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Dalton Transactions

PAPER

Inorganic-organic hybrid silica based tin complex as a novel, highly efficient and recyclable heterogeneous catalyst for the one-pot preparation of spirooxindoles in water

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In the present study, the tin complex immobilized on silica gel as a novel, green, highly efficient and heterogeneous reusable catalyst was synthesized by grafting 2-amino benzamide on to the silica gel surface as a result of the reaction between isatoic anhydride and 3-aminopropyl-functionalized silica gel, followed complexation with tin chloride. The resulting organic–inorganic hybrid material was evaluated in the one-pot three-component synthesis of spiro[indoline-pyrazolo[4′,3′:5,6]pyrido[2,3-d]pyrimidine]trione derivatives in water via the condensation reaction of isatins, barbituric acids, and 1H-pyrazol-5-amines. All reactions were completed in short reaction times and all products were obtained in high to excellent yields and high purity. Besides, the synthesized novel catalyst could be separated from the reaction mixture by simple filtration and reused up to seven runs without significant loss in activity.

Introduction

Tandem reactions are one of the best tools in modern organic synthesis and medicinal chemistry for the production of a broad spectrum of complex molecules from simple and readily available starting materials in a convergent way.[1,2] These transformations are usually operated in one-pot without the need for intermediate workups or purification steps. Tandem reactions have been widely exploited in synthesis for decreasing the number of steps along a synthetic pathway with most of the atoms incorporating from the starting materials, this is important from as atom economic standpoint.[3] These reactions have received considerable attention in synthetic chemistry for the production of a wide range of organic molecules.[4-6] Water has emerged as a versatile solvent for organic reactions in the past two decades because it is safe, nontoxic, environmentally friendly, readily available, and cheap, compared to organic solvents.[7,8] For these reasons, water has been used for multicomponent reactions (MCRs) as well, therefore designing of multicomponent reactions in water are of outstanding value in organic synthesis and green chemistry [9-11].

Notes and references
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Homogeneous catalyst, where the catalyst is in the same phase as the reactants, is gaining considerable interest by chemists.[12] One attractive possession is that all catalytic sites are accessible for the substrates. Homogeneous catalysts have remarkable merits such as; high selectivity, simple optimization of catalytic systems by modification of ligand and metals, and better yield. They are used in a number of reactions,[13-15] but the difficulty of catalyst separation from the final product makes economic and environmental barriers to use in a number of applications. To overcome these drawbacks, chemists and engineers have investigated a wide range of approaches, the usage of heterogeneous catalyst systems appears to be the best logical solution.[16] Heterogeneous catalysts have recently attracted much attention due to the increasing worldwide momentum for the development of environmentally friendly reactions in terms of green chemistry.[17]

Among various solid supports, including silica gel, alumina, and the highly acidic montmorillonite clay, silica gel as a mesoporous inexpensive, available, and nontoxic solid was found to be the most efficient because not only does it display excellent chemical and thermal stability even under acidic conditions but also its surface presents high chemical reactivity due to existence of silanol groups (Si–OH). Hence, the surface of silica gel can be easily functionalized with organic and inorganic groups.[18-20] The common structural feature that organic components anchored in

the pores of silica, called organic/inorganic hybrid. Synthesis of this hybrid could be occurred via covalently link metal complex to silica and using non-covalent interaction. [21]

Spirooxindoles, pyrimidines, and pyrazoles are very important classes of heterocyclic compounds. Spiroindoles are attractive targets in organic synthesis due to their highly evidently pharmacological properties and biological activities as well as wide-ranging utility as synthetic intermediates for alkaloids, drug candidates, and clinical pharmaceuticals.[22-24] Pyrimidines represent a class of heterocyclic compounds of great importance in biological and pharmaceutical activities such as, antitumor,[25] antibacterial,[26] antifungal,[27] antimalarial[28], and antiinflammatory properties.[29] The chemistry of pyrazole derivatives has been the subject of medical research due to their remarkable biological and pharmacological properties such as antitumor,[30] antimicrobial,[31,32] anti-inflammatory,[33] antibacterial,[34] antifungal,[35] anticancer,[36] and analgesic agents.[37] Thus, a hybrid of these three motifs could potentially lead to a series of structurally and biologically interesting compounds (Figure 1).
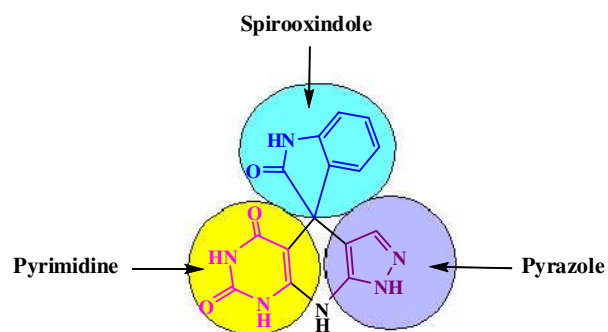

Fig. 1 Hybrid structure of some important heterocyclic compounds

In this study, we would like to present the synthesis of novel organic–inorganic hybrid materials immobilized tin catalyst as an efficient and green catalyst for the first time. At first activated silica gel was reacted with 3-aminopropyltriethoxysilane (APTES) to obtain aminopropyl silica gel. 2-Amino benzamide was then anchored on to the surface functionalized silica through the reaction between isatoic anhydride and aminopropyl silica gel, followed by metallation with tin chloride, silica immobilized tin complex was prepared. As part of our current studies on the development of new efficient strategies for the preparation of spirooxindoles,[38] Our main purpose for the design of this reusable organocatalyst is preparation of a heterogeneous and more convenient catalytic system for the application in the synthesis of spiro[indoline-pyrazolo[4′,3′:5,6]pyrido[2,3-*d*]pyrimidine]trione derivatives *via* one-pot three-component condensation of barbituric acids, 1*H*-pyrazol-5-amines and isatins in water. This methodologe has a lot of advantages such as; excellent yields, simplicity of the workup, low cost, short reaction times and green conditions.

Experimental

The chemicals used in this work were obtained from Fluka, Merck, and Aldrich was used without purification. Melting points were measured on an Electrothermal 9200 apparatus. IR spectra were recorded as KBr pellets on a Perkin-Elmer 781 spectrophotometer and an Impact 400 Nicolet FT-IR

spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 and 75.47 MHz. ^{1}H and ^{13}C NMR spectra were obtained on solutions in DMSO-d_6 solvent using tetramethylsilane as internal reference. The elemental analyses (C.H.N) were obtained from a Carlo ERBA Model EA 1108 analyzer. The content of tin in the heterogenized catalyst was determined by VISTA-PRO, CCD simultaneous ICP analyser.Thermogravimetric/differential thermal analyses (TG/DTA) was performed on a Thermal Analyzer with a heating rate of 20 °C min^{-1} over a temperature range of 25–1100 °C under flowing compressed N_2. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company).

Catalyst preparation

a) Activation of silica gel (SG):

Silica gel (Aldrich 70–270 mesh, 60 Å, Surface area > 500 m^2/G) was activated by treatment with HCl (5 M) and dried in vacuum at 120 °C.[39]

b) Preparation of the amino-functionalized silica gel (SG@NH$_2$):

Activated silica gel (1g) was added to a solution of APTES (1.8 g, 1.9 ml) in dry toluene (50 ml) and refluxed for 24h under N_2 atmosphere. The white solid was filtered and washed repeatedly with ethanol and finally dried at 50 ºC under vacuum.[40]

c) Grafting of 2-amino benzamide through isatoic anhydride on functionalized silica gel (SG@NH$_2$@2AB):

The amino-functionalized silica gel (1 g) was added to the solution of isatoic anhydride (8 mmol, 1.3 g) in ethanol (25 ml) and refluxed for 24h. The resulting solid was collected by filtration, repeatedly washed with ethanol to remove unreacted isatoic anhydride. It was dried under vacuum at 50 ºC.

d) Synthesis of tin catalyst immobilized on silica gel (SG@NH$_2$@2AB-Sn):

The catalyst was prepared by stirring a mixture of 2-amino benzamide on functionalized silica gel (SG@NH$_2$@2AB) (1 g) and tin chloride (8 mmol) in ethanol (50 ml) at reflux for 24h. After that, the catalyst was filtered, washed several times with ethanol, and dried under vacuum at 50 ºC

Typical Procedure for Preparation of 3'-phenyl-spiro[indoline-3,4'-pyrazolo [4',3':5,6] pyrido[2,3 d]pyrimidine]- 2,5',7'(6'H,8'H,9'H)-trione (4e):

A mixture of 1,3-diphenyl-1*H*-pyrazol-5-amine (0.24 g, 1 mmol), barbituric acid (0.13 g, 1 mmol), isatine (0.15 g, 1 mmol), and SG@NH$_2$@2AB-Sn as a catalyst (10 mg) under refluxing water (5 mL) was stirred (the progress of the reaction was monitored by TLC). After completion of the reaction (TLC), the solution was cooled to room temperature, then the precipitated product was filtered and washed with water (10 mL) and ethanol (5 mL), dried to afford the crude product. The crude precipitate dissolved in DMF and again filtered for catalyst separation, and finally water was added into solution and the product was extracted and recrystallized by EtOH to afford the pure product as white powder (94%); Mp >300 ˚C. IR (KBr) (v$_{max}$ /cm^{-1}): 3219, 1741, 1622. ^{1}H NMR (300 MHz, DMSO-d_6): δ$_H$ (ppm) 6.50-7.69

(14H, m, H-Ar), 9.36 (1H, s, NH), 9.93 (1H, s, NH), 10.18 (1H, s, NH), 10.67 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 48.3, 88.1, 100.7, 109.4, 121.7, 123.4, 124.1, 127.8, 128.2, 128.3, 128.9, 130.3, 132.9, 136.7, 137.4, 137.9, 142.9, 146.5, 149.8, 149.9, 162.2, 179.1. Anal. Calcd for $C_{27}H_{18}N_6O_3$: C, 68.35; H, 3.82; N, 17.71. Found: C, 68.31; H, 3.85; N, 17.74.

Results and discussion

During the past few years, significant interest has been focused on the development of new protocols for environmentally benign processes that are both economically and technologically feasible. Silica is an attractive support for the immobilization of organocatalysts as a result of its thermal and mechanical stability as well as its chemical inertness.[41] These reasons prompted us to extend our work to the grafting of organocatalyst on silica gel. The silica immobilized tin complex consists of the following steps as shown in Scheme 1. In the first step, silica gel was functionalized according to the reported procedure using 3-aminopropyltriethoxysilane (SG@NH$_2$). The amino-functionalized silica gel was allowed to react with isatoic anhydride to form immobilized bidentate ligands (SG@NH$_2$@2AB), which was complexed with tin chloride, affording the immobilized tin complex catalyst (SG@NH$_2$@2AB-Sn). The prepared novel nanocatalyst have been characterized by different physicochemical methods such as fourier transform infrared (FT-IR), thermogravimetric analysis (TGA), and ICP-AES analysis.
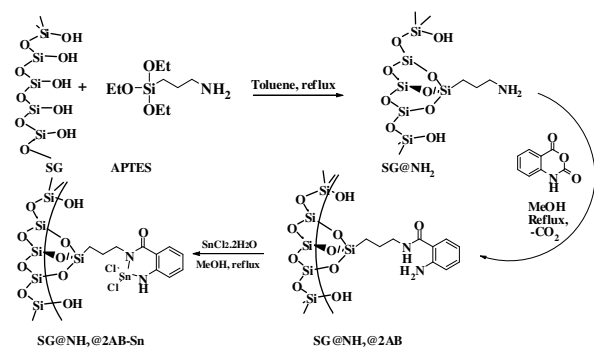
Scheme 1 Steps for fabricating tin catalyst immobilized on the surface of silica gel.

Characterization of the catalyst

FT-IR spectra:

FT-IR appears to be the best technique to confirm the modification of SG@NH$_2$@2AB-Sn. FT-IR spectrum of silica gel (SG) showed two bands at 3432 cm^{-1} and 1630 cm^{-1} due to OH stretching vibration of surface silanol.[42] Bands cantered at 1097 cm^{-1} and 799 cm^{-1} were assigned to asymmetric and symmetric Si-O-Si stretching vibrations respectively. Band at 470 cm^{-1} assigned to Si-O-Si bending Fig. 2 **(a)**. Peaks at 2930 cm^{-1} and 2851 cm^{-1} were assigned to C-H stretching vibrations of aminopropyl silica gel (SG@NH$_2$) Fig. 2 **(b)**. The spectrum of the immobilized ligand (SG@NH$_2$@2AB) showed a strong band at 1634 cm^{-1} due to the C=O of the amide stretching vibration resulting from condensation between the NH$_2$ group and isatoic anhydride, some weak bands at 1400–1500 cm^{-1} assigned to stretching vibrations of aromatic rings of 2-amino benzamide Fig.2 **(c)**. On metallation with tin chloride, C=O frequency increased to higher wave number (1714 cm^{-1}) indicative of

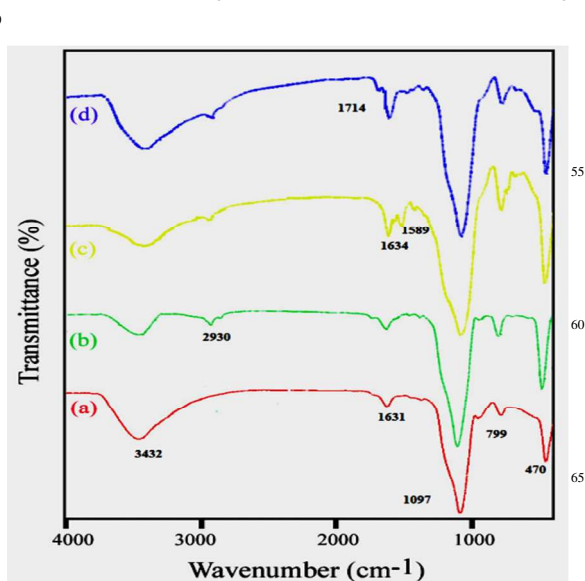formation of metal–ligand bond (SG@NH$_2$@2AB-Sn) Fig.2 **(d).**

Fig. 2 The comparative FT-IR spectra for (a) SG, (b) SG@NH$_2$, (c) SG@NH$_2$@2AB, and (d) SG@NH$_2$@2AB-Sn.

Thermo-Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA):

Differential Thermal Analysis (DTA) measurements of catalyst showed that endothermic peak at low temperature (lower than 200 °C) and exothermic signal between 200-550°C. Thermo-Gravimetric Analysis (TGA) of catalyst also supported that the endothermic peak below 200 °C showed that weight loss of this catalyst 7% can be assigned to the release of physisorbed molecules water on the surface of SG@NH$_2$@2AB-Sn. Exothermic peak accompanied with mass loss of 22% at the temperature range of 200–550 °C in the TGA curve of prepared catalyst was mainly attributed to the decomposition of organic groups grafted to the silica surface. Through the TGA analysis, the ligand content of catalyst was evaluated to be 1.2 mmol/g (Fig. 3).
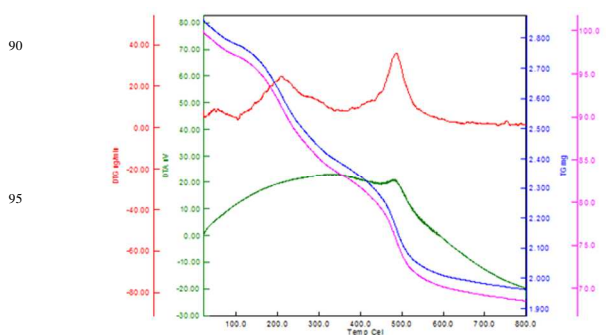
Fig. 3 Thermogravimetric and Differential Thermogravimetric of SG@NH$_2$@2AB-Sn

Inductively Coupled Plasma (ICP) and EDX analysis

5 Determination of Sn content was performed by Inductively Coupled Plasma (ICP) analyzer. According to the ICP analysis, the Sn content in the catalyst was determined which revealed the presence of 0.38 mmol/g for the catalyst. Furthermore, in order to support the above observation, catalyst was subjected to energy 10 dispersive X-rays. EDX analysis of tin confirms its immobilization on to the modified silica gel (Fig. 4).
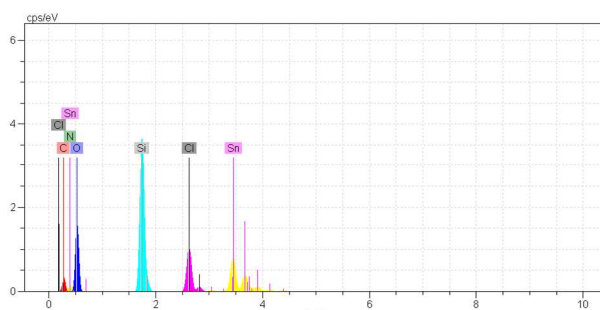

Fig. 4 EDX spectrum of catalyst (SG@NH$_2$@2AB-Sn)

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After characterizations of SG@NH$_2$@2AB-Sn, in order to study the efficiency of the silica-supported organocatalyst, we examined its catalytic activity in a model reaction between isatin **1a**, barbituric acid **2a**, and 1,3-diphenyl-1H-pyrazol-5-amine **3b** 20 for the synthesis of spiro [indoline-3, 5'-pyrimido[4,5-b]quinoline]-triones (**4e**). (Scheme 2)

1a **2a** **3b** **4e**
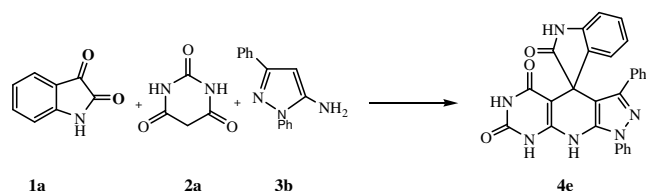
Scheme 2 Model reaction for the synthesis of 3'-phenyl-spiro[indoline-25 3,4'-pyrazolo[4′,3′:5,6]pyrido[2,3 d]pyrimidine]- 2,5',7'(6'H,8'H,9'H)-trione (**4e**)

In our initial investigations the model reaction was carried out using SG@NH$_2$@2AB-Sn (20 mg) as the catalyst in various 30 solvents. The results were summarized in Table 1.

Table 1 Screening of solvents for the synthesis of **4e**[a].

Entry	Solvent	Time	Yield (%)[b]
1	EtOH	2 h	70
2	DMSO	10 h	52
3	THF	10 h	45
4	CH$_3$CN	10 h	60
5	Toluene	24 h	-
6	n-Hexane	24 h	-
7	water	90 min	95

[a]Reaction conditions: isatin (1 mmol), barbituric acid (1mmol), and 1,3-diphenyl-1H-pyrazol-5-amine (1mmol), solvent (5 mL), catalyst (20 mg) under reflux condition.

35 [b]Isolated yields of the pure prouduct.

No product was formed in the absence of catalyst. The effect of amount of SG@NH$_2$@2AB-Sn as a catalyst on the synthesis of 3'-phenyl-spiro[indoline-3,4'-pyrazolo[4′,3′:5,6]pyrido[2,3 40 d]pyrimidine]-2,5',7'(6'H,8'H,9'H)-trione (**4e**) is presented in Table 2. As shown in Table 2, among the various amounts of the catalyst studied, 10 mg of SG@NH$_2$@2AB-Sn was found to be highly active and the catalyst afforded 94% yield of the product **4e** at 90 min in water under reflux conditions.

45

Table 2 Effect of the amount of SG-NH2-2AB-Sn as catalyst in model reaction[a]

Entry	catalyst (mg)	Time	Yield (%)[b]
1	0	10h	-
2	2	5h	73
3	5	5h	81
4	10	90 min	94
5	20	90 min	94

[a]Reaction conditions: isatin (1 mmol), barbituric acid (1mmol), 1,3-diphenyl-1H-pyrazol-5-amine (1mmol), water (5 mL), under reflux 50 condition

[b]Isolated yields of the pure prouduct.

In order to show the merit of the prepared catalyst (SG@NH$_2$@2AB-Sn), comparison of the catalytic activity of 55 some homogeneous and heterogeneous catalysts in the formation of **4e** has been presented in Table 3. The results clearly show the advantages of this method in terms of the obtained yield of the desired product and reaction time. In order to investigation of efficiency and effectiveness of SG-NH$_2$-2AB-Sn in compare with 60 2AB-Sn, the model reaction was carried out in same conditions. The obtained results are outlined in Table 3, entry 8. It can be concluded that the catalytic efficiency of SG-NH$_2$-2AB-Sn is more than 2AB-Sn due to silica possesses higher surface area and porosity

65

Table 3 Comparison of various catalysts in the synthesis of **4e**[a]

| Entry	catalyst	Time	Yield (%)[b]
1	SnCl$_2$	10h	52
2	Nano MnFe$_2$O$_4$	6h	61
3	Nano Fe$_3$O$_4$	6h	57
4	SnO$_2$	6h	<50
5	SG@NH$_2$@2AB-Sn	90 min	94
6	p-TSA	24h	90
7	Alum	24h	78
8	2AB-Sn	12h	54

[a]Reaction conditions: isatin (1 mmol), barbituric acid (1mmol), 1,3-diphenyl-1H-pyrazol-5-amine (1mmol), water (5 mL), catalyst (10 mg), under reflux condition.

5 [b]Isolated yields of the pure prouduct.

Having demonstrated the effectiveness of SG@NH$_2$@2AB-Sn as a catalyst, its reusability was investigated by using the reaction of isatin **1a**, barbituric acid **2a**, and 1,3-diphenyl-1H-pyrazol-5-
10 amine **3b**, as model substrates under optimized conditions. After completion of the reaction (TLC), the solution was cooled to r.t. Then, the precipitated product was filtered and washed with water (10 mL) and ethanol (5 mL), dried to afford the crude product. The crude precipitate dissolved in DMF and again filtered for
15 catalyst separation. The recovered catalyst was washed with hot EtOH several times followed by water and dried in oven at 70 °C before being reused to another reaction runs. The procedure was repeated and the results indicated that in seven consecutive runs, as can be seen in Figure 4, the isolated yields remained similar
20 without a significant loss of yield and catalytic activity. To determine the percent leaching of ions from the catalyst surface, the model reaction was carried out in the presence of catalyst for 20 min, in that point the catalyst was separated by filtration. The residue was then allowed to react, but no significant progress was
25 observed after 4h. It was indicated that there was no leaching of the metal ions from the supported heterogeneous catalyst, thereby establishing the truly heterogeneous nature of the catalyst (Fig. 5).
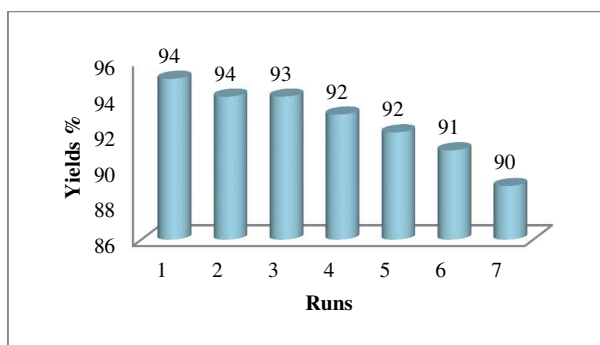
30 **Fig. 5** Recyclability of SG@NH$_2$@2AB-Sn on the synthesis of **4e**

The SEM images of fresh and recovered catalyst showed that the morphology and size of catalyst relatively remain unchanged
35 and a small aggregate was observed on the surface of recovered SG@NH$_2$@2AB-Sn (Fig. 6).
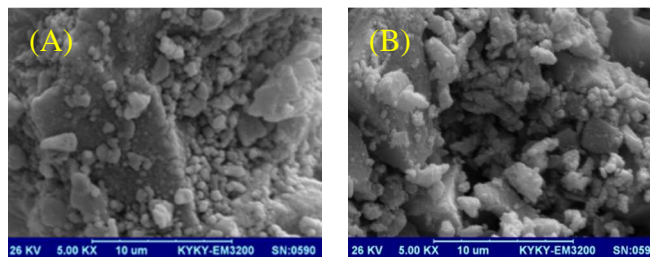
Fig. 6 The SEM images of fresh (A) and recovered catalyst (B)

40 The recovered catalyst had no obvious change in structure, referring to the FT-IR spectrum in comparison with fresh catalyst (Fig. 7).
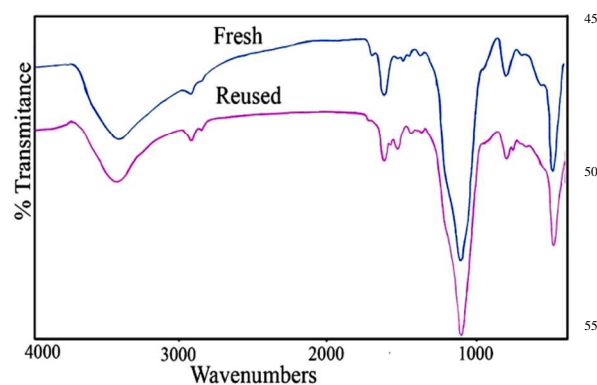
Fig. 7 FT-IR spectrum of fresh and recovered catalyst

60 Finally, to further explore the potential of this novel catalyst for spiroheterocyclic synthesis, this methodology was evaluated by using different isatins **1a-d** barbituric acids **2a-c**, and 1H-pyrazol-5-amines **3a-c**, under these appropriate reaction
65 conditions (5 mL of water, reflux, 10 mg catalyst). The results were summarized in Table 4. As can be seen in this table corresponding spirooxindole derivatives 4 were synthesized by the one-pot, three-component condensation in high to excellent yields in the presence of SG@NH$_2$@2AB-Sn as a powerful and
70 reusable catalyst.

Table 4 Synthesis of spiro[indoline-pyrazolo[4′,3′:5,6]pyrido[2,3 d]pyrimidine]trione derivatives **4**[a]
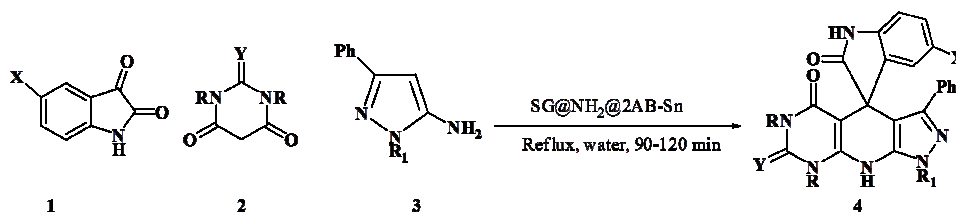
Entry	X	Y	R	R₁	Product	Yield (%)[b]
1	H	O	H	H	**4a**	83
2	Br	O	H	H	**4b**	89
3	NO₂	O	H	H	**4c**	83
4	H	S	H	H	**4d**	88
5	H	O	H	C₆H₅	**4e**	94
6	Br	O	H	C₆H₅	**4f**	92
7	NO₂	O	H	C₆H₅	**4g**	95
8	CH₃	O	H	C₆H₅	**4h**	88
9	H	S	H	C₆H₅	**4i**	92
10	Br	S	H	C₆H₅	**4j**	89
11	NO₂	S	H	C₆H₅	**4k**	94
12	NO₂	O	Me	C₆H₅	**4l**	90
13	Br	O	Me	C₆H₅	**4m**	87
14	H	O	H	4-NO₂-C₆H₄	**4n**	89
15	Br	O	H	4-NO₂-C₆H₄	**4o**	86
16	NO₂	O	H	4-NO₂-C₆H₄	**4p**	91
17	Br	S	H	4-NO₂-C₆H₄	**4q**	87

[a]Reaction conditions: Isatins **1a-d** (1 mmol), barbituric acids **2a-c** (1mmol), and 1*H*-pyrazol-5-amines **3a-c** (1mmol), catalyst (10 mg), and water (5 mL), under reflux condition.

[b]Isolated yields.

Conclusions

In this paper, tin complex immobilized on silica gel as a novel, green, heterogeneous, and reusable catalyst has been successfully prepared through sequential grafting of several organic and inorganic molecules. The application of an organic–inorganic hybrid tin catalyst has been demonstrated for the synthesis of spirooxindole derivatives through the condensation reaction of isatins, barbituric acids, and 1*H*-pyrazol-5-amines. The desired products were obtained in excellent yields, short reaction times and high purities. The prepared catalyst could be easily recovered by simple filtration and high yield of products were obtained even after the catalyst was reused seven times.

Acknowledgements

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SG@NH₂@2AB-Sn as a novel, powerful, and recoverable catalyst for the synthesis of spirooxindoles in water is reported.