

A clean and efficient synthesis of spiro[4H-pyran-oxindole] derivatives catalyzed by egg shell

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Received: 15 June 2017, Accepted: 13 May 2018, Published: 13 May 2018

Abstract

Egg shell has been utilized as a natural, green, reusable and eco-friendly reagent for the synthesis of spiro[4H-pyran-oxindole] derivatives by one-pot multicomponent reaction of isatins, 1,3-diketones, and malononitrile/ ethyl cyanoacetate. Good functional group tolerance and broad scope of usable substrates are other prominent features of the present methodology.

Keywords: Spirooxindole; eggshell; heterogeneous catalyst; isatin; green chemistry.

Introduction

The indole and indoline moiety constitutes a core structural unit of many bioactive natural products and medicinal agents [1]. Particularly, spirocyclic oxindoles are important synthetic targets due to their common occurrence in natural products and clinical pharmaceuticals and also act as potent no-peptide-inhibitors of the p53-MDM2 interaction [2-5].

Heterocycles containing the pyrans and fused pyrans have been found to be associated with a group of biological activities [6-8].

A lot of spiro-heterocycles, containing both indole and pyran heterocycles, spiro[(3'H)-indol-3',4-(4H)-pyrans], possess anticonvulsant and analgetic [9], herbicidal [10], fungicidal [11] and antibacterial activities [12]. Several synthetic methods have been reported for the preparation of spiro[(3'H)-indol-3',4-(4H)-pyrans] under classical or modified conditions [13-23].

Besides, the importance of these compounds, the development of a simple and efficient method for the synthesis of spiro-fused pyran-oxindole heterocycles will be an interesting challenge.

As it is widely known, green chemistry which has been defined as a set of principles reduces or eliminates the use or generation of hazardous substances throughout the entire life of chemical materials [24]. Along with this line, heterogeneous catalysts have gained a great deal of importance in recent years due to economic and environmental benefits [25-29]. These catalysts which are generally less expensive, highly reactive, eco-friendly are also easy to handle. They reduce reaction times, impart greater selectivity and are simple to work up. Different types of solids are used in heterogeneous catalysis. They may be metals, metals oxide, metals sulphide, clays etc [26]. Although the mentioned materials are green and heterogeneous

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catalysts with excellent yields; a large number of them are toxic. Further, they may be crystalline, microcrystalline and amorphous [25-29]. These catalysts are used in a state of fine powdered so as to give a large surface area [25-29].

In this research, we used eggshell as a heterogeneous and bioactive catalyst. Eggshell has been utilized as humidity adsorbent, as an adsorbent in the biosorption of Cr (III) ions [30], heavy metal removal [31], adsorbent for removal of dyes [32], adsorption of iron [33], removal and recovery of copper [34] and also as a low cost solid catalyst for biodiesel production [35], as a catalyst for lactose isomerization to lactulose [36], synthesis of 7,8-dihydro-4H-chromen-5(6H)-ones [37] and pyrano[3,2-c]quinolone derivatives, etc [38]. In continuation of our investigations into the synthesis of heterocyclic compounds under green condition [38-41], herein, we wish to report an efficient and green protocol for the synthesis of some spiro[(3H)-indol-3',4-(4H)-pyrans] derivatives using eggshell as green and heterogeneous catalyst with excellent yields.

Experimental

Materials and methods

All chemicals were purchased from Merck or Fluka Chemical Companies. All known compounds were identified by comparison of their melting points and spectral data with those reported in the literature. The progress of the reactions was monitored by thin layer chromatography (TLC) using silica gel SIL G/UV 254 plates. IR spectra were recorded using a Shimadzu IR-470 spectrometers with KBr plates. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance-400 MHz spectrometer.

Catalyst preparation

Empty chicken eggshells were collected from the household and washed with tap warm water. The adhering membrane was separated manually. The eggshells were washed with distilled water and dried at room temperature. The eggshells were crushed and milled into different particle sizes by mortar [37].

General procedure

A mixture of isatin derivatives **1** (1 mmol), malononitrile or ethyl cyanoacetate **2** (1 mmol) and 1,3-diketone **3** (1 mmol) was added to a vial containing a magnetic stirring bar and 0.15 g of eggshell in 3 ml EtOH. The reaction mixture was sealed and stirred at 60 °C (oil bath) until disappearance of the starting materials (monitored by TLC). After completion, the reaction mixture was filtered and the obtained precipitates were washed with hot ethanol (95.5%).

The selected spectral data

2-Amino-2',5-dioxo-5,6-dihydro-spiro[pyrano[3,2-c]quinoline-4,3'-indoline]-3-carbonitrile (**4a**)

White powder, Yield (0.33 g, 91%). M.p >300 °C. IR (KBr) cm⁻¹: 3370, 3250, 3200, 2200, 1724, 1674, 1618, 1585. ¹H NMR (400.13 MHz, DMSO-d₆): 6.83 (1H, d, *J* 7.6Hz, 7'-H), 6.88 (1H, dt, *J* 7.6 and 0.9Hz, 5'-H), 7.03 (1H, d, *J* 7.2Hz, 4'-H), 7.18 (1H, dt, *J* 7.6 and 1.2Hz, 6'-H), 7.33 (1H, t, *J* 8.0Hz, 9-H), 7.35 (1H, d, *J* 8.4Hz, 7-H), 7.45 (2H, s, NH₂), 7.62 (1H, dt, *J* 7.8 and 1.2Hz, 8-H), 7.95 (1H, dd, *J* 8.2 and 1.2Hz, 10-H), 10.52 (1H, s, NH), 11.73 (1H, s, NH) ppm.

Ethyl 2-amino-2',5-dioxo-5,6-dihydro-spiro[pyrano[3,2-c]quinoline-4,3'-indoline]-3-carboxylate (4b)

Yellow powder, Yield (0.36 g, 90%). Mp >300 °C. IR (KBr) cm^{-1} : 3300, 3200, 2950, 1720, 1690, 1670, 1620, 1365. ^1H NMR (400.13 MHz, DMSO- d_6): 0.84 (3H, t, J 7.2Hz, OCH_2CH_3), 3.70-3.82 (2H, m, OCH_2CH_3), 6.71 (1H, d, J 7.6Hz, 7'-H), 6.75 (1H, t, J 7.2Hz, 5'-H), 6.87 (1H, d, J 7.2Hz, 4'-H), 7.07 (1H, t, J 7.6Hz, 6'-H), 7.30 (1H, t, J 7.2Hz, 9-H), 7.31 (1H, d, J 8.0Hz, 7-H), 7.59 (1H, dt, J 7.8 and 1.4Hz, 8-H), 8.02 (1H, d, J 7.6Hz, 10-H), 8.05 (2H, s, NH_2), 10.27 (1H, s, NH), 11.53 (1H, s, NH) ppm.

Ethyl 2-amino-6-methyl-2',5-dioxo-5,6-dihydro-spiro[pyrano[3,2-c]quinoline-4,3'-indoline]-3-carboxylate (4c)

White powder, Yield (0.37 g, 90%). Mp >300 °C. IR (KBr) cm^{-1} : 3305, 3197, 2996, 1715, 1685, 1623, 1524, 1465, 1360, 1287. ^1H NMR (400.13 MHz, DMSO- d_6): 0.87 (3H, t, J 7.2Hz, OCH_2CH_3), 3.45 (3H, s, 6- CH_3), 3.71-3.83 (2H, m, OCH_2CH_3), 6.72 (1H, d, J 7.6Hz, 7'-H), 6.74 (1H, t, J 7.6Hz, 5'-H), 3.86 (1H, d, J 6.8Hz, 4'-H), 7.07 (1H, dt, J 7.6 and 1.2Hz, 6'-H), 7.41 (1H, t, J 7.4Hz, 9-H), 7.53 (1H, d, J 8.4Hz, 7-H), 7.71 (1H, dt, J 8.0 and 1.2Hz, 8-H), 8.08 (2H, s, NH_2), 8.15 (1H, dd, J 8.0 and 1.2Hz, 10-H), 10.29 (1H, s, NH) ppm.

Ethyl 2-amino-5'-methoxy-6-methyl-2',5-dioxo-5,6-dihydro-spiro[pyrano[3,2-c]quinoline-4,3'-indoline]-3-carboxylate (4d)

Yellow powder. Yield (0.39 g, 88%). Mp >300 °C. IR (KBr) cm^{-1} : 3350, 3280, 2965, 1705, 1685, 1645, 1593, 1484, 1358, 1282. ^1H NMR (400.13 MHz, DMSO- d_6): 0.88 (3H, t, J 6.8Hz,

OCH_2CH_3), 3.46 (3H, s, N- CH_3), 3.58 (3H, s, O- CH_3), 3.78 (2H, m, OCH_2CH_3), 6.50 (1H, d, J 2.2Hz, 4'-H), 6.62 (1H, d, J 8.0Hz, 7'-H), 6.65 (1H, dd, J 8.4 and 2.2Hz, 6'-H), 7.40 (1H, t, J 8.0Hz, 9-H), 7.53 (1H, d, J 8.4Hz, 7-H), 7.72 (1H, dt, J 7.8 and 1.6Hz, 8-H), 8.07 (2H, s, NH_2), 8.15 (1H, dd, J 8.0 and 1.2Hz, 10-H), 10.12 (1H, s, NH) ppm.

2-Amino-2',5-dioxo-5,6,7,8-tetrahydro-spiro[chromene-4,3'-indoline]-3-carbonitrile (4e)

White powder, Yield (0.28 g, 91%) Mp: >300 °C. IR (KBr) cm^{-1} : 3400, 3332, 3250, 3204, 2200, 1734, 1670, 1616, 1520, 1339. ^1H NMR (400.13 MHz, DMSO- d_6): 7.07 (1H, d, J 8.8Hz, 7'-H), 7.35 (1H, t, J 7.6 Hz, 9-H), 7.37 (1H, d, J 8.4Hz, 7-H), 7.64 (1H, t, J 8.0Hz, 8-H), 7.66 (2H, s, NH_2), 7.97 (1H, d, J 7.6Hz, 10-H), 8.13 (1H, d, J 2.4Hz, 4'-H), 8.19 (1H, dd, J 8.8 and 2.4Hz, 6'-H), 11.30 (1H, s, NH), 11.83 (1H, s, NH) ppm.

Ethyl 2-amino-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydro-spiro[chromene-4,3'-indoline]-3-carboxylate (4f)

White powder. Yield (0.35 g, 91%). Mp: 255-257 °C. IR (KBr) cm^{-1} : 3360, 3230, 3190, 1713, 1682, 1664, 1610, 1520. ^1H NMR (400.13 MHz, DMSO- d_6): 0.80 (3H, t, J 7.2Hz, OCH_2CH_3), 0.95 (3H, s, 7- CH_3), 1.02 (3H, s, 7- CH_3), 2.01 (1H, d, J 16Hz, 8- H_B), 2.15 (1H, d, J 16Hz, 8- H_A), 2.48 (1H, d, J 17.6Hz, 6- H_B), 2.58 (1H, d, J 17.6Hz, 6- H_A), 3.69-3.72 (2H, m, OCH_2CH_3), 6.67 (1H, d, J 7.6Hz, 7'-H), 6.76 (1H, t, J 7.2Hz, 5'-H), 6.83 (1H, d, J 7.2Hz, 4'-H), 7.04 (1H, t, J 7.2Hz, 6'-H), 7.86 (2H, s, NH_2), 10.14 (1H, s, NH) ppm.

2-Amino-10-benzyl-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydro-spiro[chromene-4,3'-indoline]-3-carbonitrile 4(g)

White powder. Yield (0.38 g, 92%). Mp: 265-268 °C. IR (KBr) cm^{-1} : 3396, 3304, 3200, 2200, 1717, 1678, 1655, 1596, 1347. ^1H NMR (400.13 MHz, DMSO- d_6): 1.02 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 2.13 (d, 1H, J 16.0Hz, 8- H_B), 2.22 (d, 1H, J 16.0Hz, 8- H_A), 2.58 (d, 1H, J 17.6Hz, 6- H_B), 2.64 (d, 1H, J 17.6Hz, 6- H_A), 4.88 (d, 1H, J 16.4Hz, Bn- H_B), 4.94 (d, 1H, J 16.4Hz, Bn- H_A), 6.69 (d, 1H, J 8.0Hz, 7'-H), 6.96 (t, 1H, J 7.4Hz, 5'-H), 7.09 (d, 1H, J 7.2Hz, 4'-H), 7.13 (t, 1H, J 7.6Hz, 6'-H), 7.26 (t, 1H, J 7.2Hz, Ph), 7.31 (t, 2H, J 7.6Hz, Ph), 7.34 (s, 2H, NH_2), 7.49 (d, 2H, J 7.2Hz, Ph) ppm.

Ethyl 2-amino-2',5-dioxo-5,6,7,8-tetrahydro-spiro[chromene-4,3'-indoline]-3-carboxylate 4(h)

White powder. Yield (0.29 g, 88%). Mp: 252-254 °C. IR (KBr) cm^{-1} : 3374, 3230, 3180, 1718, 1708, 1685, 1650, 1618, 1590. ^1H NMR (400.13 MHz, DMSO- d_6): 0.79 (3H, t, J 7.2Hz, OCH_2CH_3), 1.80-1.92 (2H, m, CH_2), 2.10-2.26 (2H, m, CH_2), 2.64 (2H, t, J 6.4Hz, CH_2), 3.64-3.75 (2H, m, OCH_2CH_3), 6.66 (1H, d, J 7.6 Hz, 7'-H), 6.76 (1H, dt, J 7.2 and 0.8Hz, 5'-H), 6.85 (1H, d, J 6.8Hz, 4'-H), 7.04 (1H, dt, J 7.6 and 1.2Hz, 6'-H), 7.85 (2H, s, NH_2), 10.14 (1H, s, NH) ppm.

2-Amino-2',5-dioxo-5,6,7,8-tetrahydro-spiro[chromene-4,3'-indoline]-3-carbonitrile (4i)

White powder. Yield (0.28 g, 91%). Mp: 296-298 °C. IR (KBr) cm^{-1} : 3354, 3295, 3153, 2198, 1717, 1674, 1653, 1615, 1596. ^1H NMR (400.13 MHz, DMSO- d_6): 1.91-1.95 (m, 2H, 7-H), 2.18-2.27 (m, 2H, 8-H), 2.66 (t, 2H, J 6.4Hz, 6-H), 6.78 (d, 1H, J 7.6Hz, 7'-

H), 6.89 (dt, 1H, J 7.2 and 0.8Hz, 5'-H), 7.00 (d, 1H, J 6.8Hz, 4'-H), 7.14 (dt, 1H, J 7.6 and 1.2Hz, 6'-H), 7.22 (s, 2H, NH_2), 10.40 (s, 1H, NH) ppm.

Ethyl 2'-amino-5-chloro-3'-cyano-6'-methyl-2-oxo-spiro[indoline-3,4'-pyran]-5'-carboxylate 4(j)

White powder. Yield (0.32 g, 90%). Mp: 255-257 °C 4(j). IR (KBr) cm^{-1} : 3396, 3292, 3185, 2200, 1715, 1700, 1618, 1588. ^1H NMR (400.13 MHz, DMSO- d_6): 0.84 (3H, t, J 6.8Hz, $\text{O-CH}_2\text{CH}_3$), 2.34 (3H, s, CH_3), 3.77-3.87 (2H, m, $\text{O-CH}_2\text{CH}_3$), 6.81 (1H, d, J 8.4Hz, 7-H), 7.19 (1H, d, J 2.2Hz, 4-H), 7.23 (1H, dd, J 8.4 and 2.2Hz, 6-H), 7.24 (2H, s, NH_2), 10.55 (1H, s, NH) ppm.

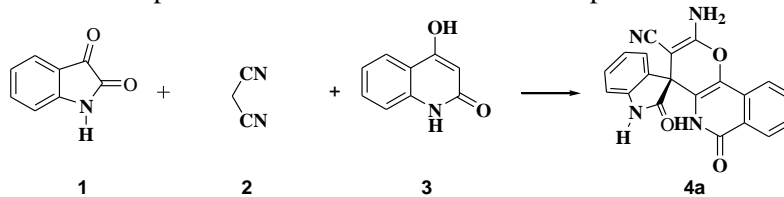
Results and discussion

Recently, Mosaddegh *et al.* have characterized the size and structure of eggshell powder by elemental analysis, X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy and laser particle sizer. Moreover, the determined the surface area of the natural eggshell was $0.0253 \text{ m}^2 \text{ g}^{-1}$ [37]. These data indicate that egg shell has porous surface. According to the useful properties of these materials, a lot of research had been done in this area [42-45] and also when the synthesis of spiro [13-23] was investigated, the results indicate that most of the used catalysts are the basic. Regarding this background and using the synthesis of **4a** as a model reaction, the reaction conditions were optimized with respect to the solvent, reaction temperature and the presence or the absence of a catalyst. This study showed that among the investigated solvents, ethanol was found to be the best (Table 1), the yields were better when the reactions were done at 60°C for 10 min (Table 1), and these results

revealed that 0.15 g of the catalyst was the best selection for carrying out the reaction. Besides, the use of excess amount of catalyst had no effect on the rate or yield of the reaction (Table 1, Entry 1). However, pure water appeared not so useful here, presumably, due to the less activity of catalyst [37]. Notably, the assistance of solvent is apparent in the table as the yield of the reaction is very low in solvent-free conditions even when the reaction mixture stood at 60 °C for 120 min. To optimize the reaction temperature, the reactions were carried out at different temperatures ranging

from 25 to 80 °C. We found that the yield of product was improved and the reaction time was shortened as the temperature was increased to 60°C. The yield did not improve when the temperature was further increased to 80 °C [37]. Since almost 90% of eggshell is composed of CaCO₃ [37], we compared the catalytic activity between CaCO₃ and eggshell in the same conditions (Table 1, Entry 14), These results which are the same as that of Mosaddegh *et al.* and Skelhorn [37,41] reveal that the activity of eggshell is higher than CaCO₃.

Table 1. Optimizations for the model three-component reaction^a



Entry	Solvent	Conditions	Time(min)	Yield ^b (%)
1	EtOH	60 °C/eggshell (0.15 g)	10	91
2	CH ₂ Cl ₂	60 °C/eggshell (0.15 g)	30	53
3	CH ₃ CN	60 °C/eggshell (0.15 g)	45	36
4	H ₂ O	60 °C/eggshell (0.15 g)	45	21
5	EtOH	25 °C/eggshell (0.15g)	10	42
6	EtOH	reflux/eggshell (0.15 g)	10	72
7	EtOH	60 °C/eggshell (0.25 g)	10	90
8	EtOH	60 °C/eggshell (0.1 g)	20	82
9	EtOH	60 °C/eggshell (0.2 g)	10	91
10	EtOH	45 °C/eggshell (0.15 g)	20	71
11	-	60 °C/eggshell (0.15 g)	60	18
12	EtOH	60 °C/-	45	Trace
13	EtOH	60 °C/CaCO ₃ (0.15 g)	20	56

^aEqual amounts (1 mmol) of the reactants were used.

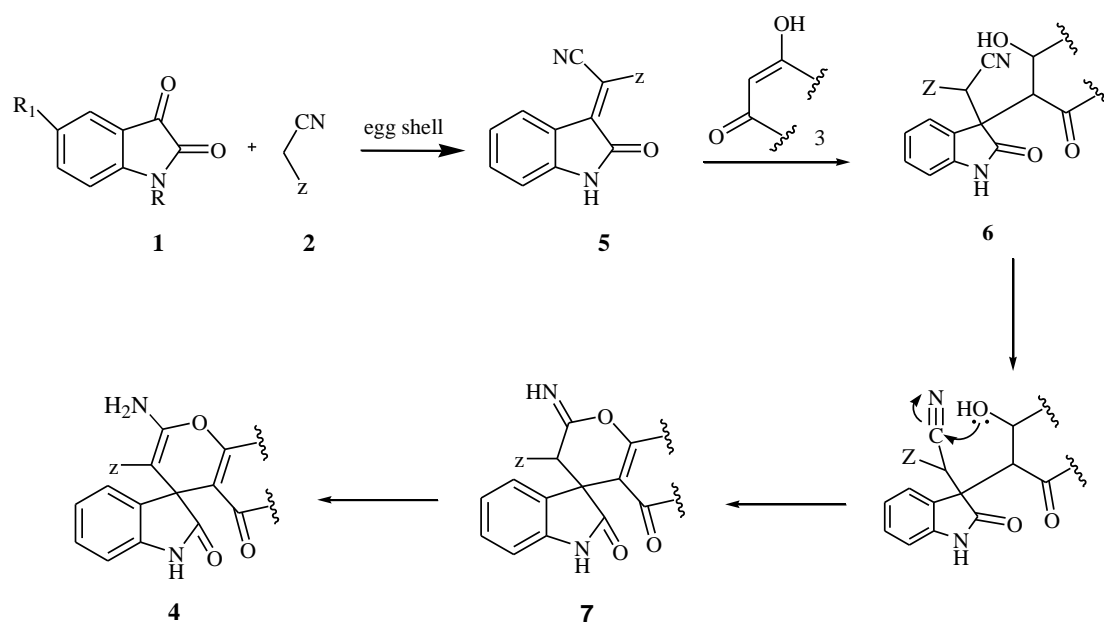
^bIsolated yields of **4a**

With this optimum condition in hand, a series derivatives were synthesized in ethanol in the presence of 0.15 g eggshell. These results are summarized in Table 2. The products have physical data consistent with those reported in the literature as well as the authentic samples prepared from previously reported methods and also the structures of compounds 4a-j which were confirmed by IR, ^1H NMR.

According to the literature [13-23], we proposed the plausible mechanism for the formation of spirooxindole derivatives **4** (Scheme 1). Firstly, we assume that the initial step is a Knoevenagel condensation between isatin derivatives **1** and malononitrile or ethyl cyanoacetate **2** catalyzed by the

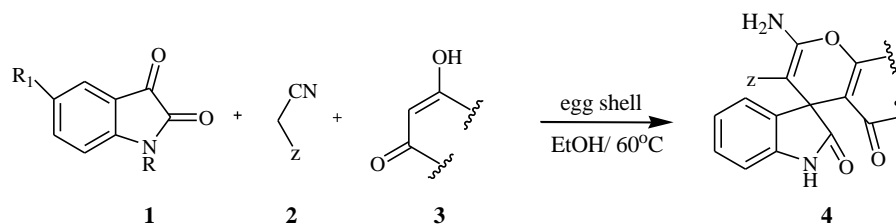
action of egg shell, resulting in the intermediate **5**. Then, the proton of 1,3-diketone **3** is abstracted from active sites of eggshell to form intermediate **6** from Michael addition, followed by cyclization and isomerization to afford the target product **4**.

In order to show the merit of the catalyst, we have compared the obtained results in the synthesis spiro[4H-pyran-oxindole] catalyzed by egg shell, with some methods, as reported in the literature (Table 3). The harsh reaction conditions, technical intricacy, use of expensive and irresability of other methods make our system a better choice [13-23].

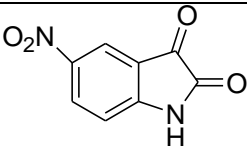
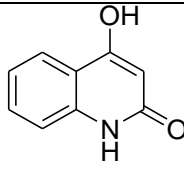
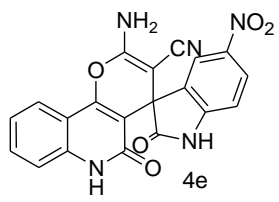
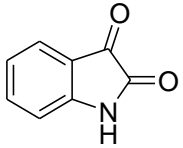
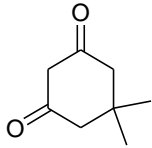
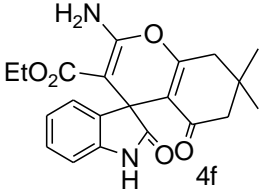
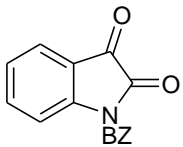
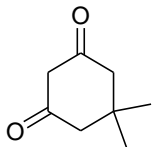
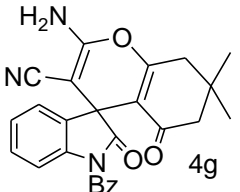
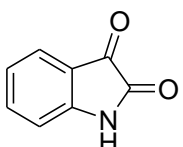
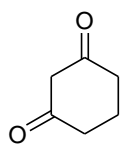
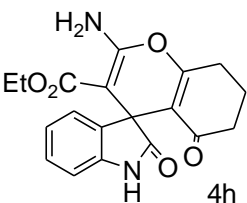
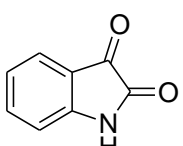
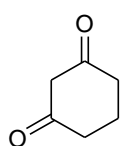
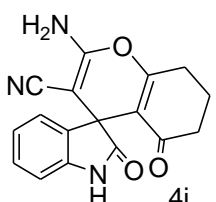
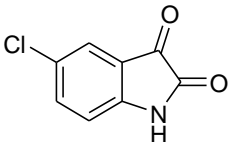
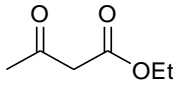
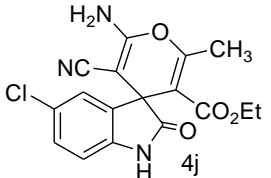


Scheme 1. A plausible mechanism for the synthesis of spiro[(3'H)-indol-3',4-(4H)-pyrans] systems **4** in the presence of eggshell as a catalyst

Table 2. Synthesis of spiro[4H-pyran-oxindole] derivatives



Entry	Isatin	Z	CH- acid	Product	Time(min)	Yield(%) ^b
1		CN			10	91
2		CO ₂ Et			15	90
3		CO ₂ Et			10	90
4		CO ₂ Et			15	88

5		CN			10	91
6		CO ₂ Et			5	91
7		CN			5	92
8		CO ₂ Et			5	89
9		CN			5	91
10		CN			15	90

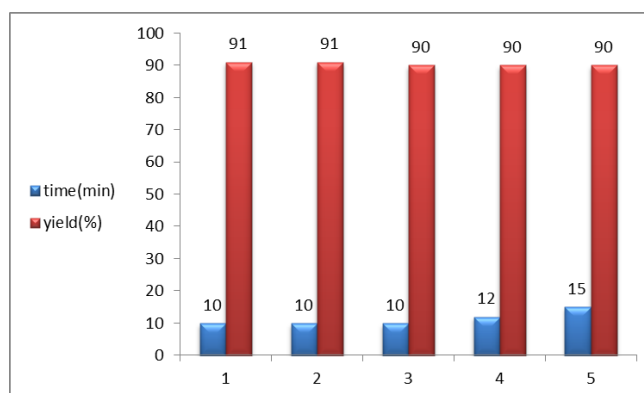
^bIsolated yield

Table 3. Comparison of egg shell with other catalysts for the synthesis of 2-Amino-2',5'-dioxo-5,6-dihydro-spiro[pyrano[3,2-c]quinoline-4,3'-indoline]-3-carbonitrile (**4a**)

Entry	Catalyst and Conditions	Reaction time (min)	Yield(%)	Ref.
1	[BMIm]Cl	5	89	[23]
2	Water/Sonation/50°C	30	90	[15]
3	EtOH/Microwave	5	89	[16]
4	EtOH/egg shell /60°C	10	91	This work

In the next phase of the study, the viability of catalysis by the recycled eggshell was evaluated. In this regard preparation of **4a** was chosen as the model. After completion of the reaction, the eggshell was washed using warm water, drying at room

temperature and then subjected to the next run with the same substrates and the same reaction time. Figure 1 displays similar high conversions obtained after consecutive recycling of the eggshell.

**Figure 1.** Reusability of the catalyst

Conclusion

In summary, an efficient method for the synthesis of spiro[4H-pyran-oxindole] derivatives using simple and readily available starting materials under catalysis of the eggshell, was introduced here. The eggshell acts as a catalyst and can be recovered to be reused several times. The promising points for the presented methodology are as follow: extremely mild and green reaction conditions, good to high yield, short reaction time, cheap and easy purification and not needing column chromatography making it a useful and

attractive process for the synthesis of these important heterocycles.

Acknowledgments

We gratefully acknowledge the financial support from the Research Council of University of Islamic Azad University, Tehran Medical Sciences Branch.

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