Tailored SnO$_2$@MWCNTs efficient and recyclable nano-catalyst for selective synthesis of 4, 5-dihydropyrrolo [1, 2-a] quinoxalines via Pictet–Spengler reaction

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Abstract
Heterocyclic compounds have a wide range of applications, and Pictet–Spengler reaction is effectual in the synthesis of heterocyclic compounds such as quinoline and isoquinoilne. The present work describes an effective Pictet–Spengler-type protocol for the selective synthesis of quinoxaline derivatives from substituted pyrroles and diverse aromatic aldehydes over tailored SnO$_2$ nanoparticles anchored multi-walled carbon nanotubes (SnO$_2$@MWCNTs) nano-catalyst under greener reaction condition. An elementary reaction process (chemical synthesis) of oxidation of MWCNTs followed by uniform dispersion of SnO$_2$ nanoparticles is used to synthesize the SnO$_2$@MWCNTs catalyst. The SnO$_2$@MWCNTs catalyst was then characterized by using modern spectroscopic and analytical techniques. The activity of catalyst was investigated toward the formation of selective quinoxaline. The reaction progressed with 100% conversion and 93–80% yield for the desired product at ambient operating conditions in just 2.30–3.30 h of reaction time. The effect of different parameters such as reaction temperature, time, and loading of SnO$_2$ on MWCNTs, SnO$_2$@MWCNTs catalyst loading were also investigated and discussed in detail. The protocol displayed high tolerance to different functionalities with respect to different substituted aromatic aldehydes to form quinoxaline derivatives in efficient
way and gave excellent yield. Plausible reaction mechanistic pathway for the selective formation of quinoxaline over SnO$_2$@MWCNTs is also proposed. It is believed that high dispersion of SnO$_2$ over MWCNTs provided sufficient Lewis acidic sites for the reaction to selectively obtain the final product. Additionally, recyclability of SnO$_2$@MWCNTs catalyst was also studied which demonstrated that the catalyst could be efficiently reused for six successive cycles without significant loss in its activity. The present work provides greener approach for synthesis of quinoxaline derivative preparation with high selectivity (free from oxidized quinoxaline as a side product) and efficient yield.

**Graphical abstract**

![Graphical abstract](image)

**Keywords** SnO$_2$ engineered MWCNTs · Quinoxaline derivatives · Pictet–Spengler-type reaction · Nano-composite · Recyclable modified CNT catalyst

**Introduction**

In recent years, organic chemists have contributed with remarkable devotion toward the development of new sustainable methods for heterocyclic synthesis [1]. Among several heterocyclic moieties, quinoxaline and its derivatives offer a broad range of biological and pharmacological properties [2–4]. Particularly, dihydropyrrolo[1,2-a]quinoxaline moiety showed significant pharmacological activities such as anticancer agents (I), anti-HIV agents (II), important intermediates (Fig. 1) for the construction of 5-HT3 receptor agonists (III), cannabinoid receptor antagonists (IV), and PARP-1 inhibitors (V) [5–11].

Literature survey revealed that insufficient work has been carried out for the sustainable catalytic synthesis of dihydropyrrolo[1,2-a]quinoxaline derivatives under mild conditions. Previously, most of the researchers reported aromatic quinoxaline derivatives following various methods such as Kalinin A. A. and Mamedov V. A. et al. have published review articles on synthesis of pyrrolo[1,2-a]quinolines, based on derivatives of quinoxalines and derivatives of pyrroles [12, 13]. Additionally, specific important methodologies (Scheme 1) for the synthesis of dihydropyrrolo[1,2-a]quinolines, such as reactions of 1-(2-aminophenyl) pyrroles with aldehydes or ketones (method I) [14–16], using 1-H
Fig. 1 Pharmacological active compounds having pyrrolo-quinazoline moiety and inset provided the structure of catalyst

Scheme 1 Common approaches for the synthesis of dihydropyrrolo[1,2-a]quinazalines
pyrrole-2-carbaldehyde with 2-iodoaniline (method II) [17], form 2-(1H-pyrrol-1-yl)anilines and alkynes in the presence of gold-catalyst (method III) [18, 19], followed by intramolecular reductive amination of 1-(2-nitrophenyl)pyrrole-2-carbaldehyde 7 (method IV) [20], from 1-(2-nitrophenyl)pyrroles and various alcohols (method V) [21] and the intramolecular substitution 1-(2-fluorophenyl)-2-(2-methylaminomethyl)pyrrole (method VI) [22], etc., were reported in the literature (Scheme 1).

In particular, the most convenient approach is to follow the Pictet–Spengler-type root, which reports good yield of dihydropyrrolo[1,2-a]quinoxaline from (2-aminophenyl)pyrrole with aldehyde and are carried out in the presence of homogenous and heterogeneous catalysts like TEMPO oxoammonium salt [23], AlCl₃ [24], Amberlite IR120H [25], sulfamic acid [14], p-dodecylbenzenesulfonic acid [15], etc. Furthermore, 4, 5-dihydropyrrolo[1,2-a]quinoxalines molecule consists of one chiral center at C-4, which directs the reaction path to form a racemic mixture of products. Several chiral catalysts like iridium [26], B(OMe)₃/(R)-BINOL [27], and phosphoramidate [28], have already been reported for optically active and enantio-selective formation of 4,5-dihydropyrrolo[1,2-a]quinoxalines (Scheme 2).

Nevertheless, all the reported approaches come with certain downsides like use of hazardous solvents, additional additives, and time-consuming process and suffer tedious work up process with low reaction selectivity with major byproducts [29, 30]. The major weakness underlying with most of the available procedures is that they provide aromatized quinazoline or mixture of dihydroquinazolines and quinoxalines [24, 31]. This particular limitation attracted attention and enforced us to design an effective protocol for selective synthesis of dihydropyrrolo[1,2-a]quinazolines. Dihydropyrrolo[1,2-a]quinazolines acts as a good precursor for the synthesis of numerous bioactive derivatives by varying the substitutions on nitrogen atom, which is one of the advantages over aromatic pyrrolo[1,2-a]quinazolines [16, 32].

Over the years, catalysis has gained significant recognition for the development of proficient and sustainable organic transformations especially for quinoxalines synthesis [33]. In this stream, both homogeneous and heterogenous catalysts systems have been explored for the effective transformations involving synthesis of quinoxaline heterocycles. Owing to separation and recovery issues related to homogeneous catalysts, heterogeneous catalysts or supported catalysts are studied extensively with
recyclability benefits for these organic conversions [34]. In the context of 2D and 3D nanomaterials of silica, oxides, alumina, and carbon allotropes are widely synthesized and employed as supports [35]. Among these, carbon nanotubes (CNTs) have been paid much attention, as they are cheap and easily obtained [36]. The carbon nanotubes-based materials have widely used as heterogeneous catalysts, sensing and organic pollutant removal [37–41] as they provide added advantage to catalysts namely, high dispersion, increased surface area, nano-size, and pronounced stability as well as selectivity [35, 42]. Multi-walled carbon nanotubes (MWCNTs) triumphs the series, especially for organic transformations, due to additional merits like active functionalization, high surface area, and strong chemical stability [42]. Therefore, MWCNTs have been screened for various organic reactions and found to exhibit excellent catalytic activity [43–46]. Efficient dispersion of metal and metal oxide nanoparticles over various support systems are dragging the attraction of researchers all over the world due to the interesting properties of nanomaterials like electronic structure, selectivity, efficiency, and recyclability[47–49].

Metals and metal oxide nanoparticle-incorporated composite systems have found applications in many areas such as organic transformations, purifications, catalysis, transparent electrodes, battery technology, gas sensors, and emission field. [50–55]. Among these, the most inspected nanoscale metal oxides is tin dioxide (SnO₂), due to its physical and chemical properties which majorly contributed for different application aspects. As an effort to enhance the electronic property and to improve surface area, SnO₂ can be incorporated on MWCNTs to form a composite material and can be used as a catalyst for organic transformation with the help of improved active sites on the surface [56]. Such attractive physicochemical properties of SnO₂@MWCNTs as nano-composite prompted us to study its catalytic efficiency in quinoxalines synthesis (Scheme 3).

Herein, taking into account our experience in the field of heterocyclic compounds synthesis using recyclable catalysts and using greener solvent under mild conditions [57–61], we introduce an efficient, sustainable protocol for the synthesis of heterocyclic molecules (quinoxaline derivatives) via Pictet–Spengler-type protocol. In particular, the selective synthesis of quinoxaline derivatives from pyrroles and diverse aromatic aldehydes were carried out using recyclable catalyst SnO₂@MWCNTs with greener solvent under mild conditions. The tailored SnO₂@MWCNTs catalyst was synthesized by a simple chemical synthesis method and characterized by
Results and discussion

In the present study, SnO$_2$ nanoparticles decorated on modified MWCNTs, namely SnO$_2$@MWCNT were synthesized, characterized, and further analyzed for its applicability in selective quinoxaline synthesis. The physicochemical properties and morphological aspects of the final SnO$_2$@MWCNTs catalyst were examined through various analytical and spectroscopic techniques and obtained results are presented and discussed below.

SnO$_2$ nanoparticles were found to catalyze the reaction with low yield and high reaction time while incorporating carboxylic acid-functionalized MWCNTs as green support enhances the catalytic activity with the added advantage of being biocompatible, inexpensive, and eco-friendly. The structure modification on MWCNT with –COOH functionality imparts secondary bonding between SnO$_2$ nanoparticles and MWCNTs. In the present study, we aim to investigate the effect of SnO$_2$ decoration on MWCNTs for the effective synthesis of dihydropyrrolo[1,2-a]quinoxaline derivatives via Pictet–Spengler Reaction.

Characterization of SnO$_2$@MWCNTs catalyst

XRD analysis

The acid-functionalized MWCNTs surface was modified by grafting with SnO$_2$ particles, and the composite formation was confirmed by X-ray diffraction (XRD) analysis. The XRD pattern of functionalized MWCNTs, pure SnO$_2$, and SnO$_2$@MWCNTs are presented and compared in Fig. 2. The XRD pattern of pure SnO$_2$...
nanoparticles indicated the presence of peaks at 2θ values ~26.1°, 33.6°, 37.9°, 51.8° and 54.7° corresponding to (110), (101), (200), (211), and (220) planes [62]. These peaks are in accordance with the JCPDS file no. 41–1445 confirming the rutile phase of cassiterite SnO₂ with a tetragonal structure [63]. Additionally, XRD pattern of functionalized MWCNTs displayed two broad peaks at 2θ values ~25.4 and 42.4 corresponding to (002) and (100) crystal planes, respectively, and confirmed the graphitic nature of MWCNTs [64]. Furthermore, the XRD pattern of prepared SnO₂@MWCNTs catalyst showed the existence of peaks belonging to both pure SnO₂ and pure MWCNTs phases indicating high-purity SnO₂ adhered to MWCNTs surface. Additionally, the calculated crystallinity and crystal sizes of respective materials were closely co-related with reported values [63]. Moreover, we observed a slight shift in the position of peaks in the XRD of SnO₂@MWCNTs catalyst which suggested a possible interaction between SnO₂ nanoparticles and MWCNTs. These results of shifting of peaks are consistent with the data reported in the literature [63, 65].

FT-IR analysis

FT-IR technique was used to study the presence of functional groups in the prepared materials of modified or oxidized MWCNTs, pure SnO₂, and final SnO₂@MWCNTs catalyst, and the results are shown in Fig. 3. FT-IR spectrum of oxidized MWCNTs displayed a broad peak centered at 3500 cm⁻¹ indicating the presence of –OH groups.
group. A short and intense peak at 2800–2900 cm\(^{-1}\) resulted due to the asymmetric stretching frequency of the C—H group due to the graphitic nature of the MWCNTs structure [66]. Other characteristic vibrations were observed at peaks corresponding to 1700 cm\(^{-1}\) for C=O stretching due to the carboxylic acid group, whereas C=C stretching of aromatic rings appeared at 1680 cm\(^{-1}\). The C—H in-plane bending vibration peak was observed at near about 1380 cm\(^{-1}\) due to graphene skeleton in CNTs. Additionally, the C—O stretching peak at 1100–1084 cm\(^{-1}\) confirms the functionalization of MWCNTs surface with the –COOH group [67].

The FT-IR spectrum of pure SnO\(_2\) nanoparticles showed peaks around 3400–3500 cm\(^{-1}\) region and also at 1600 cm\(^{-1}\) due to the stretching and bending vibration of the –OH bond, respectively. This broad peak occurred due to the –OH groups of the adsorbed water at the surface of the SnO\(_2\) nano-composite [63]. The characteristic peaks of pure SnO\(_2\) nanoparticles observed at 680–600 cm\(^{-1}\) and 520–550 cm\(^{-1}\) were obtained due to the stretching frequency of the O–Sn–O and Sn–O groups, respectively [63, 66]. The SnO\(_2\)@MWCNTs composite displayed all the peaks corresponding to the presence of MWCNTs as well as SnO\(_2\) nanoparticles, therefore, confirming the successful dispersion of SnO\(_2\) nanoparticles on the surface of MWCNTs.

UV analysis

The UV analysis of pure SnO\(_2\) and SnO\(_2\)@MWCNTs was also performed, and the spectral data are shown in Fig. 4. The UV spectrum of pure SnO\(_2\) nanoparticles presented strong absorption bands in the UV region approximately at 372 nm. However, in the case of SnO\(_2\)@MWCNTs catalyst, the absorption range extended to the visible region. Additionally, the edge of the absorption band experienced redshift from 372 to 420 nm. Thus, the obtained results showed that when compared to pure SnO\(_2\), SnO\(_2\)@MWCNTs nano-composite has the potential to be used as an efficient visible-light-activated photo-catalyst [68].

FE-SEM and EDAX analysis

FE-SEM analysis of pure SnO\(_2\) and SnO\(_2\)@MWCNTs nano-composite catalyst was performed for analyzing the surface morphology of the catalyst, and the obtained images are shown in Fig. 5. The SEM images of pure SnO\(_2\) displayed uniform and homogeneous formation of nanoparticles (Fig. 5a). The morphology of SnO\(_2\)@MWCNTs catalyst was captured at different magnifications (Fig. 5b, c and d) which indicated successful modification of MWCNTs surface with SnO\(_2\) nanoparticles. The SnO\(_2\) nanoparticles were uniformly dispersed over the surface of MWCNTs and interconnected to form a uniform network. However, the images also suggested that SnO\(_2\) agglomerated at some places, and due to this condition, we have found less surface area in BET analysis. For pure MWCNTs, we observed 78.7 m\(^2\)/g, and for SnO\(_2\)@MWCNTs, it observed as 52.3 m\(^2\)/g.

Further, SnO\(_2\)@MWCNTs catalyst was subjected to EDAX analysis to confirm the presence of elements, and the graph is shown in Fig. 6. The analysis confirmed
Fig. 3 FT-IR spectra of Fun. MWCNTs, pure SnO$_2$ and SnO$_2$@MWCNTs catalyst

Fig. 4 UV spectra of SnO$_2$ and SnO$_2$@MWCNTs catalyst
the existence of expected elements (carbon, tin and oxygen) in SnO$_2$@MWCNTs, therefore, indicating successful deposition of SnO$_2$ nanoparticles over the surface of MWCNTs. In addition, the excepted elements were present in stoichiometric ratio, and the atomic percentage of the elements is shown in Fig. 6.

**TEM analysis**

The TEM analysis of the SnO$_2$ and SnO$_2$@MWCNTs composite was performed to further explore their surface morphology. The TEM images and SAED measurements of pure SnO$_2$ nanoparticles were taken at different magnifications, and the images are shown in Fig. 7a, b and c. The images revealed the presence of SnO$_2$ nanoparticles with uniform distribution of morphology, whereas the TEM images of SnO$_2$@MWCNTs catalyst (Fig. 7e, f and g) confirmed grafting of SnO$_2$ nanoparticles over MWCNTs surface. These nanoparticles were uniformly deposited on the surface of the carbon nanotubes. Additionally, the SAED pattern of pure SnO$_2$ and SnO$_2$@MWCNTs displayed concentric rings as shown in Fig. 7d and h. The SAED pattern of SnO$_2$ nanoparticles displayed concentric circles that can be indexed to the

![SEM images of (a) pure SnO$_2$ and (b-d) SnO$_2$@MWCNTs catalyst at different magnifications](image-url)
(110), (101), (200) and (211) planes of tetragonal rutile-like SnO$_2$, suggesting the successful formation of SnO$_2$ nanoparticles [65]. The concentric rings in the SnO$_2$@MWCNTs pattern (Fig. 7h) can be indexed (inside to the outside) to the (110), (101), (200), and (211) planes of SnO$_2$ along with planes (002) and (100) of MWCNTs (indicated in white) suggesting polycrystalline nature of material [69]. The interpretations are consistent with the XRD results, which confirmed the successful formation of the SnO$_2$@MWCNTs composite.

Additionally, we can determine the particle size of synthesized SnO$_2$@MWCNTs nano-composite using the high-resolution transmission electron microscopy (HR-TEM) technique. We have screened the prepared catalyst for HR-TEM analysis shown in Fig. 8. The results of HR-TEM showed a uniform distribution of SnO$_2$ nanoparticles on the surface of MWCNT. The formulated nanoparticle was distorted in a spherical shape and in the range of 11–15 nm diameter. The average size of aggregated particles was calculated and was nearly 13 nm (mean of observed widths).

The characterization results, therefore, suggested homogeneous grafting of SnO$_2$ throughout the surface of MWCNTs, therefore, leading to the formation of SnO$_2$@MWCNTs nano-composite. These features can presumably allow reactants to easily access the active site of SnO$_2$ groups on both sides of the two-dimensional SnO$_2$@MWCNTs catalyst with limited mass allocation resistance and therefore facilitate its catalytic performance to form the desired product.

**Catalytic activity of SnO$_2$@MWCNTs catalyst toward dihydropyrrolo[1,2-a] quinoxaline synthesis**

The impact of SnO$_2$ loading on the catalytic performance of SnO$_2$@MWCNTs and the reaction outcomes have been investigated. Heterogeneous catalysts were prepared via surface modification of MWCNT through the loading of SnO$_2$ nanoparticles synthesized from 0.01 to 0.04 M of SnCl$_4$ concentration, following the same procedure as described in the experimental part. The catalytic efficiency of 10 wt. % synthesized SnO$_2$@MWCNTs nano-composites were checked for model reaction

![Fig. 6 EDX of prepared SnO$_2$@MWCNTs catalyst](image)
as 1-(2-aminophenyl)pyrrole (1 mmol), benzaldehyde (1 mmol), and magnetically stirred at 40 °C in 10-mL ethanol. The outcome of this exercise is shown in Fig. 9.

From this, it was clear that the catalyst obtained from 0.01 M of SnCl$_4$ and 0.5 g MWCNTs showed maximum catalytic proficiency for the present transformation. For SnO$_2$@MWCNTs with varying SnCl$_4$ concentrations other than 0.01 M SnCl$_4$, it could be seen that the product yield decreases along with an increase in reaction time as shown in Fig. 9. Hence, a further increase in SnO$_2$ nanoparticles on the surface of MWCNTs is observed to reduce the catalytic effectiveness, may owing to SnO$_2$ cluster formation, which reduces the active interaction between reactants.

![Fig. 7 TEM of (a-c) pure SnO$_2$ and (e-g) SnO$_2$-MWCNTs catalyst and SAED of (d) pure SnO$_2$ and (h) SnO$_2$-MWCNTs catalyst](image1)

![Fig. 8 HR-TEM of SnO$_2$@MWCNTs catalyst](image2)
summarize, SnO₂ (obtained from 0.01 M SnCl₄)-loaded MWCNTs showed excellent catalytic property with maximum yield in minimum time and hereafter optimized for further reactions.

After the successful preparation and characterization of SnO₂@MWCNTs (from 0.01 M SnCl₄) catalyst, its performance was tested toward the synthesis of dihydropyrrolo[1,2-a]quinoxaline from 1-(2-aminophenyl)pyrrole (1 mmol) and benzaldehyde (1 mmol) as a model reaction. Additionally, the reaction conditions were optimized through the screening of several reaction parameters and obtained results are summarized in Table 1.

**Influence of reaction parameters on dihydropyrrolo[1,2-a]quinoxaline synthesis**

To check the reactivity of reactants, initially, we performed the reaction without catalyst and solvent. Precisely, an appropriate amount of reactants were allowed to react at room temperature for 24 h. The reaction resulted in a negligible amount of the targeted product (Table 1, Entry 1). The same reaction was also performed at 80 °C under similar reaction conditions. However, the desired product was obtained in trace amounts (Table 1, Entry 2). This result suggested that the catalyst is required in order to improve the reaction yield. Therefore, a reaction was performed in the presence of 10 wt.% SnO₂@MWCNTs nano-composite catalyst at room temperature under solvent-free conditions. Interestingly, the catalyst assisted in achieving 60% conversion of the model reactants with 42% yield for the desired product after 18 h of reaction time (Table 1, Entry 3). Further, to investigate the solvent effect on the catalytic activity of SnO₂@MWCNTs nano-composite, a reaction was performed in the presence of ethanol solvent under a similar reaction as that of the previous reaction. The conversion (80%) and yield (67%) were observed to improve at 12 h of reaction time (Table 1, Entry 4).

![Comparison of catalytic efficiency](image-url)  
*Fig. 9* Catalytic efficiency of SnO₂@MWCNTs with varying SnCl₄ concentration
The obtained results indicated that reaction operating conditions need to be optimized in order to further improve the yield. Accordingly, the reaction temperature was varied from 20 °C to 60 °C, and its effect was studied for the model reaction in the presence of 10 wt.% SnO$_2$@MWCNTs catalyst (reaction conditions: 1-(2-aminophenyl)pyrrole (1 mmol), benzaldehyde (1 mmol) and 10 mL ethanol solvent). Initially, at 20 °C, we obtained 90% conversion of reactants with 72% yield at 8 h of reaction time (Table 1, Entry 5). With further increase in the reaction temperature to 40 °C, 100% conversion was achieved with 92% yield for the desired product in 2-h reaction time. (Table 1, Entry 6). However, a mixture of dihydropyrrolo[1,2-a]quinoxaline (72%) and pyrrolo[1,2-a]quinoxaline (25%) products were obtained when the reaction was run at 60 °C within 2 h (Table 1).

### Table 1 Effect of reaction parameters for dihydropyrrolo [1,2-a]quinoxaline synthesis$^a$

| Entry | Catalyst SnO$_2$@MWCNTs.(in wt.%) | Solvent (10 mL) | Temperature (in °C) | Reaction time$^b$ (h) | Conversion (%) | Yield$^c$ (%) |
|-------|----------------------------------|-----------------|---------------------|----------------------|----------------|---------------|
| 1     | –                                | –               | RT                  | 24                   | 0              | 0             |
| 2     | –                                | –               | 80                  | 24                   | 18             | 5             |
| 3     | 10                               | –               | RT                  | 18                   | 60             | 42            |
| 4     | 10                               | EtOH            | RT                  | 12                   | 80             | 67            |
| 5     | 10                               | EtOH            | 20                  | 08                   | 90             | 72            |
| 6     | 10                               | EtOH            | 40                  | 02                   | 100            | 92            |
| 7     | 10                               | EtOH            | 60                  | 02                   | 100            | 75(25)$^d$    |
| 8     | 10                               | EtOH            | 60                  | 06                   | 100            | 0(86)$^d$     |
| 9     | 2.5                              | EtOH            | 40                  | 05                   | 100            | 83            |
| 10    | 5                                | EtOH            | 40                  | 3.1                  | 100            | 91            |
| 11    | 7.5                              | EtOH            | 40                  | 2.2                  | 100            | 92            |
| 12    | 5                                | MeOH            | 40                  | 06                   | 100            | 58            |
| 13    | 5                                | DCM             | 40                  | 05                   | 100            | 65            |
| 14    | 5                                | Acetonitrile    | 40                  | 08                   | 100            | 44            |
| 15    | 5                                | Water           | 40                  | 24                   | 41             | 16            |

$^a$Reaction conditions: 1-(2-aminophenyl)pyrrole (1 mmol), benzaldehyde (1 mmol), and appropriate amount of SnO$_2$@MWCNTs catalyst

$^b$Reaction time was monitored by TLC

$^c$Isolated yield

$^d$yield of pyrrolo[1,2-a]quinoxaline
Further, catalyst loading was optimized by performing a series of reactions by varying the catalyst amount from 2.5 to 7.5 wt.% under optimized reaction conditions and ethanol solvent. In the presence of 2.5 wt.% catalysts, the reaction progressed with complete conversion and 83% yield for desired aromatic pyrrolo[1,2-a]quinoxaline product in 5-h reaction time (Table 1, Entry 9). With the increase in the catalyst loading to 5 wt%, there was a substantial increase in the yield for the desired product (91%) in 3.1-h reaction time (Table 1, Entry 10). There was no significant increase in the yield with a further increase in the catalyst loading up to 10 wt.% (Table 1, Entry 6, 11). Though 10 and 7.5 wt.% catalyst loading provided near about similar yield as that of 5 wt.% at shorter reaction time. For a more obvious quantitative comparison, the turnover number (TON) and turnover frequency (TOF) of these catalysts were measured. TON or TOF are one of the criteria for selecting effective catalyst that the higher the TON or TOF value, the better the catalyst. We have evaluate the catalytic activities of 10, 7.5, and 5 wt.% with TON (the mole of product form on a unit surface area) values as 0.67 × 10⁻³, 0.88 × 10⁻³ and 1.35 × 10⁻³, respectively, while TOF (per h) values are 0.33 × 10⁻³, 0.40 × 10⁻³ and 0.43 × 10⁻³, respectively.

Therefore, we choose to proceed with low catalyst loading that is 5 wt.% and was considered optimum loading for further reactions as the time and yield difference was negligible and due to the consideration of TON, TOF and green chemistry aspects.

Although the present protocol is highly efficient in ethanol solvent, the effect of different solvents for dihydropyrrolo[1,2-a]quinoxaline synthesis was also studied. In the presence of methanol solvent, 58% yield was observed with complete conversion of reactants (Table 1, Entry 12), whereas DCM and acetonitrile solvents failed to bring about the efficient conversion of reactants under consideration and produced 65% and 44% yield in 5 h and 8 h, respectively (Table 1, Entry 13 & 14). Additionally, we took one more trial of reaction with water as a solvent to make it an environmentally benign protocol; however, the reaction ended up with a poor yield for the desired product even after 24-h reaction time (Table 1, Entry 15). Therefore, all the above results emphasized that ethanol was a better solvent for the reaction under investigation. Other solvents gave lower yield and took more time for completion of reaction possibly due to the low solubility of reactants in the solvents.

**Comparative study of catalytic activity of SnO₂@MWCNTs with reported catalysts**

To compare the outstanding catalytic activity of SnO₂@MWCNTs catalyst, we conducted a series of reactions for dihydropyrrolo[1,2-a]quinoxaline synthesis.
under optimized reaction conditions in the presence of other reported homogeneous and heterogeneous catalysts, and the results are tabulated in Table 2. Initially, we checked the efficiency of some metal chlorides and sulfate as catalysts for the dihydropyrrolo[1,2-a]quinoxaline synthesis. Precisely, with 10 mol. % of AlCl₃, FeCl₃, ZnCl₂, and CuSO₄ catalysts good-to-moderate yield was achieved for the desired product. However, the yield was achieved at the expense of prolonged reaction time (Table 2, Entry 1–4). Additionally, owing to the homogeneous nature of these metal precursors, their separation from the reaction mixture was tedious.

Further, iodine catalyzed reaction ended at 70% yield after 8 h (Table 2, Entry 5), whereas sulfamic acid catalyst delivered 67% yield of dihydropyrrolo[1,2-a]quinoxaline at 8 h (Table 2, Entry 6). However, the yield obtained was not efficient, and the workup for the catalyst separation was a tedious process. Thereafter, we tested SnO₂ as a heterogeneous catalytic system which gave a good yield (84%) for the targeted

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**Table 2** Comparative study of reported homo and heterogeneous catalysts

| Entry | Catalyst (10 mol %) | Solvent (10 mL) | Temperature (°C) | Reaction timeb (h) | Yieldc (%) |
|-------|----------------------|-----------------|------------------|--------------------|------------|
| 1     | AlCl₃                | EtOH            | 40               | 6                  | 82         |
| 2     | FeCl₃                | EtOH            | 40               | 12                 | 70         |
| 3     | ZnCl₂                | EtOH            | 40               | 14                 | 63         |
| 4     | CuSO₄·5H₂O           | EtOH            | 40               | 10                 | 78         |
| 5     | Iodine               | EtOH            | 40               | 8                  | 70         |
| 6     | Sulfamic acid        | EtOH            | 40               | 8                  | 67         |
| 7     | SnO₂ (nanoparticle, 5 wt.%) | EtOH    | 40               | 6                  | 84         |
| 8     | SnO₂@MWCNTs (5 wt.%) | EtOH            | 40               | 3.1                | 91         |

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*aReaction conditions: 1-(2-aminophenyl)pyrrole (1 mmol), benzaldehyde (1 mmol), and appropriate amount of catalyst  
*bReaction time was monitored by TLC  
*cIsolated yield
product under optimized conditions after 6 h (Table 2, Entry 7). The obtained results suggested that SnO\(_2\) was appreciably active as a catalyst for the selective synthesis of dihydropyrrolo[1,2-a]quinoxaline. Further, to enhance the performance of SnO\(_2\) nanoparticles, it was supported over MWCNTs, and as expected the nano-composite resulted in 91% yield toward the desired product in just 3.10 h (Table 2, Entry 8). The reason for the high efficiency was the dispersion of SnO\(_2\) over MWCNTs in the nano-composite as evidenced by characterization results. From the observed results, we have concluded that 5 wt.% SnO\(_2\)@MWCNTs catalyst showed outstanding efficiency for the dihydropyrrolo[1,2-a]quinoxaline synthesis from 1-(2-aminophenyl) pyrrole (1 mmol), benzaldehyde (1 mmol) in ethanol solvent at 40 °C temperature in just 3.1 h of reaction time.

After the successful investigation and comparison of catalytic activity for model compound synthesis, we further investigated the substrate scope of this optimized protocol by using several substituted aromatic aldehydes, and the obtained results are summarized in Table 3. The model reaction with benzaldehyde gave a 91% yield of the targeted product in 3.10 h by using 5 wt.% SnO\(_2\)@MWCNTs catalyst (Table 3, Entry 1). With 4-nitrobenzaldehyde as a substrate reaction showed 100% conversion with satisfactory yield (90%) after 3 h reaction time under optimized conditions (Table 3, Entry 2). Further, para-substituted benzaldehydes (with Br, Cl and F) also reacted efficiently under outlined conditions displaying 87%, 88%, and 85% yield for the respective derivatives of dihydropyrrolo[1,2-a]quinoxaline (Table 3, Entry 3–5). Similarly, electron-donating methoxy group substituted benzaldehydes provided outstanding yield for the respective product. These methoxy benzaldehydes succeeded with 93 and 90% yield of corresponding derivatives after 2.30- and 3.20-h reaction time under optimized conditions (Table 3, Entries 6, 7).

Additionally, we also exercised some reactions using uncommon aldehydes like 1-naphthaldehyde (Table 3, Entry 8) and heterocyclic aldehydes such as furan-2-carbaldehyde and pyridine-2-caraldehyde (Table 3, Entries 9, 10) under similar reaction conditions, which showed satisfactory results for respective dihydropyrrolo[1,2-a]quinoxaline derivatives. The isolated yield of furan-2-carbaldehyde was to some extent not satisfactory due to the oily nature of the product, which made its separation from the reaction mixture a difficult task. Along with such exercise, we have demonstrated one more trial with aliphatic aldehyde as propionaldehyde, which also showed good reactivity with 1-(2-aminophenyl) pyrrole under offered optimized condition and gave an excellent yield of 79% for the desired product (Table 3, Entry 11). The obtained results illustrated that all substituted aldehydes offered a good-to-remarkable yield of respective dihydropyrrolo[1,2-a]quinoxaline derivatives in the presence of SnO\(_2\)@SNTs catalyst under the optimized conditions. Structures of all synthesized derivatives were confirmed by spectral analysis and physical properties and matched well with previously reported literature. [23, 24]
Table 3  Synthesis of series of dihydropyrrolo[1,2-a]quinoxaline derivatives

| Entry | Products | Reaction Time (h) | Yield (%) | Melting Point (°C) | Ref. |
|-------|----------|-------------------|-----------|-------------------|------|
| 1     | ![3a](image) | 3.10              | 91        | 97-98             | [32] |
| 2     | ![3b](image) | 3                 | 90        | 130-131           | [23] |
| 3     | ![3c](image) | 3.15              | 87        | 117-118           | [32] |
| 4     | ![3d](image) | 2.50              | 88        | 175-176           | [23] |
| 5     | ![3e](image) | 3.10              | 85        | 110-111           | [32] |
| 6     | ![3f](image) | 2.30              | 93        | 126-127           | [23] |
Herein, we have made an effort to propose a plausible mechanism for the dihydropyrrolo[1,2-a]quinoxaline over SnO$_2$@MWCNTs catalyst based on obtained results and literature background [15, 16, 70, 71]. The reaction is anticipated to follow the regular mechanism of acid-catalyzed condensation reactions and is schematically represented in Scheme 4. The reaction is initiated by the interaction of oxygen of aldehydic carbonyl group (2) over Lewis acidic sites of SnO$_2$@MWCNTs catalyst which resulted in activation of carbonyl carbon via increasing its electrophilicity (A). Subsequently, the nucleophilic attack of the –NH$_2$ group of 1-(2-aminophenyl)pyrrole (1) resulting in the formation of a tetrahedral carbon (B) which then dissociates to an imino compound (C), relieving the catalyst. Furthermore, SnO$_2$@MWCNTs catalyst interacted and activated nitrogen of imino group which was attacked by the second position of pyrrole ring (D) and resulted in an intramolecular ring closure.

Table 3 (continued)

|   | Structure | Product | Yield | Ref. |
|---|-----------|---------|-------|------|
| 7 | ![Structure 3g](image) | 3.20    | 90    | 128-129 [23] |
| 8 | ![Structure 3h](image) | 2.30    | 92    | 115-116 [23] |
| 9 | ![Structure 3i](image) | 3.30    | 80    | 210-212$^{(d)}$ [23] |
| 10| ![Structure 3j](image) | 2.40    | 88    | 124-125 [23] |
| 11| ![Structure 3k](image) | 3.50    | 79    | 55-56 [23]  |

$^a$Reaction conditions: 1-(2-aminophenyl)pyrrole (1 mmol), benzaldehyde (1 mmol), and 5 wt.% SnO$_2$@MWCNT in 10 mL EtOH

$^b$Reaction time was monitored by TLC

$^c$Isolated yield

$^d$Boiling point

**Plausible reaction mechanism**

The reaction is initiated by the interaction of oxygen of aldehydic carbonyl group (2) over Lewis acidic sites of SnO$_2$@MWCNTs catalyst which resulted in activation of carbonyl carbon via increasing its electrophilicity (A). Subsequently, the nucleophilic attack of the –NH$_2$ group of 1-(2-aminophenyl)pyrrole (1) resulting in the formation of a tetrahedral carbon (B) which then dissociates to an imino compound (C), relieving the catalyst. Furthermore, SnO$_2$@MWCNTs catalyst interacted and activated nitrogen of imino group which was attacked by the second position of pyrrole ring (D) and resulted in an intramolecular ring closure.
closure. Finally, the pyrrole ring of the intermediate (E) was stabilized by aromatization to form the final targeted moiety (dihydropyrrol[1,2-a]quinoxaline) (3). The above probable mechanism inferred that the SnO$_2$@MWCNTs catalyst played a vital role in the activation of the carbonyl group and promoting the cyclization (E) to yield the final product.

**Recyclability test of SnO$_2$@MWCNTs catalyst**

Recyclability studies have a pivotal role in heterogeneous catalysis. The recovery and reusability of the SnO$_2$@MWCNT catalyst were investigated toward the synthesis of dihydropyrrol[1,2-a]quinoxaline. After performing a fresh cycle of the reaction under optimized reaction conditions, the catalyst was recovered by simple filtration technique, washed repeatedly with water and dried in a vacuum oven at 50 °C for 12 h. The dried catalyst was further used in stoichiometric amounts for the next cycle. The catalyst was recycled up to six recycles without significant loss in its catalytic activity with respect to the selectivity and yield of dihydropyrrol[1,2-a] quinoxaline as shown in Fig. 10.

After the successful demonstration of recyclability of SnO$_2$@MWCNTs catalyst up to six runs, the recycled catalyst was characterized by FT-IR and EDAX analysis to check the stability and morphologically changes in the catalyst. We
have screened recycled catalyst (after 6th run) for FT-IR and EDAX analysis as shown in Fig. 11 which depicted the peaks were good to coincide with the IR frequencies of respective peaks observed for fresh catalyst.

Supplementary, same recycled SnO$_2$@MWCNTs catalyst was subjected to EDAX analysis to confirm the presence of elements and its stability after the

![Recyclability SnO$_2$-MWCNT Catalyst](image1)

**Fig. 10** Recyclability test of SnO$_2$@MWCNTs catalyst

![FT-IR spectra](image2)

**Fig. 11** FT-IR spectra of fresh catalyst and after completion of 6th run
recycled (displayed in Fig. 12). The analysis confirmed the existence of all elements (carbon, tin and oxygen) with near about same composition as found in fresh.

Consequently, from these screening, we have reached to conclusion that our reported catalyzed was stable and maintain its chemical composition and functionality even after the reused it up to six cycles.

**Experimental materials**

Tin chloride (SnCl$_4$, purity 99%) was procured from Sigma-Aldrich, India. Commercial MWCNTs (outer diameter—10–15 nm, inner diameter—2–6 nm, length—10 μm, 90% purity) were purchased from Iljin Nanotech (Korea). Concentrated sulfuric acid and nitric acid (95–98%) were obtained from commercial sources. Thioacetamide (C$_2$H$_5$NS, purity 99%) was also purchased from Sigma-Aldrich, India. 1-(2-aminophenyl)pyrrole and different substituted aromatic aldehydes were purchased from Sigma-Aldrich. Acetonitrile (99%), methanol (99%), ethanol (99%), n-hexane (99%), and dichloromethane (99%) solvents (purity 99%) were supplied by S D Fine Chem. Limited. Anhydrous sodium sulfate (Na$_2$SO$_4$, 99%) was purchased from Sigma-Aldrich. All chemicals were used without further purification, and solvents were purified and dried prior to use.

**Synthesis procedure of SnO$_2$@MWCNTs catalyst**

**Oxidation and preparation of functionalized MWCNTs**

The raw MWCNTs were functionalized by a reported modified hammers procedure [72]. Precisely, 0.5 g of pristine multiwall carbon nanotubes (MWCNTs) was refluxed with a mixture of conc. H$_2$SO$_4$ and conc. HNO$_3$ acid (3:1, v/v) in a round-bottom flask at 80 °C for 6 h. The obtained oxidized and functionalized MWCNTs were separated by centrifugation at 4000 rpm and subsequently

![Fig. 12 EDAX analysis SnO$_2$@MWCNTs catalyst after the recycled up to six runs](image-url)
washed with distilled water several times to get neutral pH. The separated black solid was finally dried in vacuum for 24 h at 50 °C to obtain oxidized and functionalized MWCNTs.

**Preparation of SnO$_2$@MWCNTs catalyst**

Particularly, 2.6 g (0.01 M) of SnCl$_4$ was dissolved in 100 mL of 50% distilled ethanol, followed by the addition of 6.03 g thioacetamide and 5 mL of concentrated HCl (37 wt.%). The as-synthesized functionalized MWCNTs (20 mg in 25 mL ethanol) were added slowly to the above suspension under stirring followed by sonication for 15 min. Further, the mixture was stirred for a few minutes to let the MWCNTs disperse well in the above suspension. The resultant solution was then heated at 70 °C for 3 h. The obtained precipitate was separated from the mother liquor by centrifugation at 3500 rpm and successively washed with distilled water. The final SnO$_2$@MWCNTs catalyst was obtained after drying the precipitate at 110 °C for 12 h, followed by calcination in air at 400 °C for 2 h. A schematic representation of SnO$_2$@MWCNTs catalyst synthesis is shown in Scheme 3.

**Catalyst characterization methods**

Phase and crystallinity nature of prepared materials were studied by using X-ray diffraction (XRD) on a PAN analytical X-pert diffractometer with a CuKα radiation (λ = 1.5405 Å) collected between 2θ (twice the Bragg angle) range of 05–80°. The intensity distributions of the XRD data were fitted using JADE software from JADE Software Corporation, CA. The surface morphology of catalysts was studied using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM). The elemental compositions of materials were analyzed with Hitachi S-4800 FE-SEM coupled with energy-dispersive X-ray (EDX) spectroscopy. Transmission electron microscopy (TEM) images were obtained by JOEL JEM-2010 microscope operated at an acceleration voltage at 200 kV. The presence of functional groups in the samples were characterized by Fourier transform infrared spectroscopy (FT-IR, Shimadzu FT-IR-8700) using a standard potassium bromide (KBr) pellet technique. OPTIZEN 3220 UV UV–vis spectrophotometer was used for the UV analysis of SnO$_2$@MWCNTs.

**General procedure for synthesis of dihydropyrrolo[1,2-a]quinoxaline derivatives**

Mixture of 1-(2-aminophenyl)pyrrole (1 mmol; 0.16 g), corresponding aldehydes (1 mmol; 0.10 g for benzaldehyde), and SnO$_2$@MWCNTs (5 wt.%; 0.013 g) in 10 mL ethanol was placed in a 100-mL round-bottom flask. The reactant mixture was stirred at 40 °C, and the reaction progress was monitored through thin-layer chromatography (TLC) by using hexane and ethyl acetate (8:2) solvent system. After the complete consumption of reactants, the reaction mixture was cooled at room
temperature and then poured into water. The mixture was extracted with ethyl acetate (10 mL × 3) in a separating funnel. The organic layer was collected and dried by using anhydrous Na₂SO₄ and concentrated under reduced pressure. A schematic representation of the synthesis of dihydropyrrolo[1,2-a]quinoxaline under described reaction parameters is shown in Scheme 2.

The obtained crude product was recrystallized using ethanol and further purified by column chromatography (petroleum ether–ethyl acetate system). The isolated products were further confirmed by ¹H-NMR, ¹³C-NMR, mass spectroscopy (MS), and infrared spectroscopy (IR). The catalyst was quantitatively recovered by simple filtration and washed alternatively with distilled water and ethanol. The catalyst was then dried in a vacuum oven at 50 °C for 12 h and reused for further cycles.

### Spectral data of the synthesized 4, 5-dihydropyrrolo[1,2-a]quinoxaline derivatives (3a-j)

#### 4-phenyl-4,5-dihydropyrrolo[1,2-a]quinoxaline 3a: Pale yellow solid, IR (KBr, in cm⁻¹): 3476, 3345, 2980, 1658, 1624, 1569, 1461, 1429, 1343, 1283, 1072, 965, 795, 712, 695. ¹H-NMR (CDCl₃, in δ ppm): 7.4–7.3 (m, 4H), 7.2–7.1 (m, 4H), 6.9 (dd, 2H), 6.3 (t, 1H), 6.2 (d, 1H), 5.3 (s, 1H, NH), 4.3 (s, 1H). ¹³C-NMR (CDCl₃, in δ ppm): 138.9, 136.2, 133.7, 130.9, 129.0, 128.8, 128.3, 127.6, 127.0, 124.1, 123.3, 122.5, 121.4, 108.4, 106.4, 60.8. MS (m/z): 247 (M + 1).

#### 4-(4-nitrophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline 3b: Yellow solid, IR (KBr, in cm⁻¹): 3480, 3361, 3064, 2887, 1630, 1593, 1479, 1395, 1210, 1111, 753, 712, 695. ¹H-NMR (CDCl₃, in δ ppm): 8.1 (d, 2H), 7.4 (d, 1H), 7.2 (m, 2H), 7.1–7.0 (m, 3H), 6.8 (d, 1H), 6.3 (t, 1H), 6.2 (d, 1H), 5.5 (s, 1H, NH), 4.2 (s, 1H). ¹³C-NMR (CDCl₃, in δ ppm): 149.2, 147.5, 133.8, 133.4, 131.0, 128.7, 127.1, 127.0, 124.0, 123.3, 122.5, 121.4, 108.4, 106.4, 60.51. MS (m/z): 291 (M⁺).

#### 4-(4-bromophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline 3c: Pale yellow solid, IR (KBr, in cm⁻¹): 3420, 3054, 2974, 1642, 1575, 1435, 1291, 1144, 765, 712, 647. ¹H-NMR (CDCl₃, in δ ppm): 7.8 (d, 2H), 7.4–7.3 (m, 4H), 7.1 (t, 1H), 6.7 (d, 1H), 6.6 (d, 1H), 6.2–6.1 (m, 2H), 5.4 (s, 1H, NH), 4.1 (s, 1H). ¹³C-NMR (CDCl₃, in δ ppm): 141.0, 136.4, 133.0, 130.8, 126.4, 125.8, 123.9, 121.6, 119.8, 115.4, 114.3, 110.0, 106.7, 56.1. MS (m/z): 326 (M + 1).

#### 4-(4-chlorophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline 3d: White solid, IR (KBr, in cm⁻¹): 3476, 3064, 2979, 1657, 1592, 1449, 1325, 1209, 1020, 874, 716, 695. ¹H-NMR (CDCl₃, in δ ppm): 7.4 (d, 2H), 7.3–7.2 (m, 3H), 7.2–7.1 (m, 3H), 6.9 (dd, 1H), 6.2 (t, 1H), 6.1 (d, 1H), 5.4 (s, 1H, NH), 4.2 (s, 1H). ¹³C-NMR (CDCl₃, in δ ppm): 139.9, 134.2, 133.9, 133.8, 132.6, 131.9, 130.5, 129.2, 127.3, 127.0, 124.1, 121.5, 108.5, 106.6, 60.5. MS (m/z): 282 (M + 2).

#### 4-(4-fluorophenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline 3e: Colorless solid, IR (KBr, in cm⁻¹): 3482, 2920, 1672, 1620, 1522, 1465, 1282, 1148, 780, 672. ¹H-NMR (CDCl₃, in δ ppm): 7.5 (d, 1H), 7.4–7.3 (m, 4H), 7.2–7.1 (m, 1H), 7.0–6.9 (m, 2H), 6.6 (d, 1H), 6.2 (m, 1H), 5.9 (d, 1H), 5.4 (s, 1H, NH), 4.4 (s, 1H). ¹³C-NMR (CDCl₃, in δ ppm): 162.2 (¹JC-F = 240.5 HZ), 140.0 (¹JC-F = 3.2 HZ).
Tailored SnO$_2$@MWCNTs efficient and recyclable...

HZ), 137.4, 136.9, 136.0, 131.7, 129.5, 127.9 ($^3$J$_{C,F}$ = 9.8 HZ), 125.4, 123.6, 120.0, 116.5 ($^3$J$_{C,F}$ = 21.7 HZ), 115.3, 112.8, 109.0, 58.9. MS (m/z): 265 (M + 1).

4-(4-methoxyphenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline 3f: Yellowish-white solid, IR (KBr, in cm$^{-1}$): 3384, 3186, 2917, 2848, 1624, 1590, 1498, 1315, 1246, 1155, 1056, 726, 698, 560. $^1$HNMR (CDCl$_3$, in δ ppm): 7.4 (d, 2H), 7.2–7.1 (m, 4H), 7.1 (m, 1H), 7.0 (d, 1H), 6.9 (d, 1H), 6.3 (t, 1H), 6.2 (d, 1H), 5.2 (s, 1H, NH), 4.3 (s, 1H), 3.8 (s, 3H). $^{13}$CNMR (CDCl$_3$, in δ ppm): 159.1, 138.9, 133.8, 131.0, 129.9, 128.0, 127.1, 124.2, 123.3, 122.5, 121.5, 114.5, 108.4, 106.5, 60.0, 55.2. MS (m/z): 276 (M$^+$).

4-(3-methoxyphenyl)-4,5-dihydropyrrolo[1,2-a]quinoxaline 3g: White solid, IR (KBr, in cm$^{-1}$): 3406, 3055, 2962, 1652, 1526, 1490, 1450, 1356, 1268, 1100, 752, 719, 646, 540. $^1$HNMR (CDCl$_3$, in δ ppm): 7.5 (d, 1H), 7.3 (m, 1H), 7.1–6.9 (m, 3H), 6.8 (m, 1H), 6.7–6.6 (m, 2H), 6.5 (d, 1H), 6.3 (d, 1H), 5.9–5.8 (m, 1H), 5.4 (s, 1H, NH), 4.2 (s, 1H), 3.8 (s, 3H). $^{13}$CNMR (CDCl$_3$, in δ ppm): 160.0, 145.1, 137.3, 131.5, 130.9, 126.4, 125.7, 122.0, 120.6, 118.7, 115.5, 114.0, 113.9, 113.1, 111.5, 108.2, 59.8, 55.0. MS (m/z): 276 (M + 1).

4-(Naphthalen-1-yl)-4,5-dihydropyrrolo[1,2-a]quinoxaline 3h: White solid, IR (KBr, in cm$^{-1}$): 3450, 3355, 3107, 2874, 1652, 1600, 1589, 1520, 1478, 1345, 1267, 1162, 810, 781, 714, 675, 570. $^1$HNMR (CDCl$_3$, in δ ppm): 8.2 (d, 1H), 7.8–7.7 (m, 2H), 7.6 (d, 1H), 7.5–7.3 (m, 4H), 7.2 (d, 1H), 6.9–6.8 (m, 2H), 6.2 (d, 1H), 6.0–5.9 (m, 2H), 5.3 (s, 1H, NH), 4.2 (s, 1H). $^{13}$CNMR (CDCl$_3$, in δ ppm): 138.0, 137.8, 134.7, 132.2, 130.0, 129.1, 128.9, 127.0, 126.5, 125.8, 125.0, 124.7, 123.9, 120.5, 117.4, 114.6, 113.9, 109.8, 106.4, 63.1. MS (m/z): 297 (M + 1).

4-(Furan-2-yl)-4,5-dihydropyrrolo[1,2-a]quinoxaline 3i: Yellowish oil, IR (KBr, in cm$^{-1}$): 3402, 3147, 2953, 1645, 1580, 1482, 1408, 1336, 1291, 1202, 1063, 745, 712, 632, 540. $^1$HNMR (CDCl$_3$, in δ ppm): 7.5 (d, 1H), 7.3 (d, 1H), 7.1 (m, 1H), 7.0–6.9 (m, 2H), 6.7 (d, 1H), 6.5 (t, 1H), 6.3–6.2 (m, 2H), 5.9 (d, 1H), 5.4 (s, 1H, NH), 4.4 (s, 1H). $^{13}$CNMR (CDCl$_3$, in δ ppm): 154.0, 143.1, 135.2, 126.4, 125.3, 124.9, 120.4, 116.3, 114.7, 114.3, 110.6, 109.9, 108.0, 106.4, 60.2. MS (m/z): 236 (M$^+$).

4-(pyridin-2-yl)-4,5-dihydropyrrolo[1,2-a]quinoxaline 3j: Yellow solid, IR (KBr, in cm$^{-1}$): 3468, 3068, 2980, 1652, 1601, 1516, 1482, 1420, 1346, 1278, 760, 702, 680, 635. $^1$HNMR (CDCl$_3$, in δ ppm): 8.5 (d, 1H), 7.7–7.6 (m, 1H), 7.4 (m, 2H), 7.3–7.2 (m, 2H), 7.0–6.9 (m, 2H), 6.7 (d, 1H), 6.3 (m, 1H), 6.0 (d, 1H), 5.4 (s, 1H, NH), 4.8 (s, 1H). $^{13}$CNMR (CDCl$_3$, in δ ppm): 160.5, 150.2, 137.3, 135.8, 127.0, 126.0, 124.8, 122.5, 121.7, 120.0, 116.5, 114.6, 113.9, 109.0, 106.5, 57.4. MS (m/z): 248 (M$^+$).

4-Ethyl-4,5-dihydropyrrolo[1,2-a]quinoxaline 3k: White solid, IR (KBr, in cm$^{-1}$): 3465, 3035, 2980, 2934, 1642, 1610, 1525, 1483, 1440, 1354, 1270, 1098, 762, 698. $^1$HNMR (CDCl$_3$, in δ ppm): 7.3 (d, 1H), 7.2 (m, 2H), 6.9 (m, 1H), 6.8 (d, 1H), 6.2 (t, 1H), 5.9 (s, 1H), 5.5 (s, 1H, NH), 4.2 (s, 1H), 4.2 (q, 2H), 1.2 (t, 3H). $^{13}$CNMR (CDCl$_3$, in δ ppm): 136.1, 130.2, 125.7, 124.8, 120.2, 115.2, 115.0, 110.7, 105.9, 48.3, 21.1, 10.0. MS (m/z): 198 (M$^+$).
Conclusion

Herein, we presented an effective Pictet–Spengler-type protocol for the selective synthesis of 4, 5-dihydropyrrolo[1,2-a]quinoxaline derivatives from 1-(2-aminophenyl)pyrroles and diverse aromatic aldehydes over tailored SnO$_2$@MWCNTs nano-catalyst under greener reaction condition. The SnO$_2$@MWCNTs catalyst was successfully synthesized at molecular level and characterized by using several modern analytical and spectroscopic techniques. The 5 wt.% SnO$_2$@MWCNTs catalyst showed remarkable catalytic efficiency with decent yield of the desired product under mild reaction conditions and shorter reaction time. Interestingly, the SnO$_2$@MWCNTs nano-catalyst displayed high selectivity toward dihydropyrrolo[1,2-a]quinoxaline by successfully hindering the formation of corresponding oxidized side product (pyrrolo[1,2-a]quinoxaline) making the process potentially useful for commercial applications as well. We have also explored the catalytic efficiency in synthesis of ten derivatives of targeted compound, and we obtained excellent yield (93–80%) for all the derivatives within 2.30 to 3.30 h, which suggested high tolerance of the catalyst for different functionalities. Moreover, the catalyst showed appreciable recyclability performance up to six recycles without affecting its efficiency and selectivity. Furthermore, SnO$_2$@MWCNTs being a heterogeneous catalyst its easy and simple workup process is an added advantage. Therefore, we present an efficient protocol which can be considered as a greener alternative to the existing methods for the selective synthesis of dihydropyrrolo[1,2-a]quinoxaline.

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Author contribution Authors a and d have equal contribution in the experimental work involving dihydropyrrolo[1,2-a]quinoxalines (organic synthesis section) synthesis part, while authors b and c have contributed in catalyst preparation and its characterization. Corresponding authors have major contribution in manuscript writing. All authors reviewed the manuscript.

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Declarations

Conflict of interests No, I declare that the authors have no conflict of interests as defined by Springer, or other interests that might be perceived to influence the results and/or discussion reported in this paper.

Ethical Approval This research did not contain any studies involving animal or human participants, nor did it take place on any private or protected areas. No specific permissions were required for this research work. The results/data/figures in this manuscript have not been published elsewhere, nor are they under consideration (from you or one of your Contributing Authors) by another publisher.
References

1. R. Sapra, D. Patel, D. Meshram, J. of Med. and Chem. Sci. 3, 71 (2020)
2. A. Huang, C. Ma, Mini. Rev. Med. Chem. 13, 607 (2013)
3. F.A.R. Rodrigues, I.D.S. Bomfim, B.C. Cavalcanti, C.D.O. Pessoa, J.L. Wardell, S.M.S.V. Wardell, A.C. Pinheiro, C.R. Kaiser, T.C.M. Nogueira, J.N. Low, L.R. Gomes, M.V.N.D. Souza, Bioorg. Med. Chem. Lett. 24, 934 (2014)
4. S. Sami, A. Issa, M. Ghobad, A. Sattar, Eurasian. Chem. Commun. 2, 626 (2020)
5. V. Desplat, A. Geneste, M.A. Begorre, S.B. Fabre, S. Brajot, S. Massip, D. Thiolat, D. Mossalayi, C. Jarry, J. Guillon, Enzyme Inhib. Med. Chem. 23, 648 (2008)
6. J. Milne, K.D. Normington, M. Milburn, WO Patent WO2006094210 (2006)
7. G. Maga, S. Gemma, C. Fattorusso, G.A. Locatelli, M. Persico, G. Kukreja, M.P. Romano, L. Chiasserini, L. Savini, E. Novellino, V. Nacci, S. Spadari, G. Campiani, Biochem. 44, 9637 (2005)
8. R.A. Glennon, M.K. Daoud, M. Dukat, H. Syed, Bioorg. Med. Chem. 11, 4449 (2003)
9. H.S. Parhiar, K.S. Kirschbaum, Bioorg. Med. Chem. Lett. 12, 2743 (2002)
10. G. Szabo, R. Kiss, D. Payer-Lengyel, K. Vukics, J. Szikra, A. Alarifi, Tetrahedron Lett. 56, 4619 (2015)
11. A. Preetam, M. Nath, RSC Adv. 5, 21843 (2015)
12. F. Medda, C. Hulme, Tetrahedron Lett. 55, 3328 (2014)
13. J.T. Reeves, D.R. Fandrick, Z. Tan, J.J. Song, H. Lee, N.K. Yee, C.H. Senanayake, J. Org. Chem. 75, 992 (2010)
14. Y. Harrak, S. Weber, A.B. Gomez, G. Rosell, M.D. Pujol, ARKIVOC 4, 251 (2007)
15. M.F. Pereira, V. Thiry, Org. Lett. 14, 4754 (2012)
16. A.A. Patchett, R.P. Nargund, Annu. Rev. Med. Chem. 35, 289 (2000)
17. H.R. Huo, X.Y. Tang, Y.F. Gong, SYNTHESIS 50, 2727 (2018)
18. A.K. Verma, R.R. Jha, V.K. Sankar, T. Aggarwal, R.P. Singh, R. Chandra, Eur. J. Org. Chem. 34, 6998 (2011)
19. C.S. Yi, S.Y. Yun, J. Am. Chem. Soc. 127, 17000 (2005)
20. A. Pratap, A. Kamal, S.B. Korrapati, J. Kovvuri, V. Manasa, A. Ravikumar, A. Alarifi, Tetrahedron Lett. 56, 7012 (2015)
21. H. Shu-Bo, Z. Xiao-Yong, S. Hong-Qiang, Z. Yong-Gui, Adv. Synth. Catal. 360, 1334 (2018)
22. Y. Li, Y.H. Su, D.J. Dong, Z. Wu, S.K. Tian, RSC Adv. 3, 18275 (2013)
23. Y. Wang, L. Cui, Y. Wang, Z. Zhou, Tetrahedron: Asymm. 27, 85 (2016)
24. C.S. Yi, S.Y. Yun, J. Am. Chem. Soc. 127, 17000 (2005)
25. R. Abonia, B. Insuasty, J. Quiroga, H. Kolshorn, H. Meier, J. Hetero. Chem. 38, 671 (2001)
26. D. Chamseddine, B. Raouf, K. Gilbert, C. Bertrand, D. Abdelmadjid, Tetrahedron Lett. 55, 200 (2014)
27. S Gyorgy K Robert PL Dora V Krisztina S Judit B Andrea M Laszlo F Janos M Gyorgy Keseru, Bio. Med. Chem. Lett. 19, 3471 (2009)
28. A. Kamal, S.B. Korrapati, J. Kovvuri, V. Manasa, A. Ravikumar, A. Alarifi, Tetrahedron Lett. 56, 7012 (2015)
29. H. Shu-Bo, Z. Xiao-Yong, S. Hong-Qiang, Z. Yong-Gui, Adv. Synth. Catal. 360, 1334 (2018)
30. Y. Li, Y.H. Su, D.J. Dong, Z. Wu, S.K. Tian, RSC Adv. 3, 18275 (2013)
31. Y. Wang, L. Cui, Y. Wang, Z. Zhou, Tetrahedron: Asymm. 27, 85 (2016)
32. C.S. Yi, S.Y. Yun, J. Am. Chem. Soc. 127, 17000 (2005)
33. R. Abonia, B. Insuasty, J. Quiroga, H. Kolshorn, H. Meier, J. Hetero. Chem. 38, 671 (2001)
34. D. Chamseddine, B. Raouf, K. Gilbert, C. Bertrand, D. Abdelmadjid, Tetrahedron Lett. 55, 200 (2014)
35. S Gyorgy K Robert PL Dora V Krisztina S Judit B Andrea M Laszlo F Janos M Gyorgy Keseru, Bio. Med. Chem. Lett. 19, 3471 (2009)
36. A. Kamal, K.S. Babu, Y. Poornachandra, B. Nagaraju, S.M. Ali Hussaini, S.P. Shaik, C. Ganesh Kumar, Arab J Chem. 12, 3546 (2019)
37. C.H. Griffiths, H.P.O. Horro, T.W. Smiths, J. Appl. Phy. 50, 7108 (1979)
38. M. Zhang, J. Lu, J.N. Zhang, Z.H. Zhang, Cat. Comm. 78, 26 (2016)
39. M. Baghayeri, M. Nodehi, H. Veisi, M.B. Tehrani, B. Maleki, M. Mehmandost, DARU J. Pharm. Sci. 27, 593 (2019)
40. M. Baghayeri, A. Amiri, F. Karimabadi, S.D. Masi, B. Maleki, F. Adibian, A.R. Pourali, C. Malitesta, J. Electroanal. Chem. **888**, 115059 (2021)

41. S.S. Ghasemi, M. Hadavifar, B. Maleki, E. Mohammednia, J. Water Proc. Eng. **32**, 100965 (2019)

42. P. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, S. Hu, M.H. Zhou, C. Lai, Z. Wei, C. Huang, G.X. Xie, Z.F. Liu, Sci. Total Environ. **424**, 1 (2012)

43. G.G. Wildgoose, C.E. Banks, R.G. Compton, Small **2**, 182 (2006)

44. V. Georgakilas, D. Gournis, V. Tzitzios, L. Pasquato, D.M. Guldi, M. Prato, J. Mater. Chem. **17**, 2679 (2007)

45. K. Lee, J.J. Zhang, H.J. Wang, D.P. Wilkinson, J. Appl. Electrochem. **36**, 507 (2006)

46. F. Adibian, A.R. Pourali, B. Maleki, M. Baghayeri, A. Amiri, Polyhedron **175**, 114179 (2020)

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