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ARTICLE

New Method for Synthesis of Indole Derivatives *via* Zirconium (IV) Chloride Catalyst

Seyedeh Fatemeh Hojati * and Atefeh Sadat Kaheh

Department of Chemistry, Hakim Sabzevari University, Sabzevar, 96197-76487, Iran

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Abstract: The present paper suggests a new and efficient method for the synthesis of symmetrical and unsymmetrical 3,3-di(indol-3-yl)indolin-2-ones catalyzed by $ZrCl_4$ from isatin and indole. Furthermore, it facilitates obtaining the symmetrical tris(indolyl)methane. In addition, to resolve these issues, the zirconium (IV) chloride provides the possibility of synthesizing methane-symmetric tris(indolyl) with the proposed novel method.

Keywords: 3, 3-di(indol-3-yl)indolin-2-ones, Indole, Tris(indolyl)methane, Zirconium (IV) chloride.

Introduction

Most recently, indole derivatives have attracted special attention, because they are pharmacologically and biologically active compounds[1] and can be used as versatile intermediates in the synthesis of natural products[2]. Among various indole derivatives, 3,3-di(indol-3-yl)indolin-2-ones are of great interest and display different pharmaceutical activities, such as antiproliferative[3], anti-bacterial[4], anti-inflammatory[5], laxative[6] and anticonvulsant properties[7]. Symmetrical tris(indol-3-yl)methanes are also well-known and constitute a major class of indole derivatives. These compounds can be used as hydride acceptors[8], cytotoxic agents[9] and dyes for physicochemical studies [10].

Although various pharmaceutical and industrial applications have been suggested for these compounds, relatively few methods have been published for preparing these biologically active compounds[11]. The common progress for the synthesis of 3,3-di(indol-3-yl)indolin-2-ones is the condensation of isatin with 2 equivalents of indole in the proximity of either protic or Lewis acid under different reaction conditions[12]. Despite the performance of some reported techniques, most of them suffer from several disadvantages including long reaction times, low production rates, harsh reaction condition, hard and time-consuming work-up procedure and the use of expensive and/or toxic reagent and/or solvent. Therefore, developing new methods that will take into account factors, like non-toxicity, availability, high reactivity of catalyst and operational simplicity is still in demand[13].

Given their efficiency, cost-effectiveness, easy availability and non-toxicity, zirconium salts have recently attracted much attention as catalysts in organic transformations[14-16]. The current research proposes a highly efficient method for the synthesis of symmetrical and unsymmetrical 3,3-di(indol-3-yl)indolin-2-ones and tris(indol-3-yl)methane in the proximity of catalytic amounts of $ZrCl_4$ in a non-toxic medium.

Reddy et al. have reported the use of isatin with indoles and a catalytic amount of molecular iodine[11]. But, in the case of unsymmetrical 3,3-di(indol-3-yl)indolin-2-ones, only three reports are available in the literature[12]. Wang et al. have studied an ultrasound irradiation method in the proximity of ceric ammonium nitrate (CAN) for 1-5 h[12]. Moghadam et al. have investigated the reaction in the ionic-liquid *N*,*N*,*N*,*N*-tetramethyl-guanidinium trifluoroacetate (TMGT) for 1 h[17].

In the case of 3,3-di(indol-3-yl)indolin-2-ones, Chandrasekaran et al. have conducted the

***Corresponding Author:** Seyedeh Fatemeh Hojati **Email**: hojatee@yahoo.com

synthesis of various isatines and indoles by $Cu(OTf)_2$ catalysis in 15-45 minutes[18]. Vuram et al. have proven that a time ranging of 5 minutes in the presence of solvent-free and catalyst-free reaction conditions is an attractive proposition in numerous microwave-assisted reactions[19]. Also, a reaction time of 2.5 h has been reported for using ZnO nanorods in aqueous medium[20]. EtOH and water medium (60:40) in the proximity of $FeCl_3 \cdot 6H_2O$ and ultrasonic irradiation in a range time of 5-25 minutes have been investigated by Khorshidi and Tabatabaeian[21]. Moreover, Makarem et al. have suggested a new electrochemical procedure using EtOH/propanol as a solvent with reaction time ranging from 60 to 240 minutes[22]. Also, a heterogeneous catalyst (Kaolin/KOH) in the presence of MeOH as a solvent has been reported with reaction time of 138-470 minutes[23]. Ziarani et al. have studied the synthesis of 3,3-di(indol-3-yl)indolin-2-ones utilizing sulfonic acid functionalized nanoporous SBA-Pr-SO_3H[24]. Furthermore, Nadine et al. have investigated the chemical reaction using chiral scandium(III) and indium(III) pybox complexes[25]. Recently, synthesis in an aqueous medium has been reported using diethanolamine as a base catalyst[26]. Kamal et al. reported a 10-60 minutes procedure using MeCN as a solvent in the presence of iron trichloride ($FeCl_3$) catalyst[27].

Materials and Methods

All materials used in this research were of commercial reagent grade which are produced by Merck Company. The IR spectra were obtained by using a Shimadzu 435-U-04 spectrophotometer (KBr pellets). The ^{1}H-NMR spectra were recorded on a Bruker AVANCE of 400 MHz. The melting point was measured by a Bamstead electrothermal apparatus. The elemental analyses were conducted in a Heraeus CHN-O-rapid analyzer. The mass spectra were recorded on a PLATFORM 8379E in 70 eV.

General Procedure for Synthesis of Symmetrical 3,3-di(1*H*-indol-3-yl)-2-oxindole (3a-3k)

A mixture of isatin (1 mmol), indole (2 mmol) and $ZrCl_4$ (5 mol%) in EtOH (5 ml) was stirred at 50 °C until the starting materials disappeared, as monitored by TLC (eluent: EtOAc /*n*-hexane, 3:4). After the reaction was complete, ice water was added to the mixture and the precipitate was isolated by filtration. Further, purification of the product was accomplished by recrystallization from ethanol.

General Procedure for Synthesis of Unsymmetrical 3,3-di(1*H*-indol-3-yl)-2-oxindole (5a-5h)

The catalytic amount of $ZrCl_4$ (5 mol%) was added to a 25 ml round–bottomed flask containing 3-hydroxy-3-indolylindolin-2-ones (1 mmol) and indole (1 mmol) in EtOH (5 ml) and stirred at 50 °C for an appropriate time (Table 3). After the reaction was complete, as indicated by TLC (eluent, EtOAC/*n*-hexane, 1:2), the mixture was poured into ice water and the crude product was obtained *via* filtration. The precipitate was purified by recrystallization from ethanol.

Preparation of Tris(indol-3-yl)methane (7)

$ZrCl_4$ (5 mol%) was added to a mixture of indole (3 mmol) and triethyl orthoformate (1.3 mmol) at 50 °C. The progress of the reaction was monitored by TLC (eluent, Ethyl acetate/*n*-hexane, 1:2). The residue was recrystallized in ethanol to afford the pure product. In the following, specific descriptions of the compounds selected will be discussed:

3,3-Di(1H-indol-3-yl)-2-oxindole (3a)

Mp. 310-312 ºC [**Lit**.[17] mp. 311-313 ºC]. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.79 (t, *J* = 7.7 Hz, 2H), 6.85 (s, 2H), 6.93 (t, *J* =7.5 Hz, 1H), 6.68–7.03 (m, 3H), 7.21–7.24 (m, 4H), 7.36 (d, *J* = 8.1 Hz, 2H), 10.59 (s, 1H, NH), 10.95(s, 2H, NH). IR (KBr, cm^{-1}): 3415, 3150, 1709. Anal. Calcd for $C_{24}H_{17}N_3O$: C, 79.34; H, 4.68; N, 11.57. Found: C, 79.35; H, 4.72; N 11.50%.

3-(1H-Indol-3-yl)-3-(1-methyl-1H-indol-3-yl)-2-oxindole (5a)

Mp. 297–299 ºC [**Lit.**[17] mp. 298-300 ºC]. ^{1}H-NMR (400 MHz, DMSO-*d*6): δ 3.69 (s, 3H), 6.77–6.86 (m, 4H), 6.90–7.03 (m, 3H), 7.06 (s, 1H),7.17–7.25 (m, 4H), 7.35 (d, *J* = 8.4 Hz, 1H), 10.60 (s, 1H),10.83 (s, 1H, NH), 10.94 (s, 1H, NH). IR (KBr, cm^{-1}): 3440, 3399, 3123. Anal. Calcd for $C_{25}H_{19}N_3O$: C, 79.56; H, 5.04; N 11.14. Found: C, 79.49; H, 4.97; N 11.17%.

3-Hydroxy-3-(1H-indol-3-yl)indolin-2-one (4a)

Mp. 293 – 295 ºC [**Lit**.[19] mp 293 – 295 ˚C]. ^{1}H NMR (400 MHz, DMSO-*d*6): δ 10.98 (s, 1H), 10.34 (s, 1H), 7.35 (t, 2 H), 7.27 - 7.24 (m, 2H), 7.09 (d, 1H), 7.03 - 7.02 (m, 1H), 6.98 - 6.86 (m, 4H), 6.36 (s, 1H). IR (KBr, cm^{-1}): 3263, 1710, 1616, 1549. Anal. Calcd for

$C_{16}H_{12}O_2N_2$,**:** C, 72.73; H, 4.54; N, 10.61. Found: C, 72.68; H 4.59; 10.70%.

3-Hydroxy-3-(2-methyl-1H-indol-3-yl)indolin-2-one (4b)

Mp. 177 – 179 ˚C [**Lit**.[19] mp 177– 179 ˚C]. ^{1}H-NMR (400 MHz, DMSO-d6): δ 10.87 (s, 1H), 10.32 (s, 1H), 7.24 - 7.17 (m, 3H), 6.96 - 6.88 (m, 4H), 6.73 - 6.70 (m, 1H), 6.26 (s, 1H), 2.33 (s, 3H). IR (KBr, cm^{-1}): 3348, 3229, 3034. Anal. Calcd for $C_{17}H_{14}O_2N_2$ **:**C, 73.38; H, 5.04; N, 10.07. Found: C, 73.32; H 5.11; N, 10.04%.

N-benzyl-3-hydroxy-3-(1H-indol-3-yl)indolin-2-one (4c)

Mp. 121 – 123˚C **[Lit.**[19] mp 121 - 123˚C]. ^{1}H-NMR (400 MHz, DMSO-*d*6): δ 11.02 (s, 1H), 7.38 - 7.23 (m, 9H), 7.10 (s, 1H), 7.04 - 6.97 (m, 3H), 6.82 (t, 1H), 6.58 (s, 1H), 4.92 (s, 2H). IR (KBr, cm^{-1}): υ 3295, 3029, 1698. Anal. Calcd for $C_{23}H_{18}O_2N_2$:C, 77.97; H, 5.08; N, 7.91. Found: C, 77.90; H 5.14; N, 7.88%..

3,3,3-Tris(1H-indol-3-yl)methane (7)

Mp. 236-238 ºC [**Lit.**[28] mp. 238-240 ºC]. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.19 (s, 1H), 6.88 (t, *J*=7.8 Hz, 3H), 6.92 (s, 3H), 7.03 (t, *J* =7.8 Hz, 3H), 7.37 (d, *J*= 7.8 Hz, 3H), 7.47 (d, *J*=7.8 Hz, 3H), 7.95 (s, 3H, NH). IR (KBr, cm^{-1}): 3395, 3048, 1484. Anal. Calcd for $C_{25}H_{19}N_3$: C, 83.10; H, 5.26; N, 11.63. Found: C, 83.15,;H, 5.19; N 11.59%.

Results and Discussion

At first, the reaction of isatin and two equivalent indoles was carried out in the presence of catalytic amounts of $ZrCl_4$ (Figure 1). Several experiments were performed to optimize the reaction condition (Table 1). The best result was obtained when a mixture of isatin (1 mmol) and indole (2 mmol) in EtOH (5 ml) reacted in the presence of $ZrCl_4$ (5 mol%) at 50 °C and a corresponding 3,3-di(1*H*-indol-3-yl)-2-oxindole (**3a**) was generated in 95% yield after 23 min (Table 1, entry 2). In order to investigate the generality of the current method, various isatin derivatives were made to react with substituted indoles under optimized reaction conditions (Figure 2). Corresponding symmetrical 3,3-di(1*H*-indol-3-yl)-2-oxindoles were obtained in good to excellent yields. The results are summarized in Table 2. Furthermore, pyrrole reacted efficiently with isatin under similar conditions to afford 3,3-di(pyrrol-2-yl)-2-oxindole (Table 2, entry 12).

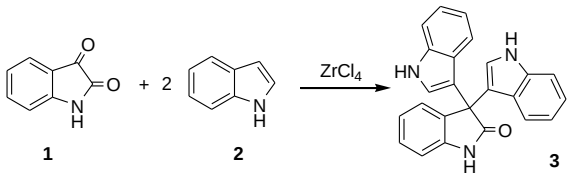
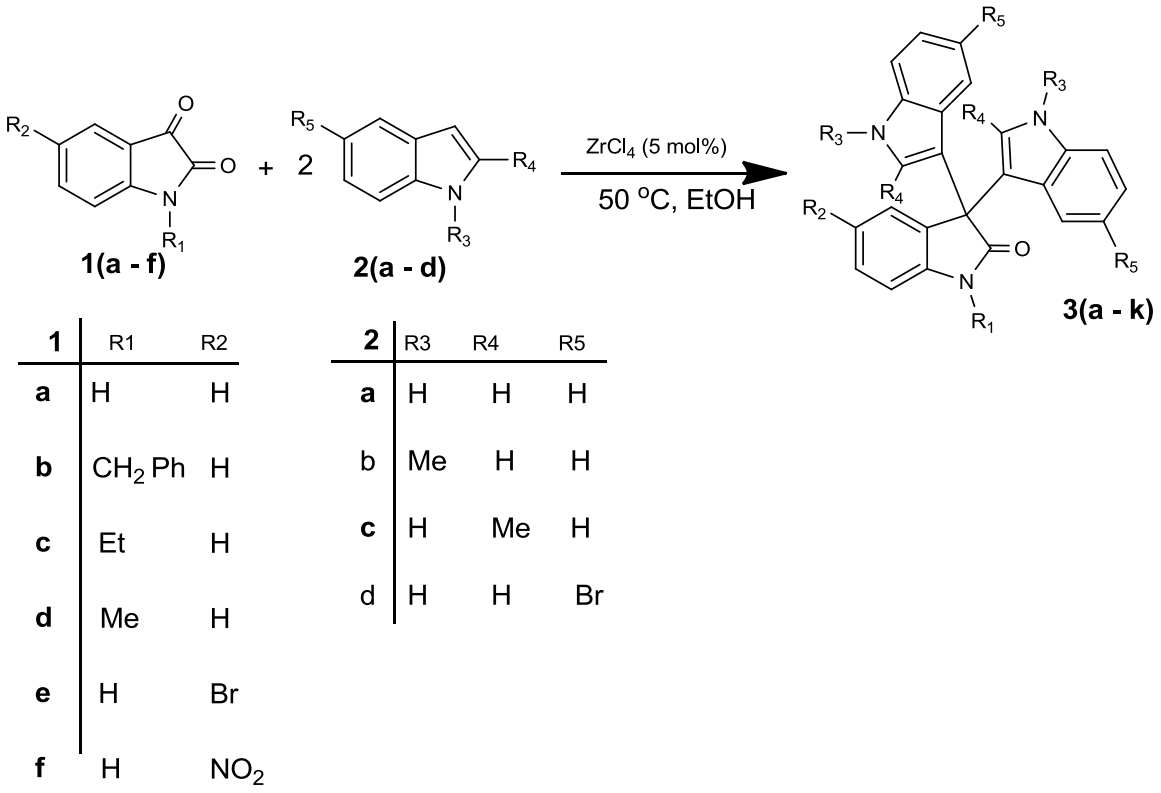


Figure 1. Model reaction.

Table 1. Optimization of reaction conditions.

Entry	Catalyst (mol%)	Solvent	Temperature (°C)	Time (min)	Yield (%)[b]
1	3	EtOH	50	30	90
2	5	EtOH	50	23	95
3	10	EtOH	50	20	95
4	15	EtOH	50	18	95
5	5	EtOH	80	40	95
6	5	EtOH	25	80	90
7	5	acetone	50	23	20
8	5	CH_2Cl_2	50	23	20
9	5	CH_3CN	50	23	50
10	5	H_2O	50	23	0
11	5	Solvent-free	50	23	10
12	5	Solvent-free	50	130	80

[a]*In all cases, isatin : indole ratio is 1:2.*
[b]*Isolated yields.*



1	R1	R2
a	H	H
b	CH_2 Ph	H
c	Et	H
d	Me	H
e	H	Br
f	H	NO_2

2	R3	R4	R5
a	H	H	H
b	Me	H	H
c	H	Me	H
d	H	H	Br

Figure 2. Synthesis of symmetrical 3,3-di(1*H*-indol-3-yl)-2-oxindoles catalyzed by $ZrCl_4$.

The results obtained from the synthesis of symmetrical 3,3-di(indol-3-yl)indolin-2-ones using $ZrCl_4$ encouraged the authors to prepare unsymmetrical ones by the same method. To this aim, first, 3-hydroxy-3-(indol-3-yl)-2-oxidole (**4a**) was synthesized according to the reported method; then, it was put in reaction with one equivalent 2-methylindole under optimized conditions (Figure 3). The desired products (**5b**) were generated in 95% yield after 15 min (Table 3, entry 2). Similarly, various 3-hydroxy-3-(indol-3-yl)-2-oxindoles were produced and then treated with indole derivatives to afford unsymmetrical 3,3-di(indol-3-yl)-2-oxindoles (**5**) in high yields and very short times (Table 3).

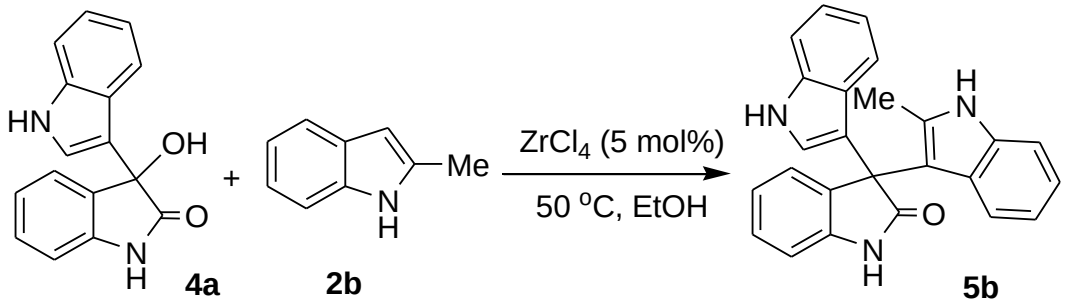
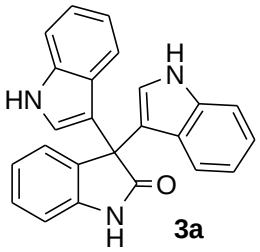
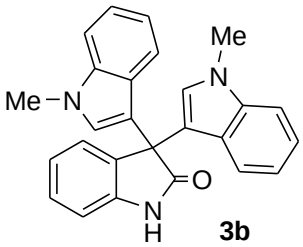
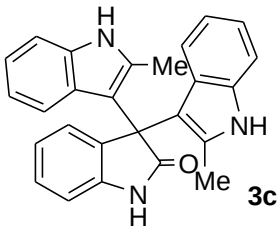
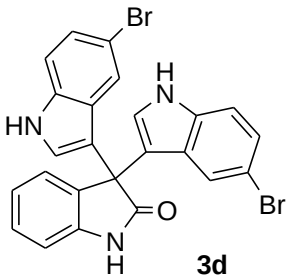
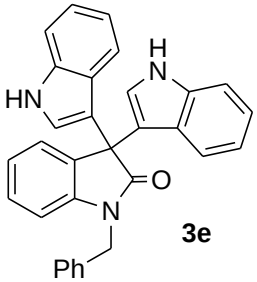
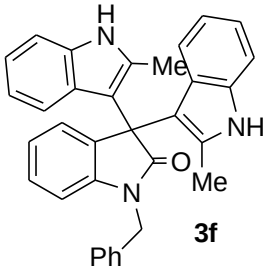
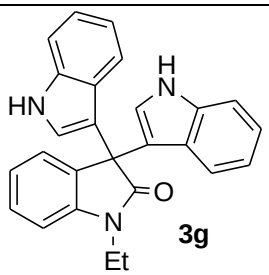
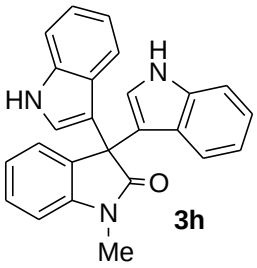
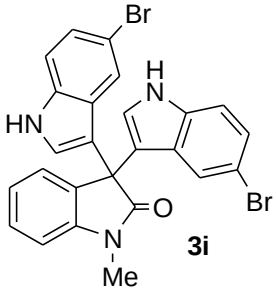
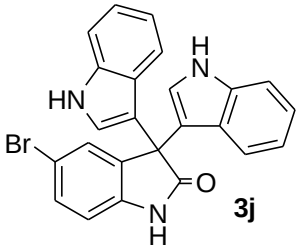
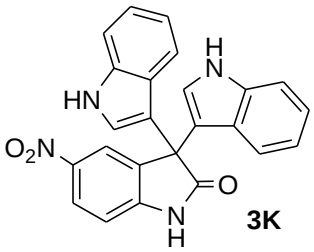
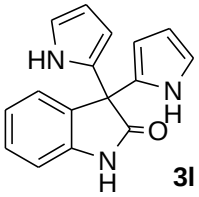


Figure 3. Synthesis of unsymmetrical 3-(1*H*-indol-3-yl)-3-(2-methyl-1*H*-indol-3-yl)-2-oxindole catalyzed by $ZrCl_4$.

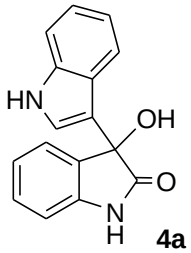
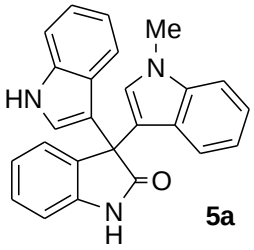
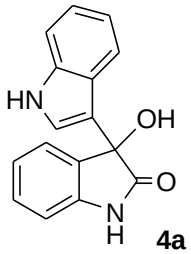
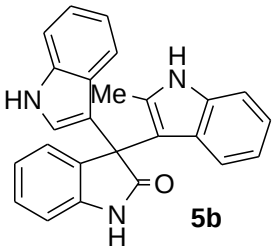
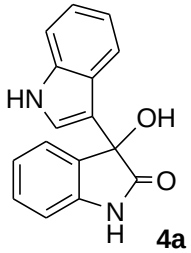
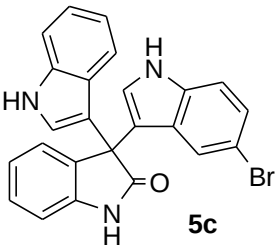
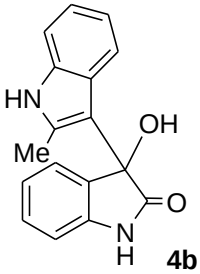
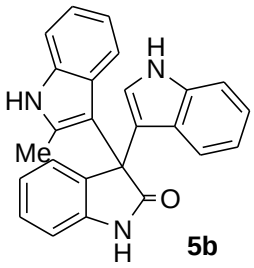
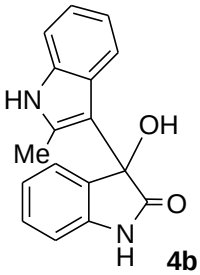
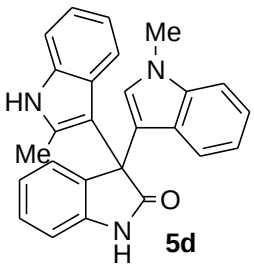
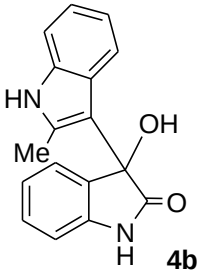
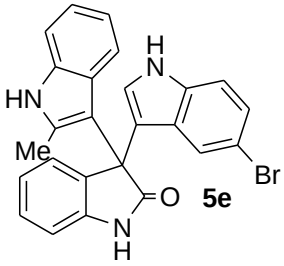
Table 2. $ZrCl_4$ catalyzed synthesis of symmetrical 3,3-di-(*1H*-indol-3-yl)-2-oxindoles.

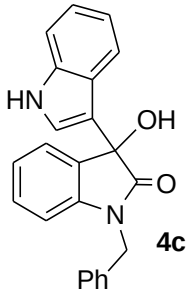
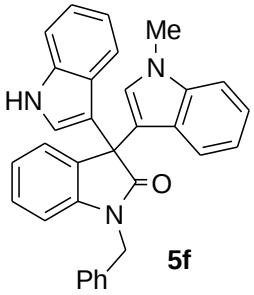
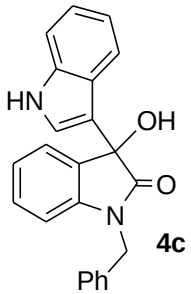
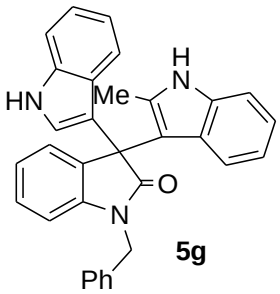
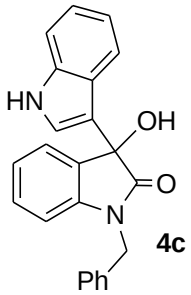
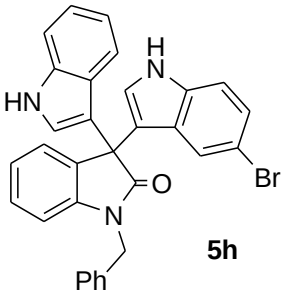
Entry	Isatin (1)	Indole (2)	Product (3)	Time (min)	Yield[a,b] (%)
1	**1a**	**2a**	 **3a**	23	95
2	**1a**	**2b**	 **3b**	90	85
3	**1a**	**2c**	 **3c**	9	98
4	**1a**	**2d**	 **3d**	54	95
5	**1b**	**2a**	 **3e**	40	91
6	**1b**	**2c**	 **3f**	11	97

Entry	Isatin (1)	Indole (2)	Product (3)	Time (min)	Yield[a,b] (%)
7	**1c**	**2a**	 **3g**	120	82
8	**1d**	**2a**	 **3h**	12	80
9	**1d**	**2d**	 **3i**	11	97
10	**1e**	**2a**	 **3j**	45	80
11	**1f**	**2a**	 **3K**	80	98
12	**1a**	Pyrrole	 **3l**	30	96

[a]*Isolated yields.*
[b]*All chemical structures and the purity of the products were characterized by physical and spectral data.*

Table 3. $ZrCl_4$ catalyzed synthesis of unsymmetrical 3,3-di-(1*H*-indol-3-yl)-2-oxindoles.

Entry	(4)	Indole (2)	Product (3)	Time (min)	Yield[a,b] (%)
1	 **4a**	**2b**	 **5a**	15	97
2	 **4a**	**2c**	 **5b**	15	95
3	 **4a**	**2d**	 **5c**	18	94
4	 **4b**	**2a**	 **5b**	10	96
5	 **4b**	**2b**	 **5d**	10	95
6	 **4b**	**2d**	 **5e**	20	93

Entry	(4)	Indole (2)	Product (3)	Time (min)	Yield[a,b] (%)
7	 **4c**	**2b**	 **5f**	17	97
8	 **4c**	**2c**	 **5g**	18	96
9	 **4c**	**2d**	 **5h**	30	97

[a]*Isolated yields.*
[b]*All chemical structures and the purity of the products were characterized by physical and spectral data.*

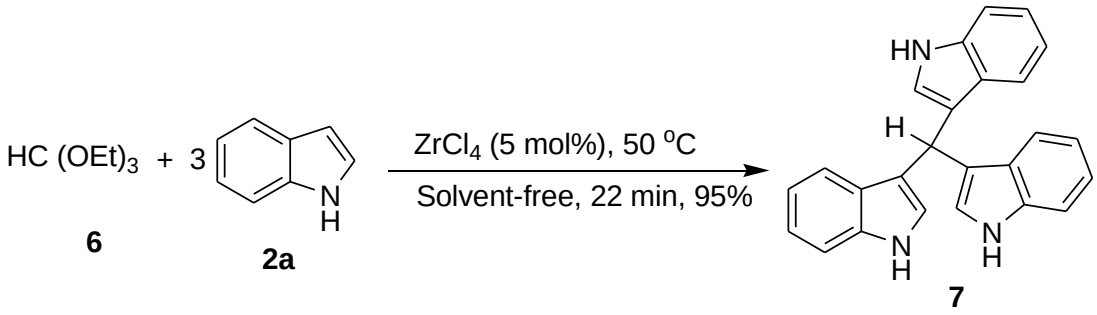


Figure 4. Synthesis of symmetrical tri(1*H*-indol-3-yl)methane catalyzed by $ZrCl_4$.

The applicability of the current procedure was also explored in the synthesis of symmetrical tris(indol-3-yl)methane due to its important biological activity. To this target, triethy1 orthoformate was stirred with 3 equivalent indoles and $ZrCl_4$ (5 mol%) in EtOH (5 ml) at 50 °C. Unfortunately, this reaction did not afford the desired product. Next, the same reaction was carried out in the absence of the solvent. This led to tris(indol-3-yl)methane in 95% yield after 22 min (Figure 4). This result indicates that $ZrCl_4$ is a highly efficient catalyst in the production of tri(1*H*-indol-3-yl)methane from orthoester and indole. According to the literature[12], a reasonable mechanism can be proposed for the synthesis of 3,3-di(indol-3-yl)-2-oxindoles catalyzed by $ZrCl_4$ (Figure 5). It is probable that $ZrCl_4$ coordinates with the non-amidic carbonyl group of isatin and activates it (**I**). Then, the nucleophilic attack of indole at **I** produces 3-hydroxy-3-(indol-3-yl)indolin-2-one (**II**) as a key intermediate which is converted

into (**III**) as a result of a loss of H_2O. The second indole is added to *N*-activated (**III**) to form the corresponding product and $ZrCl_4$ returns to the next catalytic cycle.

In order to show the superiority of the current work over previous studies, the authors have compared their proposed method with some other procedures in the synthesis of 3,3di(indol-3-y1) indolin-2-one from indole and isatin (Table 4). The findings confirm the preference of the present method in terms of its easy availability, cost-effectiveness, high activity of the catalyst, as well as reaction yield and time to those reported in the literature.

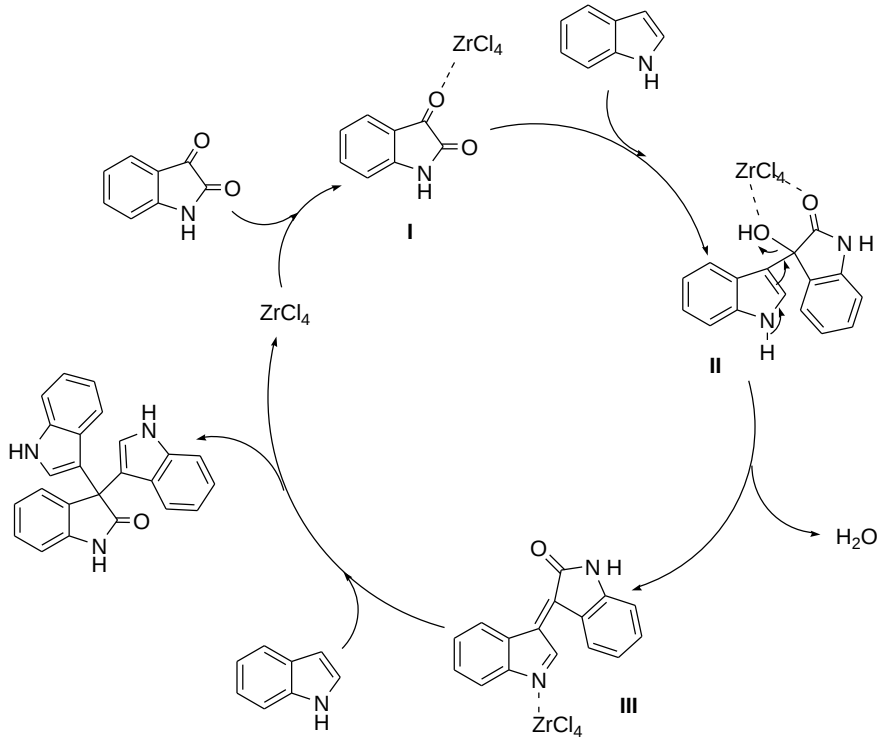


Figure 5. A reasonable mechanism for the synthesis of 3,3-di(1*H*-indol-3-yl)-2-oxindoles catalyzed by $ZrCl_4$.

Table 4. Comparison of some other procedures with the present method concerning the synthesis of 3,3-di(indol-3-yl)-2-oxindole.

Entry	Catalyst	Reaction Conditions	Time (min)	Yield (%)[Ref.]
1	CAN (10 mol%)	EtOH, ultrasound irradiation	180	95[12]
2	[BMIM]BF_4-LiCl	Ionic liquid media, rt	20	90[17]
3	Silicasulfuric acid (300% w/w)	CH_2Cl_2, rt	120	94[29]
4	I_2 (10 mol%)	CH_2Cl_2, rt	840	82[11]
5	Ru(III)-Y zeolite (10 mol%)	CH_2Cl_2, reflux	30	93[21]
6	$ZrCl_4$ (5 mol%)	EtOH, 50 °C	23	95 Present work

Conclusions

This study provided a simple, quick and efficient method for the synthesis of both symmetrical and unsymmetrical 3,3-di(1*H*-indol-3-yl)-2-oxindoles catalyzed by $ZrCl_4$. It enables acquiring symmetrical tris(indol-3-yl)methane. High yields of products, short reaction times and easy work-up, in combination with commercial availability, low cost and non-toxicity of the catalyst make this compound eco-friendly and commercially acceptable.

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