RSC Advances


This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

RSCPublishing

ARTICLE

# Synthesis of indeno and acenaphtho core containing dihydroxy indolone, pyrrole, coumarin and uracil fused heterocyclic motifs under sustainable condition exploring the catalytic role of $SnO_2$ quantum dot

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Koyel Pradhan, Sanjay Paul, Asish R. Das*

$SnO_2$ quantum dots (QDs) catalyzed approach for the synthesis of indeno and acenaphtho core containing dihydroxy indolone, pyrrole, coumarin and uracil fused derivatives has been achieved via a multicomponent one pot approach in aqueous medium. A variety of functional groups are compatible with the reaction conditions. This synthesis was established to follow the group-assistant-purification (GAP) chemistry process, which can avoid traditional chromatography. $SnO_2$ quantum dot was prepared by simple solvothermal method and characterized by XRD and TEM images. The easy recovery of the catalyst and high yield of the products make the protocol attractive, sustainable and economic. The catalyst was reused for seven cycles with almost unaltered catalytic activity. The low cost, easy to handle and the simplicity of this catalytic system render the method competitive with other strong mineral acid catalysed multicomponent protocols.

## Introduction

A wide variety of homogeneous Brønsted acids ($H_2SO_4$, p-toluenesulfonic acid, HCl and $H_3PO_4$) have been used for the synthesis of important chemicals, including pharmaceuticals, agrochemicals, and fragrances.[1–3] These acidic catalysts are economic and efficient, but have serious drawbacks associated with product isolation, equipment corrosion, solvent recycling, and reusability of the catalyst. Heterogeneous acid catalysts like zeolites, transition-metal ions, and strong acid cation exchange resins have also been used sometimes to serve this purpose.[4–6] Catalytic processes in the solution phase are important in many areas of the fine and specialty chemical industries, and the use of solid catalysts means easier catalyst separation and recovery, hence facilitating their reuse. It is widely accepted that a smaller catalyst particle means the higher activity.[7] As a result, both the activity and the stability of a solid catalyst suspended in a liquid media can benefit greatly from the use of small catalyst particles. Nano-catalysts mimic homogeneous (high surface area, easily accessible) as well as heterogeneous (stable, easy to handle) catalyst systems. Thus nano-catalysts make the system more efficient than conventional heterogeneous catalyst systems. In general, QDs are nano-materials with the grain size less than 5nm which show unique electrical and catalytic properties due to their ultra-fine grain size. Unique properties of QDs arise from two reasons. The main reason can be attributed to the completely depletion of ultra-fine grains by charge carriers. In addition the increase of the surface-to-bulk ration by decreasing the grain size of the particles plays an important role in high reactivity of the particles. All these render the catalyst cost-effective, making it promising alternatives over conventional Bronsted and Lewis acid catalysts for industrial applications.

Indeno[1,2-b]indoles are an important class of heterocyclic compounds. These molecules consist of small and planar heterocyclic frameworks. Due to the presence of this type of structural features, indeno[1,2-b]indoles (A and B, Fig. 1) serves as ATP/GTP-competitive inhibitors of CK2 and acts as DNA-intercalators and inhibitors of topoisomerase II with considerable cytotoxic activity towards cancer cells.[8]

RSC Advances Accepted Manuscript

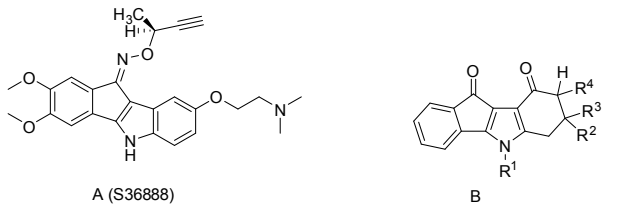



Figure 1. (A) Topoisomerase II inhibitor (B) human protein kinase CK2 inhibitor

Coumarin and uracil fused heterocycles are one of the most active classes of compounds possessing a wide spectrum of biological activity.[9] Many of the coumarin fused heterocycles show antitumor,[10] antibacterial,[11] antifungal,[12] anticoagulant,[13] anti-inflammatory,[14] and antiviral[15] activities. A large number of adenosine receptor agonists and antagonists are proved to be highly potent and subtype selective ligands.[16,17] The astonishing drug activity of these indeno[1,2-b]indoles, coumarin and uracil based heterocyclic compounds not only attracted many synthetic and medicinal chemists to synthesize this heterocyclic nucleus but also became an active research area of enduring interest.

Synthesis of $SnO_2$ nanocrystals have attracted much attention from researchers owing to their potential applications based on gas sensing,[18] field-emission,[19] electrochemical,[20] photocatalytic,[21] and photovoltaic properties.[22,23] In continuation of our research program dedicated to the synthesis and application of metal oxide nano-catalysts for design and synthesis of novel heterocyclic systems,[24] we have started our investigation with the objective of developing a clean, efficient and straightforward methodology for the synthesis of dihydroxy indeno[1,2-b]indolone, acenaphtho[1,2-b]indolone, coumarin and uracil fused indeno [1,2-b] pyrrole and acenaphtho[1,2-b] pyrrole systems utilizing a non-toxic and environmentally benign catalyst. To the best of our knowledge, only a few references exist concerning their synthesis.[25] These reported reactions have several limitations. For example, these procedures involve low yields, high reaction time, multistep approach along with less substrate scope. Thus, a simple, efficient, and green method to synthesize these highly important heterocyclic cores would be demanding as well as attractive too. Herein, we report a novel approach for the facile synthesis of dihydroxy indeno[1,2-b]indolone, acenaphtho[1,2-b]indolone, coumarin and uracil fused indeno [1,2-b] pyrrole and acenaphtho[1,2-b] pyrrole containing structural motifs by assembling the basic building blocks installing monodisperse $SnO_2$ quantum dots (QDs). Synthesis of monodisperse $SnO_2$ quantum dots (QDs)[26] and exploration of its very high catalytic activity in organic synthesis has been demonstrated in this paper.

## Results and discussion

The $SnO_2$ QDs was prepared by solvo-thermal method. Monodisperse $SnO_2$ quantum dots (QDs) were characterized by X-ray diffraction study, HRTEM and TEM images.

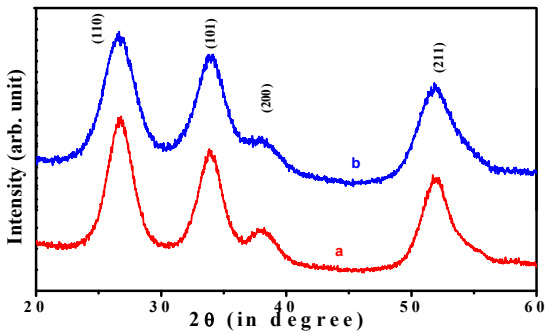



**Figure 2**: (a) XRD patterns of the $SnO_2$ QDs (b) XRD patterns of seven times reused the $SnO_2$ QDs

Fig. 2a shows the XRD patterns of the as-synthesized uncapped $SnO_2$ QDs. All the diffraction peaks matched well to the standard diffraction data for rutile $SnO_2$ (JCPDS card no. 41-1445) while no traces of other phases or impurities are found. The gradual widening of peaks indicates large decrease in dimension. The average sizes of the uncapped $SnO_2$ QDs calculated by Debye-Scherrer formula considering the instrumental broadening and strain broadening using the (110) peak of the XRD pattern is 3.9 nm.

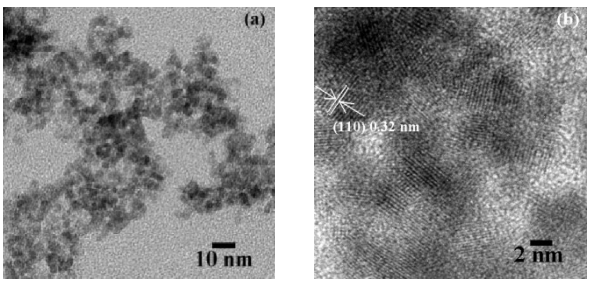



**Figure 3:** (a) Low-resolution TEM and (b) HRTEM images of $SnO_2$ QDs

From the low resolution TEM image of the $SnO_2$ QDs as displayed in Fig. 3(a), the size of the QDs is 4 nm ±10%. The HRTEM image of uncapped $SnO_2$ QDs shown in the Fig. 3(b) indicates 0.32 nm spacing between two adjacent lattice planes of a QD corresponding to the (110) lattice planes of $SnO_2$.

The composition of as synthesized $SnO_2$ QDs was deduced from the EDX measurements. The figure 4 clearly indicates that the major peaks in the bulk substrate material are due to the presence of Sn, Cu, and oxygen. The Cu peak in the EDX spectra is due to the use of Cu grids for the TEM analysis. The EDX and HRTEM clearly prove that the synthesized particle was pure $SnO_2$ which was composed of Sn and O only.

RSC Advances Accepted Manuscript


This journal is © The Royal Society of Chemistry 2012

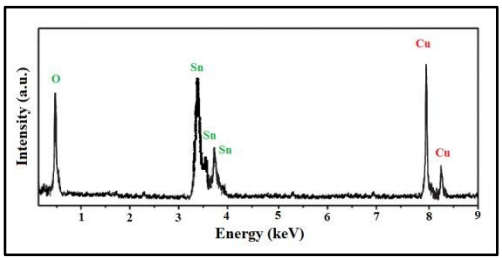
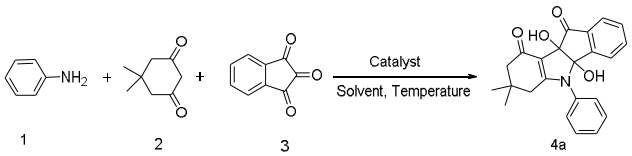



Figure 4: EDX analysis of the $SnO_2$ QDs

This $SnO_2$ quantum dots were then explored as a heterogeneous catalyst for the synthesis of fully substituted dihydroxy indeno[1,2-b]indolone derivatives applying three-component reaction (Scheme 1).




Scheme 1: Synthesis of dihydroxy indeno[1,2-b]indolone derivatives

At the commencement of our work we focused on systematic assessment of different catalysts on the model reaction (Scheme 1) for the synthesis of dihydroxy indeno[1,2-b]indolone derivatives. Initially, the one pot three-component reaction of aniline (1) (1.0 mmol), dimedone (2) (1.0 mmol) and ninhydrin (3) (1.0 mmol) as the representative substrates for the model reaction was investigated to establish the feasibility of the strategy and optimize the reaction conditions. The results are presented in Table 1. In the preliminary experiment, the above mentioned reaction was performed in the absence of any catalyst employing water as the solvent. It was evident that the reaction proceeded very slowly in the absence of catalyst and the expected product was isolated in a very small quantity after heating the reaction mixture for about 24 h at 70 $^oC$ (Table 1, entry 1). A wide array of catalysts including nano metal oxides like nano- $Fe_3O_4$, $SiO_2$, ZnO, CuO, $Al_2O_3$ (Table 1, entries 2-6) were employed to improve the yield for the specific synthesis of dihydroxy indeno[1,2-b]indolone derivative. From Table 1, it was also evident that these nano-sized particles were unable to promote this three-component reaction with comparable yields. After prolonged screening of these heterogeneous Lewis acid catalysts, we applied stronger Lewis acid catalyst nano $CuFe_2O_4$. The inefficiency of nano $CuFe_2O_4$ for the construction of this heterocyclic core made us think about a nano catalyst having greater acid character. For this we have applied $SiO_2$-$OSO_3H$ and Al-SBA15, but the results were unsatisfactory. Then we installed $SnO_2$ nano particles of different particle size for the multi-component reaction. It was evident that with the decreasing particle size, the catalytic efficiency increases for the $SnO_2$ nano particles due to the increase of surface area of the nano-catalysts. Table 1 clearly reveals that among the screened $SnO_2$ nano particles, $SnO_2$ QD having 3.9 nm particle size showed superior catalytic activity and provided the best yield of the targeted dihydroxy indeno[1,2-b]indolone derivative (4a).

**Table 1**: Optimization of reaction conditions for the synthesis[a] of dihydroxy indeno[1,2-b]indolone derivative (4a)

| Entry | Catalyst | Catalyst loading (mol%) | Solvent | Time | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | _ | _ | $H_2O$ | 24h | Trace |
| 2 | Nano $Fe_3O_4$ | 10 | $H_2O$ | 4h | 5 |
| 3 | Nano $SiO_2$ | 10 | $H_2O$ | 4h | 9 |
| 4 | Nano ZnO | 10 | $H_2O$ | 5h | 7 |
| 5 | Nano CuO | 10 | $H_2O$ | 5h | 5 |
| 6 | Nano $Al_2O_3$ | 10 | $H_2O$ | 5h | 8 |
| 7 | Nano $CuFe_2O_4$ | 10 | $H_2O$ | 4h | Trace |
| 8 | $SiO_2$-$OSO_3H$ | 10 | $H_2O$ | 5h | 37 |
| 9 | Al-SBA15 | 10 | $H_2O$ | 5h | 18 |
| 10 | Bulk $SnO_2$ | 10 | $H_2O$ | 3 | 45 |
| 11 | $SnO_2$ (20 nm) | 10 | $H_2O$ | 3 | 57 |
| 12 | $SnO_2$ (10 nm) | 10 | $H_2O$ | 3 | 62 |
| **13** | **$SnO_2$ QDs** | **10** | **$H_2O$** | **2.0h** | **89** |
| 14 | $SnO_2$ QDs | 10 | Dioxane | 2.0h | 48 |
| 15 | $SnO_2$ QDs | 10 | DMSO | 2.0h | 63 |
| 16 | $SnO_2$ QDs | 10 | $CH_3CN$ | 2.0h | 45 |
| 17 | $SnO_2$ QDs | 10 | Toluene | 2.0h | 20 |
| 18 | $SnO_2$ QDs | 10 | DMF | 2.0h | 59 |
| 19 | $SnO_2$ QDs | 8 | $H_2O$ | 2.0h | 69 |
| 20 | $SnO_2$ QDs | 12 | $H_2O$ | 2.0h | 89 |

[a] All reactions were carried out with aniline (1 mmol), dimedone (1 mmol), ninhydrin (1 mmol), and specified catalyst in 5 ml solvent at 70 $^0C$.

[b]The yield of isolated products.

Various solvents were also screened to test the efficiency of the catalysts in different reaction medium and the results are summarized in Table 1. It was evident that the polar solvents afforded better yield than the nonpolar ones and water showed superiority over the other solvents. It is noteworthy to mention that quantity of the catalyst plays a vital role in the formation of the desired product. It was found that 10 mol % of $SnO_2$ quantum dots was sufficient enough to afford 4a with 89% isolated yield (Table 1, entry 13). The yield remained unaffected when the catalyst loading was increased to 12 mol% (Table 1, entry 20). However, the yield was decreased when the catalyst loading was reduced (Table 1, entries 19).

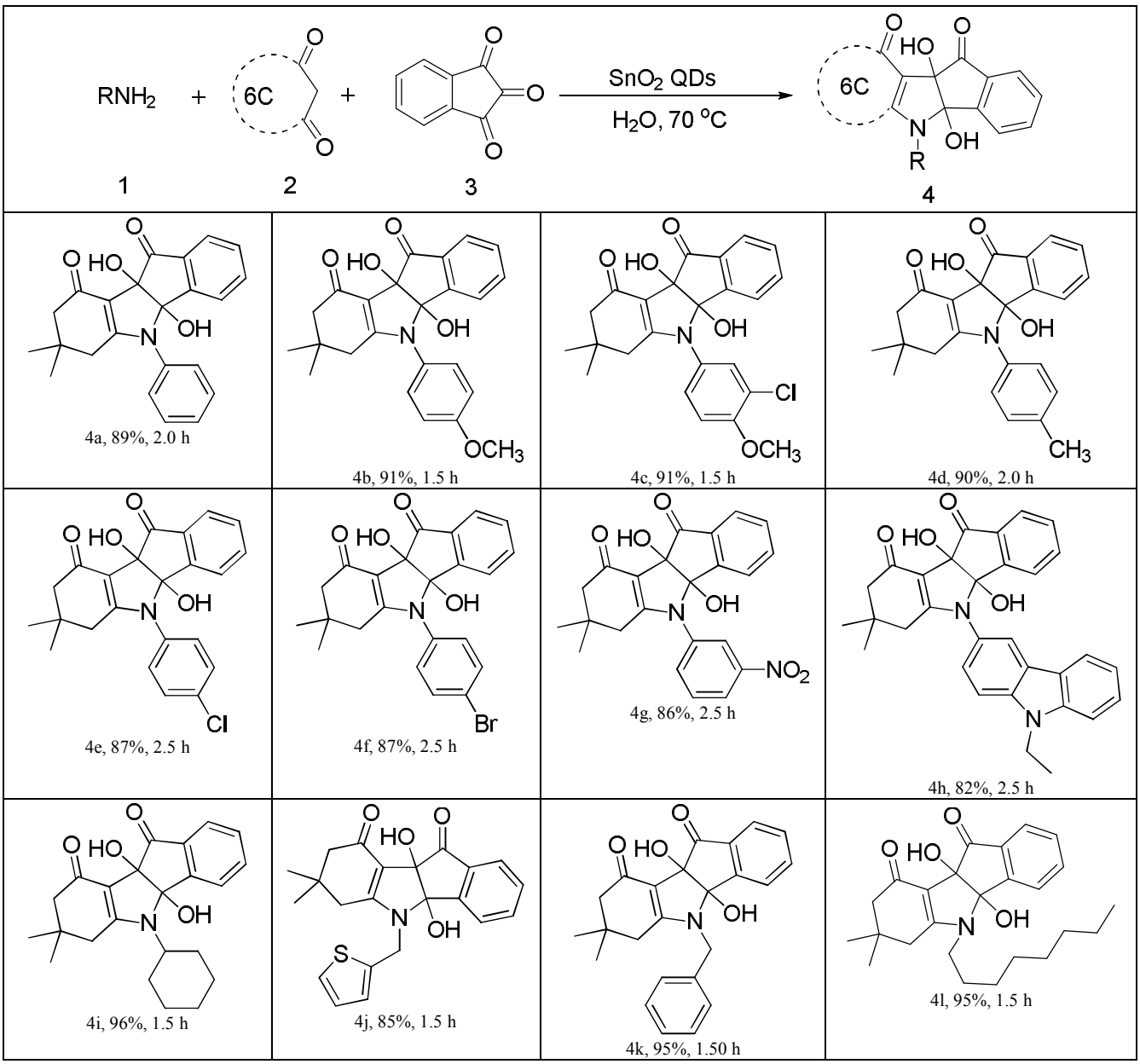
After standardization of all the reaction parameters, the proposed catalytic system was employed to synthesize dihydroxy indeno[1,2-b]indolone core in presence of a wide variety of commercially available amine derivatives. It was evident that aliphatic amine derivatives showed greater reactivity compared to aromatic amine derivatives (Table 2). The application of aromatic amine derivatives with electron releasing substituents in this three component protocol showed superior reactivity compared to that of with electron withdrawing substituent or unsubstituted aromatic amine derivatives (Table 2). Furthermore in the presence of sensitive heterocyclic core containing amine derivatives (Table 2), the reaction proceeded successfully to provide the desired products in high yields (82-86%). The catalytic system was effective for two 1,3-diketo compounds (dimedone and cyclohexane-1,3-dione) in aqueous media under thermal condition (Table 2).

RSC Advances Accepted Manuscript

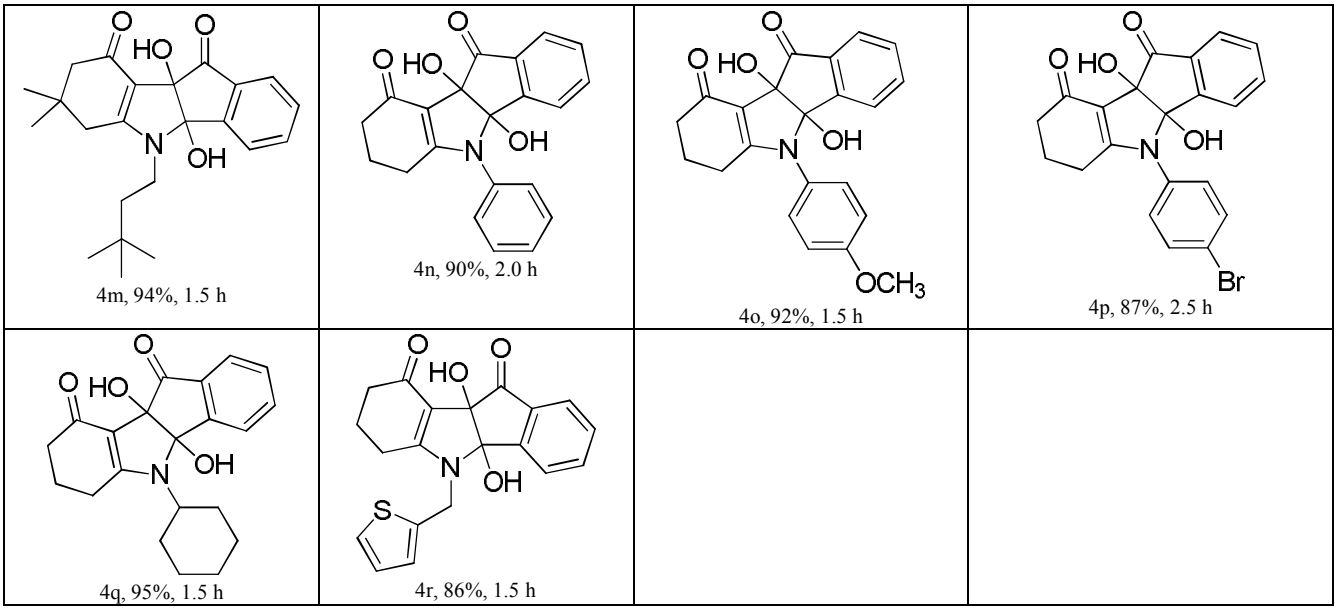
Journal Name RSCPublishing

ARTICLE

**Table 2**: Synthesis of dihydroxy indeno[1,2-b]indolone core via three-component reaction

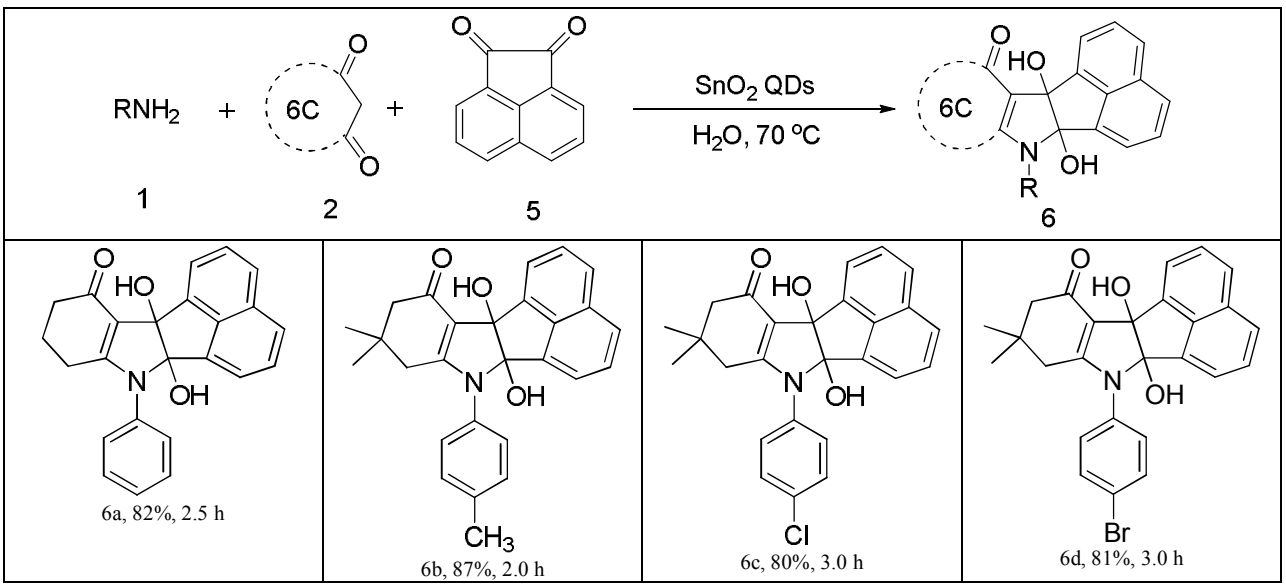



RSC Advances Accepted Manuscript




The optimized reaction conditions were thereafter employed for evaluating the scope of $SnO_2$ QDs catalyzed three component coupling reactions (Table 3). We have applied acenaphthoquinone substituting ninhydrin to obtain dihydroxy acenaphtho[1,2-b]indolone core. Unsubstituted aromic amine and aromic amine having 4-Me, 4-Cl and 4-Br groups underwent the reaction with two 1,3-diketo compounds (dimedone and cyclohexane-1,3-dione) in aqueous media to give the corresponding dihydroxy acenaphtho[1,2-b]indolone derivatives in high yield (Table 3).

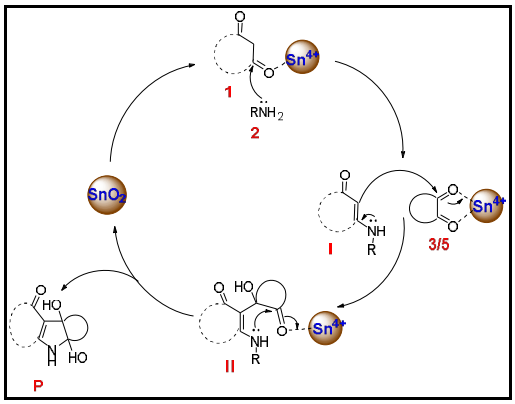
**Table 3**: Three-component synthesis of dihydroxy acenaphtho[1,2-b]indolone core




On the basis of experiment and findings thereof, we proposed a possible mechanism (Scheme 2) for the 3CRs. We believe that the reaction proceeds in a catalytic cycle which involves, synthesis of intermediate **I** (enaminone), then Michael addition and finally intra molecular cyclization catalyzed by $SnO_2$ QDs as presented in Scheme 2. The first step of the current 3CRs was the formation of intermediate **I,** through $Sn^{4+}$ (active species of $SnO_2$ QDs catalyst)-promoted condensation of 1,3-diketo compound **1** and amine derivative **2**. The strong Lewis acidic $Sn^{4+}$ ion of the $SnO_2$ nanoparticle has shown excellent catalytic activity in promoting the condensation reaction for the formation of the intermediate **I** by enhancing the electrophilicity of carbonyl groups of 1,3-diketo compound. The difference in reactivity of various aromatic amine derivatives can also be explained by the fact that in case of the aromatic amine derivatives with electron releasing substituents

RSC Advances Accepted Manuscript

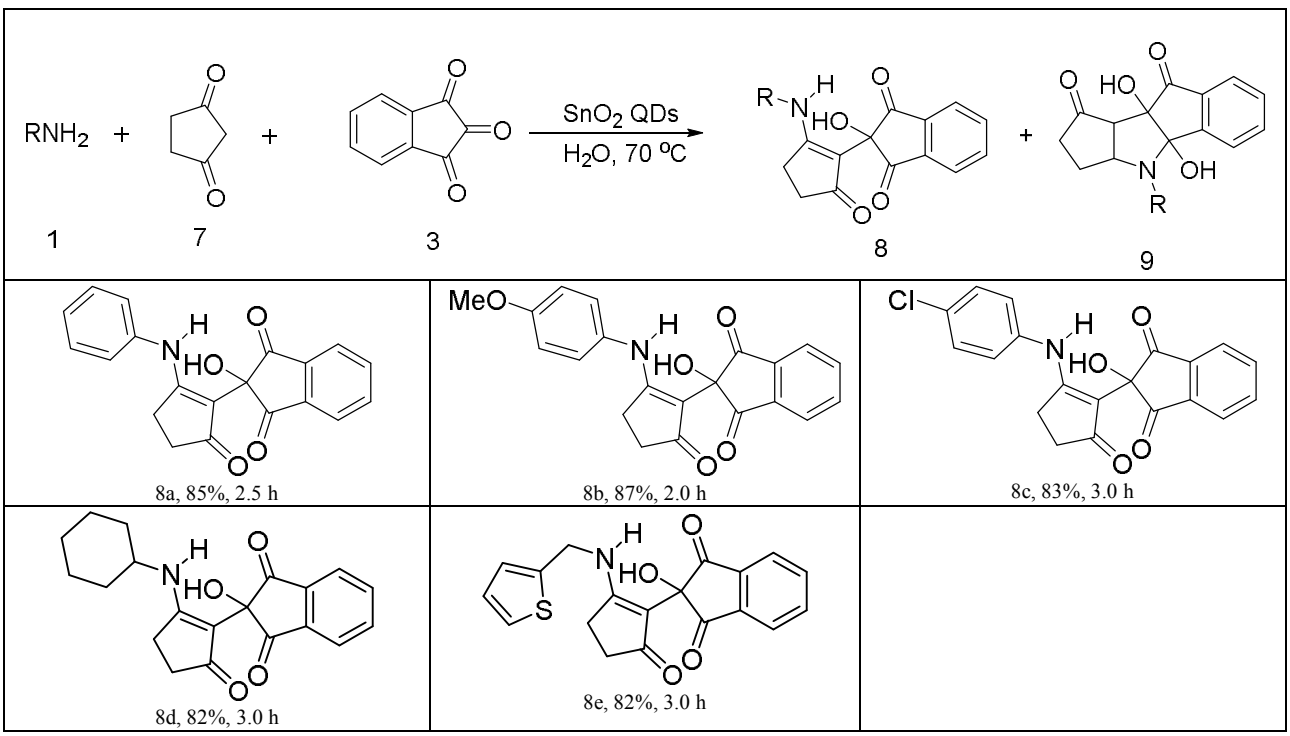
the formation of intermediate **I** is favored compared to that of with electron withdrawing substituent or unsubstituted aromatic amine derivatives. $SnO_2$ QDs then facilitated Michael addition step between intermediate **I** and 1,2-diketo compound **3/5** (ninhydrin and acenaphthoquinone) to generate the intermediate **II**. Finally, the Lewis acidic $Sn^{4+}$ interacted with the intermediate **II** which in turn facilitated intramolecular electrophilic cyclization with the formation of the five membered ring (**P**). The $SnO_2$ QDs catalyzed activation of condensation, Michael reaction and subsequent ring annulations leading to the desired heterocyclic derivatives were confirmed by the isolation of the intermediate **I**. We carried out the reaction starting from **I** (Prepared and isolated) with 1,2-diketo compound **3/5** (ninhydrin and acenaphthoquinone) and arrived at the same cyclic product **P** which further supported the proposed mechanistic course.




**Scheme 2.** The catalytic cycle for the formation of the products

The very high yield of the dihydroxy indeno[1,2-b]indolone derivatives thus directed us to expand the generality of this novel catalytic method and accordingly we turned our attention to synthesize a series of polyfunctionalized dihydroxy indeno[2,1-d]pyrrole derivatives. For this, cyclopentane-1,3-dione was examined to replace cyclohexane-1,3-dione for the formation of intermediate **I** (Scheme 2). But in practice , the reaction failed to generate the desired dihydroxy indeno[2,1-d]pyrrole derivatives **9** upon application of $SnO_2$ QDs catalyzed three component reaction. We applied aliphatic, hetero-aromatic and aromatic amines but in all the cases the acyclic intermediate **II** (Scheme 2) was isolated. This observation clearly indicates that cyclopentan-1,3-dione was not rightly compatible with the uncapped $SnO_2$ QDs catalyzed three component protocol. This observation also strenghthens the idea that the final intramolecular cyclization step is a reversible reaction. As the final step is reversible one, the dihydroxy indeno[2,1-d]pyrrole derivatives generated from the $SnO_2$ QDs catalyzed cyclization of the intermediate 8a-8e revert back to acyclic compound due to the instability of the three linearly standed highly strained five member ring containing dihydroxy indeno[2,1-d]pyrrole core.

**Table 4**: Three-component synthesis using five membered 1,3-diketo compound.




RSC Advances Accepted Manuscript


This journal is © The Royal Society of Chemistry 2012

Journal Name RSCPublishing

ARTICLE

As molecules containing coumarin and uracil linkages are prevalent in biological and pharmaceutical sciences, coumarin and uracil nuclei were then evaluated as the coupling partners for the $SnO_2$ QDs catalyzed reaction. The proposed mechanism (Scheme 2) showed that the reaction passes through the intermediate I. Like intermediate I, 4-aminocoumarin and 6-aminouracil derivatives have Michael donor and intramolecular cyclization centre (Figure 5) which encouraged us to develop a two component protocol using 1,2-diketo compound 3/5 (ninhydrin or acenaphthoquinone) and 4-aminocoumarin or 6-aminouracil.

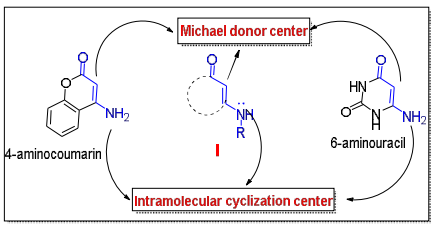
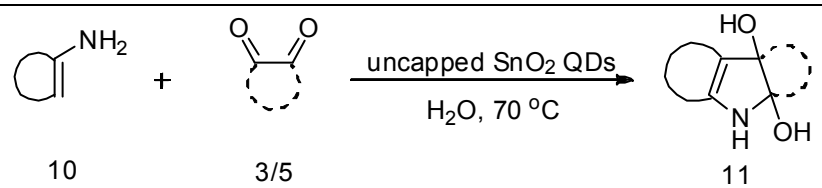


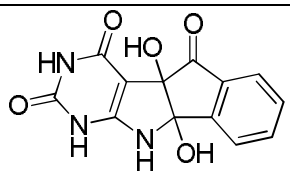

Figure 5: Structural similarities among intermediate **I**, 4-aminocoumarin and 6-aminouracil

We initiated the reaction installing 4-aminocoumarin and 6-aminouracil derivatives for the synthesis of coumarin and uracil fused dihydroxy indeno [1,2-b] pyrrole and dihydroxy acenaphtho[1,2-b] pyrrole core. The highly acid and base sensitive delicate coumarin and uracil moieties underwent SnO2 QDs catalyzed two component coupling reaction with good to excellent yield under the optimized reaction condition.

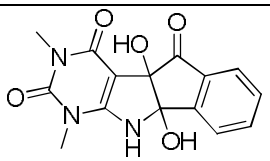
**Table 5**: Two-component synthesis of coumarin and uracil fused dihydroxy indeno [1,2-b] pyrrole and acenaphtho[1,2-b] pyrrole core.



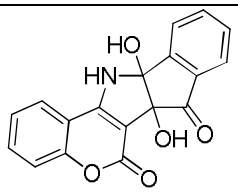

10 3/5 11



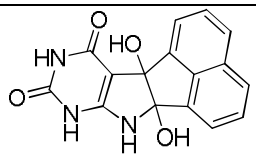
11a, 88%, 1 h



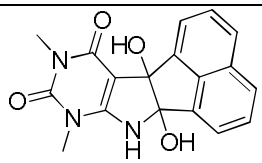
11b, 89%, 1 h



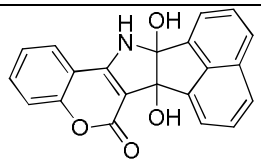
11c, 90%, 1h



11d, 82%, 1.5 h



11e, 83%, 1.5 h



11f, 83%, 1.5 h

RSC Advances Accepted Manuscript

Journal Name RSCPublishing

ARTICLE

The various products 4, 6, 8, 11 thus obtained, were characterized by IR, $^{1}$H NMR, $^{13}$C NMR and elemental analysis. Finally, the structures of two compounds **4a** and **8d** were confirmed by single-crystal X-ray diffraction (Figure 6 and 7).[27]

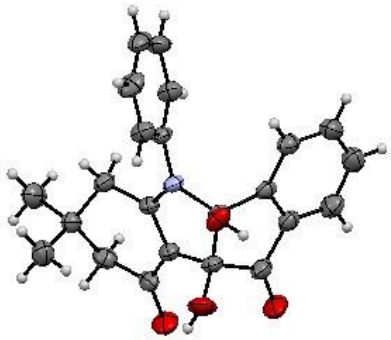


Figure 6: ORTEP Diagram of compound 4a (CCDC No. 991059)

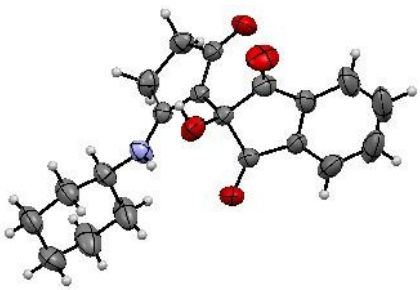


Figure 7: ORTEP Diagram of compound 8d (CCDC No. 1021234)

For useful applications of heterogeneous catalysts in practical field, the lifetime of the catalyst and its level of reusability are very important factors. Separation of the catalyst and isolation of the desired product from the reaction mixture is one of the most crucial aspects of organic synthesis. To illuminate this issue, we established a set of experiments using the recycled catalyst for the synthesis of dihydroxy indeno[1,2-b]indolone derivative (4a). The reactions were carried out under similar conditions in aqueous media. In the aforementioned developed protocol, after completion of the reaction, water was removed under reduced pressure from the reaction mixture and was stirred with 5mL methanol and then the catalyst was easily removed by filtration, leaving the clear reaction mixture as the filtrate. The recovered catalyst was then washed with 15 mL methanol and finally dried at 70 $^{0}$C for 1h. A new reaction was then performed with fresh solvent and reactants under the same conditions. To our delight, $SnO_2$ QDs catalyst could be used at least seven times without any change(loss) in activity. The X-ray diffraction (XRD) patterns (Fig. 2) and the TEM image (Fig. 8) indicated that the crystal structure of the $SnO_2$ QDs was intact even after seventh runs, which not only explained the excellent recycle results, but also reconfirmed the high stability of this catalyst.

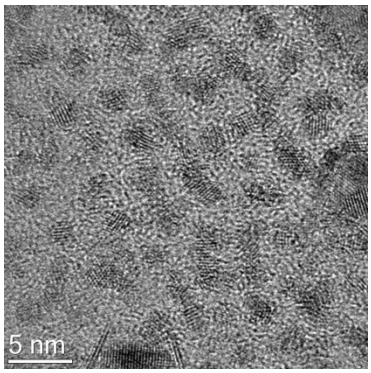



Figure 8: TEM image of the recovered SnO2 QDs catalyst after seventh run

## Conclusions

In summary, we have demonstrated $SnO_2$ QDs mediated one-pot multi-component coupling protocol for the preparation of a wide variety of heterocyclic derivatives. $SnO_2$ QDs was prepared by a simple and effective solvo-thermal method and characterized by using XRD, HRTEM and TEM images. The QDs-catalyst system encompassing very high surface area allows rapid and selective chemical transformations with excellent product yield. This is a promising approach from sustainable and practical chemistry viewpoints. This simple, environmentally benign and convenient methodology extends the scope towards a wide spectrum of novel compounds possessing an important structural subunit of a variety of biologically active molecules.

## Experimental Section

### Preparation of $SnO_2$ QDs:

The uncapped $SnO_2$ QDs was prepared by a simple solvothermal process. 5.83 mmol $SnCl_4.5H_2O$ was dissolved in a mixed solvent (18.5 ml methanol + 9.28 ml ethylenediamine) with constant magnetic stirring for 1 hr. 58.3 mmol of urea in 18.5 ml of deionised $H_2O$ was then added to the reaction mixture. The resultant solution was stirred for 30 min to obtain a white slurry which was then transferred to a 52 ml teflon lined

RSC Advances Accepted Manuscript

stainless steel chamber and heat treatment was continued at 90 ˚C for 8 hrs. After cooling down to room temperature, the product was centrifuged. The as-collected product was washed with deionised $H_2O$ and ethanol for several times to remove the impurities and dried overnight in vacuum.

**General Procedure for the synthesis of dihydroxy indeno[1,2-b]indolone and dihydroxy acenaphtho[1,2-b]indolone derivatives:**

A mixture of amine (1.0 mmol), 1,3-dicarbonyl compound (dimedone or cyclohexane-1,3-dione) (1.0 mmol), and $SnO_2$ QDs (10 mol %) were stirred in 5 ml water at 70 $^0$C. 30 minutes later, 1,2-dicarbonyl compound (ninhydrin or acenaphthenequinone) (1.0 mmol) was added. After completion of the reaction (analyzed by TLC), water was removed under reduced pressure from the reaction mixture followed by stirring with 5mL methanol (5 mins) and then the catalyst was removed by filtration, leaving the clear reaction mixture as the filtrate. Removal of solvent under reduced pressure and purification of the crude product by recrystallization from ethanol provided pure products.

**General Procedure for the synthesis of coumarin and uracil fused dihydroxy indeno [1,2-b] pyrrole and acenaphtho[1,2-b] pyrrole derivatives:**

A mixture of 6-aminouracil derivative or 4-aminocoumarin (1.0 mmol), 1,2-dicarbonyl compound (ninhydrin or acenaphthenequinone) (1.0 mmol), and $SnO_2$ QDs (10 mol %) were stirred in 5 ml water at 70 $^0$C. After completion of the reaction (analyzed by TLC), water was removed under reduced pressure from the reaction mixture followed by stirring with 5mL methanol (5 mins) and then the catalyst was removed by filtration, leaving the clear reaction mixture as the filtrate. Removal of solvent under reduced pressure and purification of the crude product by recrystallization from ethanol provided pure products.

## Acknowledgements

We gratefully acknowledge the financial support from U.G.C. and University of Calcutta. K. P. thanks U.G.C., New Delhi, India, for the grant of Senior Research fellowship.

## Notes and references

Department of Chemistry, University of Calcutta, Kolkata-700009, India. *Corresponding author. Tel.: +913323501014, +919433120265; fax: +913323519754;
E-mail address: ardchem@caluniv.ac.in, ardas66@rediffmail.com (A. R. Das)

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

1. Y. R. Leshkov, J. N. Chheda and J. A. Dumesic, *Science* 2006, **312**, 1933.
2. (a) M. Bicker, J. Hirth and H. Vogel, *Green Chem*. 2003, **5**, 280. (b) Y. R. Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature* 2007, **447**, 982.
3. J. N. Chheda, Y. Roman-Leshkov and J. A. Dumesic, *Green Chem*. 2007, **9**, 342.
4. V. V. Ordomsky, J. van der Schaaf, J. C. Schouten and T. A. Nijhuis, *J. Catal*. 2012, **287**, 68.
5. (a) Z. H. Zhang, B. Liuand, Z. B. Zhao, *Carbohydr. Polym*. 2012, **88**, 891. (b) Y. Yang, C. W. Hu and M. M. Abu-Omar, *Green Chem*. 2012, **14**, 509. (c) B. R. Caes and R. T. Raines, *ChemSusChem*, 2011, **4**, 353. (d) B. Kim, J. Jeong, D. Lee, S. Kim, H. J. Yoon, Y. S. Lee and J. K. Cho, *Green Chem*. 2011, **13**, 1503.
6. X. H. Qi, M. Watanabe, T. M. Aida and R. L. Smith, *Green Chem*. 2008, **10**, 799.
7. W. Teunissen, A. A. Bol and J. W Geus, *Catal. Today* 1999, **48**, 329.
8. C. Bal, B. Baldeyrou, F. Moz, A. Lansiaux, P. Colson, L. Kraus-Berthier, S. Léonce, A. Pierré, M.-F. Boussard, A. Rousseau, M. Wierzbicki and C. Bailly, *Biochem. Pharmacol*. 2004, **68**, 1911.
9. (a) A. A. Emmanuel-Giota, K. C. Fylaktakidou, D. J. Hadjipavlou-Litina, K. E. Litinas and D. N. Nicolaides, J. Heterocycl. Chem. 2001, 38, 717. (b) J. Neyts, E. D. Clercq, R. Singha, Y. H. Chang, A. R. Das, S. K. Chakraborty, S. C. Hong, M. H. Hsu and J. R. Hwu, J. Med. Chem. 2009, 52, 1486. (c) Soine, T. O. J. Pharm. Sci. 2006, 53, 231.
10. M. Suzuki, K. Nakagawa-Goto, S. Nakamura, H. Tokuda, S. L. Morris-Natschke, M. Kozuka, H. Nishino and K. H. Lee, Pharm. Biol. 2006, 44, 178.
11. O. Kayser and H. Z. Kolodziej, Naturforsch. 1999, 54c, 169.
12. R. C. Sharma and R. K. Parashar, J. Inorg. Biochem. 1988, 32, 163.
13. Y. L. Garazd, E. M. Kornienko, L. N. Maloshtan, M. M. Garazd and V. P. Khilya, Chem. Nat. Prod. 2005, 41, 508.
14. C. A. Kontogiorgis and D. J. Hadjipavlou-Litina, J. Med. Chem. 2005, 48, 6400.
15. J. R. Hwu, R. Singha, S. C. Hong, Y. H. Chang, A. R. Das, I. Vliegen, E. D. Clercq and J. Neyts, Antiviral Res. 2008, 77, 157.
16. (a) P. G. Baraldi, B. Cacciari, S. Moro, G. Spalluto, G. Pastorin, T. Da Ros, K. N. Klotz, K. Varani, S. Gessi and P. A. Borea, J. Med. Chem. 2002, 45, 770. (b) A. Maconi, G. Pastorin, T. Da Ros, G. Spalluto, Z. G. Gao, K. A. Jacobson, P. G. Baraldi, K. Varani, S. Moro and P. A. Borea, J. Med. Chem. 2002, 45, 3579.
17. (a) E. Ongini, A. Monopoli, B. Cacciari and P. G. Baraldi, Farmaco 2001, 56, 87. (b) K. A. Jacobson, P. Al Ijzerman and J. Linden, Drug Dev. Res. 1999, 47, 45. (c) C. E. Muller, Farmaco 2001, 56, 77.
18. L. Xiao, H. Shen, R. von Hagen, J. Pan, L. Belkoura and S. Mathur, *Chem. Commun*. 2010, **46**, 6509.
19. T. T. Baby and S. Ramaprabhu, *J. Appl. Phys*. 2012, **111**, 034311.
20. H. Ahn, H. Choi, K. Park, S. Kim and Y. Sung, J. *Phys. Chem. B* 2004, **108**, 9815.

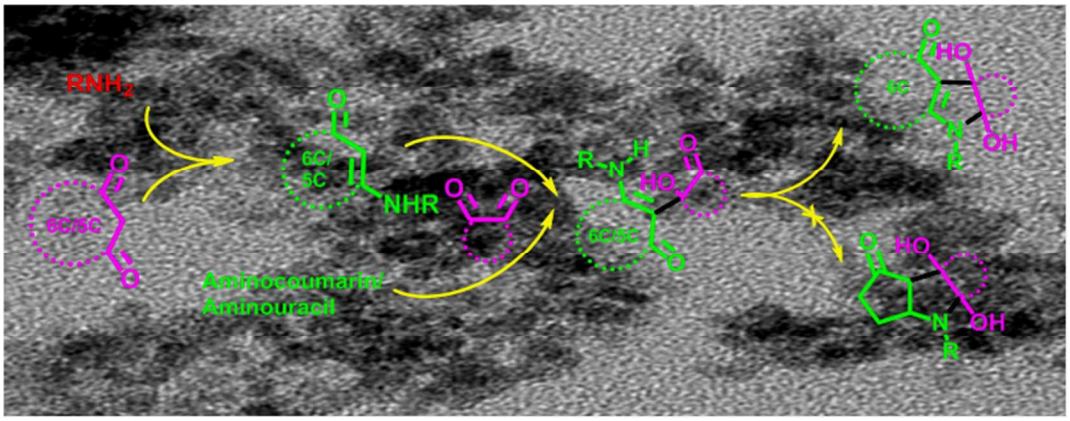
RSC Advances Accepted Manuscript

21. T. Jia, W. Wang, F. Long, Z. Fu, H. Wang and Q. Zhang, *J. Phys. Chem. C* 2009, **113**, 9071.
22. S. Gubbala, V. Chakrapani, V. Kumar and M. K. Sunkara, *Adv. Funct. Mater.* 2008, **18**, 2411.
23. N. Kudo, Y. Shimazaki, H. Ohkita, M. Ohoka and S. Ito, *Sol. Energy Mater. & Sol. Cells* 2007, **91**, 1243.
24. (a) S. Paul, P. Bhattacharyya and A. R. Das, *Tetrahedron Lett.* 2011, **52**, 4636. (b) P. Bhattacharyya, K. Pradhan, S. Paul and A. R. Das, *Tetrahedron Lett.* 2012, **53**, 4687. (c) K. Pradhan, S. Paul and A. R. Das, *Catal. Sci. Tech*. 2014, **4**, 822.
25. (a) H. J. Hemmerling and G. Reissb, *Synthesis* 2009, 985. (b) C. Hundsdörfer, H. J. Hemmerling, C. Götz, F. Totzke, P. Bednarski, M. L. Borgne and J. Jose, *Bioorg. Med. Chem*. 2012, **20**, 2282.
26. S. Paul, K. Pradhan, S. Ghosh, S. K. De and A. R. Das, Tetrahedron 2014, 70, 6088.
27. Crystallographic data for the structures 4a and 8d have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC No. 991059 and 1021234 respectively. Copies of the data can be obtained, free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 01223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

RSC Advances Accepted Manuscript

 This journal is © The Royal Society of Chemistry 2012

## Table of Content:




RSC Advances Accepted Manuscript