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One-pot, organocatalytic synthesis of spirooxindoles using citric acid in aqueous media

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Abstract

A facile and efficient multicomponent synthesis of functionalized spirooxindoles has been described through the reaction of isatin, malononitrile or ethyl cyanoacetate, and CH- acids (1,3-dicarbonyl compounds) in the presence of catalytic amount of citric acid in excellent yields with short reaction times in aqueous ethanol. Also, citric acid catalyzed synthesis of 3,3-diindolyl oxindoles by the condensation of isatin with substituted indoles.

Keywords: Isatin; malononitrile; indole; spirooxindoles; citric acid.

Introduction

The development of multicomponent reactions (MCRs) designed to produce elaborate biologically active compounds has become an important area of research in organic, combinatorial, and medicinal chemistry. The MCR strategy offers significant advantages over conventional linear-type synthesis due to its flexible, convergent, and atom efficient nature [1-3].

Compounds carrying the indole moiety exhibit antibacterial and antifungal activities [4]. Furthermore, it has been reported that sharing the indole 3-carbon atom in the formation of spiroindoline derivatives highly enhances the biological activity [5-6]. The heterocyclic spirooxindole ring is a core structure presenting in a number of pharmaceuticals and natural products, including cytostatic alkaloids such as spirotryprostatins A, B, and strychnophylline [7-8]. The unique structural array and the highly pronounced pharmacological activity displayed by the class of spirooxindole compounds have made them attractive synthetic targets [9-12].

Among the heterocyclic spirooxindole ring system, functionally substituted 4H-chromenes have received considerable attention due to their wide range of useful biological properties, which include spasmolitic-, diuretic-, anticoagulant-, anticancer-, and antianaphylactic activities [13-14]. A number of methods have been developed for the synthesis of 4H-chromenes during the past two decades. One-pot, three-component condensation of isatin, cyclic 1,3-diketones and malononitrile is the most convenient method for the preparation of these compounds. In this context, some methods and catalysts have been reported [15-21]. Despite the availability of these methods, further studies are still necessary for the

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essence of facile, environmental and economical multicomponent methodology.

Organocatalysis has emerged as an important area of research over the last decade. Compared with biocatalysts and metal catalysts, organocatalysts are usually more stable, more environmentally friendly, more readily available, less expensive and can be applied using less demanding reaction conditions, such as rigorously anhydrous or anaerobic conditions [22-24].

Considering the biomedical applications of spirooxindole derivatives and in view of our ongoing efforts to explore newer reactions for synthesis of heterocyclic compounds [25-27], we were prompted to exploit the catalytic potential of citric acid for a facile and efficient multicomponent synthesis of functionalized spirooxindoles through the reaction of isatin, malononitrile or ethyl cyanoacetate, and CH- acids (1,3-dicarbonyl compounds) in aqueous media.

Experimental

General

Chemicals were purchased from Merck, Fluka and Aldrich Chemical Companies. IR spectra were run on a Bruker Tensor 27 spectroscopy. The NMR spectra were recorded on a Bruker AC 250 MHz spectrometer for DMSO-d_6 solutions. Melting points were recorded in open capillary tubes on an Electrothermal type 9100 melting point apparatus.

General Procedure for synthesis of spirooxindols (4a-p).

A mixture of isatins (**1a-1b**, 1mmol), activated methylene (**2a-2b**, 1mmol), CH-acid compounds (**3a-3d**, 1mmol) and citric acid (0.038 g, 20 mol%) in H_2O:Ethanol(2:1, 3ml) was stirred at 80 ^oC for the appropriate time as indicated in Table 1. The progress of reactions was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature. The solid was filtered off, washed with water (3×5 mL), and cold ethanol (2×2 mL) to afford the product **4a-p**.

General procedure for the synthesis of diindolyloxindoles (6a-e)

A mixture of isatins (**1a-1b**, 1mmol), indoles (**5a-5c**, 2mmol), and citric acid (0.038 gr, 20 mol%) in H_2O:Ethanol (2:1, 3 mL) was stirred at 80 ^oC for the appropriate time as indicated in Table 2. The progress of reactions was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature. The solid was filtered off, washed with water (3×5 mL), and cold ethanol (2×2 mL) to afford the product **6a-e**.

Selected spectral data

2-Amino-5-oxo-7,7-dimethyl-spiro[(4H)-5,6,7,8 tetrahydrochromene-4,3'-(3'H)-indol]-(1'H)-2'-one carbonitrile (4a)

White powder, m.p. 295-297 °C, reported m.p. 292-294 °C [18], IR(KBr): 3306, 3135, 2960, 2192, 1718, 1682, 1652, 1603, 1468, 1347,1323, 1220, 1055, 744, 676, 611 cm^{-1}; ^{1}HNMR (250MHz, DMSO-d6): δ= 10.36 (s, 1H, NH), 7.19 (s, 2H, NH_2), 7.13– 6.73 (m, 4H, ArH), 2.52–2.47 (m, 2H, CH_2), 2.18–2.08 (m, 2H, CH_2), 1.00–0.97 (m, 6H, CH_3) ppm.

2-Amino-5,7-dioxo-spiro[(3'H)-5'-fluoro-indol-3',4,4(H)-5,6,7,8 tetrahydropyrano (2,3-d) pyrim-idine]-(1'H)-2'-one-3-carbonitrile (4g)

Light pink powder, m.p. 280-283 °C, IR(KBr): 3350, 3297, 3155, 2959,

2190, 1726, 1680, 1652, 1486, 1350, 1227, 880, 809, 794 cm^{-1}; ^{1}HNMR (250MHz, DMSO-d6): δ= 12.23(br, s, 1H, NH), 11.09(s, 1H, NH), 10.45(s, 1H, NH), 7.37(s, 2H, NH_2) , 7.12(d, 1H, J= 7.5, ArH), 6.99-6.96(m, 1H, Ar), 6.76-6.73(m, 1H, Ar) ppm; ^{13}CNMR (62.5MHz, DMSO-d6): δ= 178.2, 161.9, 160.5, 158.7, 153.9, 149.7, 138.7, 135.8, 117.3, 115.2, 114.8, 112.4, 87.8, 57.6, 47.5 ppm.

Ethyl-2-amino-5,7-dioxo-spiro[(3'H) -5'-fluoro-indol-3',4,4(H)-5,6,7,8-tetrahydro pyrano (2,3-d) pyrimidine]-(1'H)2'-one-3-carboxylate (4h)

Light pink powder, m.p. 234-235 °C, IR(KBr): 3230, 3181, 3155, 2920, 1703, 1679, 1489,1328, 1118, 808, 691, 642 cm^{-1}; ^{1}HNMR (250MHz, DMSO-d6): δ= 12.02(br, s, 1H, NH), 10.96 (s, 1H, NH), 10.26(s, 1H, NH), 7.98(s, 2H, NH_2), 7.09-6.85(m, 2H, ArH), 6.81(s, 1H, ArH), 3.70-3.39(m, 2H, CH_2), 1.03-0.77(m, 3H, CH_3) ppm; ^{13}CNMR (62.5MHz, DMSO-d6): δ= 179.8, 167.8, 161.7, 160.1, 159.4, 152.82, 149.6, 140.7, 137.6, 113.8, 111.4, 108.8, 59.6, 47.1, 13.51 ppm.

2-Amino-5-oxo-spiro[(3'H)-5'-fluoro-indol-3',4-4(H)-pyrano(3,2-c)chromen]-(1'H)-2'-one-3-carbonitrile (4k)

Light pink powder, m.p. >300 °C, IR(KBr): 3357, 3292, 3209, 2204, 1711, 1673, 1486, 1362, 1176, 1109, 976, 777, 694 cm^{-1}, ^{1}HNMR (250MHz, DMSO-d6): δ= 10.67(s, 1H, NH), 7.92(d, 1H, J= 7.5, ArH), 7.79-7.72(m, 1H, ArH), 7.68(s, 2H, NH_2), 7.56-7.42(m, 2H, ArH), 7.23(d, 1H, J= 7.5, ArH), 7.03(t, 1H, ArH), 6.85-6.80(m, 1H, ArH) ppm, ^{13}CNMR (62.5 MHz, DMSO-d6): δ= 177.6, 158.9, 155.7, 152.5, 138.87, 135.2, 135.1, 134.1, 125.4, 123.2, 117.3, 117.1, 115.4, 113.0, 112.8, 112.4, 110.7, 101.3, 57.0, 48.2 ppm.

Ethyl-2-amino-5-oxo-spiro[(3'H)-5'-fluoro-indol-3',4-4(H)-pyrano(3,2-c) chromen]-(1'H)-2'-one-3-carboxylate (4l)

White crystal, m.p. 208-210 °C, IR(KBr): 3387, 3274, 2981, 2925, 1710, 1695, 14898, 1358, 1110, 770 cm^{-1}, ^{1}HNMR (250MHz, DMSO-d6): δ= 10.42(s. 1H, NH), 8.15(s, 2H, NH_2), 8.00(d, 1H, J= 7.5, ArH), 7.75-7.69(m, 1H, rH), 7.53-7.41(m, 2H, ArH), 7.01-6.88(m, 2H, ArH), 6.72-6.67(m, 1H, ArH), 3.95-3.77(m, 2H, CH_2), 0.832(t, 3H, J=7, CH_3) ppm, ^{13}CNMR(62.5MHz, DMSO-d6): δ= 179.3, 167.5, 159.1, 158.3, 154.5, 152.4, 140.9, 136.8, 133.9, 125.2, 123.4, 116.8, 114.4, 114.1, 113.0, 111.9, 111.5, 109.2, 75.61, 59.6, 48.3, 13.6 ppm.

6-Amino-3-methyl-1-phenyl spiro[(3'H)-5'-fluoro-indol-3',4-4(H)-pyrano(3,2-d)pyrazol]-(1'H)-2'-one-5-carbonitrile (4o)

Light pink powder, m.p. 207-209 °C, IR (KBr): 3362, 3310, 3188, 2980, 2207, 1709, 1660, 1526,1488, 1401, 1182, 1073, 812, 796, 752, 695 cm^{-1}; ^{1}H NMR (250MHz, DMSO-d6): δ= 10.73(s, 1H, NH), 7.76(d, 2H, ArH), 7.58(s, 2H, J= 7.5, NH_2), 7.49(t, 2H, J= 7.5, ArH), 7.33(t, 1H, J= 7.5, ArH), 7.17-7.07(m, 2H, ArH), 6.94-6.89(m, 1H, ArH), 1.57(s, 3H, CH_3) ppm. ^{13}CNMR (62.5MHz, DMSO-d6): δ= 177.9, 161.5, 145.4, 144.3, 138.17, 137.7, 134.5, 134.3, 129.9, 127.0, 120.6, 118.3, 116.4, 116.0, 113.4, 112.9, 111.3, 96.3, 56.2, 48.8, 12.1 ppm.

Ethyl 6-amino-3-methyl-1-phenyl spiro[(3'H)-5'-fluoro-indol-3',4-4(H)-pyrano(3,2-d)pyrazol]-(1'H)-2'-one-5-carboxylate (4p)

Light pink powder, m.p. 199-200 °C, IR (KBr): 3410, 3357, 3173, 2981, 1703, 1679, 1641, 1512, 1486, 1397, 1293, 1130, 1043, 800, 763, 694 cm^{-1}, ^1H NMR (250MHz, DMSO-d6): δ= 10.57(s, 1H, NH), 8.25(s, 2H, NH_2), 7.80-7.77(m, 2H, ArH), 7.52-7.46(m, 1H, ArH), 7.35-7.29(m, 2H, ArH), 7.01-6.80(m, 3H, ArH), 3.77-3.67(m, 2H, CH_2), 1.60(s, 3H, CH_3), 0.77-0.72(m, 3H, CH_3) ppm. ^{13}CNMR (62.5MHz, DMSO-d6): δ= 179.8, 168.1, 161.8, 144.5, 138.8, 137.7, 129.8, 126.8, 120.4, 98.0, 59.53, 48.44, 13.58, 12.18 ppm.

3,3-Di(1H-indol-3-yl)indolin-2-one (6a)

White powder, m.p. 308-310 °C, reported m.p. 312°C [28], IR (KBr): 3428, 3321, 1708, 1613, 1469, 1171, 1103, 757, 736 cm^{-1}, ^1H NMR (250MHz, DMSO-d6): δ= 10.93 (s, 2H, NH), 10.58 (s, 1H, amidic NH), 7.35-7.02 (m, 6H, ArH) , 6.99-6.74 (m, 8H, ArH) ppm.

3,3-Di(5-bromo-1H-indol-3-yl)indolin-2-one (6c)

White powder, m.p. 315-317 °C, reported m.p. 320-321°C [28], IR(KBr): 3420, 3315, 1712, 1680, 1614, 1467, 1099, 885, 795, 749, 650 cm^{-1}, ^1H NMR (250MHz, DMSO-d6): δ= 11.20 (s, 2H, NH), 10.71 (s, 1H, amidic NH), 7.62-6.88 (m, 12H, ArH) ppm.

5–Fluoro-3,3-Di(1H-indol-3-yl)indolin-2-one (6d)

White powder, m.p. 315-317 °C, reported m.p. 320-321°C [28], IR(KBr): 3410, 3322, 1705, 1460, 1170, 905, 755 cm^{-1}, ^1H NMR (250MHz, DMSO-d6): δ= 11.86(s, 1H,amidic NH), 10.5(s, 2H, NH), 7.72-6.64(m, 13H, ArH), ^{13}CNMR (62.5MHz, DMSO-d6): δ= 171.2, 162.6, 138.9, 132.0, 127.4 122.8, 122.1, 120.1, 116.9, 115.3, 114.3, 111.6, 54.6 ppm.

5-Fluoro- 3,3-Di(5-bromo-1H-indol-3-yl)indolin-2-one (6e)

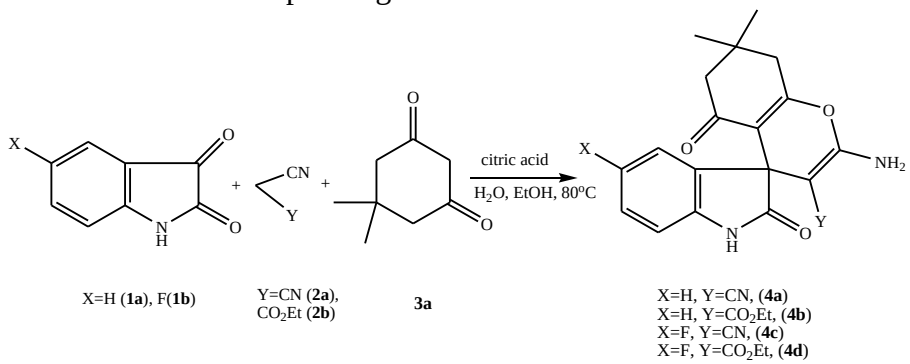
White powder, m.p. 325-326 °C, IR(KBr): 3383, 3307, 1691, 1484, 1454, 1175, 884, 793, 633 cm^{-1}, ^1H NMR (250MHz, DMSO-d6): δ= 11.26 (s, 2H, NH), 10.77 (s, 1H, amidic NH), 7.36-6.94 (m, 11H, ArH) ppm, ^{13}CNMR (62.5MHz, DMSO-d6): δ= 178.83, 137.87, 136.13, 136.0, 127.52, 126.62, 126.58, 124.94, 117.50, 117.45, 117.40, 114.36, 113.58, 112.58, 111.58, 110.50, 53.14, 56.10 ppm.

Results and discussion

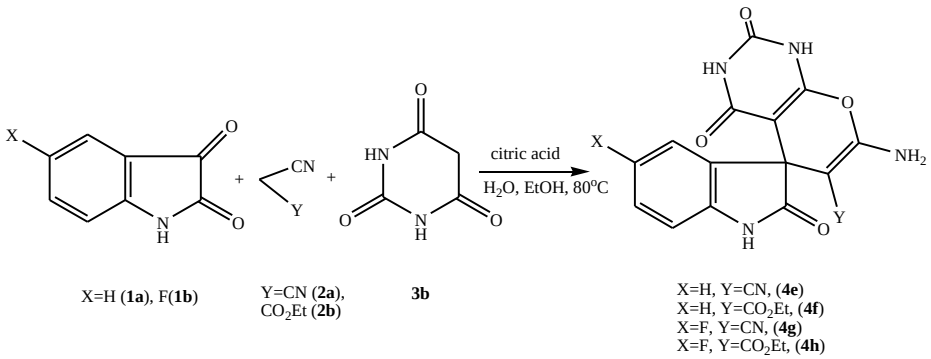
In our initial study, the evaluation of various conditions was studied for the synthesis of spirooxindole derivatives. After some preliminary experiments, it was found that a mixture of isatin, malononitrile, and dimedone in the presence of a catalytic amount of citric acid could afford 2-amino-5-oxo-7,7-dimethyl spiro[(4H)-5,6,7,8-tetrahydrochromene-4,3’-(3’H)-indol]-(1’H)-2’-one-carbonitrile **4a**. After systematic screening, the best result is obtained when the reaction is carried out for 10 min with 20 mol % of citric acid in aqueous ethanol (2:1, H_2O–EtOH) at 80 °C.

Under the optimized set of reaction conditions, isatins **1a-1b** were allowed to undergo citric acid-catalyzed multicomponent reaction with malononitrile or ethyl cyanoacetate **2a-2b** and dimedone **3a** in an equimolar ratio in aqueous ethanol at 80 °C. The results are given in Table 1. After the reactions were over (TLC), the resulting solids were filtered and washed from water to yield pure substituted spirooxindoles **4a–4d** (Scheme 1 and Entries 1-4, Table 1).

Additionally, the reaction of isatin with malononitrile or ethyl cyanoacetate and barbituric acid **3b** also proceeded smoothly and corresponding spirooxindoles **4e-4h** were prepared successfully (Scheme 2 and Entries 5-8, Table 1).



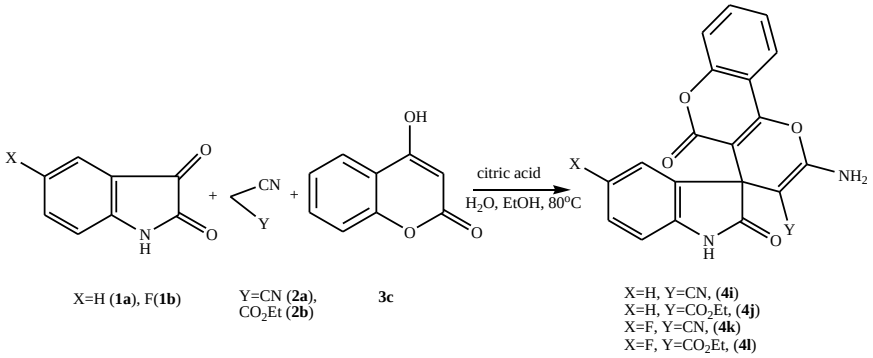
Scheme 1. Synthesis of spirooxindols (**4a-d**) from dimedone



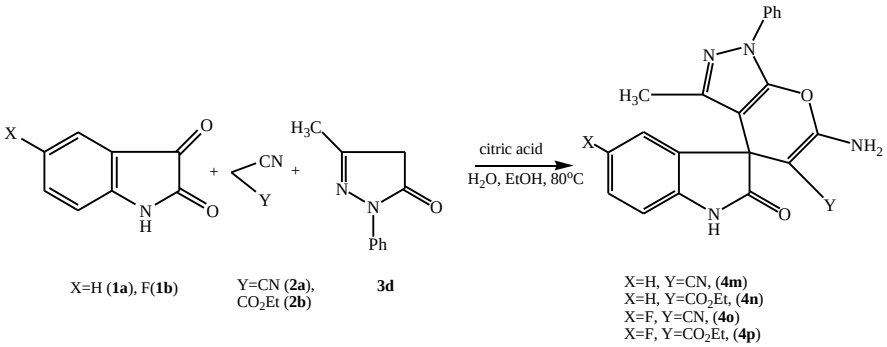
Scheme 2. Synthesis of spirooxindols (**4e-h**) from barbituric acid

To further explore the potential of this protocol for heterocyclic synthesis, we investigated one-pot reactions involving 4-hydroxy coumarin **3c**. To our delight, under the above optimized conditions, the reactions proceeded smoothly and desired spirooxindoles products **4i-4l** were obtained in good yields (Scheme 3 and Entries 9-12, Table 1).

Encouraged by these results, we carried out the reaction of 3-methyl-1-phenyl-2-pyrazolin-one (**3d**) instead of dimedone (**3a**) with isatin and malononitrile or ethyl cyanoacetate as a ternary mixture at 80 °C, which afforded the corresponding spirooxindole, through addition and cyclization in good yields within a short period of time (Scheme 4 and Entries 13-16, Table 1).



Scheme 3. Synthesis of spirooxindols (**4i-l**)



Scheme 4. Synthesis of spirooxindols (**4m-p**)

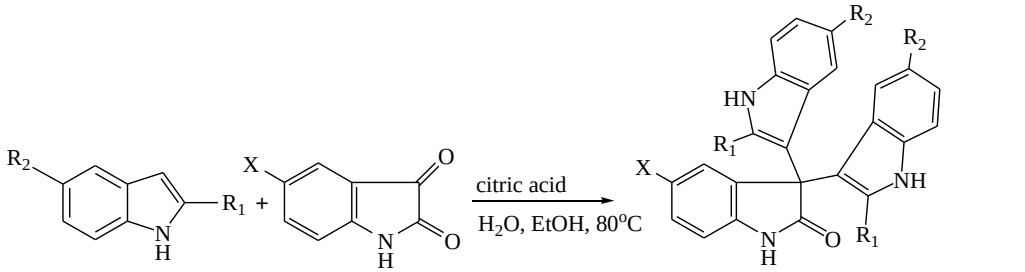
Table 1. Synthesis of spirooxindoles

Entry	X	Y	CH-acid	Product	Time (min)	Yield (%)	m.p. (˚C)
1	H	CN	**3a**	**4a**	10	81	295-297
2	H	CO_2Et	**3a**	**4b**	30	72	230-232
3	F	CN	**3a**	**4c**	10	90	296-297
4	F	CO_2Et	**3a**	**4d**	12	82	272-274
5	H	CN	**3b**	**4e**	40	85	271-274
6	H	CO_2Et	**3b**	**4f**	120	80	210-212
7	F	CN	**3b**	**4g**	30	92	280-283
8	F	CO_2Et	**3b**	**4h**	180	87	234-235
9	H	CN	**3c**	**4i**	10	95	290-291
10	H	CO_2Et	**3c**	**4j**	15	80	215-216
11	F	CN	**3c**	**4k**	10	95	>300
12	F	CO_2Et	**3c**	**4l**	13	88	208-210
13	H	CN	**3d**	**4m**	30	95	235-238
14	H	CO_2Et	**3d**	**4n**	60	70	208-210
15	F	CN	**3d**	**4o**	25	97	207-209
16	F	CO_2Et	**3d**	**4p**	180	70	199-200

These results prompted us to extend this process to the synthesis of 3,3-diindolyl oxindoles by the condensation of isatin with substituted indoles in the presence of citric acid (Scheme 5). Some methods have been developed for the synthesis of this class of compounds in the literature [28-32].

At the outset, isatins (**1a**) were reacted with indoles (**5a**) in the presence of citric acid in aqueous ethanol for 15 min, which yielded the diindolyl oxindole ***6a*** in 95% yield at 80ºC. Only 20 mol % of citric acid is sufficient to catalyze the reaction; no significant change in the yield of the products was observed using higher mol % of citric acid. But, in absence of citric acid, the reaction did not yield any product even after 4 h. As a further application of this green protocol, we turned our attention towards a range of indole derivatives. Interestingly, substituted indoles underwent smooth coupling with isatin to give the corresponding diindolyl oxindoles **6a-6e** in high yields (Scheme 5, Table 2).

Proposed mechanism for the synthesis of spirooxindole **4** was described in Scheme 6. Typically, in the first step, isatin is activated by citric acid as an acid catalyst and react with malononitrile **2a** to generate isatylidene malononitrile derivative **7** through Knoevenagel condensation. Then, **7** is attacked *via* Michael addition of dimedone **3a** to give the intermediate **8** followed by the cycloaddition of hydroxyl group to the cyano moiety to form the desired product **4a** (Scheme 6) [18].



R_1=R_2=H, (**5a**)
R_1=CH_3, R_2= H (**5b**)
R_1= H, R_2= Br (**5c**)

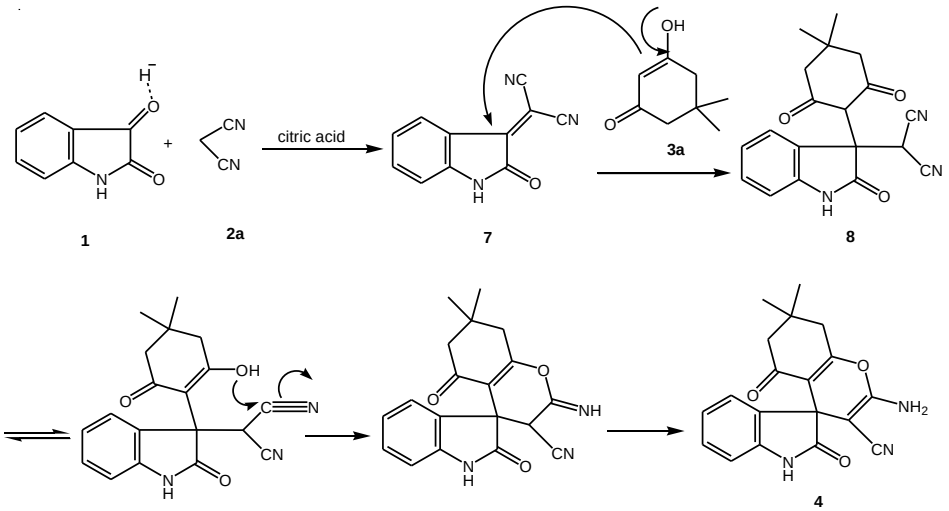
X=H (**1a**), F(**1b**)

R_1=R_2=X=H (**6a**)
R_1=CH_3, R_2=X=H (**6b**)
R_1=H, R_2=Br, X=H (**6c**)
R_1=R_2, X=F (**6d**)
R_1=H, R_2=Br, X=F (**6e**)

Scheme 5. Synthesis of 3,3-diindolyloxindoles(**6a-e**)

Table 2. Synthesis of 3,3-diindolyloxindoles **6a-e**

Entry	X	R_1	R_2	Product	Time (min)	Yield (%)
1	H	H	H	**6a**	15	95
2	H	CH_3	H	**6b**	15	70
3	H	H	Br	**6c**	15	85
4	F	H	H	**6d**	15	85
5	F	H	Br	**6e**	15	90



Scheme 6. Proposed mechanism for the synthesis of spiro derivative **4a**

Table 3. Comparison of the efficiency of various catalysts in the synthesis of **4a**

Entry	Catalyst and conditions	Time	Yield (%)	Ref.
1	$KAl(SO_4)_2.12H_2O$, H_2O, 80 °C	25 min	90	[15]
2	Sodium stearate, H_2O, 60 °C	3 h	95	[16]
3	Tetrabutylammonium bromide, neat, 100 °C	40 min	90	[17]
4	Triethylbenzylammonium chloride, H_2O, 60 °C	3 h	90	[18]
5	N-Sulfonic acid modified poly(styrene-co-maleic anhydride), EtOH, Reflux	30 min	84	[20]
6	Choline chloride/urea, 80 °C	1 h	95	[21]
7	Citric acid, H_2O/EtOH (2:1), 80 °C	10 min	81	-

In order to show the merit of the present work, this method has been compared with other reported catalysts in the reaction of isatin, malononitrile and dimedone. The results of the synthesis **4a** are collected in Table 3, which shows citric acid is a more efficient catalyst. However, citric acid as a catalyst is nontoxic, inexpensive and easy to handle.

Conclusion

In conclusion, this paper describes a convenient and efficient process for the synthesis of functionalized spirooxindoles through the one-pot reaction of isatins, malononitrile or ethyl cyanoacetate, and CH- acids (1,3-dicarbonyl compounds) using catalytic amount of citric acid in aqueous media. Also 3,3-diindolyl oxindoles have been synthesized by the condensation of isatin with substituted indoles in the presence of citric acid at 80 ^oC. The catalyst is readily available and inexpensive and can conveniently be handled and removed from the reaction mixture. The simple procedure combined with low reaction times and low cost make this method economic,

benign, and a user-friendly process for the synthesis of substituted oxindoles of biological and medicinal importance.

Acknowledgements

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