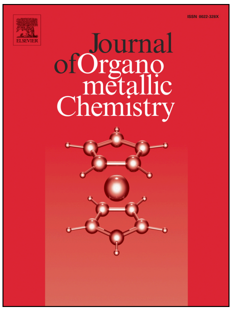

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Use of PS-Zn-anthra complex as an efficient heterogeneous recyclable catalyst for Carbon dioxide fixation reaction at atmospheric pressure and synthesis of dicoumarols under greener pathway

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Abstract

A polystyrene functionalized Zinc anthranilic acid complex catalyst has been prepared. The PS-Zn-anthra complex has been characterized by EDX, Scanning electron micrographs (FE-SEM), FTIR spectra, UV-vis spectra and thermogravimetric analyses. A greener and novel methodology was considered for the production of dicoumarol derivatives utilizing PS-Zn-anthra complex as a Lewis acid catalyst, non-toxic, mild in H_2O employing heteroaromatic/aromatic aldehydes and 4-hydroxycoumarin. The catalyst also shows good catalytic activity in the cyclo addition of CO_2 to epoxide. The results of activity of catalyst imply that the procedure adopted provides numerous advantages such as low loading of catalyst, operational simplicity, mild reaction conditions, quantitative yields, and short reaction time. The PS-Zn-anthra complex exhibited the elevated efficiency of recycling in these reactions. This catalyst can be recycled for five times without appreciable loss of its activity.

Keywords: Heterogeneous Catalyst, PS-Zn-anthra complex, Cyclic Carbonate, 4-hydroxycoumarin, aromatic/heteroaromatic aldehydes, dicoumarols

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1.Introduction

CO_2 is an extremely substantial C1 feedstock in the synthetic field of organic chemistry as it is cost-effective, non-hazardous, non-flammable and abundant in nature [1]. The global warming caused by the unlimited utility of fossil fuels, other activities of human and industrialization and to minimize it is the challenging area of current interest. In the present day, huge attention has been paid in order to establish the hazardless procedures which are environmentally benign based on reactions of CO_2 fixation [2-6]. Greater than thirteen gigatonnes of CO_2 produced yearly from the fossil fuels burning for the generation of electrical energy and heat, is a most important supplier to climate change and acidification of seawater [7]. It has been predicted by the IPCC (International Panel for Climate Change) that by the year 2100, the average universal temperature could increase by as high as 1.8-1.9°C [8]. A decrease in emissions of green house gas affecting weather change is immediately essential on a scale of the global system. One of the procedures towards decreasing emissions of carbon dioxide is CCS (capture of carbon and storage), which has the potential to diminish emissions of the future world from the use of energy by twenty percent [9]. But this method (CCS) is less cost-effective compared to CCU (carbon capture and utilization) method because of separation, purification and transportation of CO_2. The economics of capturing CO_2 could be improved if the captured carbon could be utilized. This process generates more revenue and some cases it reduces overall carbon emission. [10]. Nowadays, a wide series of heterogeneous and homogeneous catalytic systems such as functionalized polymers [11], crown ether [12], alkali metal salts [13], ionic liquids [14] or titanosilicates [15], organic bases [16-17], mixed oxides [18,19], hydrogen bond donors [20,21], metal complexes [22], zeolites [23,24], functionalized mesoporous materials [25-29] and zeolitic imidazolate frameworks [30,31] are reported in CO_2 transformation of various chemical systems. Recently, a variety of metal-free tri-s-triazine terminal-linked ionic liquids [32], urea derivative-based ionic liquids (UDILs) [33], and binary Zn-SBA-15/KI catalysts [34] were generated with higher thermal stability. These catalysts were structurally examined as well as applied to CO_2 capture and transformation under the application of mild conditions.

Dicoumarol is a naturally occurring anticoagulant drug which uses as an antagonist vitamin K. It is chemically designed as 3,3’-methylenebis[4-hydroxycoumarin] and derived from coumarin metabolism in the sweet clover (*Melilotus officinalis* and *Melilotus alba*) by *Penicillium jensi* and *Penicillium bacterial nigricans*. A recent work has exhibited that the hindrance of NAD (P) H: quinone oxidoreductase (NQO_1) with dicoumarol affects the damage of cell and oxidative strain in cancer pancreatic cells [35]. Such species have been established in clinical trials to have some action against malignant melanoma, metastatic renal cell carcinoma and prostate cancer [36–38]. Lanthanum(III) complexes of dicoumarol have been found to exhibit cytotoxic activity widely [39]. Species having this ring also imparts different other activities of the pharmacological system such as anthelmintic, HIV proteases inhibition, antioxidant, insecticidal, antifungal, hypnotic, antimicrobial and phytoalexin [40–47]. A number of schemes have been known for the production of this significant group of compounds during the last decades including utility of (Et_2AlCl_3) [48], DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) [49], molecular iodine [50], refluxing ethanol or acetic acid [51], manganous chloride [52], thermal solvent-free reaction conditions [53] and $POCl_3$ in dry DMF [54] etc. Despite their potential values, various reported procedures experience some disadvantages such as expensive reagents, long reaction time, stringent conditions, use of toxic catalysts that are detrimental to the environment and low product yields. In order to overcome these limitations, the development of new procedure are required for the generation of dicoumarol in terms of catalyst reusability, economic viability and operational simplicity. Reactions catalyzed by organic Lewis-acid in water have attracted much attention in organic synthesis as they allow access to more environmentally-benign processes under mild reaction conditions.

Polystyrene is the most usually known heterogeneous support due to its high stability in the environment and low cost. The polymer-supported zinc catalysts are obtained from Merrifield Resin, have worked in different coupling reactions [55-63], and minor leaching of zinc has appeared during the time of cross-coupling.

In the current study, we have synthesized polymer-supported Zn catalyst and utilized it in the production of dicoumarol derivatives. The characterization of polymer-supported Zn catalyst was done by different spectroscopic and physicochemical techniques. The impact of the different parameters on the catalytic activity was checked. The most remarkable character of the polymer-supported Zn catalyst involves fast reactions with outstanding transformation and absolute stability under the application of different reaction conditions. Moreover, the Zn catalyst displayed excellent recyclability for the production of dicoumarol derivatives [64].

2. Experimental Section

All chemical reagents were analytical grade. Purification of all solvents was done and dried according to standard methods. Merrifield resin was bought from Sigma-Aldrich and Zinc(II)chloride was purchased from Arora Matthey. Other chemicals were bought from Alfa aesar (India) and Merck.

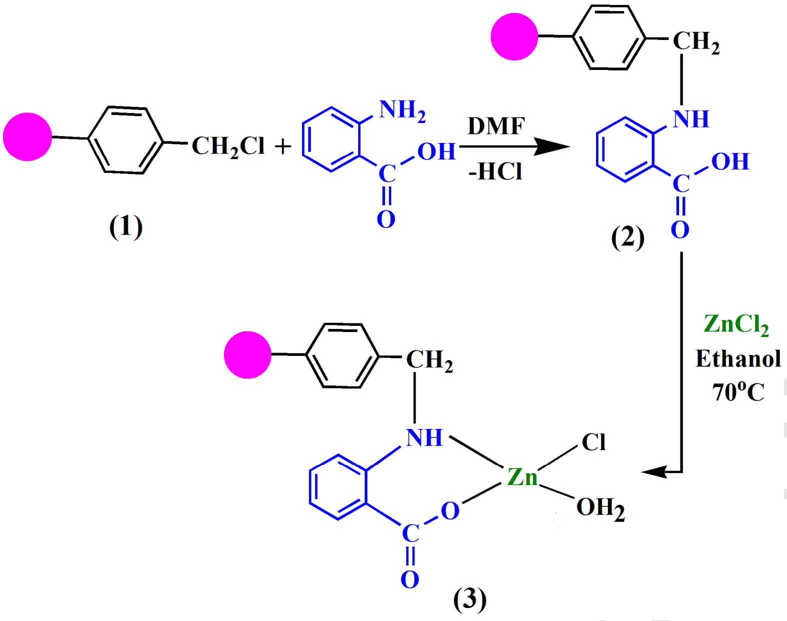
2.1. Materials

2.2. Characterization Techniques

A Perkin Elmer, 2400C, USA elemental analyzer was utilized to assemble microanalytical data (C, N and H). Analysis of surface morphology of functionalized polystyrene supported ligand and metal complex was performed with a scanning electron microscope (ZEISS EVO40, England) equipped with a facility of EDX. FTIR (Fourier transform infrared) spectra for the catalyst precursors and catalyst were recorded on a Perkin Elmer, FTIR 783, USA spectrophotometer using KBr pellets. UV-vis spectrum was recorded on a Shimadzu, Japan, UV-2401PC double beam spectrophotometer equipped with an integrating sphere attachment for solid samples. The thermal stability of the immobilized catalyst was determined with a Mettler Toledo, Switzerland, TGA/DTA 851e instrument. All reaction products were identified by using ^{1}H NMR spectra.

2.3. Synthesis of PS-Zn-anthra complex

The synthetic method of PS-Zn-anthra complex is given in Scheme 1. The complex was prepared according to the literature method [65]. Initially, the Merrifield resin (1) (500 mg) was reacted with anthranilic acid (250 mg) in DMF (5 mL) under the application of reflux condition for 32 h to give polymer-anchored ligand (2). This polymer-anchored ligand (1 g) consequently reacted with $ZnCl_2$ (0.1 g) in ethanol (10 mL) for 10 h at 70 ^{o}C to produce the resultant polymer supported Zn catalyst (3).



Scheme 1. Preparation of PS-Zn-anthra complex

Elemental analysis of PS-Zn-anthra complex by ICP spectroscopy provided a zinc loading of 4.1 wt%. Elemental analysis of PS-Zn-anthra complex provided presence of 3.74 wt% Cl. The calculated molar Cl/Zn ratio of 1.1 is in agreement with that expected for structure (3) [(PS-anthra)ZnClL]. Additionally, Elemental analysis revealed the presence of 1.12 wt% N corresponding to a molar N/Zn ratio of 1.2. Within the limit of uncertainty of elemental analysis (± 10%), this value is almost identical with expected (N/Zn = 1) based on the structure (3). Elemental analysis significantly revealed the presence of 2.42 wt% Cl (i.e elimination of 1.32 wt% Cl in ligand from 3.74 wt% Cl in complex) in PS-Zn-anthra complex. 2.42 wt% Cl in PS-Zn-anthra complex significantly came from Zinc chloride. This elemental analysis allowed for the determination of a molar Cl/Zn ratio of 1.1 for structure (3) [66, 67].

Table 1. Chemical composition polymer-anchored ligand and its Zn catalyst.

Compound	Colour	C (%)	H (%)	N (%)	Cl (%)	Zn Loading(%)
PS-anthra ligand	Pale yellow	83.27	7.34	4.23	1.32	-
PS-Zn-anthra complex	Pale yellow	80.43	7.22	1.11	3.74	4.09

2.4. Typical procedure for synthesis of cyclic carbonates at 1 atmospheric pressure of CO_2

Oxirane (5 mmol), TBAB (Bu_4NBr) (0.083 mmol, 26.7 mg) and PS-Zn-anthra complex (50 mg) were poured into a 100 ml R.B flask placed on a magnetic stirrer. The R.B flask was fitted with a stopper pierced by a CO_2 balloon under 1 atm pressure. The reaction mixture was stirred at room temperature for 6 h. The transformation of oxirane to the respective organic five-membered carbonate was checked from the data of ^{1}H NMR spectra. The isolation of organic five-membered carbonate was performed by column chromatography. The characterization of the products was analyzed from the concept of their spectroscopic data (^{1}H NMR) and was confirmed by comparison of NMR spectra with literature data.

2.5. Typical method for the production of dicoumarols

A mixture of aldehyde (1 mmol), PS-Zn-anthra complex (5 mol%), 4-hydroxycoumarin (2 mmol), and water (5 mL) was poured in a R.B. flask and refluxed at 100^{o}C for the fixed time. The progress of the reaction was checked by TLC (thin-layer chromatography). At the end of the reaction, the solution was cooled to RT. The resultant product was extracted with DCM, dried over anhydrous sodium sulphate, and resultant solution was concentrated to provide. The PS-Zn-anthra complex was separated from the reaction mixture by easy separation of organic and aqueous phases. The PS-Zn-anthra complex present in the layer of the aqueous phase was separated by precipitating the layer of aqueous phases by addition of acetone and utilized for the successive cycle.

3. Results and discussion

3.1. Characterization of PS-Zn-anthra complex

3.1.1. Microscopic analysis

Scanning electron micrographs (SEM) of the polymer-anchored ligand and the PS-Zn-anthra complex were recorded to recognize the change of morphology occurring on the polymer matrix surface. In Fig. 1 the SEM images of the polymer-supported ligand (a) and the PS-Zn-anthra complex (b) are demonstrated. SEM image exhibited a difference in morphology between PS-anthra ligand and the PS-Zn-anthra complex. EDX data established the attachment of metal on the polymer matrix surface (Fig.2). There is no change in morphology between PS-Zn-anthra complex and reused PS-Zn-anthra complex.

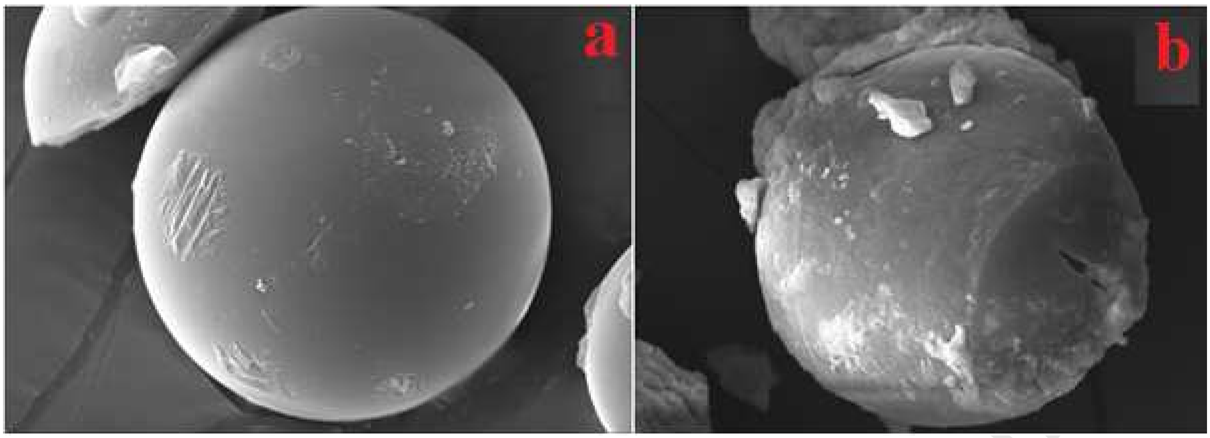


Fig.1. FE-SEM picture of PS-anthra ligand (a) and PS-Zn-anthra complex (b) respectively.

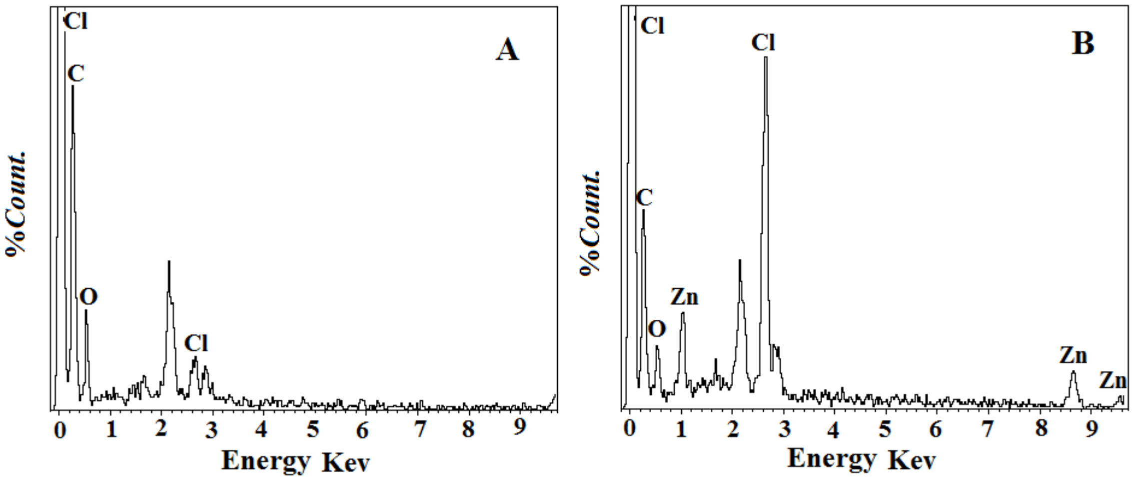


Fig. 2. EDX spectra of PS-anthra ligand (A) and PS-Zn-anthra complex (B).

3.1.2.Thermogravimetric analysis:

Thermogravimetric analyses of PS-Zn-anthra complex and PS-anthra ligand, polymer supported anthranilic acid, were taken in air atmosphere at a heating rate of 10 ^{o}C min^{-1}. PS-Zn-anthra complex is stable up to 430 ^{o}C whereas PS-anthra ligand decomposes at 390 ^{o}C (Fig. 3). After coordination with Zn, the thermal stability of PS-anthra ligand is slightly enhanced. Study of DTA supports that the stages of decomposition are exothermic in nature (not shown).

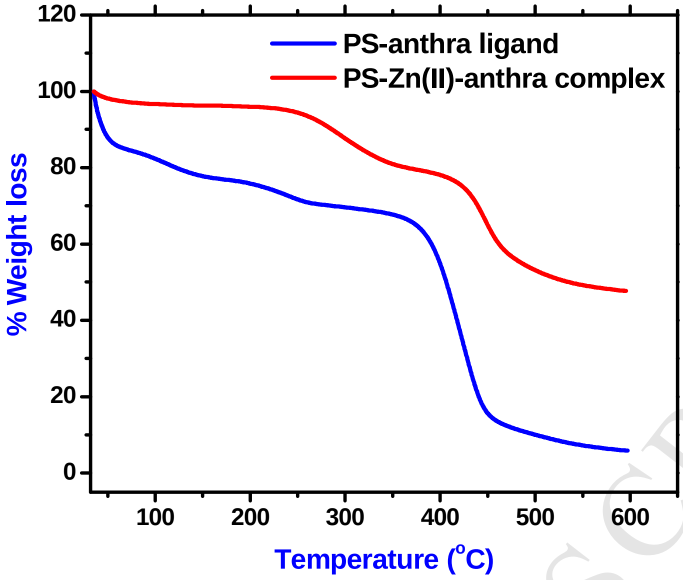


Fig. 3. Thermogravimetric analyses of PS-anthra ligand and PS-Zn-anthra complex

3.1.3. UV-visible spectra of the PS-Zn-anthra complex:

The UV-vis spectra indicated further confirmation for the existence of Zn supported on polymer. The UV-vis spectra of the Zn catalyst on polymer support has been performed in reflectance diffused spectrum mode as a disc of $BaSO_4$ owing to limitations of its solubility in ordinary organic solvents. Fig.4 indicates the UV–vis reflectance diffused spectra produced porous PS-Zn-anthra complex. The UV–vis reflectance diffused spectrum of PS-Zn-anthra complex appeared at absorption band at 251 nm. The UV-visible spectrum of PS-anthra ligand and its PS-Zn-anthra complex is shown in Fig.4. The characteristic bands at 230, 251, 342 nm for the pure ligand are due to the π-π^* transition (see supporting information). When PS-anthra ligand was coordinated with Zn, the disappearance of the band at 342 nm occurs and appearance of the new band at 370 nm is observed. It may be assigned to the charge transfers between coordinated atoms and the central zinc atom. [68].

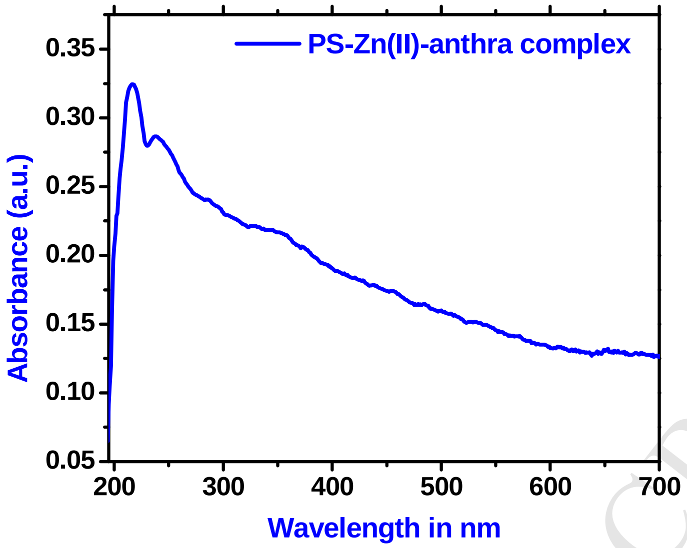


Fig. 4. The UV-visible absorption spectrum of PS-Zn-anthra complex.

3.1.4. FT IR spectra:

The attachment mode of anthranilic acid and Zn onto the polymer support is established by spectral IR data both in the far (600-50 cm^{-1}) and mid (4000-400 cm^{-1}) IR regions. The pure Merrifield resin beads exhibit a characteristic IR sharp peak at 1258 cm^{-1} (ν -CH_2-Cl group in Merrifield resin). Appearance of a strong band at 3456 cm^{-1} (ν-NH, secondary amine) and disappearance of (ν-C-Cl) band on coordinating with anthranilic acid implies the formation of covalent bond through N atom. Other peaks at 1702 (ν C=O), 3449 (ν -OH), 1410 (ν_{sym} COO) and 1560 (ν_{asym} COO) confirmed the ligand formation [69]. After coordination with metal, shifting of peaks towards higher wavelength regions (1405 ν_{sym} –COO, 1556 ν_{asym} –COO and 3280 ν N-H) implies the participation of the –NH_2 and COOH groups of the anthranilic acid in formation of complex.

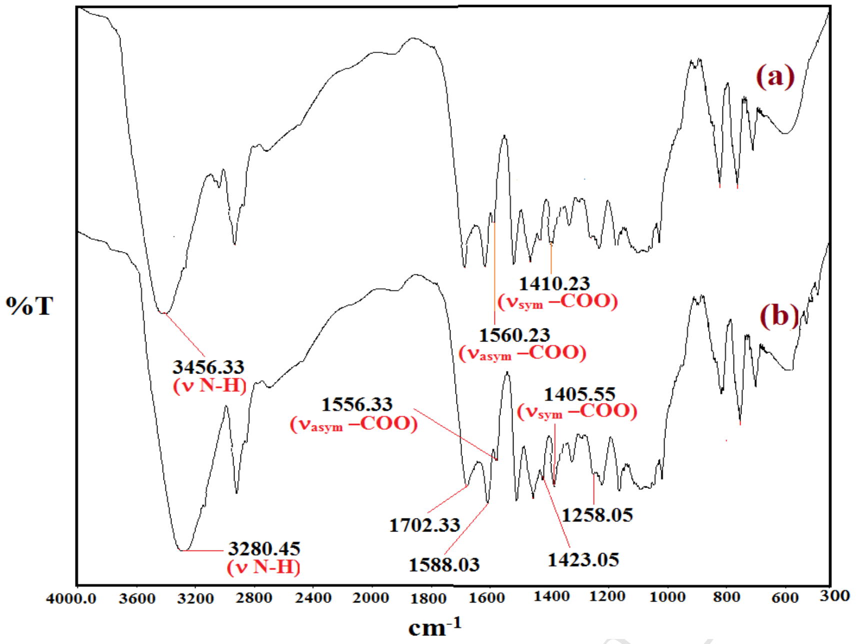
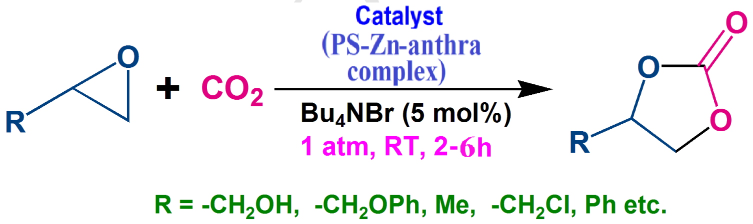


Figure 5. FT IR spectra of the PS-anthra ligand(a) and PS-Zn-anthra complex(b).

3.2.CatalyticActivity

3.2.1. Organic cyclic carbonates synthesis catalyzed by PS-Zn-anthra complex

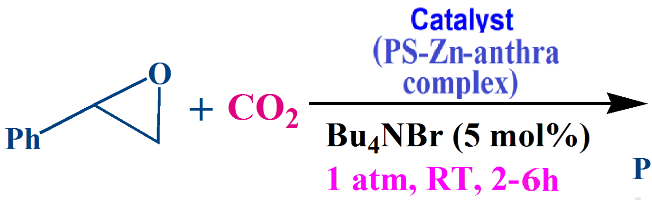
CO_2 incorporation on oxiranes leads to the production of organic cyclic carbonates over PS-Zn-anthra complex with TBAB (Bu_4NBr) as cocatalyst as shown in Scheme 2.



Scheme 2. Generation of organic cyclic carbonates from CO_2 and oxiranes

All the conditions have been screened including time of reaction, the quantity of Bu_4NBr to optimize the product yield of the cyclic five-membered organic carbonate (Table 2). The incorporation of CO_2 on SO (styrene oxide) to SC (styrene carbonate) is specified as the model reaction (Table 2). During the preliminary work, the quantity of Bu_4NBr (TBAB) has been altered to catalyze this carbon dioxide fixation. High yield of styrene carbonate was obtained using 5 mol% TBAB (Table 2, entries 8). From the table 2, time of reaction has the very essential role in the product yield (Table 2, entries 4-9). The advancement of reaction has been examined even at the tiny time period and obtained moderately better yields. When reactions took place with lesser and higher than 5 mol% of TBAB (Bu_4NBr), incomplete SO conversions and comparatively lesser yield were observed (Table 2, entry 1-3). It was also investigated that without cocatalyst and PS-Zn-anthra complex small quantity of expected product was observed (entries 9,10). Under optimized conditions of the reaction of TBAB (5 mol%) at room temperature for 6 h with just catalyst (50 mg) at 1 atmospheric CO_2 pressure, 97% yield of SC was observed (Table 2, entry 8).

Table 2. Optimization of conditions of reaction for the production of oxirane (styrene carbonate)[a]



Entry	TBAB / Bu_4NBr (mol%)	CO_2/atm	Time (h)	Yield[b] (%)	TON/TOF (h^{-1})
1	5	1	4	82	131/33
2	5	1	5	91	145/29
3	2	1	6	26	41/7
4	4	1	6	62	99/16
5	**5**	**1**	**6**	**97**	**155/26**
6	6	1	6	77	122/20
7	5	1	2	58	92/46
8	5	1	3	74	118/39
9[c]	5	1	6	Trace	-
10	0	1	6	Trace	-

[a]**Reaction conditions:** Oxirane (5 mmol of SO), PS-Zn-anthra complex (3.135×10^{-5} mol), room temperature; [b]GC yield of cyclic carbonate; [c]without catalyst

For exploring the total potential of PS-Zn-anthra complex in the carbon dioxide fixation the reaction time has been enhanced under optimized conditions of reaction until the entire transformation of SO is observed. Figure 6 explored the idea for the time of reaction with transformation and selectivity. The plot indicated the transformation of oxirane (styrene oxide) enhances linearly over the function of time from the beginning to 6 h and it kept the conversion level of 97% yield in subsequent 2 h, whereas the SC selectivity kept 100% approximately at the whole reaction period. From Figure 6 it is clear that time of reaction of 6 h is satisfactory to undergo this cycloaddition reaction at normal temperature.

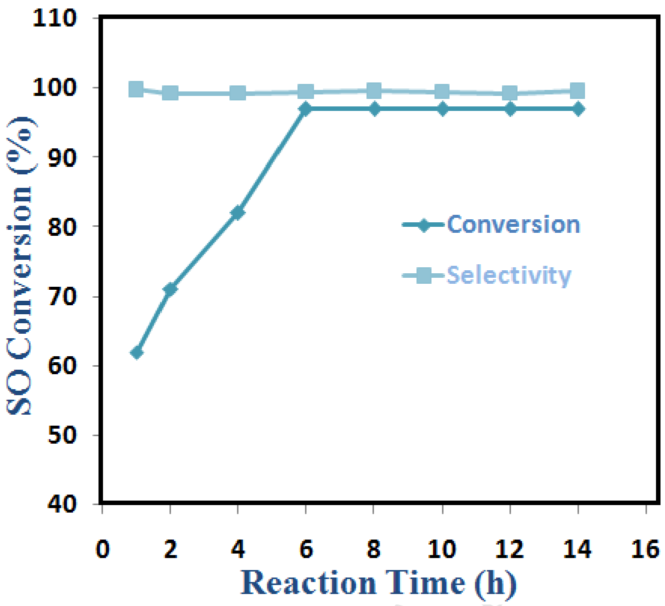
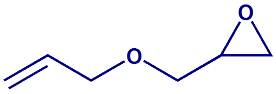
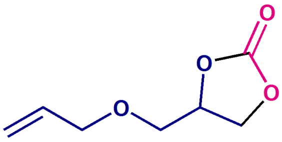
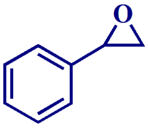
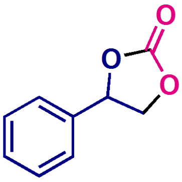
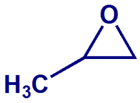
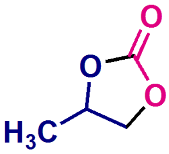
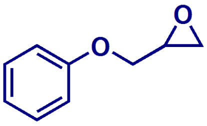
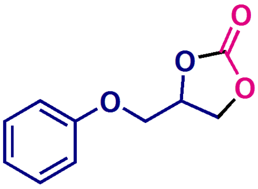
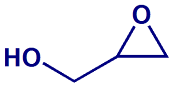
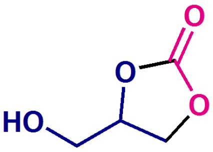
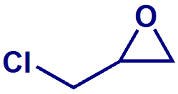
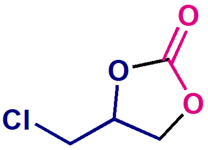


Figure 6. Influence of time of reaction on the transformation of SO to SC over PS-Zn-anthra complex

To study the possibility of applying the Zn catalyst for the chemical fixation of CO_2 with different epoxides such as allyl glycidyl ether, epichlorohydrin, propylene oxide, styrene oxide and glycidol (epoxides with substituted functional groups), aryloxy epoxides (1, 2-epoxy-3-phenoxy propane) have been used as substrates under the application of optimized conditions. The investigational results are listed in Table 3. The transformation of all the oxiranes to five-membered organic cyclic carbonate derivatives via chemical fixation undergo simply with elevated yield and exceptional selectivity. Further attempt to conduct the chemical fixation at the ideal atmospheric pressure, failed, as propylene oxide with a boiling point of 34 ^{o}C partially evaporated into the balloon at room temperature and did not participate in the cycloaddition reaction (Table 3, entry 3) [70]. It is experimental that electron-withdrawing groups (Table 3, entry 6) and electron-donating (Table 3, entries 1, 3 and 4) on terminal epoxides has no effect on the yields of cyclic carbonates.

Table 3. Production of cyclic organic five-membered carbonates over PS-Zn-anthra complex under the application of optimized conditions.

Entry	**Epoxide**	**Product**	**Time (h)**	**Yield^a (%)**	**TON/TOF (h^{-1})**
1.			6	96	153/25
2.			6	97	155/26
3.			6	90	143/24
4.			6	97	155/26
5.			5	89	141/28
6.			5	94	149/30

^{a}GC yield of five-membered organic carbonate. ^{1}H NMR spectra of the cyclic carbonate are provided in the supporting information.

The plausible mechanistic pathway for the generation of organic carbonate through the reaction of CO_2 and oxiranes over PS-Zn-anthra complex is shown in Figure 7. The active sites of PS-Zn-anthra complex activate the oxiranes through non-covalent interaction with the oxiranes O atoms, whereas the basic site present at the surface owing to amine can activate the molecules of CO_2 gas.

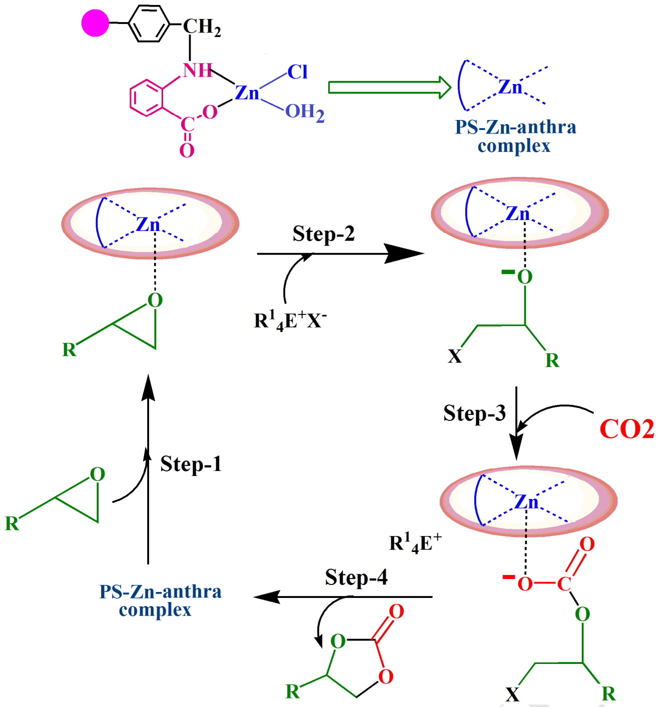
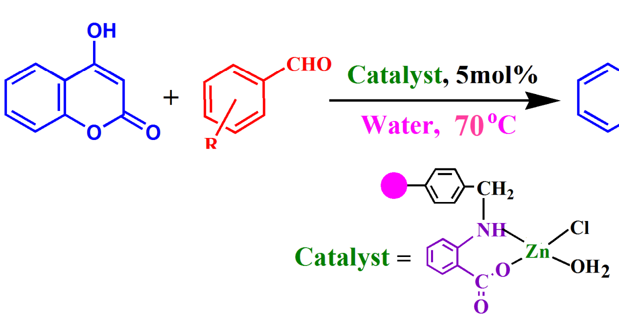


Figure 7. Probable mechanistic pathway for the formation of cyclic carbonates over PS-Zn-anthra complex.

As seen from Figure 7, the formation of a halo-alkoxide is observed through the interaction of PS-Zn-anthra coordinated oxirane with Bu_4NBr. Then the incorporation of CO_2 occurs through the bond of metal alkoxide system and generates a metal hemicarbonate [reference], which results in ring-closer to yield the organic carbonate along with the onium halide again. The synthetic step of cyclic carbonate undergoes via intra-molecularly rather than inter-molecularly and this could be attributed to the excellently elevated activity of the catalyst of Zn-anthra complex.

3.2.2. Dicoumarol synthesis catalyzed by PS-Zn-anthra complex

The plan of the current work was to sketch an effective procedure for PS-Zn-anthra complex catalyzed the reaction between a variety of aromatic/heteroaromatic aldehydes and 4-hydroxycoumarin to produce the derivatives of resultant dicoumarol with outstanding yield (93–98%) in a short time periods (3–5 min) (Table 7). Our first examinations were concerned with the PS-Zn-anthra complex catalyzed the reaction between 4-hydroxybenzaldehyde and 4-hydroxycoumarin as a model reaction. The advancement of reaction was conducted under different the reaction conditions in order to optimize solvents and catalysts conditions and the results are recorded in Tables 5 and 6. It was expected that the best results were observed for H_2O, which is an advantageous solvent from the viewpoint of green chemistry. These outstanding initial results made us thoughtful to further investigate the catalyst applicability for the production of other derivatives of dicoumarol moiety (Scheme 3 and Table 4).

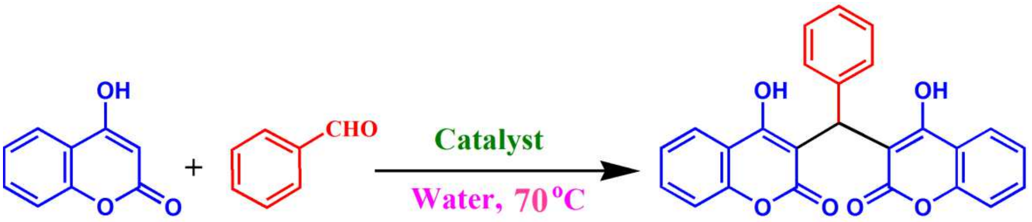


Scheme 3: Production of derivatives of dicoumarol moiety using the Zn catalyst in H_2O

Reactivity of 4-Hydroxycoumarin ring at position 3 is high owing to the existence of an electron releasing hydroxyl group at position 4 and an electron attracting C=O group at position 2. PS-Zn-anthra complex has not been utilized so far as a potential catalyst to produce dicoumarol derivatives. This encouraged us to check the efficiency of the catalyst to produce dicoumarol derivatives. As the lone pair of electrons from the oxygen atom of the hydroxyl group and the C=C bond are in conjugation, this creates the ring of coumarin moiety very suitable at C-3 to react with C=O carbon of the aldehydes. The reaction mechanism has been demonstrated to produce different dicoumarols using PS-Zn-anthra complex as catalyst (Scheme 3). In the beginning, the condensation of 4-hydroxy coumarin and 4-methoxy benzaldehyde was applied for trial as a model reaction to produce the dicoumarol derivatives using PS-Zn-anthra catalyst in water in a water bath at 100 °C. A wide series of dicoumarols have been produced.

In the present study of catalyst loading, the influence of the relative quantity of Zn catalyst on the result of the model reaction was observed. The best yield was observed with the utilization of catalyst (5 mol%). When the progress of the reaction was observed by utilizing less than 5 mol% (i.e. 1 mol % , 2 mol % and 4 mol %) of Zn catalyst, the progress of reactions was either took long time periods to complete or incomplete.

Table 4. Optimization of conditions of the reaction in production of (1) using different quantity of PS-Zn-anthra catalyst under reflux in H_2O.



(1)

Entry	Catalyst	Time (min)	Yield (%)
1.	PS-Zn-anthra (1 mol%)	3	29
2.	PS-Zn-anthra (2 mol%)	3	37
3.	PS-Zn-anthra (4 mol%)	3	79
4.	**PS-Zn-anthra (5 mol%)**	**3**	**98**

[a]**Reaction conditions:** aldehyde (1 mmol), 4-hydroxycoumarin (2 mmol), H_2O (15 mL) and 100°C.

In a relative study, various types of catalysts were utilized to exhibit the advantage of PS-Zn-anthra complex over other catalysts. General Lewis acids of different transition metals were utilized for the model reaction (Table 5). Our examination exhibited that the activity of catalyst of different transition metal chlorides was seen to be of the order PS-Zn-anthra complex > $AlCl_3$ > $NiCl_2$ > $CuCl_2$ > $FeCl_3$ > $ZnCl_2$. Initial investigation implies that PS-Zn-anthra complex was better than other catalysts in terms of reaction time and yield. When the progress of the reaction was investigated with $AlCl_3$, $NiCl_2$, $CuCl_2$ the reaction was accomplished in comparatively short time (20–30 min) and the yield of product was obtained in good to moderate amount, but these homogeneous catalysts are difficult to separate from the reaction mixture. The product was generated in small yields using $ZnCl_2$, $FeCl_3$ and L-Proline whereas formation of product was not found when the progress of reaction took place in p-toluene sulfonic acid (PTS). From Table 5 it is noticed that PS-Zn-anthra complex exhibited the maximum activity with regard to the conversion of 4-hydroxycoumarin to dicoumarol.

Table 5 Influence of different catalysts and catalyst loading on the production of dicoumarol (entry 1c)[a]

Entry	Catalyst	Time	Yield[b] (%)
1	**PS-Zn-Anthra Complex**	**3 min**	**98**

2[c]	PS-Zn-Anthra Complex	20 min	87
3[d]	PS-Zn-Anthra Complex	20 min	64
4[d,e]	PS-Zn-Anthra Complex	30 min	51
5	$AlCl_3$	20 min	91
6[d]	$AlCl_3$	20 min	56
7[d,e]	$AlCl_3$	30 min	41
8[d]	$NiCl_2$	20 min	42
9	$NiCl_2$	20 min	79
10	$CuCl_2$	30 min	51
11	$Zn(Proline)_2$	5 min	96
12[d]	$Zn(Proline)_2$	20 min	58
13[d,e]	$Zn(Proline)_2$	30 min	45
14	$FeCl_3$	30 min	21
15	$ZnCl_2$	24 h	11
16	No Catalyst	24 h	Trace

[a] Reaction conditions: aldehyde (1 mmol), 4-hydroxycoumarin (2 mmol), water (15 mL), 100^{o}C and PS-Zn-anthra (5 mol%). [b] All yields correspond to isolated products. [c] Catalyst loading was 1 mol%. [d] Catalyst loading was 0.5 mol%. [e] Ethanol was used in place of water.

To contrast, the efficiency as well as capability of the reaction under aqueous conditions, the examination of model reaction, was performed in the existence of PS-Zn-anthra complex in various solvents such as CH_3CN, CH_2Cl_2, H_2O and EtOH (Table 3). The utilization of a comparatively less aprotic polar solvent, CH_2Cl_2, generated the product in extremely low yield after a long time period (Table 6, entry 4). With the utilization of aprotic solvents of comparatively high polarity, such as MeCN (Table 6, entry 3), either formation of trace product was found or no reaction was observed. In protic polar solvents EtOH high yield was observed under reflux conditions but it required a longer reaction time of long-range, within 30 min (Table 6, entries 2). When the progress of the reaction was examined in H_2O, the resultant product was observed in high yield in 3 min (Table 6, entry 1). It was expected that the most excellent results were found for H_2O, which is an attractive solvent in green chemistry.

Table 6 Influence of solvent on the production of dicoumarol (entry 1c) in the presence of PS-Zn-anthra complex (5 mol%)

Entry	Solvent	Time[a]	Yield[b] (%)
1.	H_2O	3 min	98
2.	EtOH	30 min	84
3.	Acetonitrile	48 h	Trace
4.	DCM	48 h	46

[a] All the reactions were checked by thin layer chromatography. [b] All yields correspond to isolated products.

An attractive trend was obtained which made our option of the reaction medium, straightforward and very simple among the three protic solvents tried. With the rise in dielectric constant the PS-Zn-anthra complex was observed to provide higher yield in smaller time, and when plot of % yield/Minute against the dielectric constants of the solvents was generated, it exhibits a relationship of the monotonic system between the two (Fig. 8.).

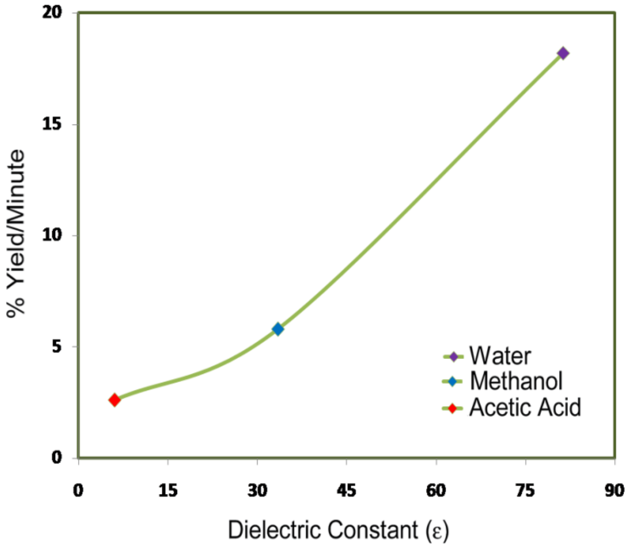
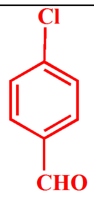
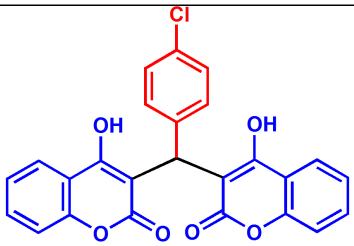
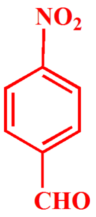
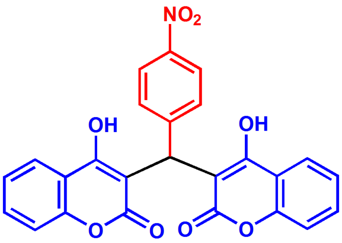
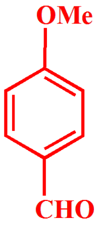
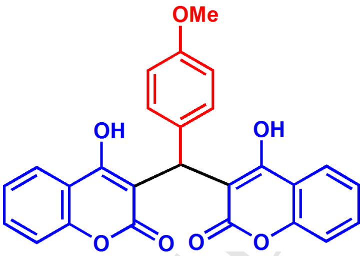
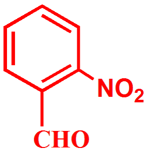
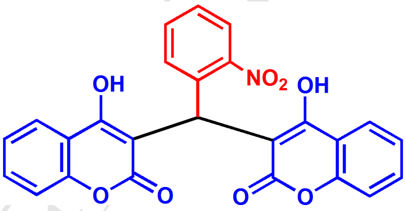
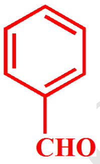
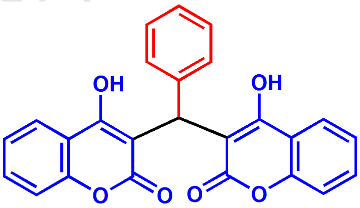
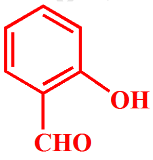
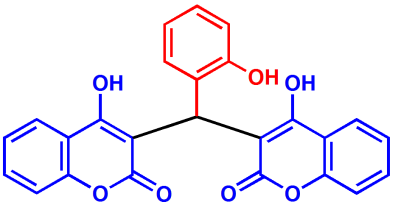
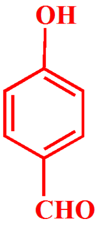
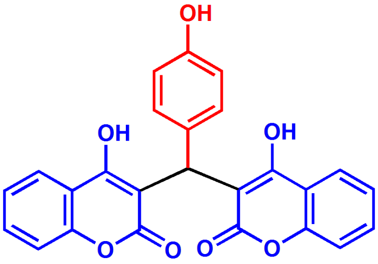
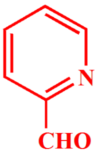
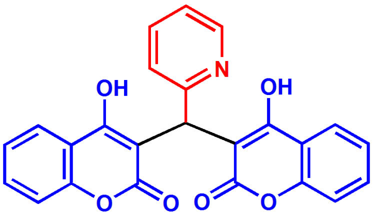
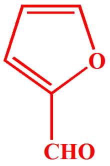
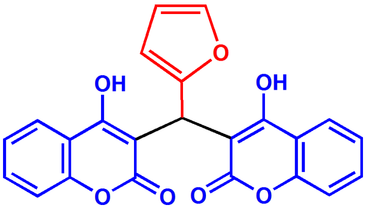
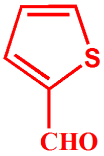
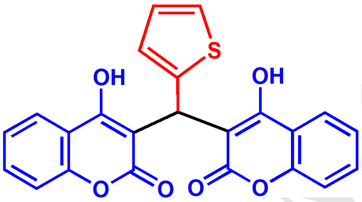


Fig.8. Comparative efficiency of some solvents which are protic in nature as medium of reaction for synthesis of the dicoumarol moiety with PS-Zn-anthra complex.

The character of the aromatic group was no considerable influence on the rate of reaction or yield of the product. Instead of some organic solvents, the utility of H_2O is more significant due to its cheapness and safety. The scheme 3 shows a proposed mechanism to produce by PS-Zn-anthra complex.

Table 7. Reaction between aromatic/heteroaromatic aldehydes and 4-hydroxycoumarin catalyzed by a PS-Zn-anthra catalyzed complex in H_2O.[a]

Entry	**Aldehyde**	**Product**	**Time[b]/min**	**Yield[c] (%)**	**TON/TOF (h^{-1})**
1a			4	94	89/1335
1b			5	93	88/1056
1c			3	98	93/1860
1d			5	94	89/1068
1e			5	97	92/1104
1f			3	96	91/1820

1g			3	98	93/1860
1h			4	96	91/1365
1i			5	94	89/1068
1j			4	96	91/1365

[a]**Reaction conditions:** aldehyde (1 mmol), 4-hydroxycoumarin (2 mmol), water (15 mL), 100°C and PS-Zn-anthra (5 mol%). [b] All the reactions were checked by TLC. [c] All yields correspond to isolated products.

The plausible mechanism for the formation of dicoumarol from 4-hydroxycoumarin and aldehydes catalysed by PS-Zn-anthra complex is shown in Figure 9. The significance of PS-Zn-anthra complex is highly observed for the formation of dicoumarol. Position 3 of 4-Hydroxycoumarin moiety is extremely reactive owing to the existence of an electron releasing hydroxyl group and an electron attracting C=O group. A lone pair of electrons from oxygen and the existence of a C=C double bond constructs the 4-hydroxycoumarin ring very suitable at position 3 to react with the C=O of aldehydes to provide derivatives of dicoumarol moiety [71, 72].

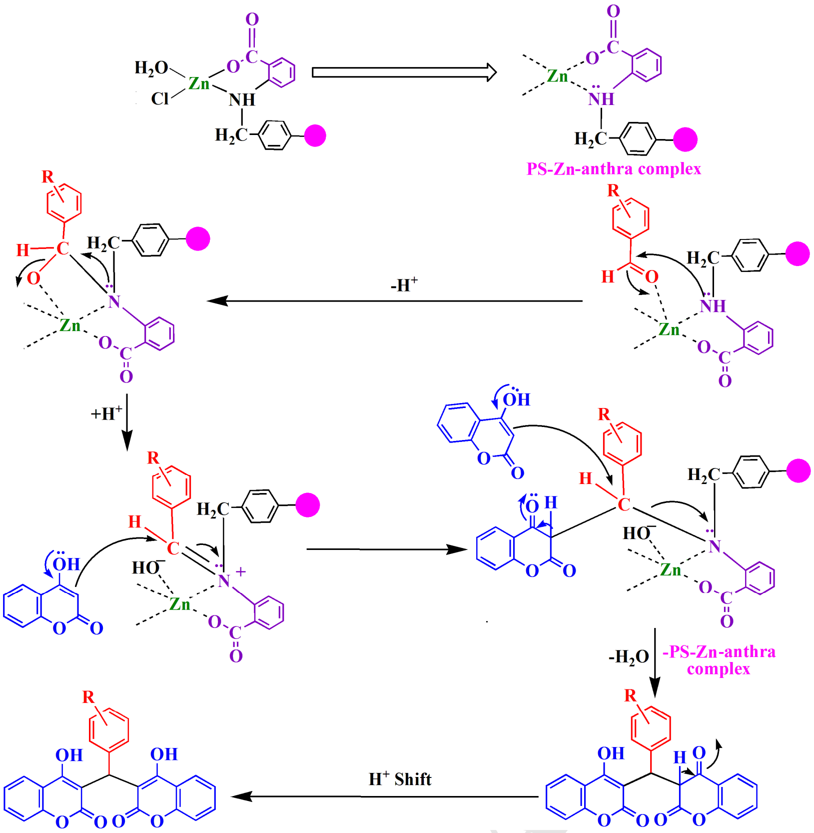


Figure 9. Plausible mechanism for the production of Dicoumarol using PS-Zn-anthra catalyst

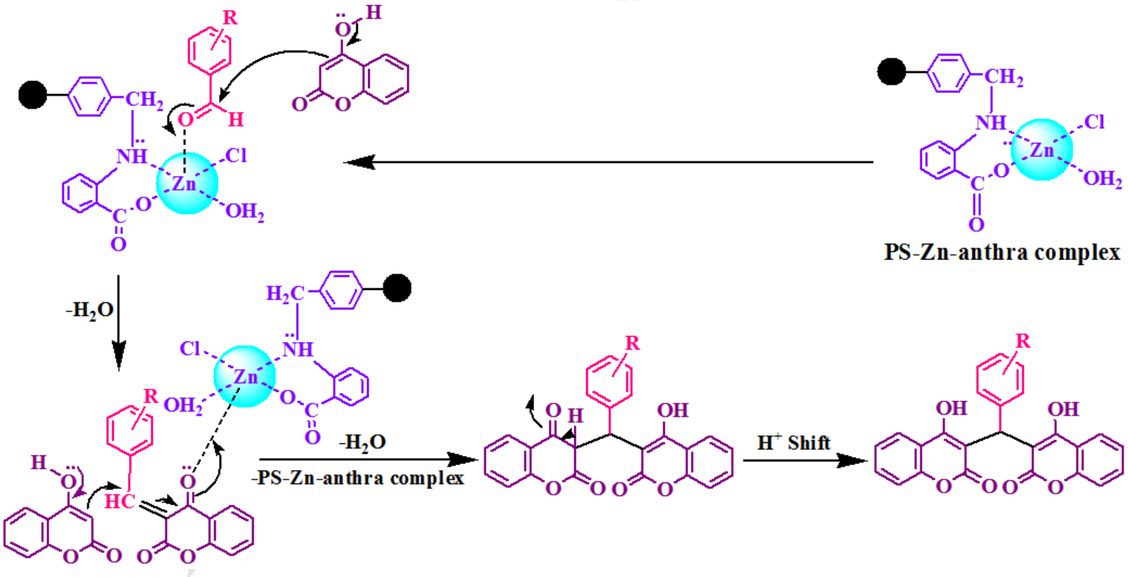


Figure 10. Another porposed mechanism for the production of Dicoumarol using PS-Zn-anthra catalyst

3.3. Recyclability of PS-Zn-anthra complex

It is significant to examine the isolation, recoverability and recyclability for a polystyrene supported catalyst. The PS-Zn-anthra complex executed outstanding reusability in the synthesis of the cyclic carbonate and dicoumarols synthesis (Fig.11). Catalyst reuse and recovery are essential issues for cyclic carbonate synthesis and synthesis of dicoumarols. Recycling in successive batch operations and easy catalyst separation can significantly enhance the reaction efficiency. The PS-Zn(II)-anthra complex was recovered by easy filtration and washed with ethyl acetate followed by acetone then dried out in low pressure at 50°C after the end of the reaction. The recovered catalyst was utilized for the next run with the extra incorporation of substrates in proper quantity under optimum conditions of reaction. The PS-Zn-anthra complex exhibits the fixed activity of catalyst up to five reaction cycles. Deterioration of catalyst was not found, supporting the elevated stability of the catalyst with heterogeneous nature under the application of reaction conditions.

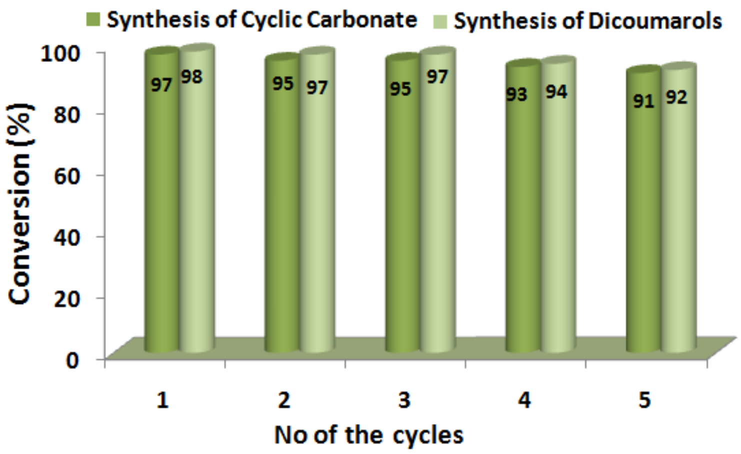


Fig.11. Recycling efficiency of PS-Zn-anthra complex catalyst for cyclic carbonate synthesis and synthesis of dicoumarols.

To explore the activity of PS-Zn-anthra complex and current method, the activity of catalyst PS-Zn-anthra has been compared with a few other reported catalytic systems and these are shown in Table 8. Compared to the some reported catalytic systems for the production of organic five-membered cyclic carbonates under the application of CO_2 and synthesis of dicoumarols, our PS-Zn(II)-anthra complex exhibited more efficiency of the catalyst under the application of optimization conditions [73-77].

Table 8: Comparison of activity of the current catalyst (PS-Zn-anthra complex) in organic five-membered carbonates preparation and the synthesis of dicoumarols with other reported heterogeneous catalysts.

Reaction	**Catalyst**	**Reaction condition**	**Yield (%)**	**Ref.**
Cyclic carbonates synthesis	HBimCl-NbCl5/HCMC	Styrene epoxide (10mmol), Cat. (0.1 g), P_{CO2} (1.5 Mpa), Time – 5h, Temp. 130^0C	96.1	73
	F-IRMOF-3	Styrene epoxide (0.2 mol), Cat. (0.17 g), P_{CO2} (2 Mpa), Time – 5h, Temp. 140^0C	84	74
	Co/POP-TPP	Styrene epoxide (12.5 mol), Cat. (50 mg), P_{CO2} (1 atm), Time – 118(48) h, Temp. 29(50) ^{0}C	77.9	75
	PS-Zn-anthra complex	**Styrene oxide (5 mmol), catalyst (50 mg), P_{CO2} (1 atm), RT, Time- 6h**	**97**	**This study**
Dicoumarol synthesis	SAMSNs	Benzaldehyde (1 mmol), 4-hydroxy coumarin (2 mmol), cat.(0.025g), H_2O (3 ml), Time – 20 min, Temp. 80^0C	96	76
	$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$	Benzaldehyde (1 mmol), 4-hydroxy coumarin (2 mmol), cat.(0.025g), EtOH-H_2O (1:1), Time – 5 h, Temp. reflux	95	77
	PS-Zn-anthra complex	Benzaldehyde (1 mmol), 4-hydroxy coumarin (2 mmol), cat.(5 mol%), H_2O (15 ml), Time – 5 min, reflux	**97**	**This study**

4.Conclusions

In conclusion, the polystyrene-supported Zn complex has been prepared as an excellent heterogeneous catalyst. The catalyst performed an exceptional activity for the production of organic five-membered cyclic carbonates from oxiranes in presence of CO_2 under atmospheric pressure at RT and active transformation of dicoumarols using H_2O as the green solvent. An efficient and simple methodology has been effectively established for the synthesis of a wide range of dicoumarols using PS-Zn-anthra complex as the recyclable catalyst. The great activity of the catalyst of PS-Zn-anthra complex for these conversions can be sustained by high yields of dicoumarols as well as the short time of the reaction. This scheme is environmentally non-hazardous and may confirm useful to both industry and academia for the change of socio-economic system.

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Research Highlights

1. A new polymer anchored zinc complex catalyst, PS-Zn-anthra complex, has been synthesized and characterized.
2. The PS-Zn-anthra complex is stable upto 430 ^{o}C using thermogravimetric analysis.
3. The PS-Zn-anthra complex showed excellent catalytic activity for the synthesis of cyclic carbonates from epoxides with CO_2 . under atmospheric pressure and at room temperature.
4. The PS-Zn-anthra complex also showed good activity for the synthesis of dicoumarols under greener pathway.
5. The catalyst is stable and reusable for several cycles without losing its catalytic activity.