



# ZnS nanostructures: An efficient heterogeneous catalyst for the synthesis of Di (indolyl) methane's (DIMs)

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## ABSTRACT

The zinc sulphide (ZnS) nanostructures were synthesized using solvothermal reaction technique at 200°C for 12 h in presence of ethylenediamine (EDA) as a solvent and was characterized by X-ray diffraction (XRD), scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). XRD indicates the formation hexagonal phase of ZnS. FESEM analysis validates the formation of submicron sized structures with spiny rod like morphology with uniform size and smooth surface having size in the range of 150 to 200 nm with the thickness of ~15 nm, at 12 h reaction time. The catalytic performance of nanostructured ZnS as a heterogeneous catalyst was investigated for the synthesis of Di (indolyl) methane's (DIMs) with several substituted aldehydes and indoles under thermal condition affording the corresponding product in excellent yield. Simplicity of operation, high yields, easy work-up, recyclability of catalyst are the major advantages of this work.

**Keywords:** Di (indolyl) methane's, ZnS nanostructures, aldehydes, recyclability, spectral analysis.

## INTRODUCTION

In recent years nanostructured ZnS has attracted much attention because of their properties in the nano forms differ considerably from those of their corresponding bulk material, hence more attention is paid to the synthesis of these nanostructured materials. Wide efforts have been taken for the synthesis of various ZnS morphologies such as nanoparticles [1], nanorods [2], nanobelts [3, 4], nanotubes [5], nanosheets [6], well aligned tetrapods [7], nanowires bundles [8, 9], and hollow spheres [10-14]. It is used preferably in various applications due to high surface to volume ratio of one-dimensional nanomaterial, which has shown the improved performance in the development of devices. ZnS nanoparticles (NPS) have been intensively explored because of their efficient heterogeneous catalyst, low Curie temperature and high coercivity [15-17]. The one-dimensional ZnS nanostructures like nanoparticles, nanorods and nanowires have been synthesized by variety methods such as electrochemical deposition, laser ablation, solvothermal method, microwave irradiation, epitaxy, sonochemical method [18-27] etc. Amongst these methods, the hydrothermal/solvothermal method is desirable due to its cost effectiveness, simplicity, high yield and to form a controlled morphology [28-30].

Synthesis of heterocyclic compounds has received considerable attention because of its wide range of pharmacological and biological applications. Di (indolyl)methane's (DIMs) are known as an important class of heterocyclic compounds which are used as bioactive intermediates in pharmaceuticals, agrochemicals and material science [31]. They exhibit a broad spectrum of biological activities such as antimicrobial and antifungal [32], antibacterial [33], analgesic and anti-inflammatory [34], antitumor [35], anticancer and antioxidant [36] etc. Recently, Maciejewska et al [37] used DNA-based electrochemical biosensors to demonstrate that bis(5-methoxy-3-indolyl) methane considerably reduces the growth of cancer cell lines such as HOP-92 (lung), A498 (renal), and MDAMB-231/ITCC (breast). Tris(indolyl)methane's (TIMs) found in bacteriaserve as bacterial metabolic and cytotoxic agents. These compounds for centuries form the basis for many common drugs such as Morphine (analgesic), Captopril (treatment of hypertension) and Vincristine (cancer chemotherapy). The condensation of aldehydes and ketones with indole is an important reaction in Organic Chemistry which afford di (indolyl)methane's. Various methods have been employed to effect this transformation using variety of reagents such as protic acids [38], silica sulfuric acid (SSA) [39], silica supported NaHSO<sub>4</sub>/amberlyst-15 [40] and Lewis acids, lithium perchlorate [41], cupric fluoroborate [42] and silicotungstic acid [43]. Recently, benzoic acid in water [44], sodium dodecylsulfate (SDS) [45] as surfactant in water, oxalic acid combination with N-acetyl-N, N, N-trimethylammoniumbromide (CTAB) [46] as surfactant in water, metal triflate in ionic liquid [47], Fe (III) salts in ionic liquid [48] and ionic liquids have been reported as effective reagents for this transformation. Most of the reported methods suffer from various disadvantages such as prolonged

reaction time, harsh reaction conditions, use of expensive Lewis acids, toxic metal ions and tedious work-up procedures.

Here in we have reported an efficient and inexpensive method for the synthesis of Di (indolyl) methane's (DIMs) derivatives. The indole and aromatic aldehydes were reacted in the presence of ZnS nanostructures as heterogeneous catalyst under thermal condition. The reaction was completed in good to excellent yields of di (indolyl) methane derivatives.

## Experimental

### Materials and reagents

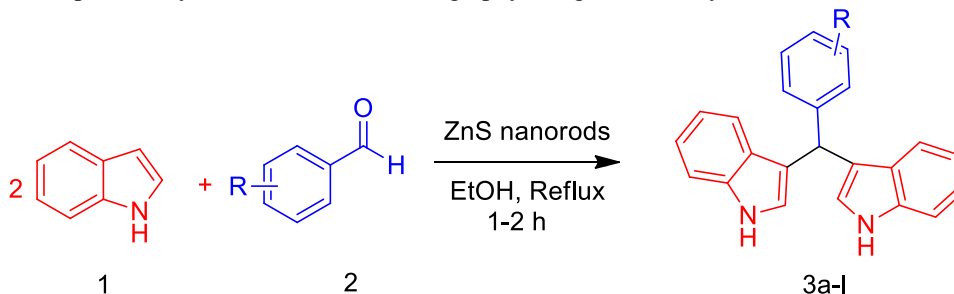
#### Synthesis of ZnS nanostructures

For the synthesis of ZnS nanostructures, zinc acetate ( $Zn(OAc)_2 \cdot 6H_2O$ ), thiourea, ethylenediamine (EDA,  $C_2H_4(NH_2)_2$ ), of Sisco Research Laboratory (SRL) make were used. All other chemicals solvents were of analytical grade and used as received without further purification.

The zinc sulphide nanostructures were synthesized using solvothermal technique by dissolving ( $Zn(OAc)_2 \cdot 6H_2O$ ) (10 mmol) and thiourea (20 mmol) separately in 30 mL of ethylenediamine (EDA) respectively and mixed together with constant stirring. The resultant mixture was stirred for 10 min, transferred into teflon lined stainless steel autoclave and was further heated at  $200^\circ C$  for 12 h in an oven. The resultant mass was centrifuged, washed with distilled water several times and finally with ethanol. It was subsequently, dried at  $80^\circ C$  for 4 h in an oven, well grinded in mortar and pestle and used for further physico-chemical analysis and evaluated its catalytic performance as a heterogeneous catalyst for the synthesis of di (indolyl) methanes.

#### General Procedure for the Synthesis of Di (indolyl) methane's:

In a 25 mL round bottom flask, aldehyde (1.0 mmol), indole (2.0 mmol), zinc sulphide (5 mol %, catalytic amount) and ethanol (5 mL) was added, reaction mixture was refluxed for 1-2 h. The progress of the reaction was monitored by TLC (30% hexane/ethyl acetate). After completion of the reaction, the catalyst was filtered and resulting crude product was extracted with ethyl acetate, dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. The crude product was purified by silica column chromatography using hexane/ethyl acetate (90:10 v/v) as eluent.



R = H,  $-NO_2$ ,  $-OCH_3$ ,  $-CH_3$ , halogens

### Scheme 1: Synthesis of di (indolyl) methanes

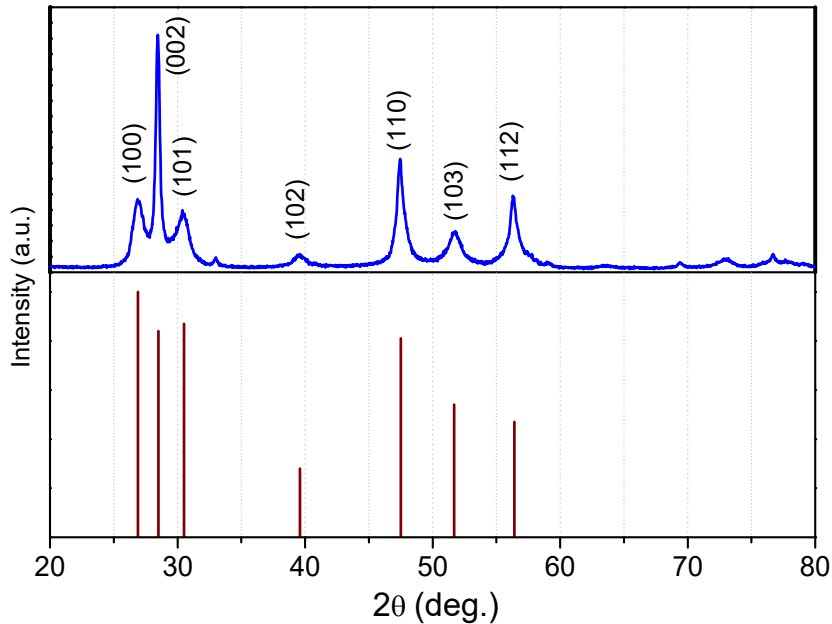
#### CHARACTERIZATION

The synthesized nanostructured ZnS was characterized using various spectroscopic techniques. All the products obtained were purified by column chromatography using neutral silica gel (60–120 mesh) and hexane, ethyl acetate as an eluant.  $^1H$  and  $^{13}C$ -NMR spectra were recorded in  $CDCl_3$  and  $DMSO-d_6$  using Varian 400 MHz NMR spectrometer. Proton chemical shifts ( $\delta$ ) are relative to TMS ( $\delta=0$ ) as internal standard and expressed in PPM. Coupling constants (J) are given in Hertz. IR spectra were recorded on a FT-IR spectrometer Perkin-Elmer 1600 A FTIR in the range of  $400-4000\text{ cm}^{-1}$ . Ultraviolet-visible absorption spectrum was recorded by using  $\lambda$ -200 double beam spectrophotometer (Perkin-Elmer/Shimadzu 3600) in the UV-Vis-NIR range of 300–1050 nm. Melting points were determined on Buchi M-560. Reaction was monitored by thin layer chromatography (TLC) on Merck's silica gel plates (60 F<sub>254</sub>).

#### X-ray diffraction analysis

The synthesized Zinc Sulphide nanostructure was analyzed by powder X-ray diffractometry to identify the crystalline phases. XRD pattern of ZnS prepared at 12 h is depicted in Fig.1. The peaks in figure with  $2\theta$  values of  $26.9^\circ$ ,  $28.5^\circ$ ,  $30.5^\circ$ ,

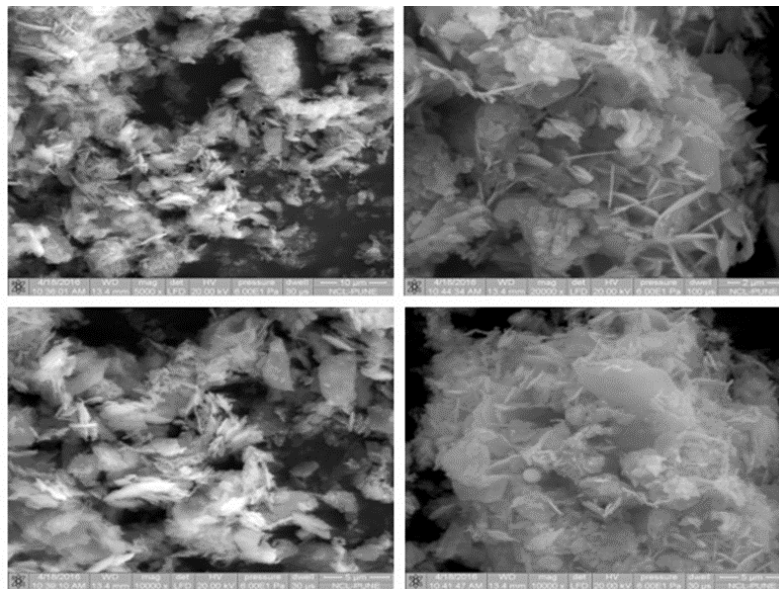
39.6°, 47.5°, 51.7°, and 56.4° corresponds to the (100), (002), (101), (102), (110), (103) & (112) planes of the hexagonal phase of ZnS (standard JCPDS data sheet no. 36-1450)



**Fig. 1: X-ray diffraction pattern of a) ZnS nanostructures b) ICDD pattern no. 36-1450**

**FESEM analysis**

The surface morphology of ZnS nanostructures was examined by FESEM, high and low resolution FESEM images are reproduced in Fig.2. ZnS prepared at 12 h of reaction time reveals the formation of submicron sized structures with spiny surface. The nanosheets agglomerated to form hierarchical structures, also rod like morphology with uniform size and smooth surfaces are observed. The observed thickness of the rods is ~15 nm and length in the range of 150 to 200 nm (Fig. 2).

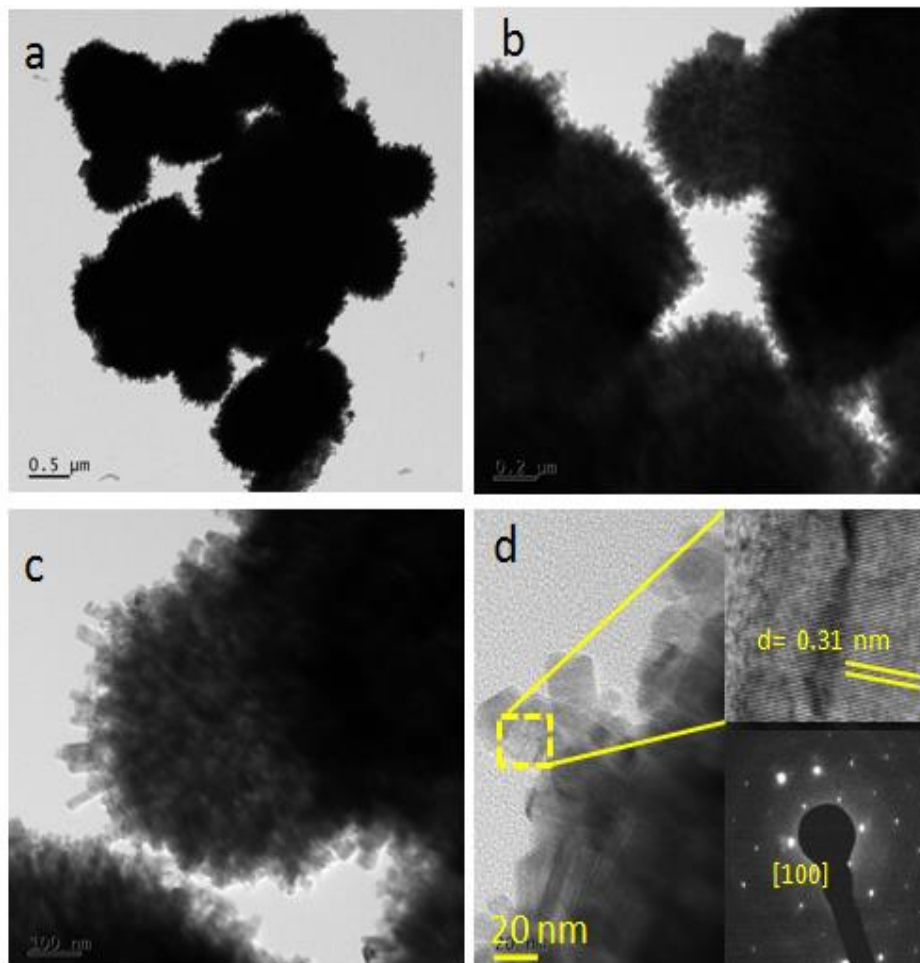


**Fig. 2: FESEM micrographs of ZnS nanostructures**

**TEM analysis**

The microstructure of synthesized zinc sulphide was investigated by TEM analysis. The high and low resolution FETEM micrographs along with selected area electron diffraction (SAED) pattern are depicted in Fig.3. TEM images of ZnS

indicate the formation of spherical shaped sub-micron size ZnS clusters made up of small rods having thickness ~20 nm and diameter ~100 nm. The nanorods agglomerated in such way that it shows the shape of spiny capsule like morphology. SAED pattern of ZnS nanostructure depicts the formation of highly crystalline hexagonal phase of ZnS (inset of Fig.3d). The high resolution FETEM indicate the interplanar spacing  $d = 0.31$  nm corresponds to (002) hkl confirms the formation of hexagonal ZnS. Overall TEM analysis supports the XRD observations and confirms the formation of wurtzite ZnS nanostructures.



**Fig. 3: FETEM of ZnS nanostructures, inset 3d SAED and HRTEM**

### **Synthesis of di (indolyl) methane's using nanostructured ZnS as a catalyst**

After the characterization of nanostructured ZnS its catalytic activity was evaluated as a heterogeneous catalyst in organic transformation for synthesis of di (indolyl) methane's

#### **Effect of amount of catalyst**

To establish the general reaction conditions for the synthesis of di(indolyl) methane's model reaction of indole and p-nitro benzaldehyde was studied with and without ZnS nanostructured material as a catalyst. The reaction was sluggish and did not proceed in the absence of catalyst even after extended reaction time. The use of ZnS nanostructured material afforded good yield of desired di(indolyl) methane's.

In order to find the appropriate concentration of ZnS for synthesis, the amount of catalyst varied from 0.5 mol% to 10 mol%, the results are represented in Table 1. With increase in catalyst amount the yield of the reaction increases from 70 % to 93 %. With higher catalyst amount (>5 mol%) the yield of the product was around 94% this indicates that there was not much increase in the yield. The increase in catalyst amount did not show any substantial enhancement in the yield of resultant product. Based on the above observations 5mol % catalyst was used for the synthesis of di(indolyl) methane's

derivatives.

**Table 1: Effect of amount of catalyst**

Entry	ZnS (x mmol)	Yield (%)
1	0.5	70
2	1.0	80
3	2.5	89
4	5.0	93
5	7.5	94
6	10.0	94

Reaction Conditions: Aldehyde (1 mmol), Indole (2 mmol), catalyst ZnSnanostructures (x mol %) were stirred in 5 mL ethanol at reflux temperature, time 1-5 h. Isolated yield after chromatographic separation.

#### Effect of Solvent

The influence of various solvents on the yield of DIMs was also investigated using 5 mol % ZnS nanostructures and results are depicted in Table 2. The reaction in water afforded lower yields ( $\leq 10\%$ ) after prolonged reaction time; the lower yield may be due to the inhomogeneity of reactants. Yield of DIMs in ethanol was almost more than 93%. The polar aprotic solvents such as CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub>, THF, CHCl<sub>3</sub> and DMF afforded reasonable yield (Table 2, entry 3 to 6, 8) while non-polar solvents like 1, 4-dioxane and toluene afforded the low yield of corresponding product which require longer reaction time. (Table 2, entry 7, 9). Amongst the studied solvents ethanol gave the excellent yield of di(indolyl)methane's within 1 h under reflux reaction condition. For further investigation we used 5 mol% of catalyst and ethanol as a solvent system.

**Table 2: Effect of Solvents**

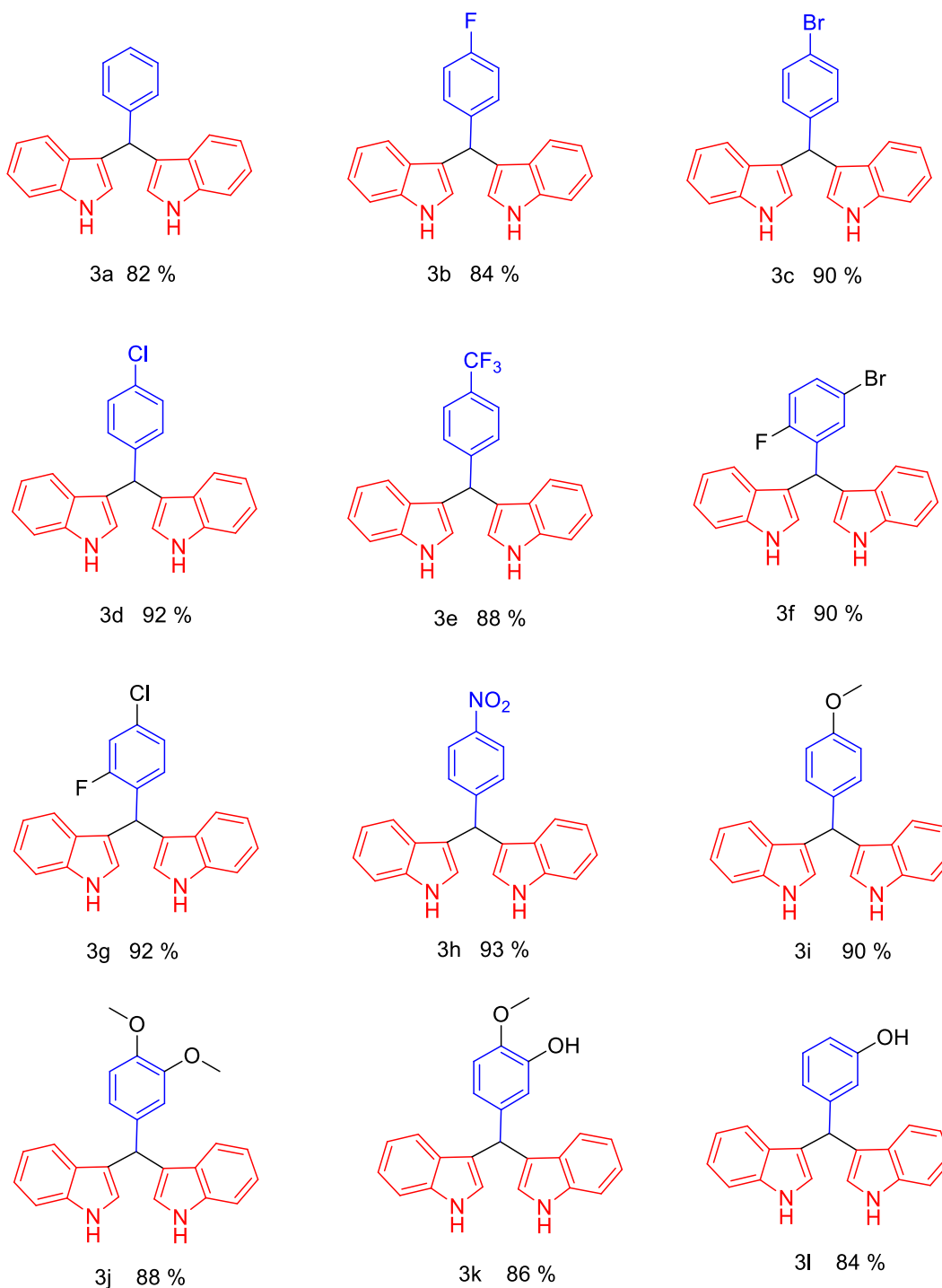
Entry	Solvent	Time (h)	Yield (%)
1	H <sub>2</sub> O	5	$\leq 10$
2	EtOH	1	93
3	Acetonitrile	1	85
4	DCM	1.5	80
5	THF	1	78
6	CHCl <sub>3</sub>	1.5	80
7	1,4 dioxane	1	74
8	DMF	1.5	60
9	Toluene	1	42

Reaction Conditions: Aldehyde (1 mmol), Indole (2 mmol), catalyst ZnSnanostructures (x mol %) were stirred in 5 mL solvent under reflux temperature, time 1-2 h. Isolated yield after chromatographic separation.

#### Synthesis of DIM's

To investigate the further applicability of this reaction using optimized reaction conditions, we extended the methodology for the synthesis of diverse derivatives of di(indolyl)methane's using various aromatic aldehydes with either electron-releasing or electron-withdrawing substituents in the ortho, meta and para positions (scheme I), the results are summarized in Table 3. Unsubstituted aromatic aldehyde (benzaldehyde) afforded 82% yield (Table 3 entry 3a), however amongst halogenated aldehydes 4-chlorobenzaldehyde (Table 3 entry 3d) furnished 92% yield of the resultant di(indolyl)methane's derivative within 1h of reaction time, whereas other halogenated aldehydes afforded ~ 90% yield (Table 3, entries 3b, c). Trifluoro benzaldehyde afforded 88% yield of corresponding DIMs (Table 3, entry 3e). Di substituted halogenated benzaldehyde under similar reaction condition leads to ~ 90-92% yield of DIM (Table 3, entry 3f, 3g). The reaction of 4-nitrobenzaldehyde was completed within 1 h giving 93% yield of corresponding product (Table 3, entry 3h). Aldehydes having electron releasing groups also reacted within 1-2 h with good to excellent yield (84-90%) of di(indolyl)methane's derivatives. (Table 3 entries 3i-l)

Table 3: Synthesis of di(indolyl)methane derivatives

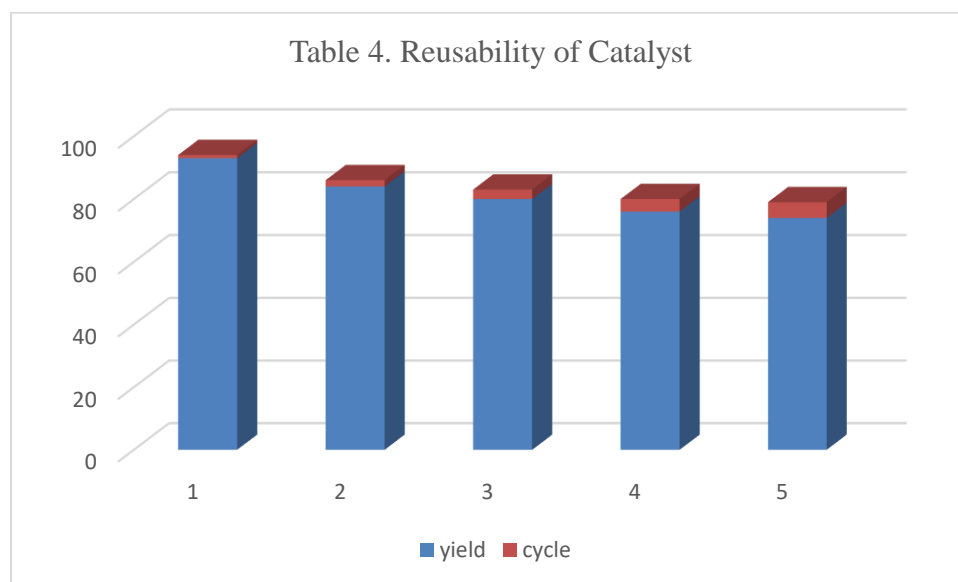


Reaction Conditions: Aldehyde (1 mmol), Indole (2 mmol), catalyst ZnSnanostructures (x mol %) were stirred in 5 mL solvent at reflux temperature, time 1-2 h. Isolated yield after chromatographic separation.

#### Reusability Study

The reusability of the catalyst was also studied under optimized reaction conditions. After completion of reaction the catalyst was recovered, filtered and washed repetitively with ethyl acetate and dried. It was reused under optimized reaction

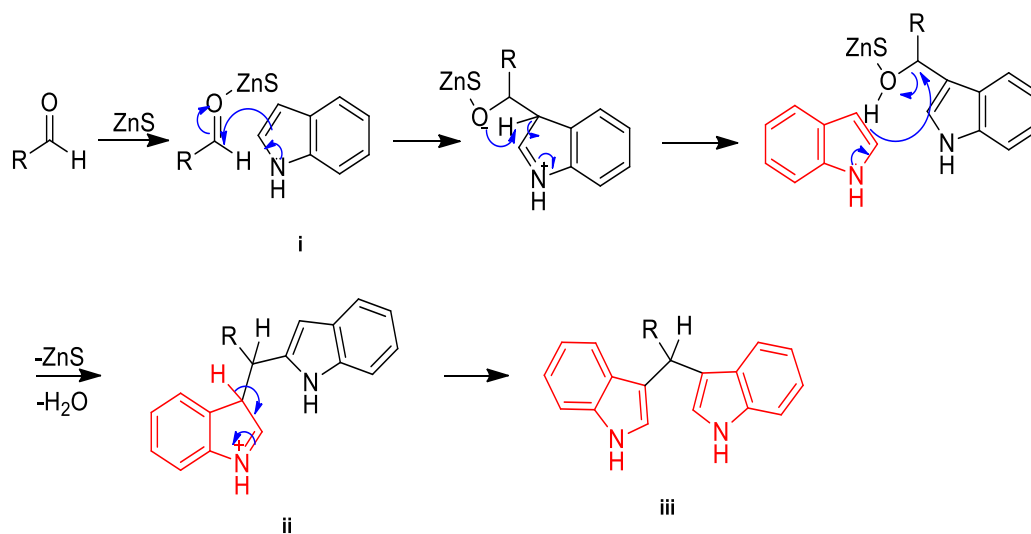
conditions and was found that yield of di(indolyl)methane's were almost comparable. The catalyst recovered after the first cycle was used for successive four cycles and the yield of corresponding product obtained in each cycle is summarized in (Table 4). It was observed that the % yield of these derivatives was marginally lowered even after five cycles. These observations suggest that the catalyst surface remains active during successive cycles. Although the slight decrease in the catalytic activity of ZnS might be due to the deactivation of active sites of catalyst. The reusability of catalyst checked for four cycles and the corresponding yields obtained in each cycle is summarized in Table 4.



### Plausible reaction Mechanism for the synthesis of di(indolyl)methane's

A Plausible reaction mechanism for the synthesis of di(indolyl)methane derivatives using hierarchical ZnS nanostructures is illustrated in scheme II

In this reaction ZnS acts as Lewis acid, hierarchical ZnS nanostructure co-ordinates with carbonyl oxygen and enhances the electrophilicity of the carbonyl carbon of aldehydes hence electrophilic condensation reaction most likely proceeds through activation of a carbonyl group (intermediate i) followed by attack of Indole to give Azafulvenium salt (intermediate ii). Further, another molecule of Indole reacts with intermediate (ii) followed by subsequent loss of H<sub>2</sub>O and ZnS to give corresponding di(indolyl)methane's (iii).



**Scheme II: Plausible reaction Mechanism for the synthesis of di(indolyl)methane's**

## CONCLUSION

In the present work we have successfully synthesized ZnS nanostructures as a reusable, readily available, inexpensive and efficient catalyst using solvothermal reaction technique. XRD analysis indicate the formation of highly crystalline hexagonal phase of ZnS. FE-SEM and TEM analysis confirms the presence of nanosized plates and rods agglomerated in such way to form micron sized hierarchical nanostructures. Furthermore, the effective use of synthesized ZnS nanostructures as a heterogeneous catalyst was evaluated for the synthesis of variety of biologically active di(indolyl)methane's having moderate to good yield. Overall, the catalytic performance of ZnS nanostructures were comparable due to its ability to act as Lewis acids. In addition, the catalyst could be easily recovered by simple filtration and reused for several cycles without significant loss in its catalytic activity.

## ACKNOWLEDGMENT

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## ANALYTICAL AND SPECTRAL DATA

### **3,3 di(indolyl)-phenylmethane, Pink Solid**

$\delta$ H(400 Hz, DMSO- $d_6$ , Me $_4$ Si) 5.8(1H, s, CH), 6.7 (2H,d, J = 2 Hz), 6.86 (2H, t, J = 7.6 and 14.6 Hz), 7.1(2H, t, J = 8 and 14.80 Hz), 7.02 (1H, t, J = 7.2 and 14.40 Hz, Ph), 7.4 (4H, t, J = 8 and 16 Hz, Ph), 7.2(4H, m), 10.8 (2H, br s, NH);  $\delta$  (200 Hz, CDCl $_3$ ) 144.8,136.4, 128.19, 127.9, 126.54, 125.64, 123.41, 120.74, 118.98,118.03, 117.97, 111.32; mp 124–126 $^{\circ}$ C

### **3,3 di(indolyl)-4-fluorophenylmethane**

$\delta$ H(400 Hz, CDCl $_3$ , Me $_4$ Si) 5.8(1H, s, CH), 6.8(2H, s, Ph), 6.93–7.02 (4H, m, Ph), 7.1–7.2 (2H, m, Ph), 7.27–7.30 (3H, m, Ph), 7.4 (4H, dd, J = 2 and 7.60 Hz, Ph), 7.8(2H, br s, NH); mp 82–84 $^{\circ}$ C

### **3,3 di(indolyl)-3,4-dimethoxyphenylmethane**

$\delta$ H(400 Hz, CDCl $_3$ , Me $_4$ Si) 3.7 (3H, s, OMe), 3.8 (3H, s, OMe), 5.8 (1H, s, CH), 6.6 (2H, s, Ph), 6.77 (1H, d, J = 8.4 Hz, Ph), 6.83 (1H, m, Ph), 6.9 (1H, s, Ph), 7.0 (2H, t, J = 7.6 and 16 Hz, Ph), 7.1 (2H, t, J = 8.0 and 14.8 Hz, Ph), 7.3(4H, dd, J = 8.0 Hz, Ph), 7.9 (2H, bs, Ph);  $\delta$ (200 Hz, CDCl $_3$ ) 40.0, 50.6, 110.9, 111.0, 112.2, 119.1, 119.8, 119.9, 120.5, 121.8, 123.5, 127.0, 136.7, 147.2, 148.6; mp 180–190 $^{\circ}$ C.

### **3,3 di(indolyl)-3-hydroxy-4-methoxyphenylmethane**

$\delta$ H(400 Hz, CDCl $_3$ , Me $_4$ Si) 3.8 (3H, s, OMe), 5.5 (1H, bs, OH), 5.8 (1H, s, CH), 6.6 (2H, s, Ph), 6.7 (1H, d, J = 8.4 Hz, Ph), 6.83 (1H, dd, J = 8.0 Hz, Ph), 6.9 (1H, s), 7.0 (2H, t, J = 7.2 and 14.4 Hz, Ph), 7.1 (2H, t, J = 7.6 and 15.2 Hz, Ph), 7.3 (2H, d, J = 8.0 Hz, Ph), 7.4 (2H, d, J = 8.0 Hz, Ph), 7.8 (2H, bs, NH); mp 110–115 $^{\circ}$ C.

### **3,3 di(indolyl)-4-(N,Ndimethylamino)phenylmethane**

$\delta$ H(400 Hz, CDCl $_3$ , Me $_4$ Si) 2.9 (6H, s, Nme $_2$ ), 5.8 (s, 1H, CH), 6.67 (4H, d, Ph), 6.9 (2H, m, Ph), 7.2–1.12 (4H, m, Ph), 7.3 (2H, d, J = 8.4 Hz, Ph), 7.4 (2H, d, J = 8.0, Ph), 7.8 (2H, bs, NH); mp 180–194 $^{\circ}$ C.

### **3,3 di(indolyl)-4-methoxyphenylmethane**

$\delta$ H(400 Hz, CDCl $_3$ , Me $_4$ Si) 3.7 (3H, s, 3OMe), 5.8 (1H, s, CH), 6.6 (2H, s, Ph), 6.8 (2H, dd, J = 4.80 Hz, Ph), 7.0 (2H, m, Ph), 7.14 (2H, t, J = 7.2 and 14.4 Hz, Ph), 7.25 (2H, m, Ph), 7.37 (3H, dd, J = 12.0 Hz, Ph), 7.8 (2H, bs, NH); mp 165–170 $^{\circ}$ C

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