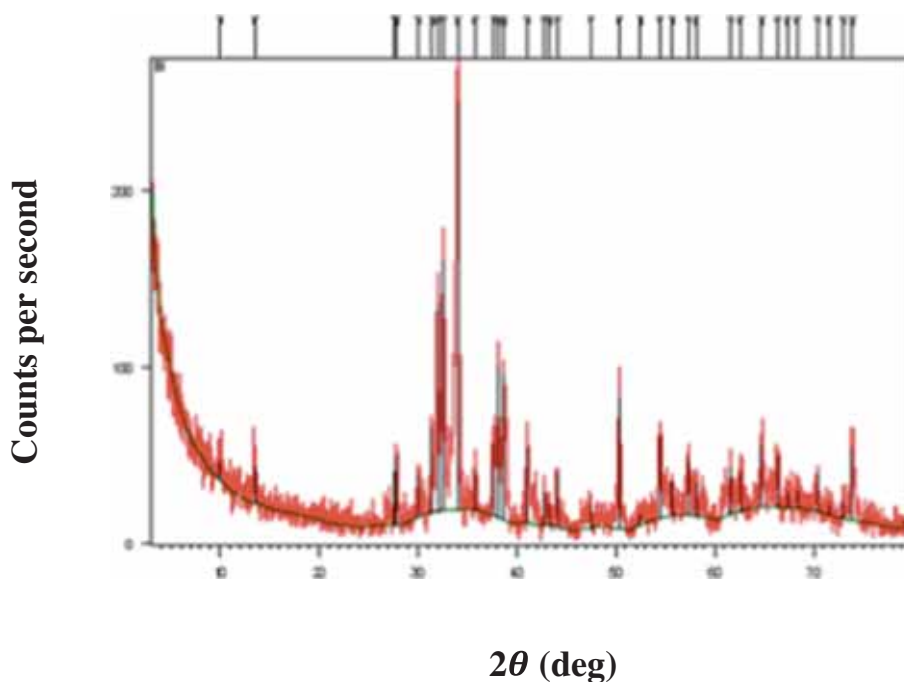
temperature effects revealed that performing the reaction at 50°C in water medium yielded the best results (Table 1, entries 1–8). Changing the catalyst amount, affirmed that 0.55 mmol (0.28 g) of the nano  $\text{MgBi}_2\text{O}_4$  is the best choice (Table 1, entries 5, 9, and 10).

Eventually, on the basis of optimized conditions, the pseudo four-component condensation of various isatins, anilines, and acetone was performed in the presence of nano-size  $\text{MgBi}_2\text{O}_4$  (0.55 mmol 0.28 g) in the presence of water at 50°C. The results are summarized in Table 2.

As could be seen at Table 2, the protocol is very effective for the condensation of isatin (**1a**) with different anilines consisting electron-withdrawing (entries 1–4)



**Figure 3.** EDX image of synthesized  $\text{MgBi}_2\text{O}_4$  nano catalyst.



**Figure 4.** XRD spectrum of synthesized nano  $\text{MgBi}_2\text{O}_4$ .

as well as electron-donating groups (entries 6, 7). N-Benzylisatin (**1b**), as an electron-donating isatin, reacted with 4-chloro- and 4-bromoaniline, respectively, to obtain **3g** and **3h** (entries 7, 8) successfully. We also performed the reaction with electron-withdrawing isatins such as 5-nitroisatin with anilines but the data was not satisfactory.

The reusability of nano-size  $\text{MgBi}_2\text{O}_4$  for the MCR to afford **4c** was also investigated for three additional

runs. According to optimized reaction conditions, isatin **1a** (4 mmol), 4-bromoaniline **2c** (2 mmol), and acetone **3** (4 mL) in  $\text{H}_2\text{O}$  (10 mL) at  $50^\circ\text{C}$  in the presence of  $\text{MgBi}_2\text{O}_4$  (1.1 mmol, 0.56 g) mixed and stirred magnetically until completion of reaction (15 min); Then the mixture was diluted with ethanol (20 mL). The catalyst was separated by filtration, washed with more ethanol (10 mL) and air-dried. Subsequently the residue was heated in oven at  $100^\circ\text{C}$  for 20 min and used for another

**Table 1.** Screening the reaction conditions in the preparation of **4c**.<sup>a</sup>

Entry	Conditions	Time (min)	Yield (%) <sup>b</sup>
1	MgBi <sub>2</sub> O <sub>4</sub> (0.28 g), r.t., solvent-free	135	41
2	MgBi <sub>2</sub> O <sub>4</sub> (0.28 g), 80°C, solvent-free	450	92
3	MgBi <sub>2</sub> O <sub>4</sub> (0.28 g), r.t., H <sub>2</sub> O (5 mL)	35	91
4	MgBi <sub>2</sub> O <sub>4</sub> (0.28 g), 40°C, H <sub>2</sub> O (5 mL)	25	91
5	MgBi <sub>2</sub> O <sub>4</sub> (0.28 g), 50°C, H <sub>2</sub> O (5 mL)	15	93
6	MgBi <sub>2</sub> O <sub>4</sub> (0.28 g), reflux, H <sub>2</sub> O (2 mL)	15	93
7	MgBi <sub>2</sub> O <sub>4</sub> (0.28 g), r.t., CH <sub>3</sub> CN (5 mL)	135	43
8	MgBi <sub>2</sub> O <sub>4</sub> (0.28 g), reflux, CH <sub>3</sub> CN (5 mL)	570	92
9	MgBi <sub>2</sub> O <sub>4</sub> (0.20 g), 50°C, H <sub>2</sub> O (5 mL)	40	91
10	MgBi <sub>2</sub> O <sub>4</sub> (0.32 g), 50°C, H <sub>2</sub> O (5 mL)	15	93

<sup>a</sup>**1a** (2 mmol), **2c** (1 mmol), and **3** (2 mL).

<sup>b</sup>Isolated yields.

**Table 2.** Synthesis of 1'-aryl-2'-(2-oxoindolin-3-yl)spiro[indoline-3,5'-pyrroline]-2,3'-diones in the presence of MgBi<sub>2</sub>O<sub>4</sub>.<sup>a</sup>

Entry	R	R <sub>1</sub>	Product	Time (min)	Yield (%) <sup>b</sup>	M.p. (°C)	Lit M.p. (°C)
1	H	H	<b>4a</b>	35	95	224	–
2	H	Cl	<b>4b</b>	15	92	251-254	248-251
3	H	Br	<b>4c</b>	15	93	222	–
4	H	NO <sub>2</sub>	<b>4d</b>	45	71	201	–
5	H	CH <sub>3</sub>	<b>4e</b>	35	90	228-233	232-235
6	H	OCH <sub>3</sub>	<b>4f</b>	15	93	235-239	238-241
7	PhCH <sub>2</sub>	Cl	<b>4g</b>	45	91	238-243	–
8	PhCH <sub>2</sub>	Br	<b>4h</b>	45	94	230	–

<sup>a</sup>Reaction conditions: isatins (2 mmol), anilines (1 mmol) and acetone (2 mL) in H<sub>2</sub>O (5 mL) at 50°C in the presence of MgBi<sub>2</sub>O<sub>4</sub> (0.55 mmol, 0.28 g).

<sup>b</sup>Isolated yields.

cycle without a considerable loss of catalytic activity during 3 runs. The yields for runs 1–4 were 93%, 92%, 90% and 90%, respectively.

#### 4. Conclusions

In conclusion, nanocrystalline MgBi<sub>2</sub>O<sub>4</sub> has been prepared for the first time *via* a simple co-precipitation method using available salt precursors and CTAB as organic surfactant. The characterization has been performed *via* SEM, FT-IR, EDX, and XRD techniques. Its catalytic activity has been examined for the synthesis of novel 1'-aryl-2'-(2-oxoindolin-3-yl)spiro[indoline-3,5'-pyrroline]-2,3'-diones successfully. This research have several advantages such as, short reaction times, high yields of products, absence of any bi-products due to the aldol condensation of acetone, ambient temperature, and utilizing easy to handle, inexpensive and non-toxic nano catalyst. The procedure happened in water media and hasn't required and hazardous organic solvents, which follows the green chemistry. Also the catalyst

could be successfully recycled and reused at least for 4 runs without significant loss in activity.

#### Supplementary Information (SI)

All additional information pertaining to characterization of the derivatives **4a**, **4c–d**, and **4g–h**, IR spectra (Figures S1, S3, S5, S7, S10) and <sup>1</sup>H NMR spectra (Figures S2, S4, S6, S8, S10) are available in Supplementary Information at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

#### Acknowledgements

Authors greatly appreciate the Iran National Science Foundation (INSF) for the financial support for this study.

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